Supporting Information

Transition-Metal-Free Fast Track to Flavones and 3-Arylcoumarins

Mostafa Golshani, Mehdi Khoobi,* Nafiseh Jalalimanesh, Farnaz Jafarpour* and Alireza Ariafard

mkhoobi@tums.ac.ir; Mehdi.khoobi@gmail.com,
jafarpur@ut.ac.ir;
Alireza.Ariafard@utas.edu.au

Contents

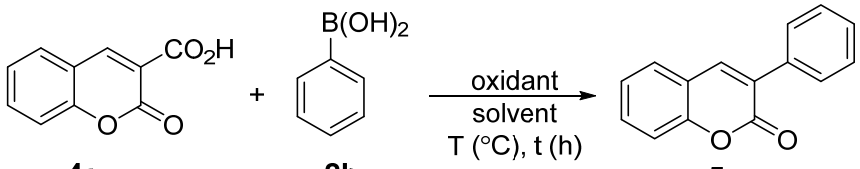
1 General remarks. Synthesis of coumarin and chromone derivatives were performed according to literature procedures. Other reagents were commercially available and used as received. The reactions were carried out in an oil bath using Microwave Vials (2-5 ml). ^{1}H and ^{13}C NMR spectra were recorded at room temperature on 400, 500 and 100, 125 MHz spectrometers respectively, using $CDCl_3$ and DMSO as the NMR solvents. ^{1}H NMR and ^{13}C NMR spectra are referenced from the solvent central peaks. Chemical shifts are given in ppm.

2 General experimental procedure

A vial equipped with a stir bar was charged with coumarin- or chromone carboxylic acid (0.5 mmol, 1eq), aryl boronic acid (0.5 mmol, 1eq), $K_2S_2O_8$ (1 mmol, 2eq). Water (2.4 ml) and dichloromethane (0.6 mL) were added next and the vial was capped. The resulting mixture was heated in an oil bath at 100 °C for 2 h, cooled then filtered through a short plug of silica. Removal of the solvent gave a crude mixture which was purified by column chromatography (petroleum ether /EtOAc gradient).

3 Optimization of reaction conditions

Table S1. Optimization of reaction conditions for arylation of coumarin 4a[a]



Entry	Solvent	Oxidant (equiv.)	T (°C)	t (h)	Yield[%]
1	DMSO	$K_2S_2O_8$ (2.0)	100	2	0
2	EtOH	$K_2S_2O_8$ (2.0)	100	2	0
3	CH_3CN	$K_2S_2O_8$ (2.0)	100	2	0
4[b]	DME	$K_2S_2O_8$ (2.0)	100	2	0
5	mestylene	$K_2S_2O_8$ (2.0)	100	2	0
6	NMP	$K_2S_2O_8$ (2.0)	100	2	0
7	Dioxan	$K_2S_2O_8$ (2.0)	100	2	0
8	DCE	$K_2S_2O_8$ (2.0)	100	2	0
9	H_2O	$K_2S_2O_8$ (2.0)	100	2	50
10	H_2O/CH_3CN 1:1	$K_2S_2O_8$ (2.0)	100	2	40
11	H_2O/DMSO 1:1	$K_2S_2O_8$ (2.0)	100	2	trace
12	H_2O/DMF 1:1	$K_2S_2O_8$ (2.0)	100	2	trace
13	H_2O/EtOH 1:1	$K_2S_2O_8$ (2.0)	100	2	trace
14	H_2O/DCE 1:1	$K_2S_2O_8$ (2.0)	100	2	53
15	$H_2O/CHCl_3$ 1:1	$K_2S_2O_8$ (2.0)	100	2	45
16	H_2O/acetone 1:1	$K_2S_2O_8$ (2.0)	100	2	20
17	H_2O/mestylene 1:1	$K_2S_2O_8$ (2.0)	100	2	30
18	H_2O/EtOAc	$K_2S_2O_8$ (2.0)	100	2	15
19	H_2O/DCE 8:2	$K_2S_2O_8$ (2.0)	100	2	60
20	H_2O/DCE 2:8	$K_2S_2O_8$ (2.0)	100	2	40
21	H_2O/DCE 8:2	$Na_2S_2O_8$(1.0)	100	2	35
22[c]	H_2O/DCE 8:2	-	100	2	0
23[c]	DMSO	-	100	2	0
24	H_2O/DCE 8:2	Benzoyl Peroxide(1.0)	100	2	20
25	H_2O/DCE 8:2	H_2O_2 (1.0)	100	2	5
26[d]	H_2O/DCE 8:2	TBHP (1.0)	100	2	12
27[e]	H_2O/DCE 8:2	*m*-CPBA (1.0)	100	2	10
28	H_2O/DCE 8:2	KIO_3 (1.0)	100	2	0
29	H_2O/DCE 8:2	$K_2S_2O_8$ (2.0)	100	2	60
30	H_2O/DCE 8:2	$K_2S_2O_8$ (3.0)	100	2	55
31	H_2O/DCE 8:2	$K_2S_2O_8$ (4.0)	100	2	50
32	H_2O/DCE 8:2	$K_2S_2O_8$ (5.0)	100	2	48
33	H_2O/DCE 8:2	$K_2S_2O_8$ (2.0)	rt	2	10
34	H_2O/DCE 8:2	$K_2S_2O_8$ (2.0)	40	2	15
35	H_2O/DCE 8:2	$K_2S_2O_8$ (2.0)	60	2	32
36	H_2O/DCE 8:2	$K_2S_2O_8$ (2.0)	80	2	45

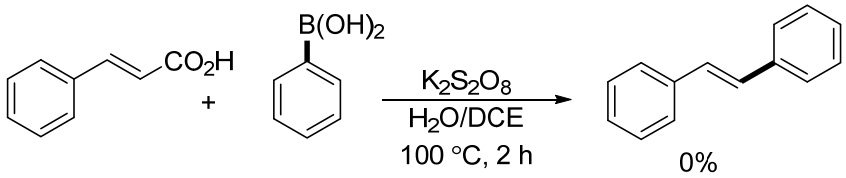
37	H_2O/DCE 8:2	$K_2S_2O_8$ (2.0)	120	2	55
38	H_2O/DCE 8:2	$K_2S_2O_8$ (2.0)	140	2	41
39	H_2O/DCE 8:2	$K_2S_2O_8$ (2.0)	100	1	45
40	H_2O/DCE 8:2	$K_2S_2O_8$ (2.0)	100	4	60
41	H_2O/DCE 8:2	$K_2S_2O_8$ (2.0)	100	6	60
42	H_2O/DCE 8:2	$K_2S_2O_8$ (2.0)	100	8	55
43	H_2O/DCE 8:2	$K_2S_2O_8$ (2.0)	100	10	52
44	H_2O/DCE 8:2	$K_2S_2O_8$ (2.0)	100	24	45

[a]Reaction conditions: Coumarin-3-carboxylic acid (0.5 mmol, 1.0 equiv.), phenyl boronic acid (0.5 mmol, 1.0 equiv); [b]DME= dimethoxyethane; [c]K_2CO_3 (1.0 equiv.); [d]TBHP= t-BuOOH; [e]*m*-CPBA= *meta*-chloroperbenzoic acid.

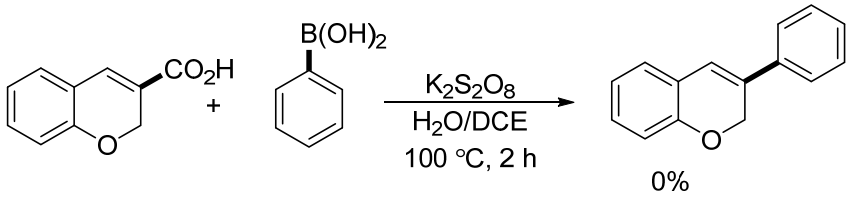
4 Complementary Experiments

When phenylboronic acid was allowed to react with cinnamic acid (Scheme S1) and 2*H*-chromene-3-carboxylic acid (Scheme S2) under standard reaction conditions, the reactions failed to deliver any arylated adducts. Employing coumarin instead of coumarin-3-carboxylic acid diminished the yield to 40% (Scheme S3).

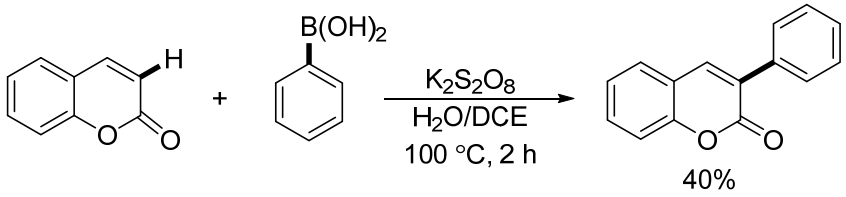
Scheme S1: Reaction of cinnamic acid and phenylboronic acid



Scheme S2: Reaction of 2*H*-chromene-3-carboxylic acid with Phenylboronic acid



Scheme S3: Reaction of Coumarin-3-carboxylic acid with Phenylboronic acid



5 DFT Calculations

5.1 Computational Methods

All DFT calculations were carried out in Gaussian 09.[1] Geometry optimization in water using CPCM solvation model were performed at the B3LYP level of theory[2] with the 6-31+G(d) basis set.[3] Harmonic frequency calculation were performed at the same level to evaluate its zero-point vibrational energy (ZPVE) and thermal corrections at 298 K. The transition structures showed only one imaginary vibration which were further confirmed by IRC analysis of Gaussian 09. To further improve the energies obtained from the B3LYP/6-31+G(d) calculations, we carried out single-point energy calculations in water using CPCM solvation model computed at the M06-2X/6-311+G(2d,p) level.

In order to probe the mechanism of the reaction and in particular to explain the regioselectivity observed, as well as to identify in which step decarboxylation reaction occurs, we have carried out a detailed computational study by the DFT calculation. Two major pathways were considered for arylation of chromone-2-carboxylic acid with arylboronic acid (Figure S1). First, we investigated on the addition of phenyl radical on two possible C-2 and C-3 positions of chromone-2-carboxylic acid (path **I**). Remarkably, the computational data showed that transition state related to addition of phenyl radical to chromone ring at C-3 (TS_2) has a lower energy than that of addition to chromone ring at C-2 (TS_1) and later, 3-phenylchromone-2-carboxylic acid radical intermediate **7** remains 7.6 kcal/mol more stable than 2-phenylchromone-2-carboxylic acid radical intermediate **6**. Subsequent decarboxylation involves sulfate radical anion ($SO_4^{\bullet-}$) mediated H-atom abstraction from carboxylic acid intermediate **8**. Protonation of sulfate radical anion reduces its reduction potential. After H-atom abstraction, outer sphere single electron transfer from SO_4 to C-2 occurs followed by decarboxylation via TS_3. As the $\Delta G^{\ddagger}$ for decarboxylation reaction is 7.7 kcal/mol, decarboxylation step at this point seems not to be the rate determining step. Decarboxylation leaves one electron on C-2 and hence generates a triplet carbene intermediate which in turn converts to singlet state and next a phenyl group migration from C-3 to C-2 via TS_4 produces 2-phenyl chromone **3b**.

Next we considered a decarboxylation/arylation cascade. Oxidative decarboxylation of carboxylic acids and their derivatives with potassium persulfate have been reported previously and its mechanism have been studied.[4] We also have proposed a mechanism for oxidative decarboxylation of chromone-2-carboxylic acid (Figure S1, path **II**). First, hydrogen abstraction from chromon-2 carboxylic acid to sulfate radical anion occurs which is followed by an electron transfer and subsequent decarboxylation to afford chromone radical. Finaly, hydrogen abstraction from reaction media produces chromone. As the overall computed $\Delta G^{\ddagger}$ for decarboxylation of chromone-2-carboxylic acid was obtained 19.1 kcal/mol, decarboxylation/arylation reaction appears to be less viable than direct arylation of chromon 2-carboxylic acid and subsequent decarboxylation.

Based on these results, density functional theory calculations point to a direct C-3 arylation of chromone-2-carboxylic acid and subsequent C-3 to C-2 aryl migration mechanism for regioselective arylation of chromones (Figure S1, path **I**).

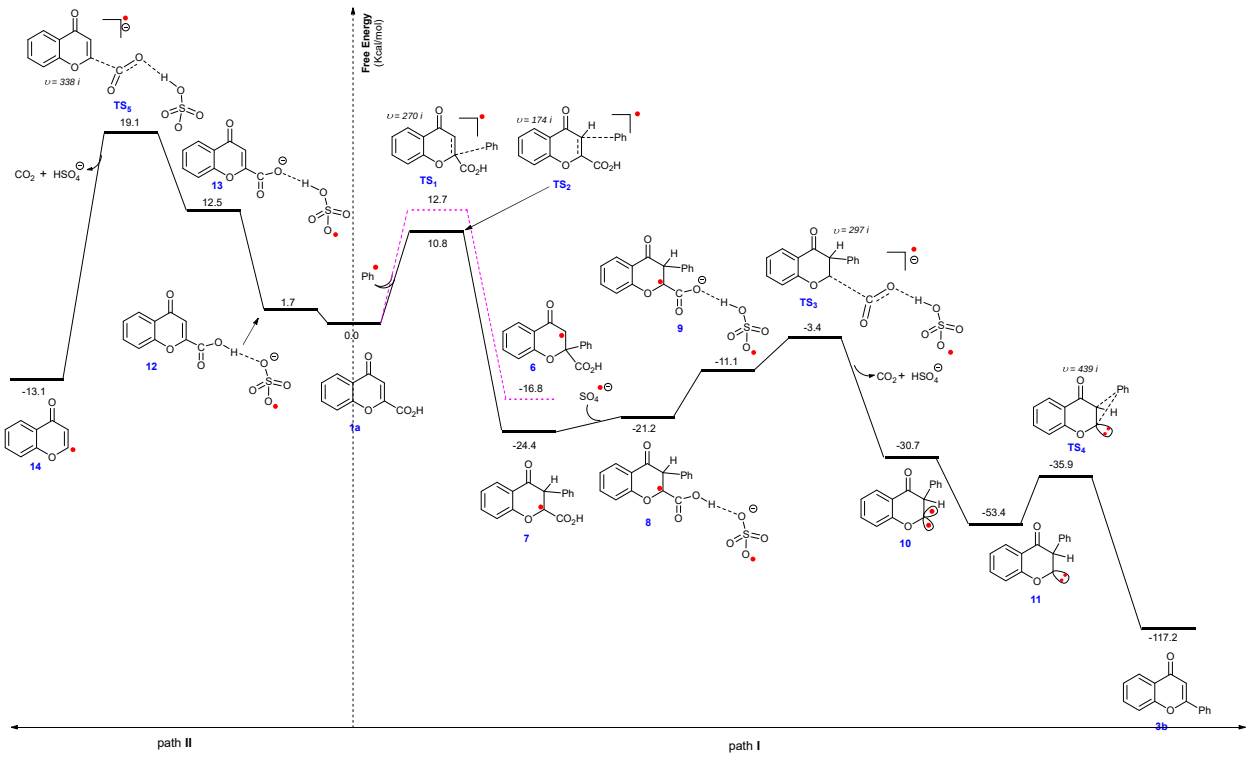


Figure S1. Free energy (kcal/mol) profiles for the proposed mechanism of metal-free regioselective arylation of chromone-2-carboxylic acid.

Next the mechanism of regioselective arylation of coumarin-3-carboxylic acid was studied and a plausible mechanism very similar to that of chromone was proposed (Figure S2).

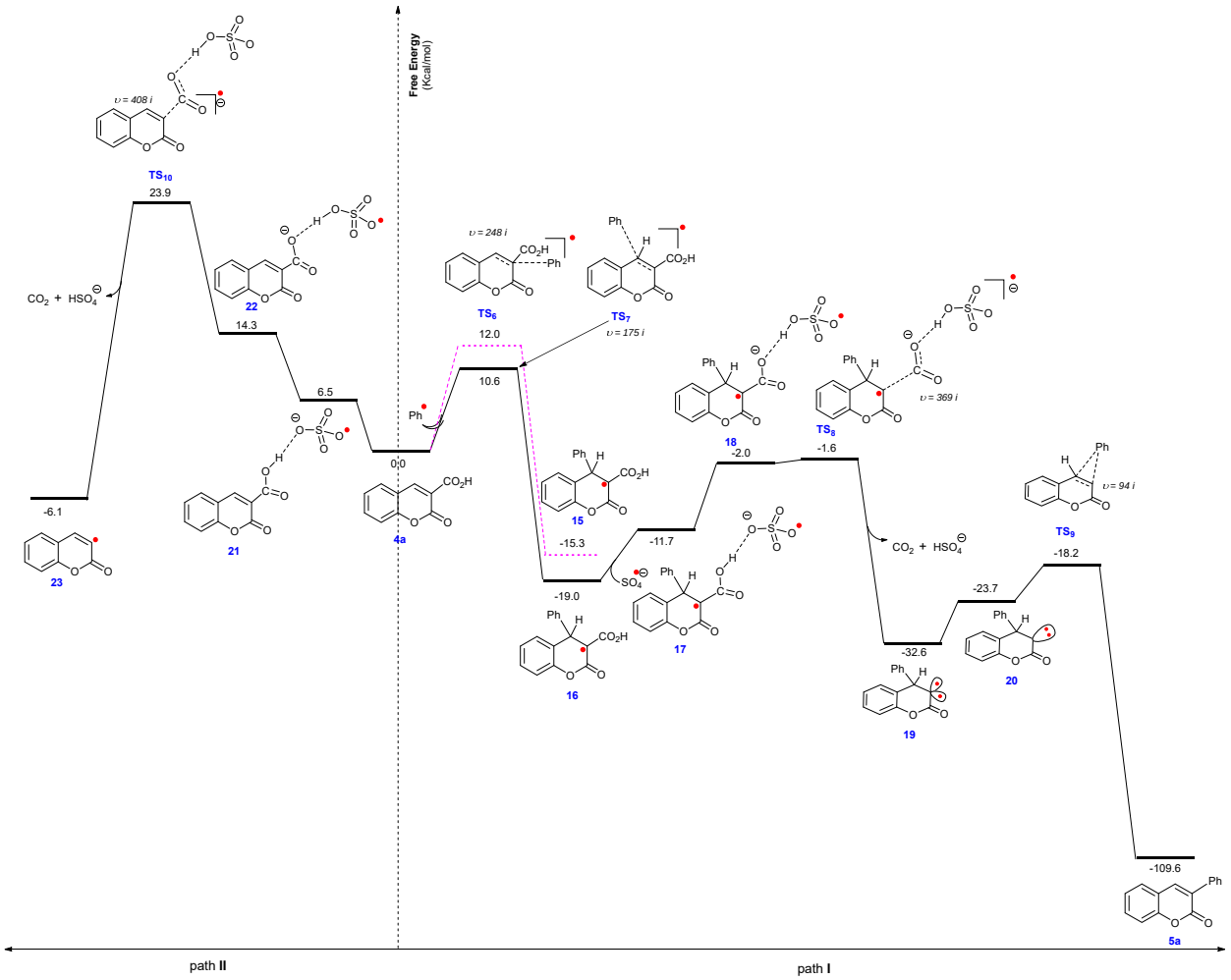


Figure S2. Free energy (kcal/mol) profiles for the proposed mechanism of metal-free regioselective direct arylation of coumarin-3-carboxylic acid.

Table S2. Activation energy (ΔG, kcal/mol) and their smallest calculated vibrational frequencies (ν_{min}, i) for transition structures calculated at M06-2X/6-311+G(2d,p) level with CPCM solvation model for water

Structure	ΔG	ν_{min}	Structure	ΔG	ν_{min}
TS_1	12.7	270	**TS_6**	12.0	248
TS_2	10.8	174	**TS_7**	10.6	175
TS_3	7.7	297	**TS_8**	0.4	369
TS_4	17.5	439	**TS_9**	5.5	94
TS_5	32.2	338	**TS_{10}**	30.0	408

5.2 Coordinates and Energies (kcal/mol) of Stationary Points

4a -685.5647431

C	3.70620500	0.31596500	-0.00007600
C	2.63451800	1.20402600	0.00001200
C	1.34291200	0.68300000	0.00005600
C	1.10082100	-0.70515600	0.00002000
C	2.20744700	-1.58152800	-0.00005800
C	3.49677700	-1.07457900	-0.00010900
H	4.71868000	0.70755100	-0.00012400
H	2.78099200	2.27848000	0.00002900
C	-0.25959800	-1.13830200	0.00009900
H	2.02940900	-2.65266100	-0.00008200
H	4.34691500	-1.74871000	-0.00017600
C	-1.28971000	-0.24340100	0.00010600
C	-1.00801900	1.18561100	0.00005200
O	0.30117600	1.57518900	0.00009500
O	-1.85290500	2.07829500	0.00001000
C	-2.70238100	-0.74680500	0.00014500
O	-3.67228200	0.17553100	-0.00042500
H	-3.25664900	1.07836200	-0.00039000
O	-2.96389500	-1.93604200	0.00021200
H	-0.48991700	-2.19979200	0.00013500

TS_7 -917.090306994

C	-3.64223400	1.93952400	0.05929800
C	-3.32385200	0.83269100	-0.72180000
C	-2.20474000	0.07558700	-0.38003200
C	-1.39443100	0.40349900	0.72128600
C	-1.74052800	1.52924100	1.49557200
C	-2.85528500	2.28741300	1.17010400
H	-4.51255500	2.53671600	-0.19452300
H	-3.92372200	0.54511800	-1.57835000
H	-1.12041900	1.79213800	2.34738600
H	-3.11933400	3.15106200	1.77166600
C	-0.25887700	-0.44053400	0.99467800
C	-0.07863600	-1.61153800	0.27664100
C	-0.92144700	-1.89865500	-0.86807500
O	-1.92798600	-1.02127400	-1.16080800
C	1.48849400	0.95550000	0.11056900
C	1.13520000	2.05409100	-0.64211500
C	2.77150800	0.56981600	0.43500000
C	2.19078800	2.85477300	-1.11022500
H	0.10213600	2.30511200	-0.86320700
C	3.80754800	1.39006400	-0.04287500
H	2.97693300	-0.31836600	1.02403600

C	3.51479400	2.52173200	-0.80979400
H	1.96844700	3.73560800	-1.70735000
H	4.83915000	1.13555000	0.18716900
H	4.32333900	3.14751300	-1.17661700
O	-0.81589200	-2.88013800	-1.60469700
C	0.99151800	-2.56468400	0.69053400
O	1.13906000	-3.67342100	-0.04514700
H	0.47759700	-3.65120900	-0.78786600
O	1.70617500	-2.35780600	1.65932100
H	0.29863400	-0.30926200	1.91570800

TS_6 -917.0877979

C	4.19382600	1.22071900	0.56386300
C	3.22288200	0.62782600	1.36887100
C	2.15064700	-0.00924400	0.75470900
C	2.01528300	-0.06960300	-0.64840000
C	3.02223300	0.53220900	-1.43778700
C	4.09571300	1.17075700	-0.83739900
H	5.03630200	1.72247900	1.02940500
H	3.28723200	0.64831000	2.45132500
H	2.93371600	0.49080500	-2.51927600
H	4.86273200	1.63442300	-1.44926000
C	0.87314500	-0.73041500	-1.18214300
C	-0.12181400	-1.21500900	-0.34738100
C	0.13341600	-1.26828600	1.09745500
O	1.22474200	-0.61647800	1.57580300
C	-1.65288000	0.57246300	-0.03050500
C	-2.60161900	0.55266600	0.97086300
C	-1.49050800	1.57668800	-0.96044600
C	-3.47157100	1.65356800	1.03729700
H	-2.67721500	-0.26210200	1.68508200
C	-2.37080900	2.66701400	-0.87581800
H	-0.72126000	1.53835500	-1.72737100
C	-3.35367000	2.70031300	0.11814100
H	-4.23569400	1.68562800	1.80992000
H	-2.28330000	3.48406400	-1.58756500
H	-4.03079200	3.54758400	0.17773400
O	-0.57368400	-1.85101200	1.91592000
C	-1.21514900	-2.05844400	-0.95687000
O	-1.99968900	-2.73637500	-0.11155100
H	-1.68042900	-2.58207400	0.81635300
O	-1.37822800	-2.12323300	-2.15987600
H	0.74884100	-0.83001300	-2.25542500

16 -917.1409236

C	4.02286100	-1.16972600	0.13227200

C	3.46985600	-0.11124000	-0.58490300
C	2.14734900	0.24827100	-0.33545700
C	1.35546500	-0.41121900	0.60222600
C	1.93361800	-1.46892600	1.31422600
C	3.25523500	-1.84817200	1.08510500
H	5.05265200	-1.46090100	-0.05036300
H	4.04111900	0.43859800	-1.32541600
H	1.33395600	-1.99615400	2.05132100
H	3.68676200	-2.66962400	1.64861800
C	-0.08343800	0.00553500	0.81190700
C	-0.33595100	1.37991900	0.27410400
C	0.49931000	1.93906800	-0.78287400
O	1.65489000	1.31433700	-1.09537000
C	-1.09443100	-0.96088600	0.14934900
C	-0.92430800	-1.37763200	-1.17877800
C	-2.20737500	-1.40903200	0.87084800
C	-1.84529600	-2.24421000	-1.76867900
H	-0.06509600	-1.04115500	-1.75250900
C	-3.12518600	-2.27958900	0.28062600
H	-2.35365000	-1.07614200	1.89372800
C	-2.94762000	-2.69825600	-1.04047400
H	-1.69964200	-2.56424600	-2.79651700
H	-3.97747500	-2.63174400	0.85504200
H	-3.66361300	-3.37413400	-1.49939100
O	0.21180000	2.95504800	-1.41850400
C	-1.49409400	2.14800300	0.81339800
O	-1.83450600	3.28368800	0.19419100
H	-1.21397700	3.43017500	-0.56636700
O	-2.10519000	1.75628700	1.79497700
H	-0.31297300	0.01899000	1.88212400
15	**-917.1342292**		
C	4.33056100	0.96467000	0.21916600
C	3.40856800	0.39085500	1.10318200
C	2.19328700	-0.04234500	0.60718700
C	1.82606400	0.07410900	-0.75713900
C	2.79734200	0.64449600	-1.63027800
C	4.01975800	1.08152700	-1.14644100
H	5.28820000	1.31062200	0.59438900
H	3.63077600	0.27076000	2.15831800
H	2.55269300	0.73981400	-2.68418000
H	4.74244300	1.51990300	-1.82795500
C	0.56467000	-0.36834300	-1.17214000
C	-0.49014900	-0.77000300	-0.17862600
C	0.11431500	-1.11720700	1.18654800
O	1.33403300	-0.66579400	1.51182700
C	-1.49583000	0.41779800	-0.00023100

C	-1.57212600	1.16332700	1.18267400
C	-2.30283300	0.78164800	-1.08891700
C	-2.44511800	2.25010400	1.27561700
H	-0.96231500	0.91232600	2.04467600
C	-3.17459100	1.86549000	-0.99032300
H	-2.25682300	0.21344900	-2.01235800
C	-3.24905700	2.60489800	0.19233300
H	-2.49252700	2.81637500	2.20130500
H	-3.79628900	2.12951200	-1.84103900
H	-3.92757700	3.44955800	0.26823100
O	-0.49310500	-1.75669200	2.03176200
C	-1.32169300	-1.97174100	-0.74405800
O	-2.02047400	-2.69312300	0.13137300
H	-1.74592800	-2.43876300	1.04968400
O	-1.38690200	-2.18382000	-1.93574500
H	0.27992600	-0.34381700	-2.21611900

17 -1616.293965

C	4.27723300	-3.18718200	-0.75774900
C	3.56011200	-2.91646300	0.40656600
C	2.66227600	-1.85043700	0.41187300
C	2.45854100	-1.04671900	-0.70985300
C	3.18306700	-1.33974200	-1.87043400
C	4.08876500	-2.40001900	-1.89842200
H	4.97928000	-4.01542700	-0.77405100
H	3.68314400	-3.51366800	1.30416400
H	3.03192200	-0.72650400	-2.75503200
H	4.64334800	-2.61381300	-2.80704100
C	1.47079800	0.09709600	-0.63278100
C	0.43857600	-0.19560500	0.42031700
C	0.86060400	-0.83853500	1.67055900
O	1.99892500	-1.60523700	1.61193200
C	2.11887700	1.46666800	-0.32128500
C	3.21773900	1.58119300	0.54118000
C	1.57426400	2.62703500	-0.88880100
C	3.77210900	2.83265500	0.81636600
H	3.65735700	0.69446200	0.98828600
C	2.13180100	3.87682700	-0.61582800
H	0.70991000	2.54592700	-1.54062600
C	3.23223900	3.98384400	0.23848400
H	4.62861100	2.90536000	1.48092400
H	1.70660900	4.76643600	-1.07244100
H	3.66600700	4.95681500	0.45173200
O	0.31387700	-0.72916300	2.75015900
C	-0.95236100	0.24427500	0.17198800
O	-1.83962500	-0.13618200	1.09047900

H	-2.74164500	0.18142800	0.81059800
O	-1.24451300	0.88374200	-0.83366700
H	0.95092100	0.19835400	-1.58865000
O	-4.37345100	0.72254400	0.48530000
S	-5.24431400	-0.22593600	-0.36693600
O	-5.89164000	-0.89378300	0.87288000
O	-4.42497600	-1.18328200	-1.13077700
O	-6.23538300	0.51964600	-1.16130100

18 -1616.280139

C	5.38639600	-1.39390500	-0.84862600
C	4.49327000	-1.96246000	0.05518100
C	3.18616600	-1.47560300	0.11859800
C	2.74763600	-0.43290300	-0.69628900
C	3.66241600	0.12252700	-1.60070400
C	4.97033100	-0.34956800	-1.68237900
H	6.40455100	-1.76735000	-0.90415800
H	4.78572700	-2.77661500	0.71033900
H	3.33680400	0.93751700	-2.24201400
H	5.66291300	0.09350500	-2.39150300
C	1.32760200	0.07705500	-0.59440700
C	0.46496700	-0.81531300	0.25274100
C	1.00339300	-1.86048700	1.11032500
O	2.35716800	-2.09703700	1.04315700
C	1.24272200	1.51985200	-0.05185300
C	1.88543700	1.87104700	1.14383400
C	0.49493200	2.48560400	-0.73500100
C	1.79077500	3.17148600	1.63944700
H	2.47116000	1.13125200	1.68319500
C	0.40190200	3.78843300	-0.23902800
H	-0.01593900	2.21768000	-1.65566900
C	1.04889900	4.13420600	0.94891200
H	2.29668200	3.43263200	2.56481700
H	-0.17464000	4.53119200	-0.78344400
H	0.97682600	5.14714900	1.33490000
O	0.35786500	-2.56111700	1.87072100
C	-1.02367400	-0.57042900	0.24281400
O	-1.66030400	-0.58564300	1.31239200
H	-3.26089300	-0.52106100	1.23805500
O	-1.46918500	-0.33471800	-0.93870300
H	0.88127200	0.09697900	-1.59743100
O	-4.27138700	-0.47925800	1.13177800
S	-4.58206100	-0.40187700	-0.44644200
O	-4.47770400	-1.75394100	-1.01006500
O	-3.51289700	0.55783800	-1.00058700
O	-5.89237100	0.26011300	-0.55812000

TS_8 -1616.271769

C	5.79575500	-1.20682400	0.04706900
C	4.71788600	-1.95445100	0.51183300
C	3.41799300	-1.52019600	0.24677200
C	3.17143800	-0.34566200	-0.47021100
C	4.26998300	0.38911100	-0.93334500
C	5.57289300	-0.03310900	-0.68014700
H	6.80800300	-1.54220300	0.25090900
H	4.86086600	-2.87093900	1.07458100
H	4.09217800	1.30420400	-1.49107300
H	6.41029300	0.55192800	-1.04749300
C	1.74232000	0.13743800	-0.76031700
C	0.82473900	-0.88897800	-0.23347500
C	1.08154300	-2.09103600	0.50008300
O	2.40873200	-2.34309700	0.74536100
C	1.44010600	1.53648200	-0.20175600
C	1.60247800	1.81245800	1.16272200
C	0.98574600	2.54406000	-1.05833500
C	1.31476500	3.08280800	1.66019000
H	1.96087500	1.03788200	1.83548000
C	0.69937900	3.81750400	-0.55882400
H	0.85740000	2.33635200	-2.11758400
C	0.86232300	4.08858500	0.80042200
H	1.44449000	3.28788300	2.71906800
H	0.35160200	4.59424900	-1.23390000
H	0.64038500	5.07820700	1.18958900
O	0.24027100	-2.87423700	0.90676800
C	-1.08420800	-0.69370300	-0.60832300
O	-1.49144800	-0.18973600	0.40006000
H	-3.32654500	0.44478500	0.81793200
O	-1.16847400	-1.13234100	-1.71494900
H	1.61257300	0.18706000	-1.85262100
O	-4.26445900	0.71221100	0.89473000
S	-5.13561000	-0.36081800	-0.04151700
O	-5.22654500	-1.60764300	0.75510800
O	-4.33312900	-0.50406200	-1.28319500
O	-6.41909700	0.35350100	-0.20722700

19 -727.8779086

C	-2.93022500	-2.26908800	0.42594100
C	-3.07514700	-0.89356400	0.58086000
C	-2.06520200	-0.03884700	0.13244200
C	-0.90305700	-0.53766300	-0.46768000
C	-0.77945800	-1.92490400	-0.61615600
C	-1.77970600	-2.78883000	-0.17621100
H	-3.71520800	-2.93348500	0.77448800

H	-3.95796800	-0.46387200	1.04300700
H	0.11932600	-2.32345800	-1.07880700
H	-1.66236100	-3.86093000	-0.30117500
C	0.20100400	0.40433500	-0.96825800
C	-0.23766300	1.78743600	-0.72135700
C	-1.41606500	2.28435400	-0.09620900
O	-2.31107300	1.31646300	0.33005100
C	1.57998300	0.12882900	-0.34851300
C	1.76144000	0.17587800	1.04068300
C	2.67428000	-0.15624400	-1.17134400
C	3.01822400	-0.06463600	1.59537400
H	0.91799400	0.39356100	1.69082100
C	3.93337800	-0.39922800	-0.61557600
H	2.54325700	-0.19098600	-2.25003900
C	4.10813300	-0.35316700	0.76838600
H	3.14679400	-0.02679500	2.67355700
H	4.77412200	-0.62459400	-1.26578600
H	5.08639600	-0.54141300	1.20173900
O	-1.70099100	3.45636500	0.09418500
H	0.30463600	0.26139200	-2.05598400

20 -727.862578

C	-2.66757900	-2.48514500	0.31019200
C	-2.93187700	-1.17243400	0.69925500
C	-2.01753400	-0.17749700	0.36039800
C	-0.83854700	-0.46274100	-0.33623400
C	-0.59904600	-1.78122100	-0.73183300
C	-1.50931000	-2.78902500	-0.41157200
H	-3.37314900	-3.26973500	0.56625400
H	-3.83199000	-0.90793000	1.24382200
H	0.31492900	-2.02110700	-1.26641900
H	-1.30679000	-3.81198900	-0.71335900
C	0.15705400	0.69091300	-0.59177300
C	-0.37376700	1.94423900	-0.03159300
C	-1.78168200	2.11928700	-0.14190100
O	-2.31829800	1.13598900	0.73343200
C	1.59454100	0.36060900	-0.21467300
C	2.00288100	0.42229600	1.12399800
C	2.51795300	-0.02451000	-1.19238000
C	3.31313100	0.10279700	1.47853500
H	1.29216000	0.72906000	1.88769300
C	3.83179600	-0.34547000	-0.83876900
H	2.21503400	-0.06756800	-2.23627600
C	4.23135600	-0.28358100	0.49697400
H	3.61847900	0.15603400	2.51995100
H	4.54044400	-0.63860300	-1.60835700

H	5.25235500	-0.53173400	0.77329800
O	-2.48335300	2.95874500	-0.65243600
H	0.11551700	0.89461000	-1.68631900

TS_9 -727.8557265

C	-3.05549500	-2.01254300	0.36175800
C	-2.84496600	-0.74905000	0.91274700
C	-1.82039400	0.04122500	0.39732300
C	-0.98606400	-0.39667100	-0.63550100
C	-1.22659100	-1.66193600	-1.18281800
C	-2.25569200	-2.46559000	-0.69326700
H	-3.85392400	-2.63811100	0.74945900
H	-3.46644300	-0.36356000	1.71423200
H	-0.58884000	-2.02108900	-1.98644700
H	-2.42848700	-3.44652400	-1.12538000
C	0.18290400	0.47721100	-1.03628100
C	0.13889200	1.89729100	-0.58348000
C	-1.11203900	2.26173700	0.07561700
O	-1.67702200	1.32932800	0.93033700
C	1.52078900	0.04480200	-0.37078900
C	1.55257200	-0.39829200	0.95751700
C	2.71873700	0.14197300	-1.09447900
C	2.76540800	-0.76983300	1.54439700
H	0.63495100	-0.47387400	1.53190800
C	3.92385600	-0.23584100	-0.50844400
H	2.70212000	0.50179400	-2.11959800
C	3.95139400	-0.69230700	0.81487900
H	2.77733900	-1.11864000	2.57299100
H	4.84267700	-0.17964200	-1.08522500
H	4.89304400	-0.98510600	1.27021700
O	-1.64631200	3.34368300	-0.07482800
H	0.35436600	0.44760700	-2.12130100

5a -728.0068301

C	-4.57743200	-0.15352900	-0.03864800
C	-3.66384300	0.88512900	0.11778400
C	-2.30164000	0.58893200	0.07710900
C	-1.83323700	-0.72153400	-0.11654700
C	-2.77949700	-1.75445800	-0.27467900
C	-4.13788000	-1.47334900	-0.23519400
H	-5.64092000	0.06350600	-0.00838600
H	-3.98429800	1.91049200	0.26922600
H	-2.42773400	-2.77112100	-0.42641400
H	-4.86208000	-2.27276300	-0.35639700
C	-0.41244500	-0.92085700	-0.14989800
C	0.47387200	0.10495000	0.00629300

C	-0.04359400	1.46723200	0.20945500
O	-1.41952000	1.62414300	0.23036800
C	1.94065700	-0.11869300	-0.00270700
C	2.47578300	-1.26802900	0.60637700
C	2.82267400	0.77280300	-0.63990200
C	3.84571800	-1.52654900	0.56917100
H	1.81578100	-1.95319800	1.13100600
C	4.19177300	0.51079600	-0.67771700
H	2.43232000	1.66721600	-1.11069900
C	4.70989800	-0.63822300	-0.07478200
H	4.23735500	-2.41752900	1.05217800
H	4.85584700	1.20715500	-1.18259200
H	5.77780700	-0.83627000	-0.10174700
O	0.61626800	2.47620800	0.36966600
H	-0.04289800	-1.92801500	-0.32313600

21

C	5.97391600	-0.46418900	0.24595900
C	5.15825200	0.66321200	0.23680300
C	3.78152400	0.49014300	0.08958600
C	3.21207700	-0.78981100	-0.04602600
C	4.06198800	-1.91610000	-0.03391400
C	5.43084900	-1.75436600	0.11050100
H	7.04682800	-0.34149600	0.35942900
H	5.56472900	1.66354100	0.33983000
C	1.79246800	-0.86172700	-0.18352800
H	3.62531700	-2.90504400	-0.13871100
H	6.08454000	-2.62046400	0.11968200
C	0.99986000	0.25000400	-0.18657100
C	1.60550900	1.58043500	-0.06079900
O	2.99580200	1.60432800	0.07933300
O	1.05862700	2.66089500	-0.06765000
C	-0.47551100	0.03250500	-0.32712400
O	-1.21712400	1.13174700	-0.23875300
H	-2.17924400	0.87933400	-0.35324700
O	-0.94277300	-1.08625600	-0.50000400
H	1.31433500	-1.83139800	-0.28722400
O	-3.84359200	0.70719300	-0.65844700
S	-4.64252200	-0.23984500	0.17224900
O	-4.07172300	-0.46849400	1.51047300
O	-6.11153900	0.19754000	0.22355500
O	-4.92039600	-1.54540100	-0.58164000

22 -1384.703277

C	5.99973700	0.01190100	0.54323100
C	5.02902800	1.00077300	0.41269000

C	3.71814500	0.61570800	0.14088800
C	3.36494000	-0.74411300	-0.00205200
C	4.37137800	-1.72577100	0.13544800
C	5.67617500	-1.35007400	0.40567100
H	7.02431600	0.30172400	0.75502700
H	5.26779800	2.05335100	0.51693500
C	1.99994800	-1.04389400	-0.27952600
H	4.10274900	-2.77206000	0.02555900
H	6.44982100	-2.10312700	0.51168200
C	1.07787300	-0.04257600	-0.39947300
C	1.45218800	1.35744200	-0.24856800
O	2.78290000	1.60789900	0.01816300
O	0.70196100	2.30961400	-0.33725500
C	-0.32058900	-0.35449000	-0.68441900
O	-1.23494400	0.52991100	-0.80771300
H	-3.13231300	-0.00591500	-1.01112200
O	-0.78790500	-1.51422400	-0.84514400
H	1.68848200	-2.07915200	-0.39683100
O	-4.09839400	-0.13266400	-1.11606900
S	-4.77114300	-0.10612700	0.40857700
O	-4.48082800	1.24584600	0.94518300
O	-6.19652200	-0.35497000	0.10425400
O	-4.09570400	-1.19718900	1.15335500

TS_{10} -1384.685733

C	5.60411200	-1.08896900	0.66094000
C	4.96070500	0.13505000	0.81929500
C	3.66269200	0.27770300	0.33085800
C	3.00429600	-0.78575000	-0.32186800
C	3.67721400	-2.01459600	-0.46954900
C	4.96718900	-2.16320300	0.01786200
H	6.61337700	-1.21029200	1.04200500
H	5.44109300	0.97304000	1.31233400
C	1.67101800	-0.53627500	-0.81947300
H	3.17271300	-2.83579200	-0.96964700
H	5.48540000	-3.10949100	-0.09829300
C	1.11548000	0.65127400	-0.54102100
C	1.77158700	1.79000600	0.06051600
O	3.06022700	1.49964300	0.49886900
O	1.34290100	2.90984200	0.22050900
C	-0.87754600	0.91810400	-0.83284200
O	-1.32833800	1.24742500	0.22056200
H	-3.26974300	1.13309600	0.50003500
O	-0.89733200	0.65823500	-1.99835800
H	1.14739800	-1.30816400	-1.37716500
O	-4.23633600	0.97648000	0.49339900

S	-4.45469200	-0.66547000	0.29484900
O	-4.12854300	-1.27521600	1.60658000
O	-5.88471900	-0.73632800	-0.07358300
O	-3.50981500	-1.04194900	-0.78737400

23 -496.2894935

C	2.52959600	-1.06635700	0.00009600
C	1.20692900	-1.49947900	0.00005300
C	0.18538100	-0.54883500	0.00001100
C	0.47131900	0.83215600	0.00001300
C	1.81690700	1.24463500	0.00005700
C	2.83750000	0.30330700	0.00009900
H	3.32937500	-1.80068500	0.00012800
H	0.95237300	-2.55397000	0.00004900
C	-0.65683100	1.74574400	-0.00003200
H	2.04216000	2.30721300	0.00005900
H	3.87362900	0.62668000	0.00013300
C	-1.88431900	1.21812400	-0.00007700
C	-2.22438200	-0.17860000	-0.00009100
O	-1.10515800	-1.01767200	-0.00003400
O	-3.32155800	-0.69509100	-0.00010500
H	-0.47640900	2.81870800	-0.00003000

CO_2 -188.5805295

C	0.00000000	0.00000000	-0.00005600
O	0.00000000	0.00000000	-1.16897800
O	0.00000000	0.00000000	1.16902100

$SO_4^{\bullet-}$ -699.1493195

O	-0.88305000	1.24121800	-0.00014600
S	-0.08087600	0.00020800	-0.00001300
O	0.96590200	-0.00115800	1.12802400
O	0.96577100	-0.00158300	-1.12809200
O	-0.88687100	-1.23889200	0.00024100

HSO_4^- -699.8308354

H	1.97706800	0.49684500	0.01146600
O	1.49564500	-0.35069300	0.00704600
S	-0.14140200	0.01658000	-0.00071000
O	-0.35291500	0.80870500	-1.23546400
O	-0.37152800	0.78259000	1.24708400
O	-0.73553100	-1.33586900	-0.01868000

$Ph^{\bullet}$ -231.5234122

C	1.21536200	0.63304900	-0.00000100
C	1.22781800	-0.77251100	0.00000400

C	0.00000000	-1.40039800	-0.00000100
C	-1.22781900	-0.77251000	-0.00000300
C	-1.21536300	0.63304800	0.00000200
C	0.00000100	1.32527100	0.00000000
H	2.15579100	1.17899700	-0.00000300
H	2.16520000	-1.32270200	0.00000100
H	-2.16519800	-1.32270400	-0.00000500
H	-2.15578900	1.17900000	0.00000100
H	-0.00000100	2.41170900	-0.00000200

1a **-685.5415823**

C	-3.03253400	-1.60242700	0.00001000
C	-1.66423300	-1.83656900	-0.00000300
C	-0.79626300	-0.74007800	-0.00001000
C	-1.27427200	0.58010500	-0.00000700
C	-2.66571400	0.78743000	0.00000700
C	-3.53798200	-0.28925500	0.00001600
H	-3.71667000	-2.44548400	0.00001700
H	-1.25451600	-2.84095400	-0.00000500
C	-0.32361600	1.70784000	-0.00002200
H	-3.02785100	1.81024600	0.00001000
H	-4.61064900	-0.12342000	0.00002600
C	1.08122600	1.30212300	-0.00001300
C	1.43220200	-0.00420700	-0.00001800
H	1.84730100	2.06675800	-0.00000700
O	-0.67550400	2.89151400	0.00001400
O	0.54603300	-1.02420000	-0.00001800
C	2.83787600	-0.52166300	-0.00001900
O	3.11960500	-1.70036500	0.00001100
O	3.73458700	0.47779100	0.00002500
H	4.62449500	0.07514200	0.00005400

TS_2 **-917.0658223**

C	3.84336500	-1.23372100	-1.33849900
C	3.14076700	-0.03619100	-1.35609200
C	2.09772800	0.14475700	-0.44222700
C	1.74930700	-0.85238400	0.48376800
C	2.48239800	-2.05267700	0.48356200
C	3.51726900	-2.24610000	-0.41799500
H	4.65479600	-1.38480500	-2.04395600
H	3.38097800	0.75890400	-2.05381200
H	2.20836600	-2.81611600	1.20432500
H	4.07620300	-3.17655100	-0.41695900
C	0.64040500	-0.62512100	1.42758200
O	0.33219800	-1.42499500	2.31493000
C	-0.07073600	0.64626700	1.22666900

C	0.42392800	1.58679500	0.36440200
H	-0.82972900	0.93301900	1.94175800
O	1.45003500	1.35136100	-0.48814900
C	-1.94475300	-0.48752600	0.05493900
C	-2.49212800	-1.58541000	0.68504500
C	-2.42205200	0.09401100	-1.10073700
C	-3.63126600	-2.15296600	0.09039900
H	-2.06018900	-1.99817900	1.59239100
C	-3.56032900	-0.49125400	-1.68007200
H	-1.95045700	0.96071500	-1.55705900
C	-4.15773000	-1.60630700	-1.08427000
H	-4.10015000	-3.02089300	0.54793900
H	-3.97401500	-0.07150200	-2.59387000
H	-5.03834100	-2.05203400	-1.53828700
C	-0.09933000	2.96956500	0.21232200
O	0.37393200	3.79719600	-0.54028500
O	-1.15933100	3.19169800	1.01281800
H	-1.44319200	4.11493600	0.87024300

TS_1 -917.0636527

C	-3.62757800	1.39488800	-1.28216800
C	-2.46032000	0.74398900	-1.66185900
C	-1.74662800	0.02628500	-0.69784000
C	-2.18305800	-0.05440600	0.63373600
C	-3.36767200	0.61323900	0.98981700
C	-4.08447600	1.33308200	0.04580200
H	-4.18883600	1.95638000	-2.02290700
H	-2.09195900	0.77850000	-2.68174900
H	-3.69849200	0.54441900	2.02098700
H	-4.99771000	1.84730100	0.32848000
C	-1.41353100	-0.84507100	1.61752100
O	-1.76755600	-0.98174900	2.79640000
C	-0.22006400	-1.46673600	1.07727800
C	0.17663100	-1.25293700	-0.22532400
O	-0.60200900	-0.60249400	-1.13032600
C	1.26486500	-2.08938000	-0.83691100
O	1.97712600	-2.82185500	-0.18031800
O	1.33842200	-1.94959700	-2.16765200
H	2.06352000	-2.52617500	-2.47799100
C	1.80343500	0.40834700	0.06039000
C	1.60463900	1.55394000	-0.68030900
C	2.80980100	0.20999200	0.98209500
C	2.51663200	2.60247700	-0.47378400
H	0.79452000	1.65003700	-1.39674000
C	3.71005100	1.27073800	1.17017400
H	2.91650500	-0.72162900	1.53029600

C	3.55865700	2.45795400	0.44680900
H	2.40663000	3.52596300	-1.03671500
H	4.52437400	1.16277300	1.88221800
H	4.25788500	3.27484700	0.60065600
H	0.39739300	-2.08526100	1.71607700

7 -917.1267921

C	4.06632600	-0.62188200	-1.03211700
C	3.12934800	0.39943800	-1.15754100
C	1.98486300	0.36493600	-0.35985000
C	1.76057400	-0.67538100	0.55610400
C	2.72918700	-1.68796700	0.67160800
C	3.87188600	-1.66756900	-0.11587400
H	4.95898800	-0.60161400	-1.64988100
H	3.27092000	1.22232600	-1.84990000
H	2.54991300	-2.48623700	1.38458300
H	4.61132400	-2.45686300	-0.02668900
C	0.52923400	-0.70174500	1.36137800
O	0.34162100	-1.48812800	2.27860300
C	-0.57265100	0.28729500	0.94197100
C	-0.02211400	1.48402700	0.23012200
H	-1.05608300	0.63063200	1.86118800
O	1.11770200	1.42287400	-0.49852600
C	-1.62845300	-0.48203100	0.12633200
C	-2.69420100	-1.09498900	0.79750300
C	-1.52592500	-0.61845800	-1.26362700
C	-3.64581000	-1.82969000	0.08897300
H	-2.77833200	-0.99512400	1.87616500
C	-2.47986700	-1.35276000	-1.97179300
H	-0.70852100	-0.14717000	-1.80222600
C	-3.54142500	-1.96036900	-1.29833900
H	-4.47085600	-2.29529700	0.62097800
H	-2.39108300	-1.44781200	-3.05040300
H	-4.28411200	-2.52928700	-1.85050200
C	-0.68152300	2.77300100	0.15039000
O	-0.25903300	3.74591500	-0.46175600
O	-1.84559500	2.78537100	0.85319400
H	-2.21641100	3.68305200	0.76312900

6 -917.113542

C	-3.71756400	1.18542100	-1.25328500
C	-2.46350800	0.71268600	-1.62706900
C	-1.65600600	0.08165900	-0.67429600
C	-2.10558200	-0.08275000	0.64699900
C	-3.37490400	0.40278200	1.00072000
C	-4.17923500	1.03682400	0.06393200

H	-4.34104700	1.67756800	-1.99413800
H	-2.09549900	0.82189000	-2.64205300
H	-3.70535000	0.26092900	2.02479000
H	-5.15836700	1.41184300	0.34471200
C	-1.25908900	-0.80220400	1.61854700
O	-1.62882000	-1.06458400	2.77903200
C	0.02883700	-1.21231900	1.13436000
C	0.56506400	-0.79438300	-0.20017400
O	-0.44552200	-0.37626600	-1.12063400
C	1.32053100	-1.97823600	-0.85197500
O	1.95103100	-2.78743200	-0.20530000
O	1.24661500	-1.96842500	-2.18582100
H	1.78431400	-2.71749100	-2.51165800
C	1.59445500	0.35241700	0.01452000
C	1.38461800	1.61084200	-0.55858100
C	2.73444900	0.13023100	0.80077700
C	2.30549100	2.63853000	-0.34140200
H	0.51421500	1.78918700	-1.17821300
C	3.65148800	1.15992200	1.01080500
H	2.91602600	-0.84693000	1.23626200
C	3.43853800	2.41845800	0.44332200
H	2.13420500	3.61176000	-0.79267200
H	4.53229500	0.97581800	1.61919800
H	4.15199300	3.22041000	0.60974800
H	0.67527100	-1.79061000	1.78260600

8 -1616.287566

C	-4.19058800	-3.23318900	-0.94410300
C	-2.89317200	-2.80409300	-1.20565300
C	-2.34388400	-1.79374700	-0.41411400
C	-3.07532600	-1.20316600	0.62960000
C	-4.37973400	-1.66460400	0.88075300
C	-4.93829600	-2.66779100	0.10140700
H	-4.62302700	-4.01890400	-1.55622700
H	-2.29658600	-3.24081400	-1.99940100
H	-4.93528900	-1.20533200	1.69204700
H	-5.94861600	-3.01305500	0.29596200
C	-2.48334300	-0.11531000	1.42426200
O	-2.99654700	0.33237800	2.44042200
C	-1.18898300	0.49754800	0.86255700
C	-0.41999200	-0.47770200	0.02778400
H	-0.56756400	0.77341400	1.71905000
O	-1.04449700	-1.44560400	-0.68984100
C	-1.55659800	1.79730400	0.12095400
C	-1.67346400	2.98759900	0.85092600
C	-1.81584600	1.81197200	-1.25496800

C	-2.03858100	4.17420600	0.21396900
H	-1.47786500	2.98315300	1.91968400
C	-2.17957200	3.00082500	-1.89199300
H	-1.72706000	0.90042300	-1.83910100
C	-2.29234000	4.18439100	-1.16030200
H	-2.11979800	5.09131600	0.79100700
H	-2.37366000	2.99864600	-2.96100300
H	-2.57300800	5.10896600	-1.65691500
C	1.01699400	-0.42421900	-0.20076300
O	1.62227500	-1.20509500	-0.93114500
O	1.59688800	0.57335500	0.48905800
H	2.57879500	0.56847300	0.30412200
O	4.24692300	0.79533800	0.02639000
S	5.17510900	-0.36654500	0.13931200
O	5.45309100	-0.99661500	-1.23047500
O	6.61509600	0.11628300	0.35409300
O	4.75405500	-1.35775400	1.14398400

9 -1616.273471

C	-3.71831800	-3.44336900	-0.98409100
C	-2.45027600	-2.91076500	-1.19459700
C	-2.02557000	-1.84550900	-0.39893000
C	-2.85153600	-1.30166200	0.59838300
C	-4.12366300	-1.86710500	0.79845500
C	-4.55900900	-2.92633800	0.01466700
H	-4.05437600	-4.27231800	-1.59965200
H	-1.78257600	-3.30848400	-1.95134200
H	-4.75351700	-1.44329300	1.57400200
H	-5.54500200	-3.35239900	0.16977100
C	-2.39109700	-0.15589400	1.39933400
O	-2.99059500	0.26474500	2.37871300
C	-1.12204600	0.55413300	0.89345100
C	-0.24207600	-0.36765300	0.11094500
H	-0.56134100	0.88277000	1.77282100
O	-0.74699300	-1.39289900	-0.62155100
C	-1.55127500	1.81612800	0.12270400
C	-1.75640300	3.00828900	0.82957900
C	-1.78237700	1.79275600	-1.25825900
C	-2.18089200	4.15984100	0.16558800
H	-1.58224800	3.03309900	1.90178400
C	-2.20571300	2.94644200	-1.92235600
H	-1.62480200	0.87940200	-1.82503700
C	-2.40672100	4.13221900	-1.21321300
H	-2.33031500	5.07916700	0.72521000
H	-2.37731300	2.91554000	-2.99475600
H	-2.73405900	5.02943200	-1.73099400

C	1.20416100	-0.15554700	0.00578200
O	1.83261800	-1.02371500	-0.71936000
O	1.70237900	0.81763200	0.62606000
H	3.28173000	0.89222700	0.75377300
O	4.29877700	0.90097700	0.82174400
S	4.83784600	-0.40297800	0.04209400
O	3.95344200	-0.49378400	-1.20713800
O	6.21349800	-0.06977500	-0.36880600
O	4.69126700	-1.56609100	0.93112200

TS_3 -1616.254167

C	-4.67644200	-2.98399200	-0.77537600
C	-3.38873500	-2.63811500	-1.17674600
C	-2.69175700	-1.69426700	-0.42753200
C	-3.24845300	-1.08253500	0.70657800
C	-4.55017500	-1.45437200	1.09083800
C	-5.25863300	-2.39735000	0.35977300
H	-5.23026000	-3.72138000	-1.34826600
H	-2.91898200	-3.08608300	-2.04551400
H	-4.98095200	-0.97956300	1.96635500
H	-6.26115200	-2.68093300	0.66307800
C	-2.51084700	-0.05174500	1.45613400
O	-2.90134400	0.44791400	2.49540800
C	-1.15646700	0.45020300	0.83598200
C	-0.65074300	-0.66831400	-0.00592000
H	-0.47767400	0.58812900	1.68106500
O	-1.41490200	-1.36039300	-0.85666400
C	-1.36503400	1.80105700	0.15013000
C	-1.14467600	2.97354300	0.88609100
C	-1.80351600	1.89825900	-1.17764700
C	-1.36102300	4.22355500	0.30515800
H	-0.80417400	2.90597100	1.91579500
C	-2.01609200	3.14964600	-1.75802900
H	-1.96938900	1.00174100	-1.76744500
C	-1.79721200	4.31480500	-1.01884500
H	-1.18326300	5.12464600	0.88539300
H	-2.35132700	3.21246500	-2.78940500
H	-1.96143500	5.28770700	-1.47328800
C	1.23183800	-0.39134700	-0.75870900
O	1.19182000	-1.00218000	-1.77947700
O	1.74947000	0.27700600	0.09071800
H	3.64457800	0.68768700	0.15003200
O	4.61349400	0.83382400	0.16309600
S	5.32673300	-0.67203000	0.22157500
O	4.67927600	-1.44251600	-0.86965500
O	6.74805400	-0.33788800	-0.01086900

O	5.03339400	-1.20102900	1.57565800

10 -727.8537775

C	-3.75750500	-0.82424900	-0.99881900
C	-2.94495900	-1.41947800	-0.03906100
C	-1.86567200	-0.69551900	0.46659600
C	-1.57269100	0.60652400	0.02486200
C	-2.41808900	1.18525800	-0.94151600
C	-3.49913300	0.48104200	-1.45058700
H	-4.60388100	-1.37711500	-1.39525500
H	-3.13607200	-2.42114600	0.33101500
H	-2.19085800	2.19084100	-1.28086100
H	-4.14283700	0.93411600	-2.19780400
C	-0.39473900	1.33787500	0.52658200
O	-0.18772100	2.52136700	0.30187200
C	0.63331100	0.50471800	1.35505900
C	-0.14712300	-0.55909800	2.03503000
H	1.03255100	1.19030700	2.10958800
O	-1.08375600	-1.30692000	1.42949200
C	1.79178200	0.04940300	0.45439400
C	2.77504200	0.98224500	0.09454600
C	1.88272200	-1.25900200	-0.03440900
C	3.83088900	0.61205000	-0.73887100
H	2.70854300	2.00096100	0.46706000
C	2.94158300	-1.62947100	-0.86738000
H	1.13387200	-1.99555700	0.24080800
C	3.91757400	-0.69652900	-1.22236400
H	4.58831400	1.34402900	-1.00594700
H	3.00227600	-2.64981600	-1.23613900
H	4.74195400	-0.98681700	-1.86775000

11 -727.8913971

C	-3.87737400	-0.87796000	-0.69432700
C	-3.01130100	-1.32830900	0.30300100
C	-1.88145500	-0.57303700	0.58921000
C	-1.59159400	0.61733900	-0.08489400
C	-2.48058600	1.05807700	-1.07711500
C	-3.61416400	0.31295900	-1.38452500
H	-4.76472500	-1.45705600	-0.93082000
H	-3.20262700	-2.24088800	0.85736400
H	-2.25541400	1.98349400	-1.59715300
H	-4.29574400	0.65309900	-2.15762900
C	-0.37721600	1.36792000	0.27997200
O	-0.14869200	2.50258000	-0.11852000
C	0.59487200	0.62196100	1.19121100
C	0.10177700	-0.56133300	2.01843000

H	0.99714800	1.34678900	1.90924400
O	-1.05819100	-1.06205500	1.62964500
C	1.78671500	0.09938200	0.37393900
C	3.02170300	0.75819100	0.43784600
C	1.65578500	-1.02769100	-0.45029200
C	4.10441100	0.30358900	-0.31586600
H	3.13395600	1.62972500	1.07658400
C	2.74121300	-1.48259800	-1.20190500
H	0.70818300	-1.55524800	-0.51408700
C	3.96747800	-0.81844800	-1.13734900
H	5.05533400	0.82592700	-0.25892000
H	2.62577200	-2.35728600	-1.83565500
H	4.81159400	-1.17300300	-1.72195900

TS_4 -727.8640985

C	-3.77611400	-1.26369000	-0.23026400
C	-2.65008400	-1.56308700	0.52598900
C	-1.60324600	-0.63544700	0.59240900
C	-1.68903500	0.59159500	-0.09593800
C	-2.84270500	0.87286000	-0.85307000
C	-3.87859900	-0.04393800	-0.92395700
H	-4.58677900	-1.98443800	-0.28471600
H	-2.55844100	-2.50015400	1.06513700
H	-2.89270800	1.82374000	-1.37384200
H	-4.76514600	0.17400500	-1.51088300
C	-0.59198500	1.55378100	0.02362700
O	-0.55801200	2.64636600	-0.53633100
C	0.49973800	1.11591000	0.96147700
C	0.51636800	-0.11773400	1.66683400
H	1.09488200	1.93914500	1.34570200
O	-0.51321600	-0.99666800	1.34311900
C	1.73572400	0.01726600	0.44227200
C	3.05558900	0.36616700	0.82438300
C	1.54094200	-0.69741100	-0.75727600
C	4.13383000	-0.02149600	0.04735900
H	3.21251300	0.92549500	1.74171000
C	2.63789900	-1.09847300	-1.52057200
H	0.54153300	-0.96775400	-1.07977800
C	3.93314900	-0.76237400	-1.12895500
H	5.14004300	0.24385600	0.35843600
H	2.47167500	-1.66581400	-2.43161900
H	4.78342000	-1.06924600	-1.73035300

3b -727.9964453

C	3.61970300	-1.92159000	0.13596000
C	2.23080200	-1.94393100	0.13851400

C	1.53940600	-0.73096500	0.05823900
C	2.21169900	0.49622700	-0.02339900
C	3.61738000	0.49042900	-0.02417500
C	4.31794500	-0.70375400	0.05500400
H	4.16755800	-2.85714000	0.19788400
H	1.67349200	-2.87273500	0.20125800
H	4.12909200	1.44528700	-0.08875100
H	5.40361000	-0.70191400	0.05453400
C	1.43425400	1.74922900	-0.11402400
O	1.97064200	2.86304100	-0.19512800
C	-0.00484600	1.55940800	-0.11133000
C	-0.57948600	0.32893600	-0.01272000
O	0.17000300	-0.80400900	0.07108200
C	-2.02599700	0.04445500	0.00220800
C	-2.49966100	-1.24557700	-0.29617900
C	-2.95404600	1.05503700	0.31110900
C	-3.86775800	-1.51142800	-0.29862400
H	-1.79492700	-2.03422500	-0.53391300
C	-4.31980500	0.78363000	0.30780800
H	-2.61024900	2.04968200	0.57514400
C	-4.78233300	-0.49931200	0.00110600
H	-4.21896600	-2.51122800	-0.53699300
H	-5.02361700	1.57339000	0.55363000
H	-5.84813100	-0.70887300	0.00068400
H	-0.62656700	2.44074000	-0.20808100

12 -1384.704632

C	5.07131100	-1.96621900	0.13314000
C	3.69101500	-1.99233100	-0.01280600
C	2.99525100	-0.77916600	-0.04004300
C	3.65748400	0.45341500	0.07562900
C	5.05646000	0.44974800	0.22279900
C	5.75893600	-0.74450500	0.25148500
H	5.62222100	-2.90163100	0.15571000
H	3.14194100	-2.92332300	-0.10557700
C	2.88424200	1.70982700	0.04120300
H	5.56053700	1.40653900	0.31255000
H	6.83850400	-0.74096100	0.36513900
C	1.44508600	1.51735700	-0.11564400
C	0.90707700	0.28001000	-0.21834800
H	0.79952400	2.38532200	-0.15010400
O	3.40464400	2.82651500	0.13603400
O	1.63413400	-0.85933800	-0.18556400
C	-0.55890000	-0.01604600	-0.38145300
O	-0.98675800	-1.15210000	-0.46988800
O	-1.28692800	1.09286300	-0.41254500

H	-2.25980500	0.85877000	-0.52598200
O	-3.87477100	0.64664600	-0.82174600
S	-4.67029000	-0.11789100	0.18572000
O	-4.01780100	-0.19239200	1.50325300
O	-6.10244200	0.42231200	0.26114600
O	-5.07333500	-1.49338000	-0.35556800

13 -1384.688955

C	4.67528200	-2.14742900	0.02469800
C	3.29300900	-2.04854100	-0.05941000
C	2.70874500	-0.77792700	-0.04630000
C	3.48282000	0.38947200	0.04790400
C	4.88080100	0.25918400	0.13217900
C	5.47401500	-0.99335400	0.12101600
H	5.14053500	-3.12846600	0.01554000
H	2.65893900	-2.92558000	-0.13421700
C	2.82511400	1.71097300	0.05656400
H	5.47218900	1.16606400	0.20523000
H	6.55353900	-1.08723600	0.18598900
C	1.36939300	1.65046800	-0.03904400
C	0.72009200	0.46777100	-0.12617300
H	0.79587400	2.56842300	-0.04005300
O	3.44858800	2.77455900	0.13816700
O	1.33941200	-0.73362800	-0.13102400
C	-0.79378900	0.37266300	-0.22260000
O	-1.24351200	-0.82093300	-0.19536600
O	-1.42984200	1.44179400	-0.30390700
H	-3.02362700	1.36646700	-0.16313800
O	-4.03033200	1.25542100	-0.07035900
S	-4.32293400	-0.31282200	0.13959700
O	-4.04390400	-0.65904100	1.53863500
O	-5.70069900	-0.52454400	-0.33319400
O	-3.37013500	-1.01540500	-0.84744100

TS_5 -1384.671925

C	5.23588200	-1.84405900	0.35272600
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C	3.13594300	-0.76851700	-0.00439000
C	3.71757400	0.49847300	0.10995500
C	5.10148400	0.57204200	0.35126800
C	5.85296300	-0.58697000	0.47206200
H	5.82743900	-2.74919500	0.44799500
H	3.37170500	-2.90444700	0.01524700
C	2.89412100	1.71715900	-0.01742600
H	5.55494200	1.55373900	0.44024300
H	6.91997700	-0.52531200	0.66014900

C	1.45169600	1.46978200	-0.24697800
C	1.06147600	0.19494000	-0.34425900
H	0.76899000	2.30393900	-0.32197100
O	3.33923700	2.85765300	0.07022400
O	1.76973600	-0.90392000	-0.25685100
C	-0.84409900	-0.18245400	-0.74792200
O	-0.80436400	-1.32589800	-1.09337800
O	-1.40984100	0.85263800	-0.52644000
H	-3.34369900	0.94814800	-0.73061100
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S	-4.84322200	-0.16899700	0.35790100
O	-4.74218900	0.59156100	1.62694400
O	-6.22767800	-0.44797100	-0.07949200
O	-3.91856900	-1.32838800	0.28496000

14 -496.2791048

C	-2.67755700	-0.23769200	0.00001000
C	-1.71567400	-1.24223200	0.00000000
C	-0.37380600	-0.86732100	-0.00000300
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C	-2.30016800	1.11561500	0.00001600
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C	1.47941000	0.82591100	0.00000100
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C	2.38807500	-0.33235400	-0.00001300
C	1.83887000	-1.55503500	-0.00001700
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O	1.88162600	1.98969100	0.00000100
O	0.57203200	-1.89701300	-0.00001300

5.3 References

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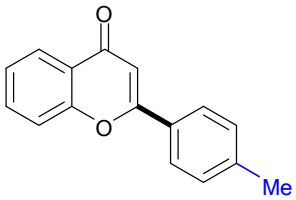
4. (a) D. D. Tanner, S. A. A. Osman, *J. Org.* Chem., 1987, **52,** 4689; (b) J. M. Anderson, J. K. Kochi, *J. Am. Chem. Soc.,* 1970, **92**, 1651; (c) Y. Gong, L. Lin, *Molecules*, 2011, **16**, 2714.

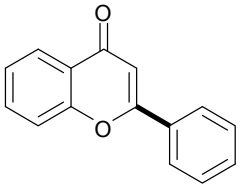
6 Compounds characterization data

2-(p-Tolyl)-4*H*-chromen-4-one 3a



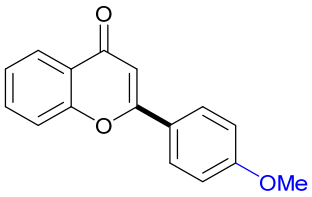
White solid; Yield 82% (97 mg); mp 112-144 °C; Eluent: Petroleum ether /EtOAc 90:10; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.43 (s, 3H), 6.78 (s, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.40 (t, *J* = 7.0 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.68 (t, *J* = 8.0 Hz, 2H), 7.81 (d, *J* = 7.5 Hz, 2H), 8.22 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.5, 107.0, 118.0, 124.0, 125.1, 125.7, 126.2, 129.0, 129.7, 133.6, 142.2, 156.2, 163.6, 178.4; IR 763.7, 1377, 1468, 1603, 1647, 3066 cm^{-1}. Anal. Calcd for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: C, 81.68; H, 5.24.

2-Phenyl-4*H*-chromen-4-one 3b



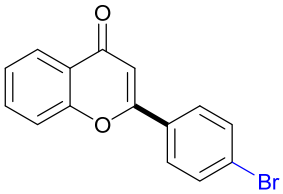
White solid; Yield 40% (44 mg); mp 88-92 °C; Eluent: Petroleum ether /EtOAc 90:10; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.83 (s, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.51-7.55 (m, 3H), 7.57 (d, *J* = 7.5 Hz, 1H), 7.70 (t, *J* = 7.5 Hz, 3H), 7.93 (d, *J* = 6.5 Hz, 2H), 8.24 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 107.6, 118.1, 124.0, 125.2, 125.8, 126.2, 129.0, 131.6, 131.9, 133.7, 156.3, 163.4, 178.4; IR 752.1, 817.7, 1124, 1371, 1466, 1645, 2916, 3033 cm^{-1}. Anal. Calcd for $C_{15}H_{10}O_2$: C, 81.07; H, 4.54. Found: C, 81.36; H, 4.65.

2-(4-Methoxyphenyl)-4*H*-chromen-4-one 3c



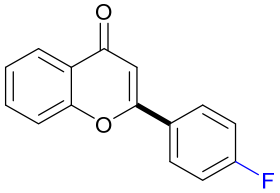
White solid; Yield 86% (108 mg); mp 220-224 °C; Eluent: Petroleum ether /EtOAc 70:30; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.86 (s, 3H), 6.71 (s, 1H), 6.99 (d, *J* = 8.0 Hz, 2H), 7.38 (m, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.65 (m, 1H), 7.85 (d, *J* = 8.0 Hz, 2H), 8.20 (d, *J* = 7.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.4, 106.1, 114.4, 117.8, 123.9, 124.0, 124.9, 125.6, 127.9, 133.4, 156.1, 162.4, 163.3, 178.2; IR 829, 1259, 1435, 16.22, 2927 cm^{-1}. Anal. Calcd for $C_{16}H_{12}O_3$: C, 76.18; H, 4.79. Found: C, 76.50; H, 4.93.

2-(4-Bromophenyl)-4*H*-chromen-4-one 3d



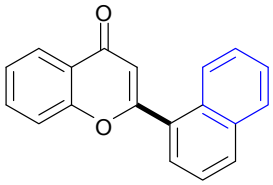
White solid; Yield 41% (62 mg); mp 174-178 °C; Eluent: Petroleum ether /EtOAc 90:10; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.80 (s, 1H), 7.42 (t, *J* = 7.0 Hz, 1H), 7.56 (d, *J* = 8.5 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.70 (t, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 2H), 8.23 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 107.7, 118.0, 124.0, 125.4, 125.8, 126.3, 127.7, 130.7, 132.4, 133.9, 156.2, 162.3, 178.2; IR 756, 837, 1373, 1466, 1662, 2931 cm^{-1}. Anal. Calcd for $C_{15}H_9BrO_2$: C, 59.83; H, 3.01. Found: C, 60.08; H, 3.12.

2-(4-Fluorophenyl)-4*H*-chromen-4-one 3e



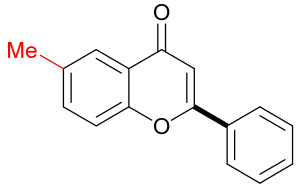
White solid; Yield 38% (46 mg); mp 140-144 °C; Eluent: Petroleum ether /EtOAc 90:10; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.76 (s, 1H), 7.22 (t, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 7.0 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.70 (t, *J* = 8.0 Hz, 1H), 7.93 (t, *J* = 7.0 Hz, 2H), 8.23 (d, *J* = 8.0 Hz, 1H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ 107.4, 116.2 (d, $J_{C\text{-}F}$ = 21.9 Hz), 118.0, 123.9, 125.3, 125.7, 128.0, 128.5 (d, $J_{C\text{-}F}$ = 7.7 Hz), 133.8, 156.2, 162.4, 164.8 (d, $J_{C\text{-}F}$ = 247.2 Hz), 178.2; IR 752, 835, 1232, 1377, 1466, 1508, 1658, 2924, 3055 cm^{-1}. Anal. Calcd for $C_{15}H_9FO_2$: C, 75.00; H, 3.78. Found: C, 75.26; H, 3.90.

2-(Naphthalen-1-yl)-4*H*-chromen-4-one 3f



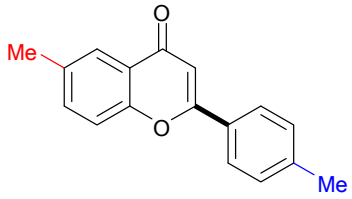
White solid; Yield 65% (88 mg); mp 142-144 °C; Eluent: Petroleum ether /EtOAc 90:10; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.61 (s, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.48-7.52 (m, 3H), 7.64 (t, *J* = 7.6 Hz, 1H),7.69 (d, *J* = 7.2 Hz, 1H), 7.87 (m, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 8.05 (m, 1H), 8.23 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 113.1, 118.3, 124.0, 124.9, 125.1, 125.4, 125.9, 126.6, 127.5, 128.0, 128.8, 130.4, 130.7, 131.5, 133.7, 133.9, 156.7, 165.5, 178.3. Anal. Calcd for $C_{19}H_{12}O_2$: C, 83.81; H, 4.44. Found: C, 83.54; H, 4.30.

6-Methyl-2-phenyl-4*H*-chromen-4-one 3g



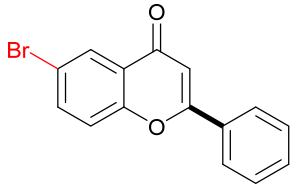
White solid; Yield 43% (51 mg); mp 108-112 °C; Eluent: Petroleum ether /EtOAc 90:10; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.46 (s, 3H), 6.81 (s, 1H), 7.46-7.52 (m, 5H), 7.91 (d, *J* = 7.0 Hz, 2H), 8.02 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.9, 107.5, 117.8, 123.6, 125.0, 126.2, 129.0, 131.4, 131.9, 134.9, 135.2, 154.6, 163.2, 178.5; IR 819.6, 1360, 1643, 2918, 3064 cm^{-1}. Anal. Calcd for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: C, 81.59; H, 5.22.

6-Methyl-2-(p-tolyl)-4*H*-chromen-4-one 3h



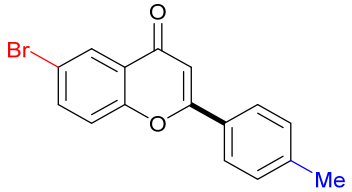
White solid; Yield 53% (66 mg); mp 151-153 °C; Eluent: Petroleum ether /EtOAc 90:10; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.45 (s, 3H), 2.48 (s, 3H), 6.80 (s, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.8 Hz, 1H), 7.52 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 2H), 8.03 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.9, 21.5, 106.8, 117.8, 123.6, 125.0, 126.2, 129.1, 129.8, 134.9, 135.1, 142.1, 154.5, 163.5, 178.6. Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.88; H, 5.77.

6-Bromo-2-phenyl-4*H*-chromen-4-one 3j



Yellow solid; Yield 45% (68 mg); mp 190-195 °C; Eluent: Petroleum ether /EtOAc 90:10; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.84 (s, 1H), 7.47 (d, *J* = 8.5 Hz, 1H), 7.53-7.55 (m, 3H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.92 (d, *J* = 7.0 Hz, 2H), 8.37 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 107.6, 118.7, 120.0, 125.2, 126.5, 128.5, 129.4, 131.5, 131.9, 136.7, 155.1, 163.8, 177.0; IR 678.8, 769.5, 1354, 1456, 1651, 2925, 3082 cm^{-1}. Anal. Calcd for $C_{15}H_9BrO_2$: C, 59.83; H, 3.01. Found: C, 59.08; H, 3.15.

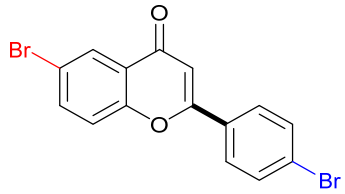
6-Bromo-2-(p-tolyl)-4*H*-chromen-4-one 3k



Yellow solid; Yield 40% (63 mg); mp 197-199 °C; Eluent: Petroleum ether /EtOAc 90:10; ^{1}H NMR (500 MHz, DMSO) δ 2.47 (s, 3H), 7.13 (s, 1H), 7.46-7.47 (m, 2H), 7.86-7.87 (m, 1H), 8.07-

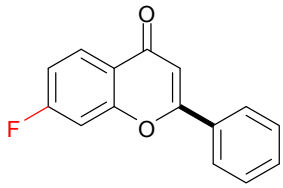
8.17 (m, 4H); ^{13}C NMR (125 MHz, DMSO) δ 21.0, 106.2, 117.9, 121.3, 125.0, 126.4, 126.9, 128.1, 129.7, 136.8, 142.5, 154.9, 163.4, 175.8. Anal. Calcd for $C_{16}H_{11}BrO_2$: C, 60.98; H, 3.52. Found: C, 61.23; H, 3.63.

6-Bromo-2-(4-bromophenyl)-4*H*-chromen-4-one 3l



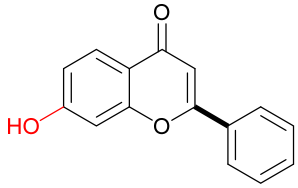
Yellow solid; Yield 36% (68 mg); mp 245-247 °C; Eluent: Petroleum ether /EtOAc 90:10; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.81 (s, 1H), 7.46 (d, J = 8.8 Hz, 1H), 7.66 (d, J = 8.7 Hz, 2H), 7.76-7.79 (m, 3H), 8.34 (d, J = 2.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 107.7, 118.9, 120.0, 125.2, 126.6, 127.7, 128.4, 130.4, 132.4, 136.9, 154.9, 162.6, 176.8. Anal. Calcd for $C_{15}H_8Br_2O_2$: C, 47.41; H, 2.12;. Found: C, 47.74; H, 2.25.

7-Fluoro-2-phenyl-4*H*-chromen-4-one 3m



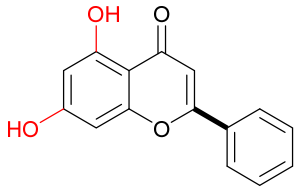
Yellow solid; Yield 55% (66 mg); mp 134-136 °C; Eluent: Petroleum ether /EtOAc 90:10; ^{1}H NMR (500 MHz, DMSO) δ 7.15 (s, 1H), 7.47 (dd, J = 8.8, 2.4 Hz, 1H), 7.66-7.69 (m, 3H), 7.84 (dd, J = 9.0, 2.4 Hz, 1H),8.17-8.21 (m, 3H); ^{13}C NMR (100.6 MHz, DMSO) δ 105.4 (d, $J_{C\text{-}F}$ = 25.7 Hz), 106.9, 114.0 (d, $J_{C\text{-}F}$ = 23.1 Hz), 120.5, 126.3, 127.6 (d, $J_{C\text{-}F}$ = 10.9 Hz), 129.1, 130.8, 131.9, 139.8, 156.8 (d, $J_{C\text{-}F}$ = 28.7 Hz), 162.9, 165.0 (d, $J_{C\text{-}F}$ = 251.8 Hz), 176.3. Anal. Calcd for $C_{15}H_9FO_2$: C, 75.00; H, 3.78. Found: C, 75.29; H, 3.93

7-Hydroxy-2-phenyl-4*H*-chromen-4-one 3n



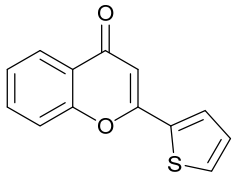
Yellow solid; Yield 63% (75 mg); mp 265-268 °C; Eluent: Petroleum ether /EtOAc 90:10; ^{1}H NMR (400 MHz, DMSO) δ 6.92 (s, 1H), 6.94 (dd, J = 8.6, 2.0 Hz, 1H), 7.02 (d, J = 2.0 Hz, 1H), 7.57-7.59 (m, 3H), 7.89 (d, J = 8.6 Hz, 1H), 8.06-8.08 (m, 2H), 10.86 (bs, 1H); ^{13}C NMR (100.6 MHz, DMSO) δ 102.5, 106.6, 115.0, 116.1, 126.2, 126.5, 129.1, 131.3, 131.5, 157.5, 161.9, 162.7, 176.4. Anal. Calcd for $C_{15}H_{10}O_3$: C, 75.62; H, 4.23. Found: C, 75.90; H, 4.37.

5,7-Dihydroxy-2-phenyl-4*H*-chromen-4-one 3o



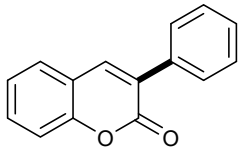
Yellow solid; Yield 41% (52 mg); mp 283-284 °C; Eluent: Petroleum ether /EtOAc 90:10; ^{1}H NMR (400 MHz, DMSO) δ 6.18 (d, *J* = 2.1 Hz, 1H), 6.47 (d, *J* = 2.1 Hz, 1H), 6.90 (s, 1H), 7.49-7.56 (m, 3H), 7.99 (d, *J* = 8.5 Hz, 2H), 10.88 (s, 1H), 12.80 (s, 1H); ^{13}C NMR (125 MHz, DMSO) δ 94.5, 99.4, 104.4, 105.6, 126.8, 129.5, 131.1, 132.3, 157.8, 161.9, 163.5, 164.8, 182.2. Anal. Calcd for $C_{15}H_{10}O_4$: C, 70.86; H, 3.96. Found: C, 71.10; H, 4.07.

2-(Thiophen-2-yl)-4*H*-chromen-4-one 3p



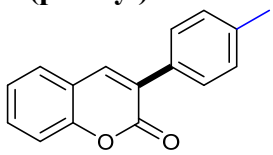
Yellow solid; Yield 35% (40 mg); mp 283-284 °C; Eluent: Petroleum ether /EtOAc 90:10; ^{1}H NMR (500 MHz, DMSO) δ 6.85 (s, 1H), 7.23-7.24 (m, 1H), 7.41-7.44 (m, 1H), 7.60 (d, *J* = 8.2 Hz, 1H), 7.73-7.76 (m, 1H), 7.92 (d, *J* = 4.2 Hz, 1H), 7.97 (s, 2H); ^{13}C NMR (125 MHz, DMSO) δ 105.7, 118.6, 123.8, 125.2, 125.9, 129.4, 130.0, 132.2, 134.6, 134.6, 155.7, 159.0, 176.8. Anal. Calcd for $C_{28}H_{18}O_4S$: C, 68.40; H, 3.53; S, 14.05. Found: C, 68.69; H, 3.66; S, 14.21.

3-Phenyl-2*H*-chromen-2-one 5a



White solid; Yield 60% (67 mg); mp 135-140 ºC; Eluent: Petroleum ether /EtOAc 90:10; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (td, *J* = 7 Hz, *J* = 1.0 Hz, 1H), 7.37 (d, *J* = 8 Hz, 1H) 7.39-7.42 (m, 1H), 7.43-7.47 (m, 2H), 7.51-7.55 (m, 2H), 7.69-7.72 (m, 2H), 7.81 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 116.4, 119.7, 124.4, 127.9, 128.4, 128.5, 128.8, 131.3, 134.7, 139.7, 153.6, 160.5; IR 694.3, 754, 954.6, 1119, 1450, 1606, 1722, 3057 cm^{-1}. Anal. Calcd for $C_{15}H_{10}O_2$: C, 81.07; H, 4.54. Found: C, 80.85; H, 4.41.

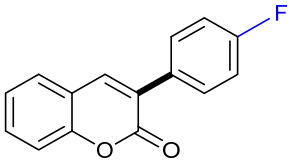
3-(p-Tolyl)-2*H*-chromen-2-one 5b



White solid; Yield 75% (89 mg); mp 142-148 ºC; Eluent: Petroleum ether /EtOAc 90:10; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.40 (s, 3H), 7.26 (d, *J* = 8 Hz, 2H), 7.29 (d, *J* = 7.0 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.50-7.54 (m, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.78 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.3, 116.4, 119.8, 124.4, 127.8, 128.4, 129.2, 131.2, 131.8, 138.9, 139.1, 139.2, 153.4, 160.7;

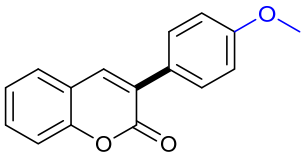
IR 752.1, 819.6, 1111, 1608, 1716, 2918, 3033 cm^{-1}. Anal. Calcd for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: C, 81.63; H, 5.25.

3-(4-Fluorophenyl)-2*H*-chromen-2-one 5c



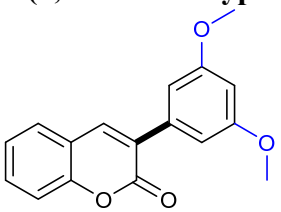
White solid; Yield 30% (36 mg); mp 191-194 ºC; Eluent: Petroleum ether /EtOAc 90:10; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13 (t, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 7.0 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.52-7.55 (m, 2H), 7.71-7.73 (m, 2H), 7.79 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.1(d, J_{C-F} = 247.8 Hz), 160.5, 153.4, 139.7, 131.5, 130.7, 130.4 (d, J_{C-F} = 8.1 Hz), 127.9, 127.3, 124.6, 119.5, 116.5, 115.5 (d, J_{C-F} = 3.1 Hz); IR 746.3, 823.5, 1232, 1512, 1604, 1712, 3053 cm^{-1}. Anal. Calcd for $C_{15}H_9FO_2$: C, 75.00; H, 3.78. Found: C, 75.26; H, 3.88.

3-(4-Methoxyphenyl)-2*H*-chromen-2-one 5d



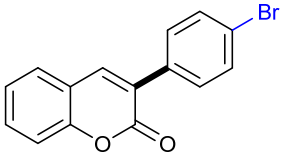
yellow solid; Yield = 50% (63 mg); m.p. = 138 ºC; Eluent: Petroleum ether /EtOAc 80:20; ^{1}H NMR (500 MHz, DMSO) δ 3.78 (s, 3H), 7.00 (d, *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 7 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.60 (t, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 1H), 8.19 (s, 1H); ^{13}C NMR (125 MHz, DMSO) δ 55.2, 113.6, 115.8, 119.6, 124.6, 126.4, 126.8, 128.4, 129.8, 131.2, 139.1, 152.7, 159.6, 159.8; IR 757.9, 1254, 1450, 1512, 1608, 1724, 2945, 3062 cm^{-1}. Anal. Calcd for $C_{16}H_{12}O_3$: C, 76.18; H, 4.79. Found: C, 75.90; H, 4.66.

3-(3,5-Dimethoxyphenyl)-2*H*-chromen-2-one 5e



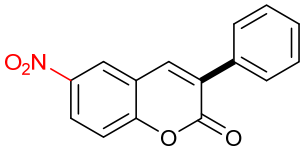
Yellow solid; Yield 40% (56 mg); mp 161-165 ºC; Eluent: Petroleum ether /EtOAc 70:30; ^{1}H NMR (500 MHz, DMSO) δ 3.92 (s, 3H), 3.94 (s, 3H), 6.93 (d, *J* = 8.0 Hz, 1H), 7.27-7.31 (m, 3H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.49-7.54 (m, 2H), 7.78 (s, 1H); ^{13}C NMR (125 MHz, DMSO) δ 55.9, 56.0, 111.0, 111.8, 116.3, 119.7, 121.2, 124.4, 127.4, 127.7, 131.0, 138.6, 138.7, 148.7, 149.7, 153.2, 160.6; IR 763.7, 1022, 1254, 1516, 1606, 1711, 2931, 3078 cm^{-1}. Anal. Calcd for $C_{17}H_{14}O_4$: C, 72.33; H, 5.00. Found: C, 72.60; H, 5.11.

3-(4-Bromophenyl)-2*H*-chromen-2-one 5f



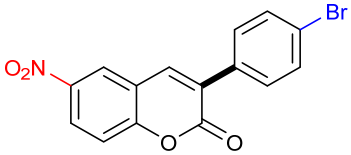
White solid; Yield 80% (120 mg); mp 190-194 ºC; Eluent: Petroleum ether /EtOAc 90:10; ^{1}H NMR (500 MHz, DMSO) δ 7.41-7.44 (m, 2H), 7.46-7.50 (m, 2H), 7.71 (d, *J* = 7.0 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 1H), 8.02 (s, 1H), 8.21 (s, 1H); ^{13}C NMR (125 MHz, DMSO) δ 116.5, 119.5, 123.2, 124.6, 127.2, 127.9, 130.1, 131.7, 133.5, 139.9, 153.6, 160.2 ; IR 725.1, 817.7, 954.6, 1606, 1716 cm^{-1}. Anal. Calcd for $C_{15}H_9BrO_2$: C, 59.83; H, 3.01. Found: C, 60.12; H, 3.14.

6-Nitro-3-phenyl-2*H*-chromen-2-one 5g



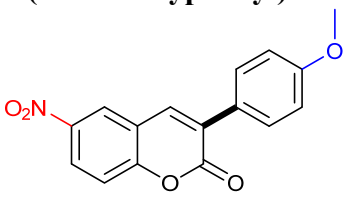
White solid; Yield 50% (67 mg); mp 261-264 ºC; Eluent: Petroleum ether /EtOAc 70:30; ^{1}H NMR (500 MHz, DMSO) δ 7.47-7.52 (m, 3H), 7.66 (d, *J* = 9.0 Hz, 1H), 7.73 (d, *J* = 7.5 Hz, 2H), 8.41 (s, 1H), 8.43 (s, 1H), 8.75 (s, 1H); ^{13}C NMR (125 MHz, DMSO) δ 117.4, 119.9, 124.3, 126.0, 128.2, 128.5, 128.9, 129.2, 133.9, 139.2, 143.6, 156.5, 158.7; IR 825.4, 952.7, 1105, 1344, 1523, 1614, 1728, 3060 cm^{-1}. Anal. Calcd for $C_{15}H_9NO_4$: C, 67.42; H, 3.39; N, 5.24. Found: C, 67.73; H, 3.55; N, 5.43.

3-(4-Bromophenyl)-6-nitro-2*H*-chromen-2-one 5h



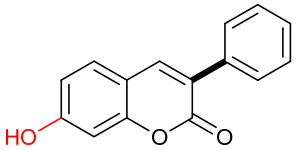
Yellow solid; Yield 75% (130 mg); mp 209-212 ºC; Eluent: Petroleum ether /EtOAc 70:30; ^{1}H NMR (500 MHz, DMSO) δ 7.63-7.64 (m, 5H), 8.38-8.39 (m, 2H), 8.66 (s, 1H); ^{13}C NMR (125 MHz, DMSO) δ 117.9, 120.1, 123.0, 124.8, 126.7, 127.9, 130.9, 131.8, 133.5, 139.9, 144.0, 157.0, 158.9; IR 744.4, 825.4, 941.1, 1103, 1352, 1533, 1614, 1741 cm^{-1}. Anal. Calcd for $C_{15}H_8BrNO_4$: C, 52.05; H, 2.33; N, 4.05. Found: C, 52.32; H, 2.45; N, 4.23.

3-(4-Methoxyphenyl)-6-nitro-2*H*-chromen-2-one 5i



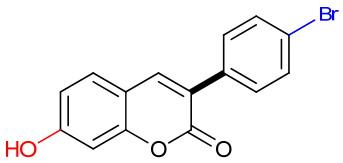
Yellow solid; Yield 70% (103 mg); mp 229-232 ºC; Petroleum ether /EtOAc 70:30; ^{1}H NMR (500 MHz, DMSO) δ 3.78 (s, 3H), 7.02-7.03 (m, 2H), 7.66-7.67 (m, 3H), 8.32-8.33 (m, 2H), 8.68 (s, 1H). ^{13}C NMR (125 MHz, DMSO) δ 55.7, 114.3, 114.4, 117.7, 124.5, 126.2, 126.3, 126.5, 130.3, 130.6, 138.2, 138.3, 144.1, 160.5; IR 746.3, 825.4, 1097, 1254, 1348, 1522, 1610, 1749 cm^{-1}. Anal. Calcd for $C_{16}H_{11}NO_5$: C, 64.65; H, 3.73; N, 4.71. Found: C, 64.31; H, 3.60; N, 4.49.

7-Hydroxy-3-phenyl-2*H*-chromen-2-one 5j



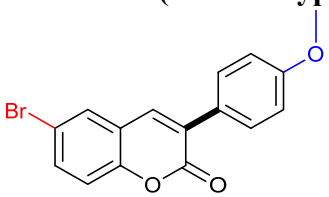
Yellow solid; Yield 83% (99 mg); mp 188-190 °C; Eluent: Petroleum ether /EtOAc 70:30; ^{1}H NMR (500 MHz, DMSO) δ 6.75 (s, 1H), 6.82 (d, *J* = 8.5 Hz, 1H), 7.37 (d, *J* = 6.5 Hz, 1H), 7.43 (t, *J* = 7.0 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 7.0 Hz, 2H), 8.12 (s, 1H), 10.61 (bs, 1H); ^{13}C NMR (100 MHz, DMSO) δ 101.9, 111.9, 113.6, 122.2, 128.0, 128.1, 128.3, 130.0, 135.1, 141.1, 154.9, 160.1, 161.3; IR 825, 1105, 1244, 1344, 1523, 1614, 1728, 3060 cm^{-1}. Anal. Calcd for $C_{15}H_{10}O_3$: C, 75.62; H, 4.23. Found: C, 75.25; H, 4.21.

3-(4-bromophenyl)-7-hydroxy-2H-chromen-2-one 5k



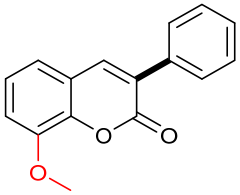
White solid; Yield = 20% (32 mg); m.p. = 273-275 °C; Eluent: Petroleum ether /EtOAc, 70:30; ^{1}H NMR (500 MHz, DMSO) δ 6.74 (s, 1H), 6.82 (d, *J* = 8.5 Hz, 1H), 7.58-7.67 (m, 5H), 8.18 (s, 1H), 10.65 (bs, 1H); ^{13}C NMR (125 MHz, DMSO) δ 101.7, 111.9, 113.5, 120.8, 121.2, 130.1, 130.3, 131.1, 134.3, 141.4, 155.0, 159.8, 161.5; IR 825, 1105, 1244, 1344, 1523, 1614, 1728, 3060 cm^{-1}. Anal. Calcd for $C_{15}H_9BrO_3$: C, 56.81; H, 2.86. Found: C, 56.51; H, 2.72.

6-Bromo-3-(4-methoxyphenyl)-2*H*-chromen-2-one 5l



White solid; Yield 88% (146 mg); mp 200-204 ºC; Eluent: Petroleum ether /EtOAc 80:20; ^{1}H NMR (500 MHz, DMSO) δ 3.80 (s, 3H), 7.02 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.7 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 8.7 Hz, 1H), 7.97 (s, 1H), 8.1 (s, 1H). ^{13}C NMR (125 MHz, DMSO) δ 55.2, 1143.7, 116.0, 118.0, 12.5, 126.4, 127.4, 129.8, 130.2, 133.5, 137.5, 151.7, 159.3, 159.8; IR 815.7, 960.4, 1032, 1122, 1255, 1417, 1512, 1610, 1722, 3423 cm^{-1}. Anal. Calcd for $C_{16}H_{11}BrO_3$: C, 58.03; H, 3.35. Found: C, 58.29; H, 3.48.

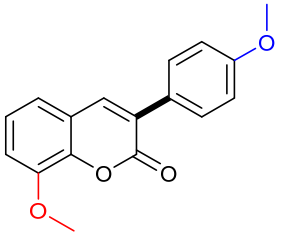
8-Methoxy-3-phenyl-2*H*-chromen-2-one 5m



White solid; Yield 60% (76 mg); mp 154-156 °C; Eluent: Petroleum ether /EtOAc 90:10; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.97 (s, 3H), 7.07 (d, *J* = 7.8 Hz, 1H), 7.10 (d, *J* = 7.4 Hz, 1H), 7.19-7.22

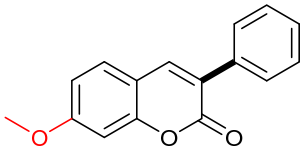
(m, 1H), 7.37-7.44 (m, 3H), 7.70 (d, J = 7.3 Hz, 2H), 7.78 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.2, 113.3, 119.3, 120.3, 124.3, 128.4, 128.5, 128.8, 134.6, 139.8, 139.9, 143.2, 147.0, 159.9; IR 702, 784.9, 935.3, 1101, 1286, 1356, 1475, 1576, 1728 cm^{-1}. Anal. Calcd for $C_{16}H_{12}O_3$: C, 76.18; H, 4.79. Found: C, 76.49; H, 4.95.

8-Methoxy-3-(4-methoxyphenyl)-2*H*-chromen-2-one 5n



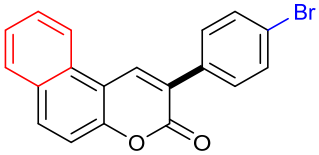
Yellow solid; Yield 60% (85 mg); mp 156-160 °C; Eluent: Petroleum ether /EtOAc 70:30; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.85 (s, 3H), 3.98 (s, 3H), 6.96 (d, J = 8.0 Hz, 2H), 7.05 (d, J = 8.0 Hz, 1H), 7.09 (d, J = 8.0 Hz, 1H), 7.20 (t, J = 8.0 Hz, 1H), 7.68 (d, J = 8.8 Hz, 2H), 7.73 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.3, 56.2, 112.9, 113.9, 119.2, 120.5, 124.2, 127.1, 128.1, 129.8, 138.4, 138.5, 142.8, 147.0, 160.2; IR 729, 838.9, 931.5, 1095, 1184, 1277, 1514, 1606, 1707, 2947, 3404 cm^{-1}. Anal. Calcd for $C_{17}H_{14}O_4$: C, 72.33; H, 5.00. Found: C, 72.08; H, 4.90.

7-Methoxy-3-phenyl-2*H*-chromen-2-one 5o



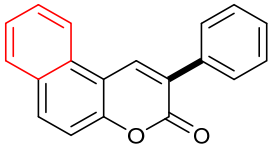
Yellow solid; Yield 85% (107 mg); mp 112-116 °C; Eluent: Petroleum ether /EtOAc 70:30; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.88 (s, 3H), 6.86 (s, 1H), 6.88 (s, 1H), 7.38 (d, J = 7.0 Hz, 1H), 7.42-7.45 (m, 3H), 7.69 (d, J = 7.0 Hz, 2H), 7.76 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.8, 100.4, 112.8, 113.4, 124.8, 128.4, 128.8, 135.0, 140.0, 155.3, 160.8, 162.6; IR 688.5, 779.1, 983.5, 1032, 1269, 1360, 1441, 1502, 1618, 1728, 3055 cm^{-1}. Anal. Calcd for $C_{16}H_{12}O_3$: C, 76.18; H, 4.79. Found: C, 76.40; H, 4.91.

2-(4-Bromophenyl)-3*H*-benzo[f]chromen-3-one 5p



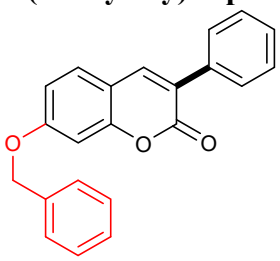
White solid; Yield 80% (140 mg); mp 278-280 ºC; Eluent: Petroleum ether /EtOAc 90:10; ^{1}H NMR (500 MHz, DMSO) δ 7.54-7.62 (m, 2H), 7.65-7.74 (m, 3H), 7.85 (d, J = 9.0 Hz, 2H), 8.03 (d, J = 7.8 Hz, 1H), 8.17 (d, J = 9.0 Hz, 1H), 8.70 (d, J = 8.2 Hz, 1H), 9.00 (s, 1H); ^{13}C NMR (125 MHz, DMSO) δ 113.4, 116.4, 121.9, 122.7, 124.8, 128.2, 128.8, 128.9, 129.9, 130.9, 131.1, 133.2, 133.9, 136.6, 137.0, 152.7, 159.5. IR 813, 1109, 1209, 1344, 1483, 1574, 1712, 2966, 3053 cm^{-1}. Anal. Calcd for $C_{19}H_{11}BrO_2$: C, 64.98; H, 3.16. Found: C, 65.23; H, 3.28.

2-Phenyl-3*H*-benzo[f]chromen-3-one 5q



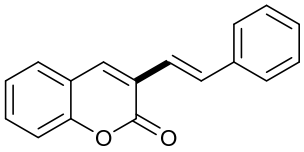
yellow solid; Yield = 70% (95 mg); m.p = 140-142 °C; Eluent: Petroleum ether /EtOAc 90:10; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43-7.49 (m, 4H), 7.55-7.58 (m, 1H), 7.68 (t, *J* = 7.0 Hz, 1H), 7.79 (d, *J* = 7.0 Hz, 2H), 7.91 (d, *J* = 7.0 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 8.28 (d, *J* = 8.0 Hz, 1H), 8.56 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 113.7, 116.7, 121.4, 126.0, 127.3, 128.2, 128.5, 128.9, 129.0, 129.1, 130.3, 132.7, 135.1, 135.7, 152.9, 160.6; IR 817.7, 952.7, 1101, 1215, 1568, 1718, 2927, 3066 cm^{-1}. Anal. Calcd for $C_{19}H_{12}O_2$: C, 83.81; H, 4.44. Found: C, 83.52; H, 4.29.

7-(Benzyloxy)-3-phenyl-2*H*-chromen-2-one 5r

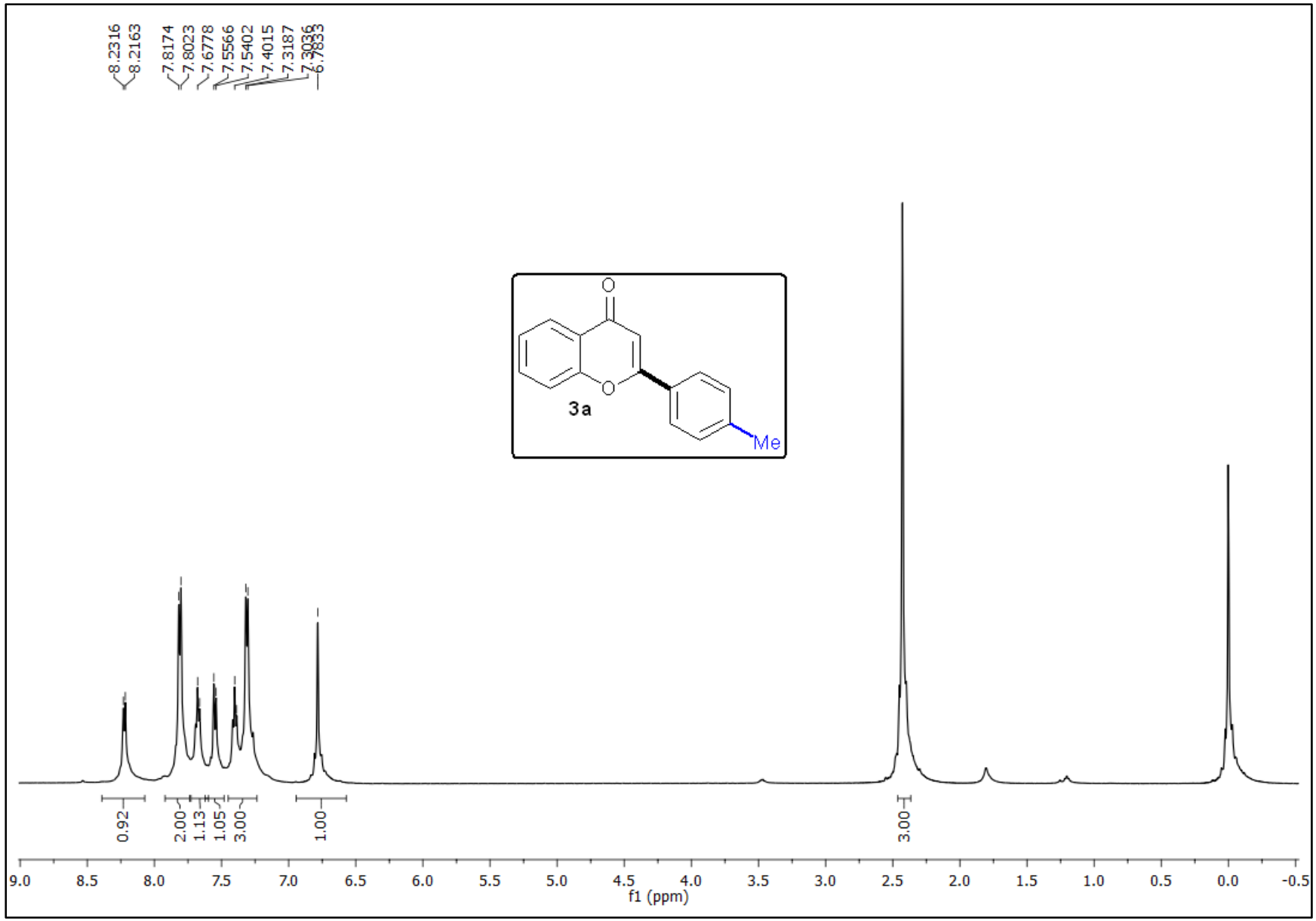


Yellow solid; Yield 58% (95 mg); mp 135-138 °C; Eluent: Petroleum ether /EtOAc 90:10; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.13 (s, 2H), 6.90-6.94 (m, 2H), 7.36-7.42 (m, 9H), 7.67 (d, *J* = 7.0 Hz, 2H), 7.73 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 70.5, 101.5, 113.4, 113.5, 125.0, 127.5, 128.3, 128.4, 128.7, 128.8, 135.0, 135.8, 139.9, 155.2, 160.8, 161.6; IR 694.3, 823.5, 997, 1122, 1169, 1265, 1358, 1500, 1612, 1714, 2931, 3032 cm^{-1}. Anal. Calcd for $C_{22}H_{16}O_3$: C, 80.47; H, 4.91. Found: C, 80.79; H, 5.06.

(E)-3-Styryl-2*H*-chromen-2-one 5s



Yellow solid; Yield 70% (87 mg); mp 159-162 ºC; Eluent: Petroleum ether /EtOAc 90:10; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (d, *J* = 16.5 Hz, 1H), 7.26-7.38 (m, 5H), 7.47-7.55 (m, 4H), 7.6 (d, *J* = 16.5 Hz, 1H), 7.8 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 116.5, 119.7, 122.0, 124.5, 125.0, 127.0, 127.6, 128.4, 128.7, 131.1, 133.7, 136.6, 136.8, 152.9, 160.6; IR 748.3, 973.9, 1063, 1448, 1603, 1714, 3030, cm^{-1}. Anal. Calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87. Found: C, 82.55; H, 5.02.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7.4015
7.3187
7.3036
6.7833
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2.00
1.13
1.05
3.00
1.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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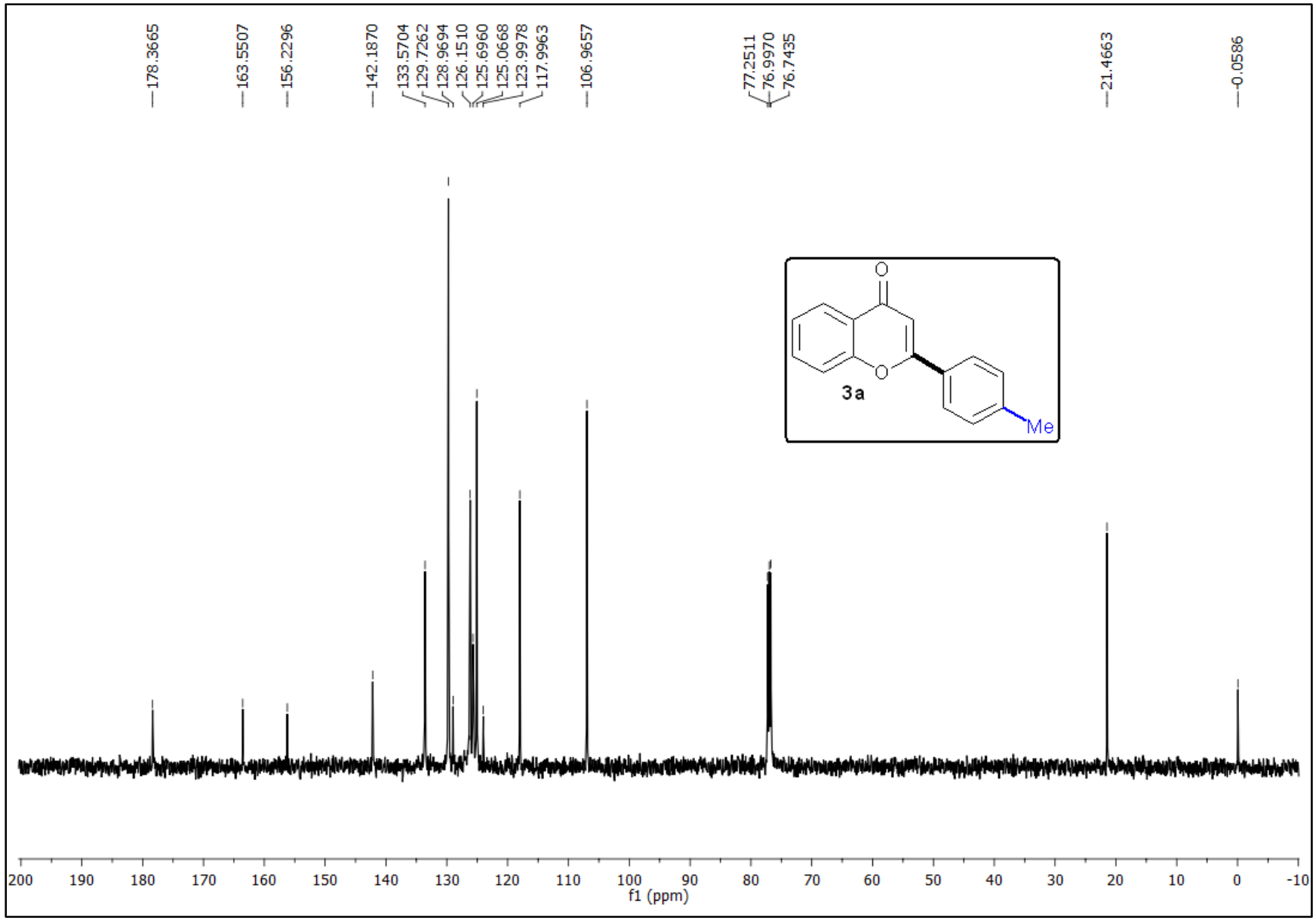
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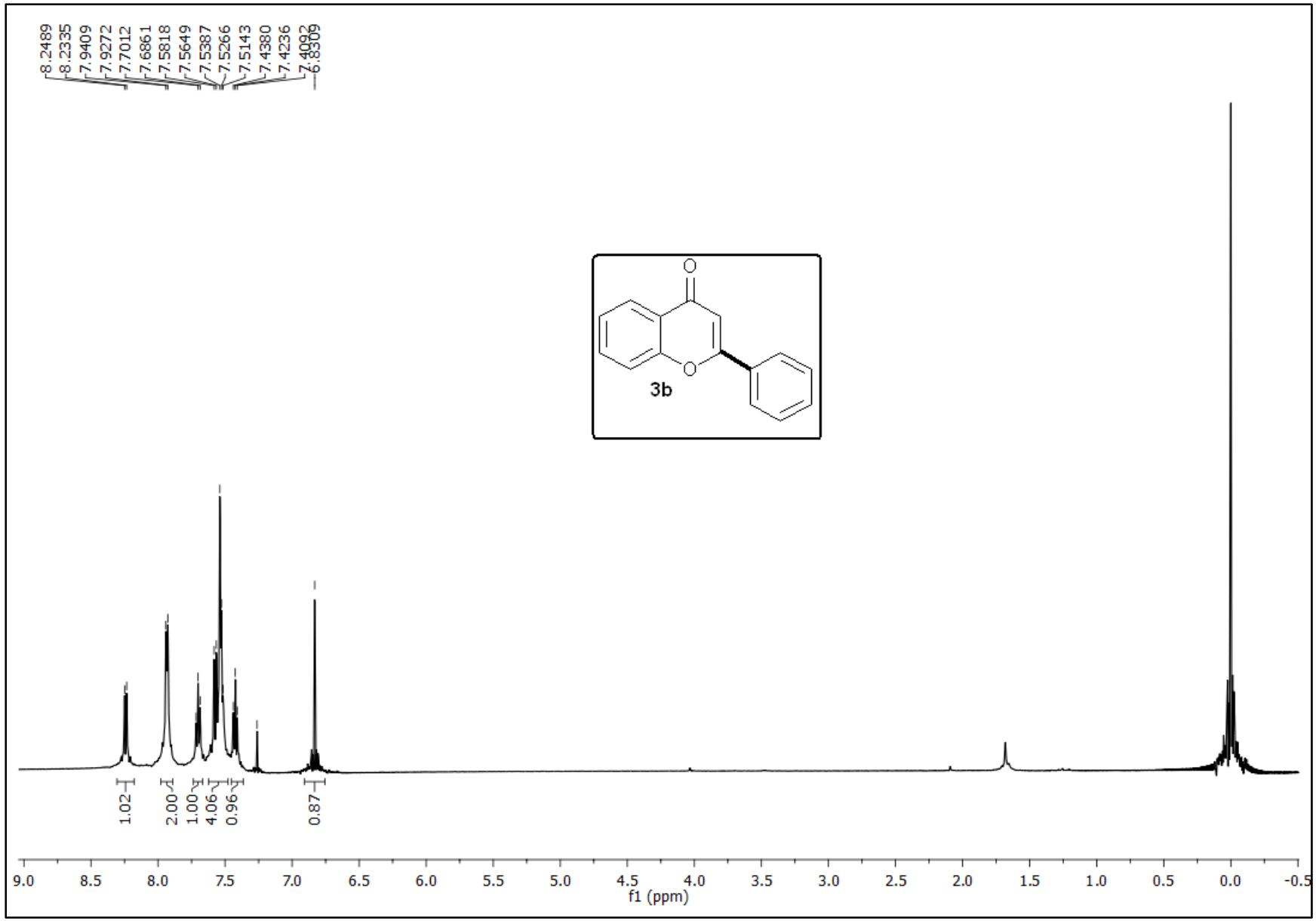
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7.4380
7.4236
7.4092
6.8309
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1.00
4.06
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8.0
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6.5
6.0
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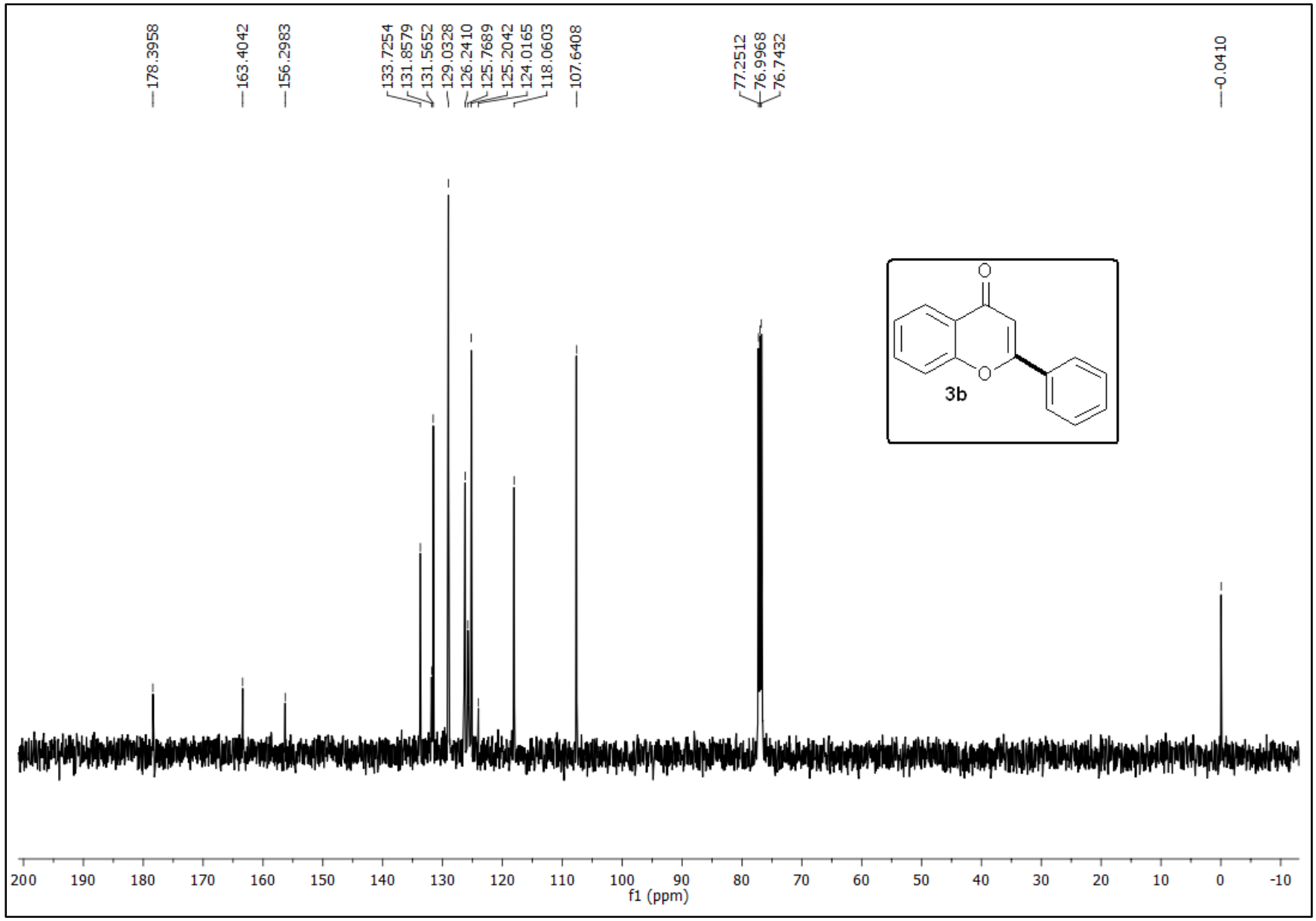
f1 (ppm)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76.9968
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3b
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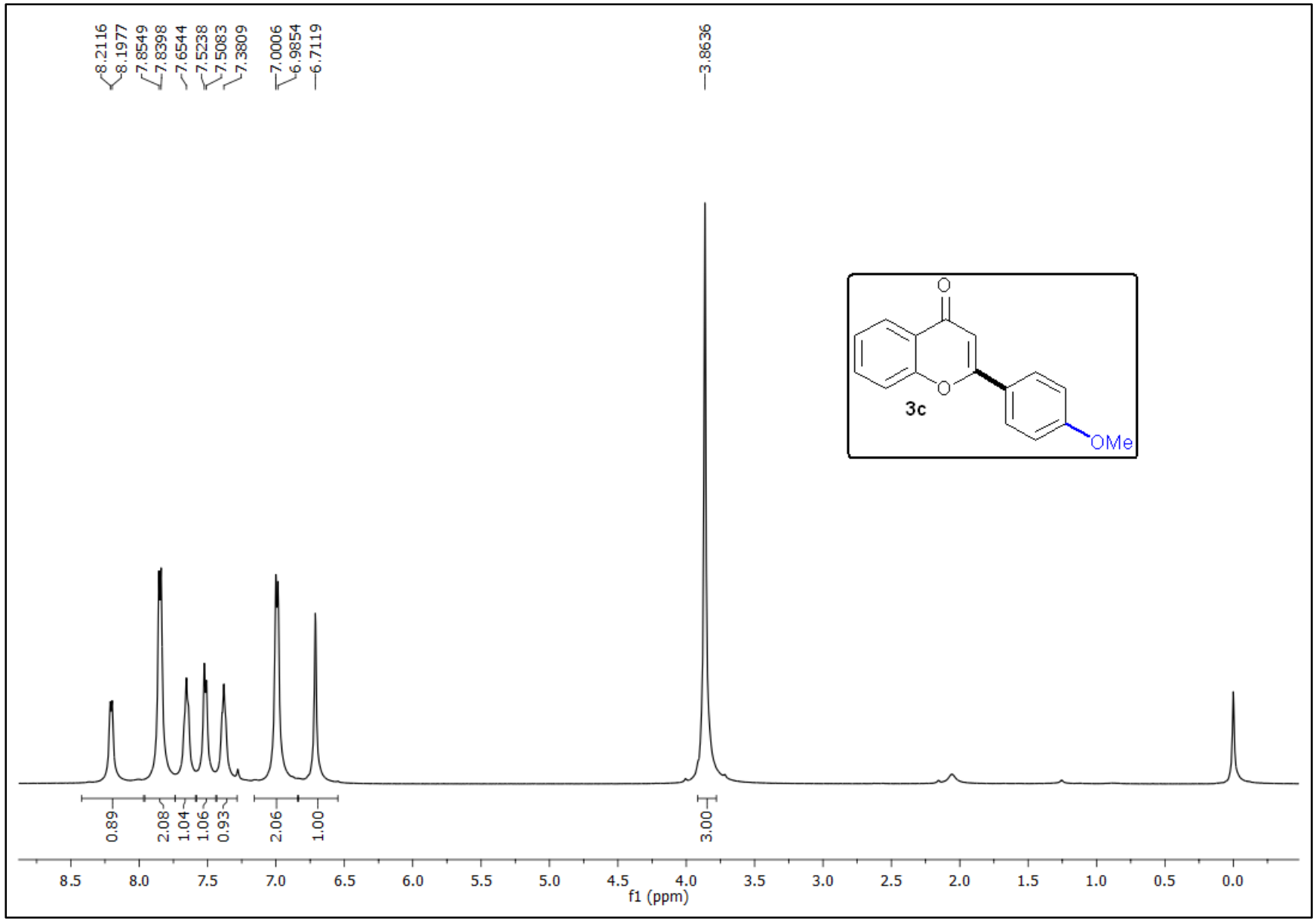
f1 (ppm)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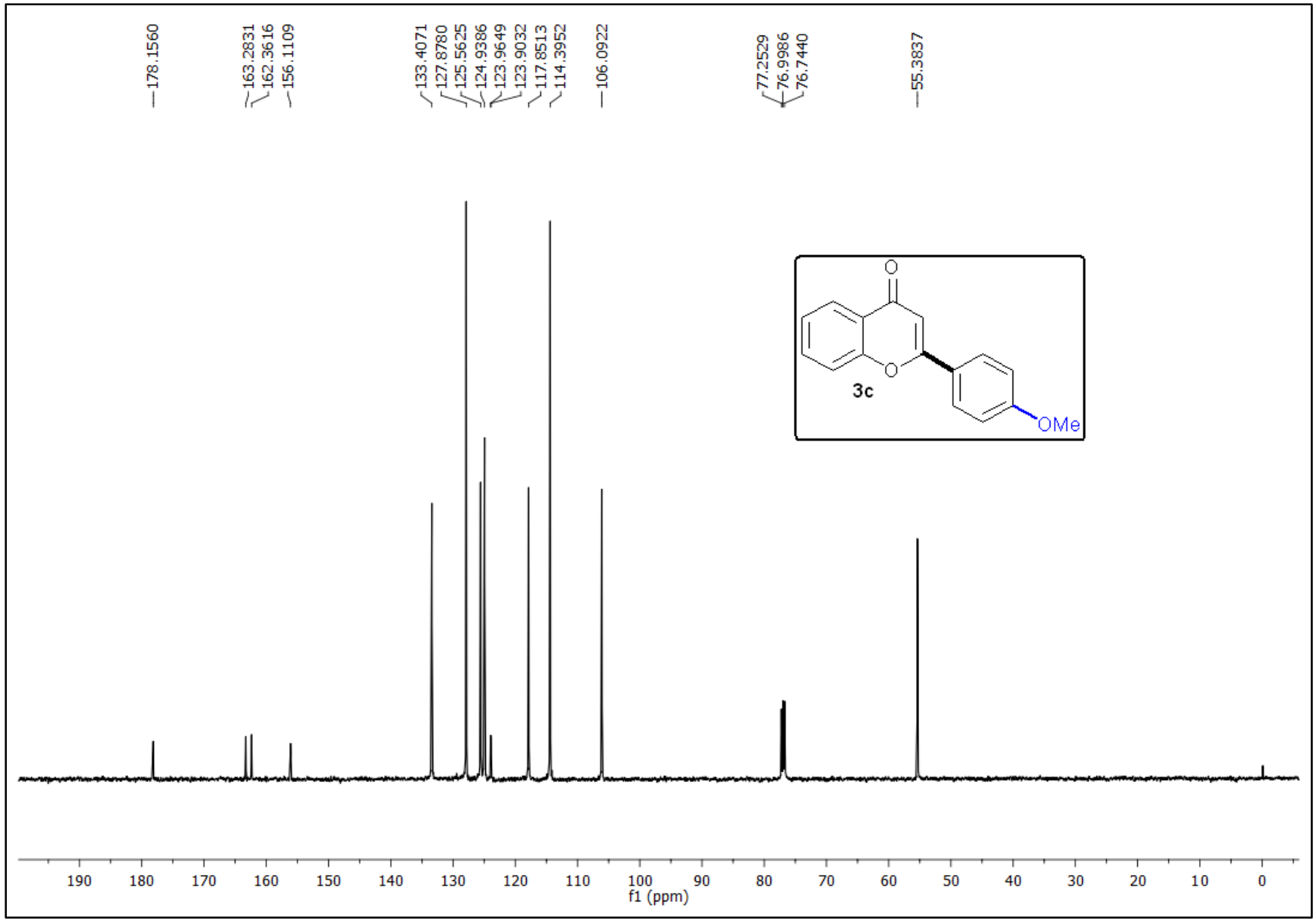
f1 (ppm)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3c
OMe
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180
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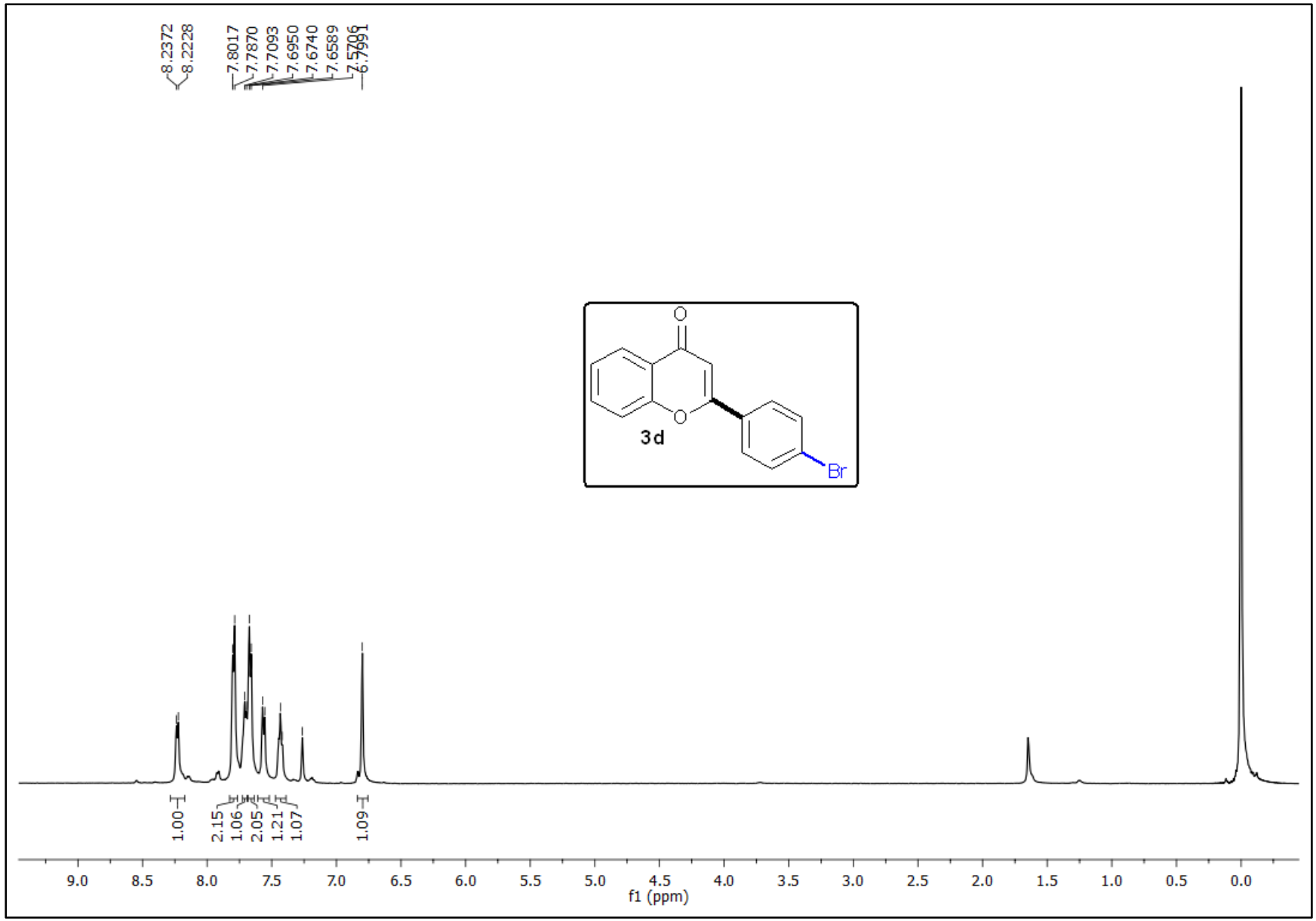
f1 (ppm)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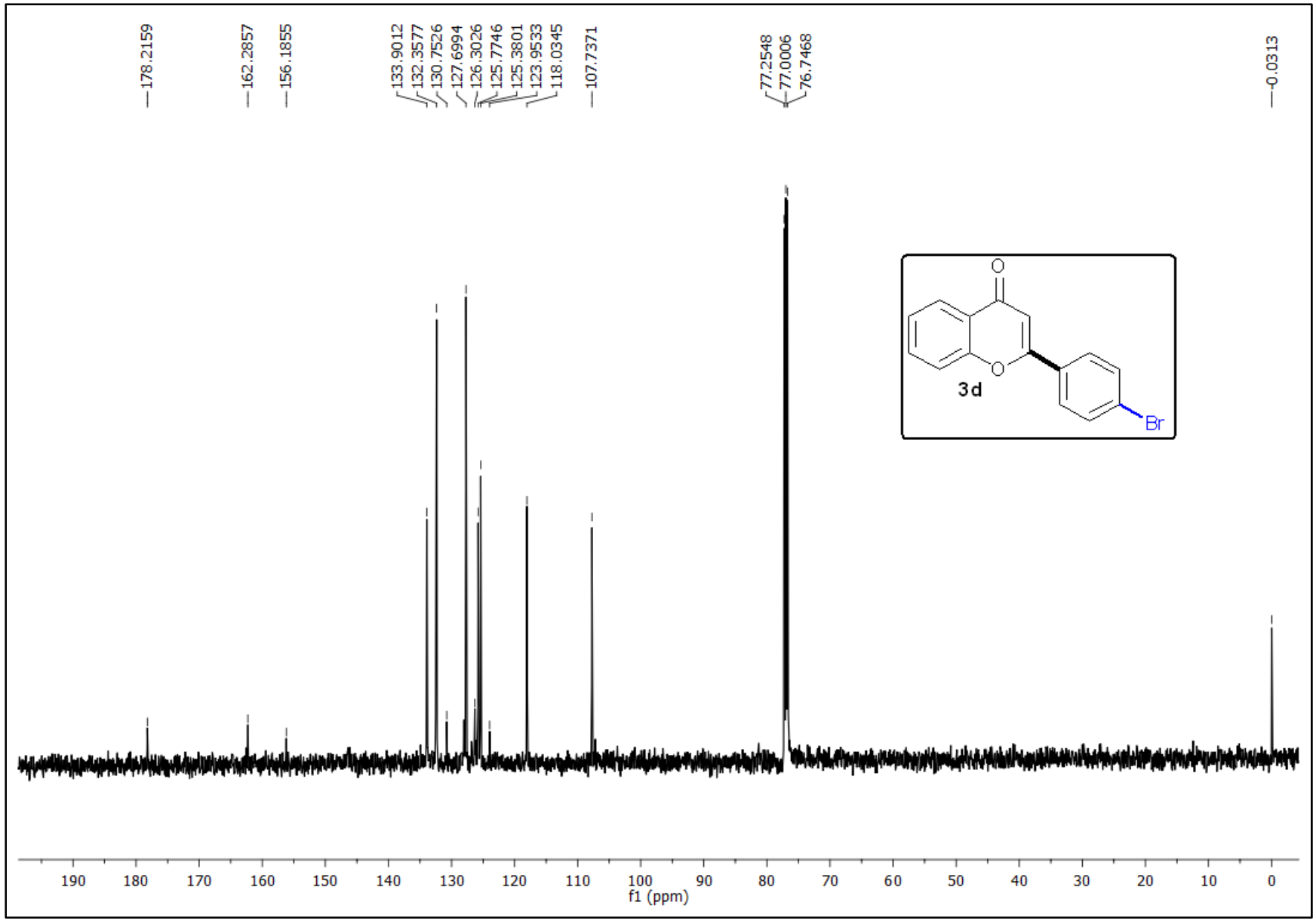
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O
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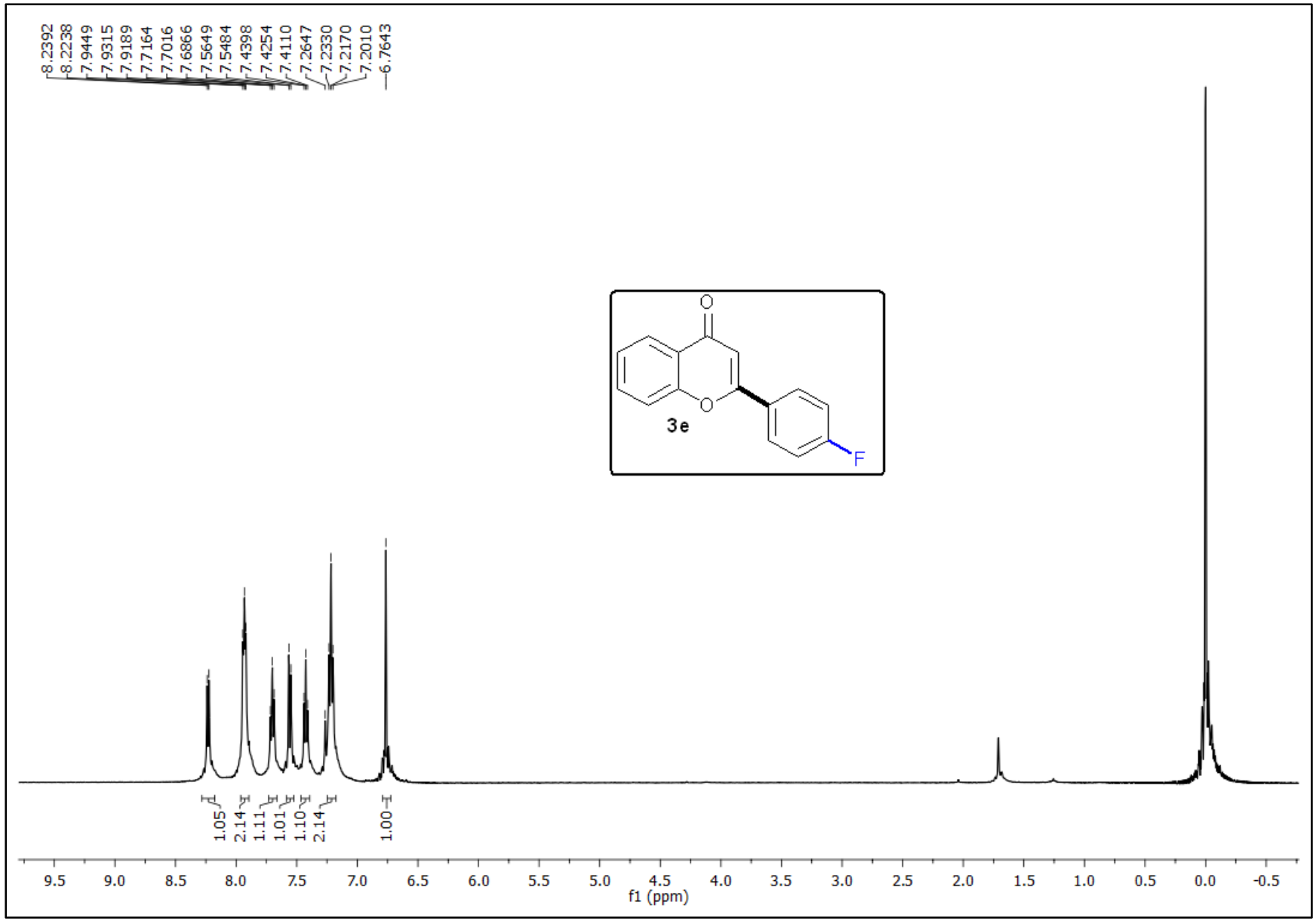
f1 (ppm)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1.01
1.10
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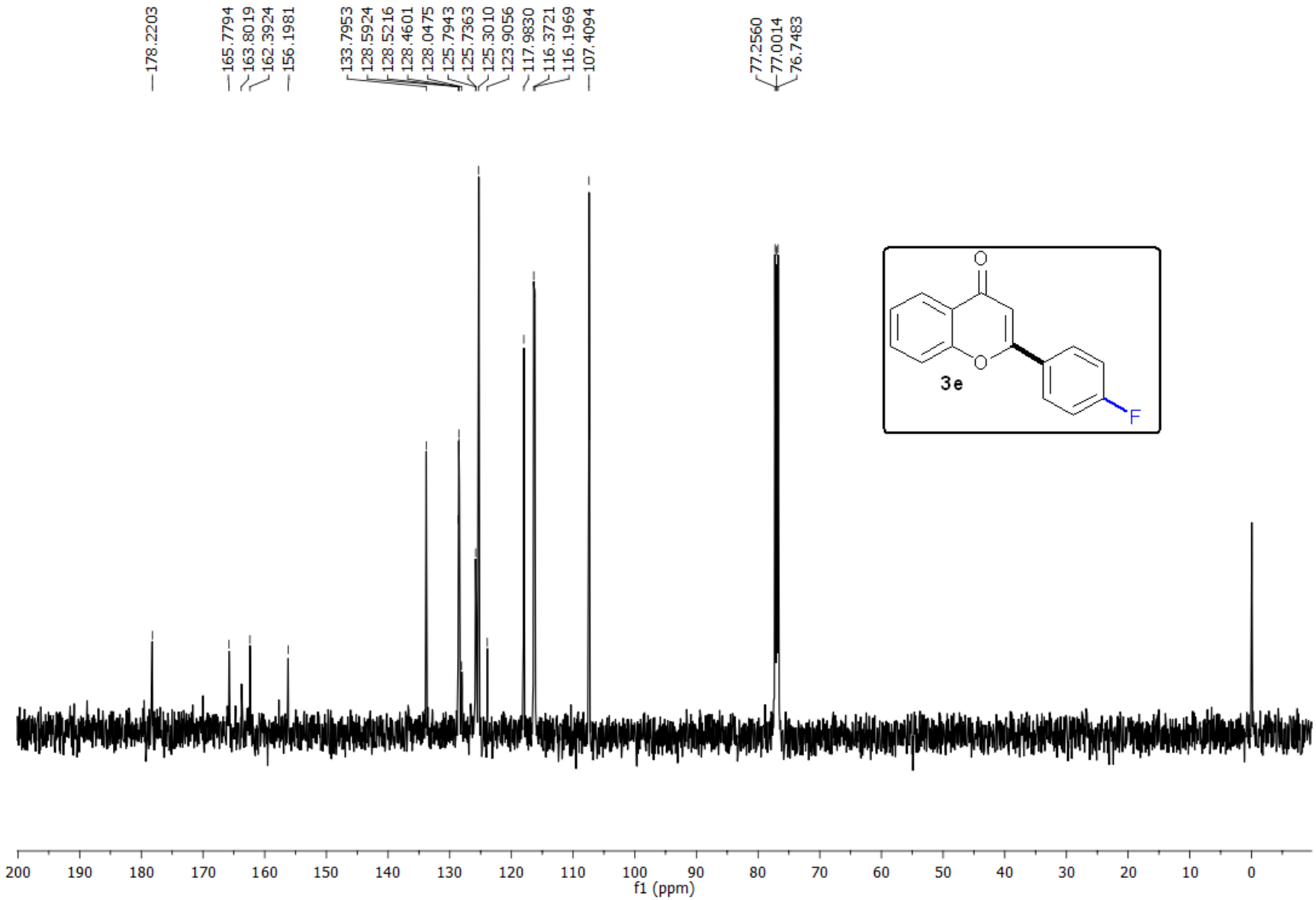
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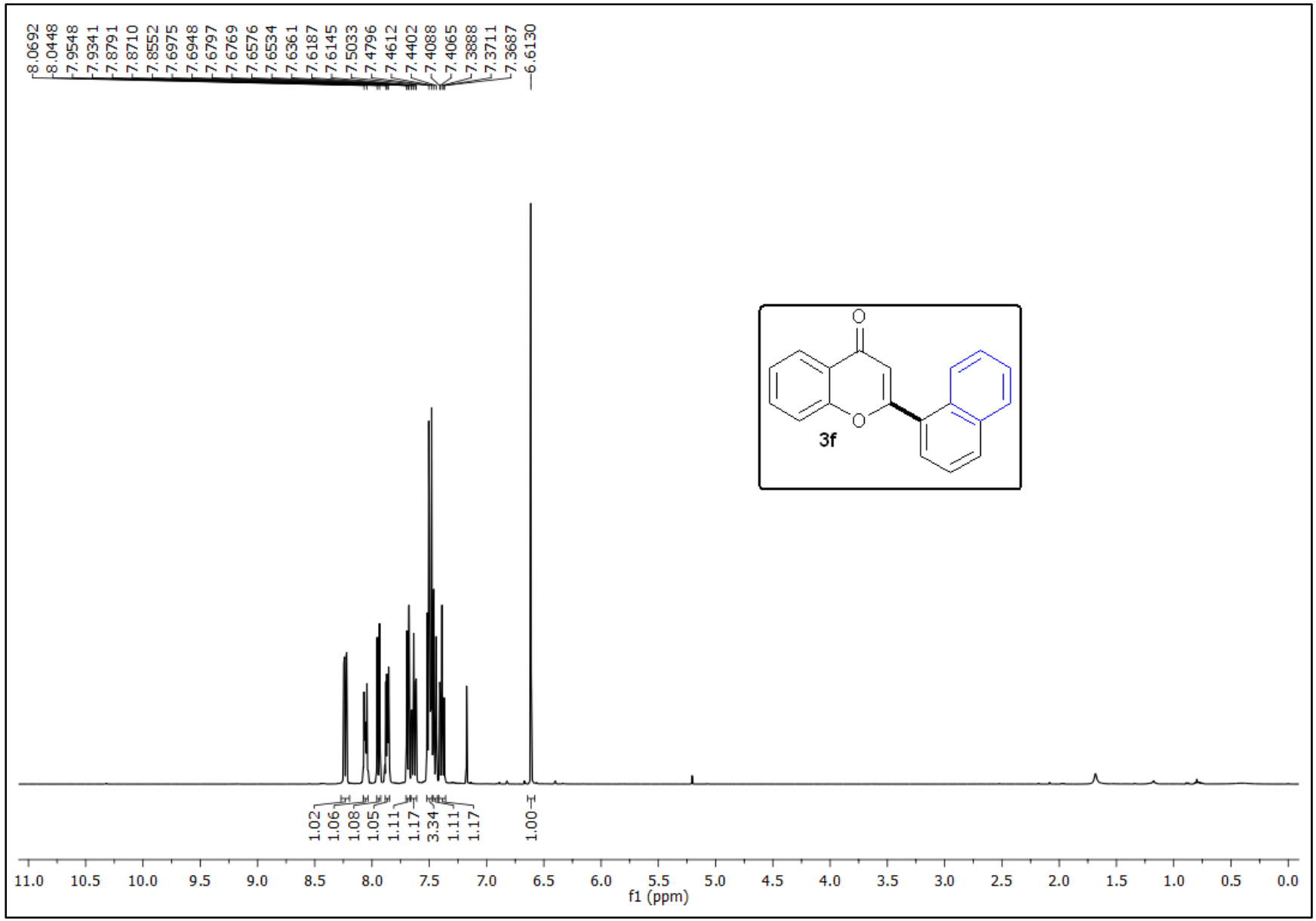
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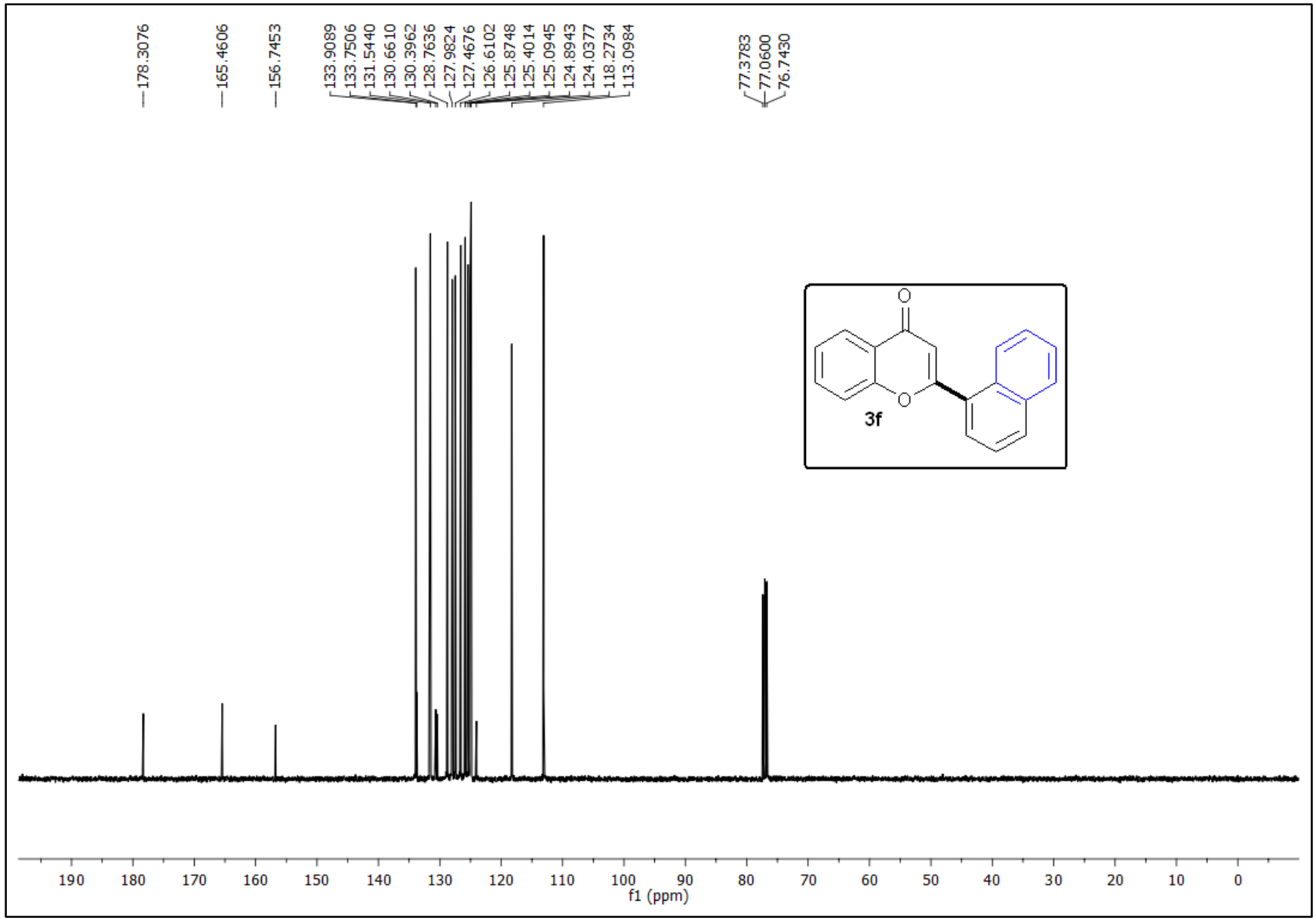
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3f
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180
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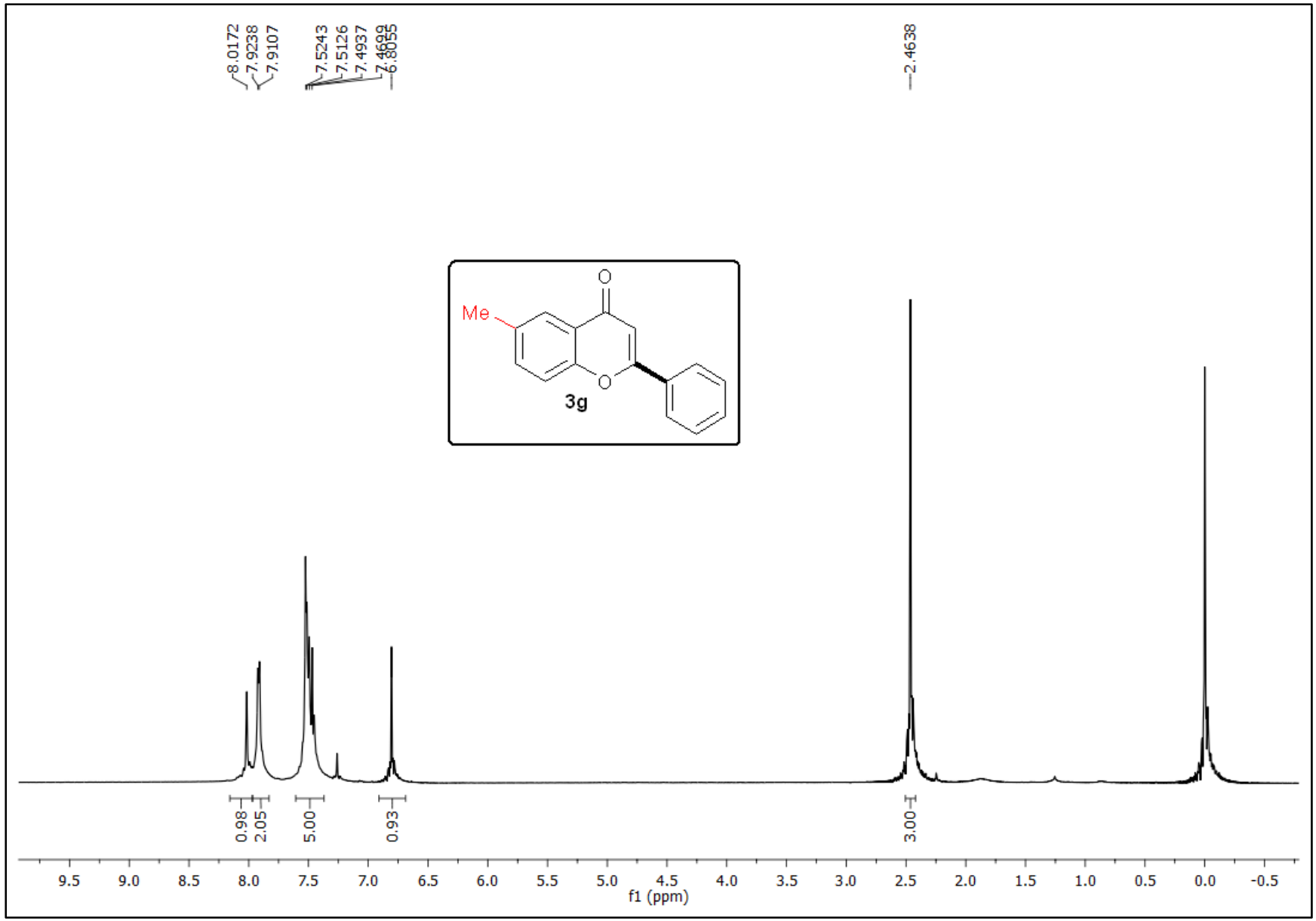
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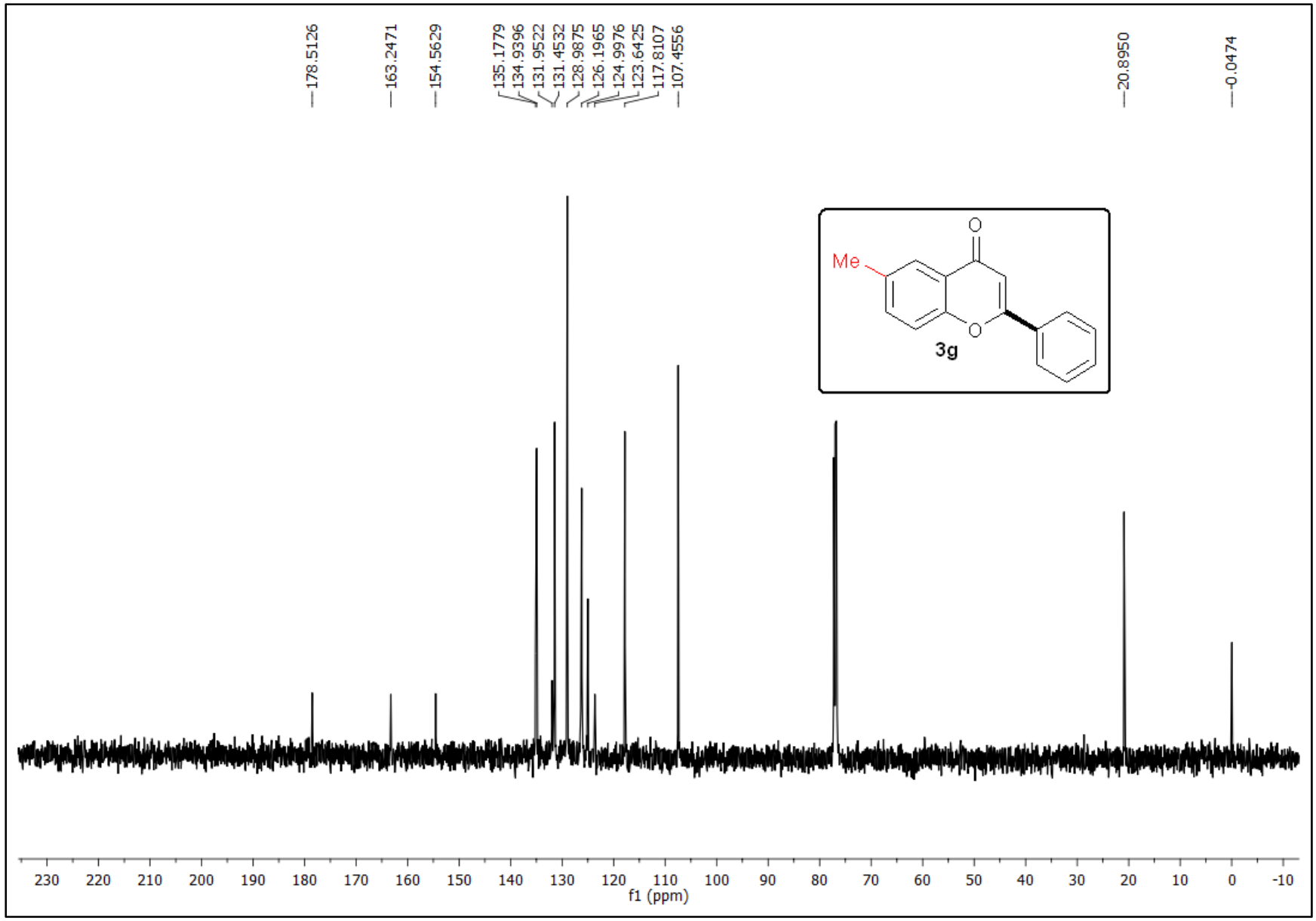
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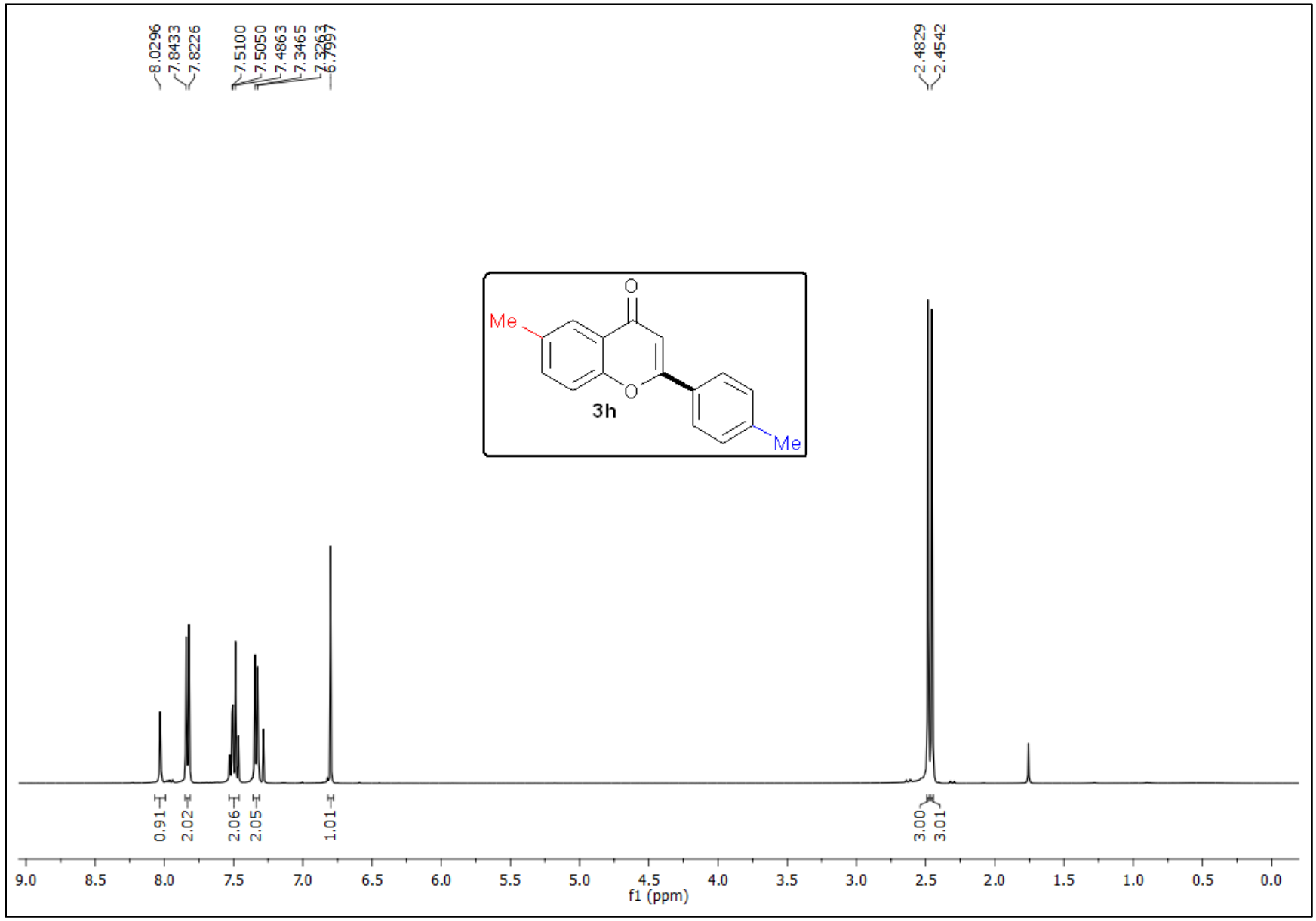
f1 (ppm)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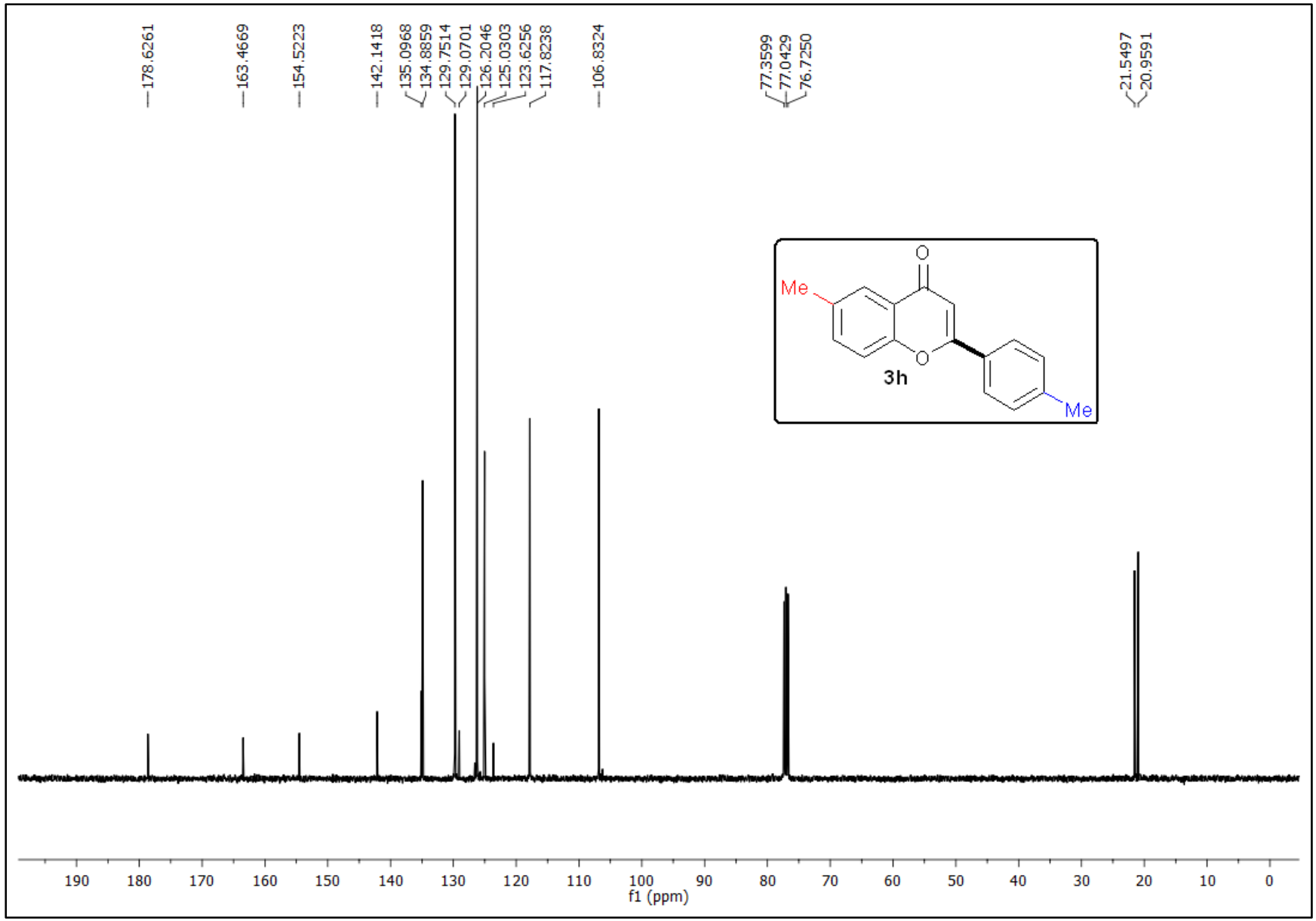
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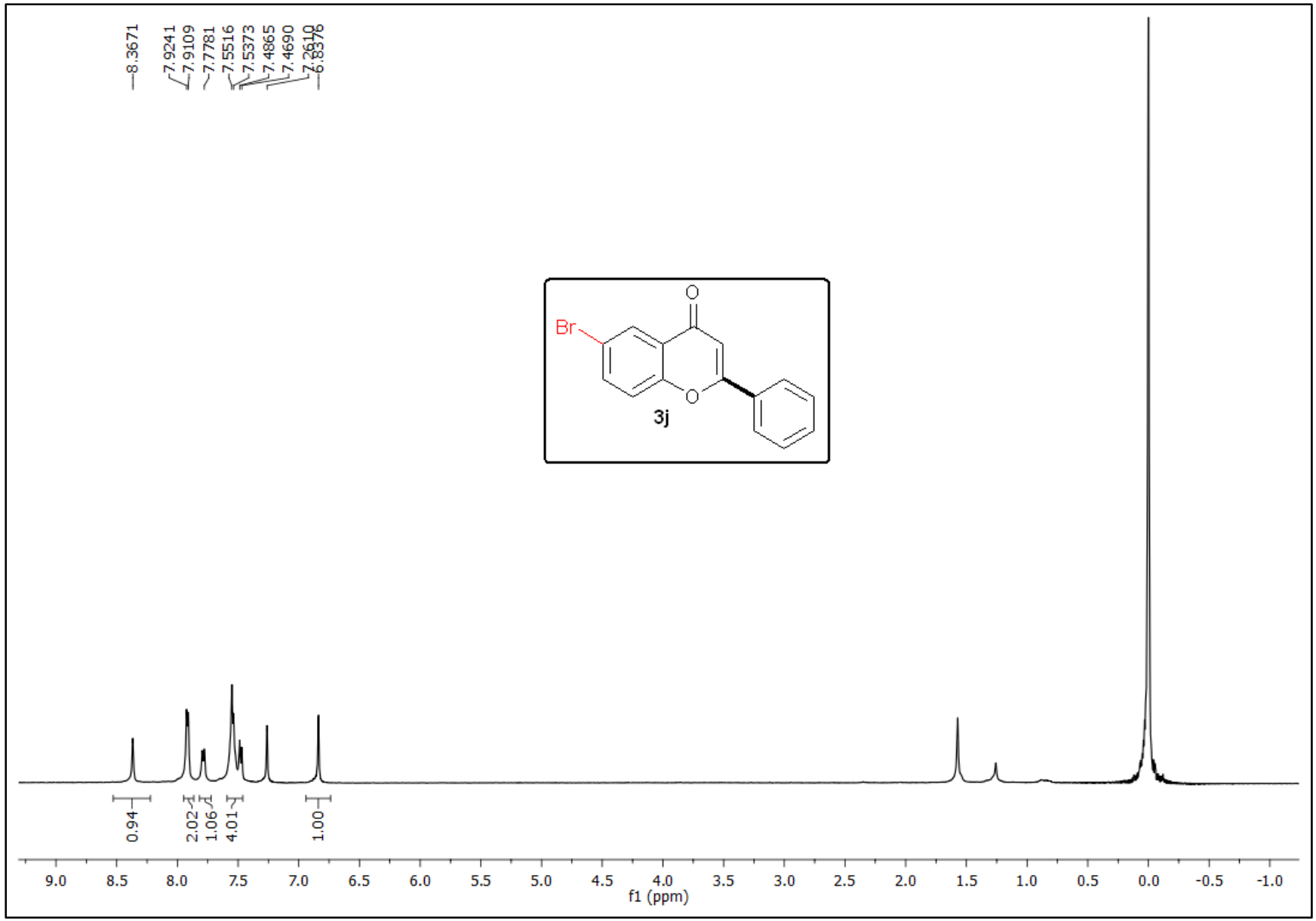
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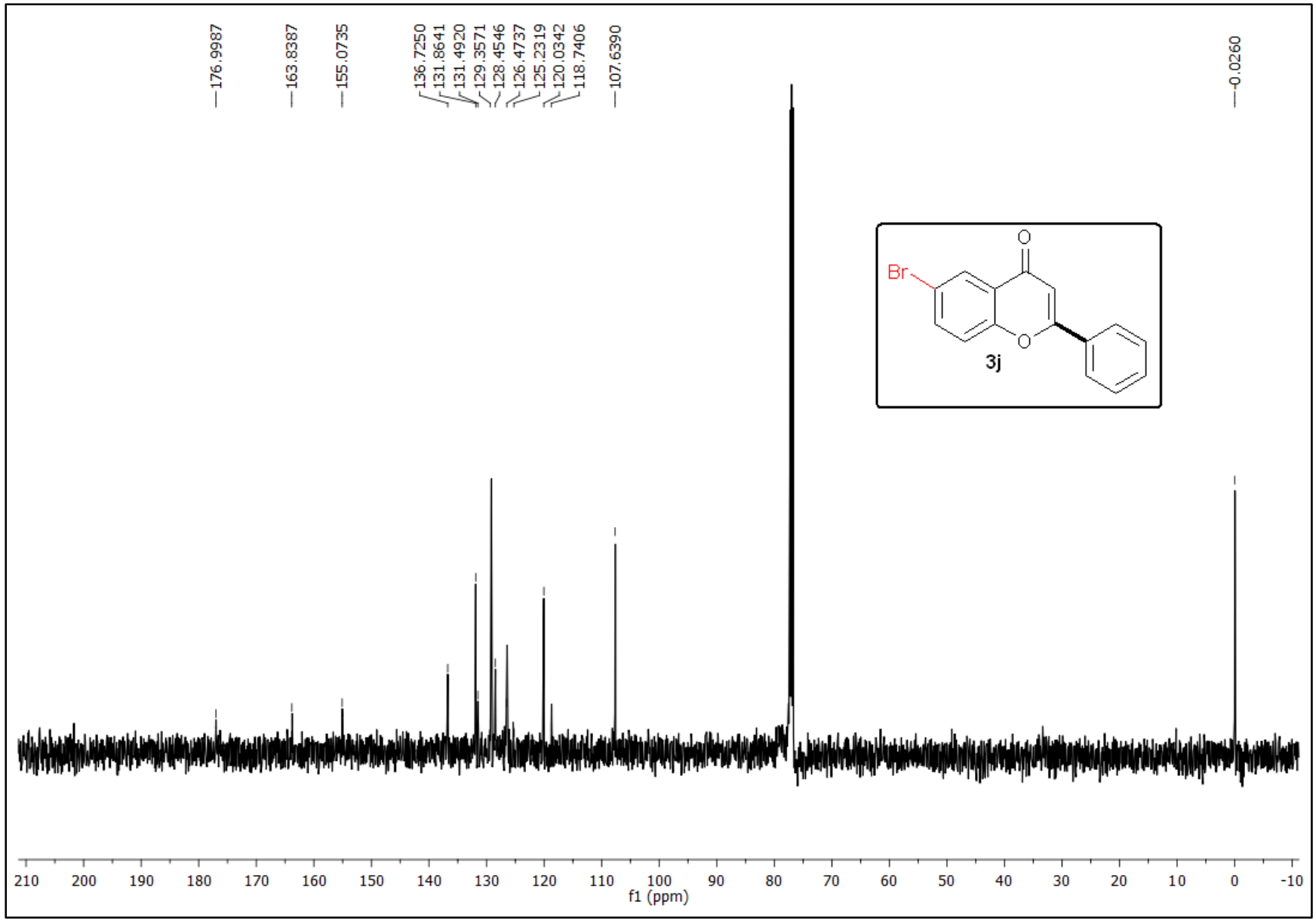
f1 (ppm)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180
170
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30
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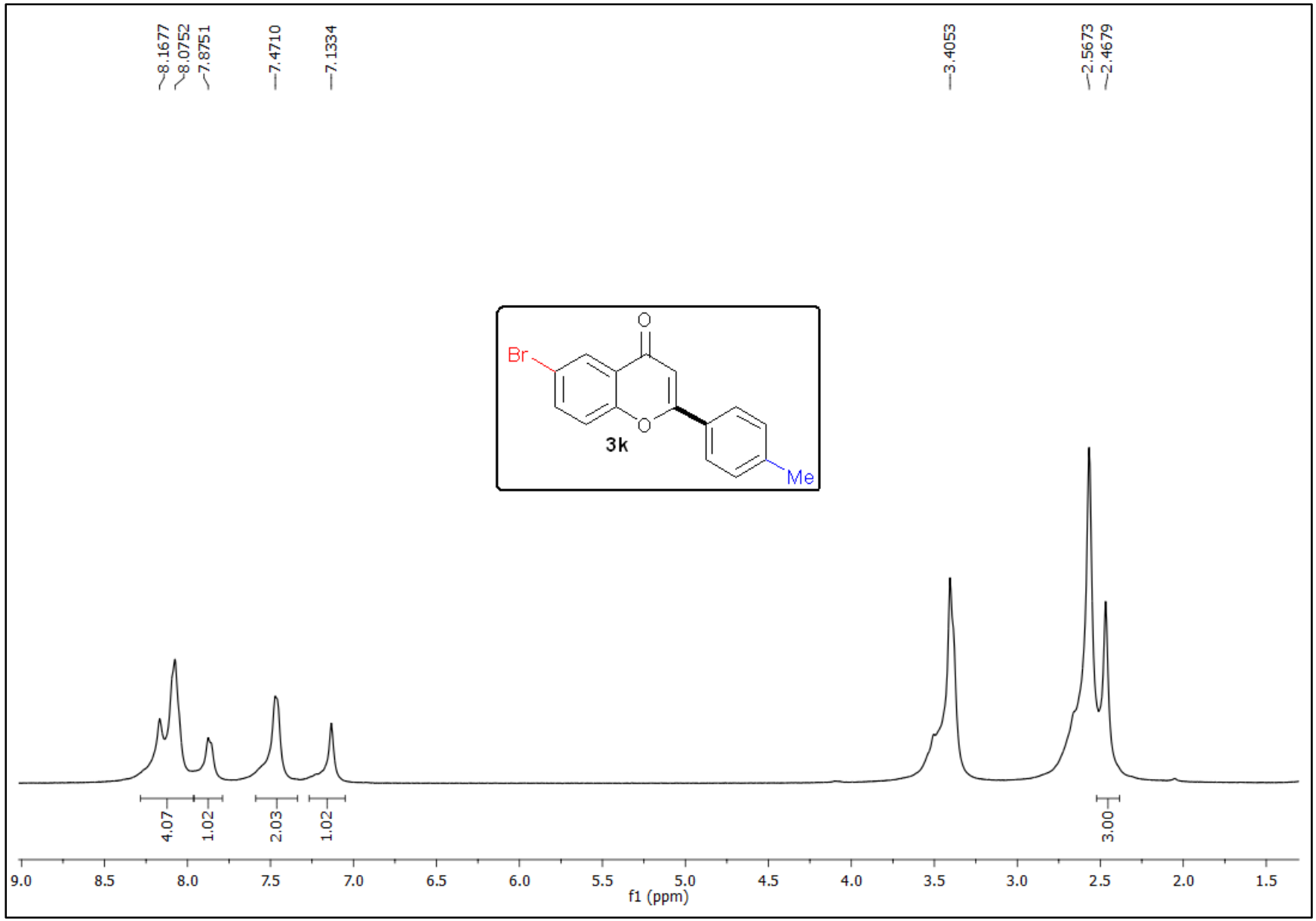
-10
f1 (ppm)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Br
O
O
3k
Me
4.07
1.02
2.03
1.02
3.00
9.0
8.5
8.0
7.5
7.0
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6.0
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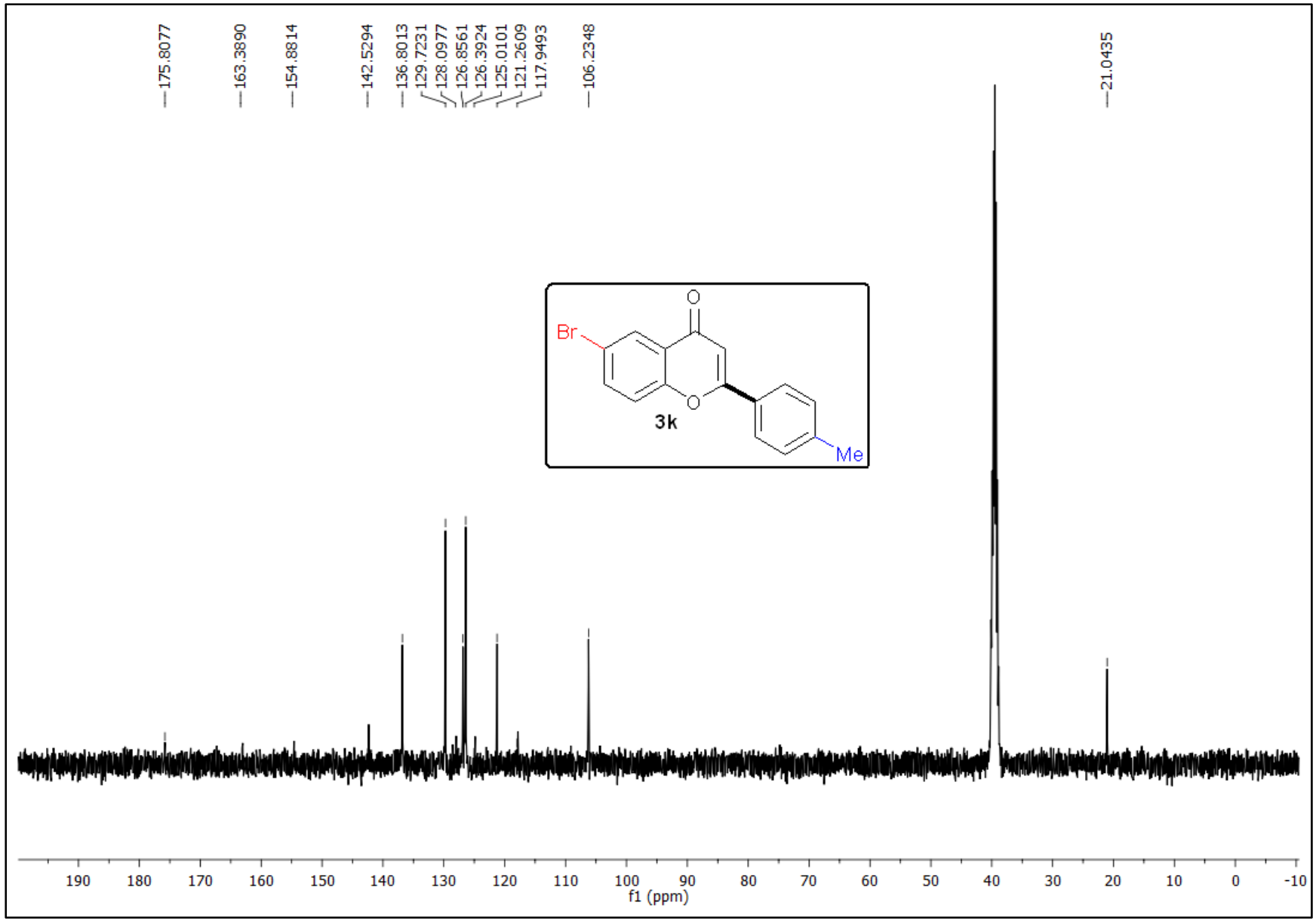
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)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128.0977
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125.0101
121.2609
117.9493
106.2348
21.0435
Br
O
O
3k
Me
190
180
170
160
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140
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120
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100
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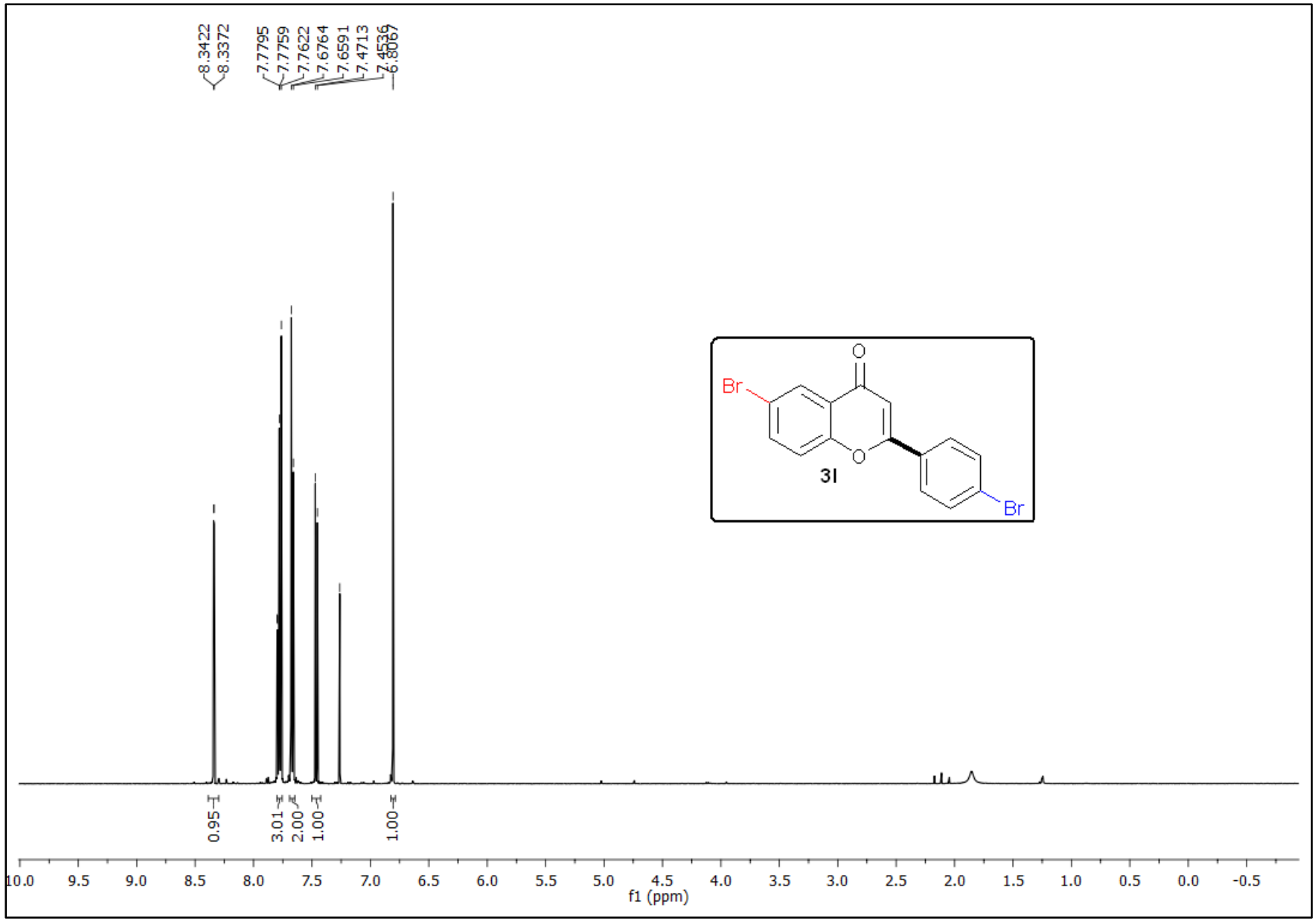
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.7622
7.6764
7.6591
7.4713
7.4536
7.4067
Br
O
O
Br
3l
0.95
3.01
2.00
1.00
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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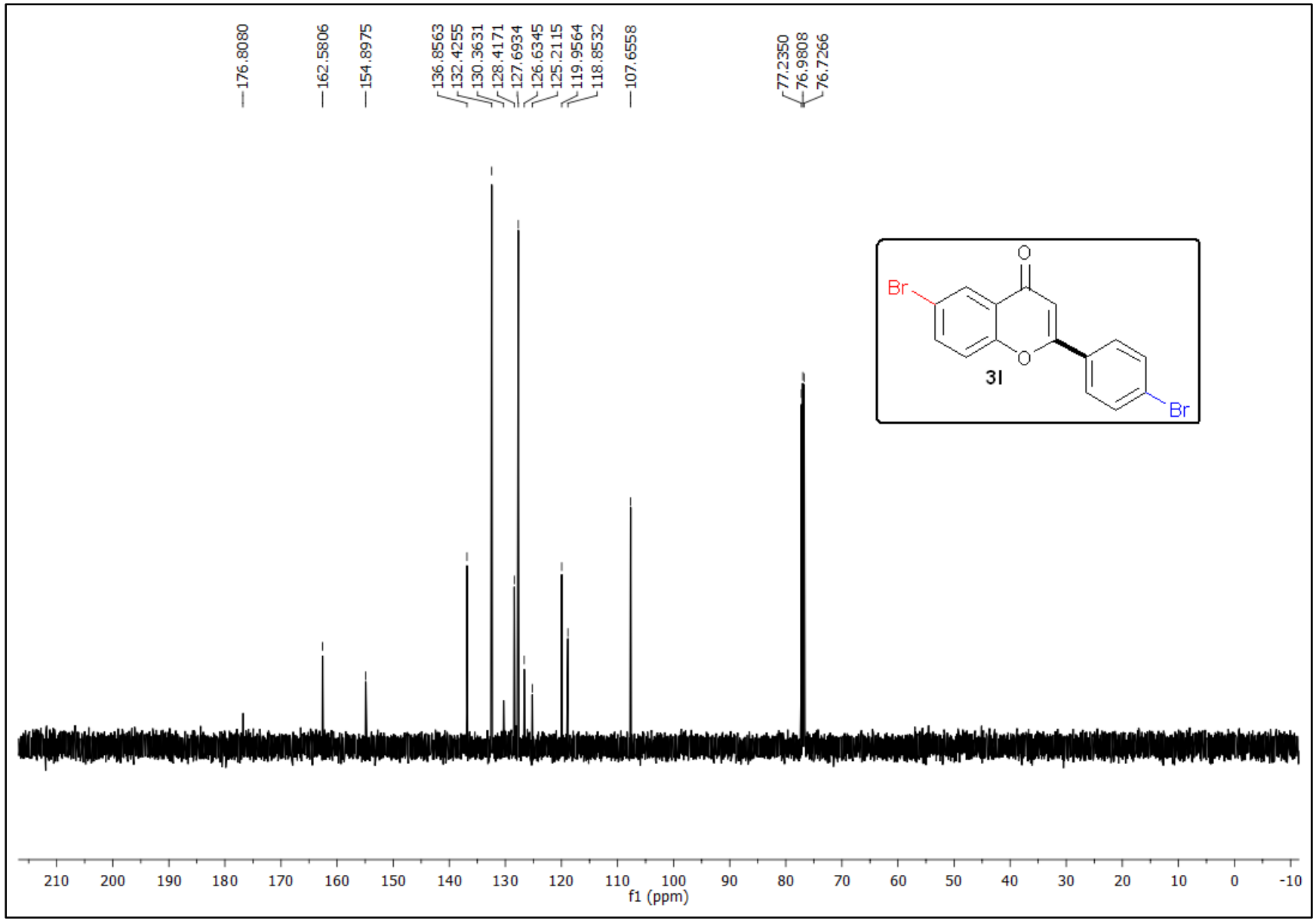
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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128.4171
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119.9564
118.8532
107.6558
77.2350
76.9808
76.7266
Br
O
O
Br
3l
210
200
190
180
170
160
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110
100
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80
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50
40
30
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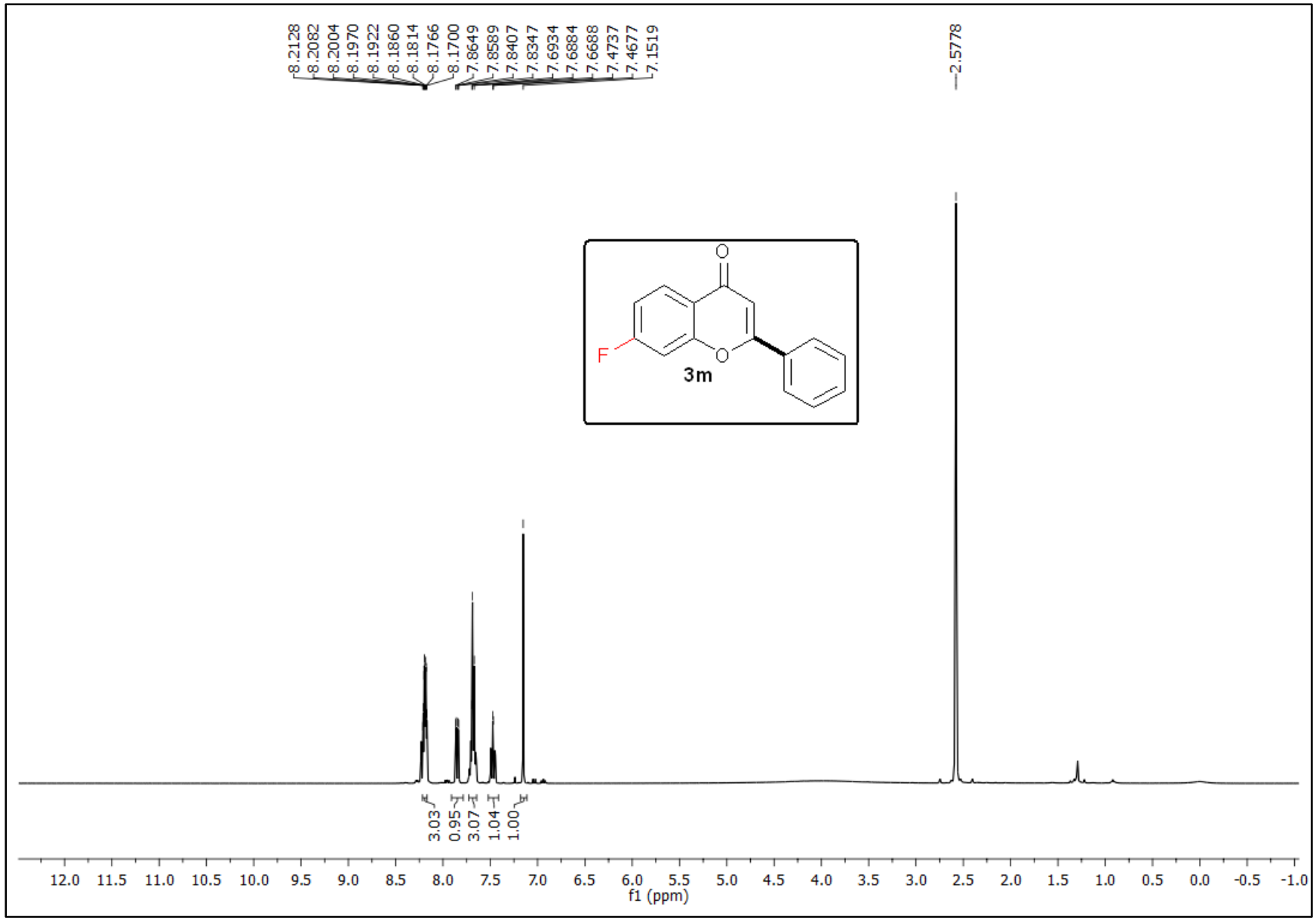
0
-10
f1 (ppm)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8.1970
8.1922
8.1860
8.1814
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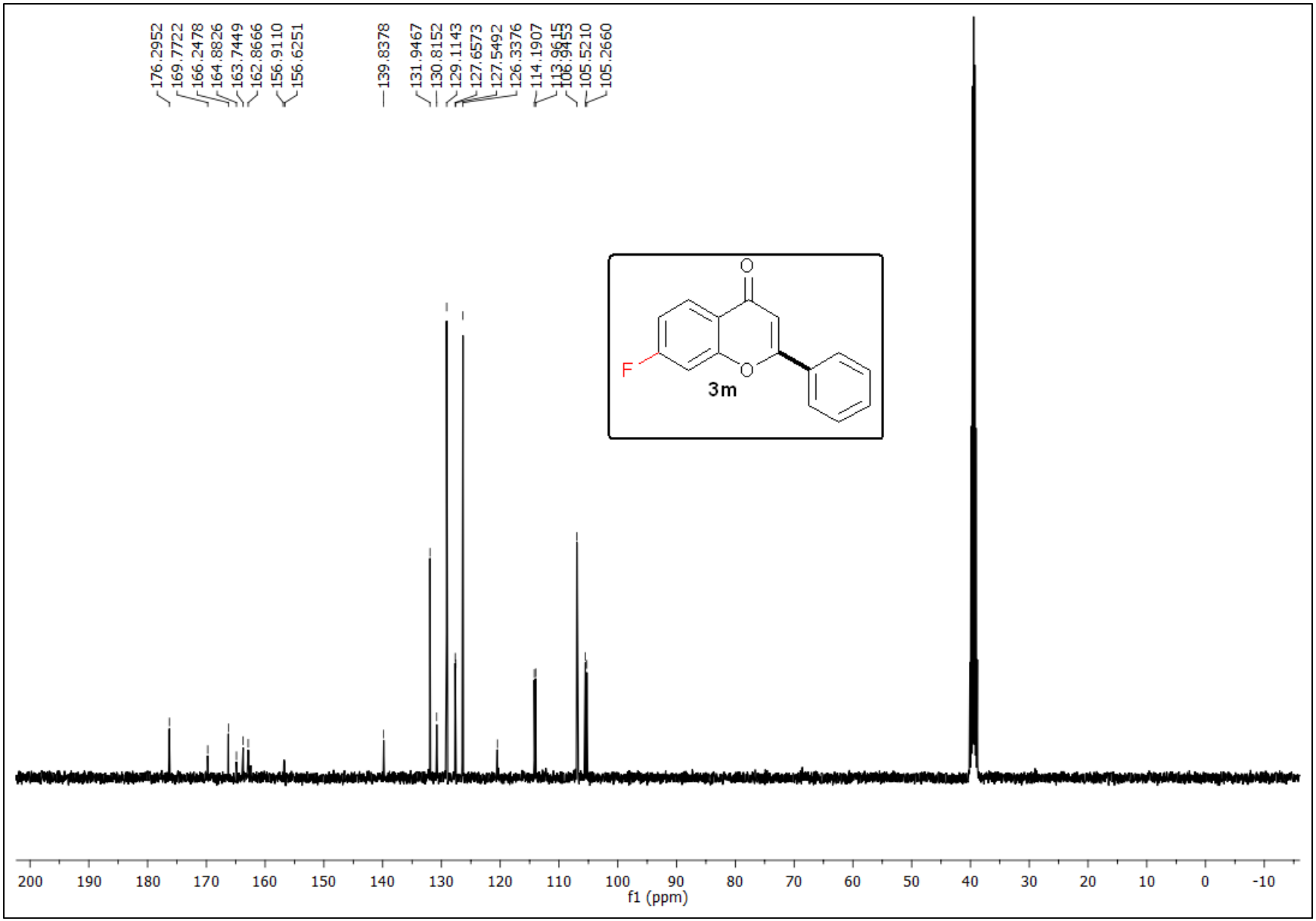
8.1700
7.8649
7.8589
7.8407
7.8347
7.6934
7.6884
7.6688
7.4737
7.4677
7.1519
2.5778
F
O
O
3m
3.03
0.95
3.07
1.04
1.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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156.6251
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129.1143
127.6573
127.5492
126.3376
114.1907
113.9615
106.9453
105.5210
105.2660
O
F
O
3m
200
190
180
170
160
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140
130
120
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100
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80
70
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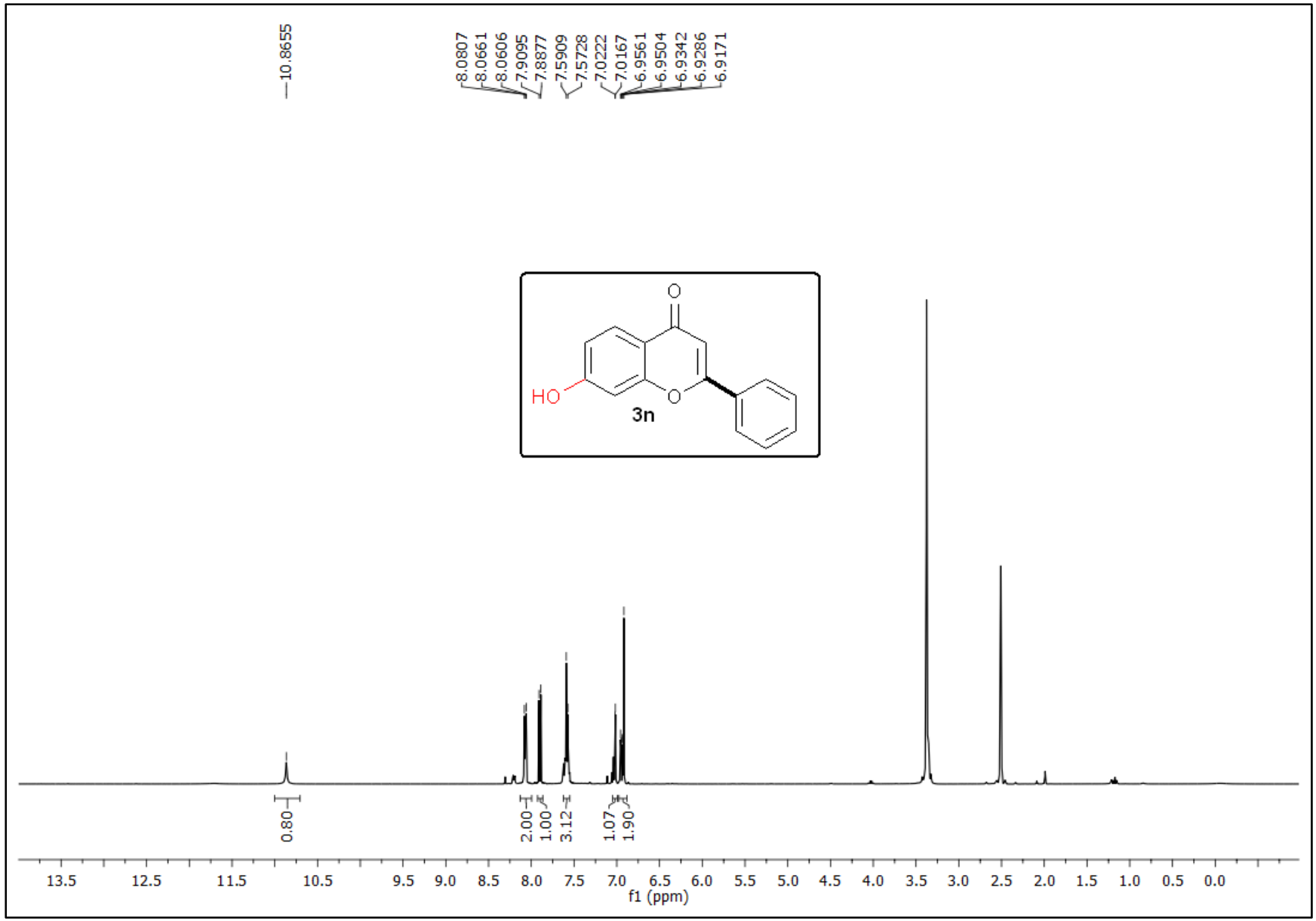
30
20
10
0
-10
f1 (ppm)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8.0661
8.0606
7.9095
7.8877
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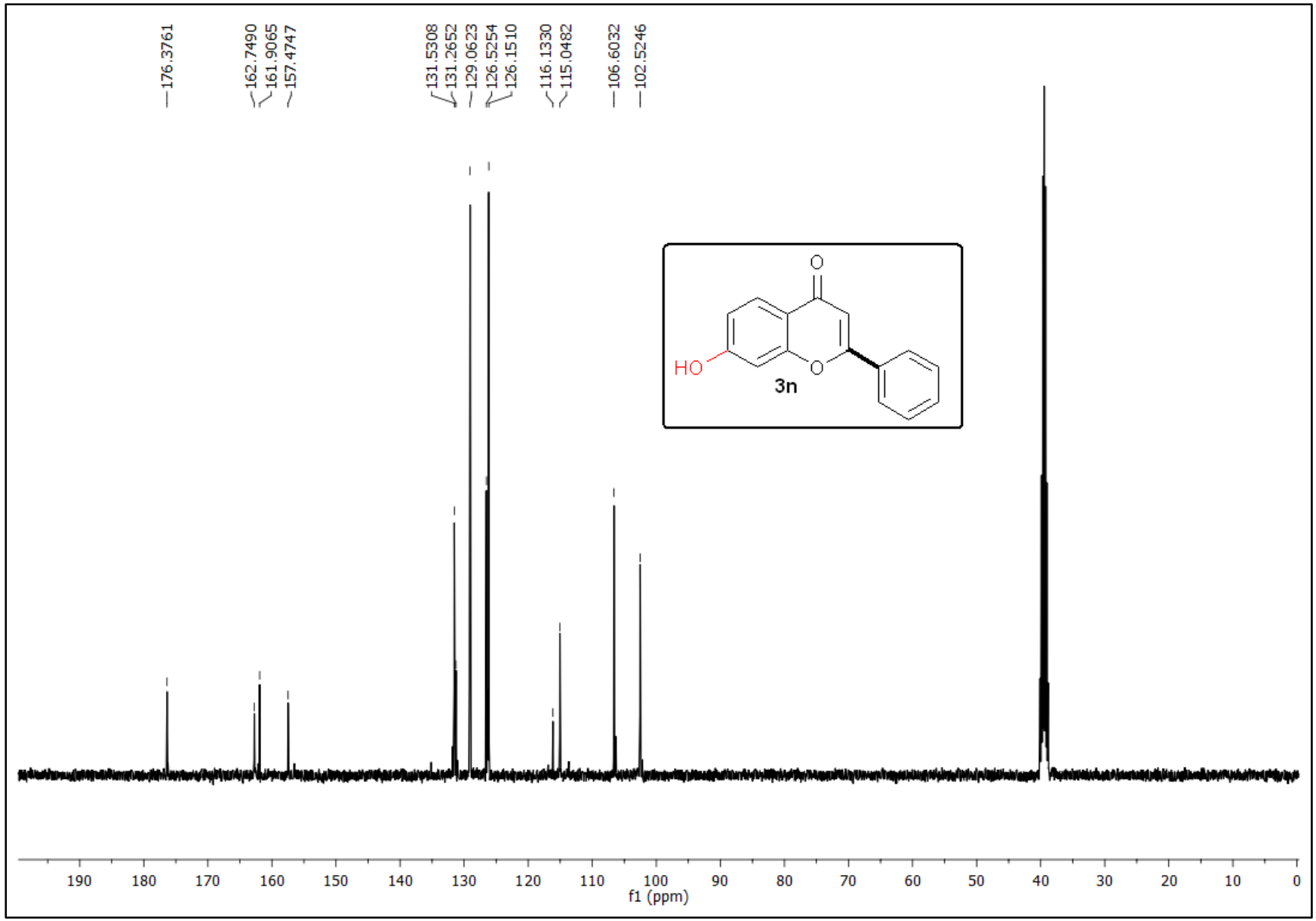
7.5728
7.0222
7.0167
6.9561
6.9504
6.9342
6.9286
6.9171
HO
O
O
3n
0.80
2.00
1.00
3.12
1.07
1.90
13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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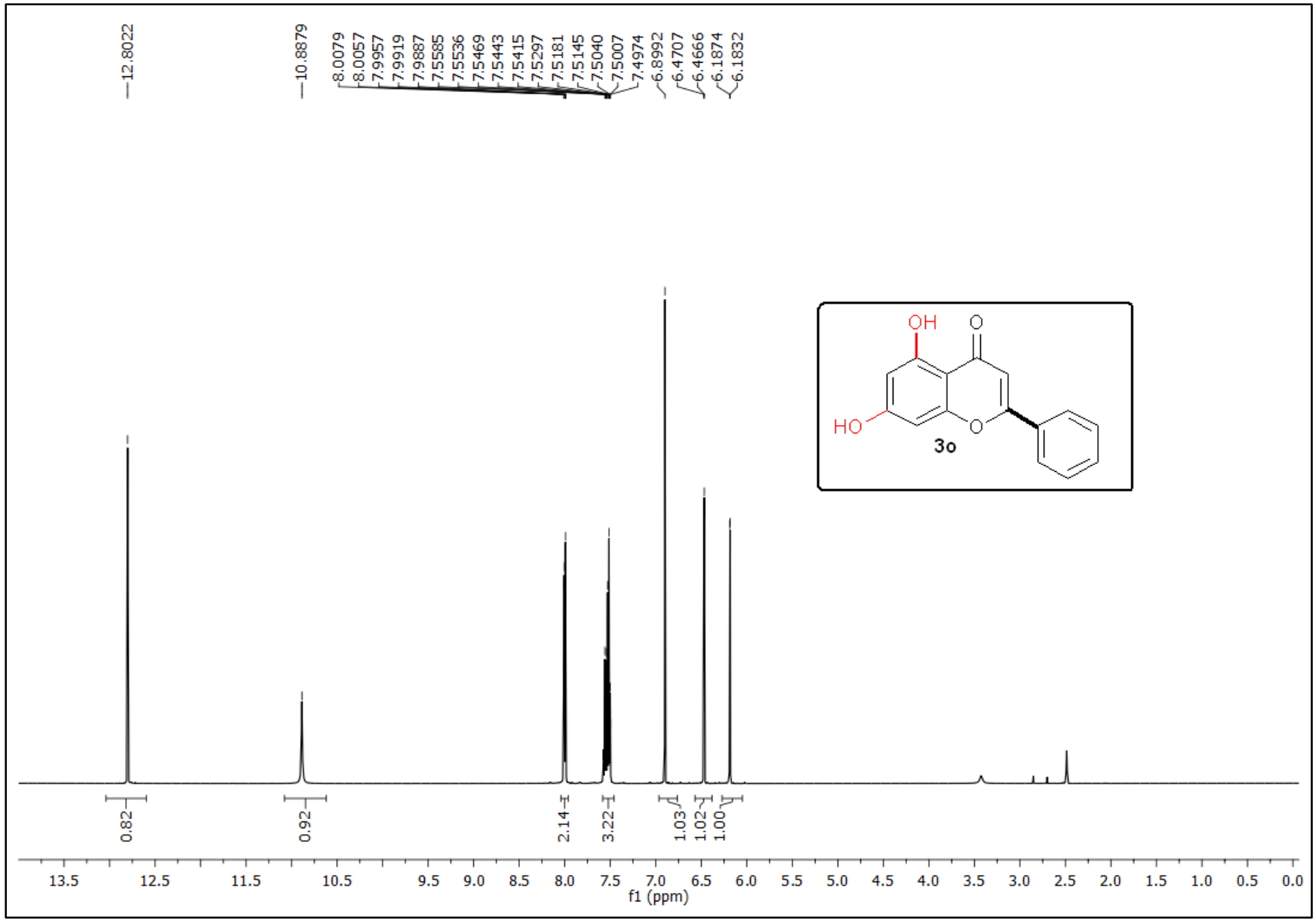
161.9065
157.4747
131.5308
131.2652
129.0623
126.5254
126.1510
116.1330
115.0482
106.6032
102.5246
HO
O
O
3n
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.0079
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7.9957
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7.9887
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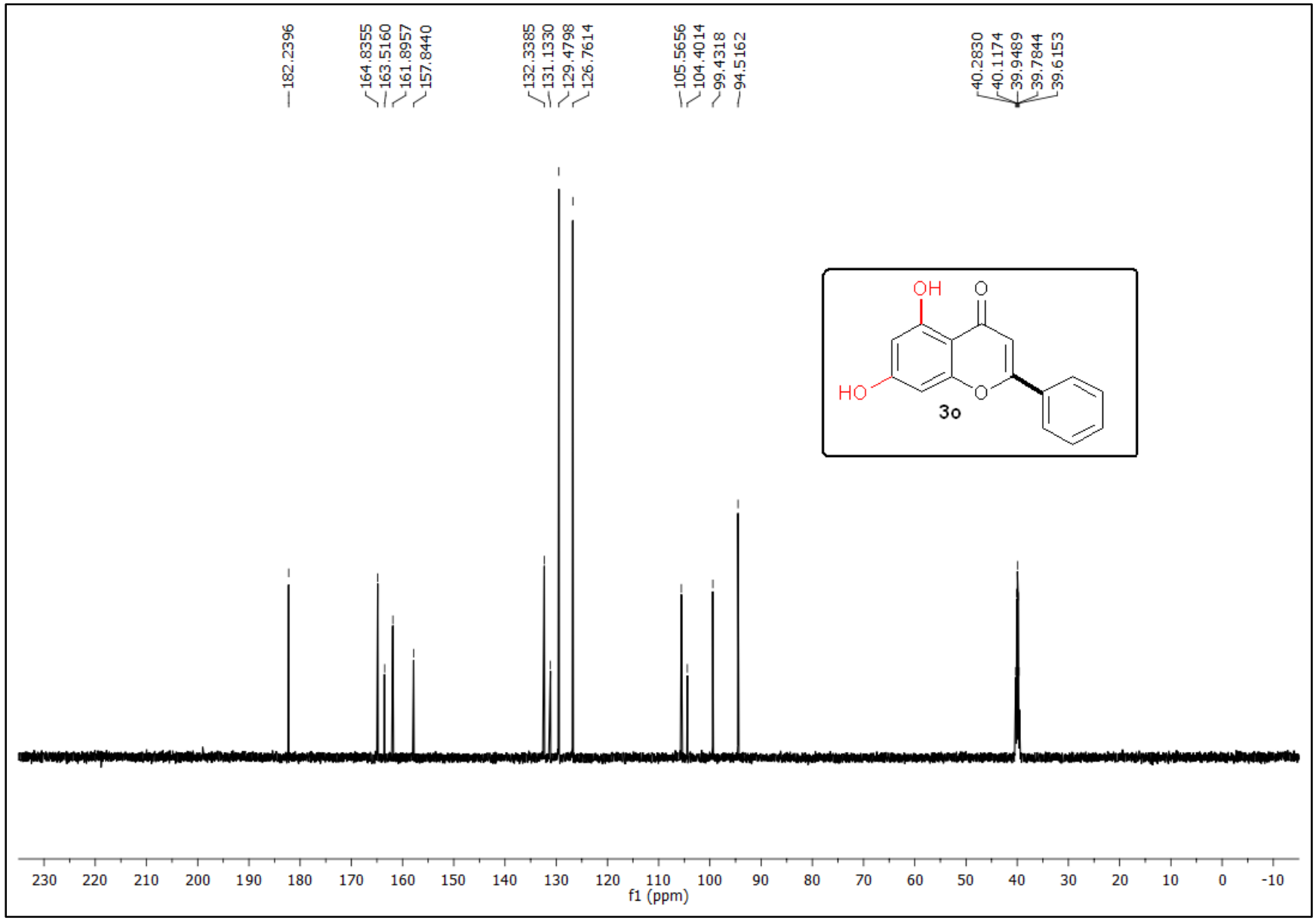
7.5536
7.5469
7.5443
7.5415
7.5297
7.5181
7.5145
7.5040
7.5007
7.4974
6.8992
6.4707
6.4666
6.1874
6.1832
OH
O
HO
O
3o
0.82
0.92
2.14
3.22
1.03
1.02
1.00
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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163.5160
161.8957
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131.1330
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105.5656
104.4014
99.4318
94.5162
40.2830
40.1174
39.9489
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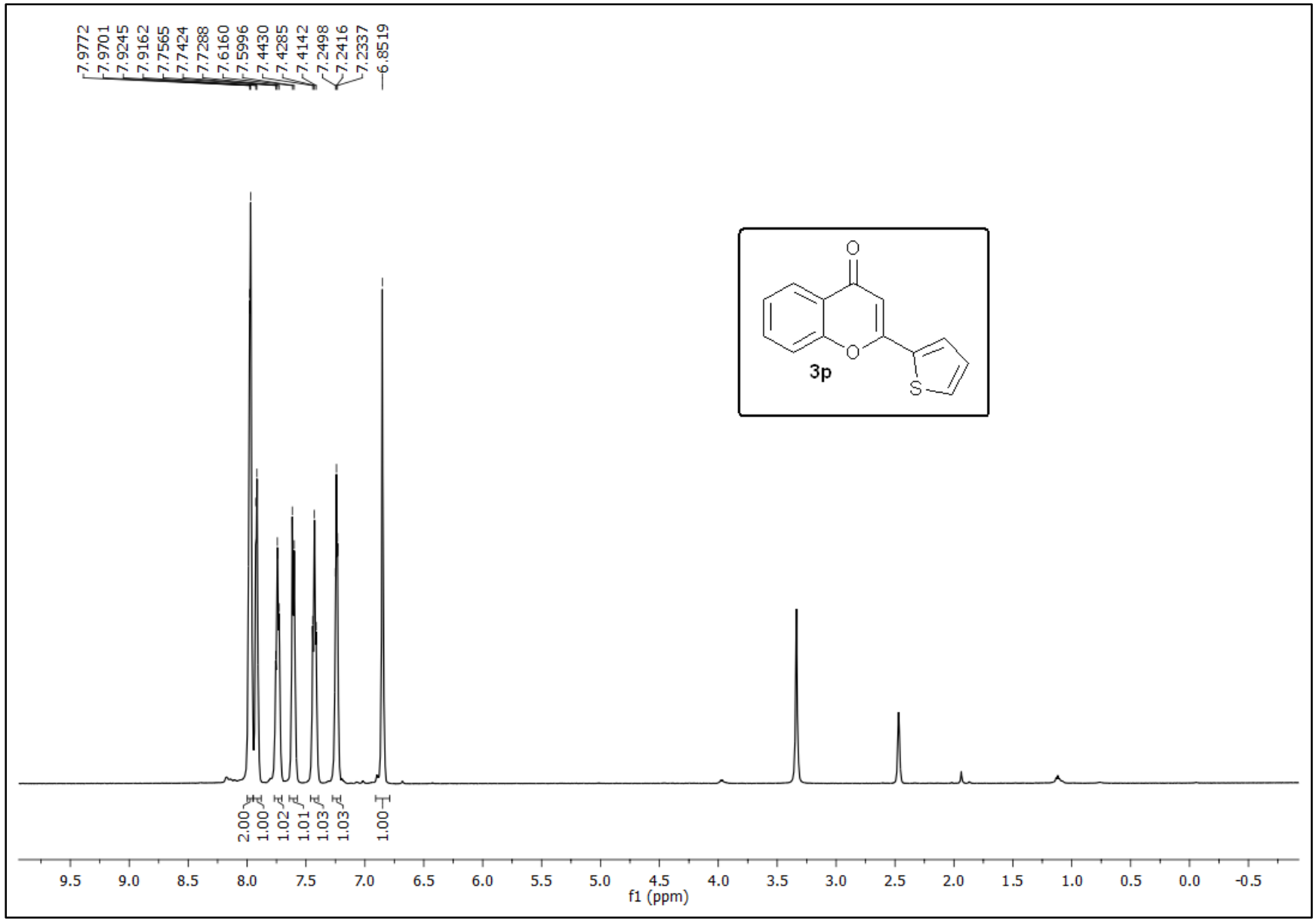
OH
O
HO
O
3o
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.6160
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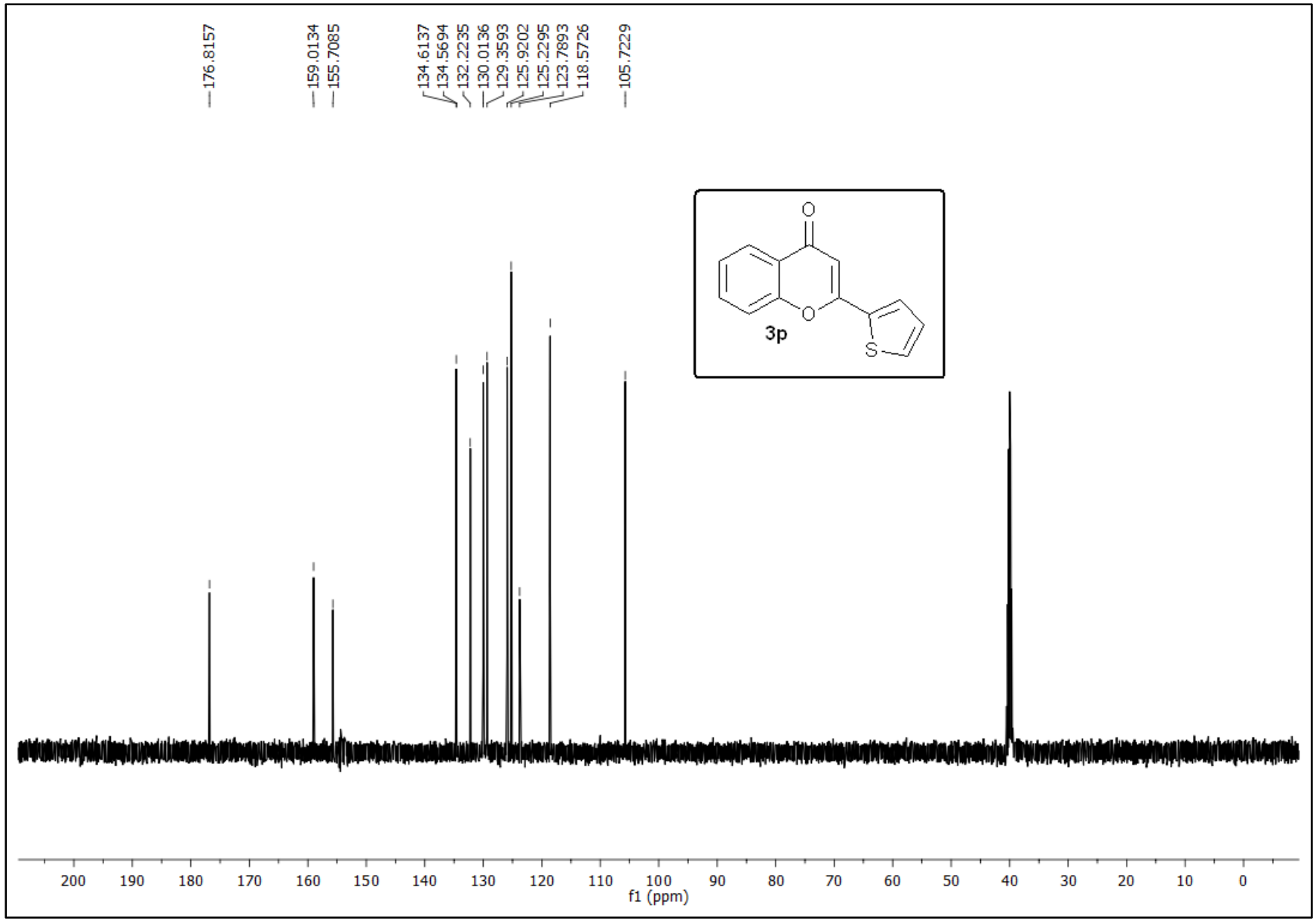
7.4285
7.4142
7.2498
7.2416
7.2337
6.8519
3p
O
O
S
2.00
1.00
1.02
1.01
1.03
1.03
1.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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130.0136
129.3593
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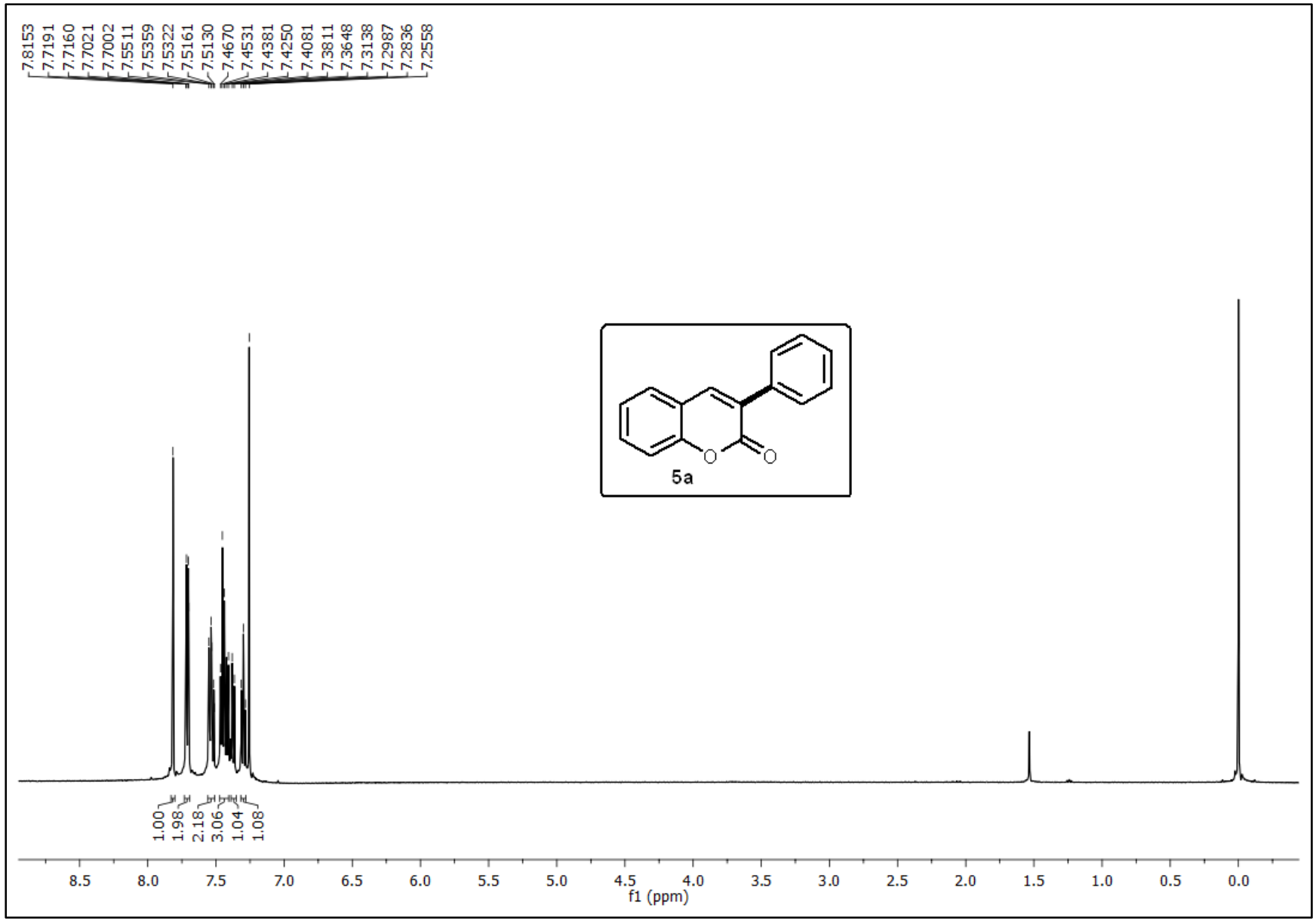
125.2295
123.7893
118.5726
105.7229
O
O
S
3p
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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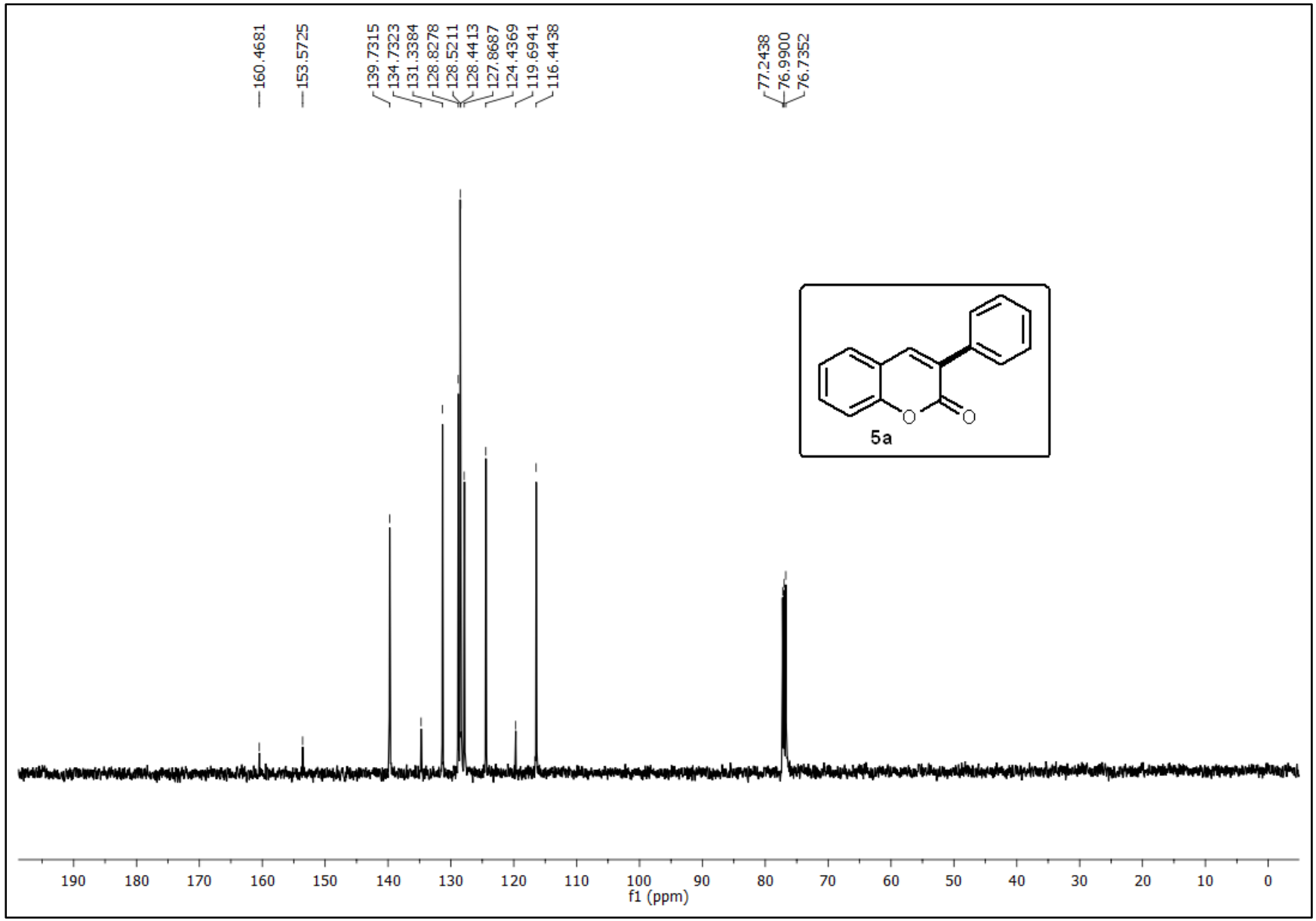
7.5130
7.4670
7.4531
7.4381
7.4250
7.4081
7.3811
7.3648
7.3138
7.2987
7.2836
7.2558
5a
1.00
1.98
2.18
3.06
1.04
1.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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116.4438
77.2438
76.9900
76.7352
5a
190
180
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150
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110
100
90
80
70
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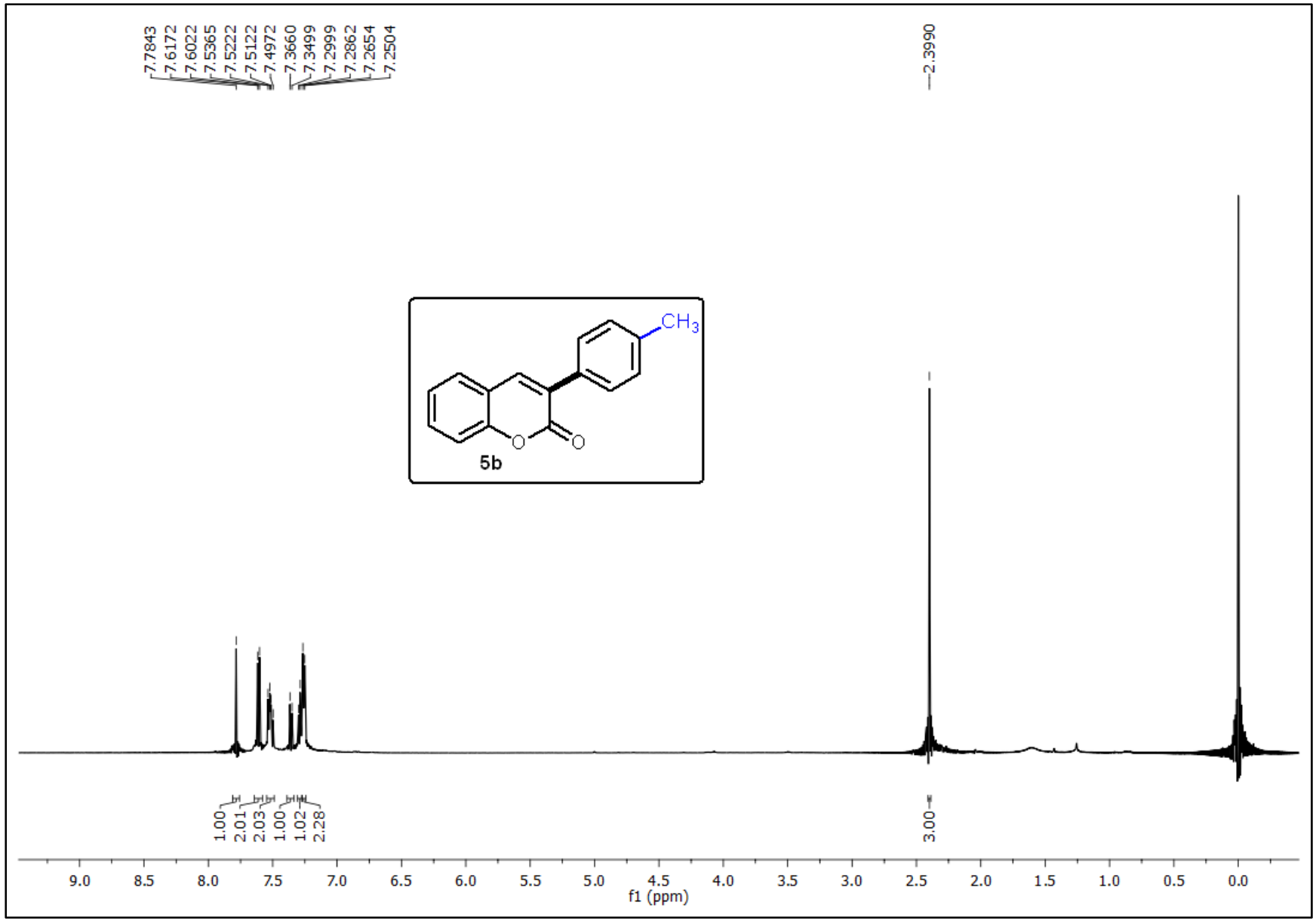
50
40
30
20
10
0
f1 (ppm)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7.2862
7.2654
7.2504
2.3990
CH3
O
O
5b
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2.01
2.03
1.00
1.02
2.28
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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3.5
3.0
2.5
2.0
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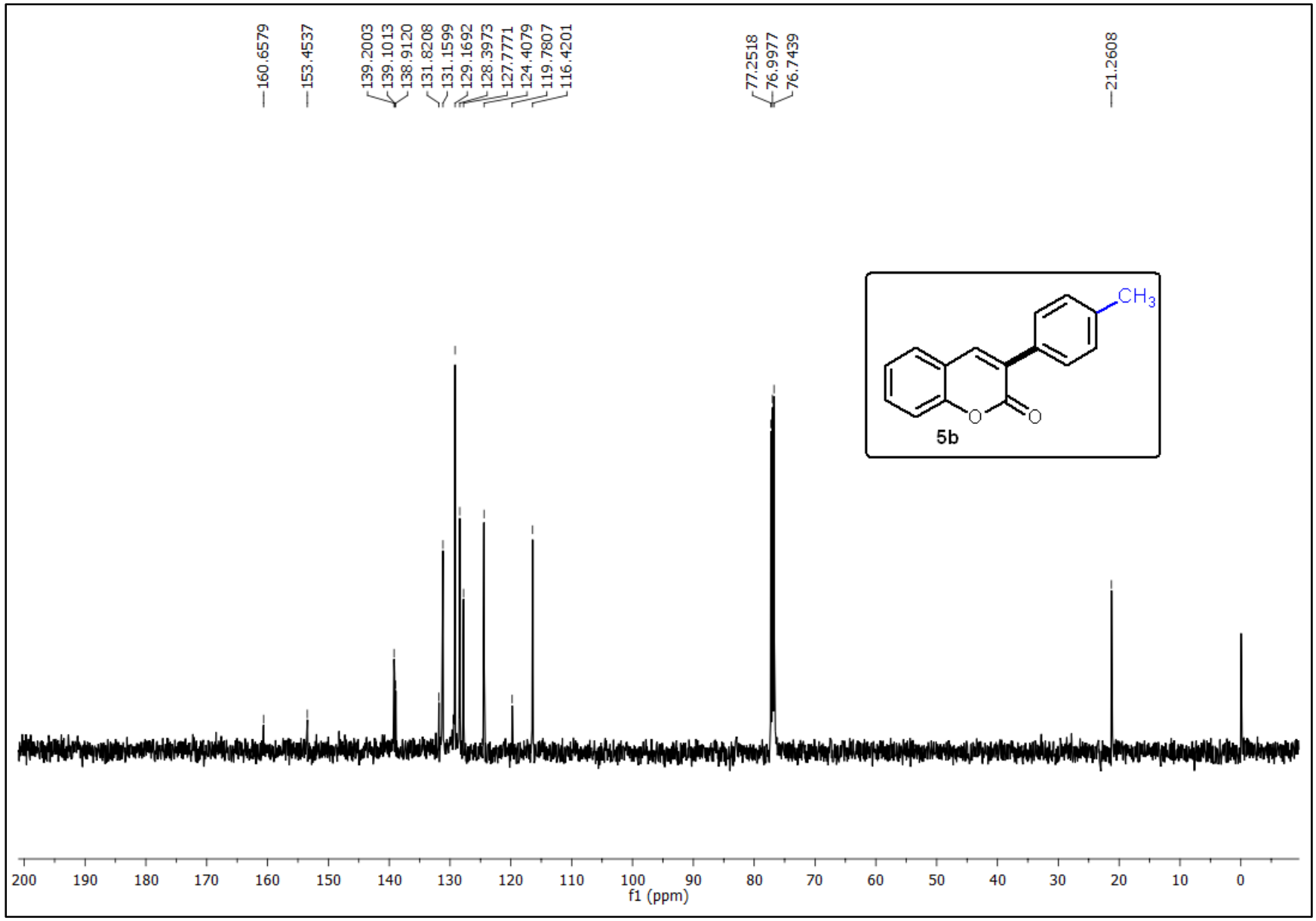
f1 (ppm)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116.4201
77.2518
76.9977
76.7439
21.2608
CH3
O
O
5b
200
190
180
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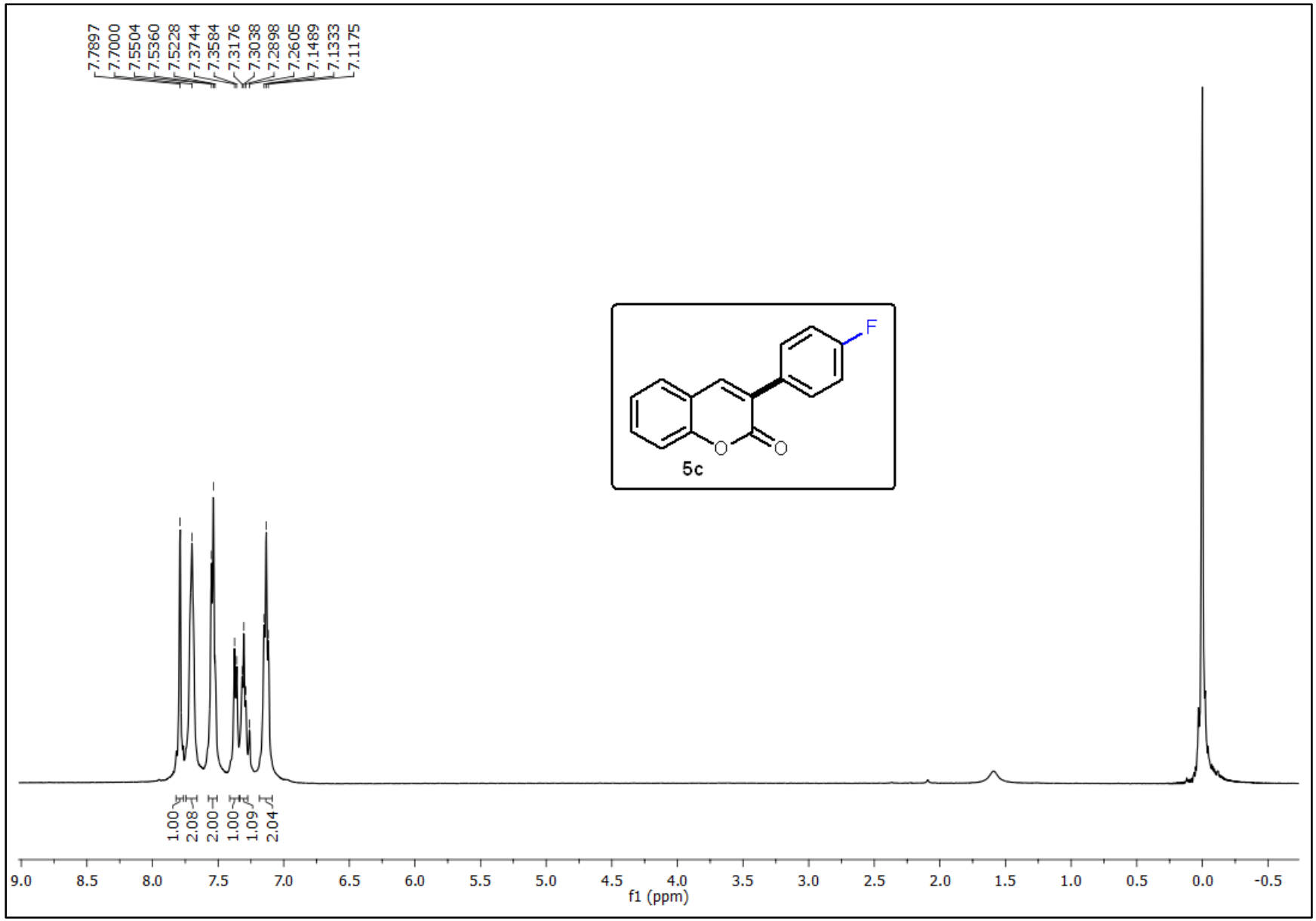
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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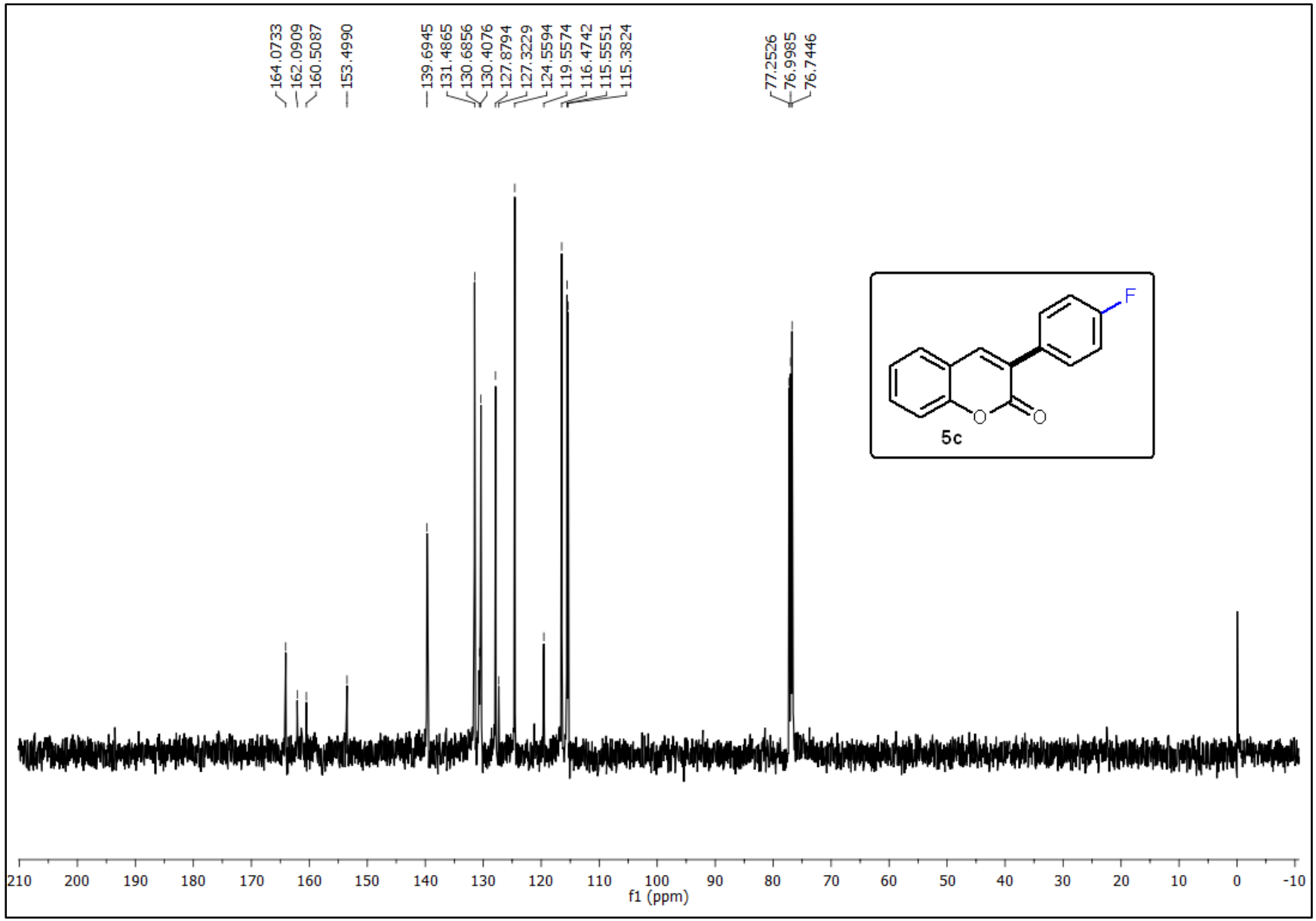
7.1489
7.1333
7.1175
F
O
O
5c
1.00
2.08
2.00
1.00
1.09
2.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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116.4742
115.5551
115.3824
77.2526
76.9985
76.7446
F
O
O
5c
210
200
190
180
170
160
150
140
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120
110
100
90
80
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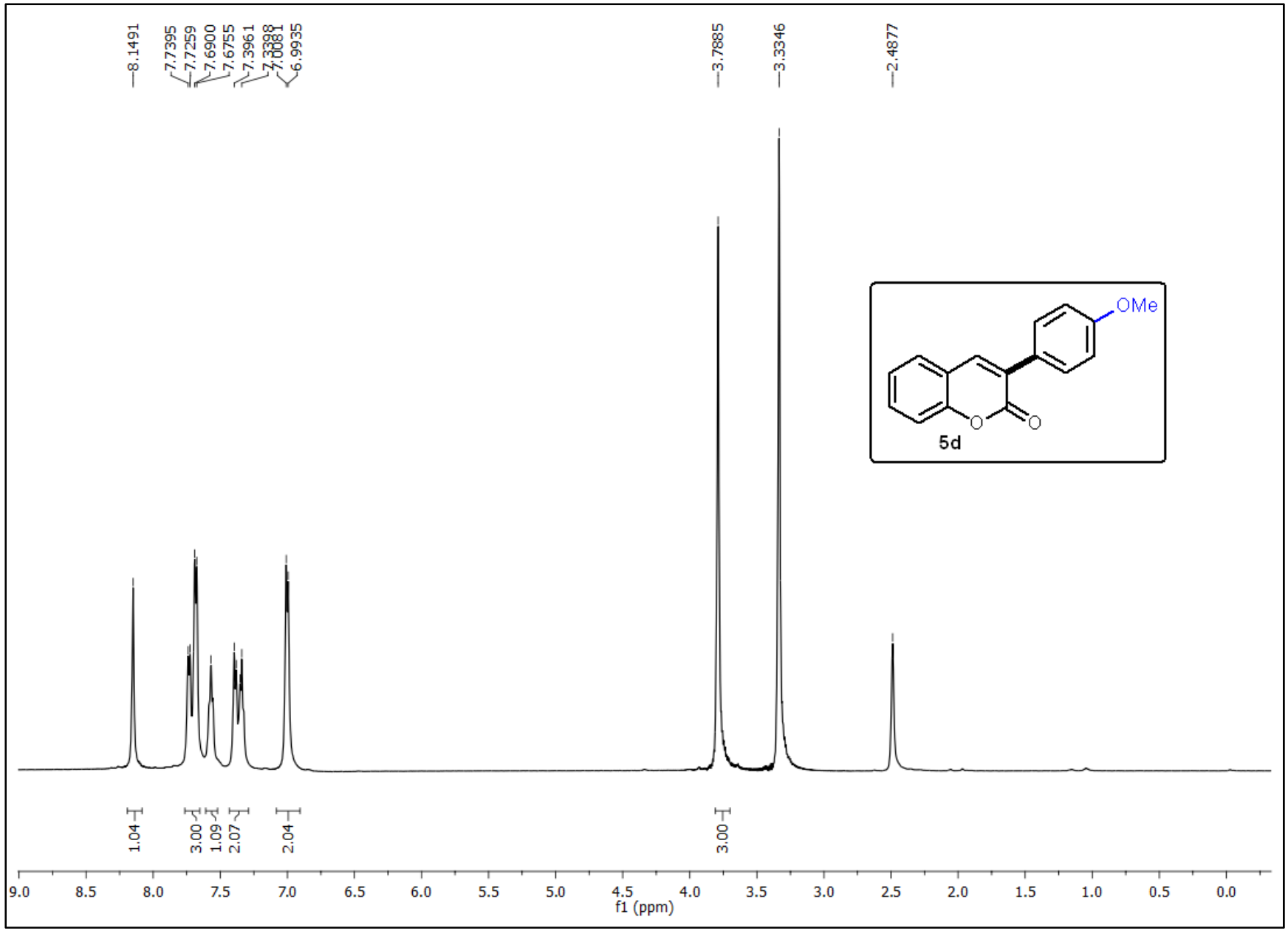
60
50
40
30
20
10
0
-10
f1 (ppm)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3.3346
2.4877
OMe
O
O
5d
1.04
3.00
1.09
2.07
2.04
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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1.0
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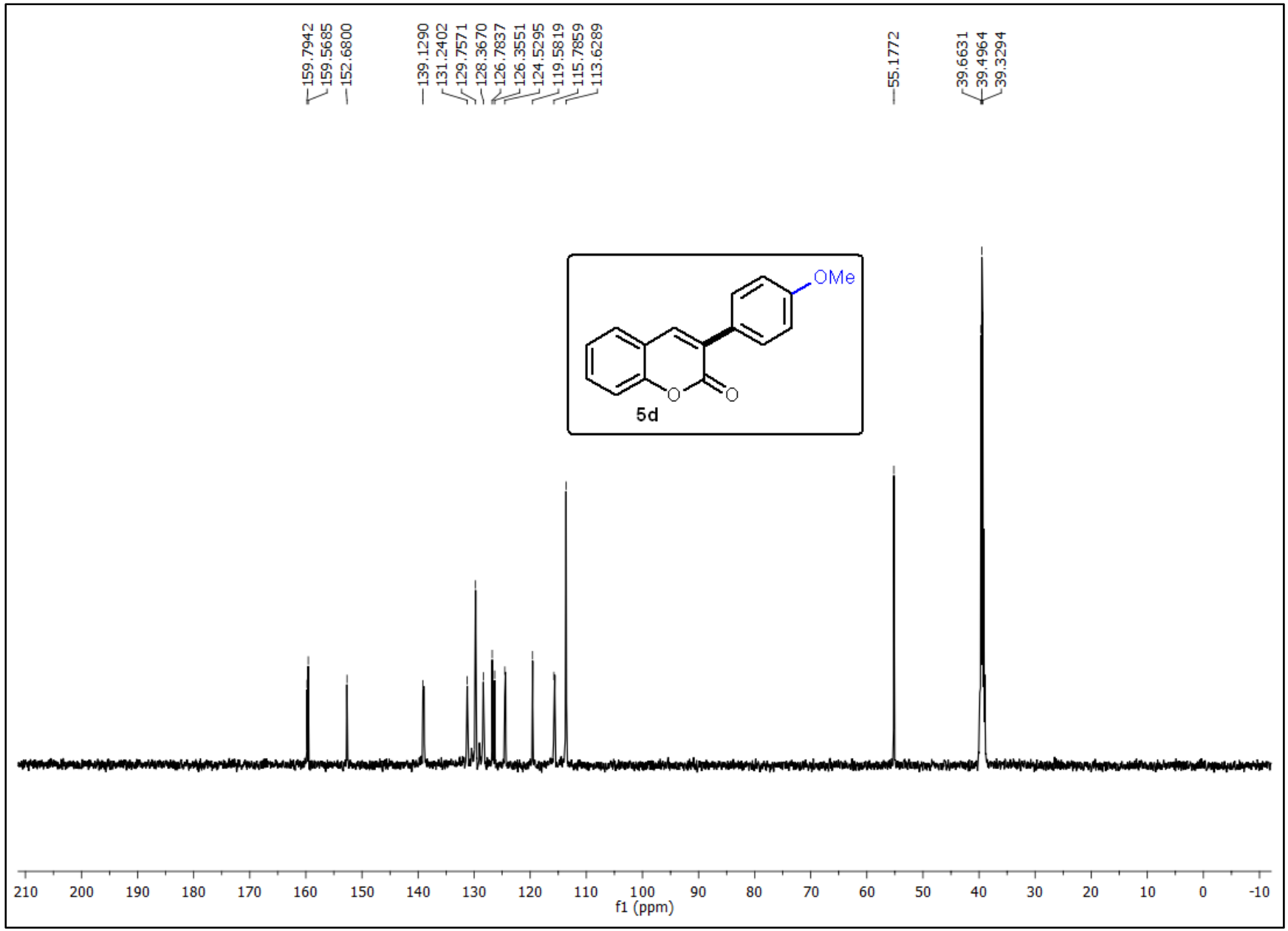
f1 (ppm)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115.7859
113.6289
55.1772
39.6631
39.4964
39.3294
OMe
O
O
5d
210
200
190
180
170
160
150
140
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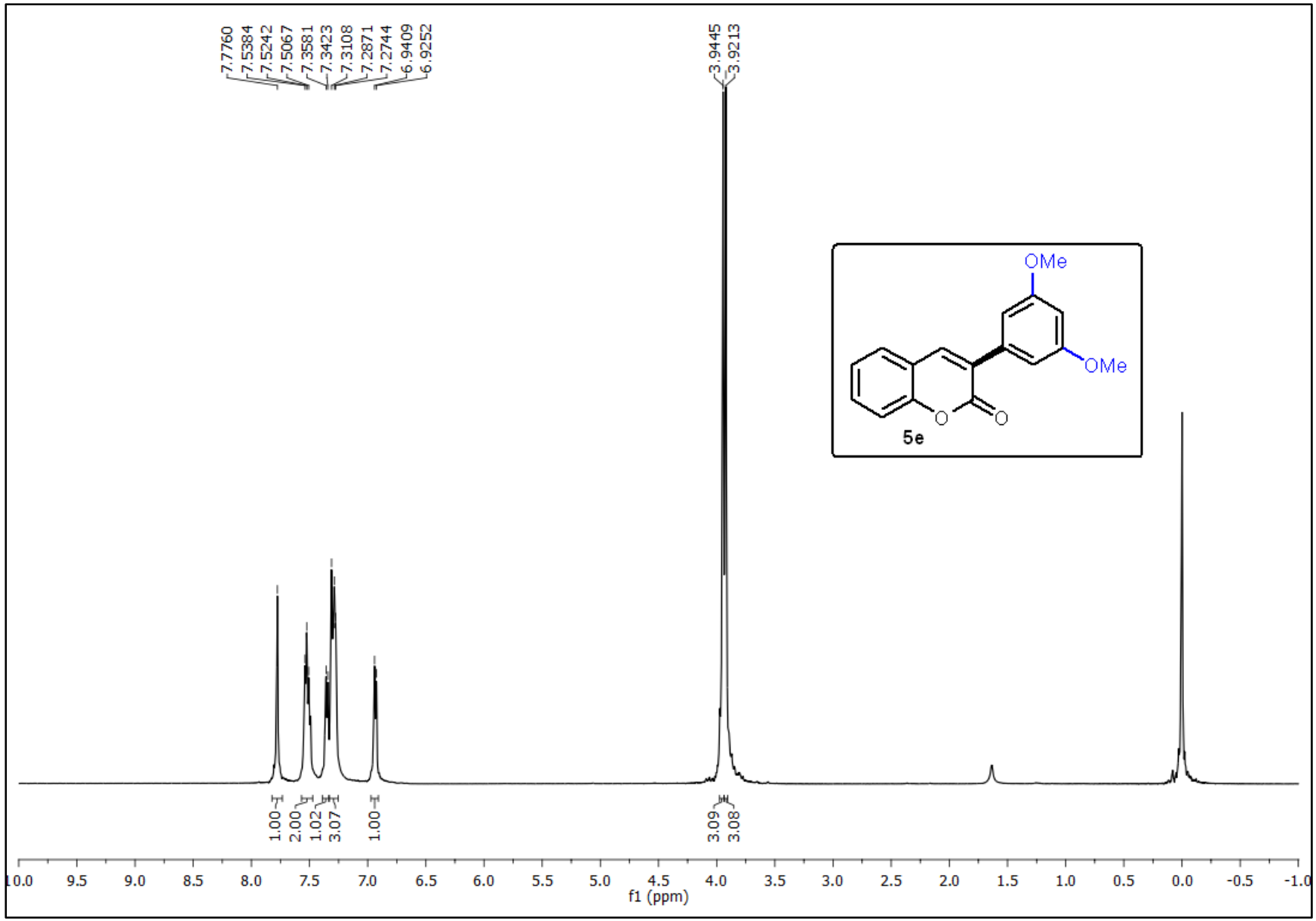
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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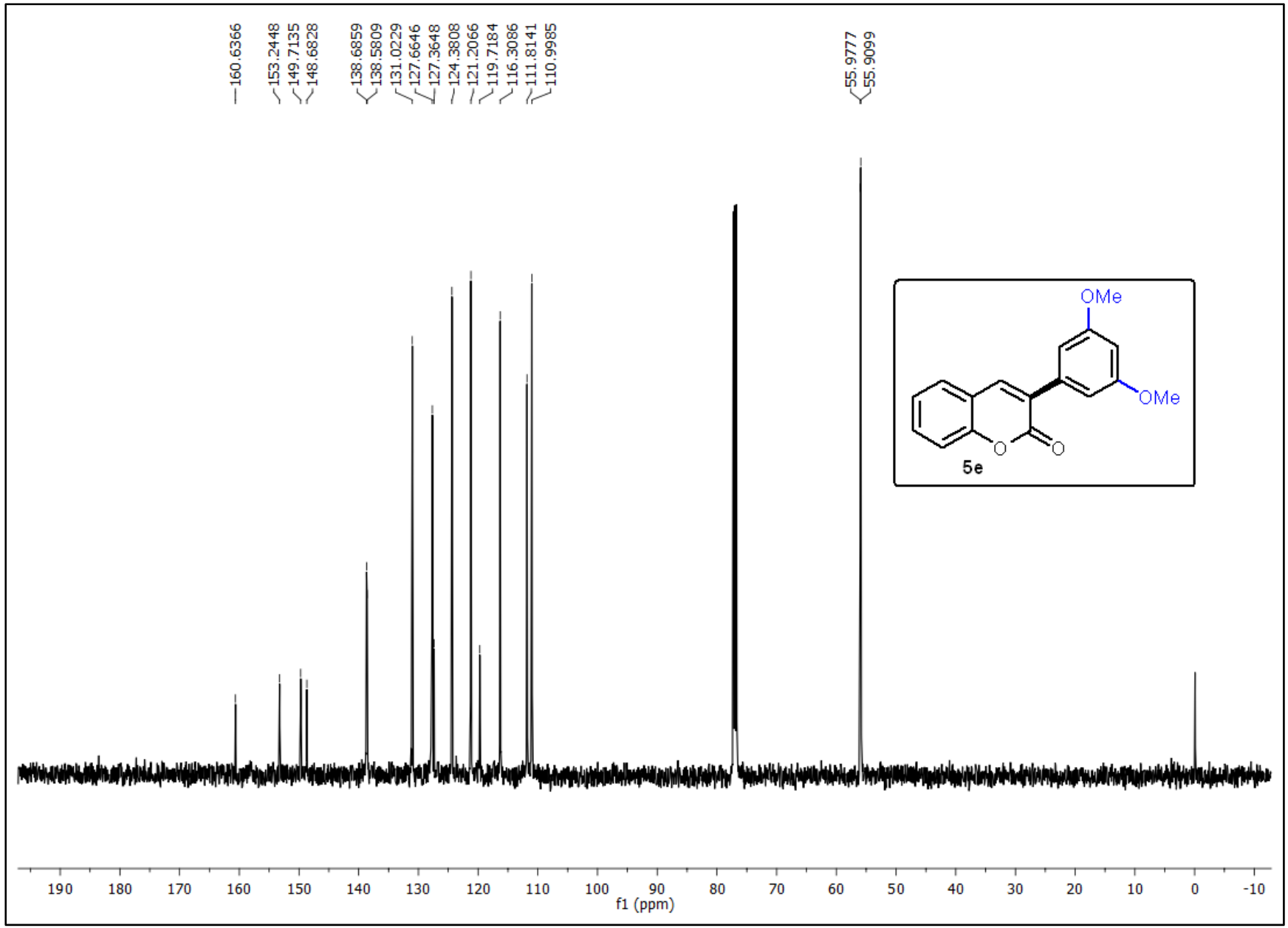
6.9252
3.9445
3.9213
OMe
OMe
O
O
5e
1.00
2.00
1.02
3.07
1.00
3.09
3.08
f1 (ppm)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55.9099
OMe
OMe
O
O
5e
190
180
170
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100
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80
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60
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40
30
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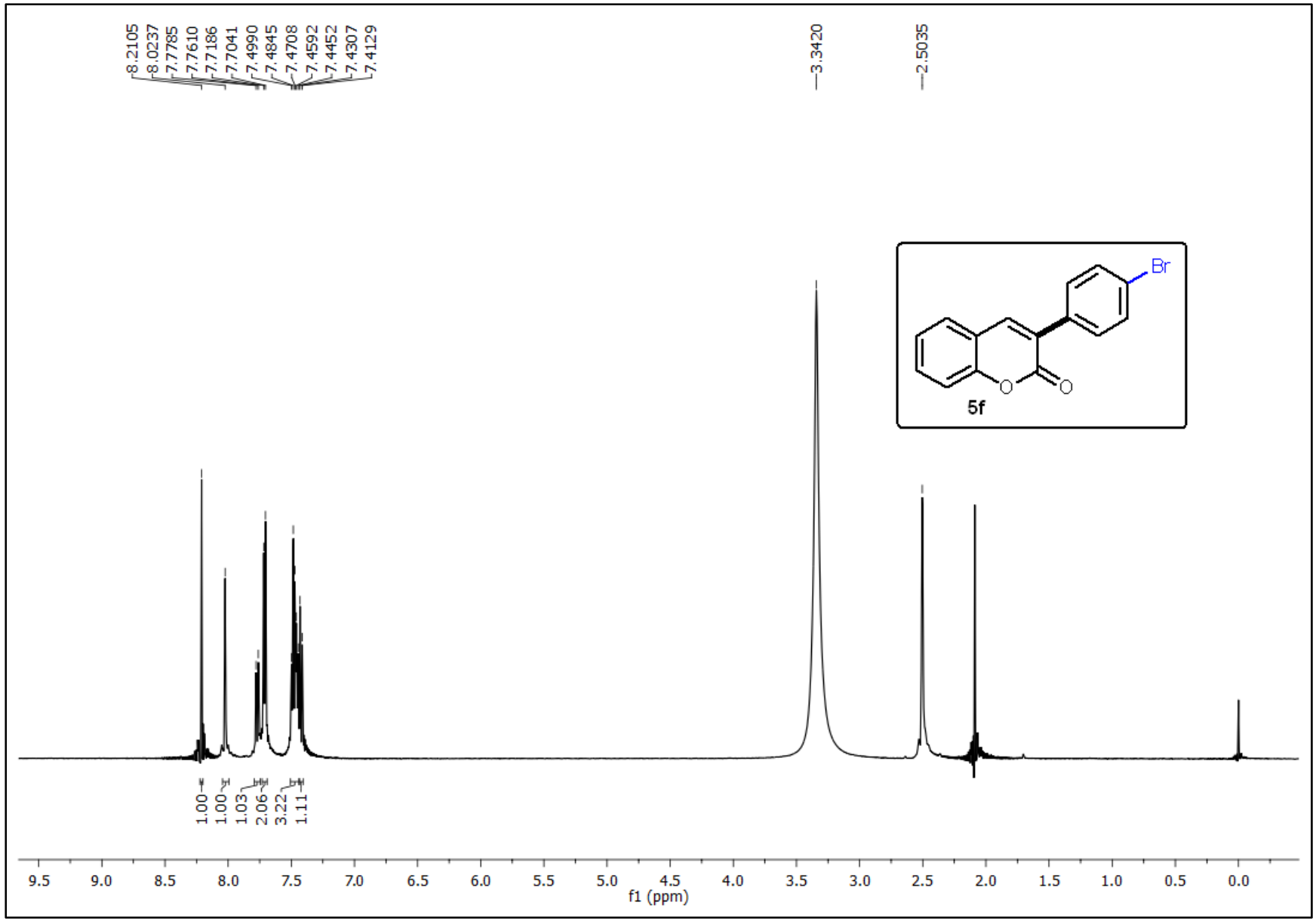
0
-10
f1 (ppm)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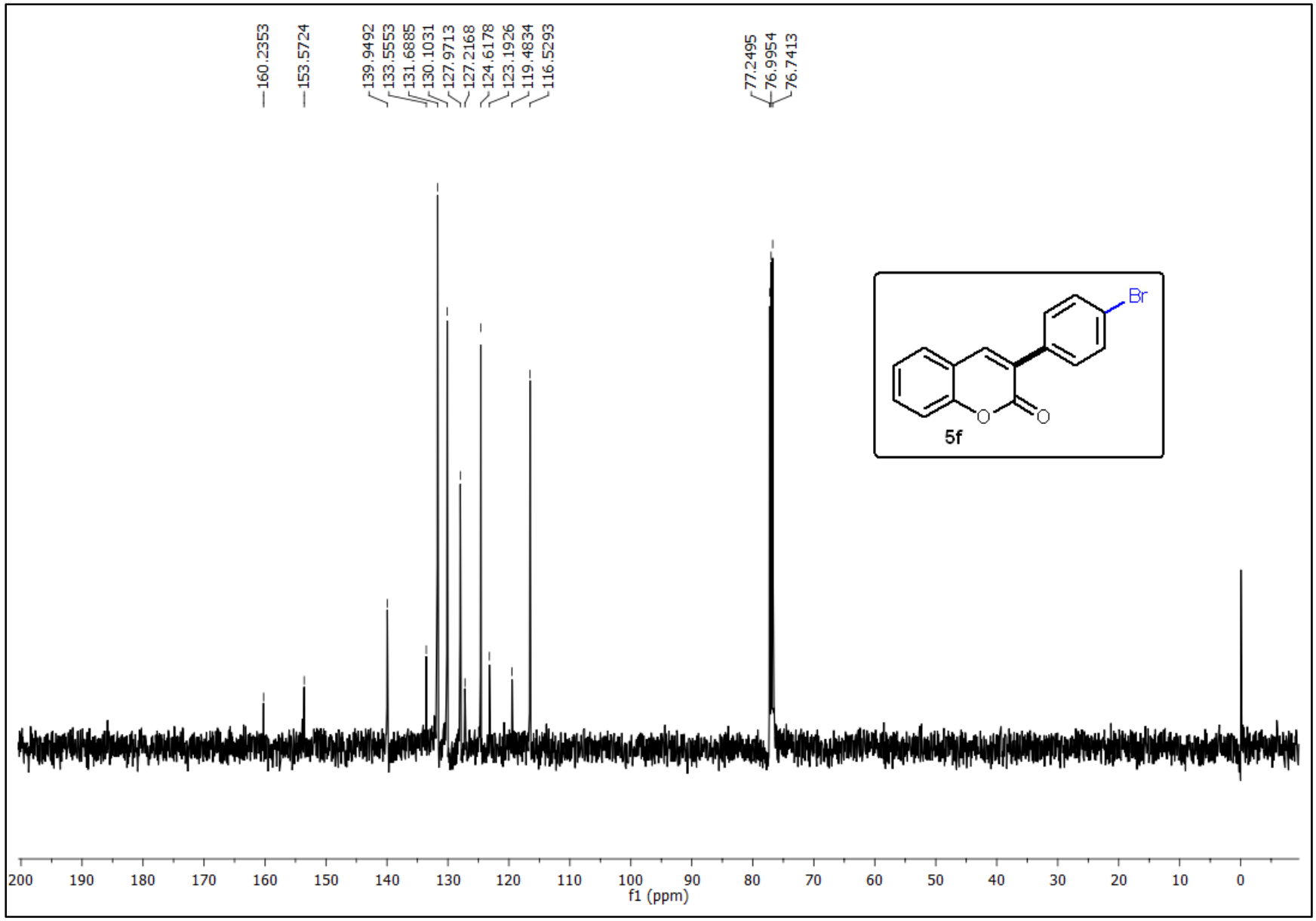
7.4452
7.4307
7.4129
3.3420
2.5035
Br
O
O
5f
1.00
1.00
1.03
2.06
3.22
1.11
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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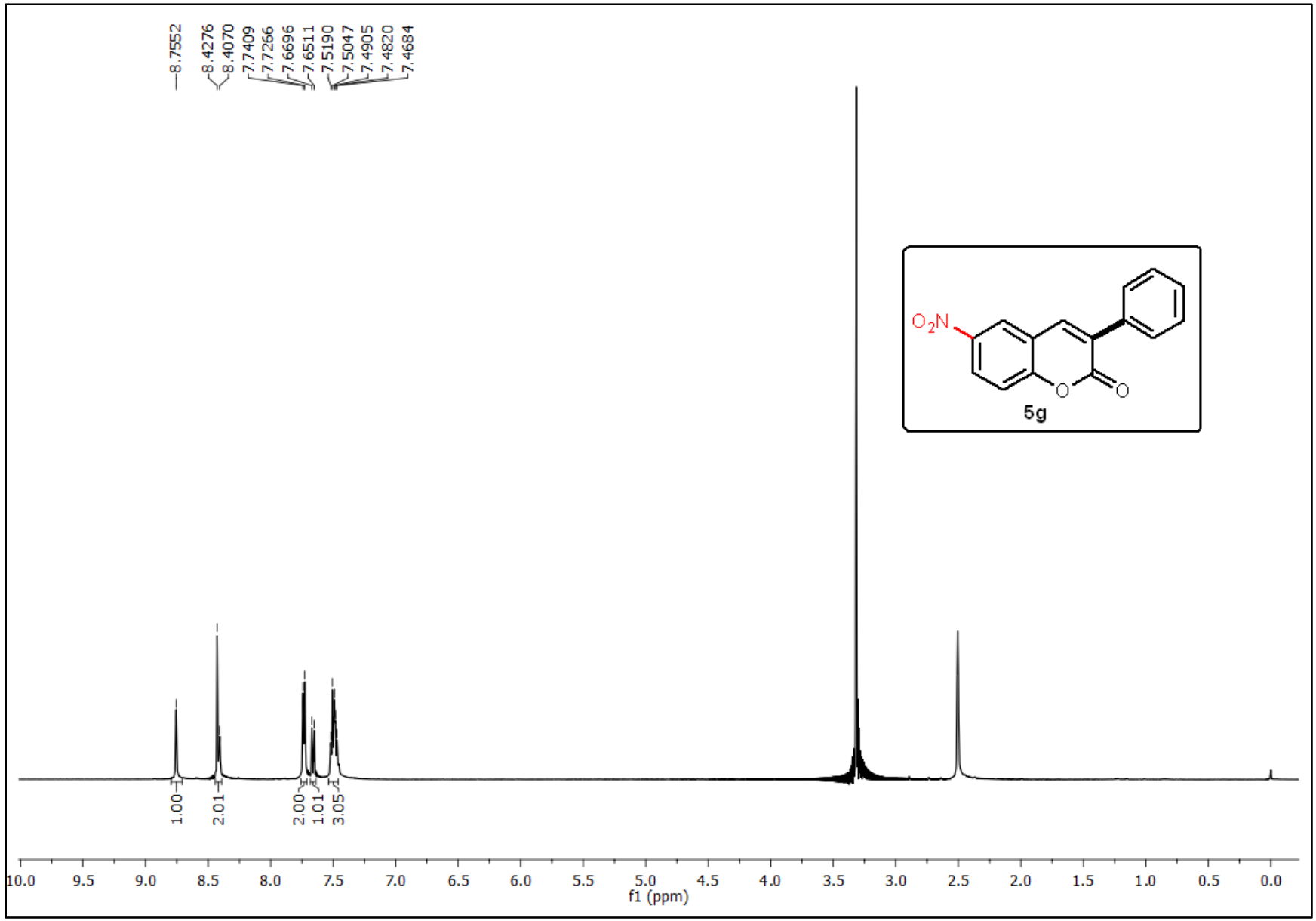
116.5293
77.2495
76.9954
76.7413
Br
O
O
5f
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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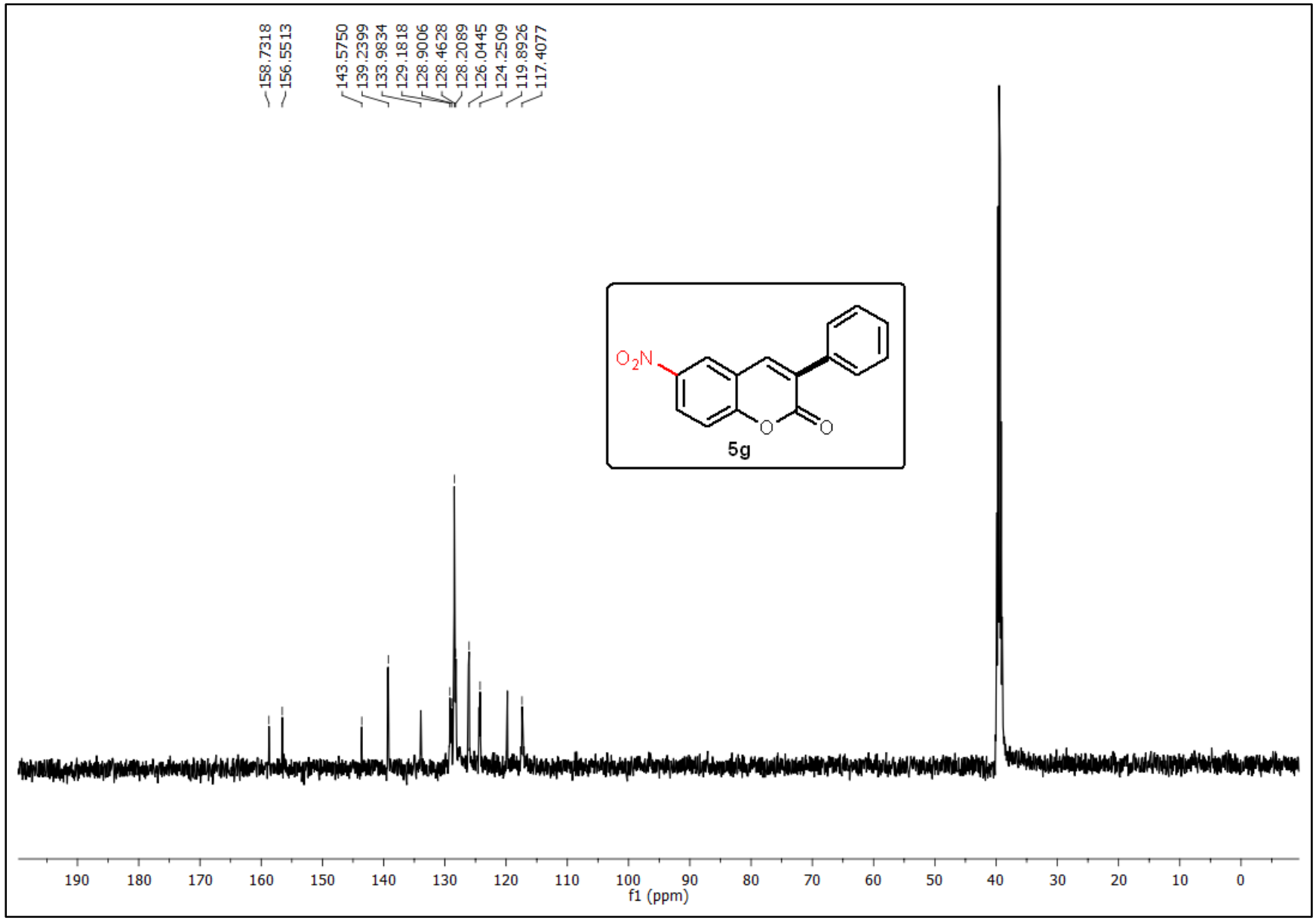
8.4276
8.4070
7.7409
7.7266
7.6696
7.6511
7.5190
7.5047
7.4905
7.4820
7.4684
1.00
2.01
2.00
1.01
3.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
O2N
O
O
5g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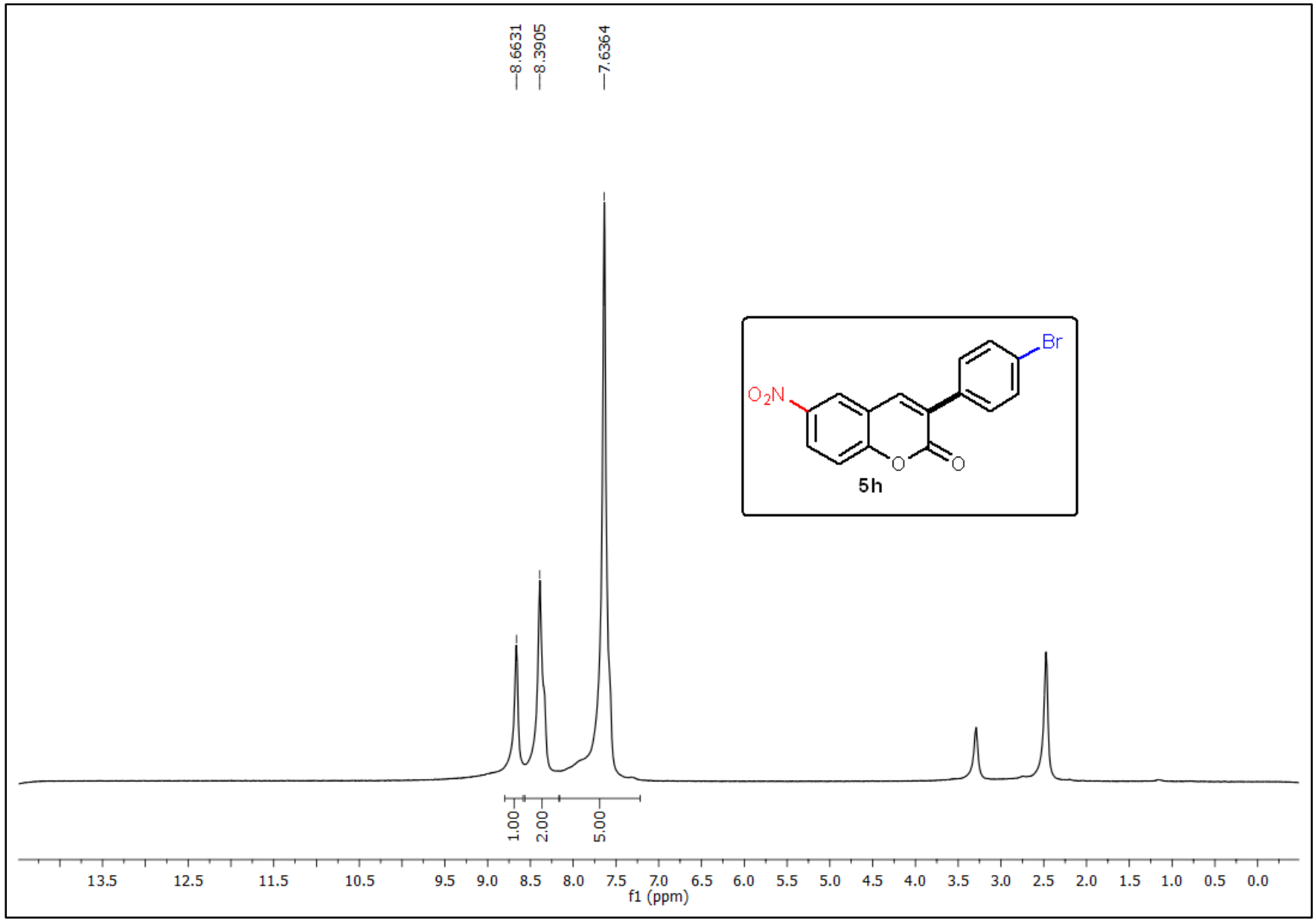
156.5513
143.5750
139.2399
133.9834
129.1818
128.9006
128.4628
128.2089
126.0445
124.2509
119.8926
117.4077
O2N
O
O
5g
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.3905
7.6364
Br
O2N
O
O
5h
1.00
2.00
5.00
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12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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1.0
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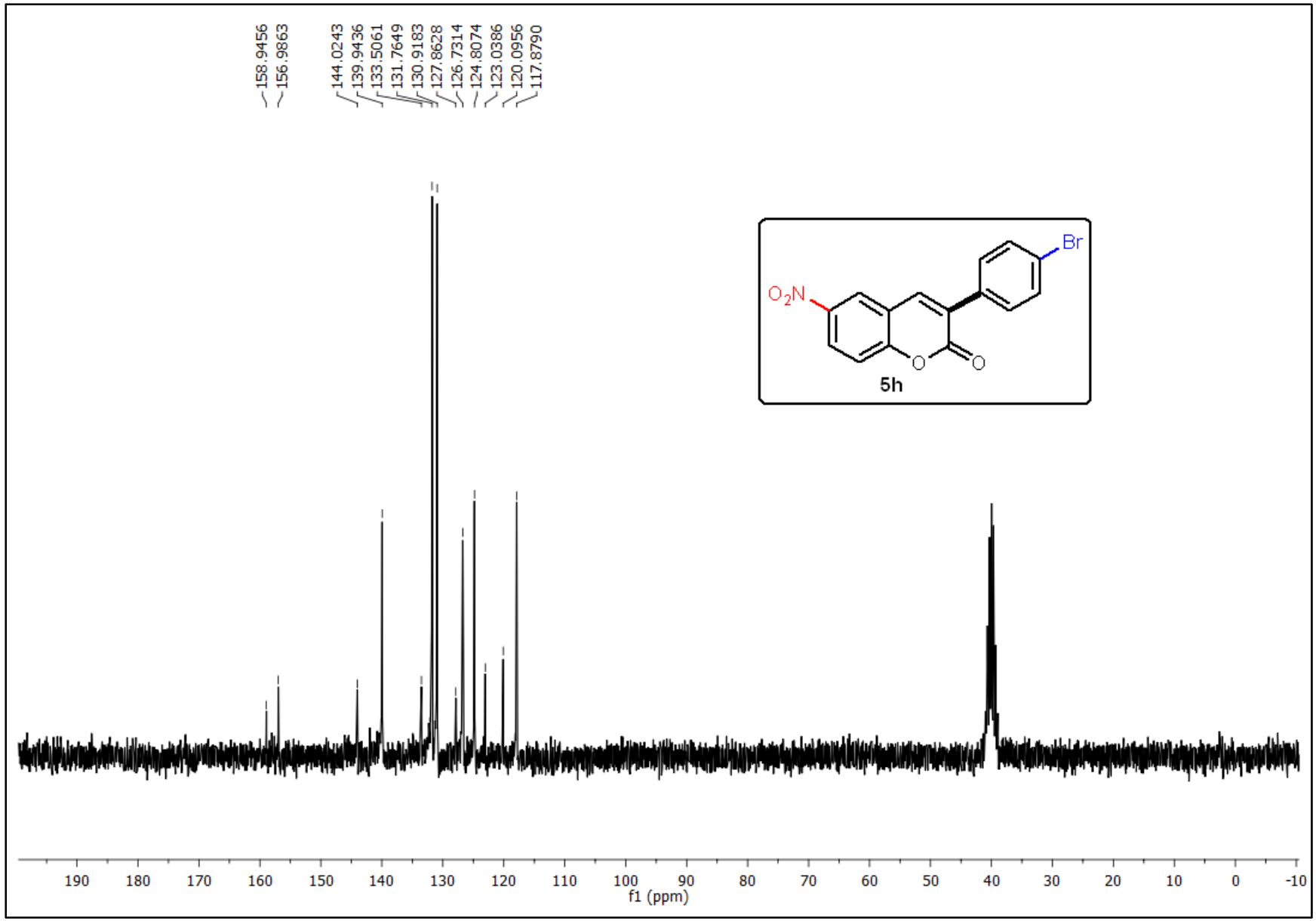
0.0
f1 (ppm)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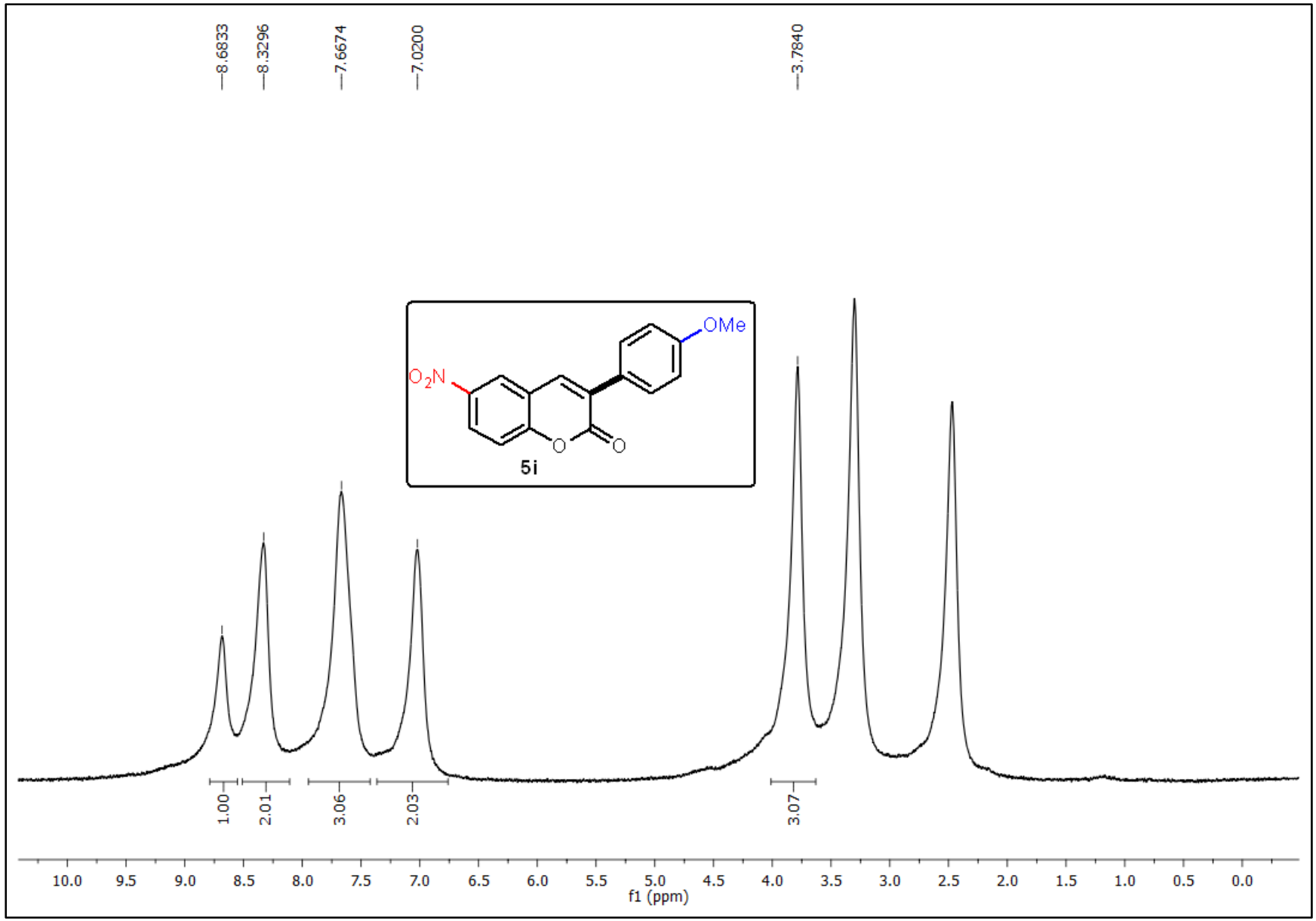
144.0243
139.9436
133.5061
131.7649
130.9183
127.8628
126.7314
124.8074
123.0386
120.0956
117.8790
Br
O2N
O
O
5h
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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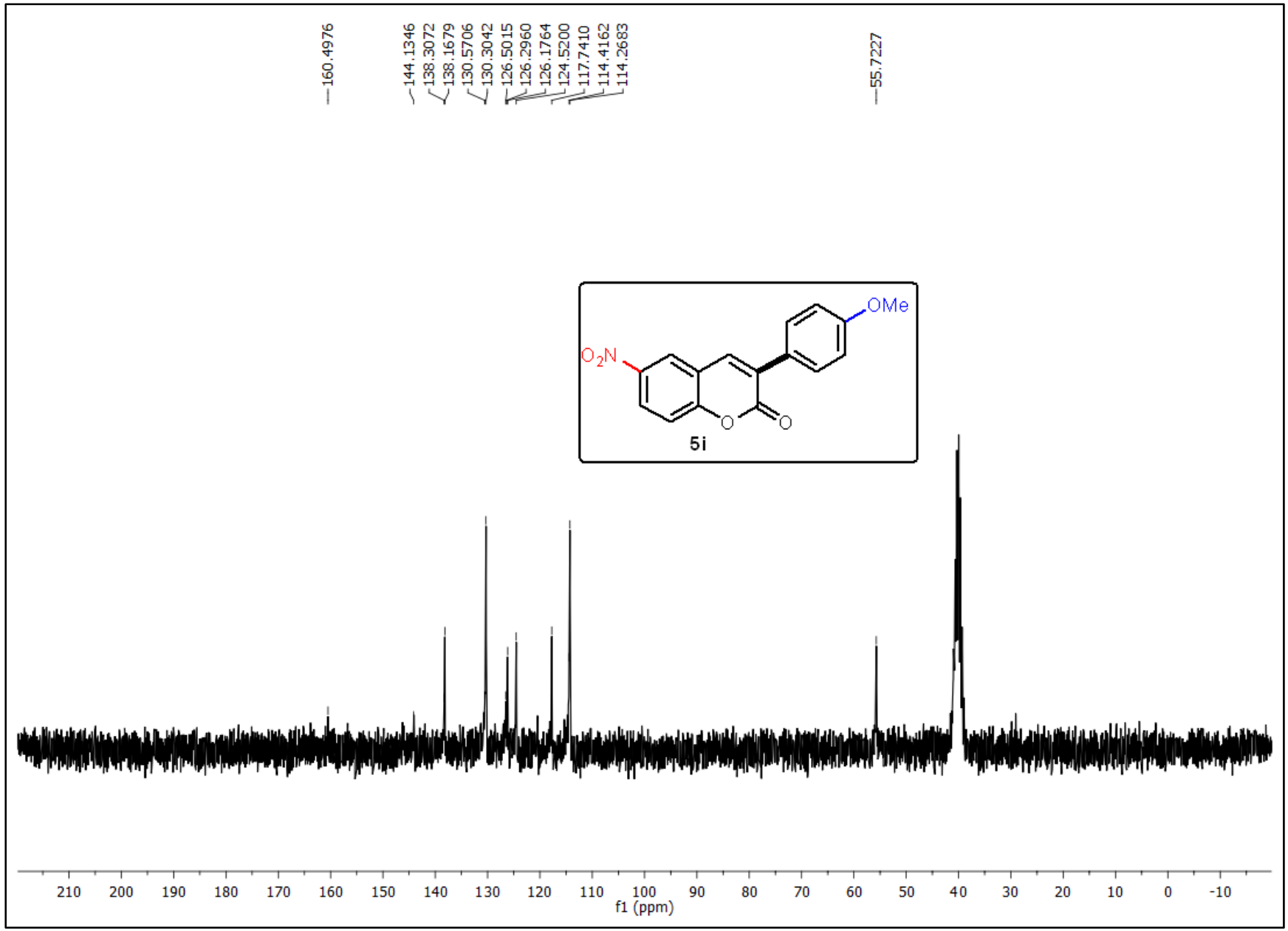
8.3296
7.6674
7.0200
3.7840
OMe
O2N
O
O
5i
1.00
2.01
3.06
2.03
3.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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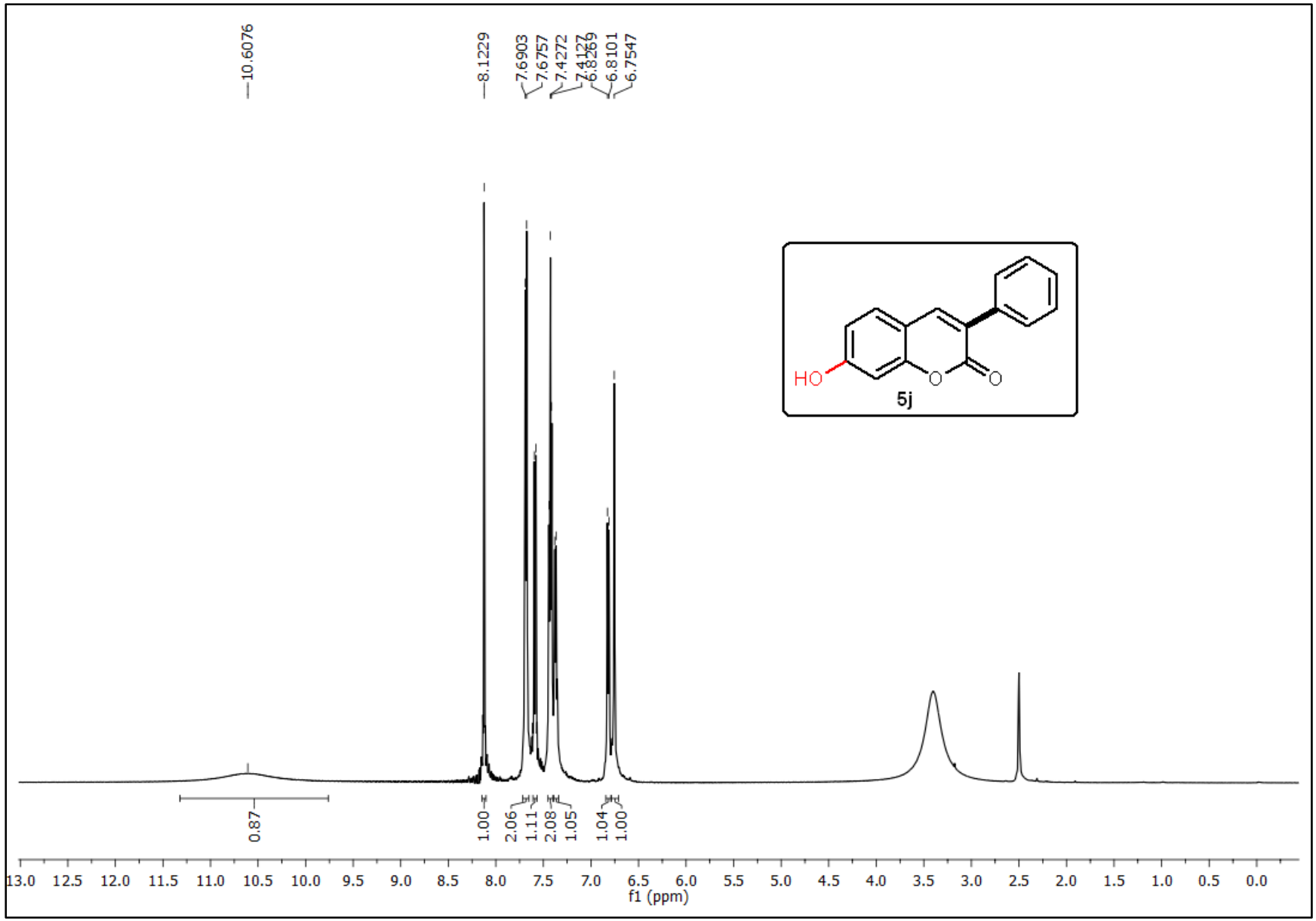
138.3072
138.1679
130.5706
130.3042
126.5015
126.2960
126.1764
124.5200
117.7410
114.4162
114.2683
55.7227
OMe
O2N
O
O
5i
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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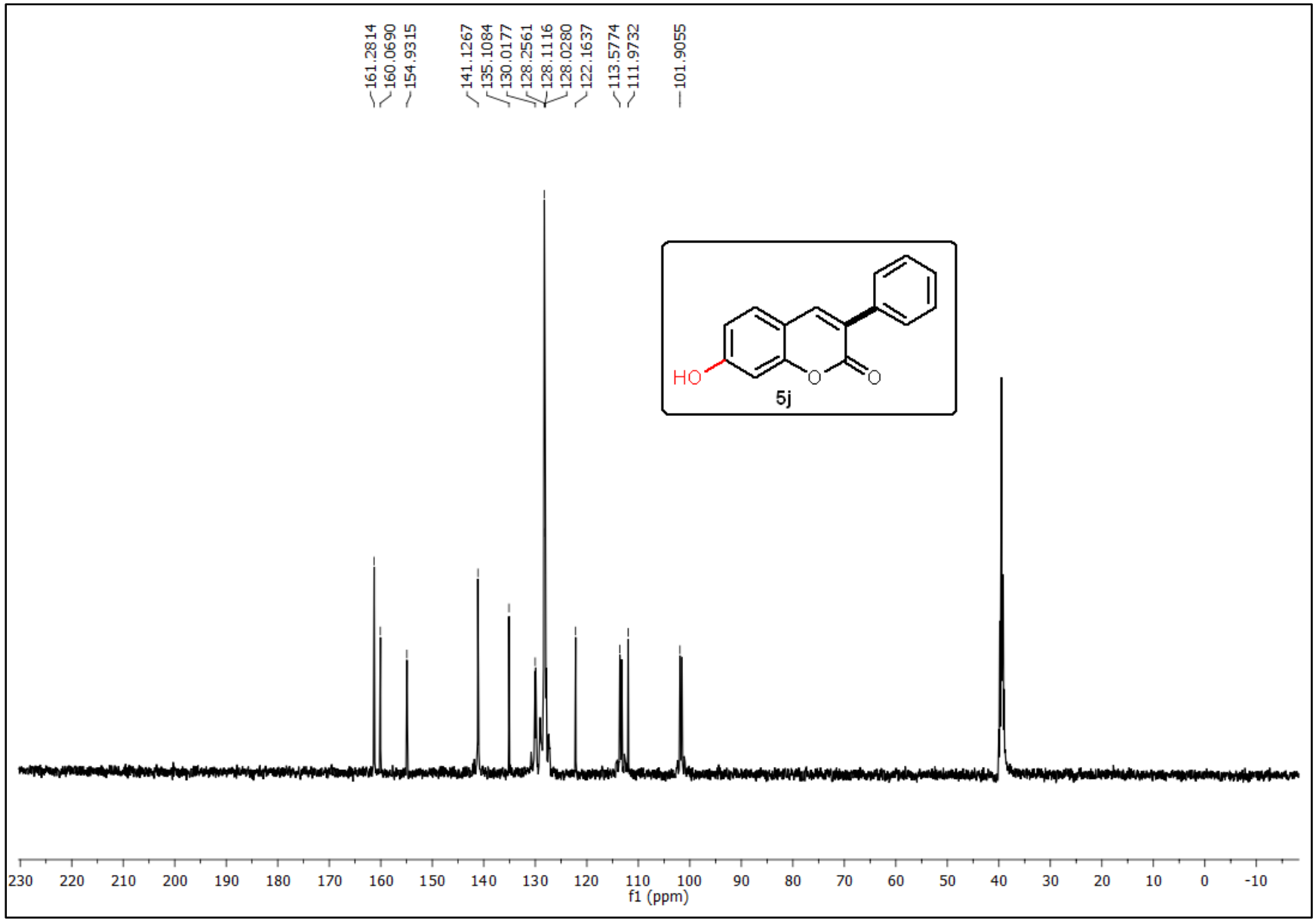
8.1229
7.6903
7.6757
7.4272
7.4127
6.8269
6.8101
6.7547
HO
O
O
5j
0.87
1.00
2.06
1.11
2.08
1.05
1.04
1.00
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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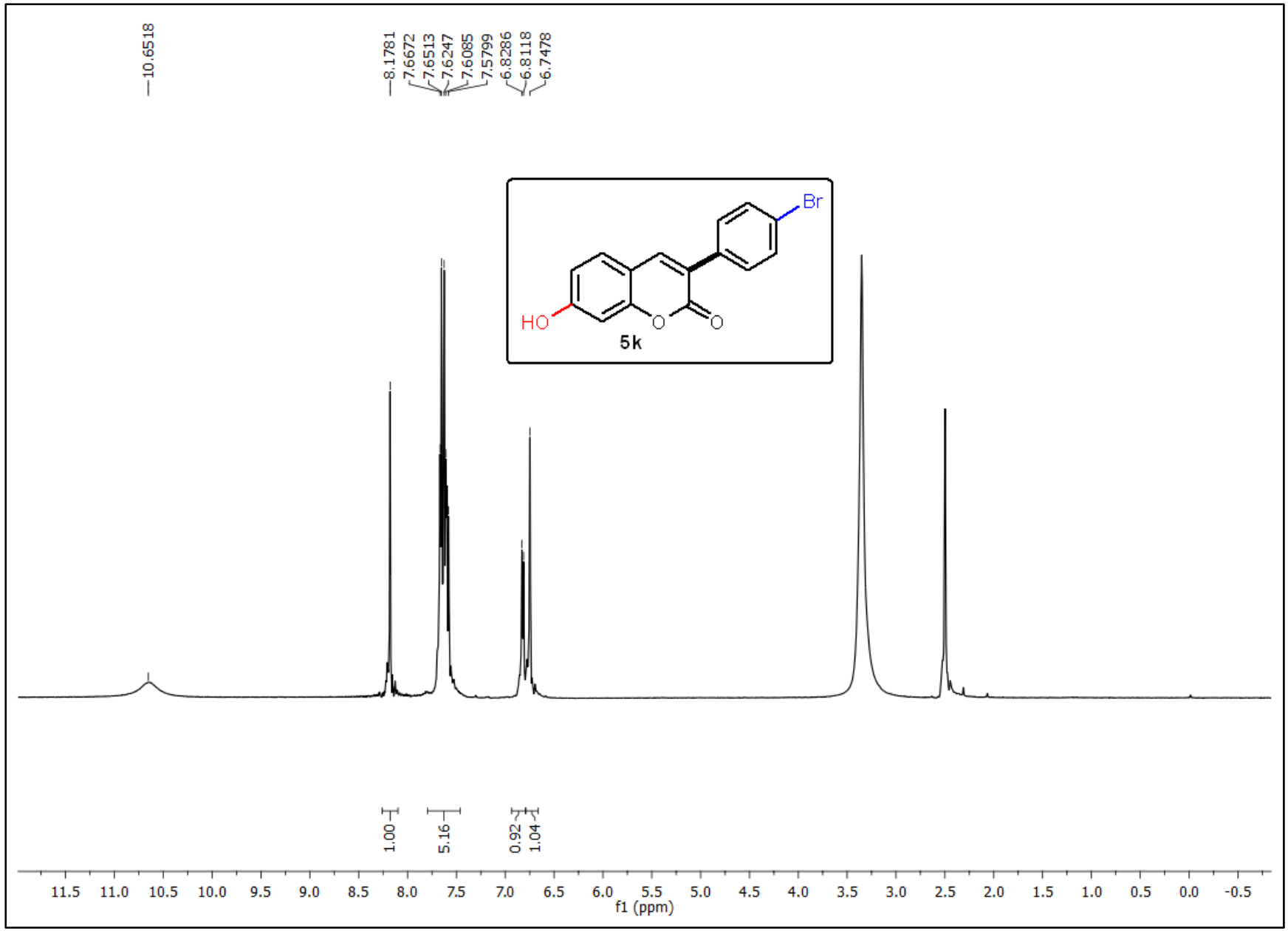
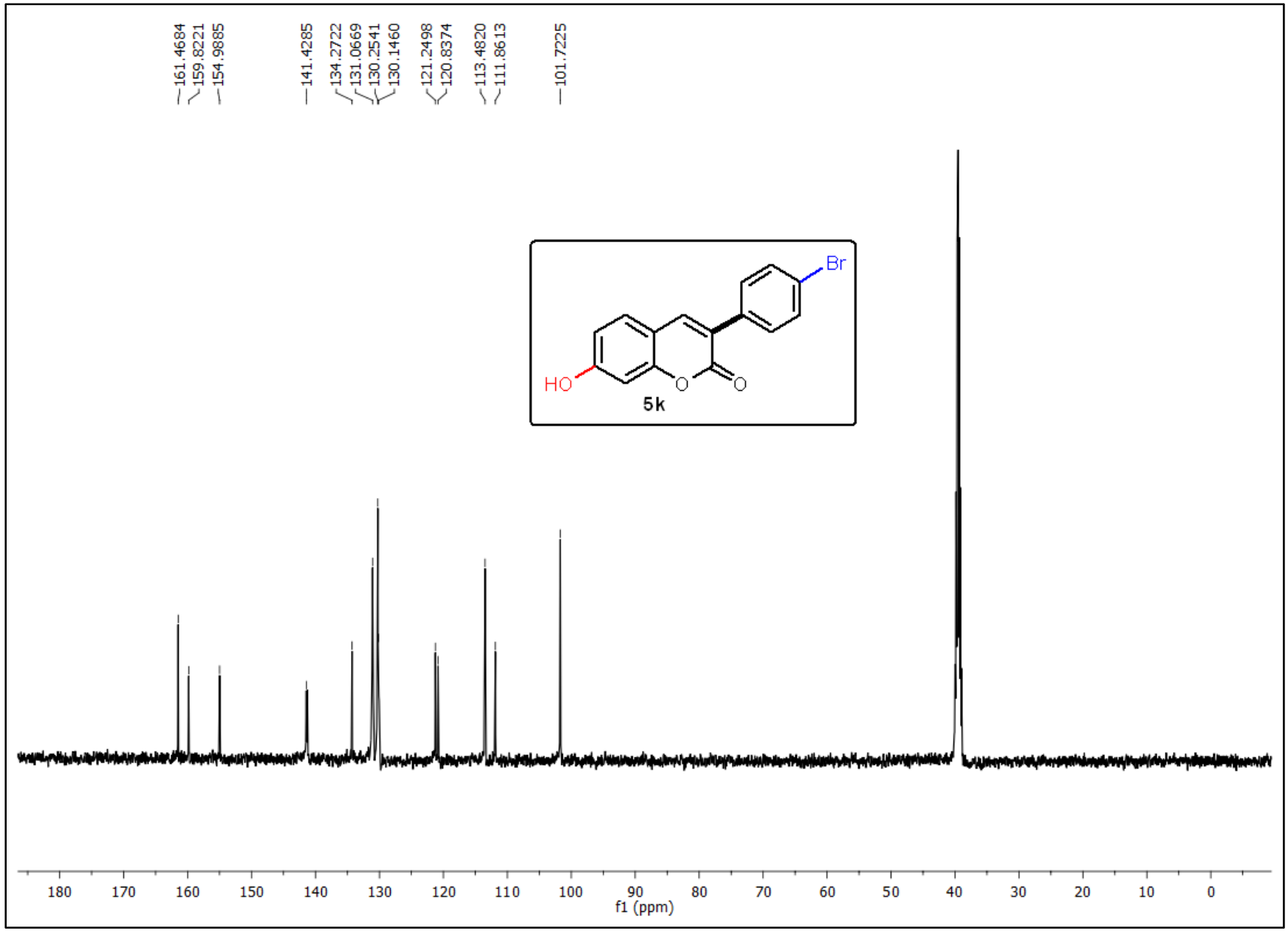
160.0690
154.9315
141.1267
135.1084
130.0177
128.2561
128.1116
128.0280
122.1637
113.5774
111.9732
101.9055
HO
O
O
5j
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


10.6518
8.1781
7.6672
7.6513
7.6247
7.6085
7.5799
6.8286
6.8118
6.7478
Br
HO
O
O
5k
1.00
5.16
0.92
1.04
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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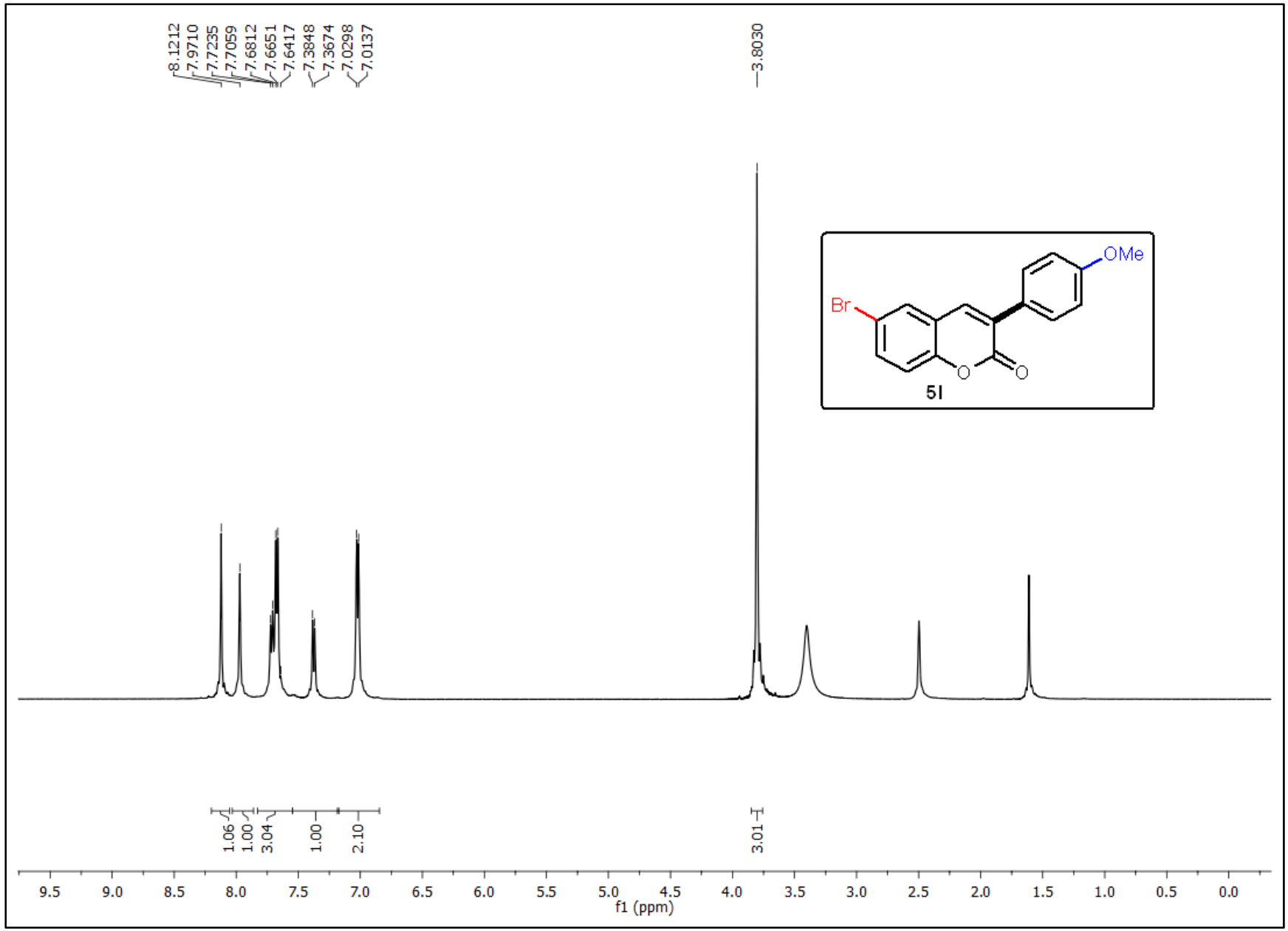
154.9885
141.4285
134.2722
131.0669
130.2541
130.1460
121.2498
120.8374
113.4820
111.8613
101.7225
Br
HO
O
O
5k
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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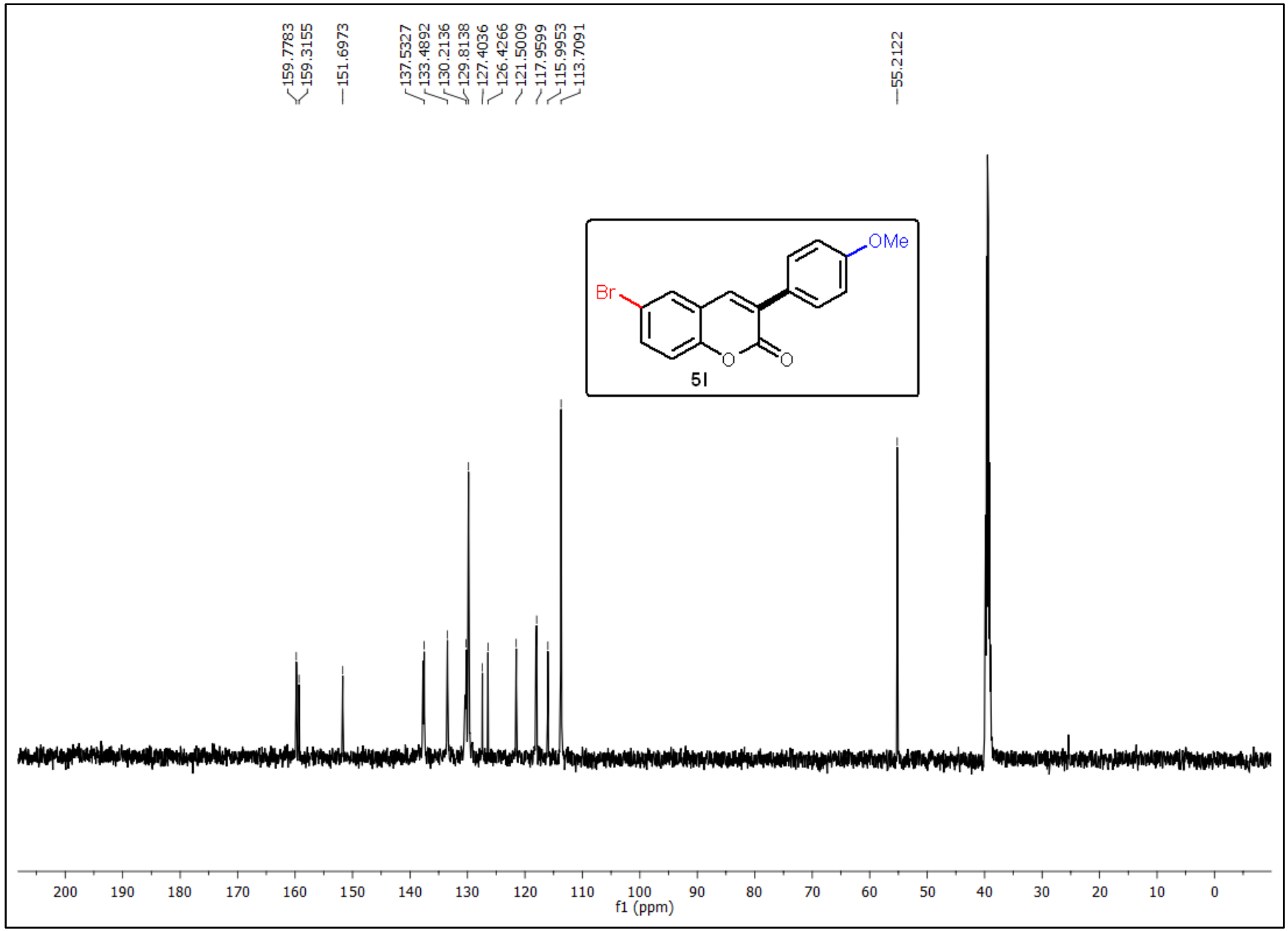
7.7235
7.7059
7.6812
7.6651
7.6417
7.3848
7.3674
7.0298
7.0137
3.8030
OMe
Br
O
O
5l
1.06
1.00
3.04
1.00
2.10
3.01
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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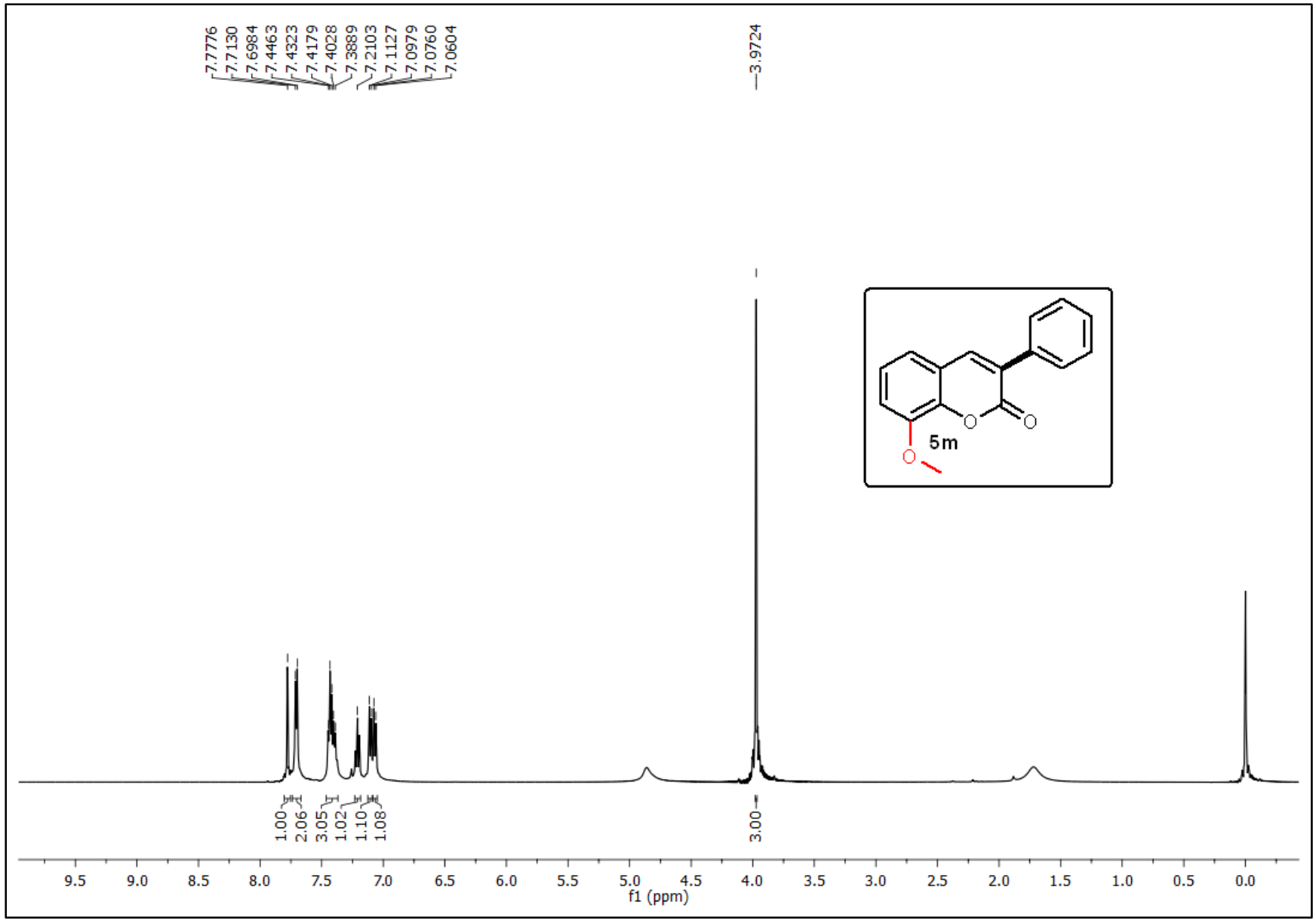
159.3155
151.6973
137.5327
133.4892
130.2136
129.8138
127.4036
126.4266
121.5009
117.9599
115.9953
113.7091
55.2122
OMe
Br
O
O
5l
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.4323
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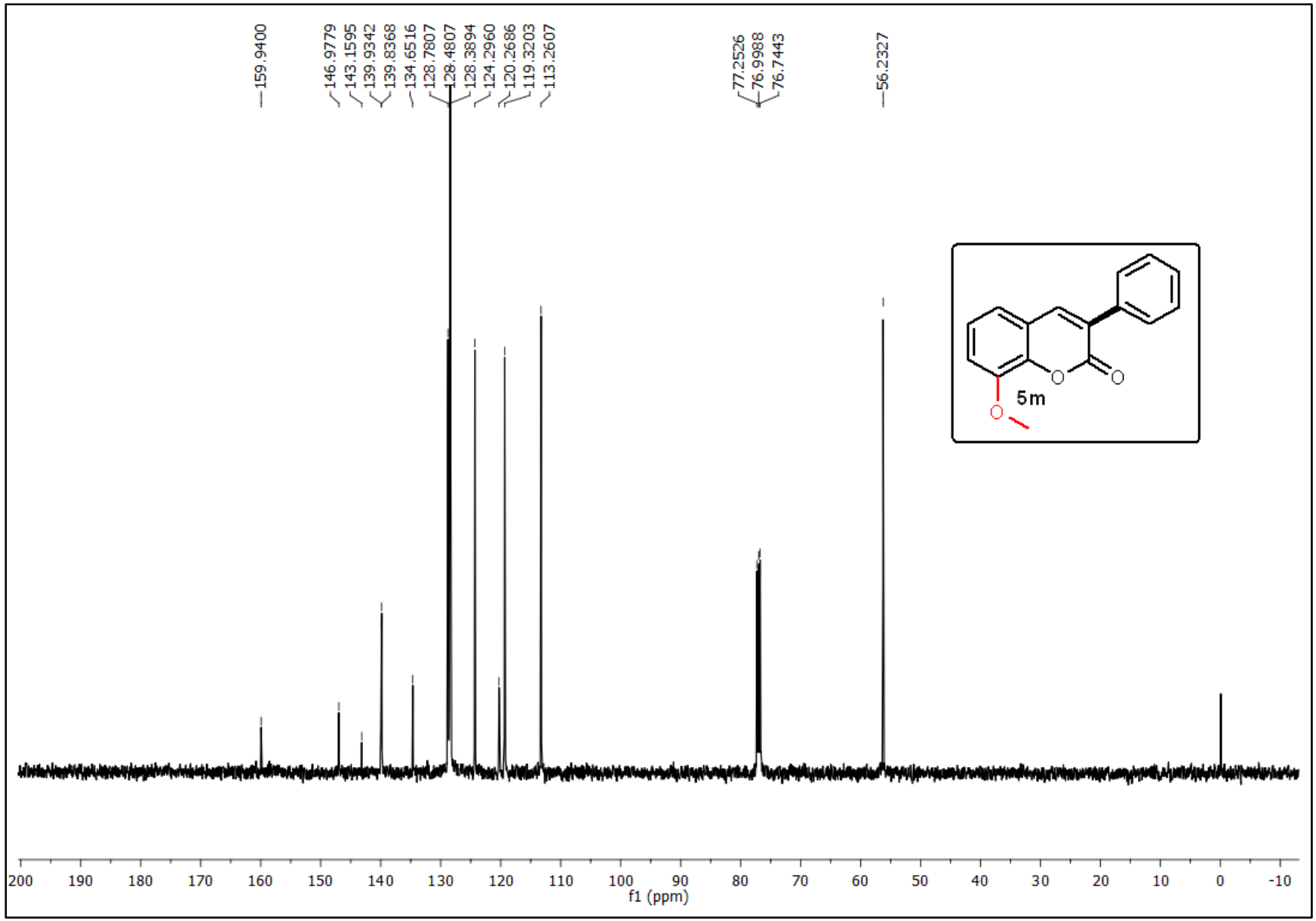
7.4028
7.3889
7.2103
7.1127
7.0979
7.0760
7.0604
3.9724
5m
1.00
2.06
3.05
1.02
1.10
1.08
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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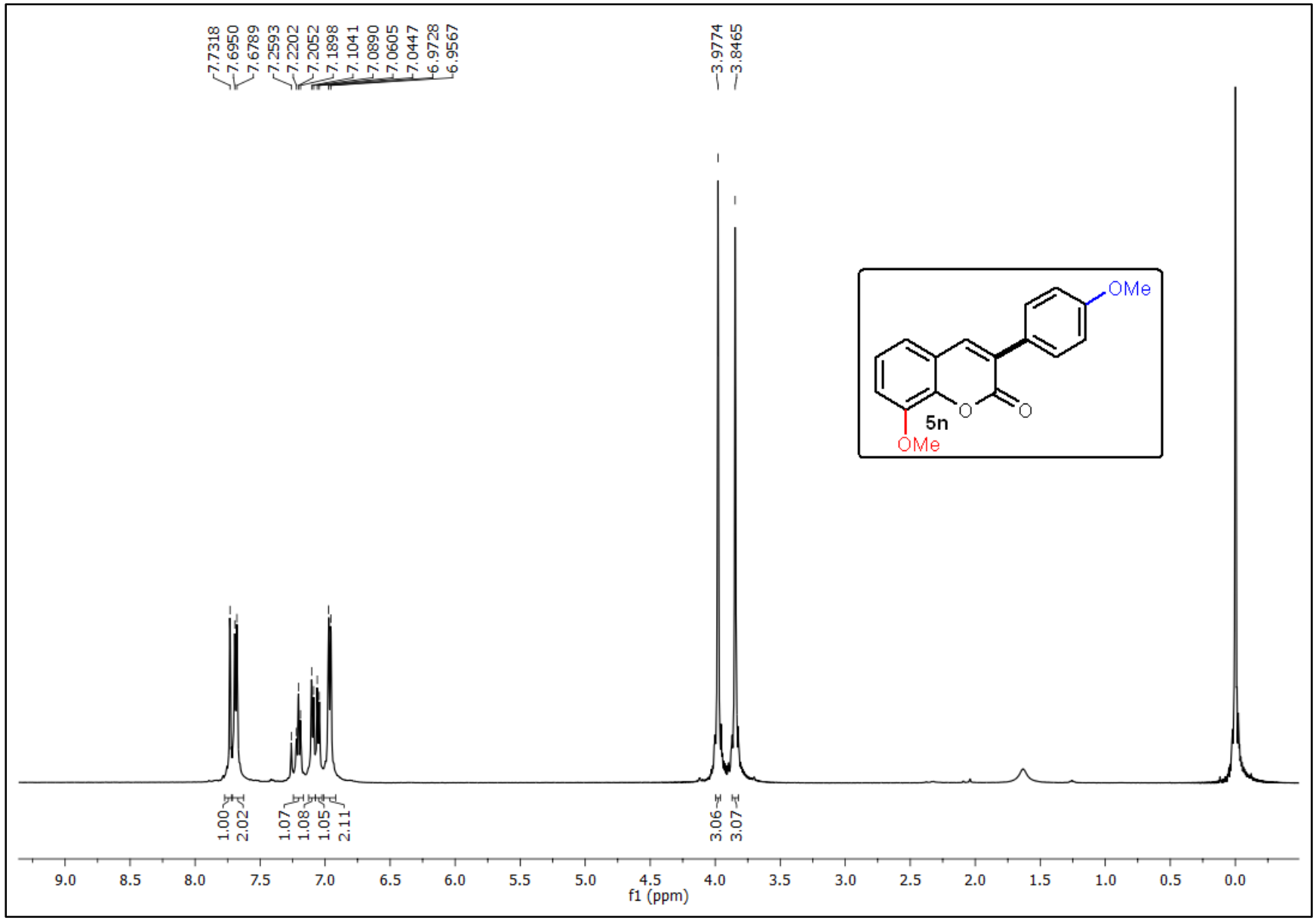
128.4807
128.3894
124.2960
120.2686
119.3203
113.2607
77.2526
76.9988
76.7443
56.2327
5m
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.2052
7.1898
7.1041
7.0890
7.0605
7.0447
6.9728
6.9567
3.9774
3.8465
OMe
5n
OMe
1.00
2.02
1.07
1.08
1.05
2.11
3.06
3.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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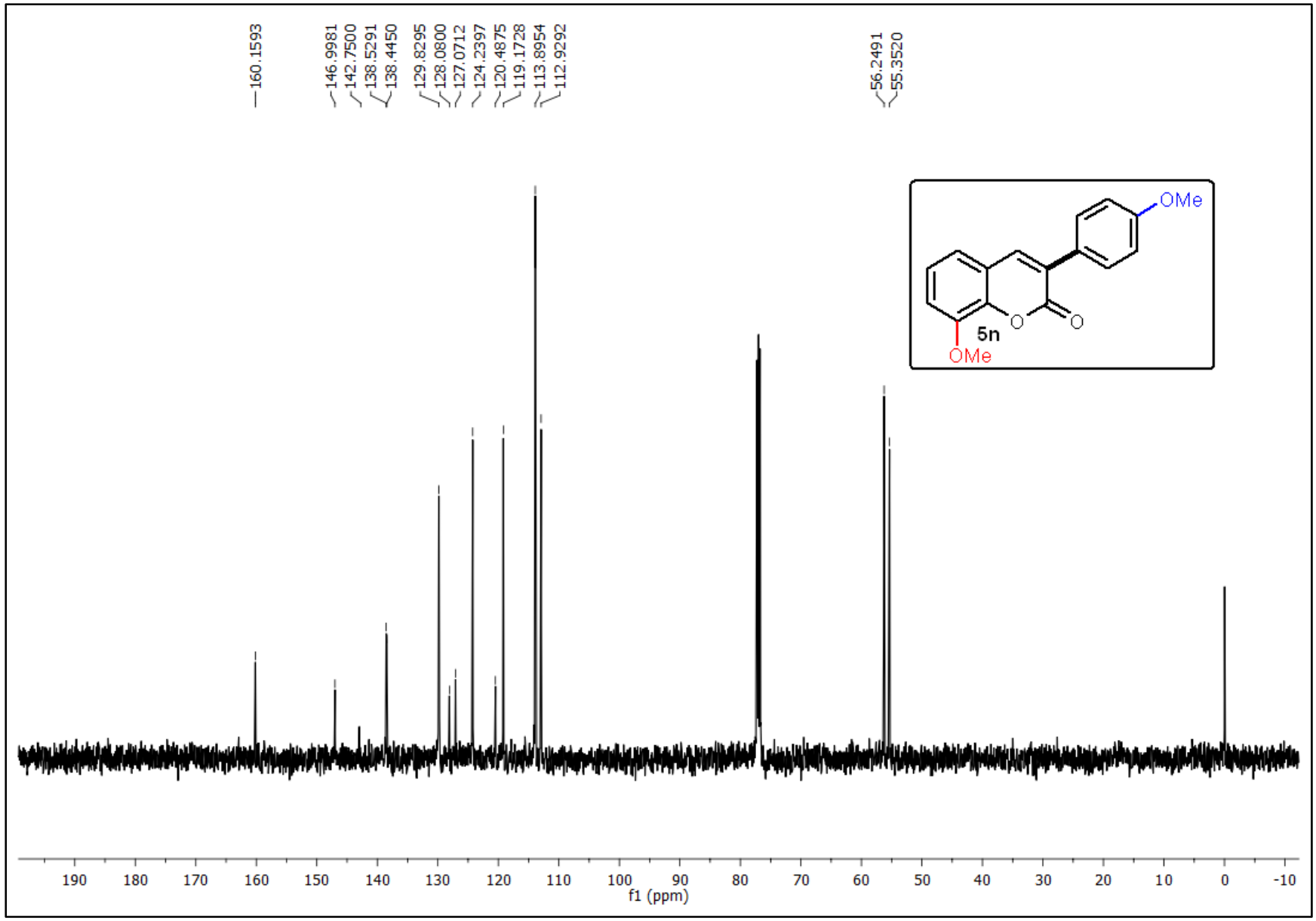
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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138.4450
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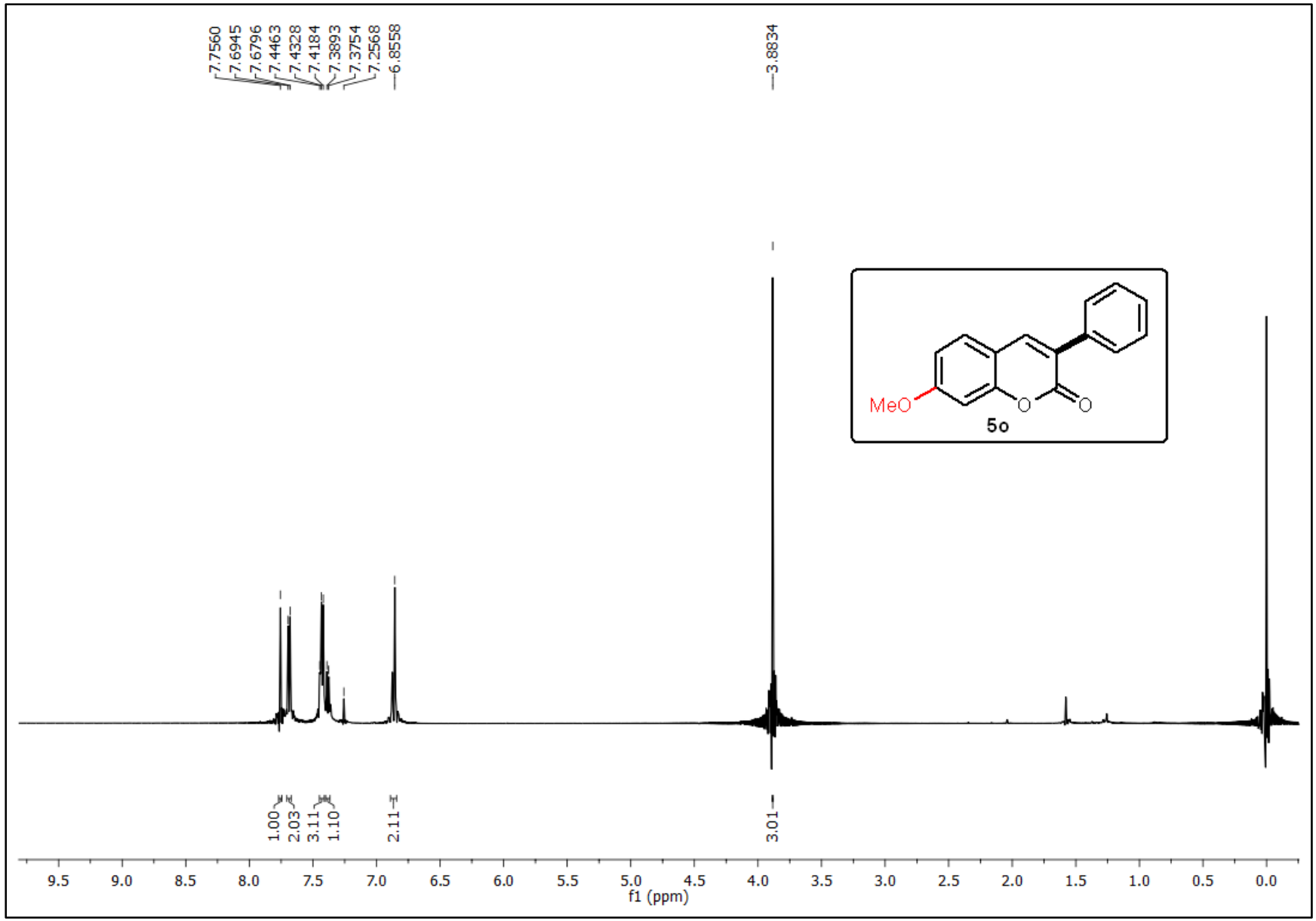
128.0800
127.0712
124.2397
120.4875
119.1728
113.8954
112.9292
56.2491
55.3520
OMe
5n
OMe
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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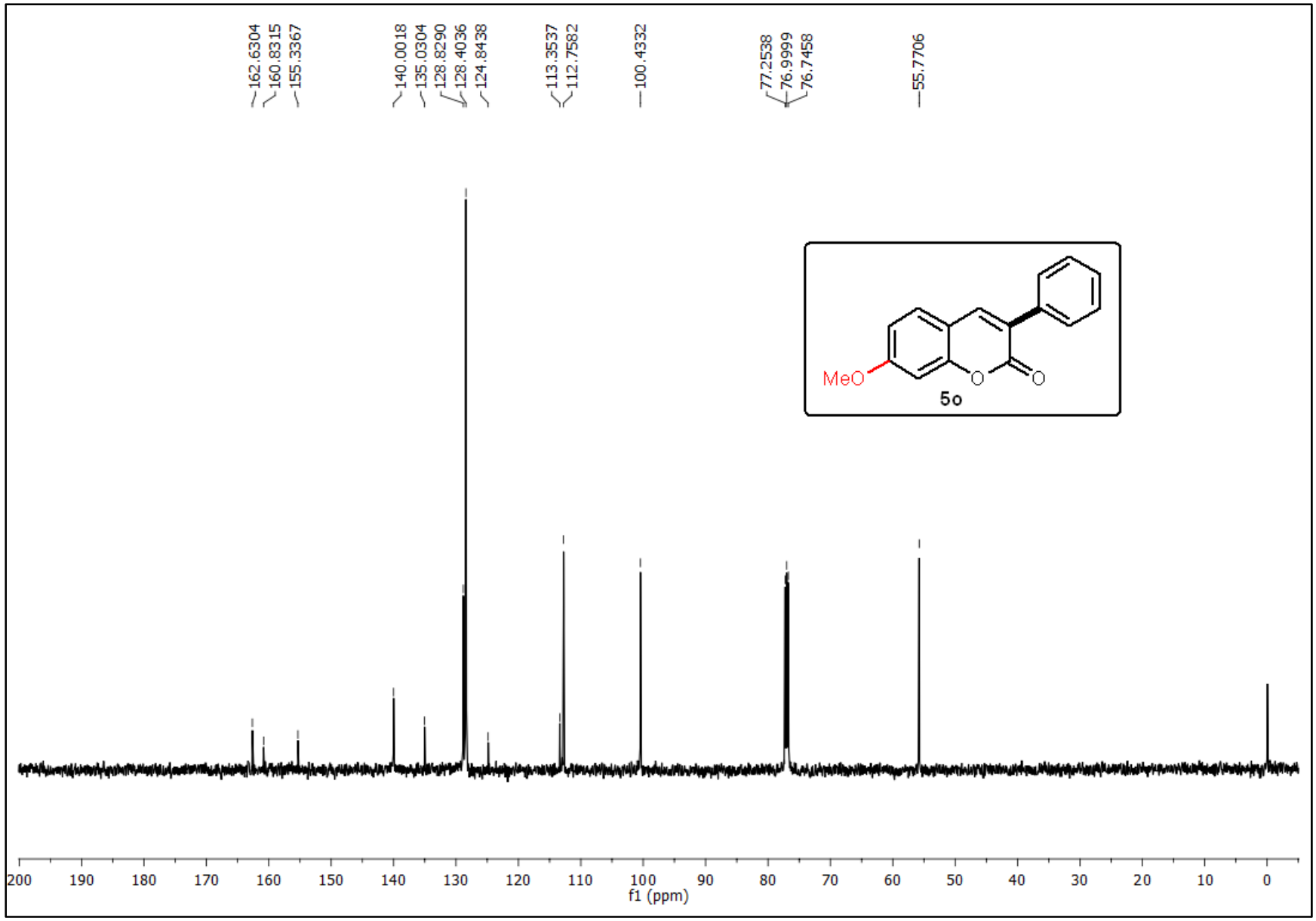
7.4184
7.3893
7.3754
7.2568
6.8558
3.8834
MeO
O
O
5o
1.00
2.03
3.11
1.10
2.11
3.01
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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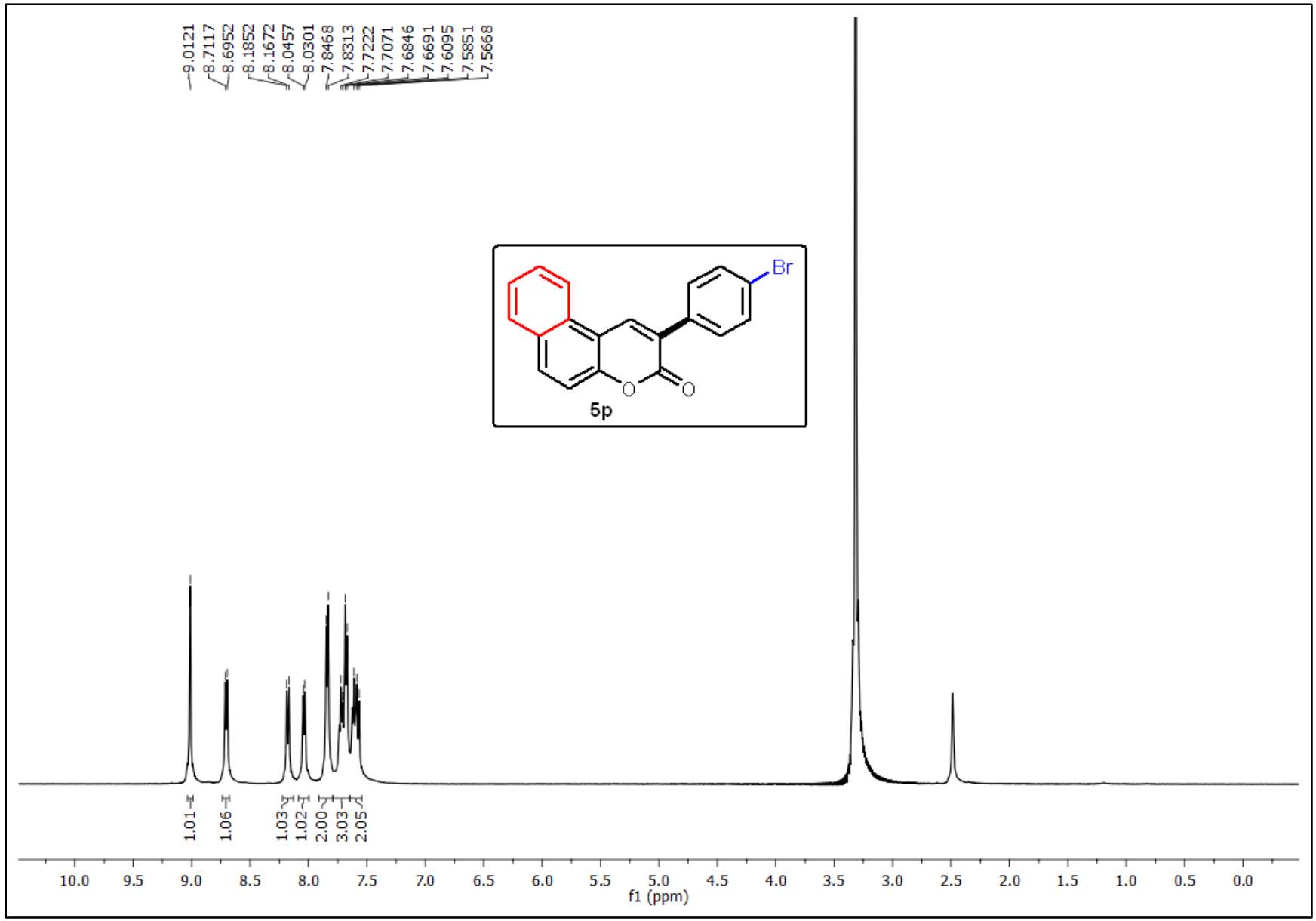
128.4036
124.8438
113.3537
112.7582
100.4332
77.2538
76.9999
76.7458
55.7706
MeO
O
O
5o
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.1852
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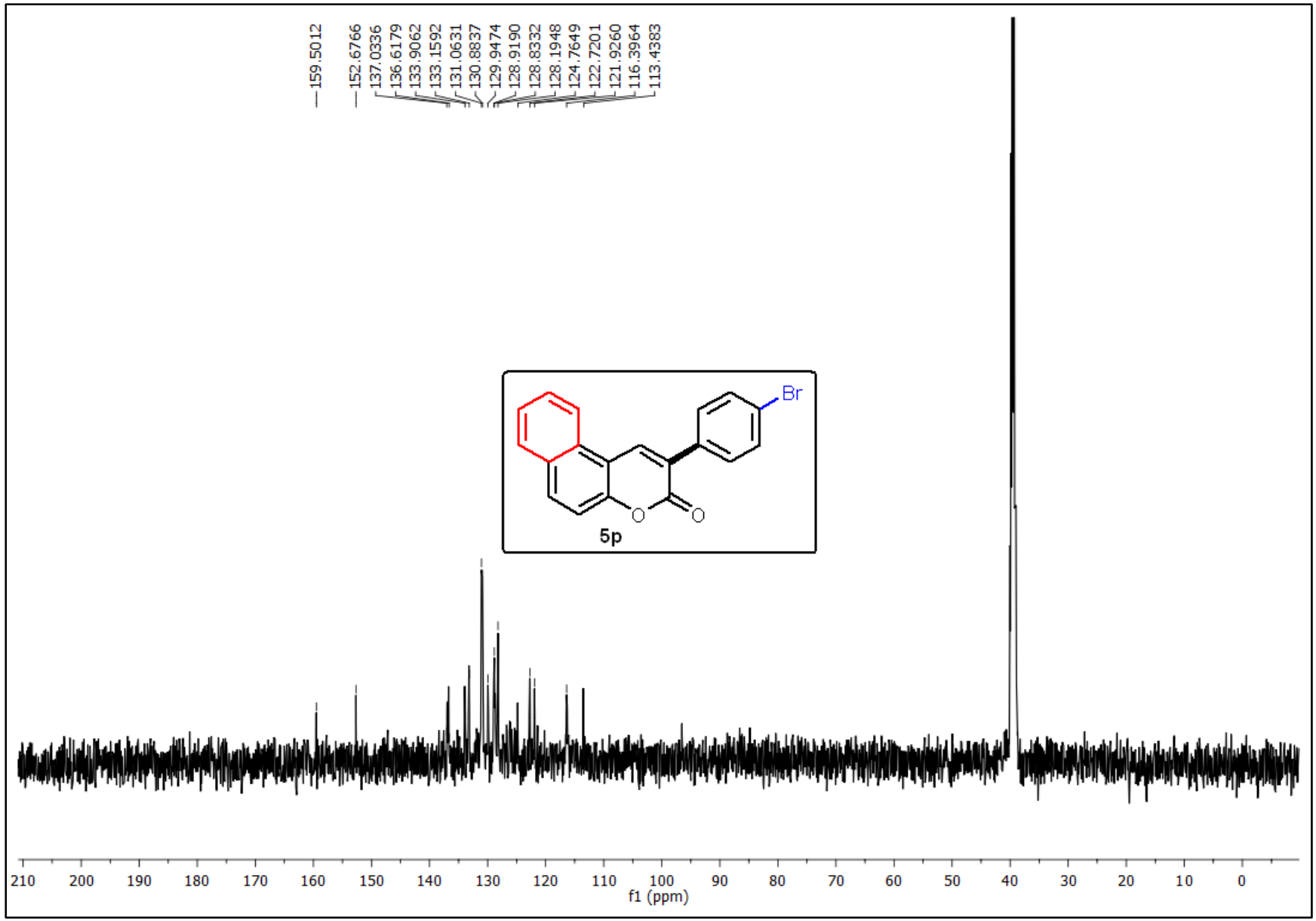
8.0457
8.0301
7.8468
7.8313
7.7222
7.7071
7.6846
7.6691
7.6095
7.5851
7.5668
Br
O
O
5p
1.01
1.06
1.03
1.02
2.00
3.03
2.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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128.8332
128.1948
124.7649
122.7201
121.9260
116.3964
113.4383
Br
O
O
5p
210
200
190
180
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110
100
90
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70
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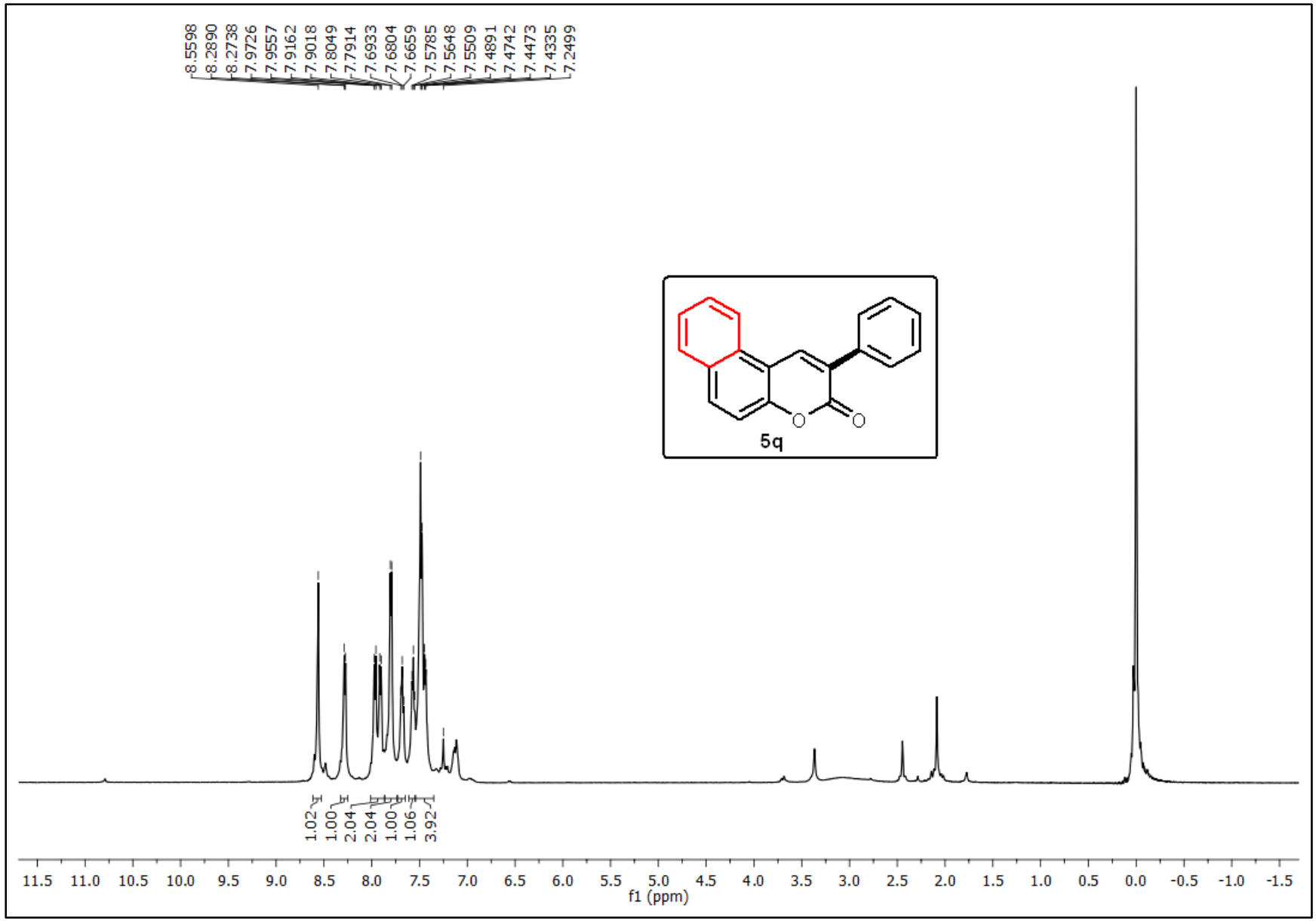
50
40
30
20
10
0
f1 (ppm)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7.6659
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7.5648
7.5509
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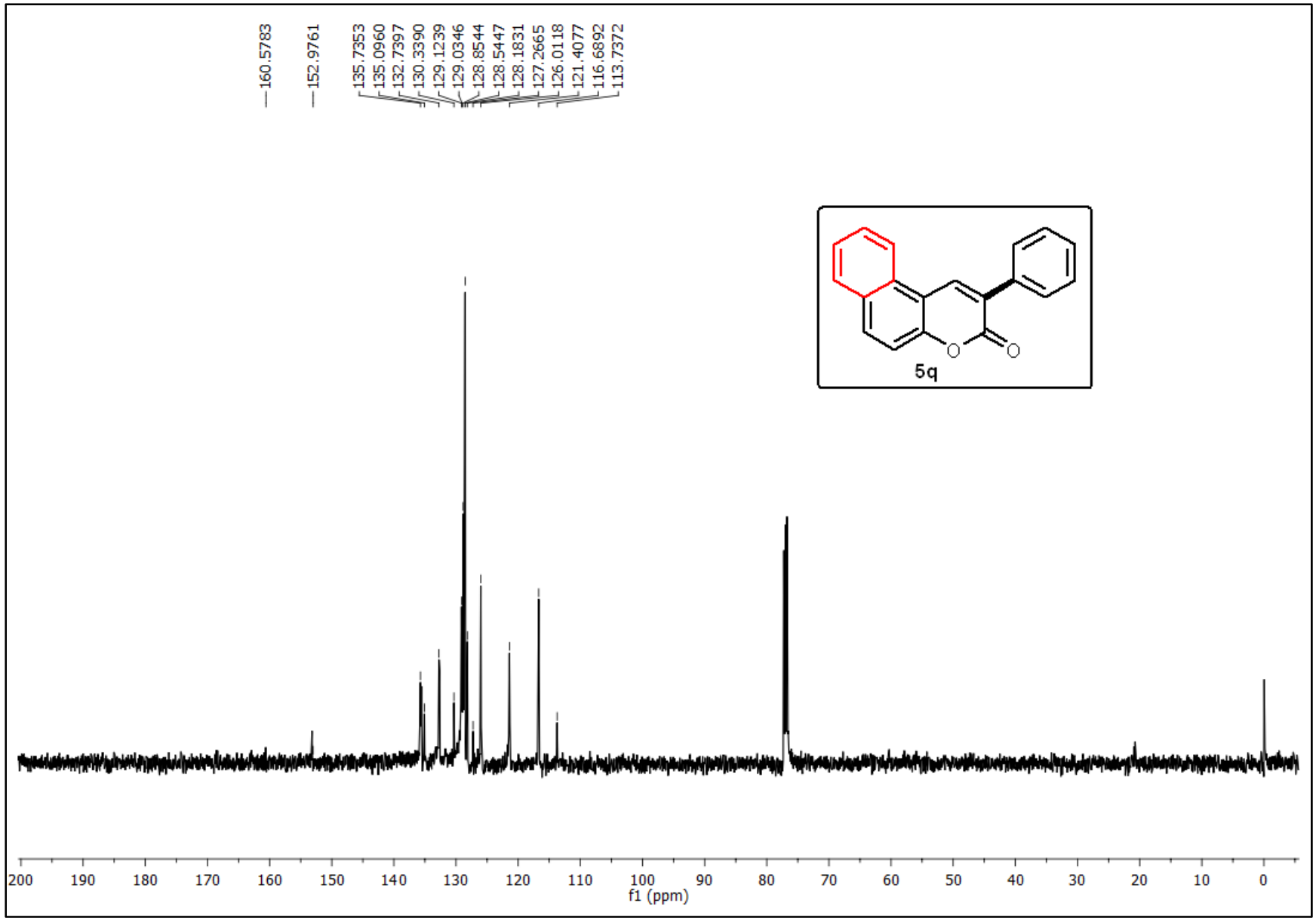
7.4473
7.4335
7.2499
5q
1.02
1.00
2.04
2.04
1.00
1.06
3.92
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)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129.1239
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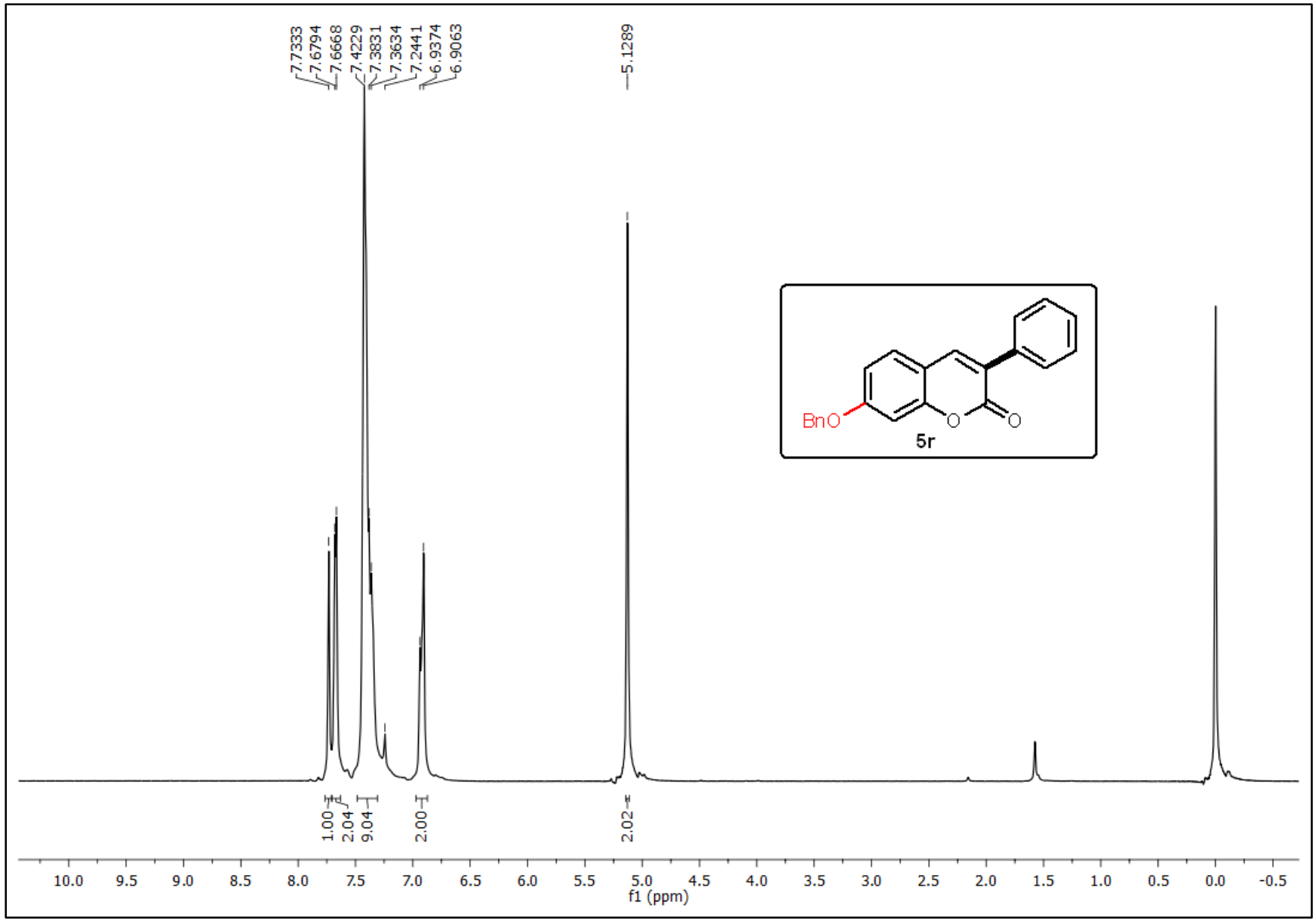
128.1831
127.2665
126.0118
121.4077
116.6892
113.7372
5q
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.2441
6.9374
6.9063
5.1289
BnO
O
O
5r
1.00
2.04
9.04
2.00
2.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
1.5
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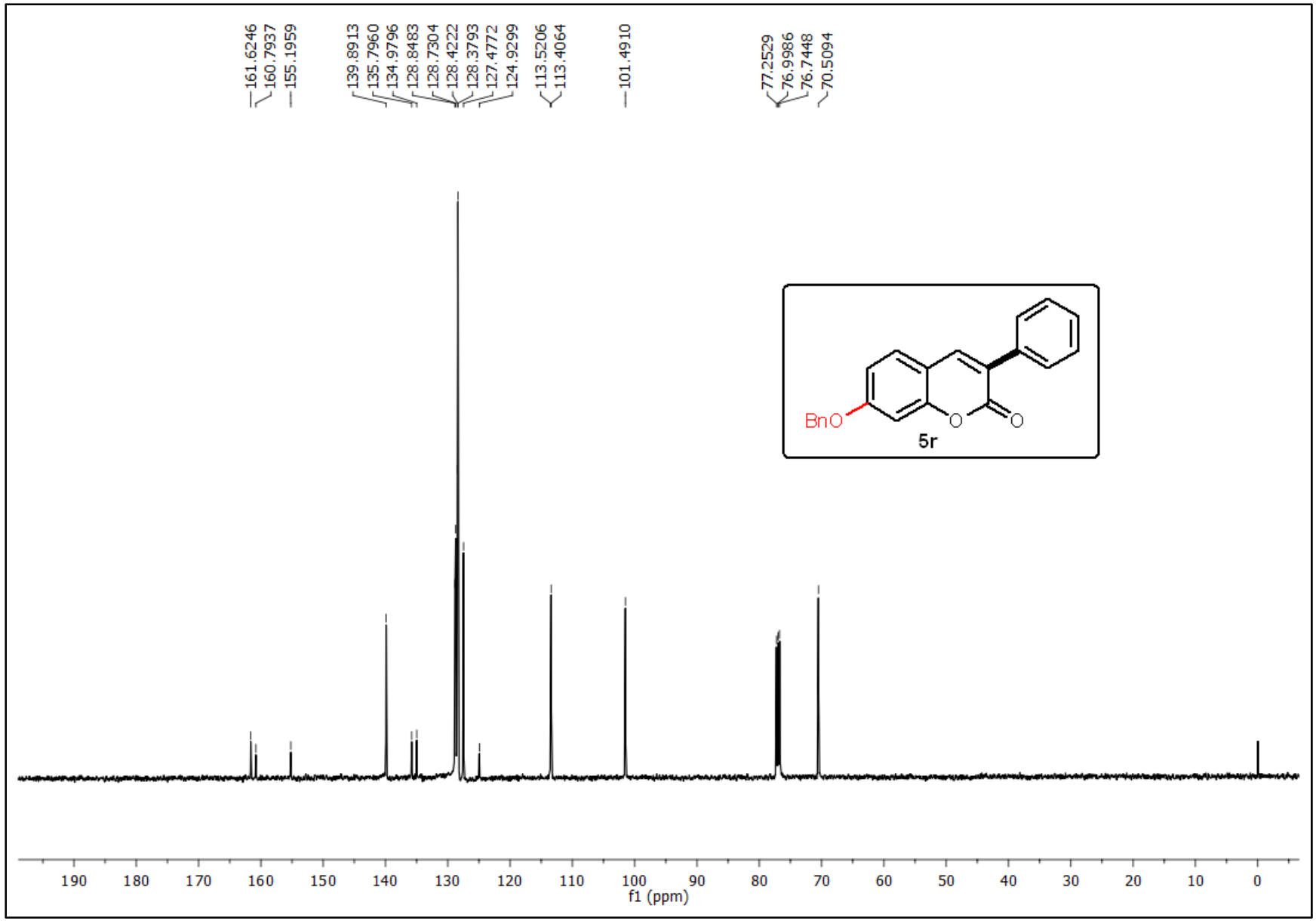
0.0
-0.5
f1 (ppm)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113.5206
113.4064
101.4910
77.2529
76.9986
76.7448
70.5094
BnO
O
O
5r
190
180
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130
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110
100
90
80
70
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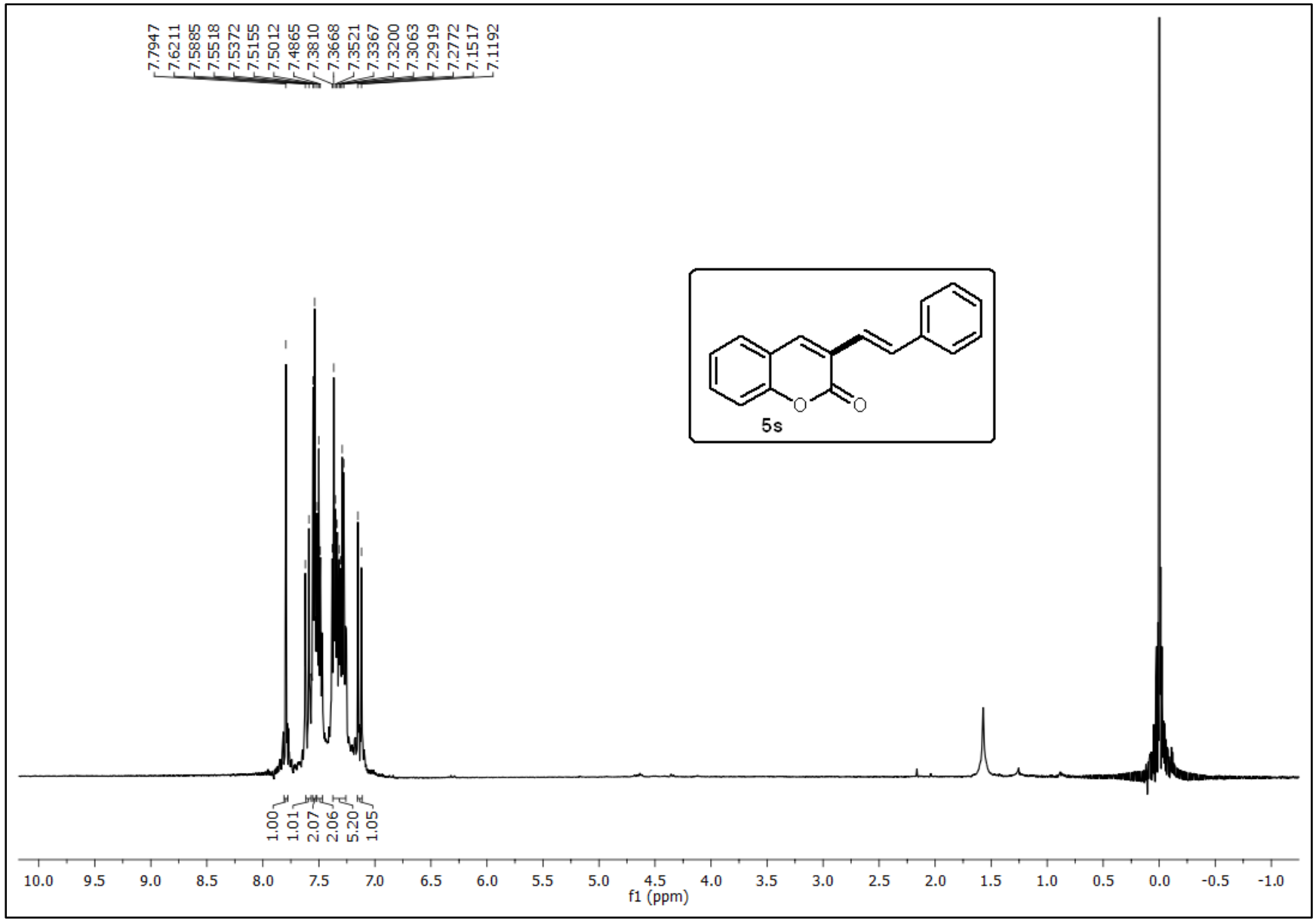
50
40
30
20
10
0
f1 (ppm)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7.3367
7.3200
7.3063
7.2919
7.2772
7.1517
7.1192
5s
1.00
1.01
2.07
2.06
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10.0
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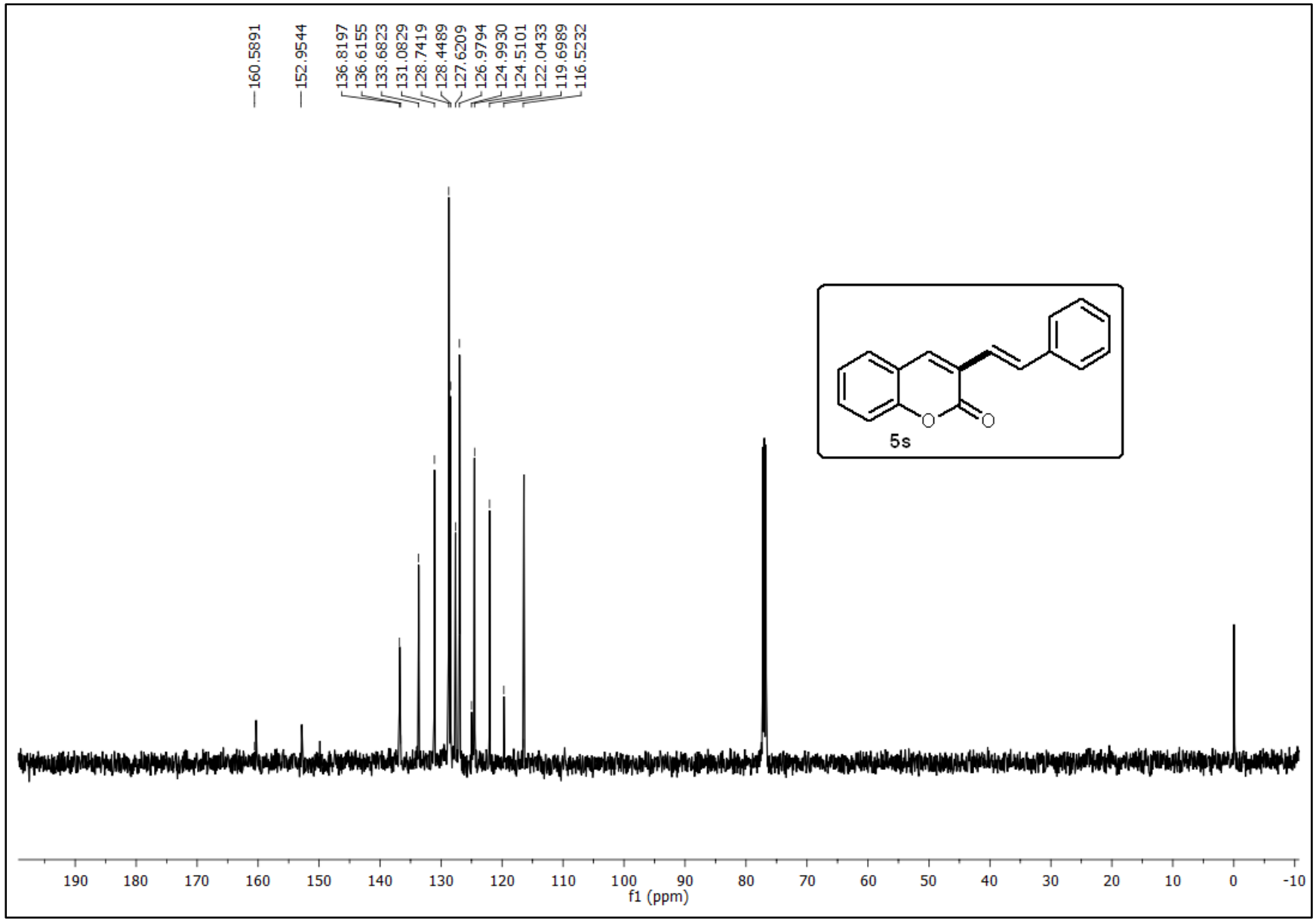
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


160.5891
152.9544
136.8197
136.6155
133.6823
131.0829
128.7419
128.4489
127.6209
126.9794
124.9930
124.5101
122.0433
119.6989
116.5232
5s
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)