Organic & Biomolecular Chemistry

SUPPORTING INFORMATION

Metal-free synthesis of nitrile based partially reduced thia- and oxa-thia[5]helicenes: Conformation and dynamics

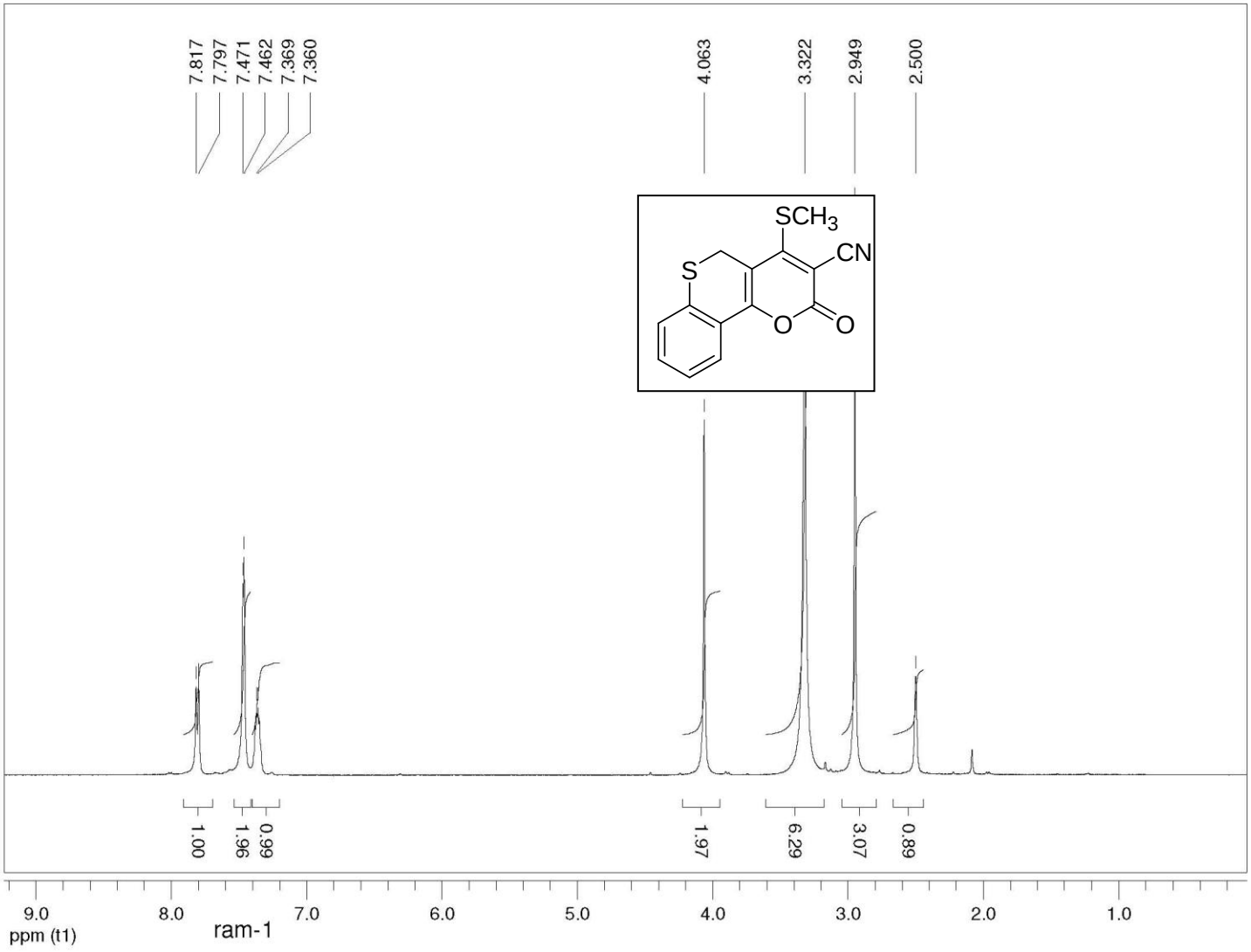
Ramendra Pratap,[a] Abhinav Kumar,[b] Rigoberg Pick,[c] Volker Huch,[d] and Vishnu Ji. Ram[b,*]

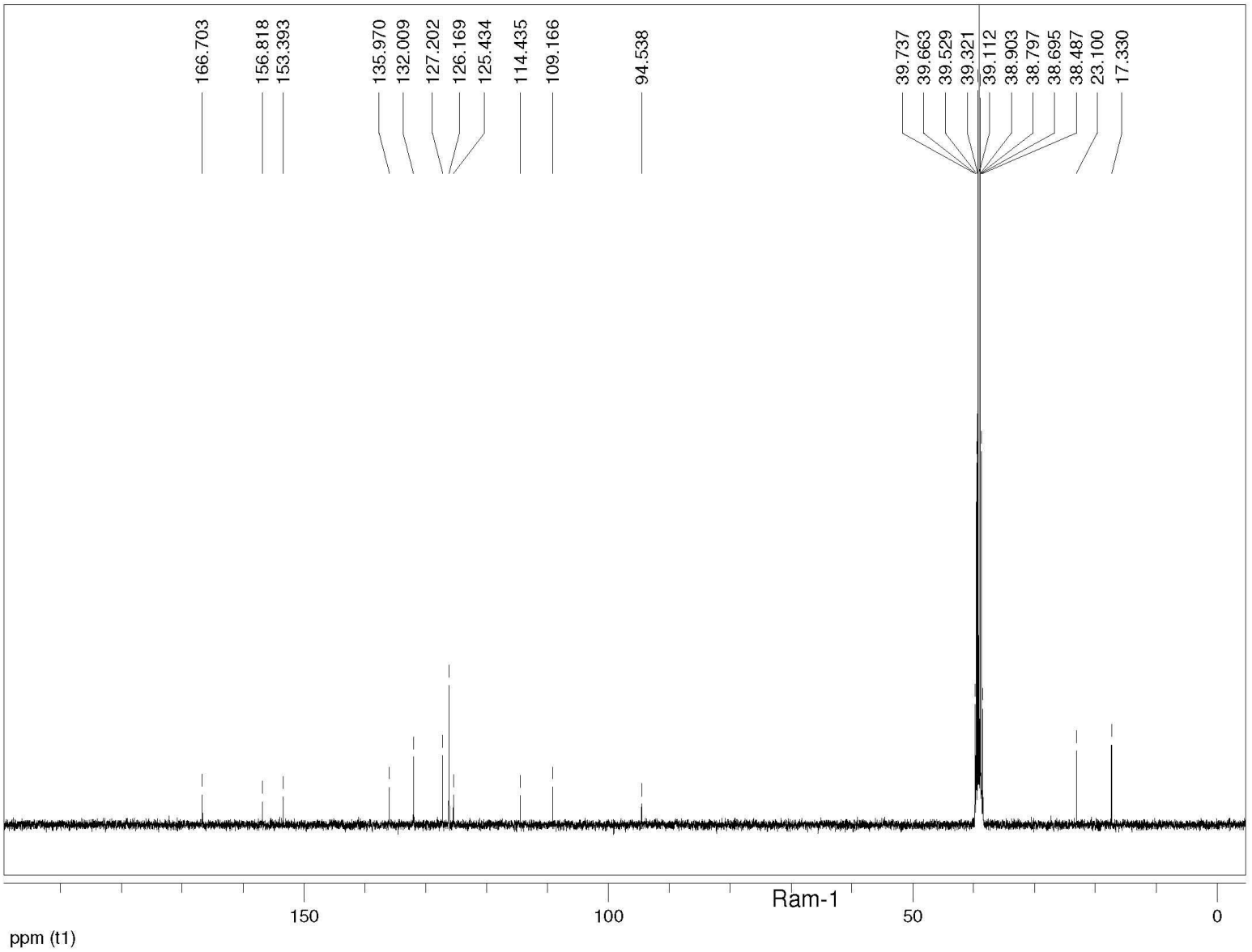
ramendrapratap@gmail.com, vjiram@yahoo.com

2-31: **NMR spectra of the compounds**

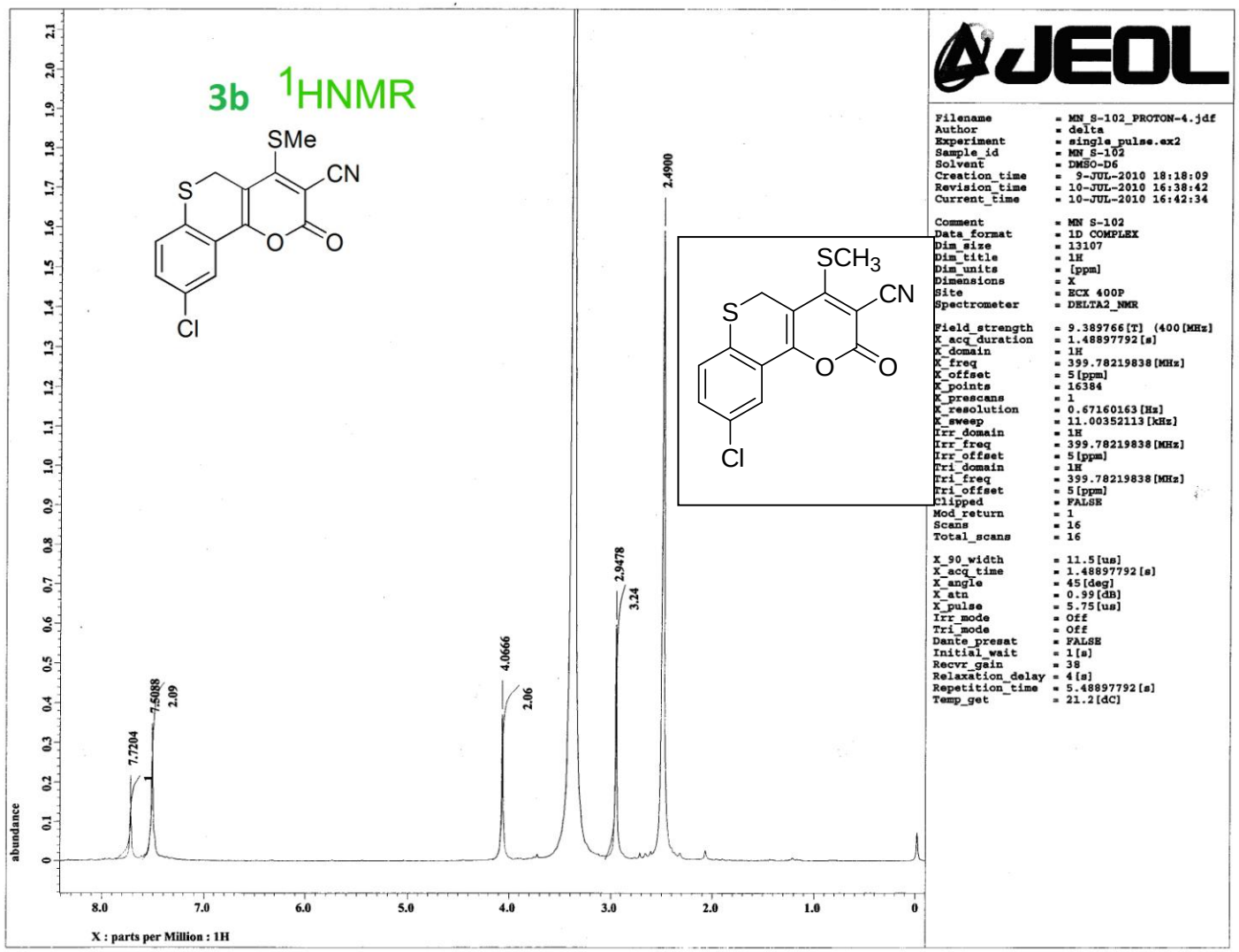
32-39: **Quantum Chemical Calculation detail of 7a**

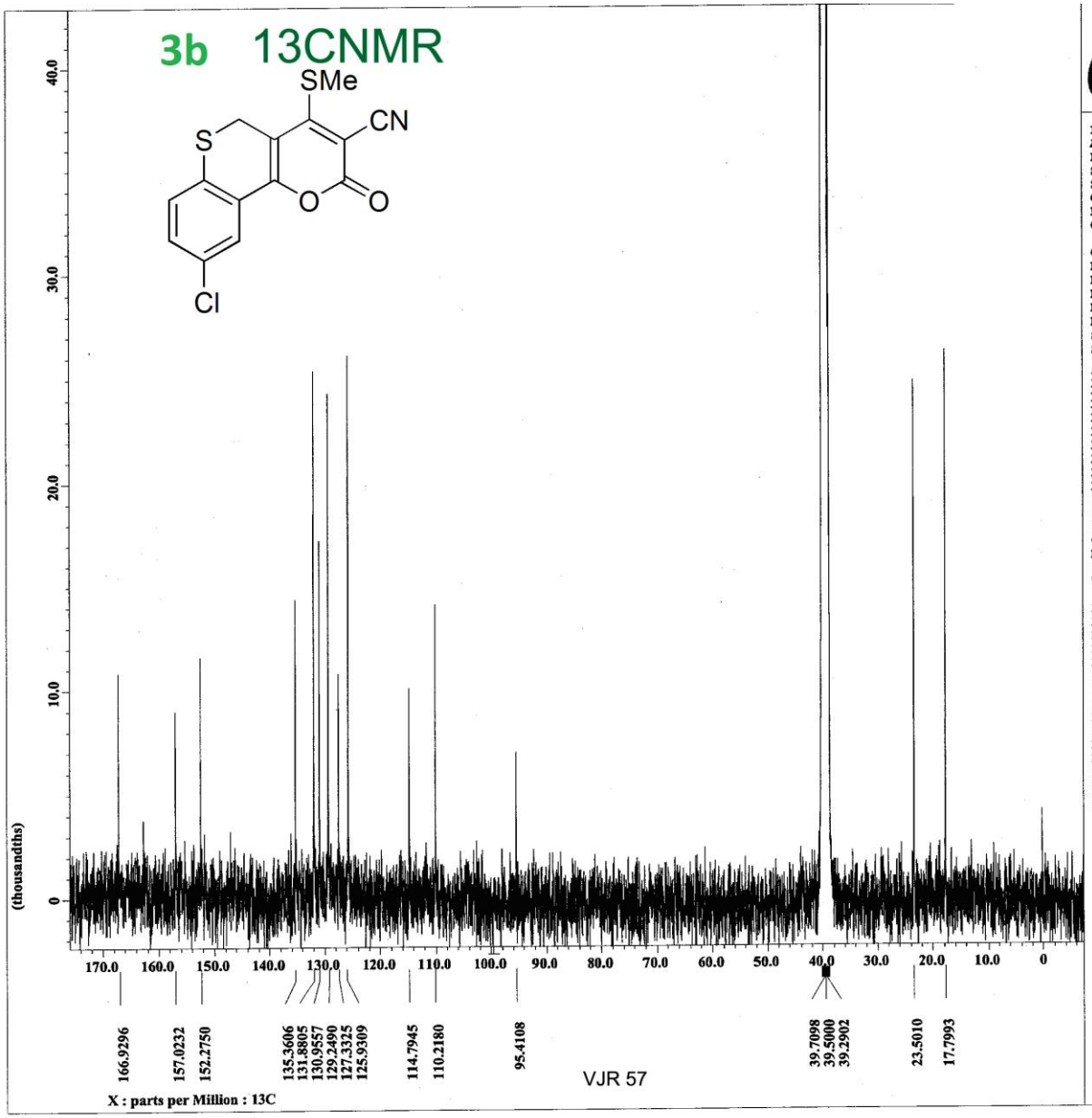
3a: 1-Methylsulfanyl-3-oxo-3*H*,10*H*-4-oxa-9-thiaphenanthrene-2-carbonitrile





3b: 6-Chloro-1-methylsulfanyl-3-oxo-3*H*,10*H*-4-oxa-9-thiaphenanthrene-2-carbonitrile





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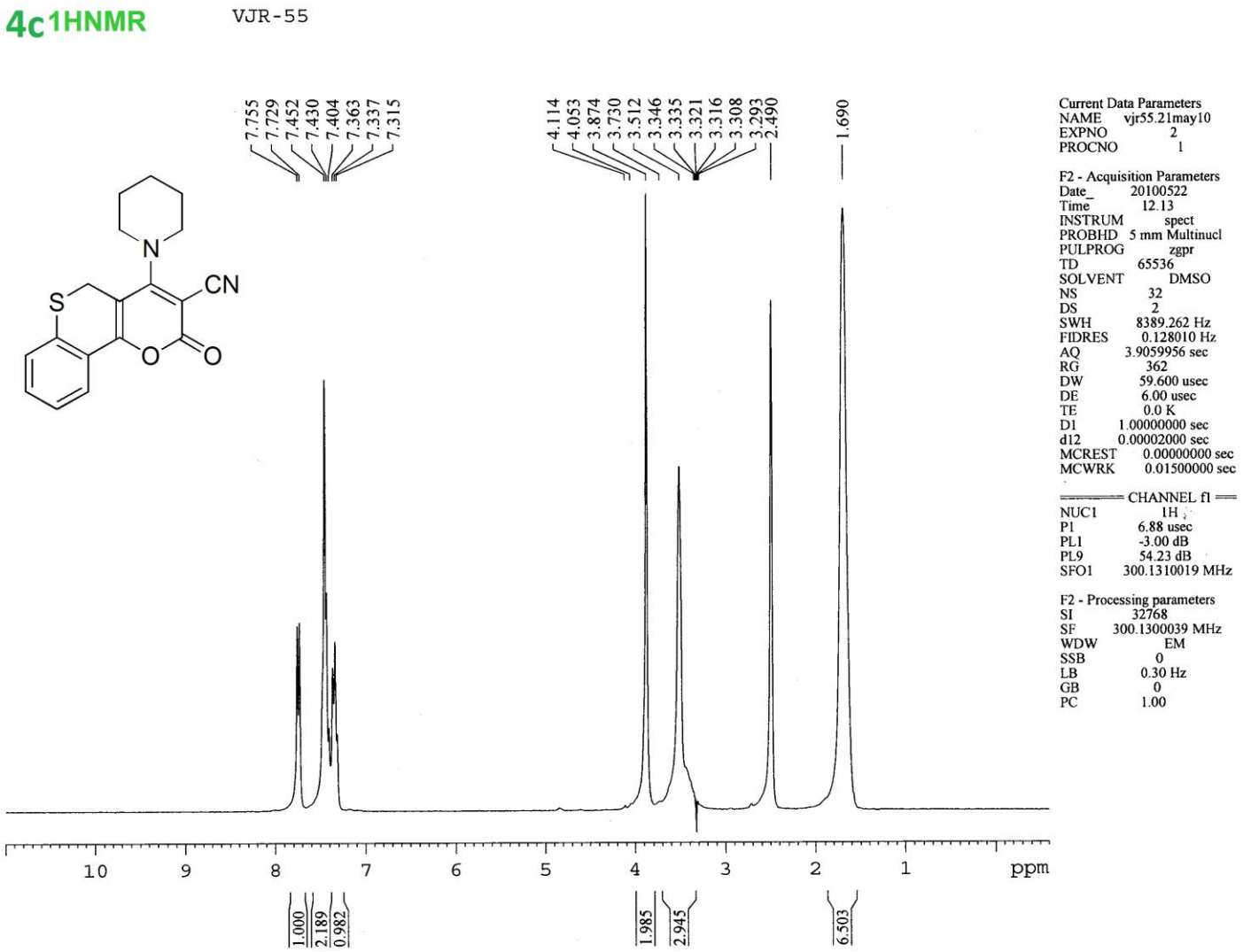
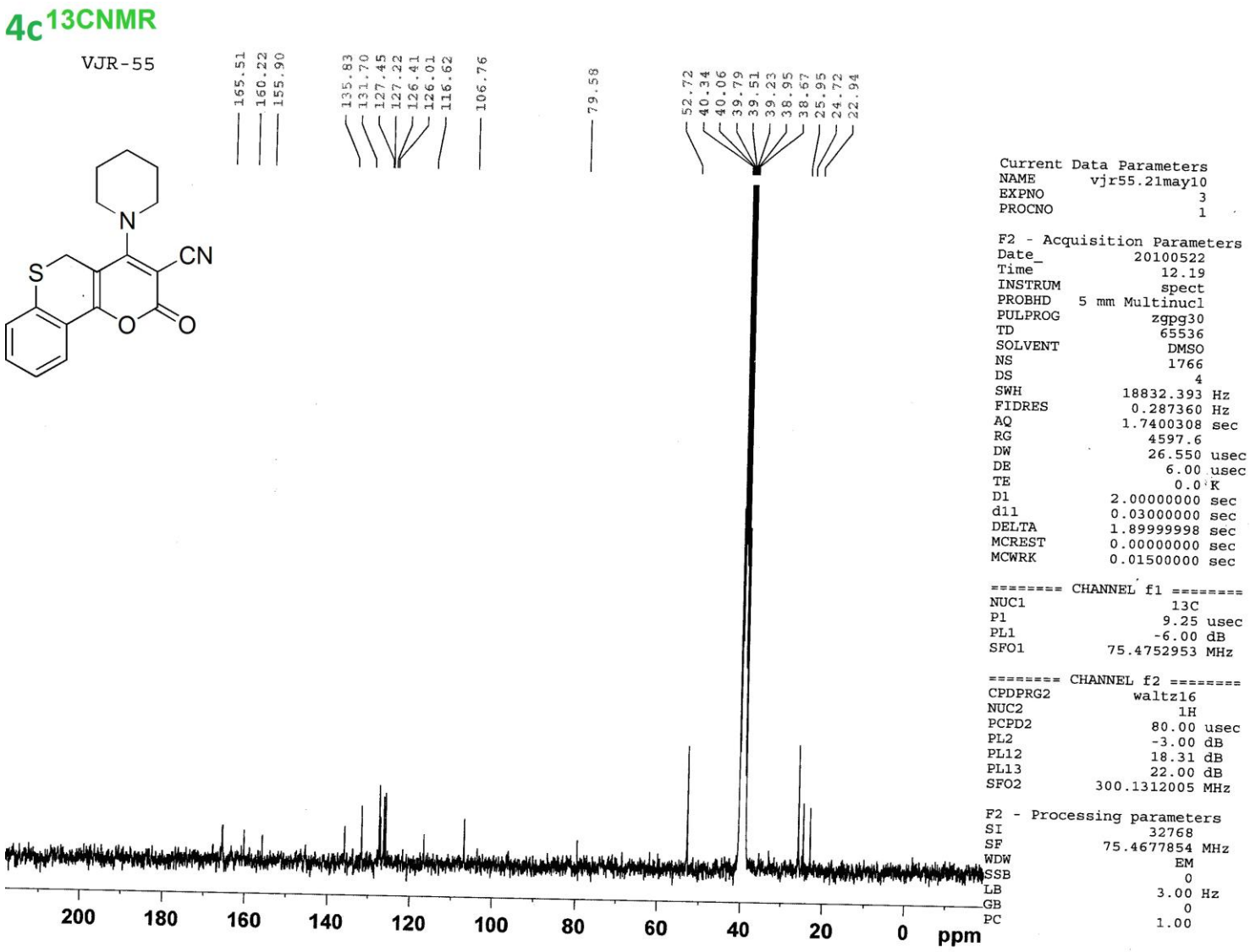
4a: 2-Oxo-4-(piperidin-1-yl)-2,5-dihydrothiochromeno[4,3-*b*]pyran-3-carbonitrile

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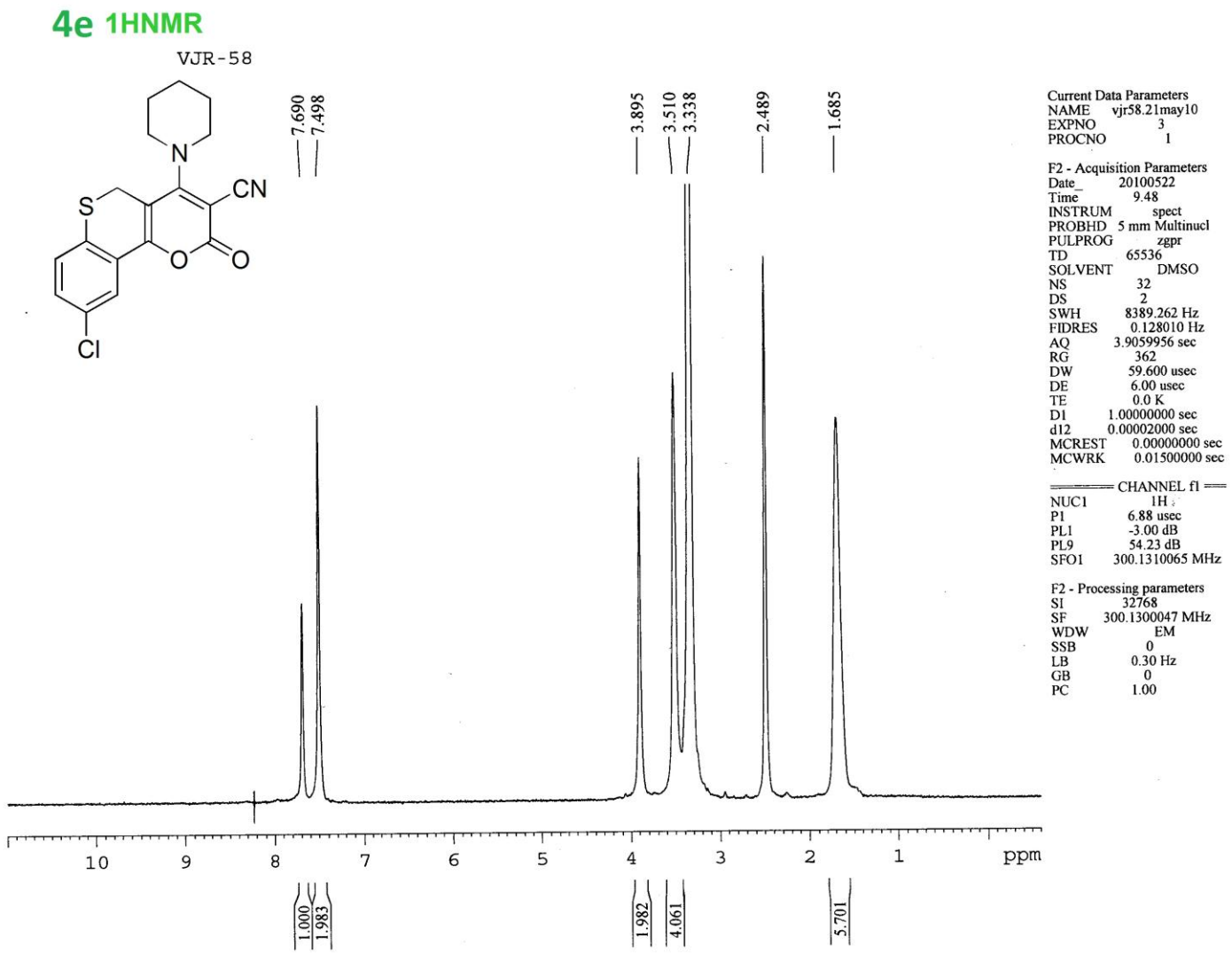
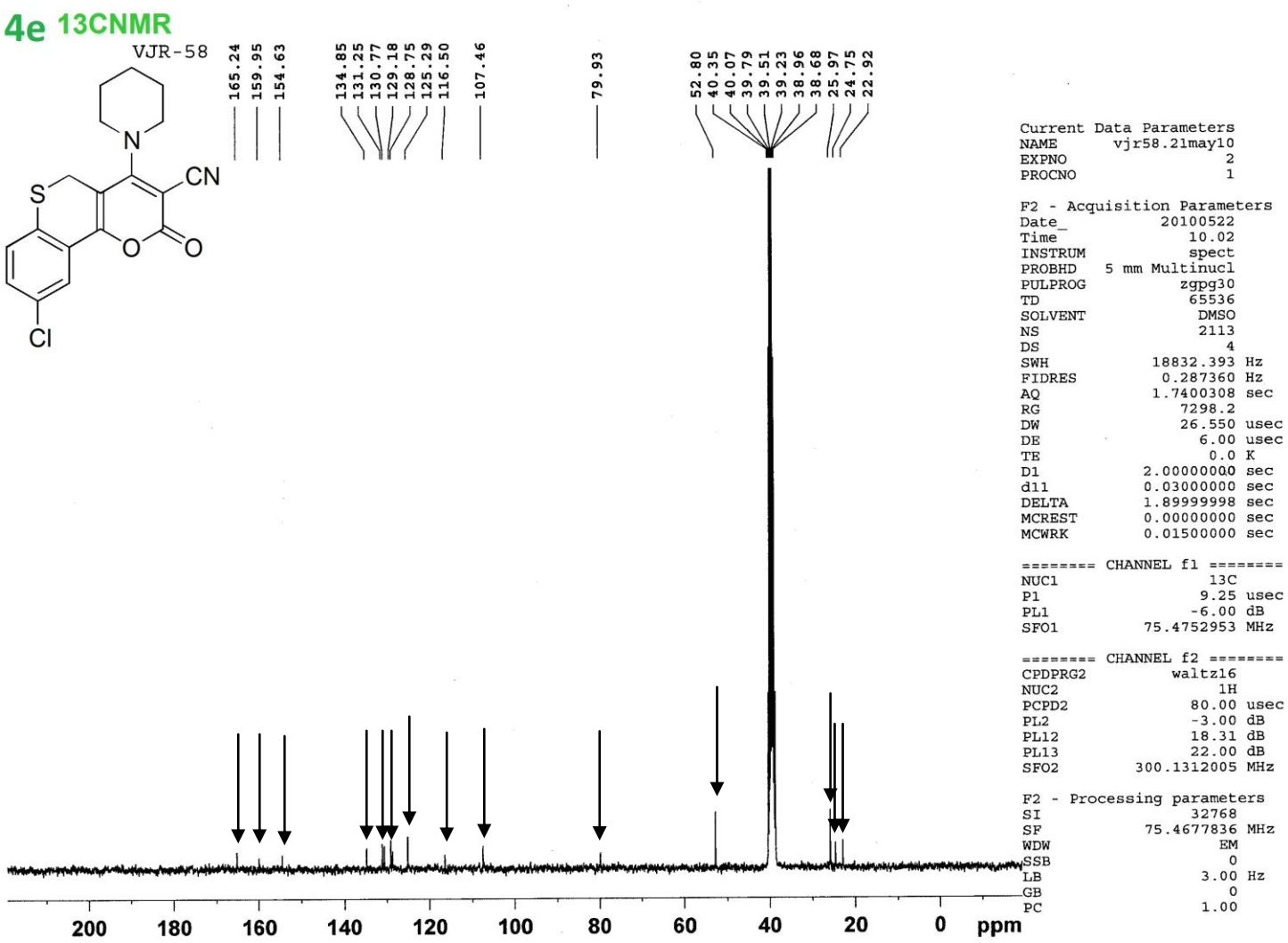
4b: 9-Chloro-2-oxo-4-(piperidin-1-yl)-2,5-dihydrothiochromeno[4,3-*b*]pyran-3-carbonitrile



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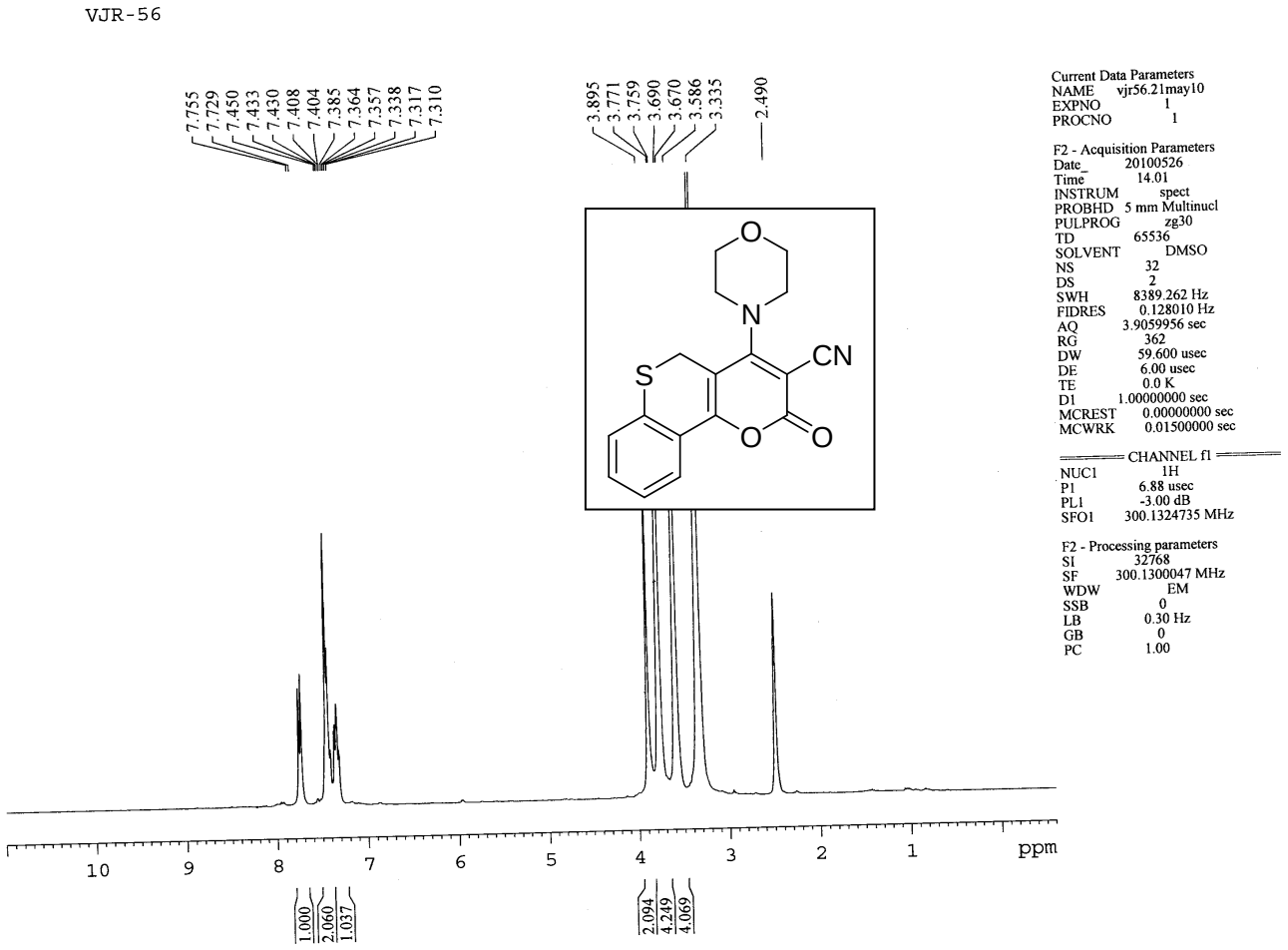
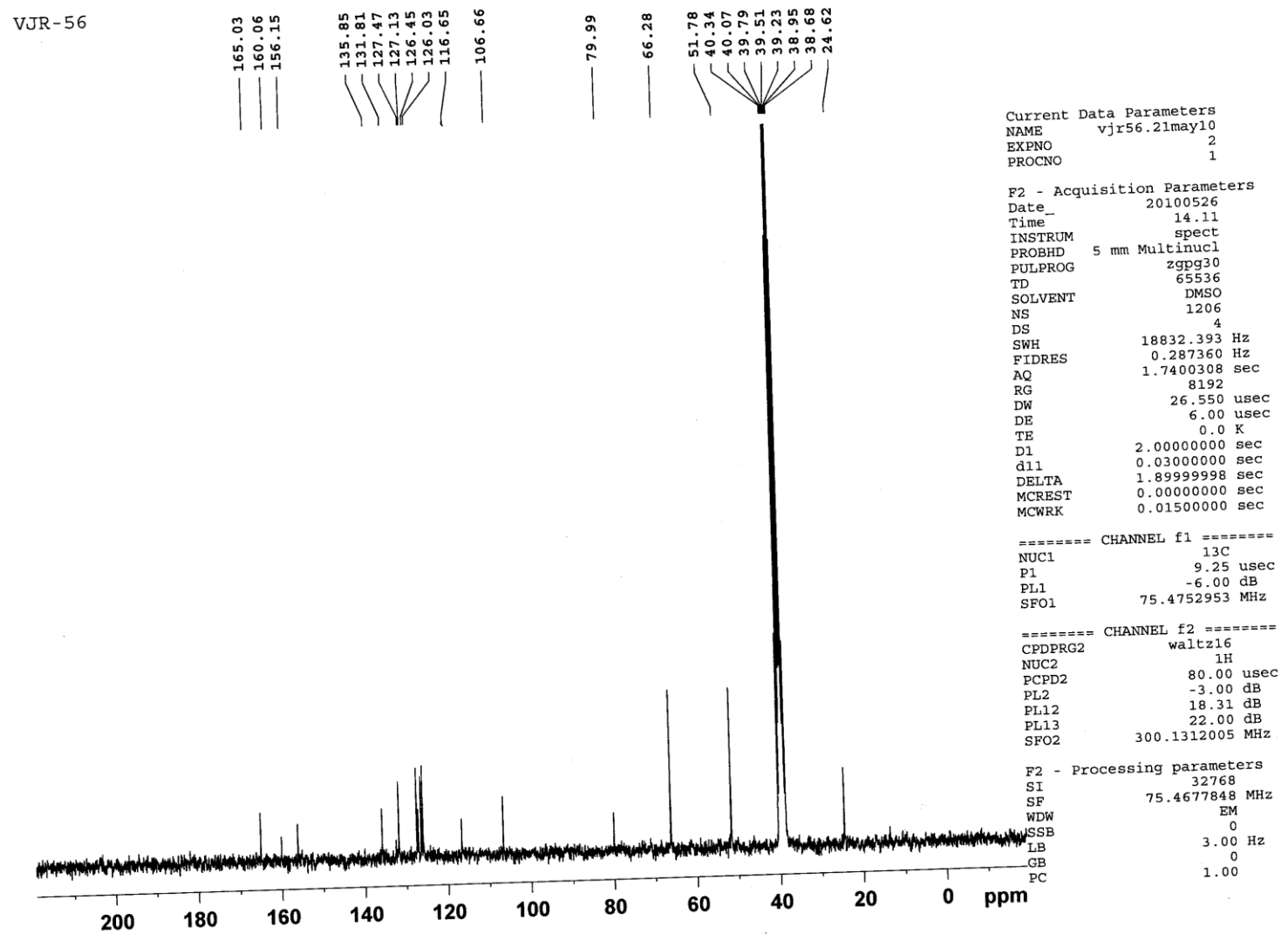
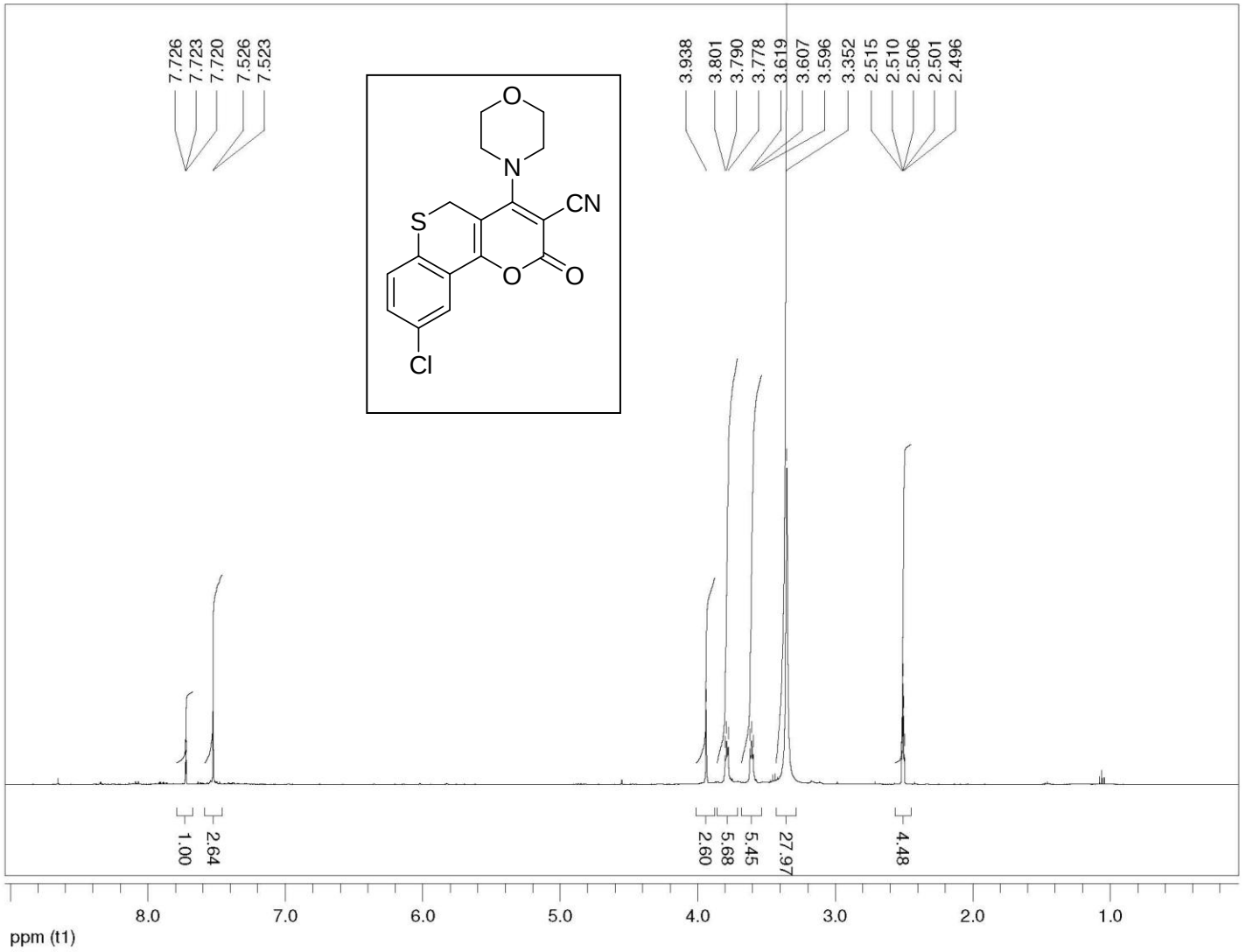
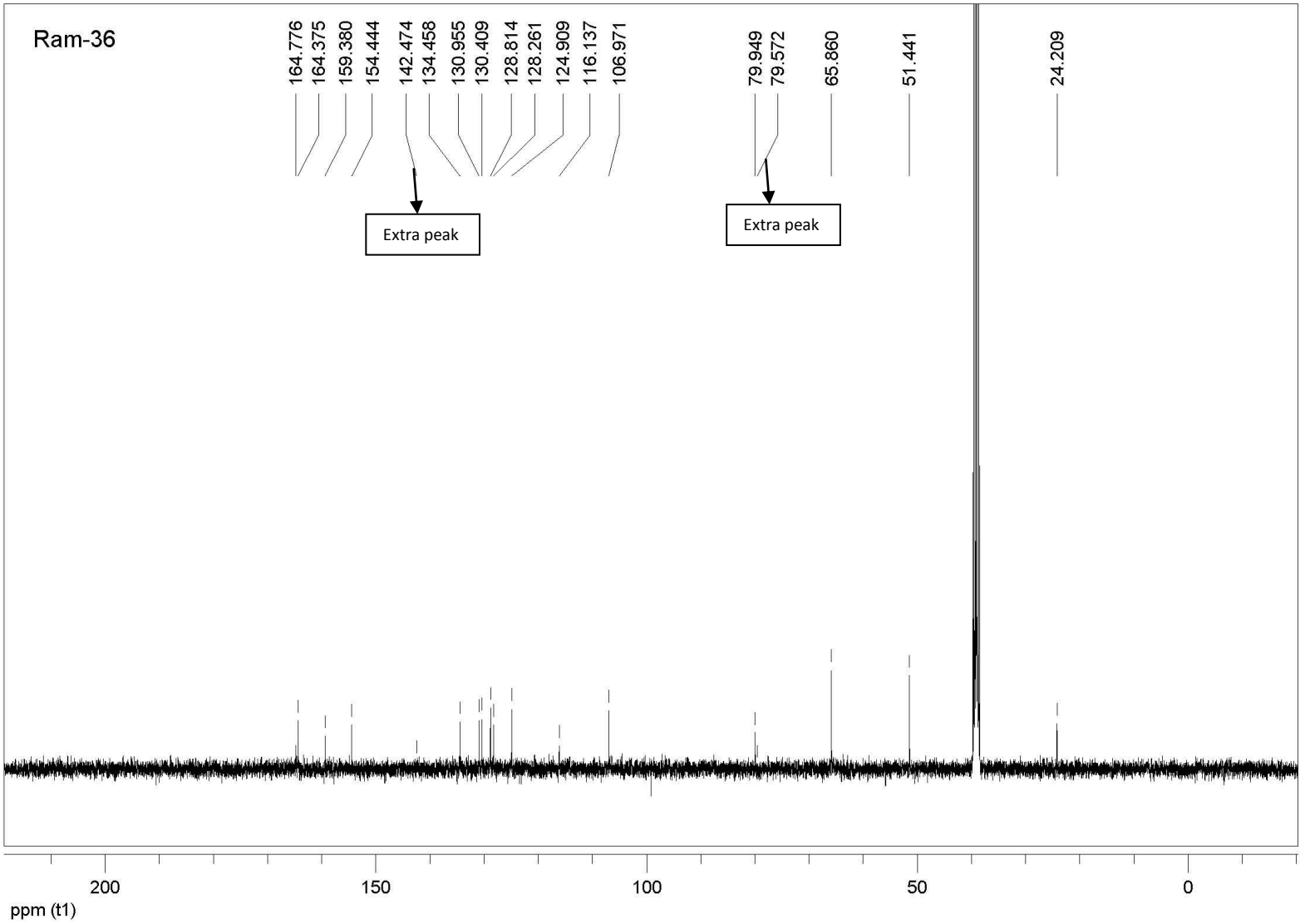
4c: 4-Morpholino-2-oxo-2,5-dihydrothiochromeno[4,3-*b*]pyran-3-carbonitrile



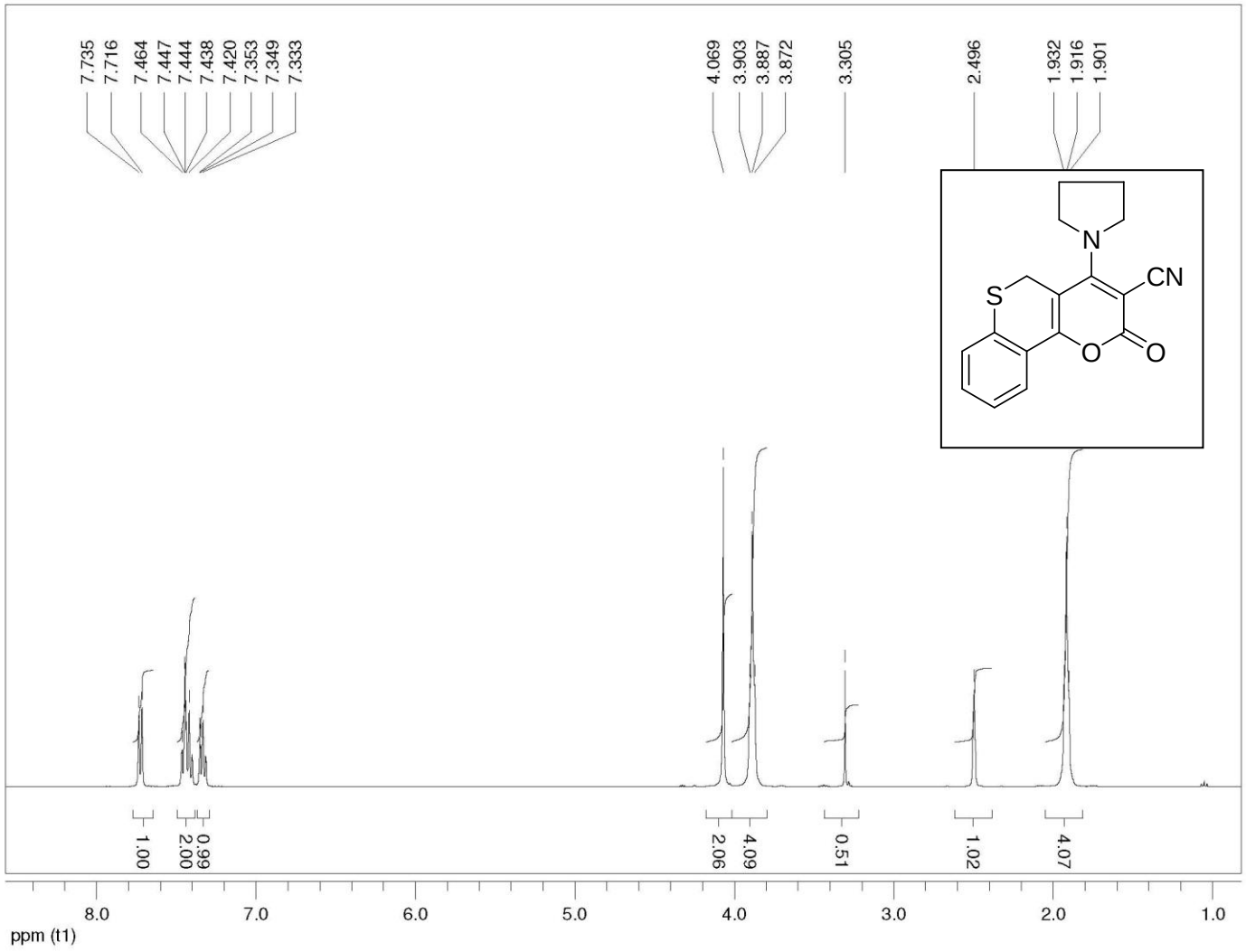


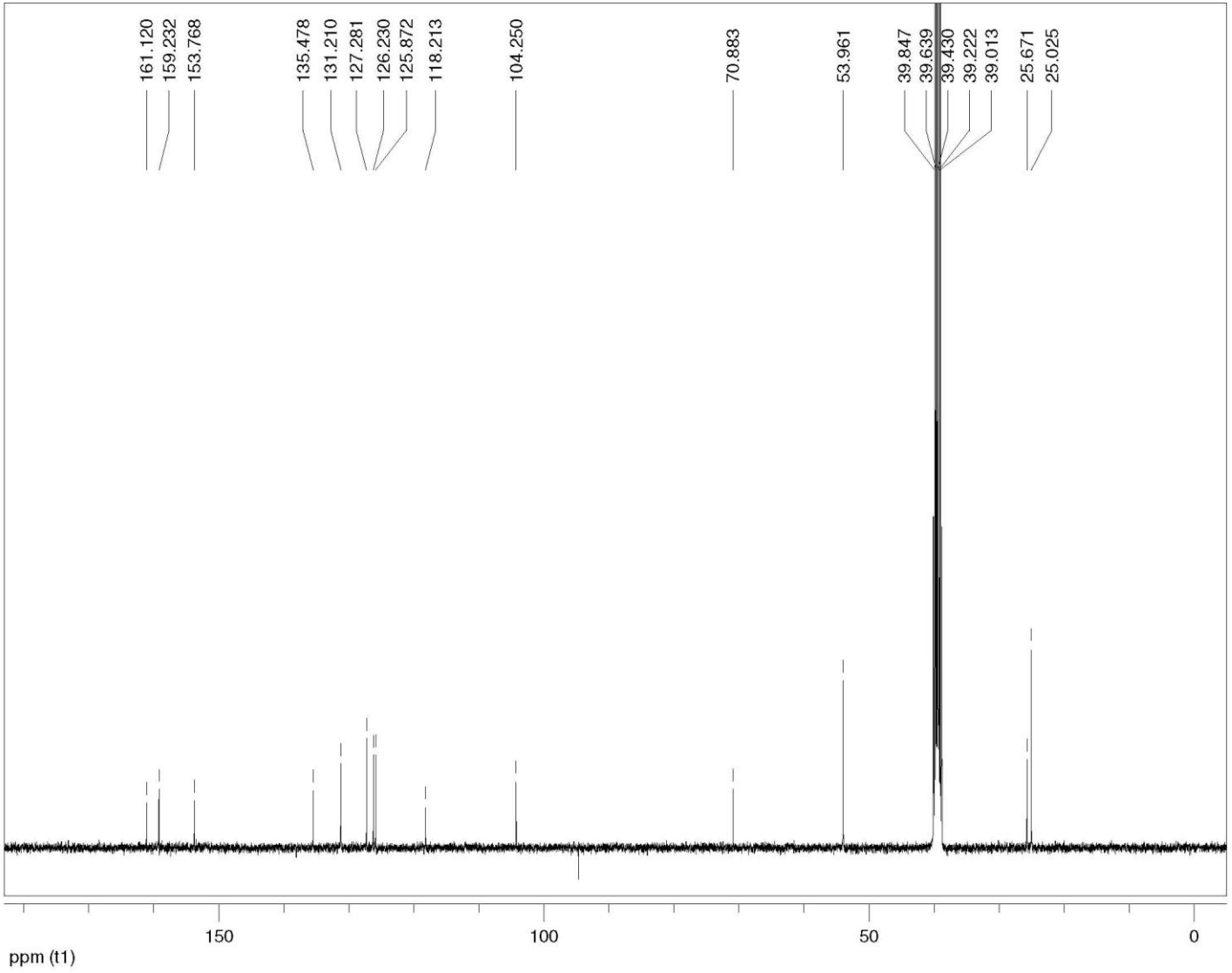
4d: 9-Chloro-4-morpholino-2-oxo-2,5-dihydrothiochromeno[4,3-*b*]pyran-3-carbonitrile



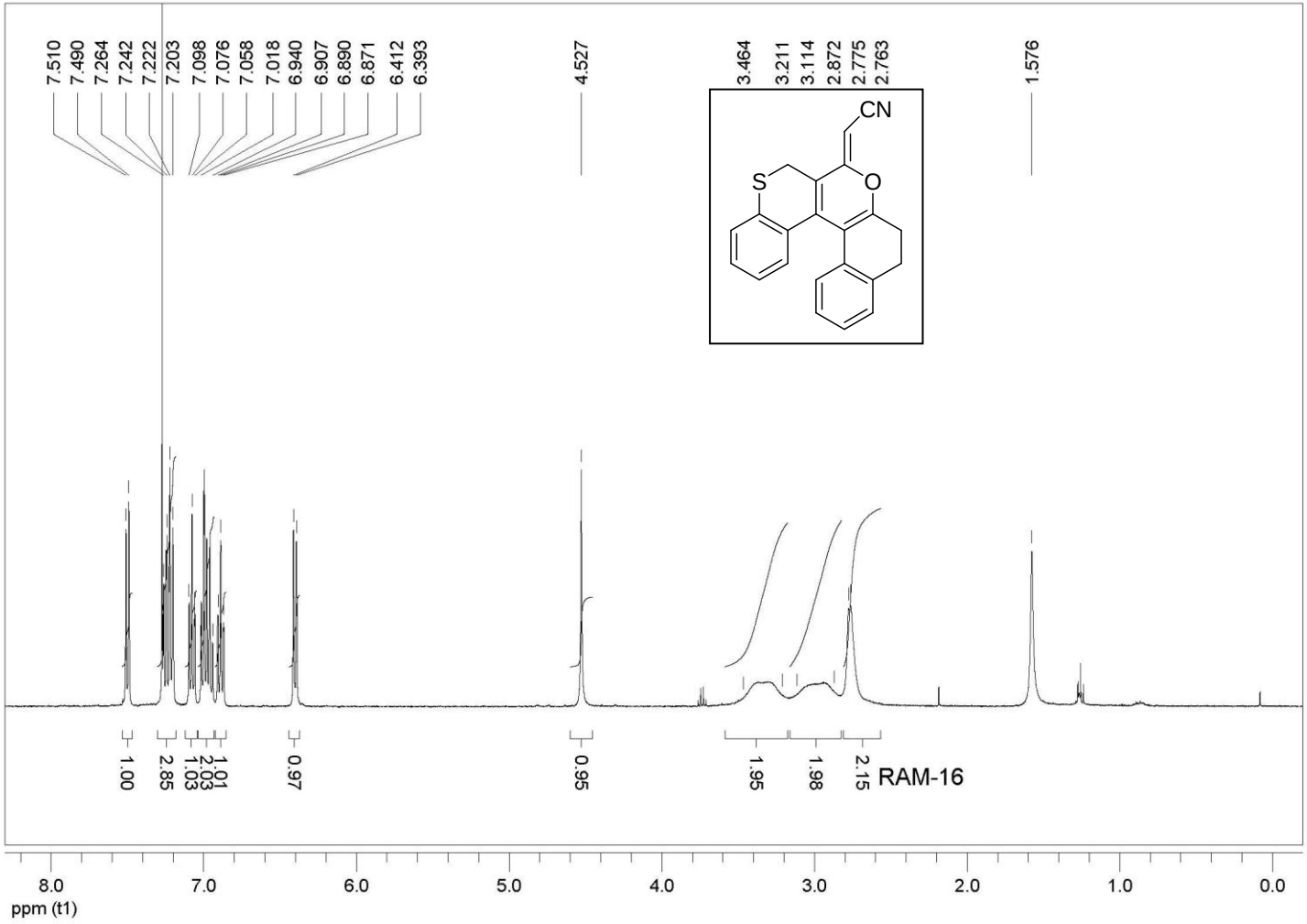


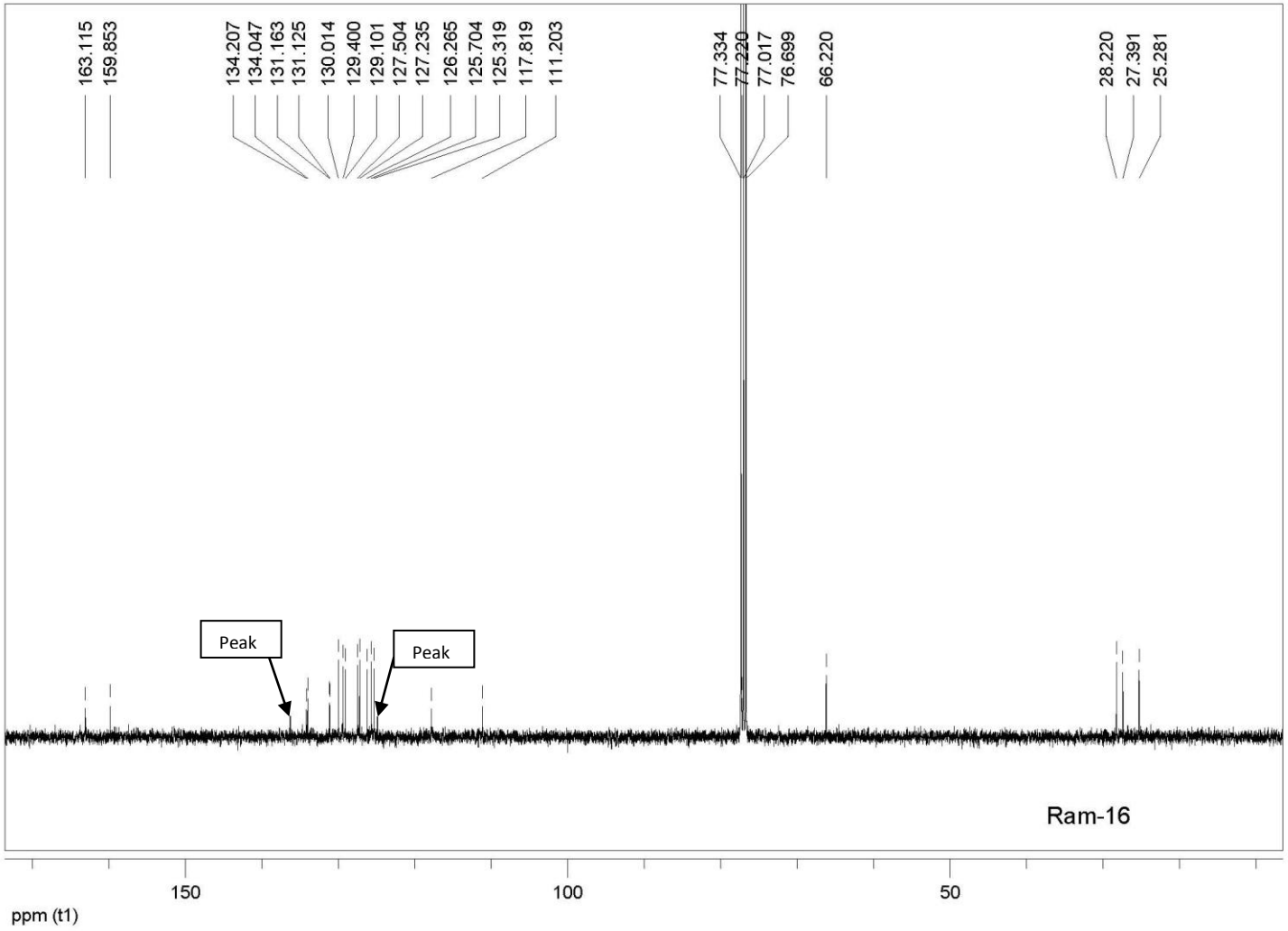
4e: 2-Oxo-4-(pyrrolidin-1-yl)-2,5-dihydrothiochromeno[4,3-*b*]pyran-3-carbonitrile





6a: (*Z*)-2-(5,6-Dihydrobenzo[*f*]thiochromeno[3,4-*c*]chromen-3(2*H*)-ylidene)acetonitrile





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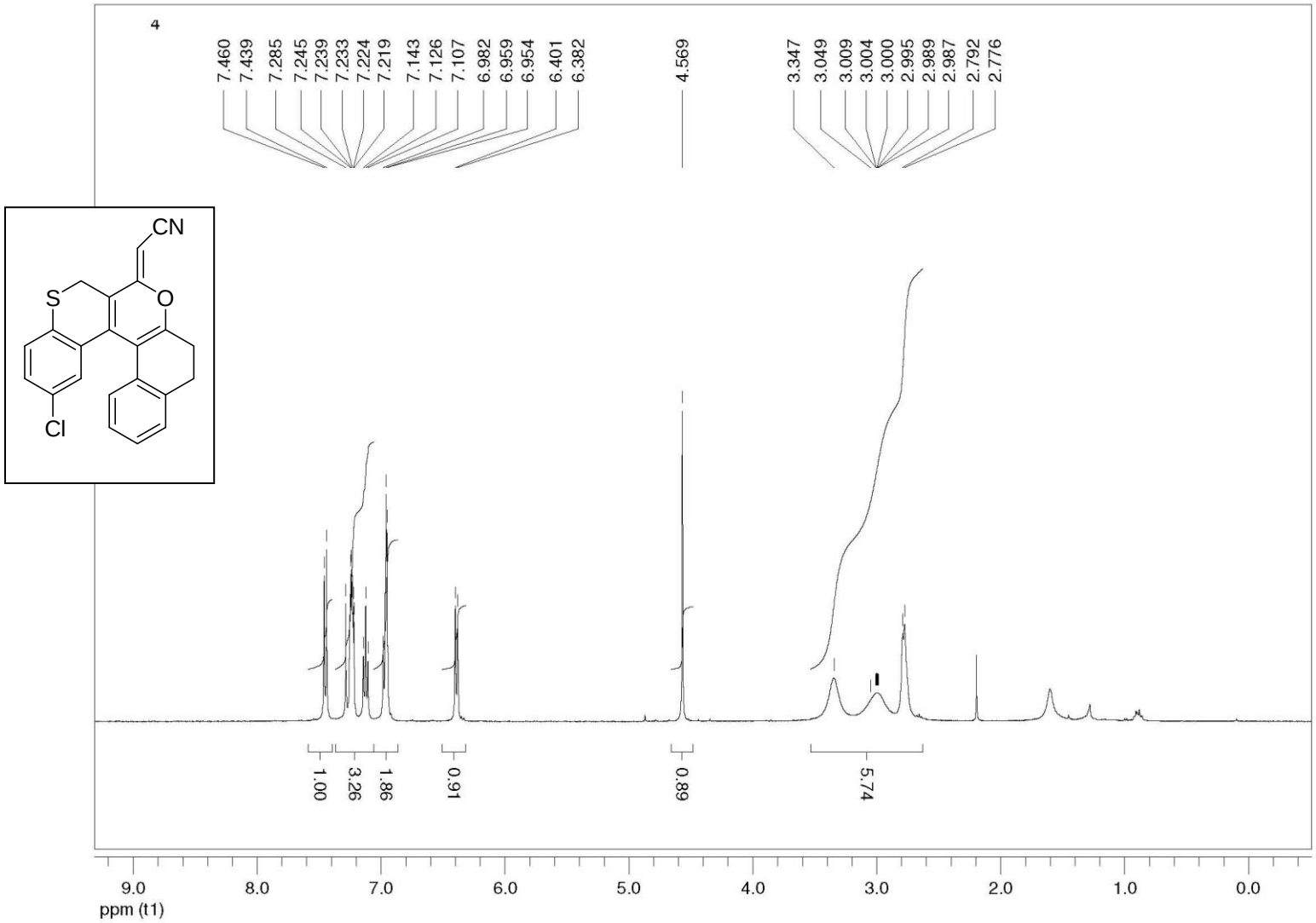

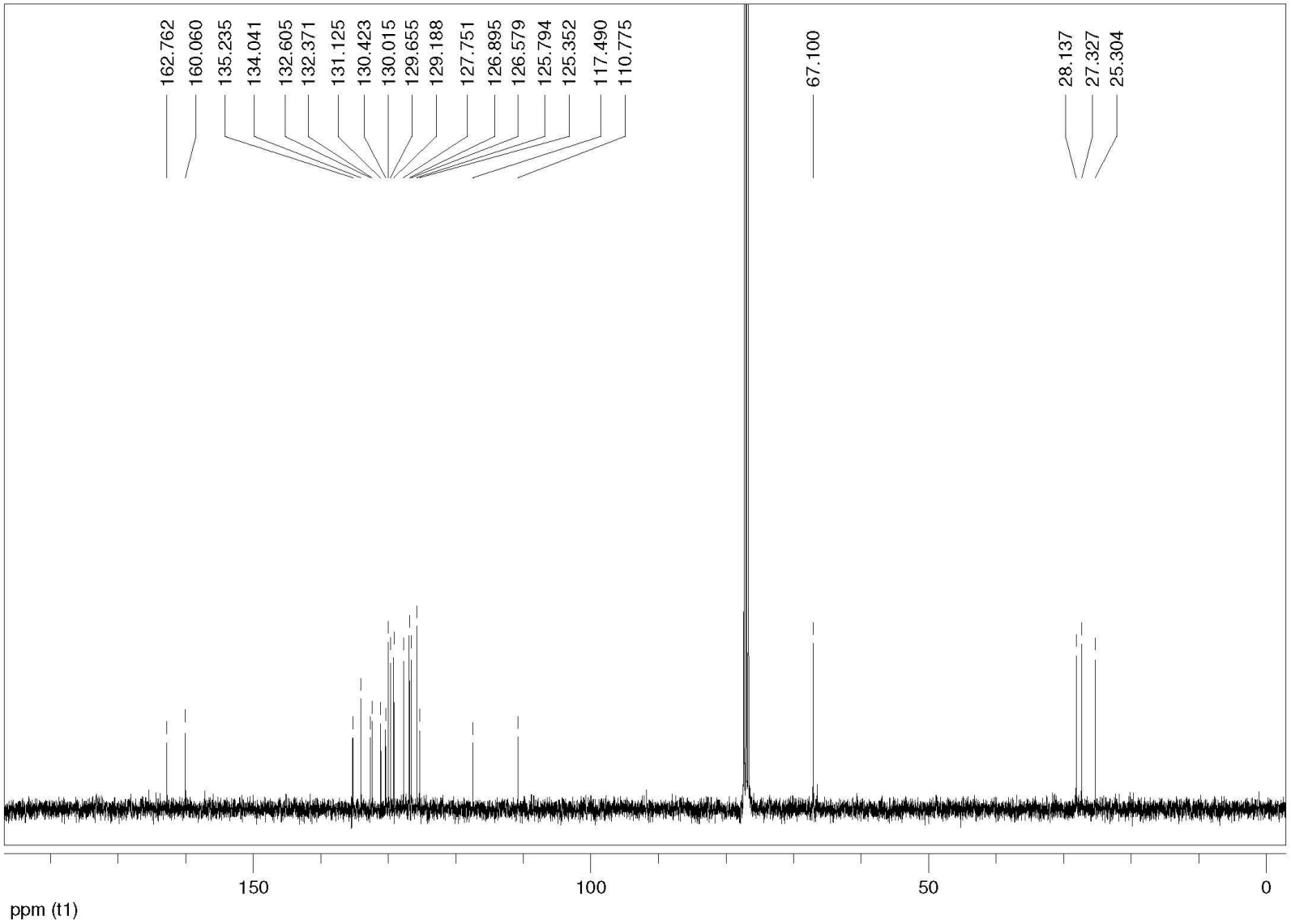

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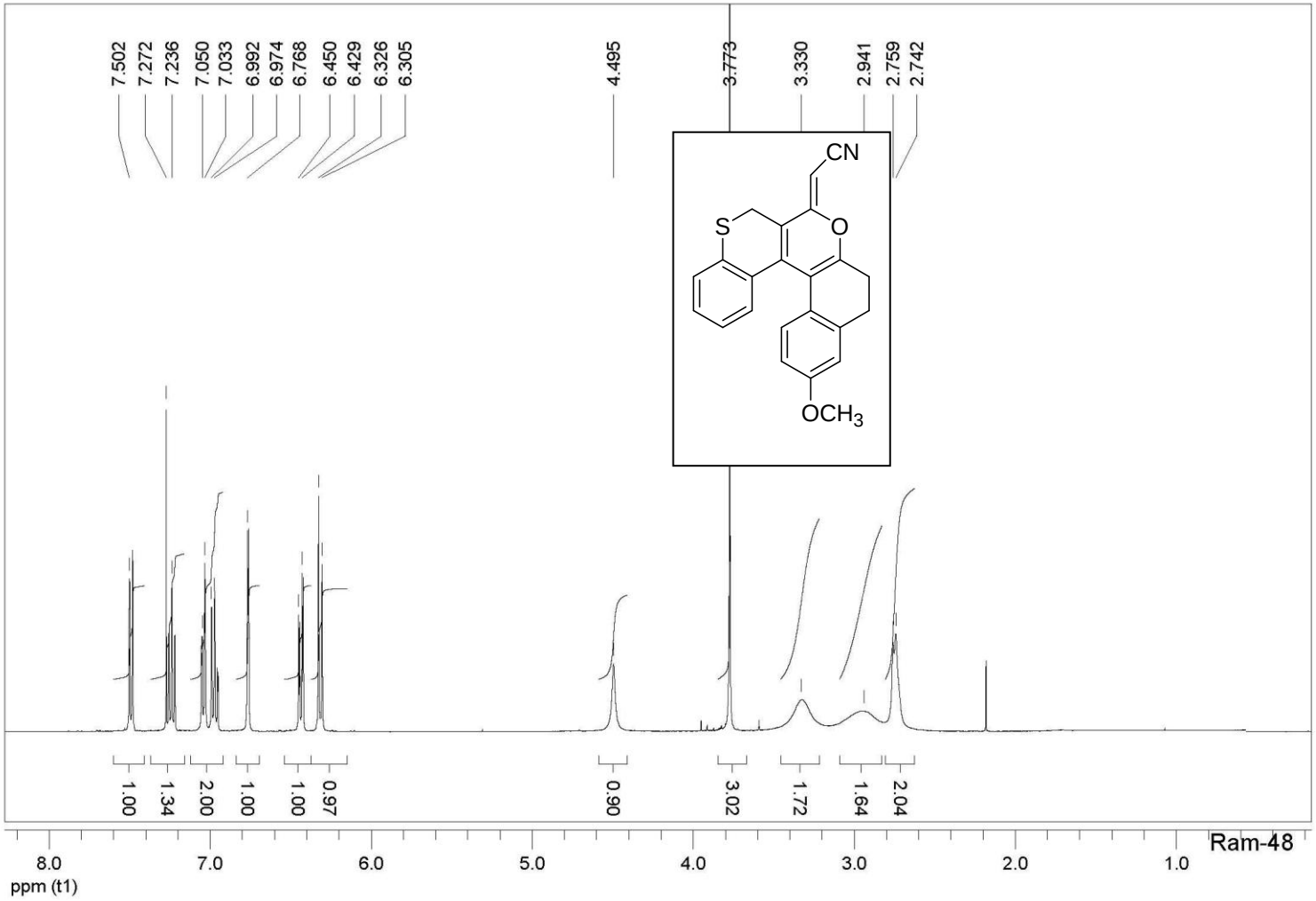
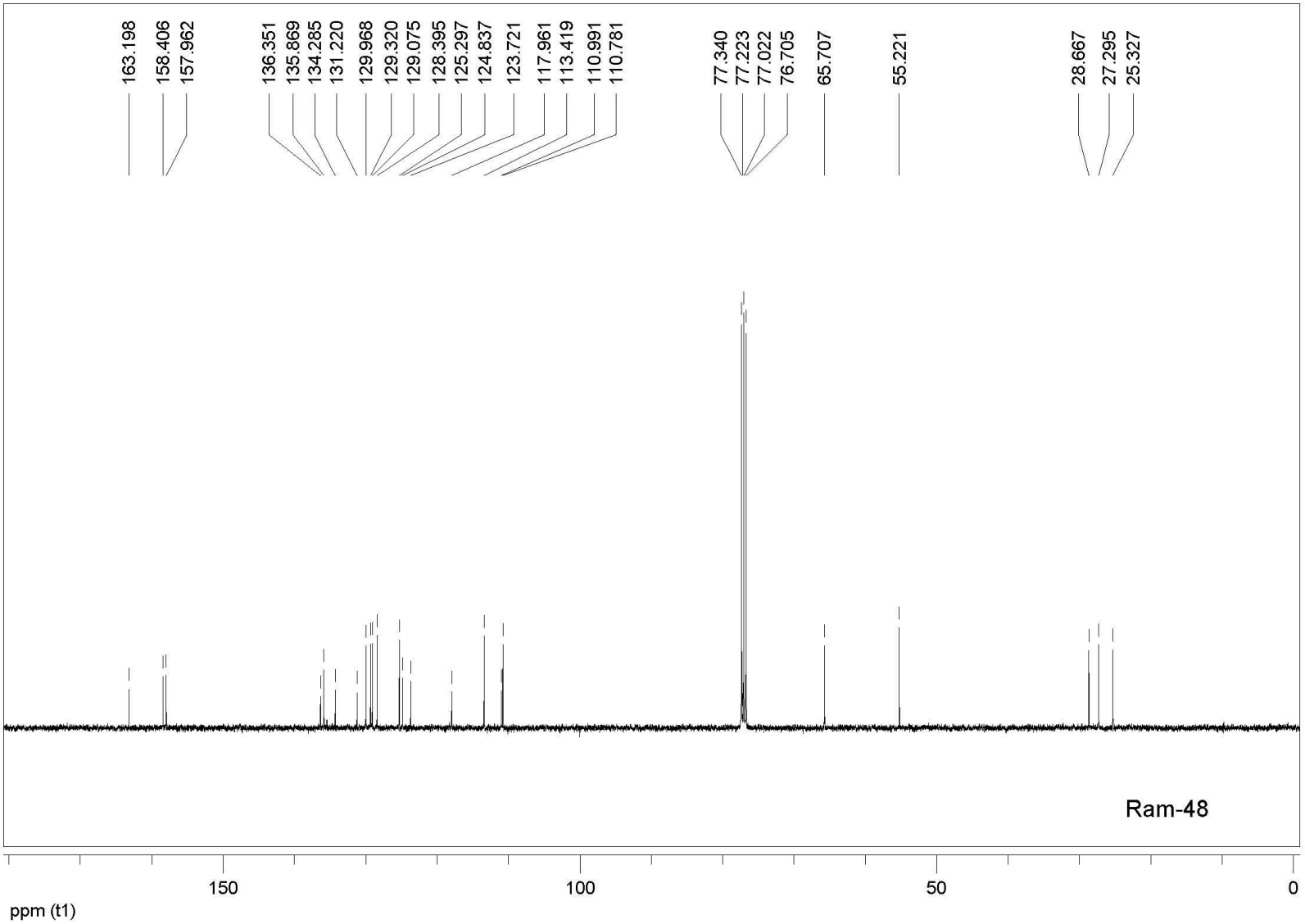
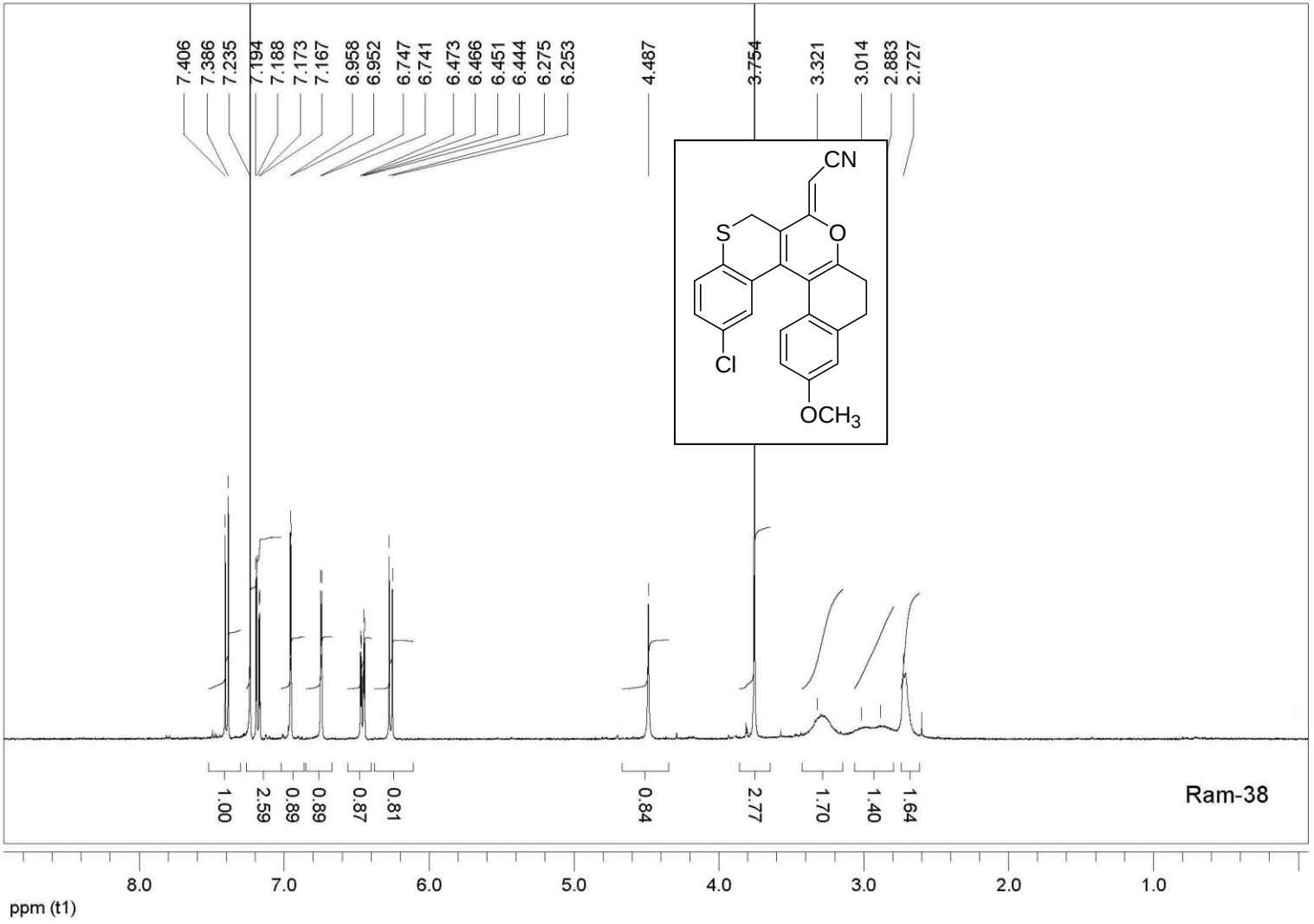
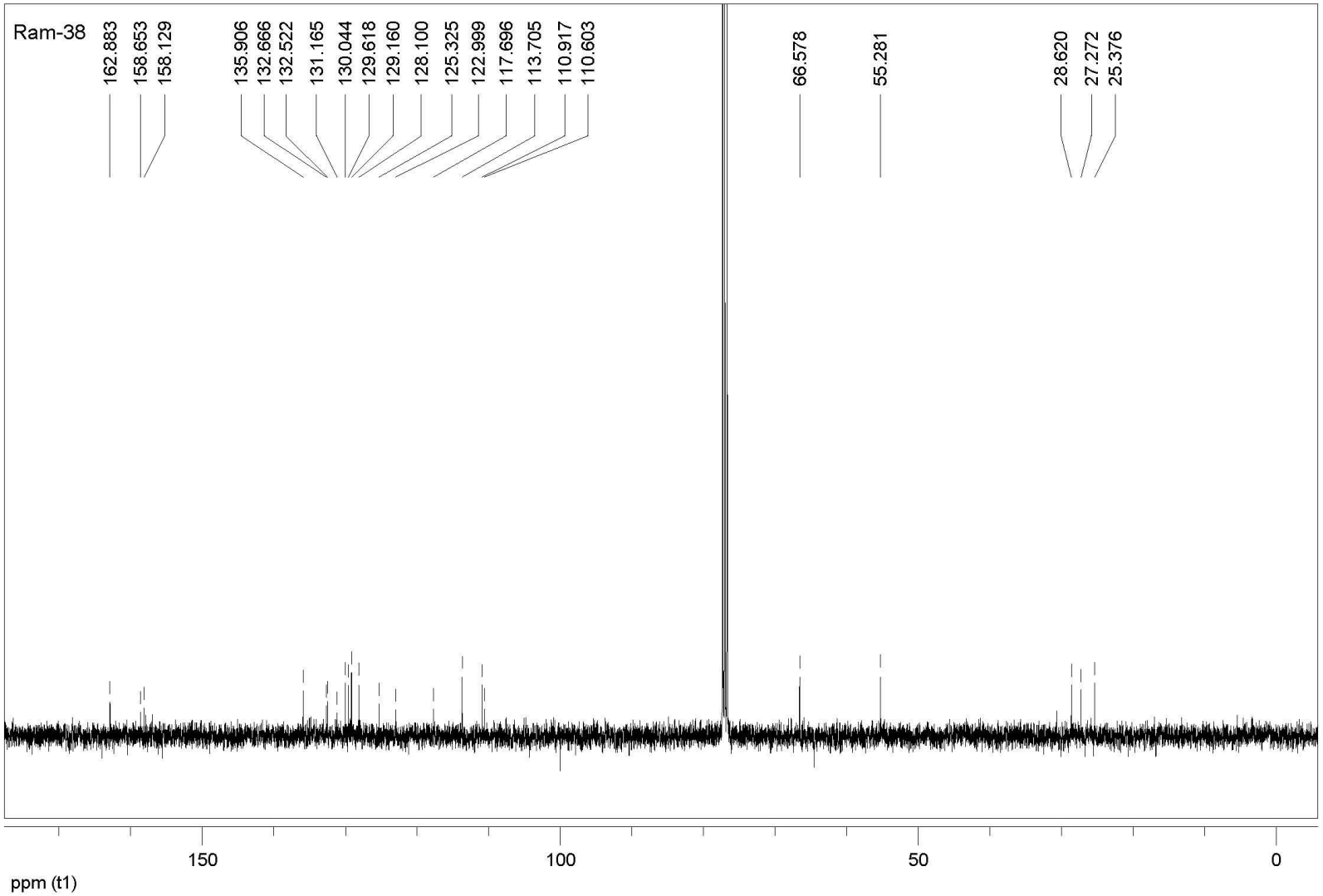
6c: (*Z*)-2-(8-Methoxy-5,6-dihydrobenzo[*f*]thiochromeno[3,4-*c*]chromen-3(2*H*)-ylidene)acetonitrile



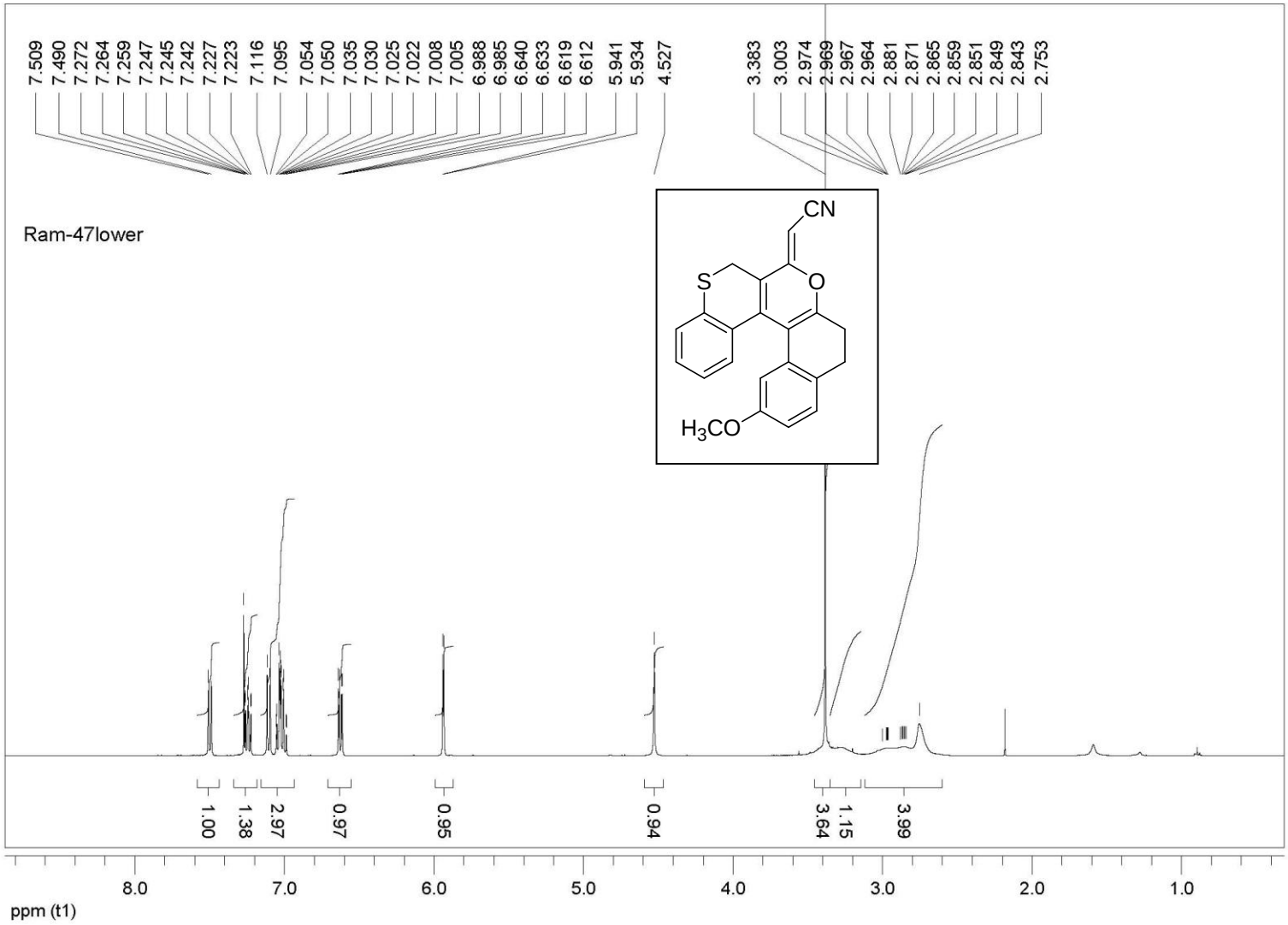


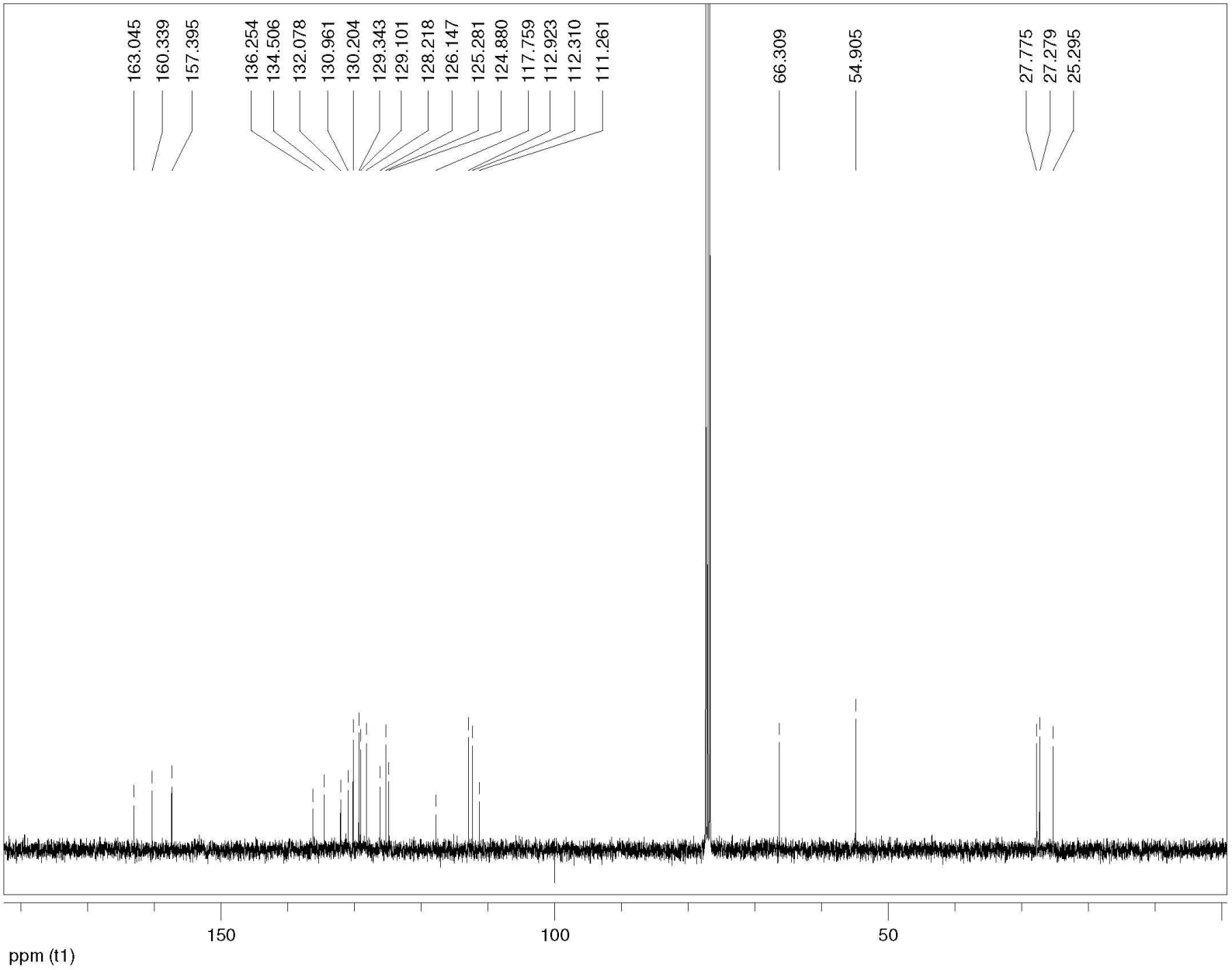
6d: (*Z*)-2-(12-Chloro-8-methoxy-5,6-dihydrobenzo[*f*]thiochromeno[3,4-*c*]chromen-3(2*H*)-ylidene)acetonitrile



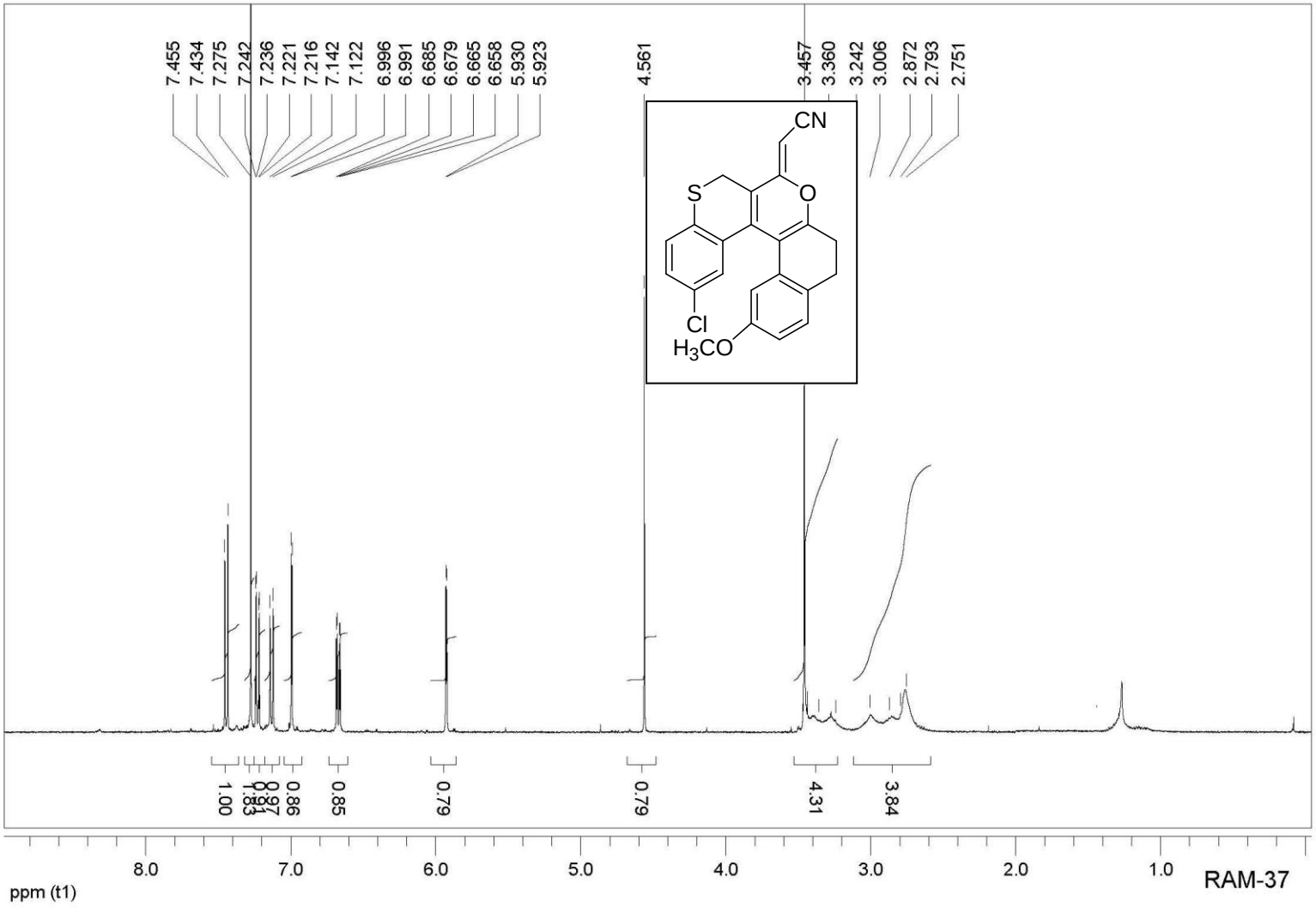


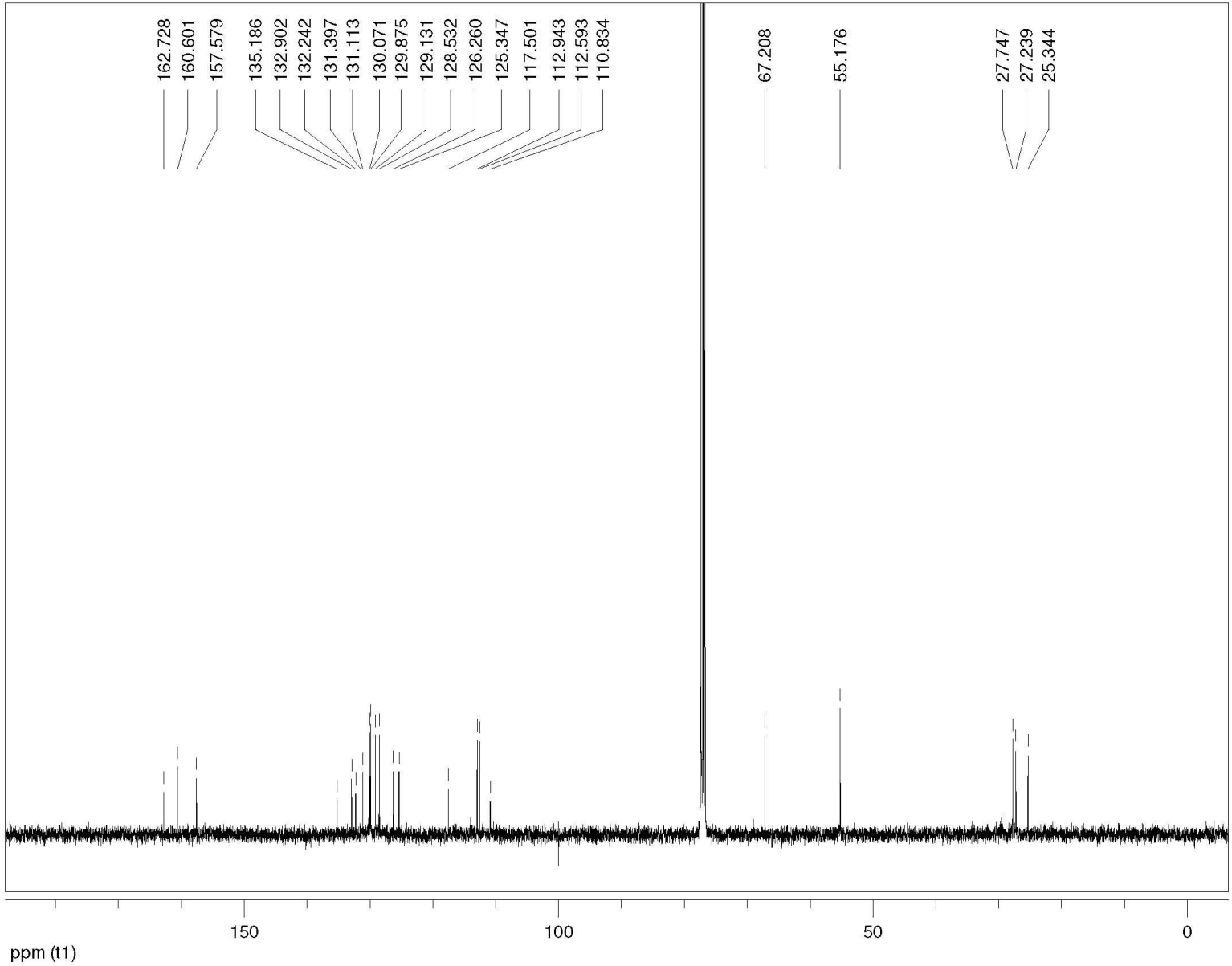
6e: **(*Z*)-2-(9-Methoxy-5,6-dihydrobenzo[*f*]thiochromeno[3,4-*c*]chromen-3(2*H*)-ylidene)acetonitrile**



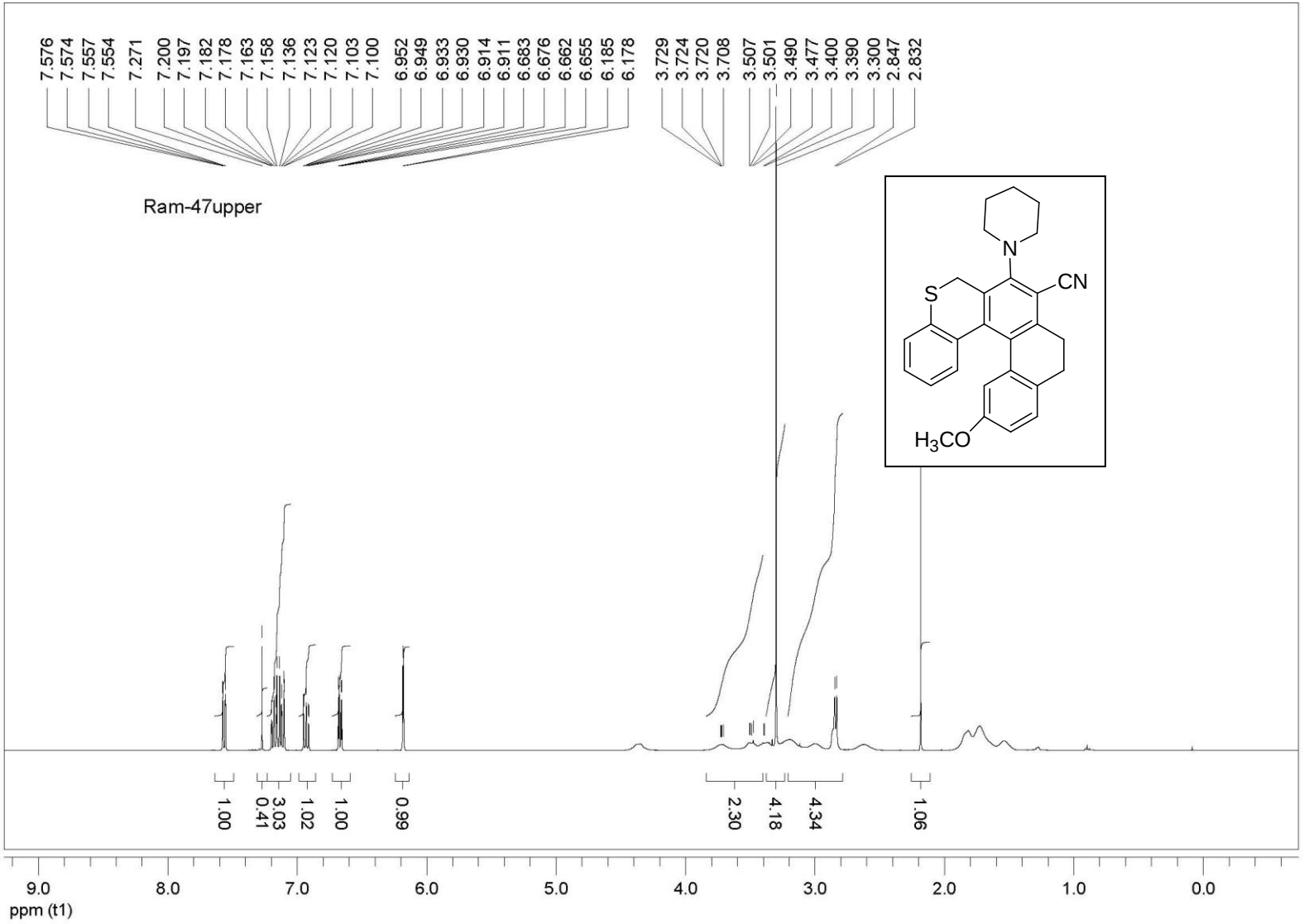


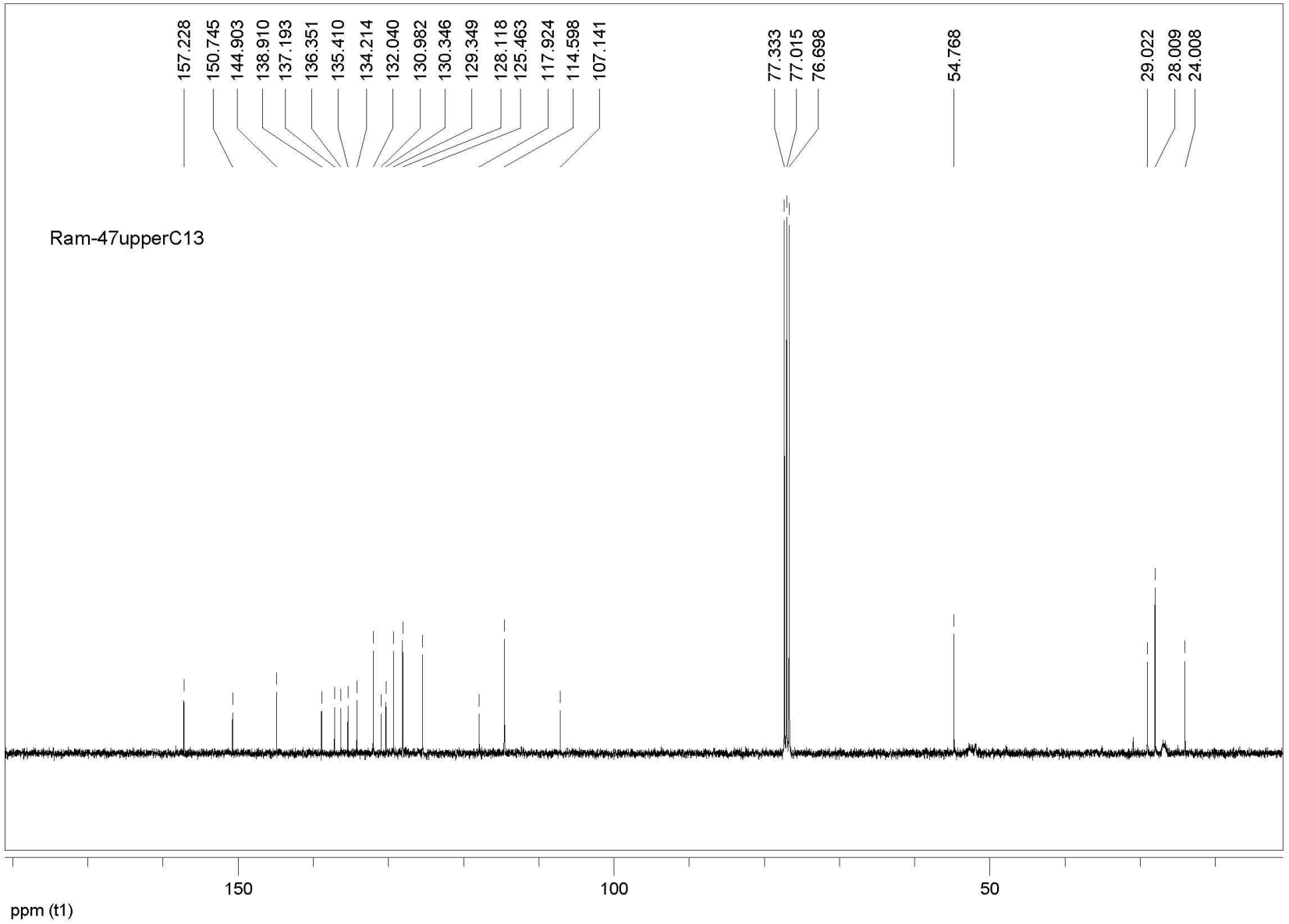
6f: **(Z)-2-(12-Chloro-9-methoxy-5,6-dihydrobenzo[*f*]thiochromeno[3,4-*c*]chromen-3(2*H*)-ylidene)acetonitrile**



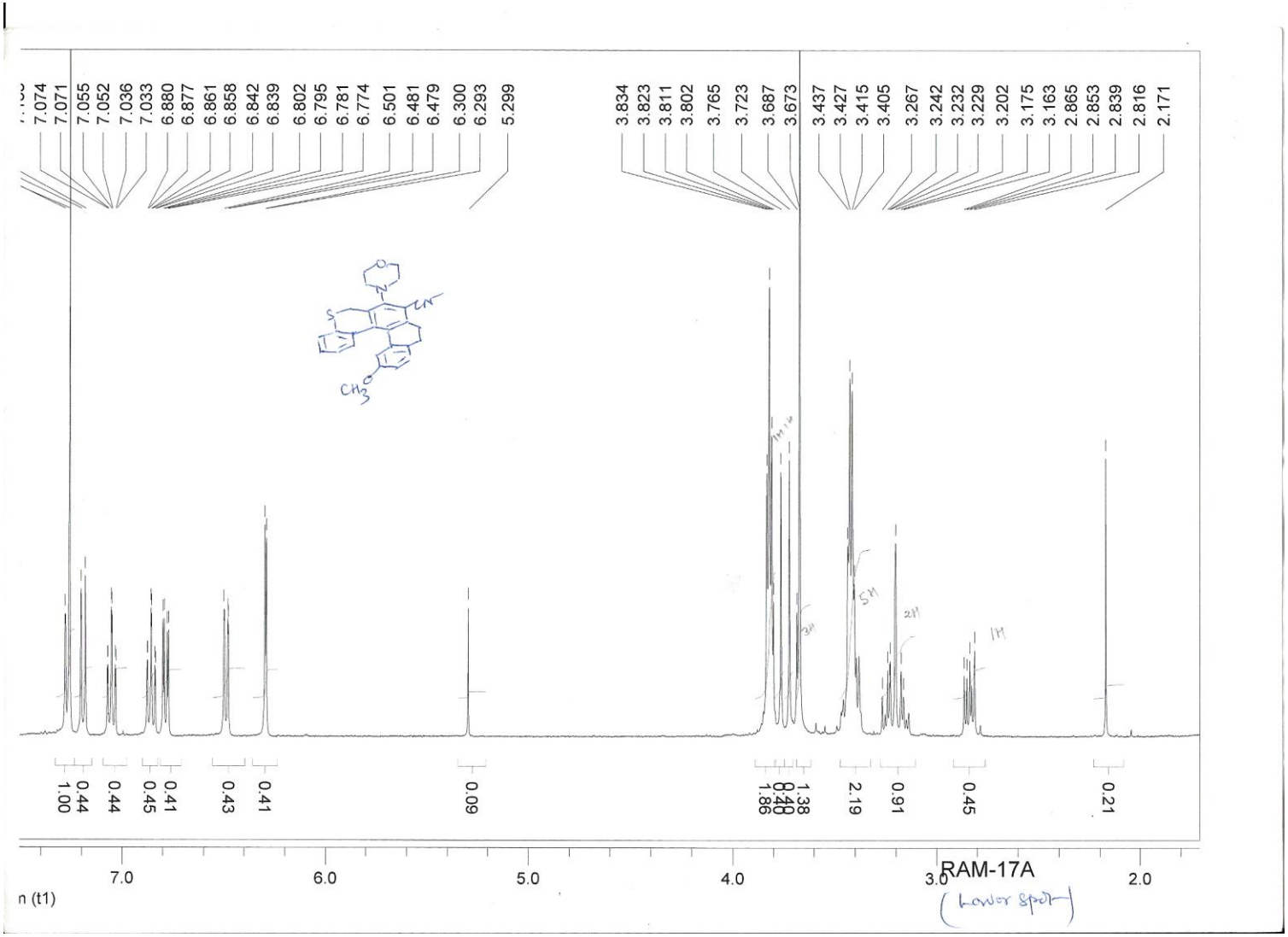


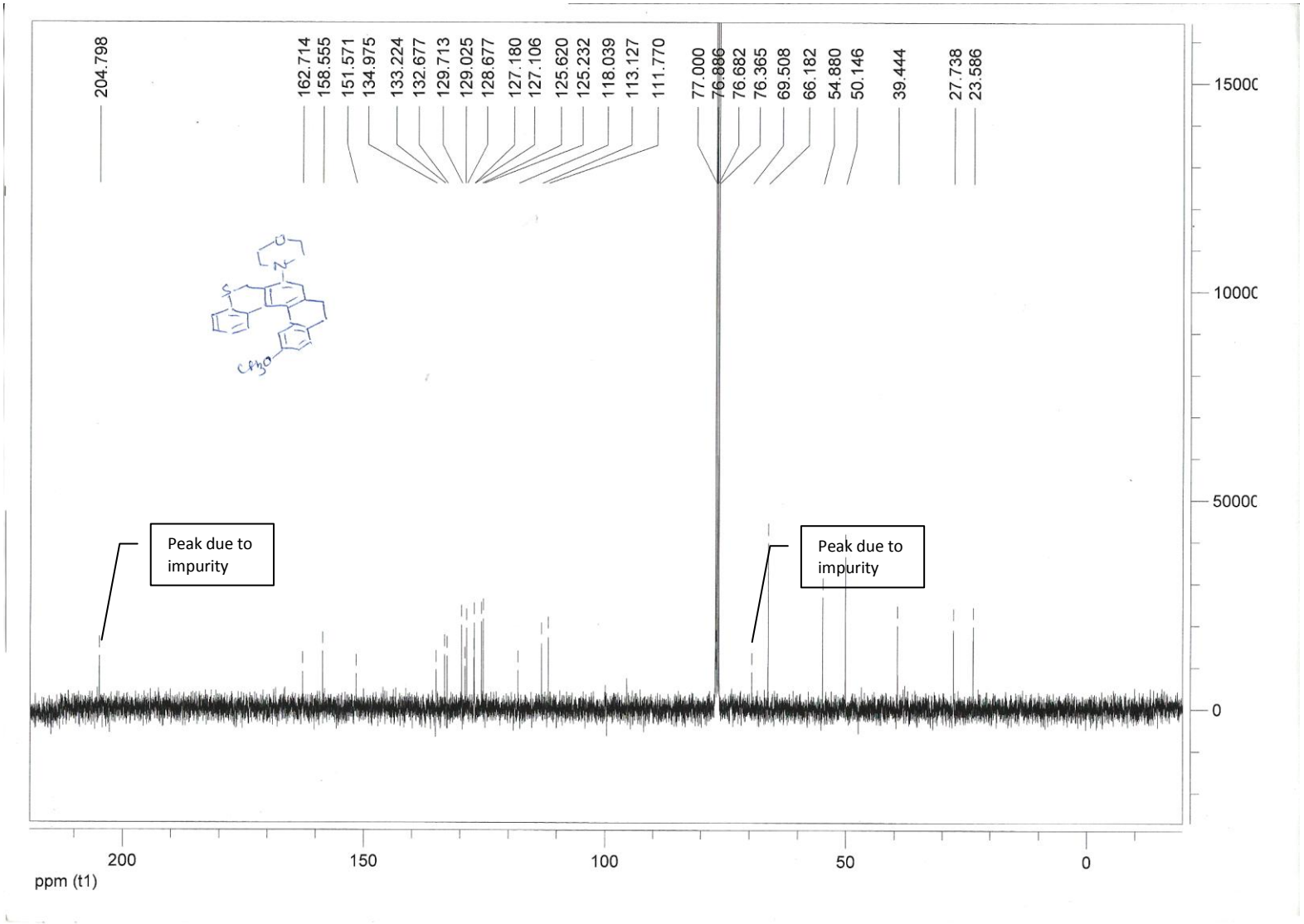
7a: **9-Methoxy-3-(piperidin-1-yl)-5,6-dihydro-2*H*-phenanthro[3,4-*c*]thiochromene-4-carbonitrile**





7b: 9-Methoxy-3-(morpholin-4-yl)-5,6-dihydro-2*H*-phenanthro[3,4-*c*]thiochromene-4-carbonitrile





Quantum Chemical Calculation detail of 7a:

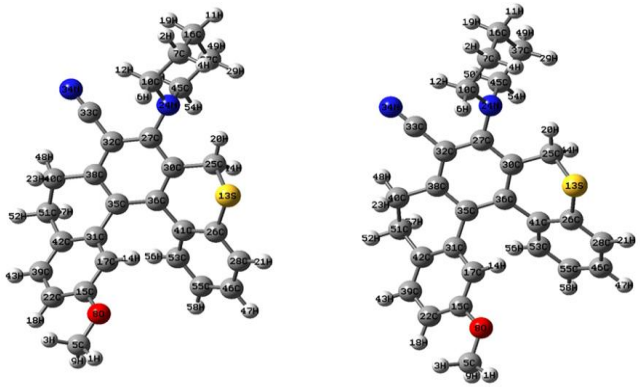


Figure S1: The optimized structures for the ground (left) and transition (right) states for **7**.

TABLE S1: Key optimized structural parameters for **7**.

	Ground state	**Transition state**
Dihedral angle (°)		
C17-C31-C35-C36	33.38878	33.33793
C31-C35-C36-C41	18.16384	18.36053
C35-C36-C41-C53	38.47154	38.61200
C38-C25-S13-C26	59.83068	59.63594
C25-S13-C26-C28	-37.44048	-37.53963
C25-C13-C26-C41	-37.44048	-37.53963
C36-C38-C25-C13	-42.21962	-41.81075
Bond angle (°)		
C25-S13-C26	94.65063	94.70556
Non-bonding distance (Å)		
H14···H56	3.25237	3.25967
C17···C53	3.10125	3.10537
	Ground state	**Transition state**

Dihedral angle (°)		
C17-C31-C35-C36	33.38878	33.33793
C31-C35-C36-C41	18.16384	18.36053
C35-C36-C41-C53	38.47154	38.61200
C38-C25-S13-C26	59.83068	59.63594
C25-S13-C26-C28	-37.44048	-37.53963
C25-C13-C26-C41	-37.44048	-37.53963
C36-C38-C25-C13	-42.21962	-41.81075
Bond angle (°)		
C25-S13-C26	94.65063	94.70556
Non-bonding distance (Å)		
H14···H56	3.25237	3.25967
C17···C53	3.10125	3.10537

XYZ Coordinate Ground State

1	**1**	**0**	**6.811991**	**0.615942**	**2.366734**
2	**1**	**0**	**-5.989097**	**-0.309305**	**2.530820**
3	**1**	**0**	**6.515204**	**-1.139977**	**2.337541**
4	**1**	**0**	**-5.257606**	**1.186191**	**1.947092**
5	**6**	**0**	**6.408695**	**-0.204880**	**1.776042**
6	**1**	**0**	**-3.502126**	**-0.508625**	**2.225394**
7	**6**	**0**	**-5.492786**	**0.152163**	**1.671294**
8	**8**	**0**	**5.044551**	**0.115658**	**1.548396**
9	**1**	**0**	**6.966988**	**-0.280833**	**0.836010**
10	**6**	**0**	**-4.191011**	**-0.601336**	**1.382256**
11	**1**	**0**	**-7.321113**	**0.720769**	**0.642203**

12	1	0	-4.418243	-1.669619	1.255388
13	16	0	-0.601322	3.184219	0.974209
14	1	0	2.624999	0.544642	1.093518
15	6	0	4.284323	-0.757415	0.825648
16	6	0	-6.415010	0.139785	0.445922
17	6	0	2.949085	-0.386262	0.649114
18	1	0	5.779295	-2.265553	0.400031
19	1	0	-6.736691	-0.890141	0.247240
20	1	0	-2.709390	2.167295	0.445371
21	1	0	1.519965	4.930585	0.119098
22	6	0	4.750169	-1.955535	0.280768
23	1	0	0.454714	-3.724149	0.641039
24	7	0	-3.534264	-0.024831	0.196193
25	6	0	-1.733008	2.150933	-0.032675
26	6	0	0.813156	2.913041	-0.074264
27	6	0	-2.152789	-0.326502	0.001900
28	6	0	1.686313	3.968096	-0.350309
29	1	0	-5.473377	1.754561	-0.642660

30	**6**	**0**	**-1.241270**	**0.730206**	**-0.121265**
31	**6**	**0**	**2.069121**	**-1.190088**	**-0.075557**
32	**6**	**0**	**-1.662562**	**-1.646046**	**-0.125971**
33	**6**	**0**	**-2.575000**	**-2.748195**	**-0.171600**
34	**7**	**0**	**-3.292054**	**-3.652698**	**-0.230843**
35	**6**	**0**	**0.628853**	**-0.836984**	**-0.236407**
36	**6**	**0**	**0.134818**	**0.488086**	**-0.325779**
37	**6**	**0**	**-5.683645**	**0.688643**	**-0.785593**
38	**6**	**0**	**-0.286650**	**-1.907818**	**-0.231554**
39	**6**	**0**	**3.856426**	**-2.781187**	**-0.402197**
40	**6**	**0**	**0.233810**	**-3.323459**	**-0.357053**
41	**6**	**0**	**1.009145**	**1.645313**	**-0.661048**
42	**6**	**0**	**2.523987**	**-2.429141**	**-0.577163**
43	**1**	**0**	**4.209350**	**-3.730853**	**-0.791171**
44	**1**	**0**	**-1.815491**	**2.617566**	**-1.018543**
45	**6**	**0**	**-4.365114**	**-0.052988**	**-1.019841**
46	**6**	**0**	**2.730230**	**3.796496**	**-1.250940**
47	**1**	**0**	**3.398966**	**4.622415**	**-1.464868**

48	**1**	**0**	**-0.534550**	**-3.966155**	**-0.790071**
49	**1**	**0**	**-6.310025**	**0.598248**	**-1.678728**
50	**1**	**0**	**-4.576627**	**-1.088027**	**-1.334793**
51	**6**	**0**	**1.510698**	**-3.350005**	**-1.205625**
52	**1**	**0**	**1.905360**	**-4.366474**	**-1.271737**
53	**6**	**0**	**2.030405**	**1.521010**	**-1.617180**
54	**1**	**0**	**-3.801557**	**0.421830**	**-1.827058**
55	**6**	**0**	**2.881965**	**2.576950**	**-1.910376**
56	**1**	**0**	**2.161993**	**0.574455**	**-2.125585**
57	**1**	**0**	**1.268245**	**-3.030733**	**-2.227712**
58	**1**	**0**	**3.663677**	**2.448607**	**-2.649804**

XYZ Coordinate Transition State

1	**1**	**0**	**6.793261**	**0.650883**	**2.391507**
2	**1**	**0**	**-5.993027**	**-0.422457**	**2.518616**
3	**1**	**0**	**6.506156**	**-1.106565**	**2.361383**
4	**1**	**0**	**-5.213579**	**1.084289**	**2.033394**

5	6	0	6.398161	-0.172336	1.798602
6	1	0	-3.515582	-0.685677	2.193911
7	6	0	-5.482435	0.078967	1.690365
8	8	0	5.034053	0.140613	1.561808
9	1	0	6.963344	-0.245735	0.862418
10	6	0	-4.206160	-0.695030	1.347355
11	1	0	-7.292166	0.773153	0.704421
12	1	0	-4.469438	-1.742838	1.145005
13	16	0	-0.615078	3.169251	0.976818
14	1	0	2.613745	0.553905	1.095092
15	6	0	4.282716	-0.737347	0.835464
16	6	0	-6.405713	0.176604	0.468955
17	6	0	2.946026	-0.374748	0.652157
18	1	0	5.789135	-2.236280	0.418423
19	1	0	-6.761742	-0.827294	0.205683
20	1	0	-2.717435	2.139169	0.462819
21	1	0	1.490796	4.930287	0.113984
22	6	0	4.758788	-1.932825	0.293680

23	**1**	**0**	**0.472394**	**-3.731633**	**0.630709**
24	**7**	**0**	**-3.531544**	**-0.056892**	**0.204677**
25	**6**	**0**	**-1.746058**	**2.131510**	**-0.025987**
26	**6**	**0**	**0.796270**	**2.908401**	**-0.077843**
27	**6**	**0**	**-2.152140**	**-0.348998**	**-0.002429**
28	**6**	**0**	**1.661972**	**3.968996**	**-0.355898**
29	**1**	**0**	**-5.417642**	**1.827596**	**-0.519798**
30	**6**	**0**	**-1.246542**	**0.714082**	**-0.124557**
31	**6**	**0**	**2.074685**	**-1.184697**	**-0.076211**
32	**6**	**0**	**-1.653896**	**-1.664919**	**-0.139581**
33	**6**	**0**	**-2.560213**	**-2.769648**	**-0.209945**
34	**7**	**0**	**-3.273158**	**-3.676273**	**-0.293955**
35	**6**	**0**	**0.632751**	**-0.841811**	**-0.242012**
36	**6**	**0**	**0.130118**	**0.480283**	**-0.331355**
37	**6**	**0**	**-5.658383**	**0.778942**	**-0.727936**
38	**6**	**0**	**-0.275757**	**-1.918194**	**-0.241016**
39	**6**	**0**	**3.873797**	**-2.764352**	**-0.393678**
40	**6**	**0**	**0.254144**	**-3.330194**	**-0.367724**

41	6	0	0.998120	1.642280	-0.665855
42	6	0	2.540043	-2.420763	-0.575641
43	1	0	4.234754	-3.711761	-0.780517
44	1	0	-1.841371	2.602503	-1.008589
45	6	0	-4.360405	0.017598	-1.010024
46	6	0	2.705068	3.803815	-1.258803
47	1	0	3.368151	4.633810	-1.474148
48	1	0	-0.508069	-3.976699	-0.805999
49	1	0	-6.287415	0.762432	-1.623701
50	1	0	-4.597556	-0.990646	-1.388891
51	6	0	1.535591	-3.347358	-1.209943
52	1	0	1.936956	-4.361274	-1.275473
53	6	0	2.018685	1.523902	-1.623478
54	1	0	-3.783657	0.525717	-1.786897
55	6	0	2.863418	2.585030	-1.918087
56	1	0	2.154929	0.578145	-2.132040
57	1	0	1.296090	-3.028253	-2.232827
58	1	0	3.644795	2.461327	-2.658543