Supporting Information

New Insights into the Lewis Acidity of Guanidinium Species: Lewis Acid Interaction Provides Reactivity

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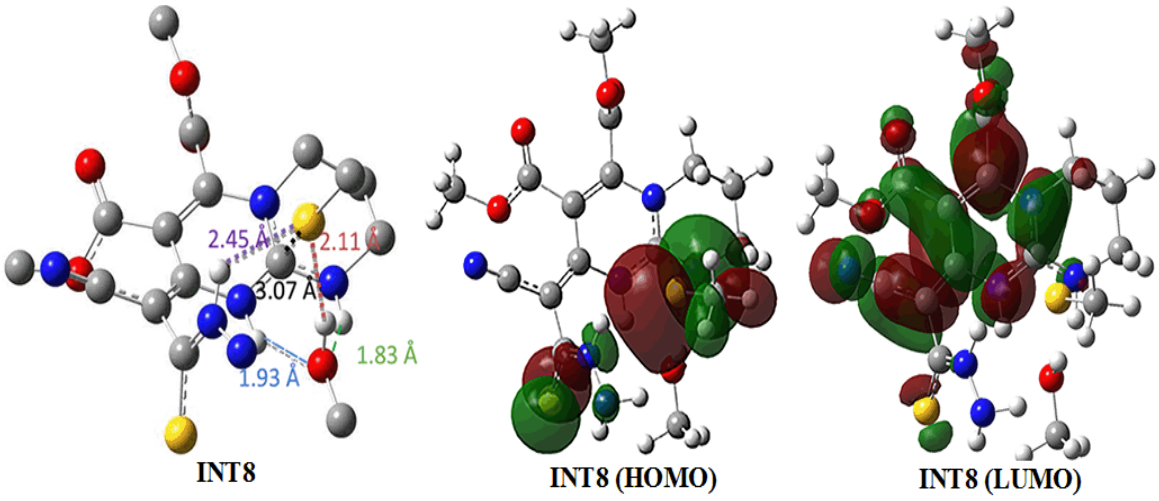
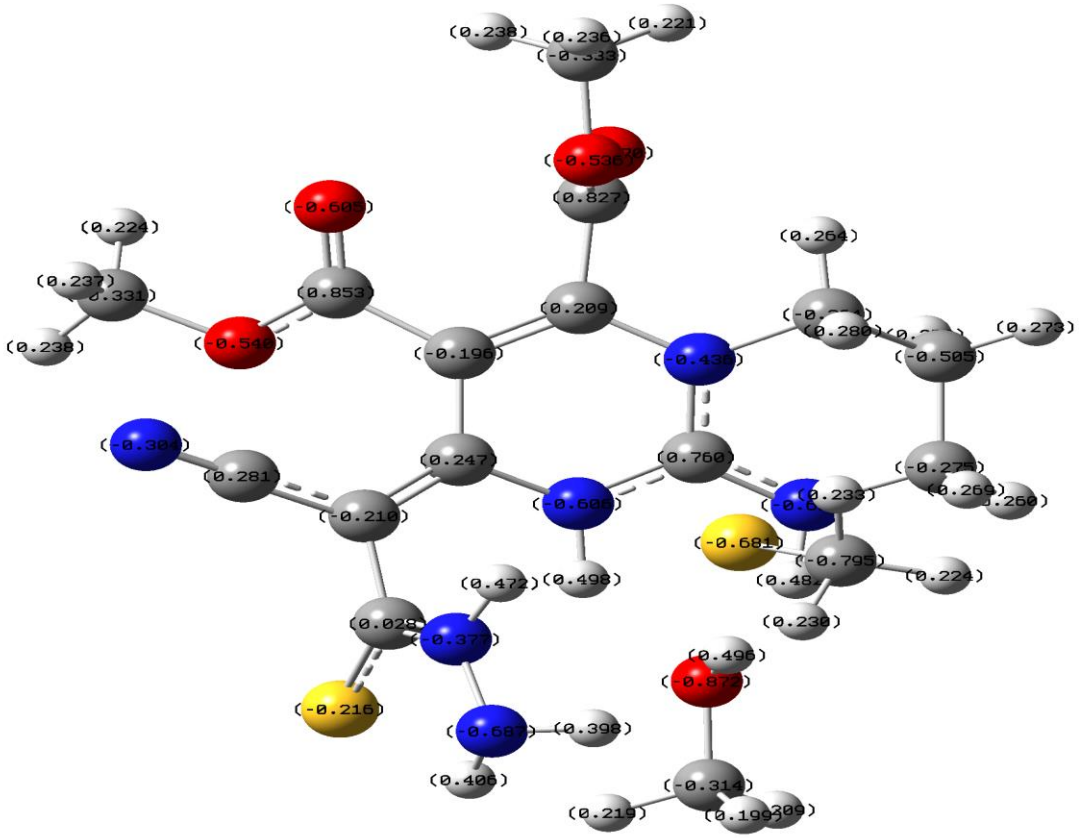
General information:

Melting points measured on an Electrothermal 9100 apparatus. IR spectra were recorded as KBr pellets on a NICOLET FT-IR 100 spectrometer. ^{1}H NMR (300 and 500 MHz) and ^{13}C NMR (75 and 100 MHz) spectra were obtained using Bruker DRX-300 AVANCE and Bruker DRX-500 AVANCE spectrometers. All NMR spectra at room temperature were recorded in DMSO-d_6. Chemical shifts are reported in parts per million (δ) downfield from an internal tetramethylsilane reference. Coupling constants (*J* values) are reported in hertz (Hz), and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Elemental analyses for C, H and N performed using a Heraeus CHN–O–Rapid analyzer. Mass spectra were recorded on a FINNIGAN-MATT 8430 mass spectrometer operating at an ionization potential of 70 eV. The Cartesian coordinates of all optimized structures are separately attached as .xyz files.



Scheme S1. Optimized structure and molecular orbitals of INT8.

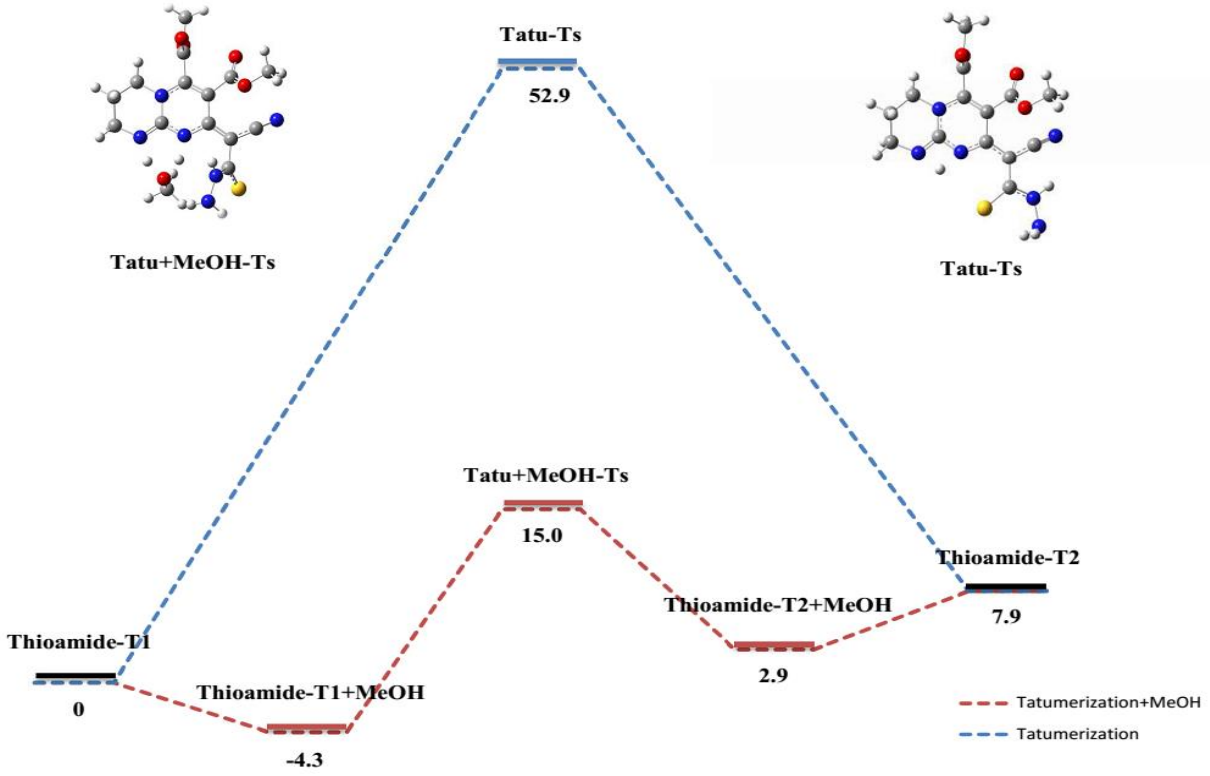
Inspection of the HOMO and LUMO revealed the overlap of the molecular orbital cloud between Lewis acid (CN_3) and Lewis base (MeS^-).



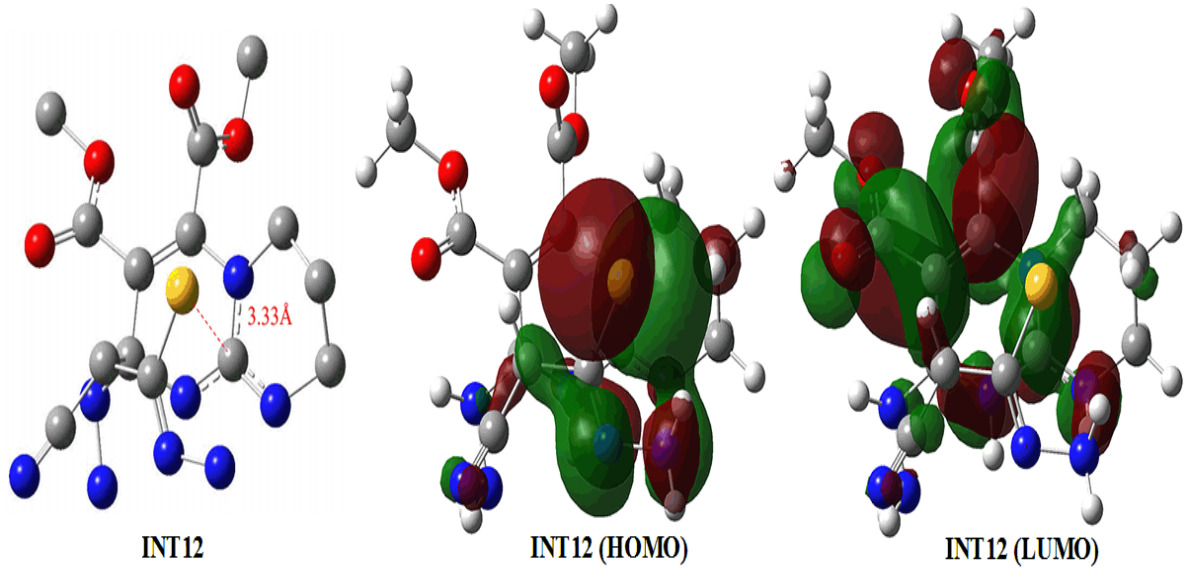
Scheme S2. NBO analysis of INT8

The Lewis acidity of guanidinium is further evidenced by NBO charge analysis (see supporting information). In **INT8**, the atomic charge on the central carbon atom of CN_3 group is +0.76 that

pairs with the strongly negative charge on the MeS^- counteranion (−0.68). Noteworthy, the electron deficiency in central carbon is even greater than *t*-butyl cation (+0.51). Also, the calculation shows the strong negative charge on the neighboring nitrogen atoms in CN_3 (N_1: −0.60, N_5: −0.43, and N_9: −0.61).



Scheme S3. Energy profile of tautomerization



Scheme S4. Optimized structure and molecular orbitals of INT12.

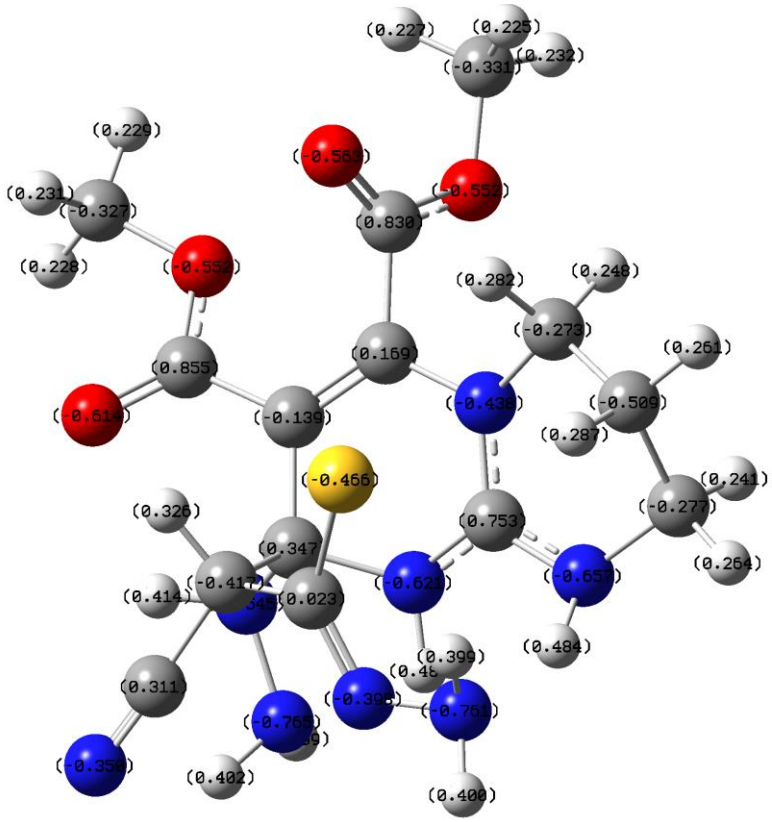
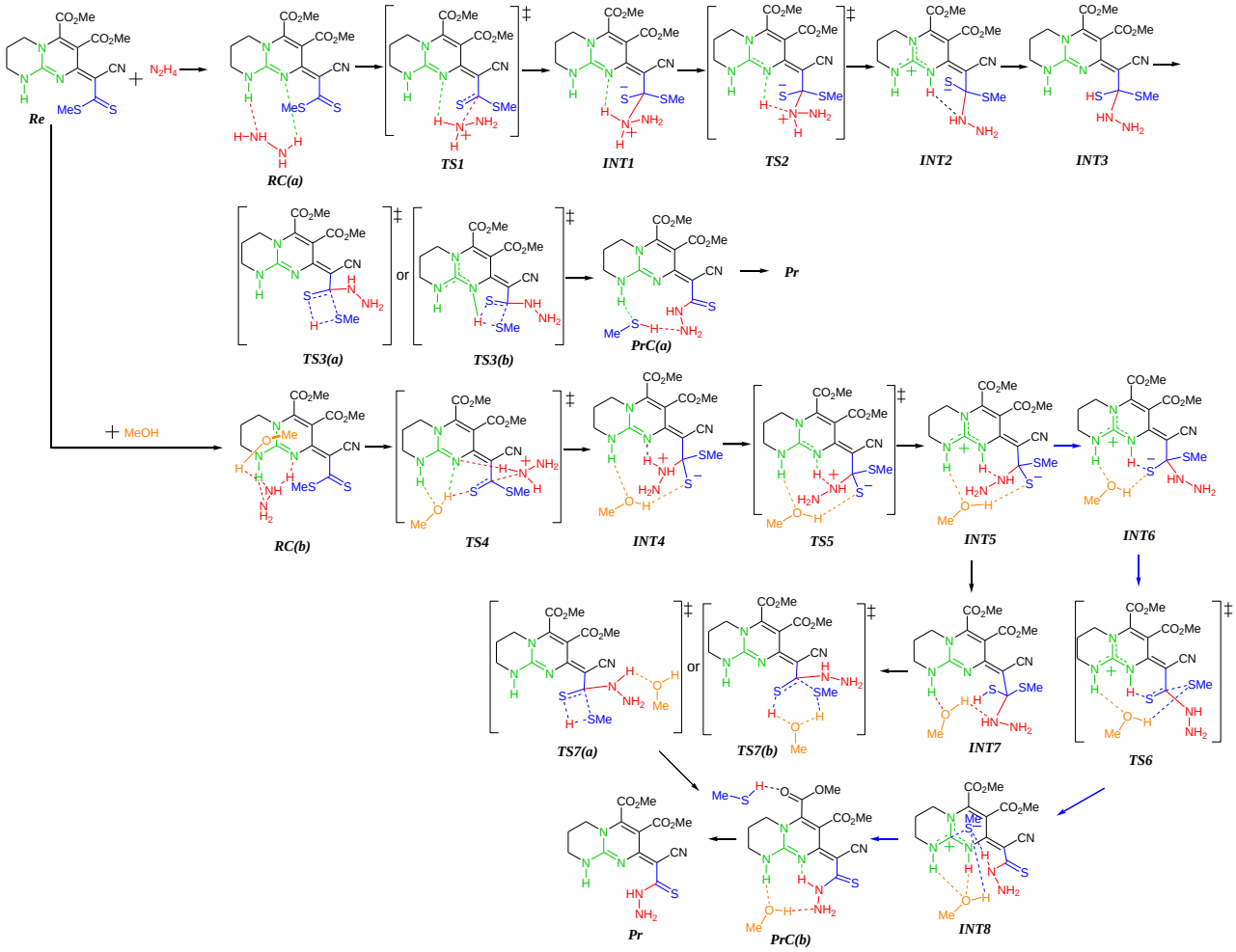
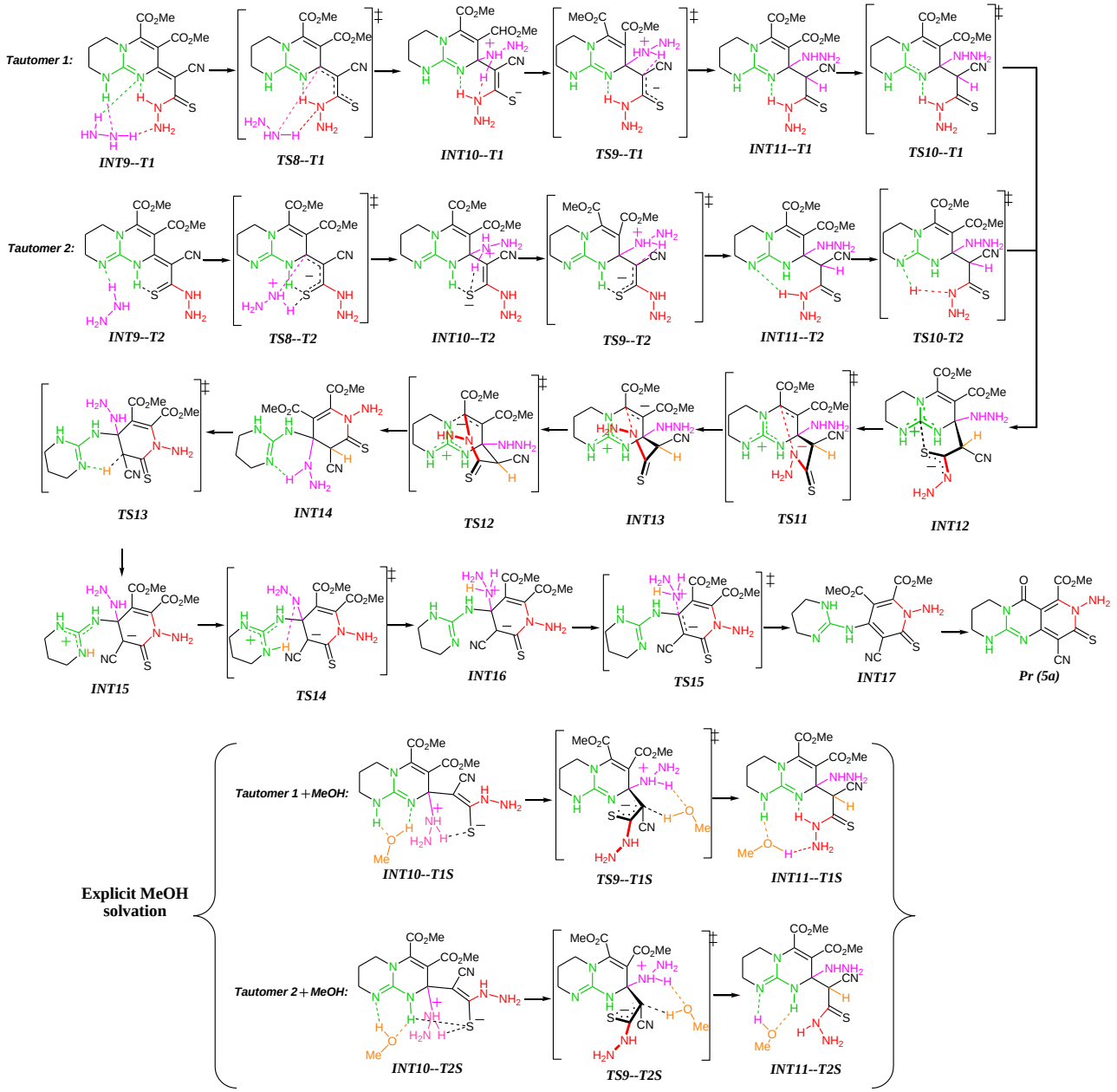


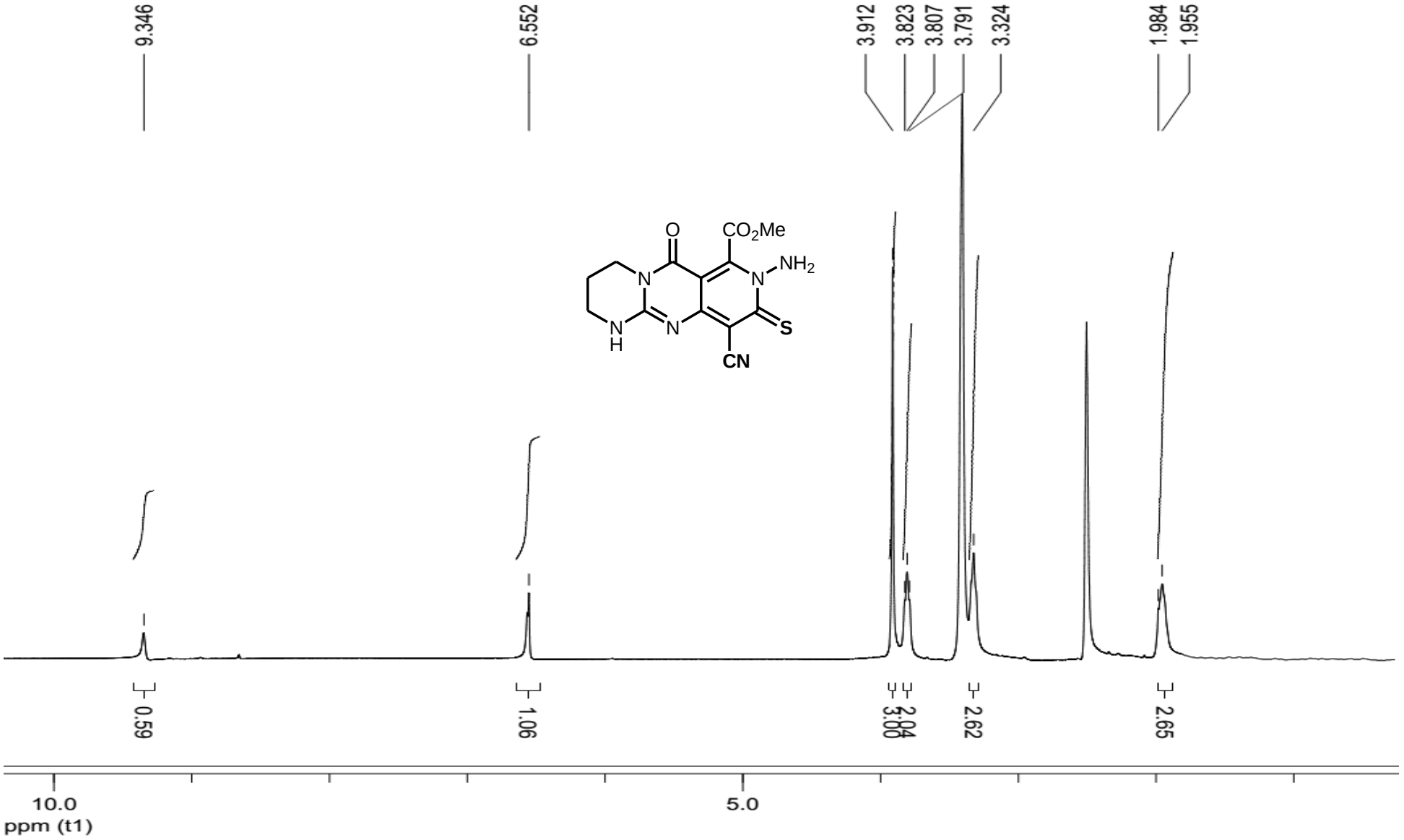
Figure S5. NBO analysis of INT12



Scheme S6: Thioamidation sequence



Scheme S7. *N*-Michael addition sequence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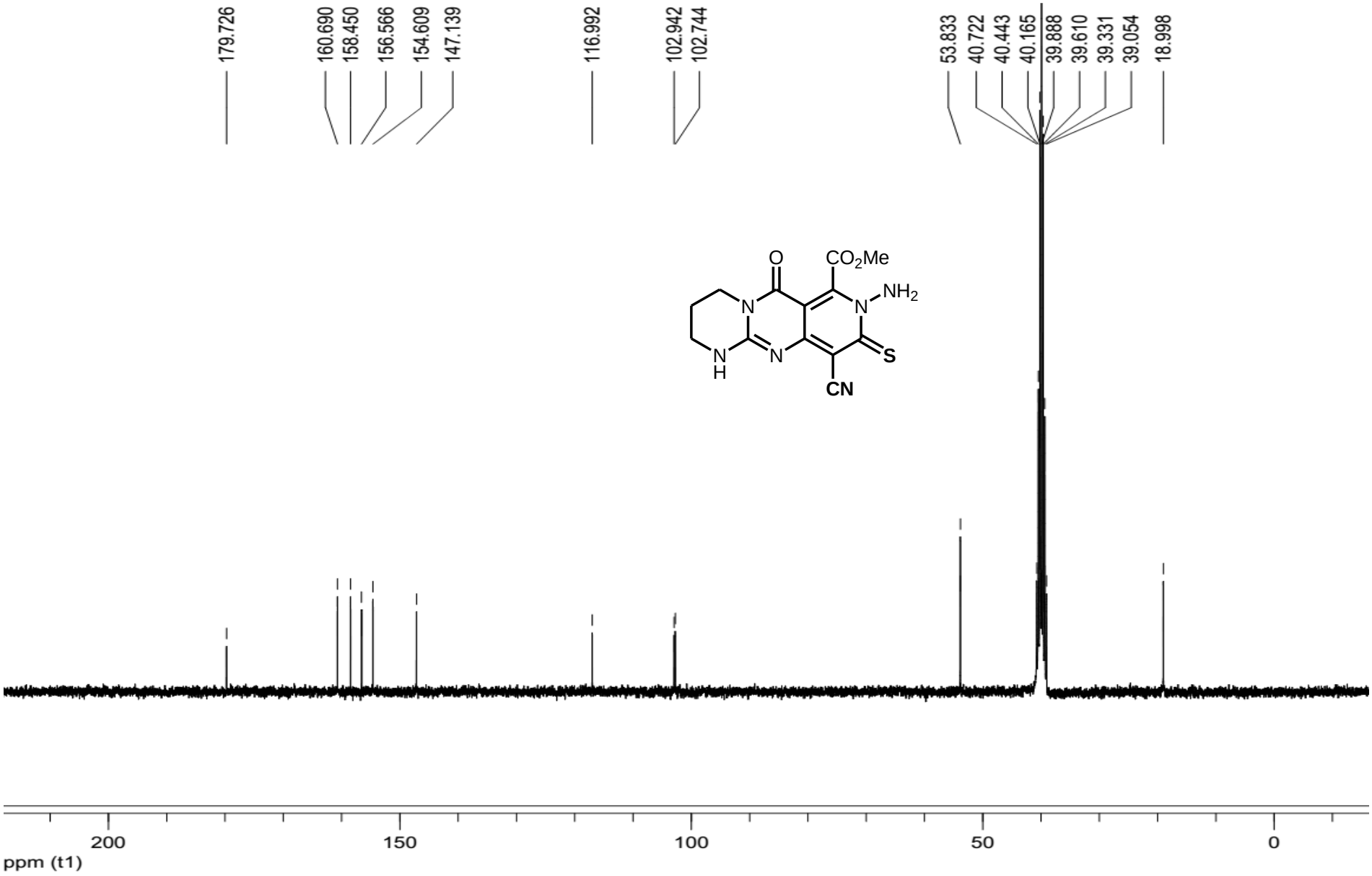
6.552
3.912
3.823
3.807
3.791
3.324
1.984
1.955
O
CO2Me
NH2
N
N
N
H
N
S
CN
0.59
1.06
3.00
3.04
2.62
2.65
10.0
ppm (t1)
5.0

^{1}H NMR of **5a**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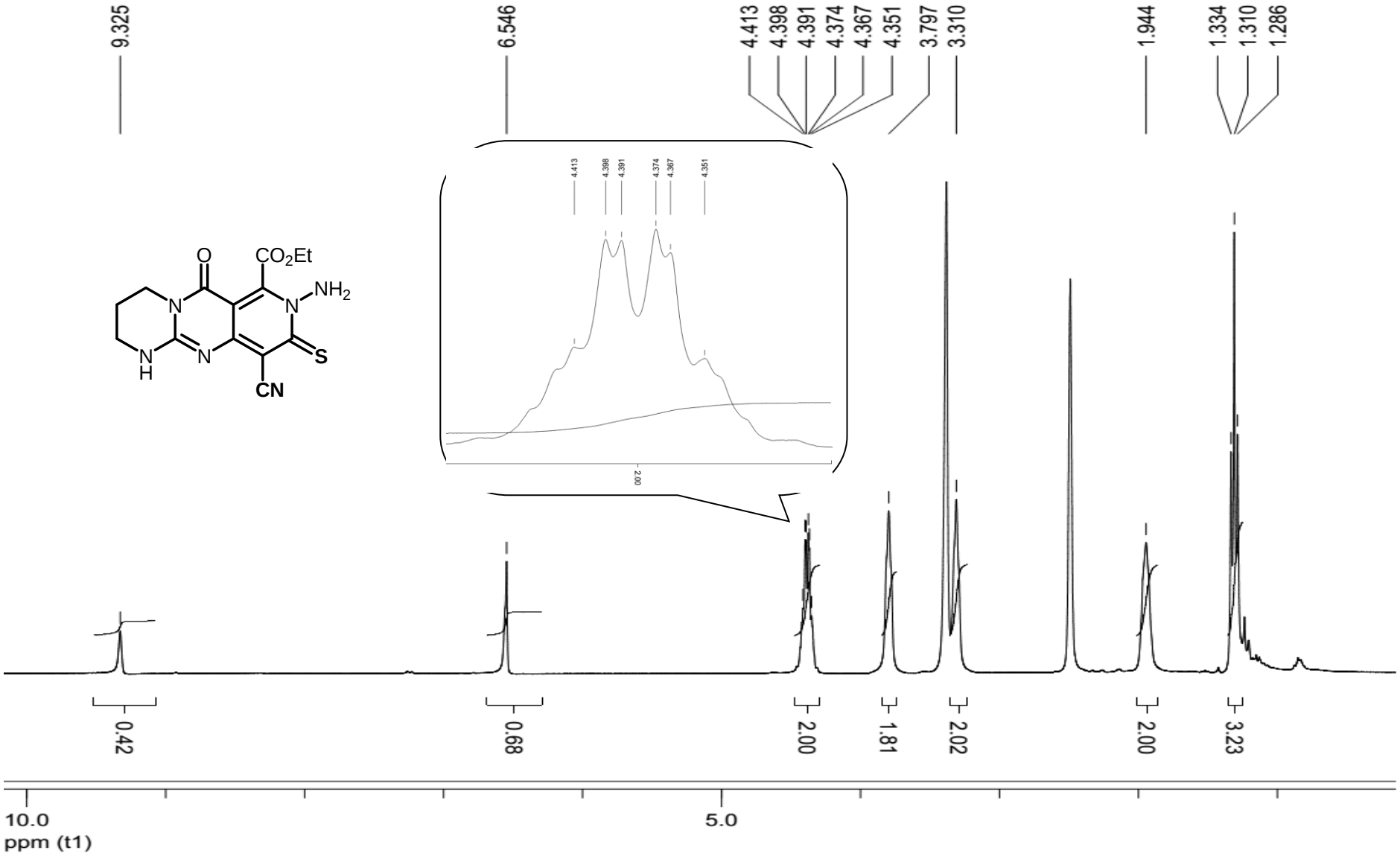
158.450
156.566
154.609
147.139
116.992
102.942
102.744
53.833
40.722
40.443
40.165
39.888
39.610
39.331
39.054
18.998
O
CO2Me
NH2
N
N
N
H
S
CN
200
150
100
50
0
ppm (t1)

^{13}C NMR of **5a**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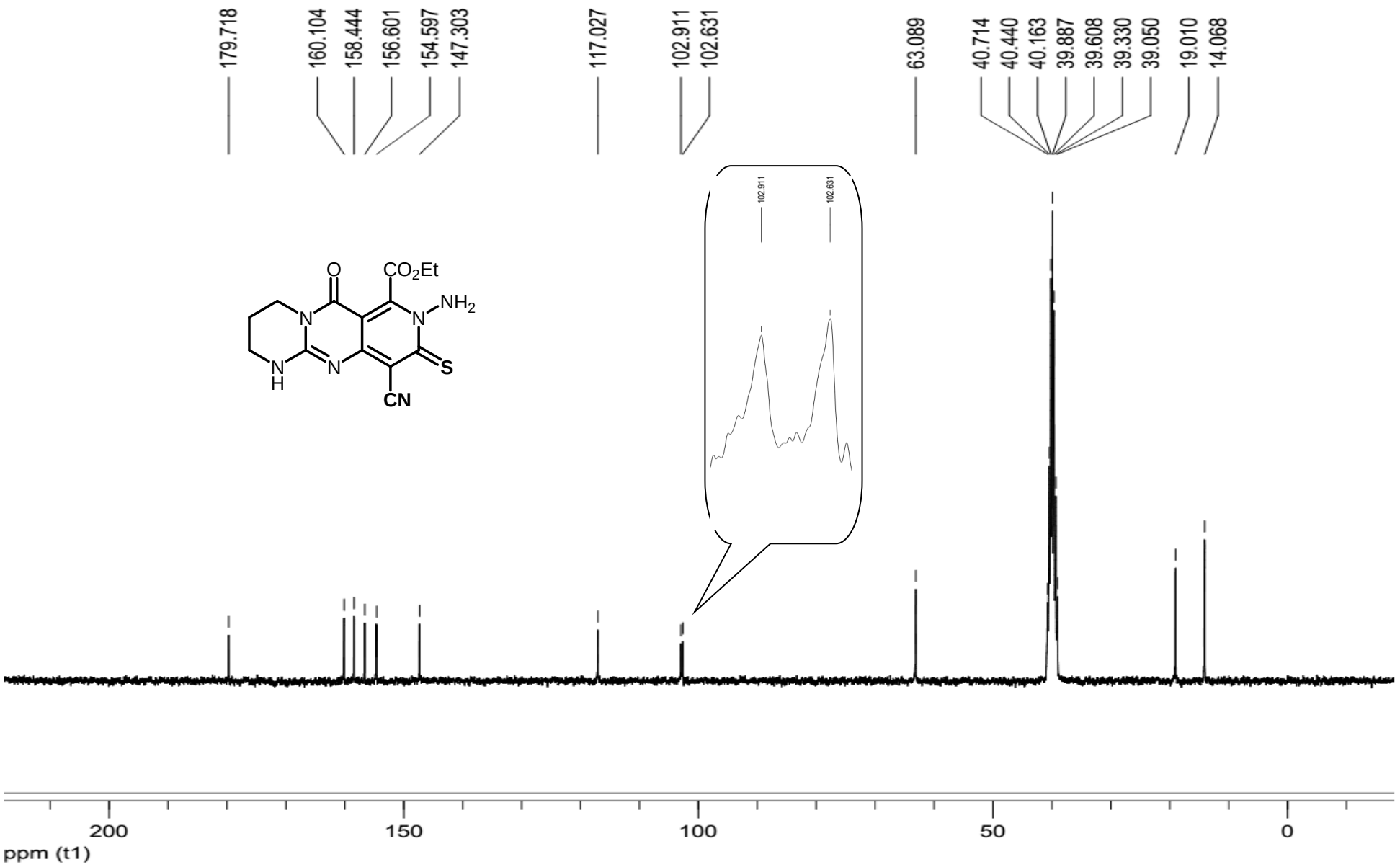
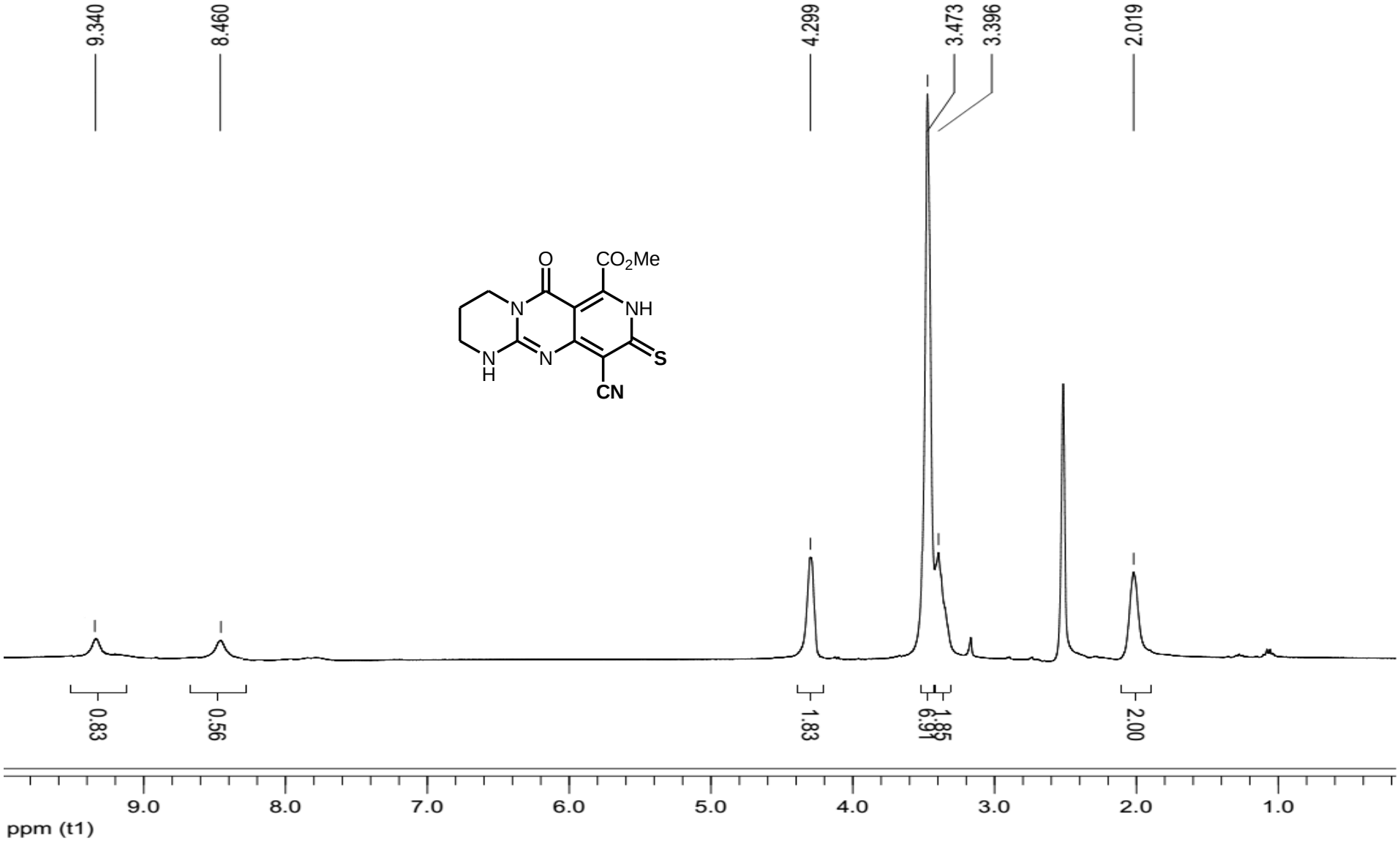
6.546
4.413
4.398
4.391
4.374
4.367
4.351
3.797
3.310
1.944
1.334
1.310
1.286
O
CO2Et
NH2
N
N
N
H
N
S
CN
0.42
0.68
2.00
1.81
2.02
2.00
3.23
10.0
ppm (t1)
5.0

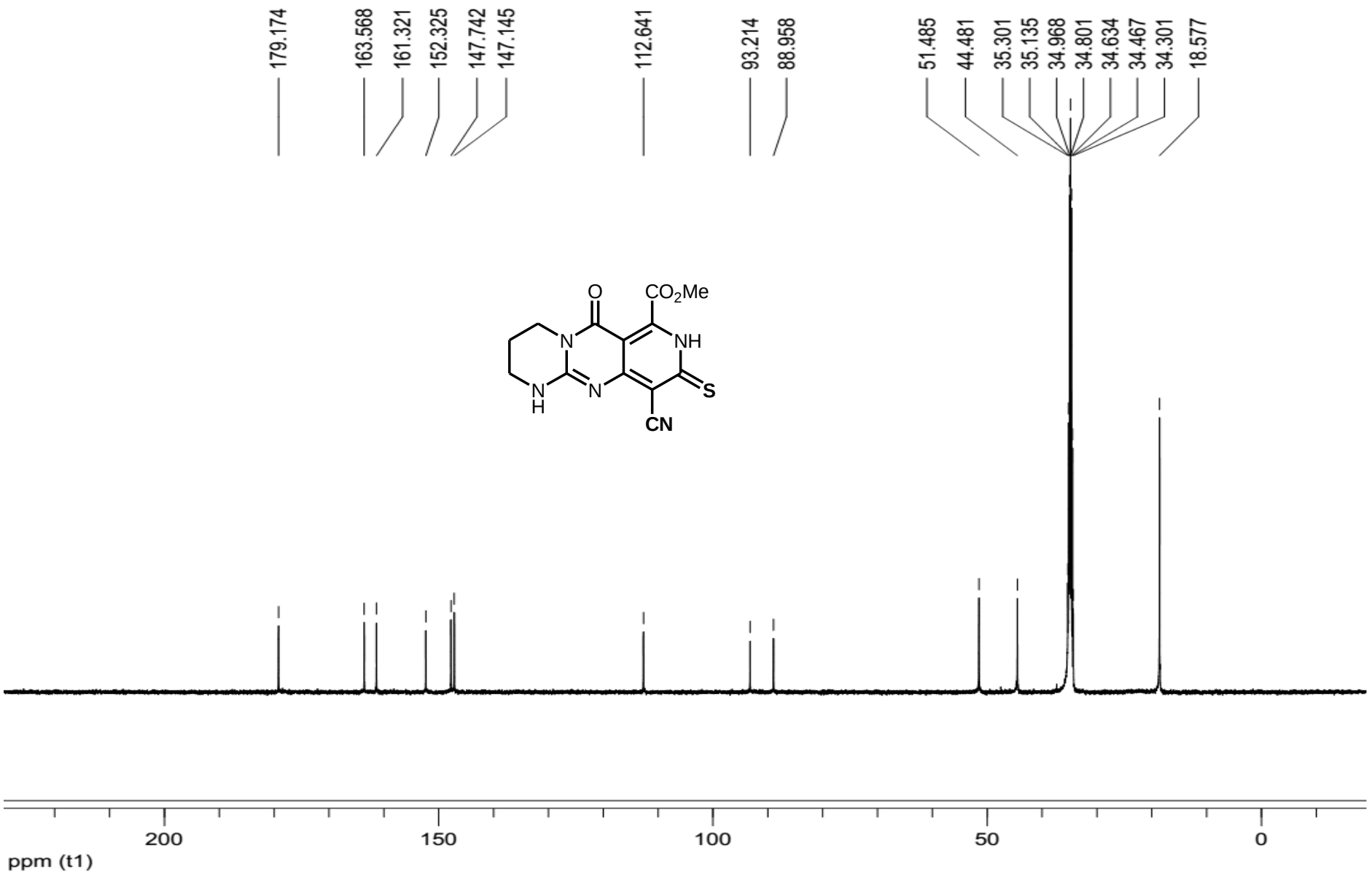
^{1}H NMR of **5b**


179.718
160.104
158.444
156.601
154.597
147.303
117.027
102.911
102.631
63.089
40.714
40.440
40.163
39.887
39.608
39.330
39.050
19.010
14.068
O
CO2Et
NH2
N
N
N
H
N
S
CN
200
150
100
50
0
ppm (t1)

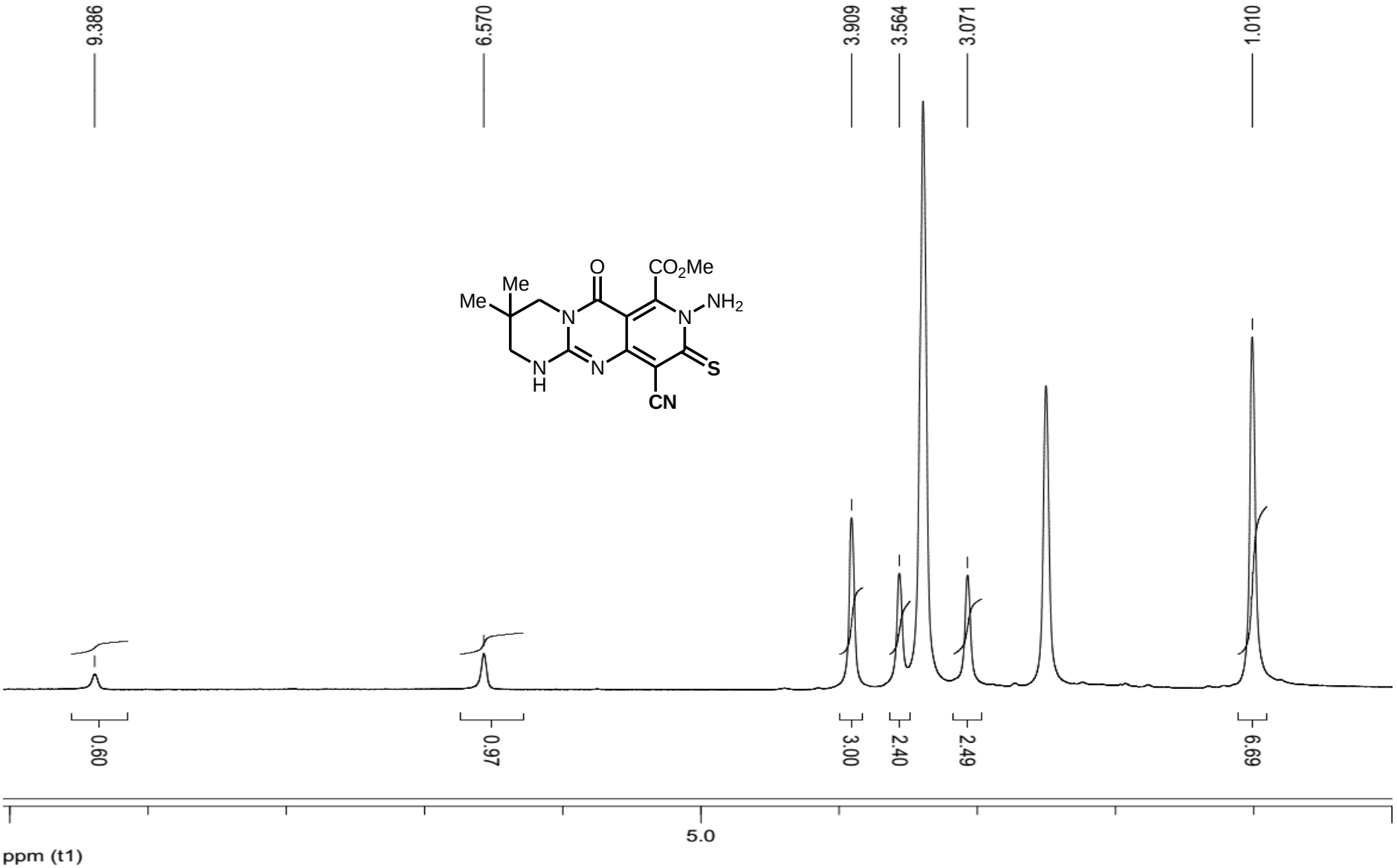
^{13}C NMR of **5b**


9.340
8.460
4.299
3.473
3.396
2.019
O
CO2Me
N
NH
N
H
N
S
CN
0.83
0.56
1.83
6.61
1.85
2.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

^{1}H NMR of **5c**


179.174
163.568
161.321
152.325
147.742
147.145
112.641
93.214
88.958
51.485
44.481
35.301
35.135
34.968
34.801
34.634
34.467
34.301
18.577
O
CO2Me
N
NH
N
H
N
S
CN
200
150
100
50
0
ppm (t1)

^{13}C NMR of **5c**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3.909
3.564
3.071
1.010
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CO2Me
Me
Me
NH2
N
N
N
H
N
S
CN
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3.00
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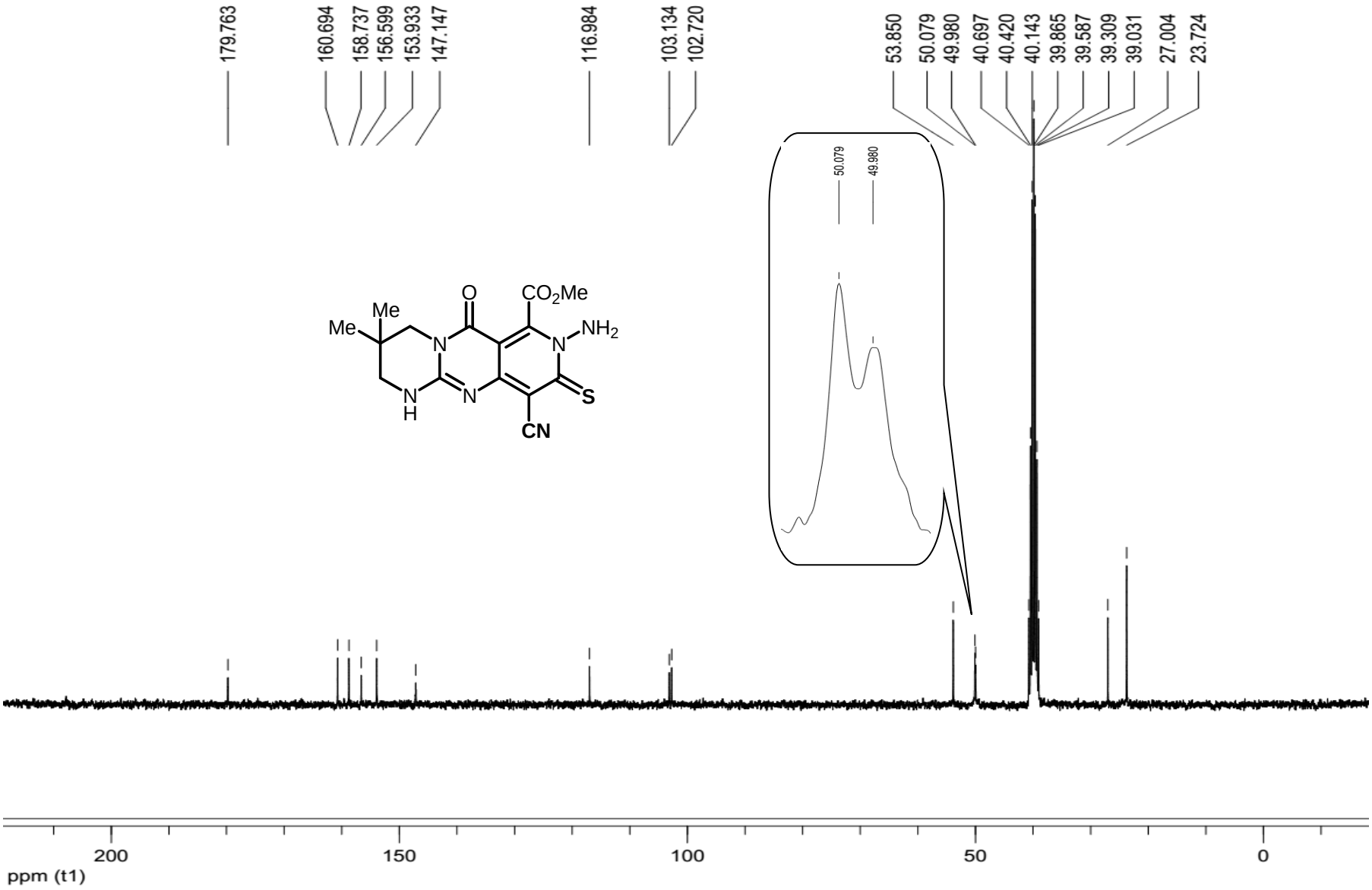
2.49
6.69
5.0
ppm (t1)

^{1}H NMR of **5d**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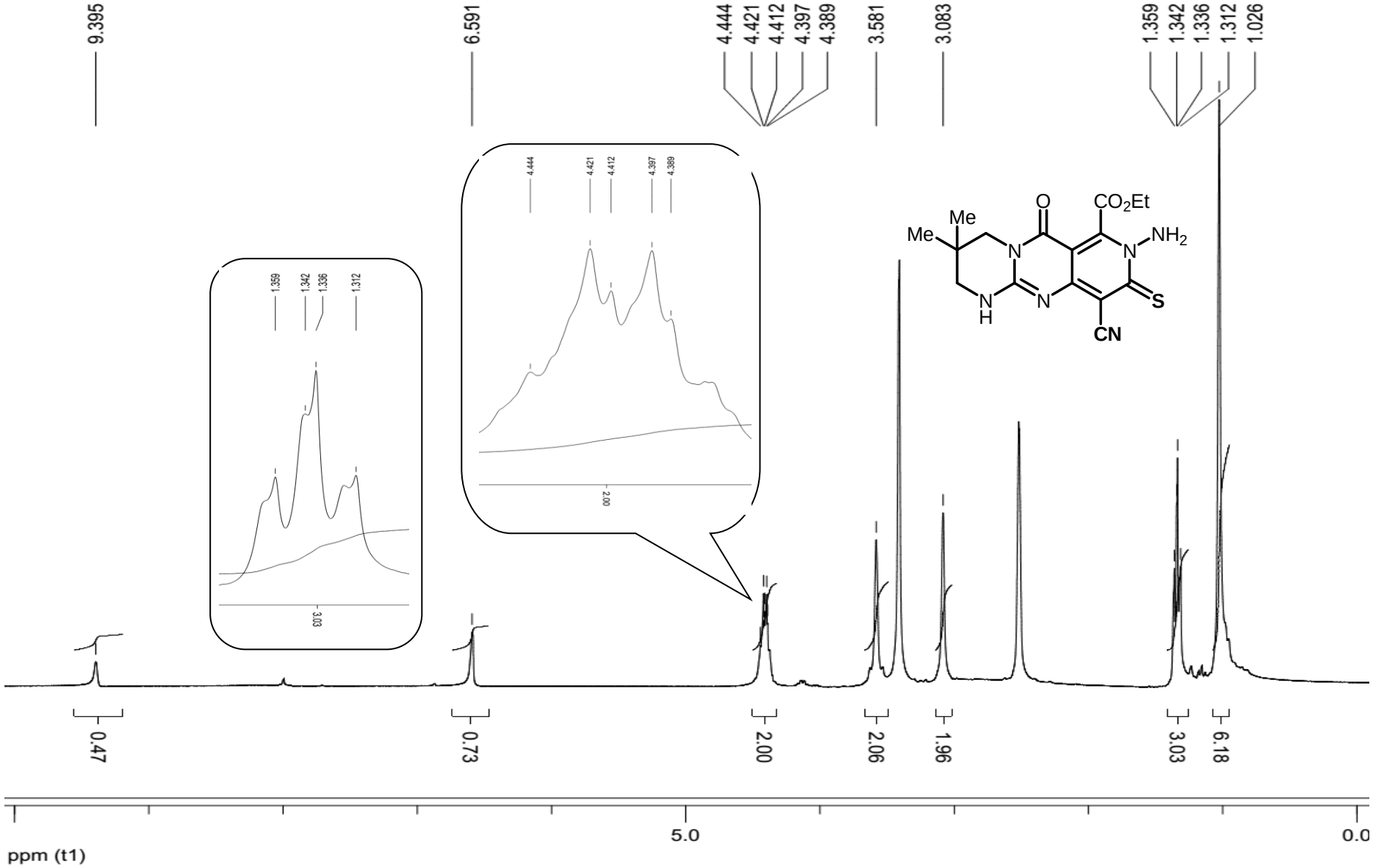
160.694
158.737
156.599
153.933
147.147
116.984
103.134
102.720
53.850
50.079
49.980
40.697
40.420
40.143
39.865
39.587
39.309
39.031
27.004
23.724
50.079
49.980
O
CO2Me
Me
Me
NH2
N
N
N
H
N
S
CN
200
150
100
50
0
ppm (t1)

^{13}C NMR of **5d**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4.397
4.389
3.581
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1.359
1.342
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1.312
1.026
Me
Me
O
CO2Et
NH2
N
N
N
H
N
S
CN
0.47
0.73
2.00
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1.96
3.03
6.18
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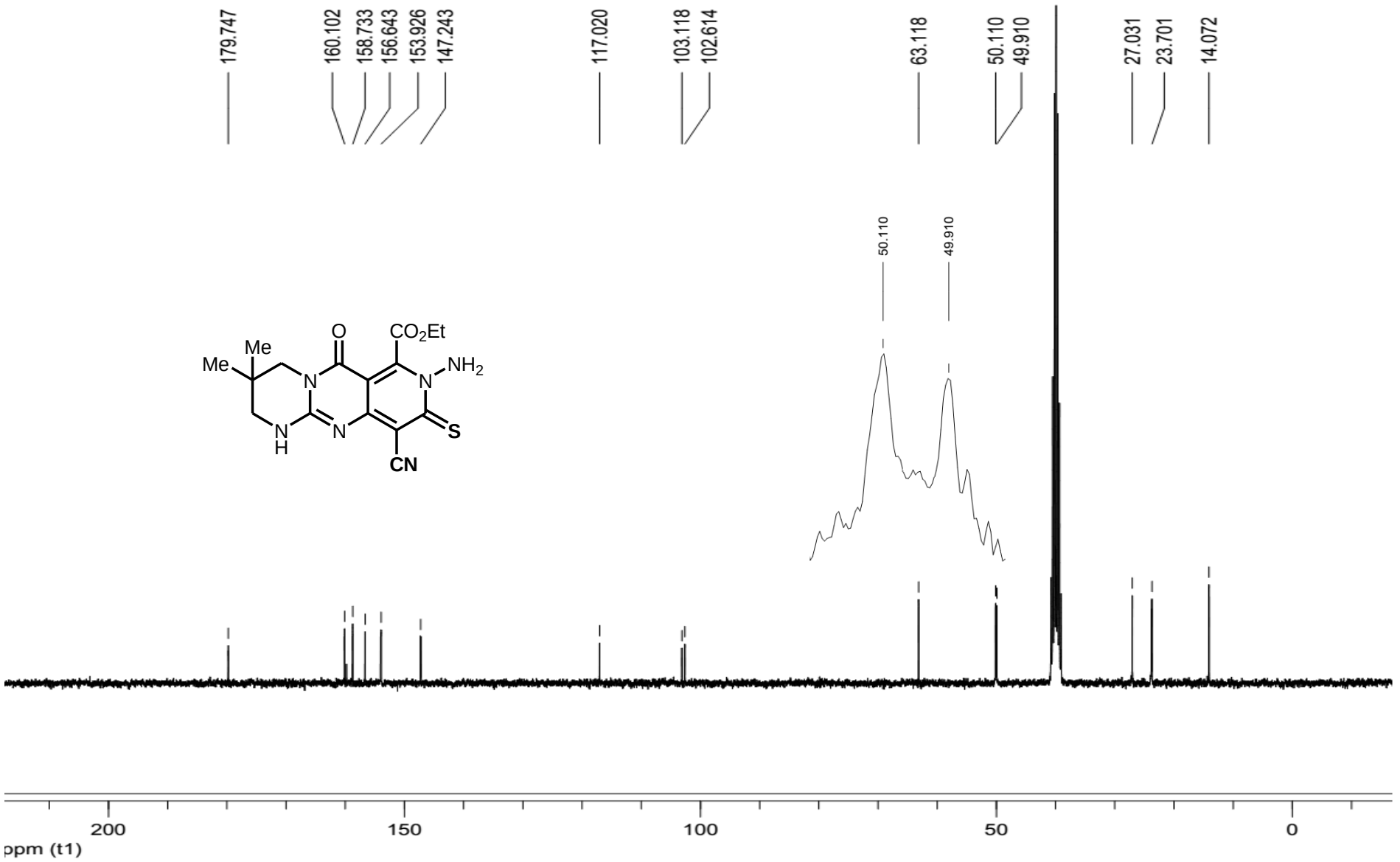
0.0
ppm (t1)

^{1}H NMR of **5e**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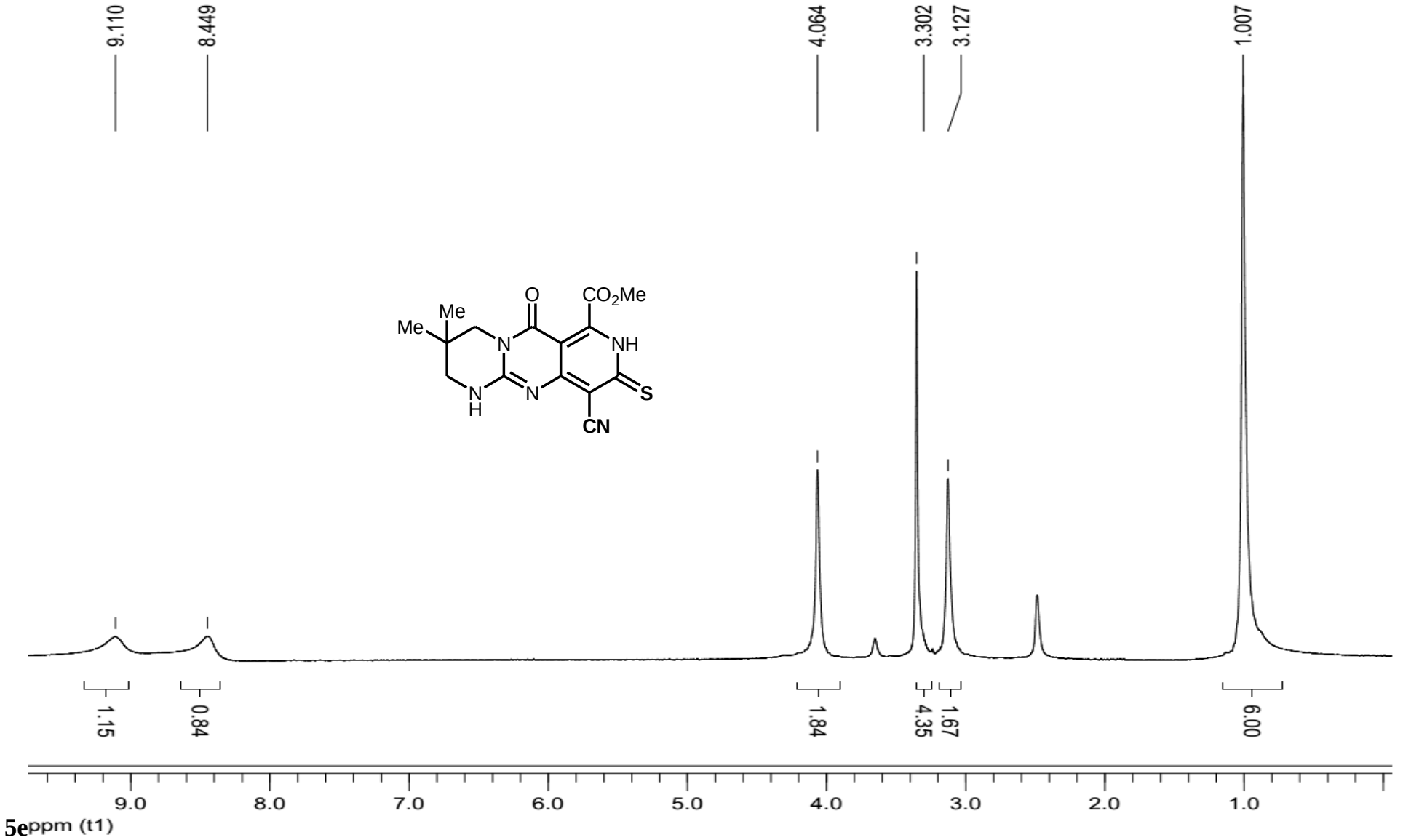
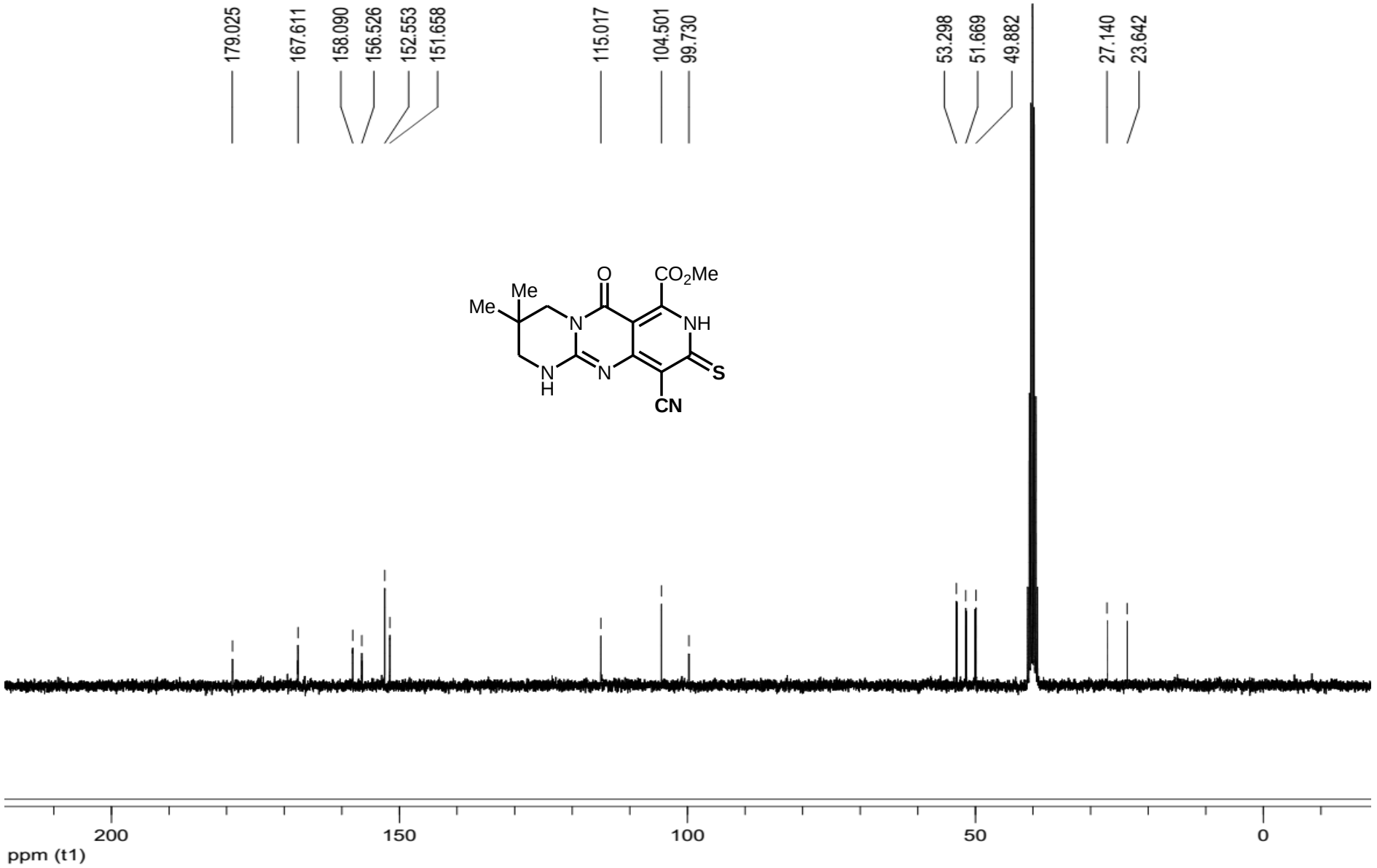
158.733
156.643
153.926
147.243
117.020
103.118
102.614
63.118
50.110
49.910
27.031
23.701
14.072
50.110
49.910
O
CO2Et
Me
Me
N
NH2
N
N
H
N
S
CN
200
150
100
50
0
ppm (t1)

^{13}C NMR of **5e**



5e

^{1}H NMR of **5f**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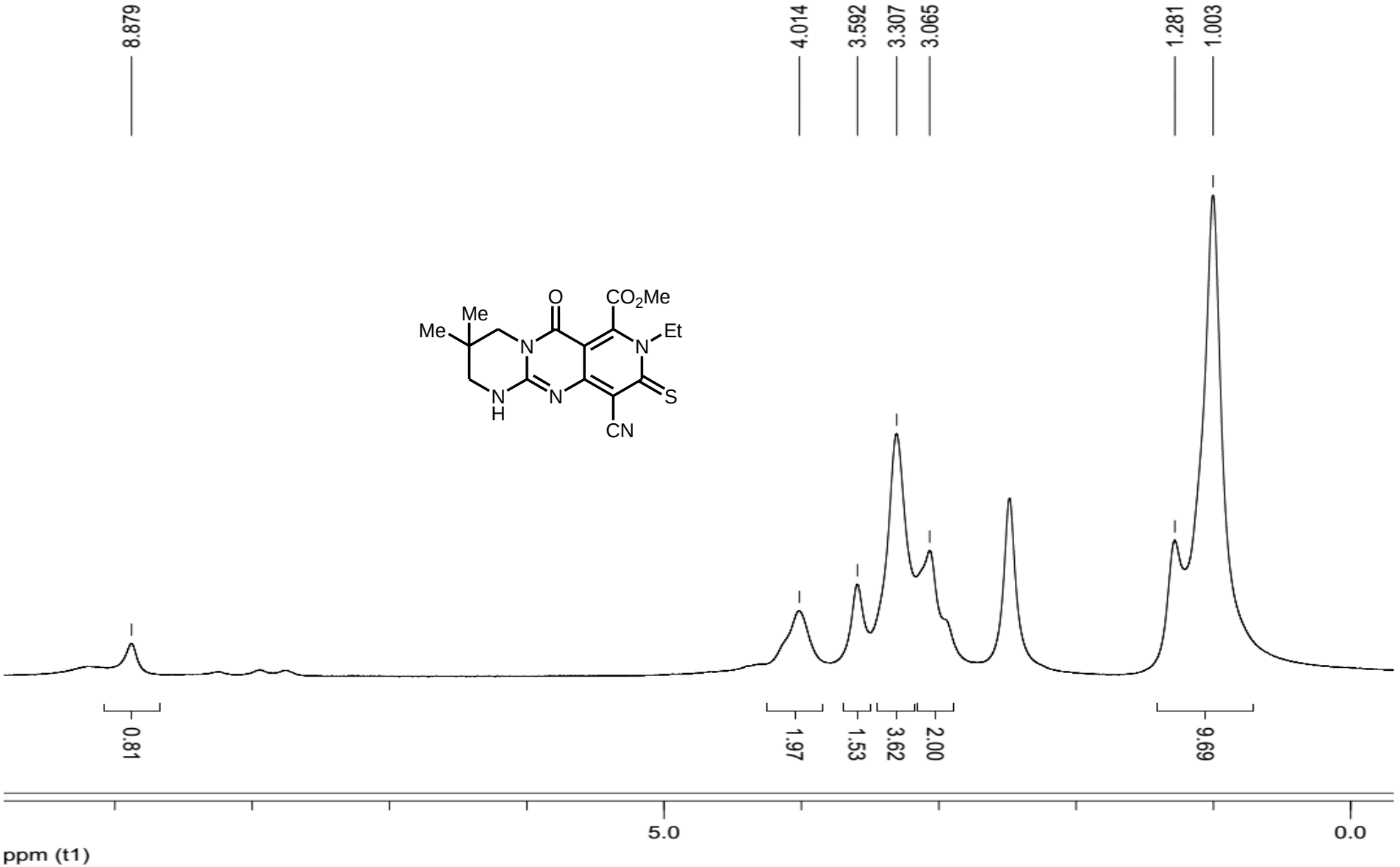
158.090
156.526
152.553
151.658
115.017
104.501
99.730
53.298
51.669
49.882
27.140
23.642
O
CO2Me
Me
Me
N
NH
N
H
N
S
CN
200
150
100
50
0
ppm (t1)

^{13}C NMR of **5f**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3.307
3.065
1.281
1.003
Me
Me
O
CO2Me
Et
N
N
N
H
N
S
CN
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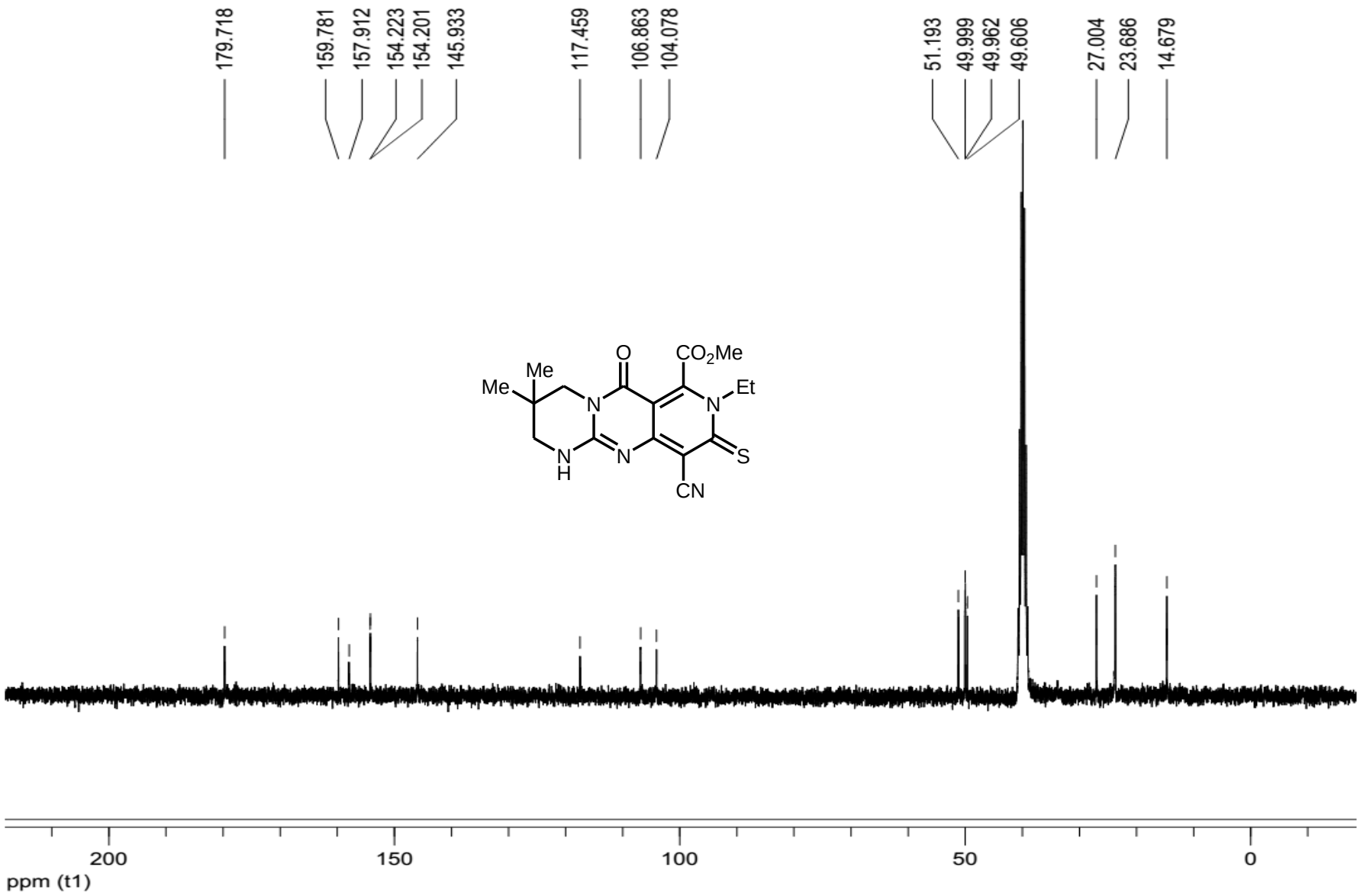
1.97
1.53
3.62
2.00
9.69
5.0
0.0
ppm (t1)

^{1}H NMR of **5g**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157.912
154.223
154.201
145.933
117.459
106.863
104.078
51.193
49.999
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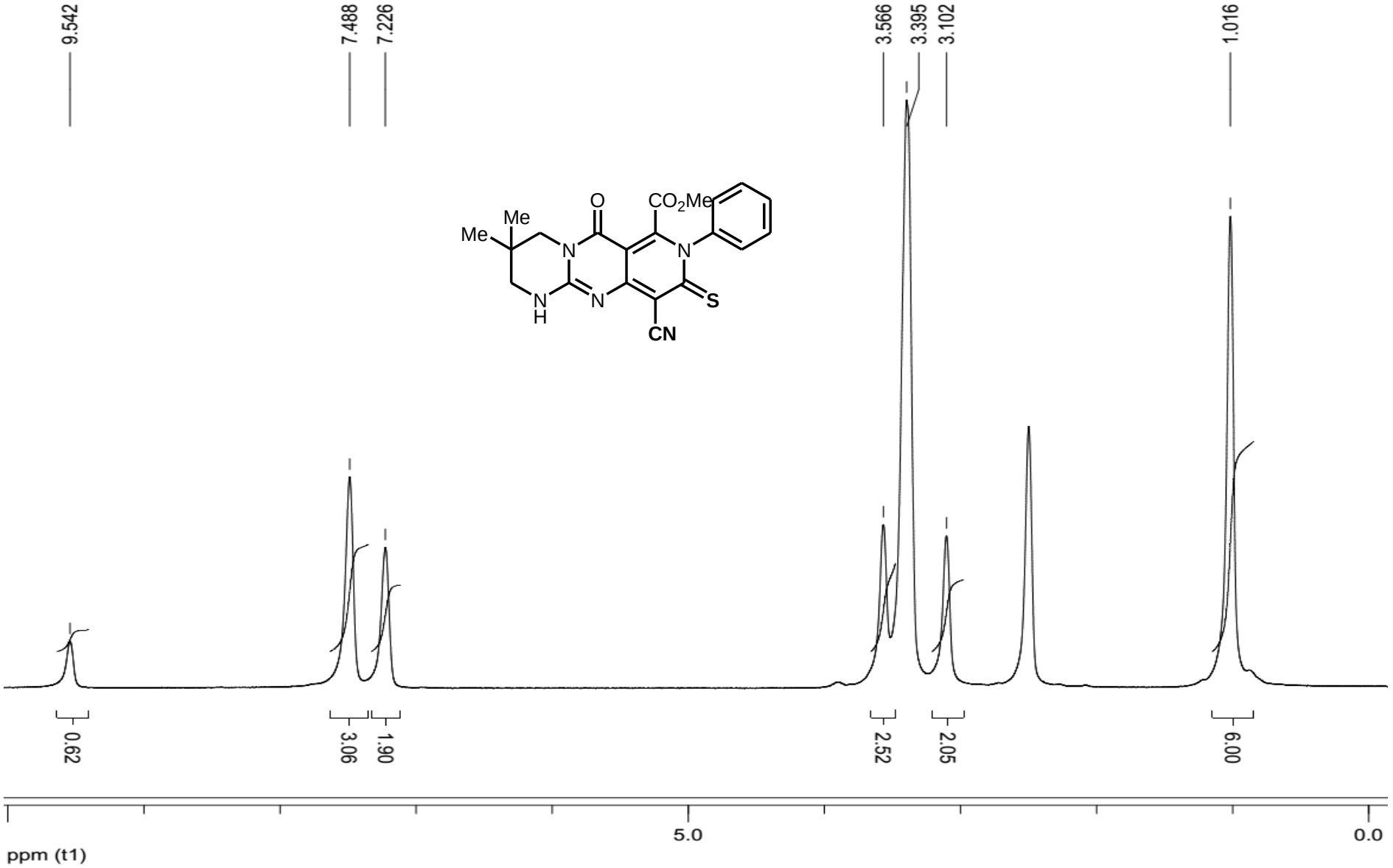
49.606
27.004
23.686
14.679
O
CO2Me
Me
Me
N
N
Et
N
H
N
S
CN
200
150
100
50
0
ppm (t1)

^{13}C NMR of **5g**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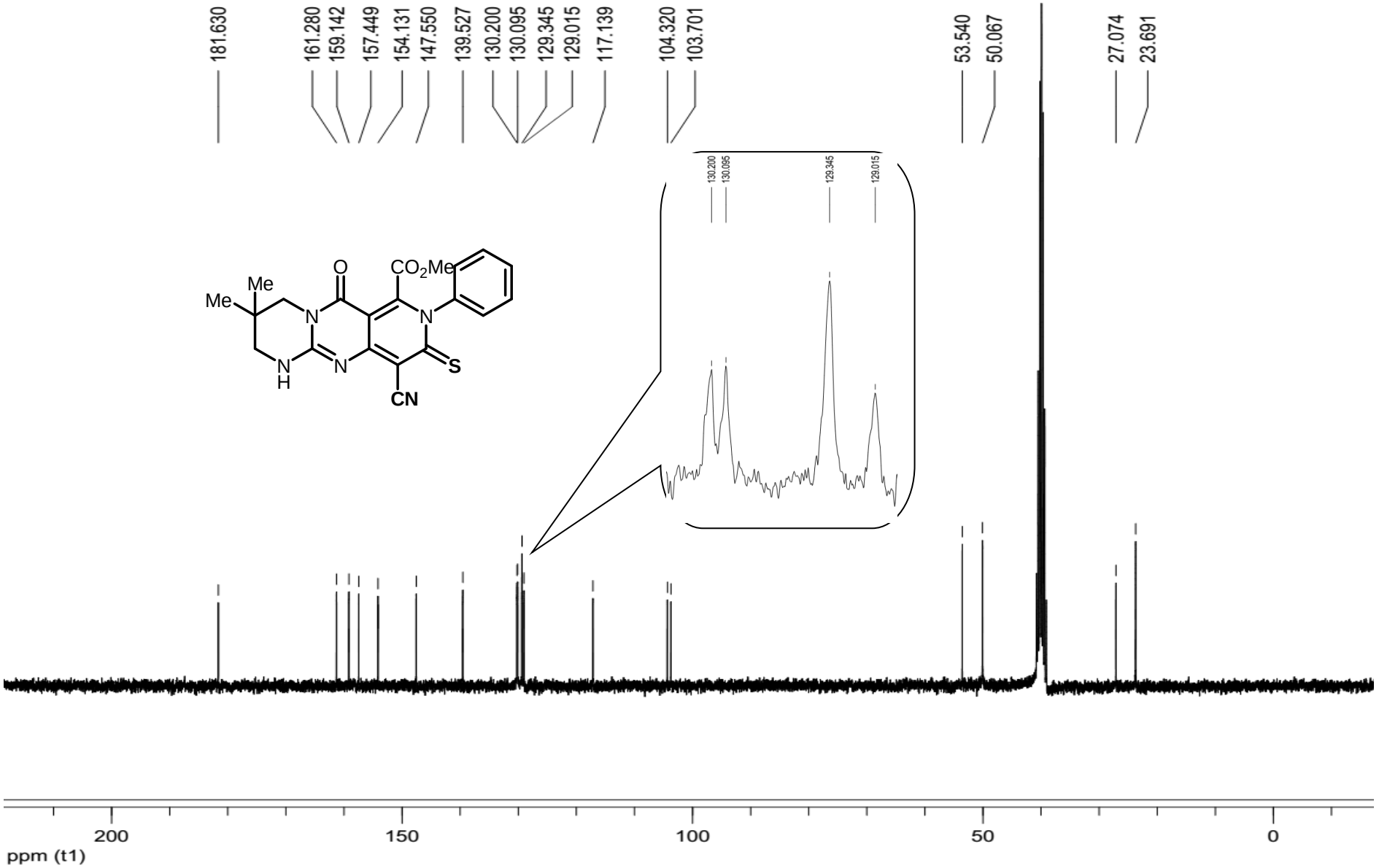
7.226
3.566
3.395
3.102
1.016
Me
Me
O
CO2Me
N
N
N
H
N
S
CN
0.92
3.06
1.90
2.52
2.05
6.00
5.0
0.0
ppm (t1)

^{1}H NMR of **5h**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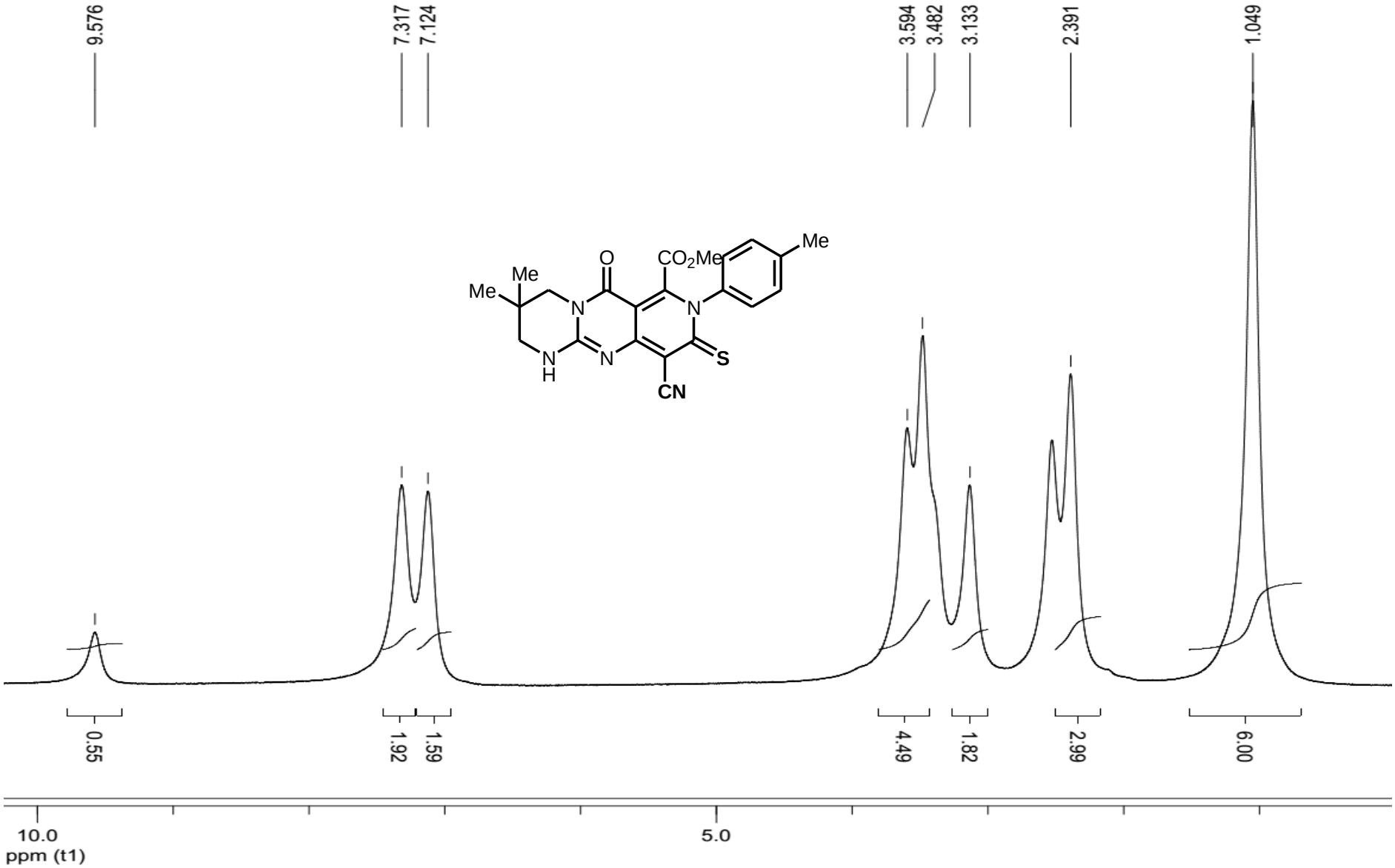
161.280
159.142
157.449
154.131
147.550
139.527
130.200
130.095
129.345
129.015
117.139
104.320
103.701
53.540
50.067
27.074
23.691
130.200
130.095
129.345
129.015
O
CO2Me
Me
Me
N
N
N
H
N
S
CN
200
150
100
50
0
ppm (t1)

^{13}C NMR of **5h**


9.576
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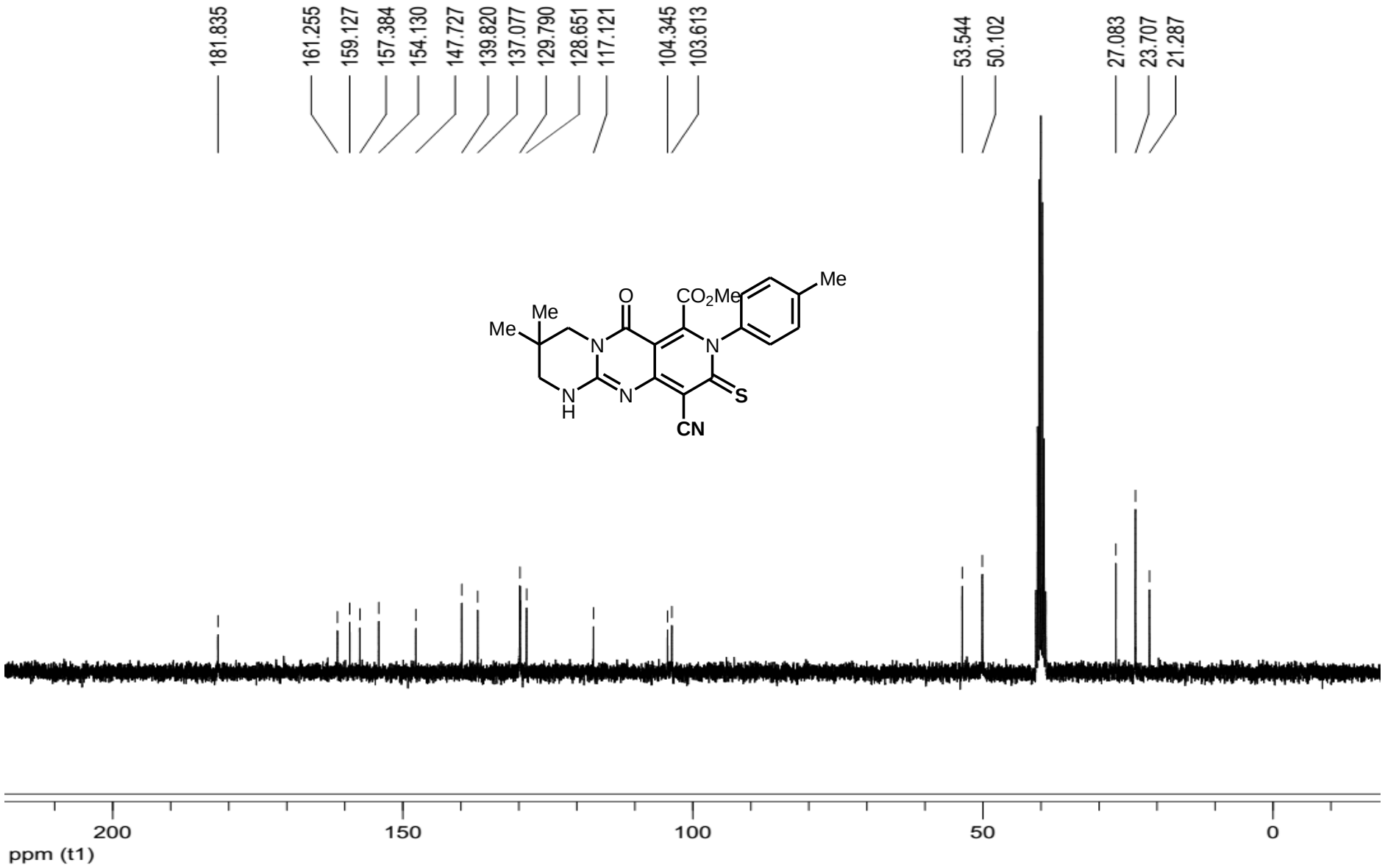
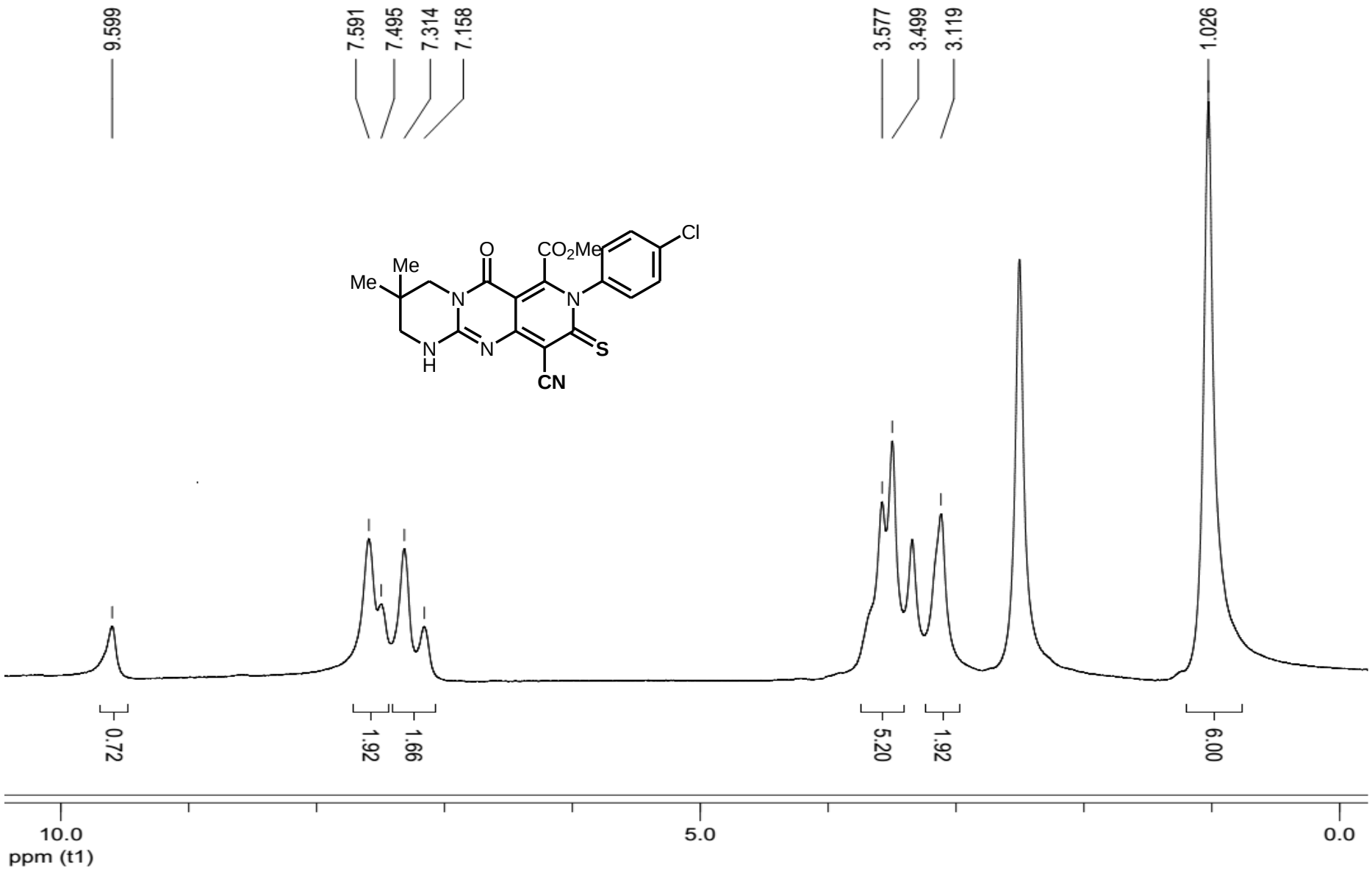
7.124
3.594
3.482
3.133
2.391
1.049
Me
Me
Me
O
CO2Me
N
N
N
H
N
S
CN
0.55
1.92
1.59
4.49
1.82
2.99
6.00
10.0
ppm (t1)
5.0

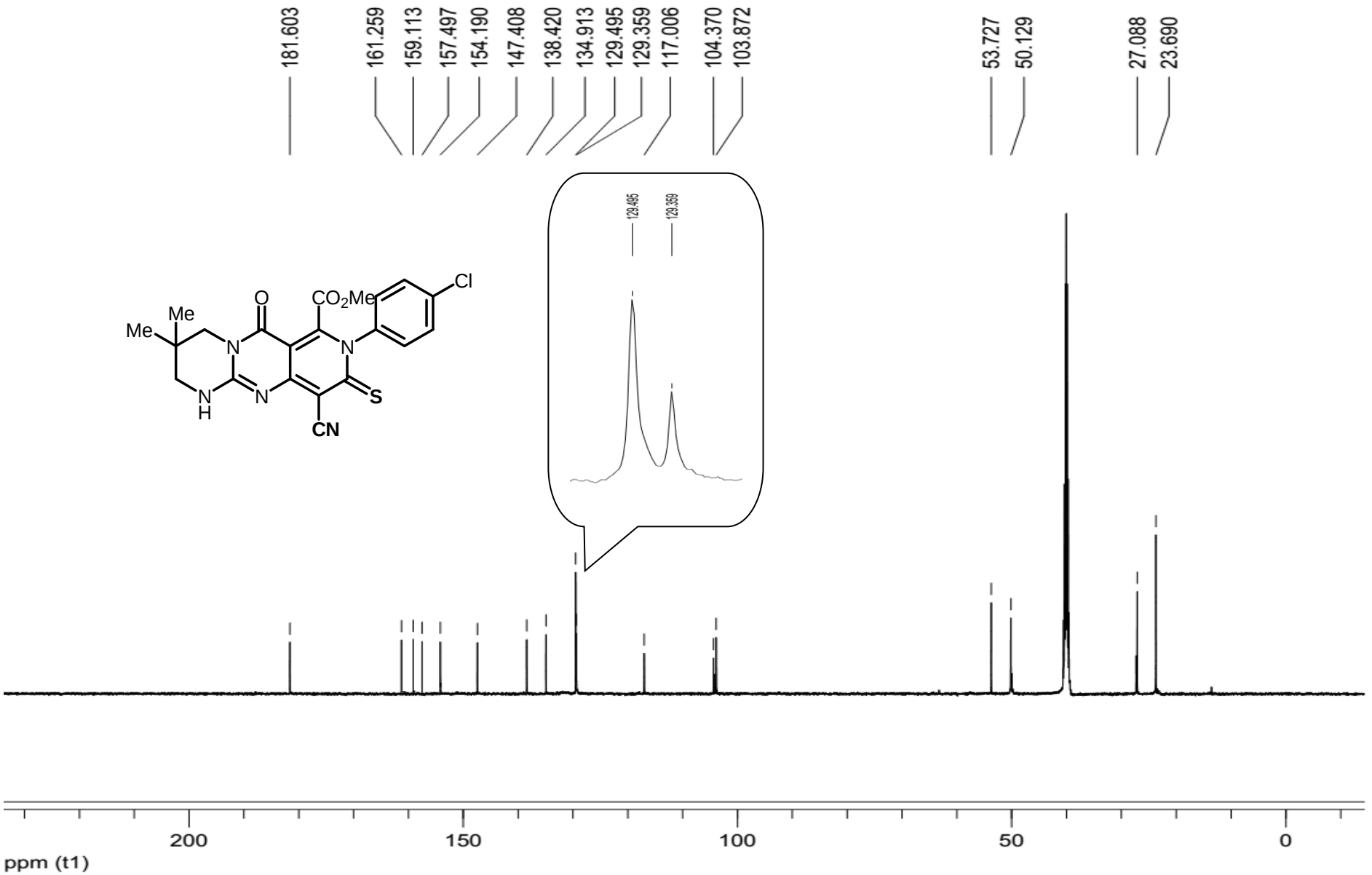
^{1}H NMR of **5i**


181.835
161.255
159.127
157.384
154.130
147.727
139.820
137.077
129.790
128.651
117.121
104.345
103.613
53.544
50.102
27.083
23.707
21.287
Me
Me
Me
O
CO2Me
N
N
N
H
N
S
CN
200
150
100
50
0
ppm (t1)

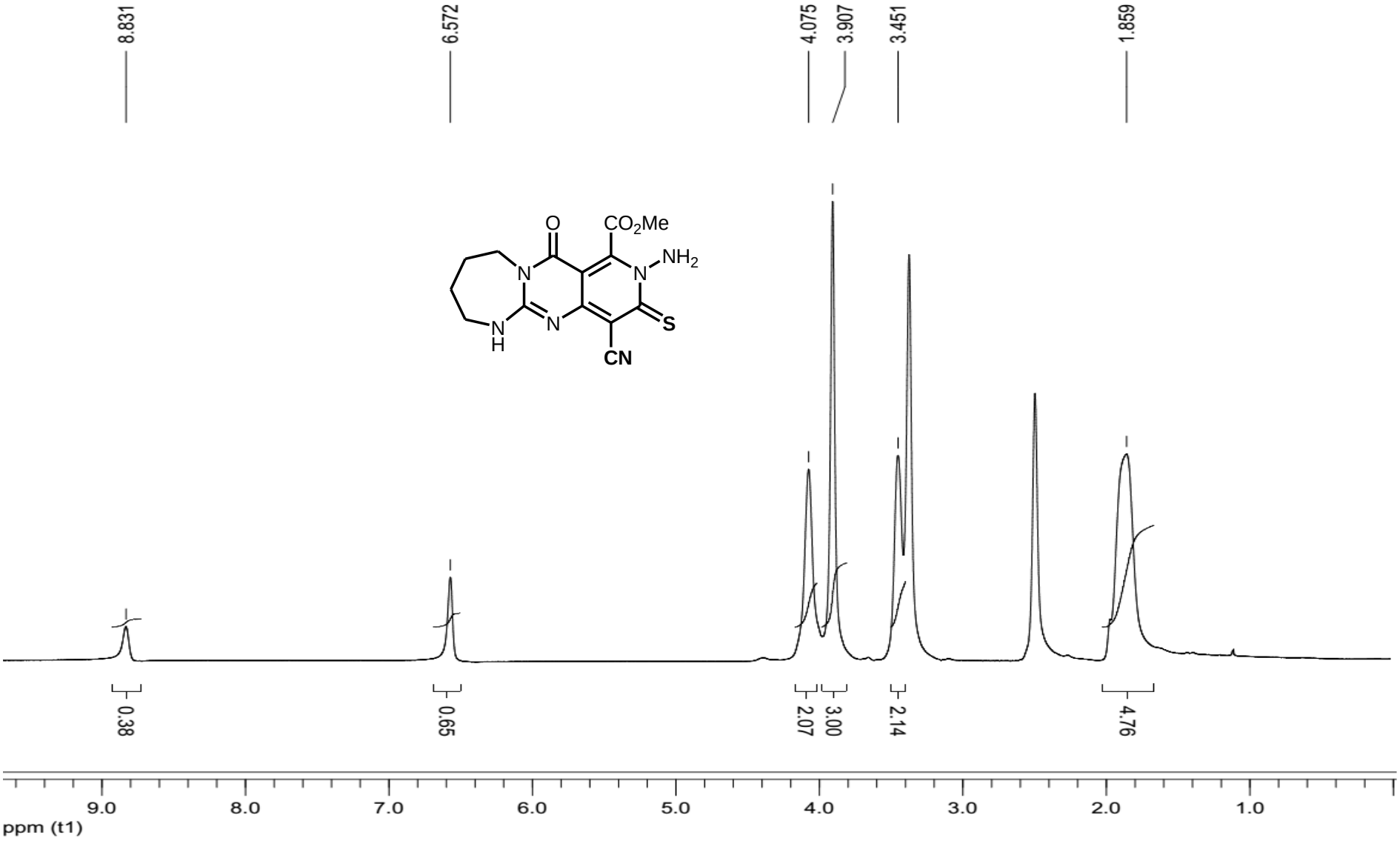
^{13}C NMR of **5i**


9.599
7.591
7.495
7.314
7.158
3.577
3.499
3.119
1.026
Me
Me
O
CO2Me
Cl
N
N
N
H
N
S
CN
0.72
1.92
1.99
5.20
1.92
6.00
10.0
ppm (t1)
5.0
0.0

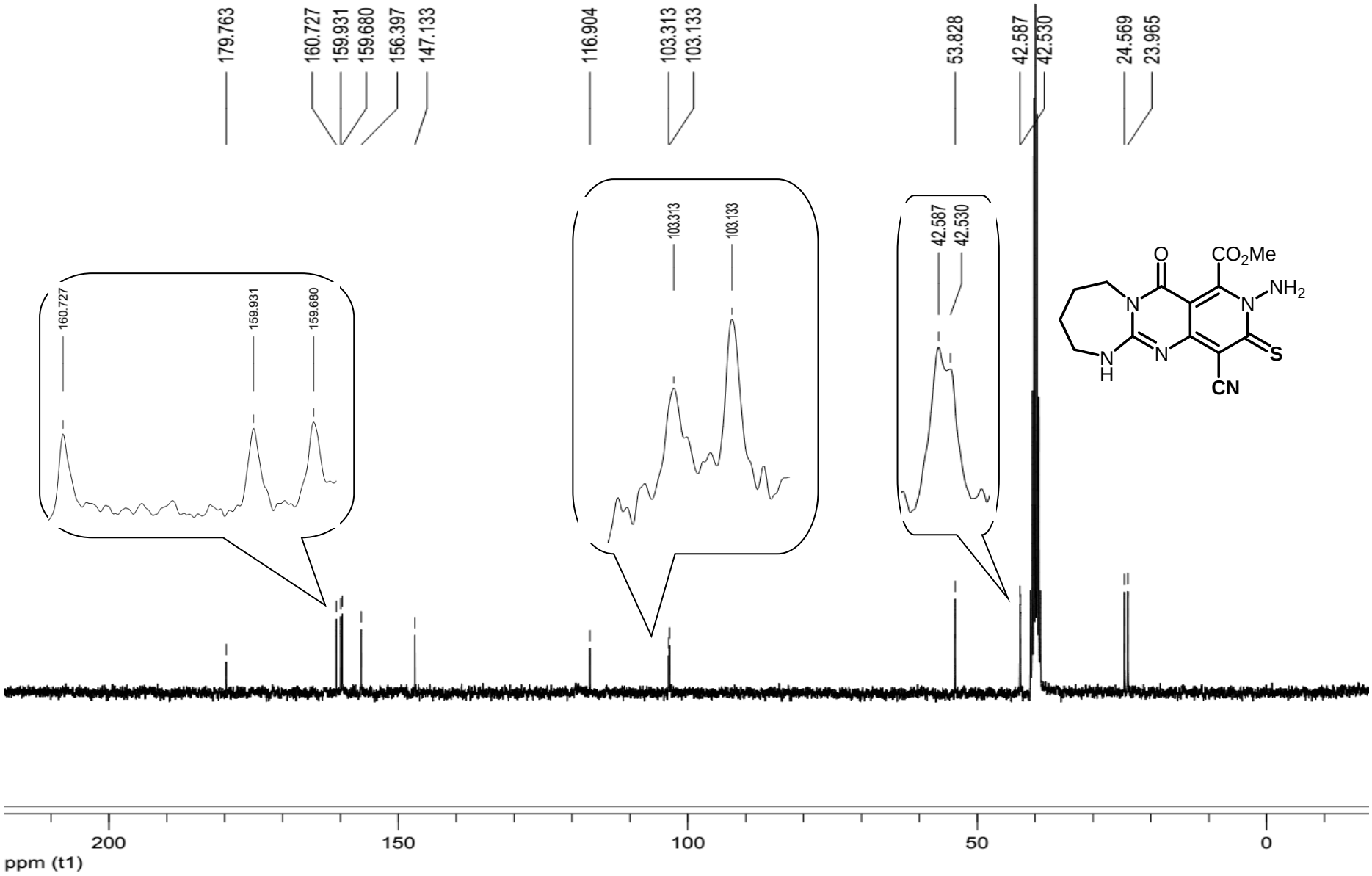
^{1}H NMR of **5j**


181.603
161.259
159.113
157.497
154.190
147.408
138.420
134.913
129.495
129.359
117.006
104.370
103.872
53.727
50.129
27.088
23.690
129.495
129.359
Me
Me
O
CO2Me
Cl
N
N
N
H
N
S
CN
200
150
100
50
0
ppm (t1)

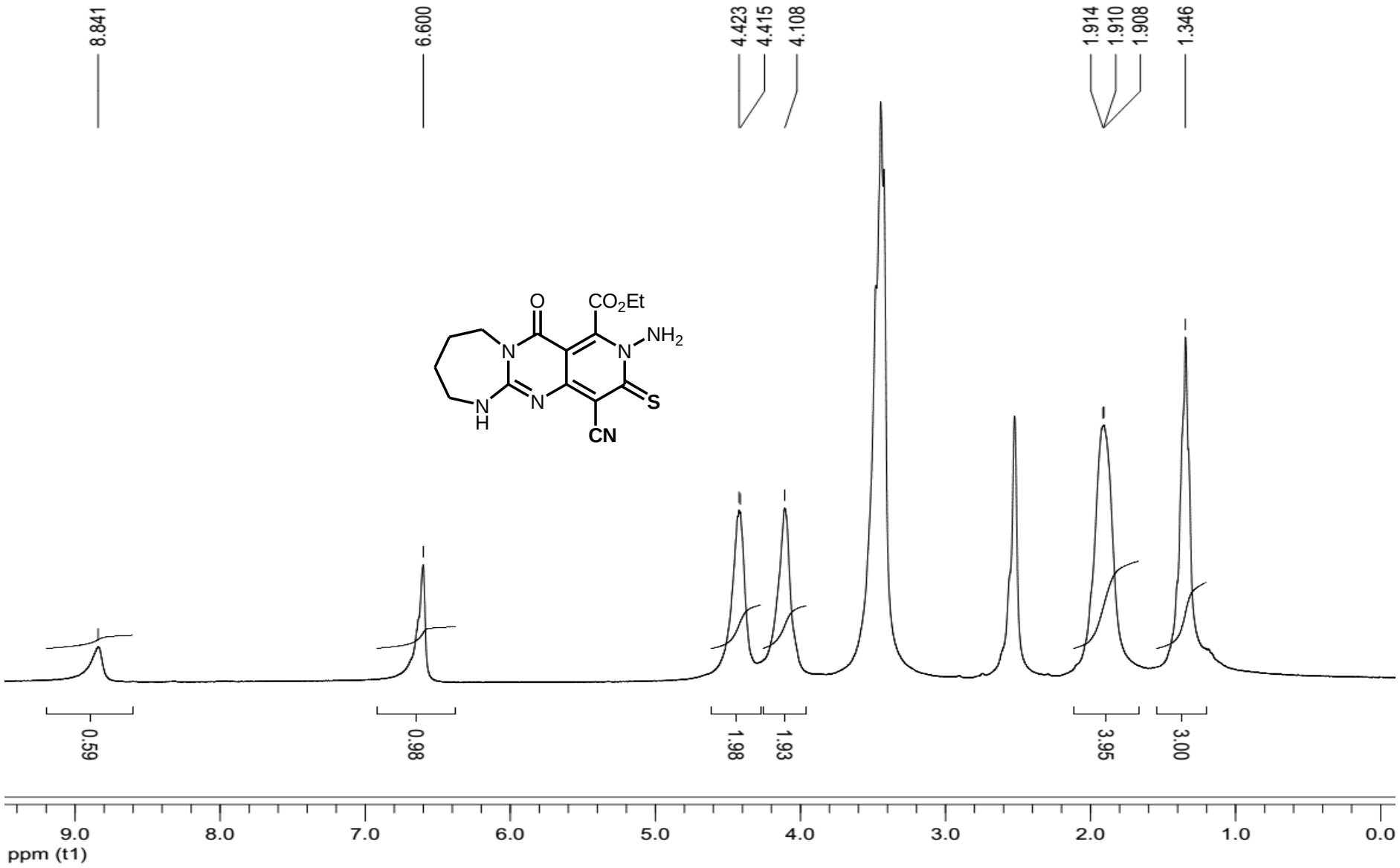
^{13}C NMR of **5j**


8.831
6.572
4.075
3.907
3.451
1.859
O
CO2Me
NH2
N
N
N
H
N
S
CN
0.38
0.65
2.07
3.00
2.14
4.76
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

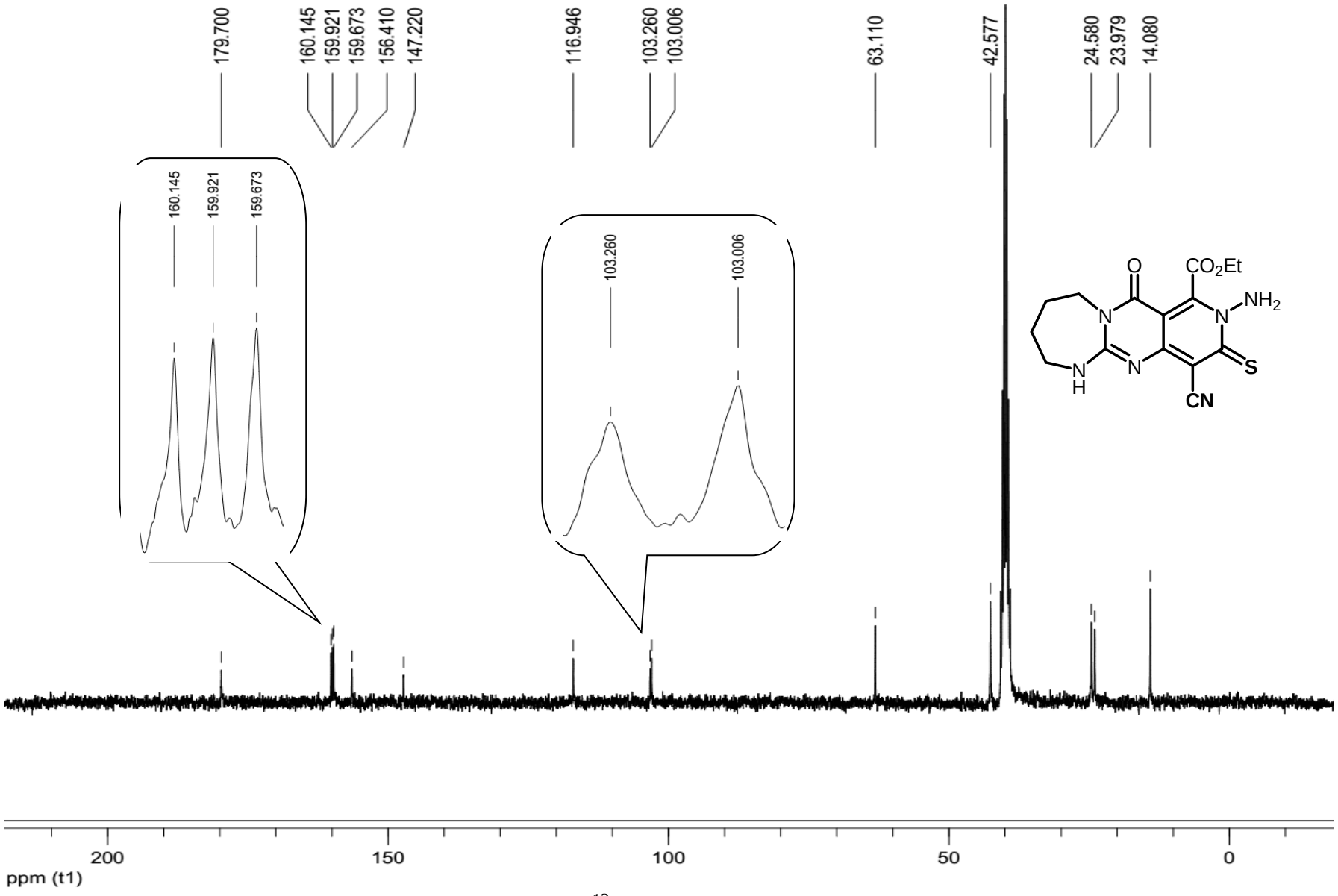
^{1}H NMR of **5k**


179.763
160.727
159.931
159.680
156.397
147.133
116.904
103.313
103.133
53.828
42.587
42.530
24.569
23.965
O
CO2Me
NH2
N
N
N
H
N
S
CN
200
150
100
50
0
ppm (t1)

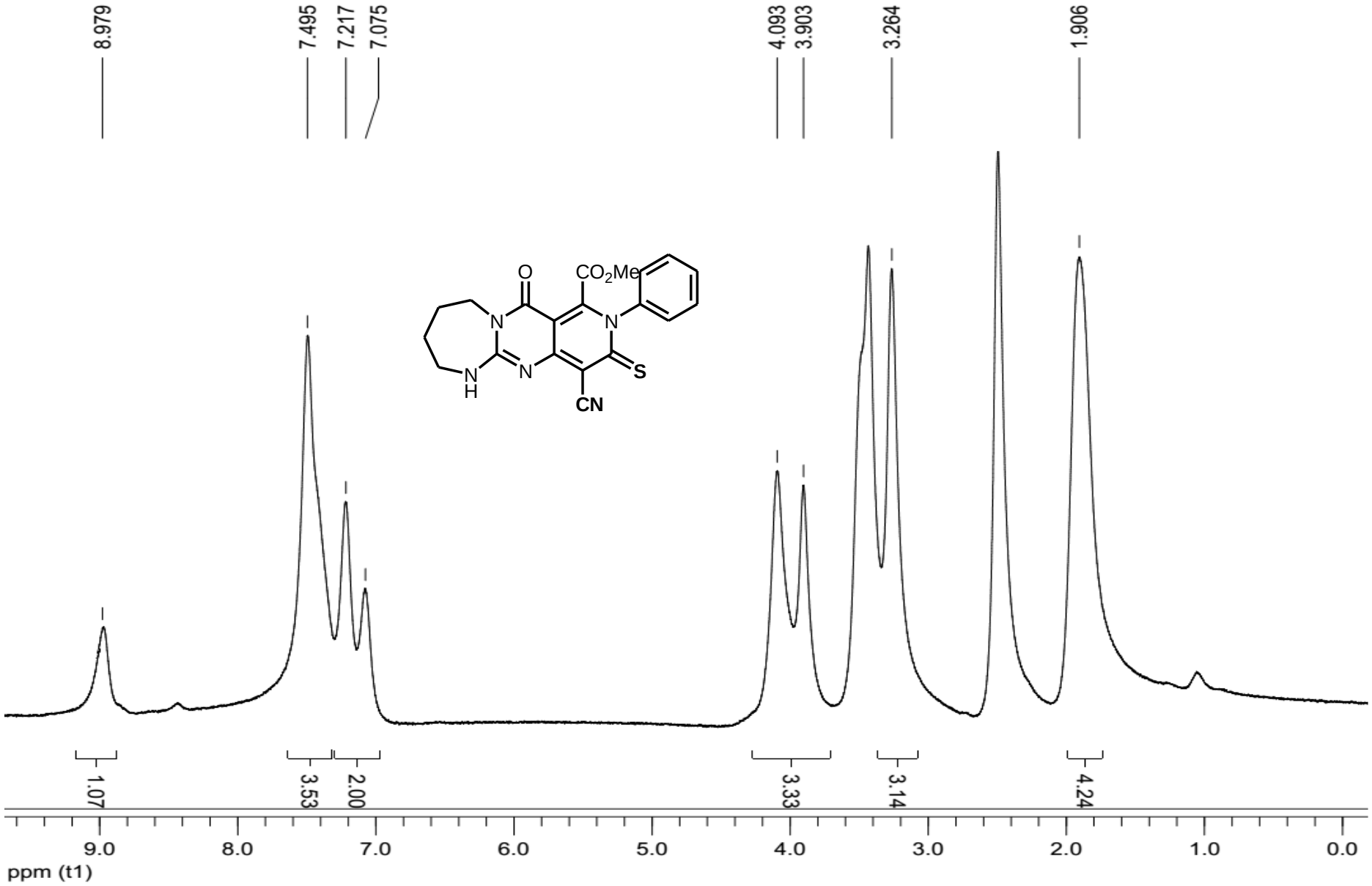
^{13}C NMR of **5k**


8.841
6.600
4.423
4.415
4.108
1.914
1.910
1.908
1.346
O
CO2Et
NH2
N
N
N
H
N
S
CN
0.59
0.98
1.98
1.93
3.95
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

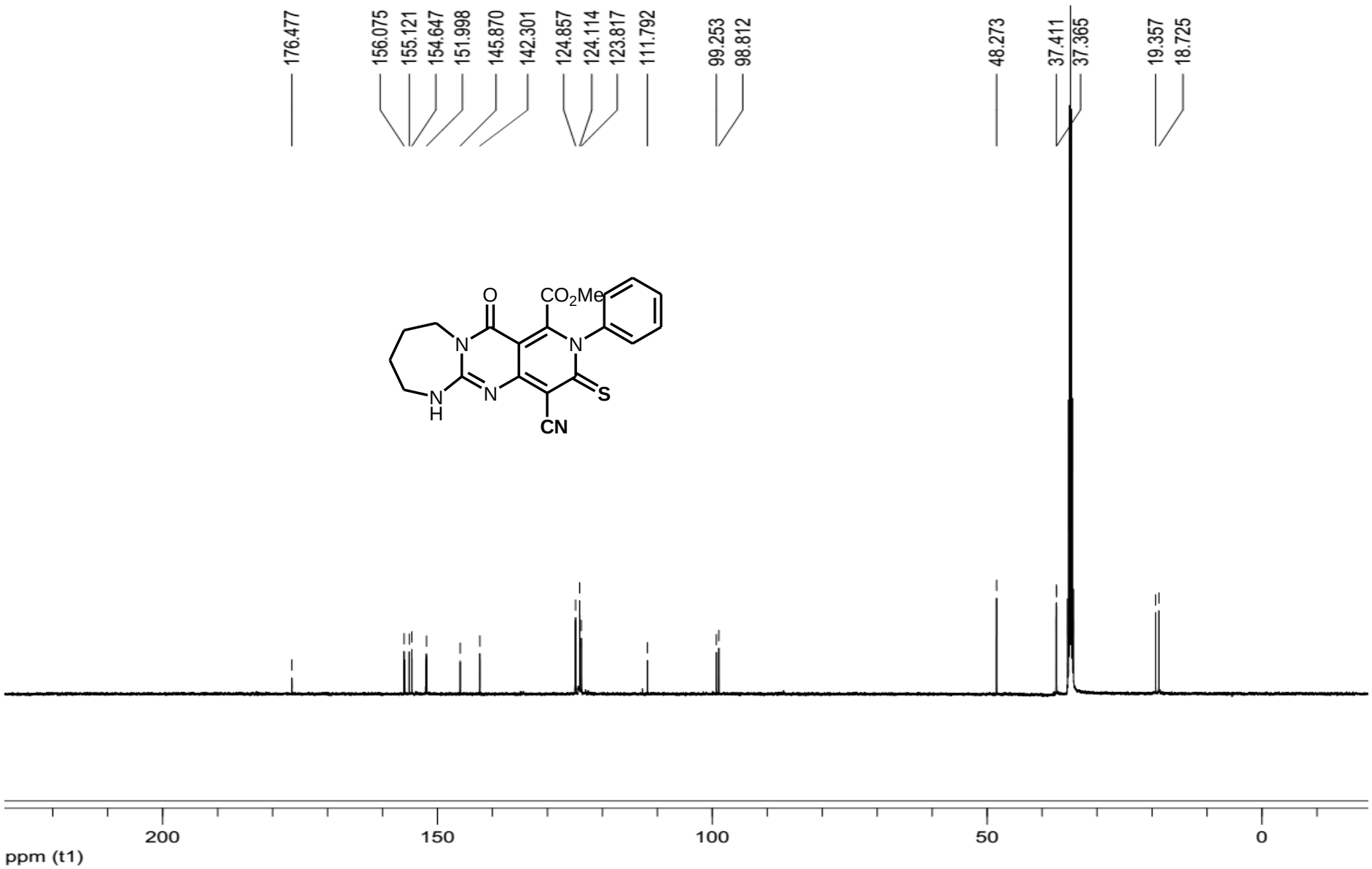
^{1}H NMR of **5l**


179.700
160.145
159.921
159.673
156.410
147.220
116.946
103.260
103.006
63.110
42.577
24.580
23.979
14.080
160.145
159.921
159.673
103.260
103.006
O
CO2Et
NH2
N
N
N
H
N
S
CN
200
150
100
50
0
ppm (t1)

^{13}C NMR of **5l**


8.979
7.495
7.217
7.075
4.093
3.903
3.264
1.906
O
CO2Me
N
N
N
H
N
S
CN
1.07
3.53
2.00
3.33
3.14
4.24
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

^{1}H NMR of **5m**


176.477
156.075
155.121
154.647
151.998
145.870
142.301
124.857
124.114
123.817
111.792
99.253
98.812
48.273
37.411
37.365
19.357
18.725
O
CO2Me
N
N
N
H
N
S
CN
200
150
100
50
0
ppm (t1)

^{13}C NMR of **5m**