Development and Scope of the Arene-Fused Michael/Mannich/N-Alkylation Reaction: Application to the Total Syntheses of *Aspidosperma* Alkaloids (−)-Aspidospermidine, (−)-Tabersonine, and (−)-Vincadifformine

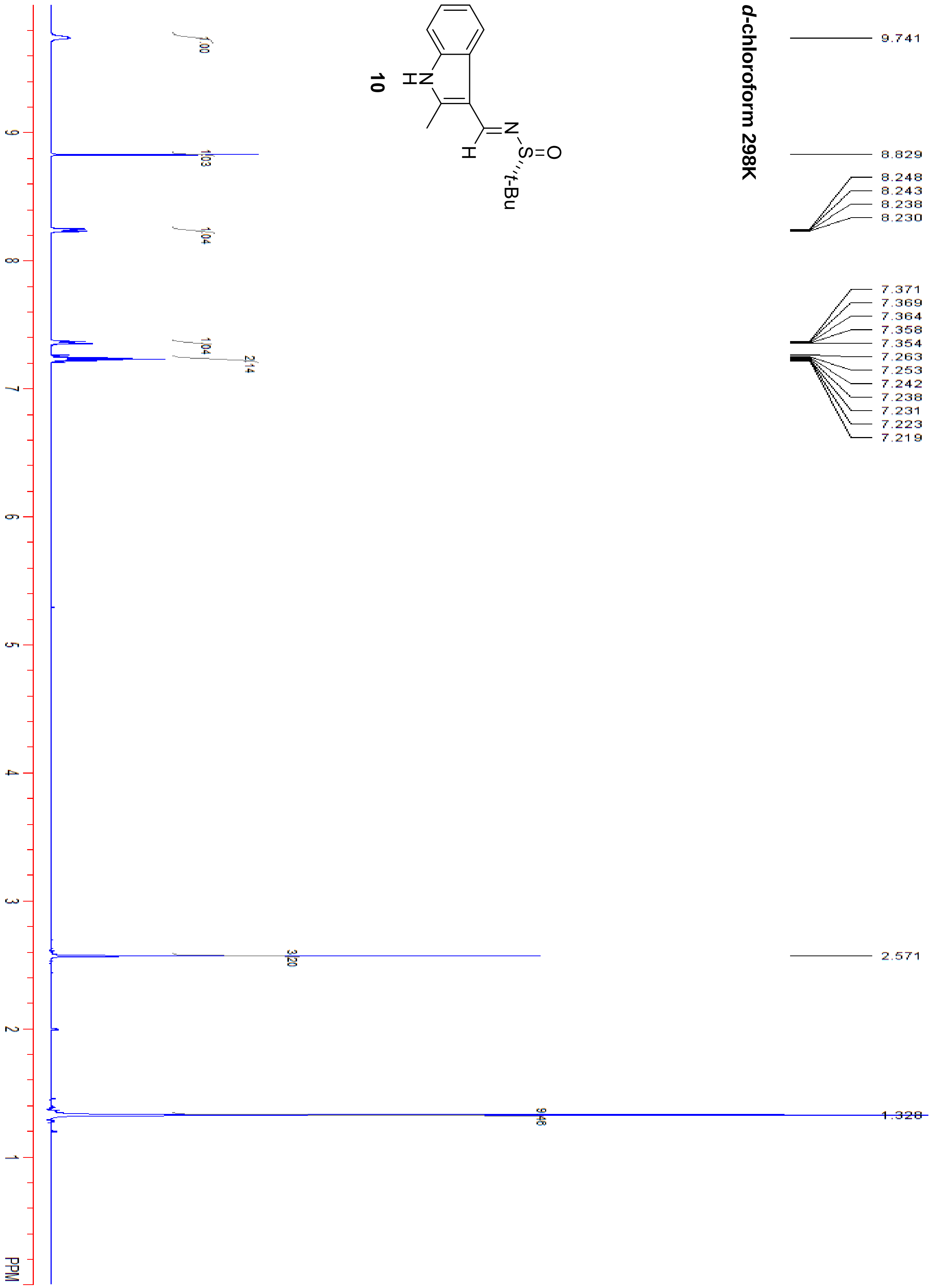
Senzhi Zhao and Rodrigo B. Andrade*

Department of Chemistry, Temple University, Philadelphia, PA 19122.

SUPPORTING INFORMATION

Table of Contents

General Information. Single crystal X-ray diffraction was performed with a Mo Kα radiation obtained from a sealed molybdenum tube with a monochromator. The structure was solved using direct methods and refined using full-matrix least squares (SHELXTL). Additional experimental and sample details are given in the crystallographic tables.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7.354
7.263
7.253
7.242
7.238
7.231
7.223
7.219
2.571
1.328
10
N
H
O
S
t-Bu
1.00
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2
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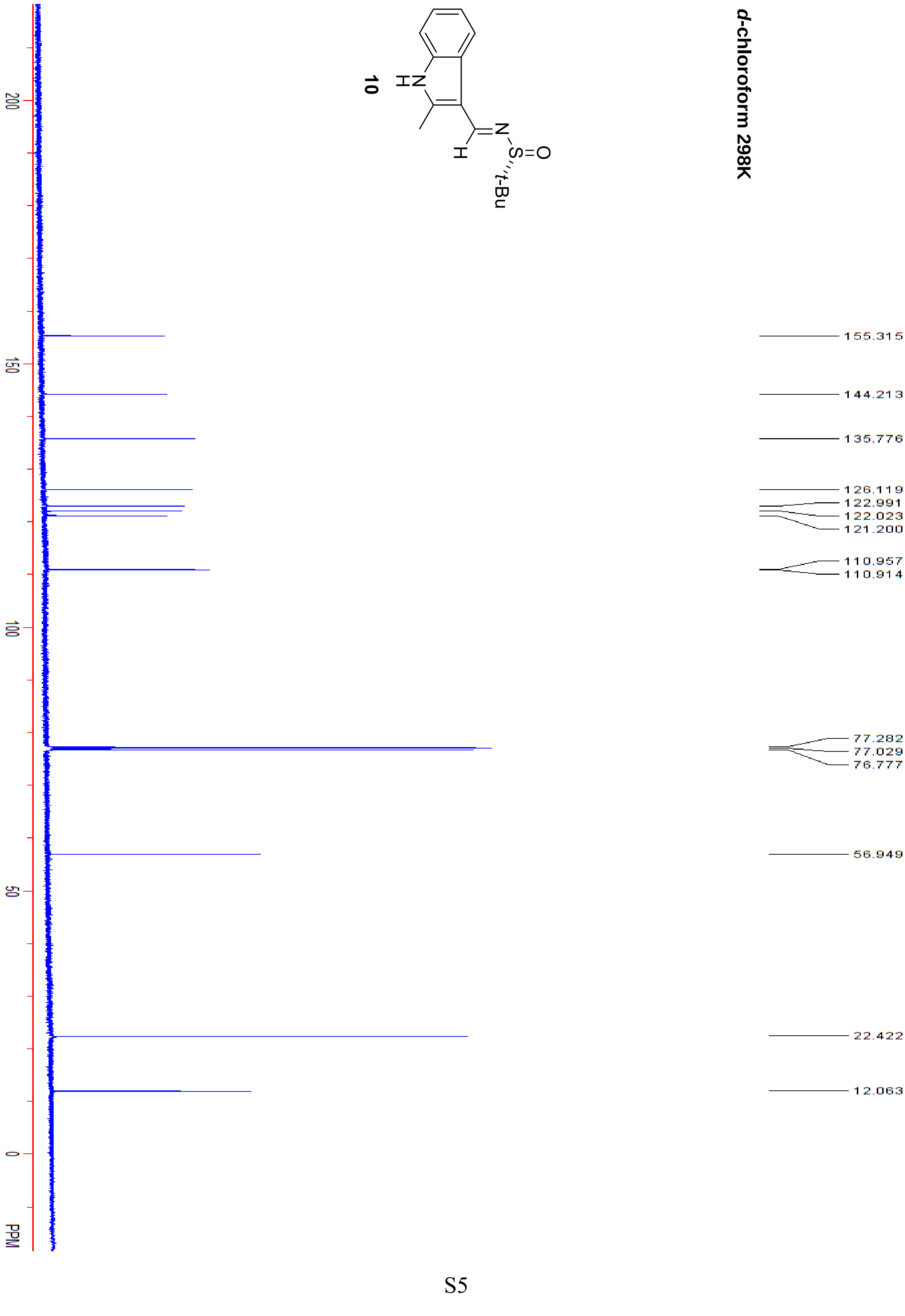
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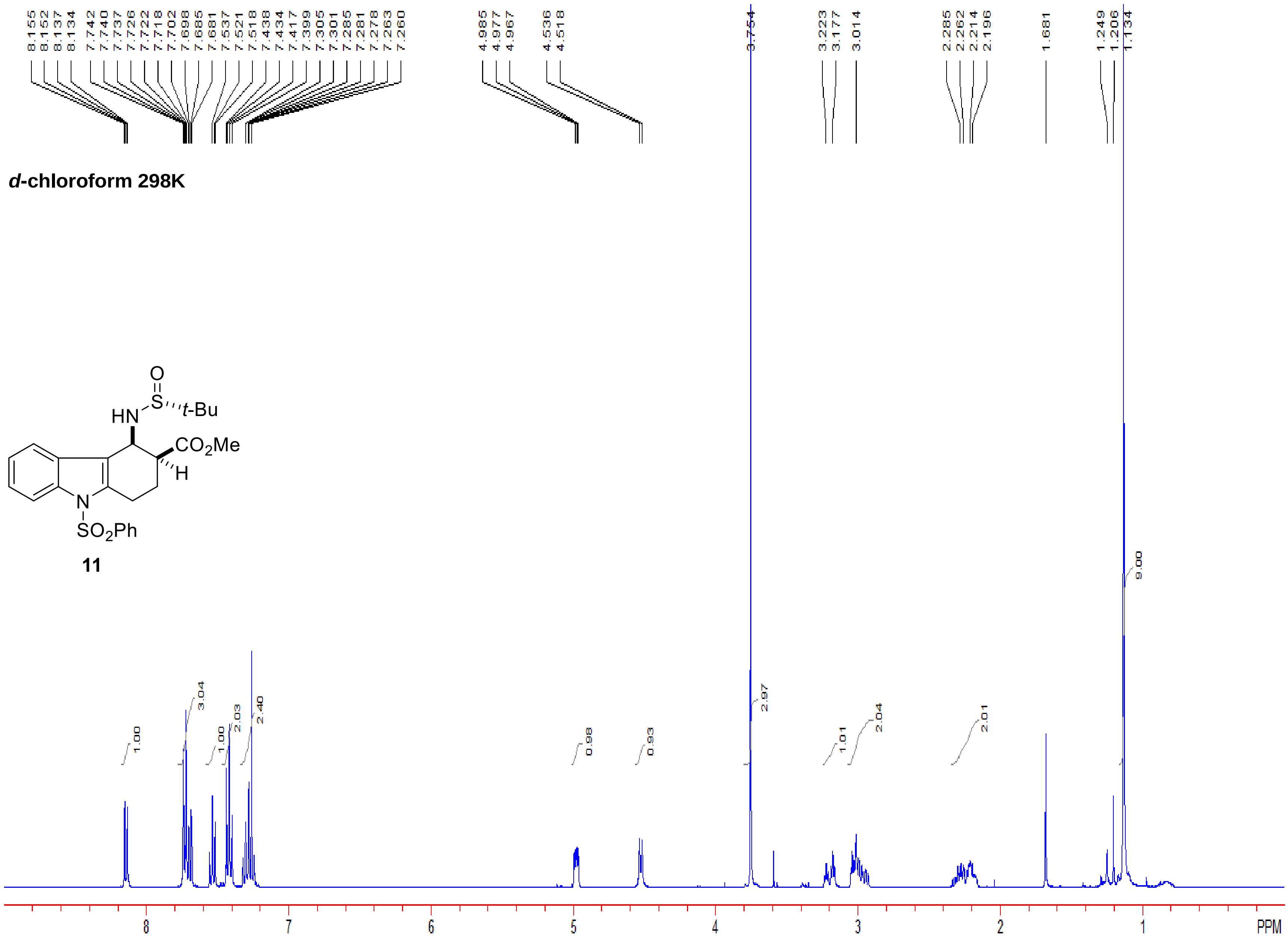
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4.985 4.977 4.967 4.536 4.518
3.754
3.223 3.177 3.014
2.285 2.262 2.214 2.196
1.681
1.249 1.206 1.134
1.00 3.04 1.00 2.03 2.40 0.98 0.93 2.97 1.01 2.04 2.01 9.00
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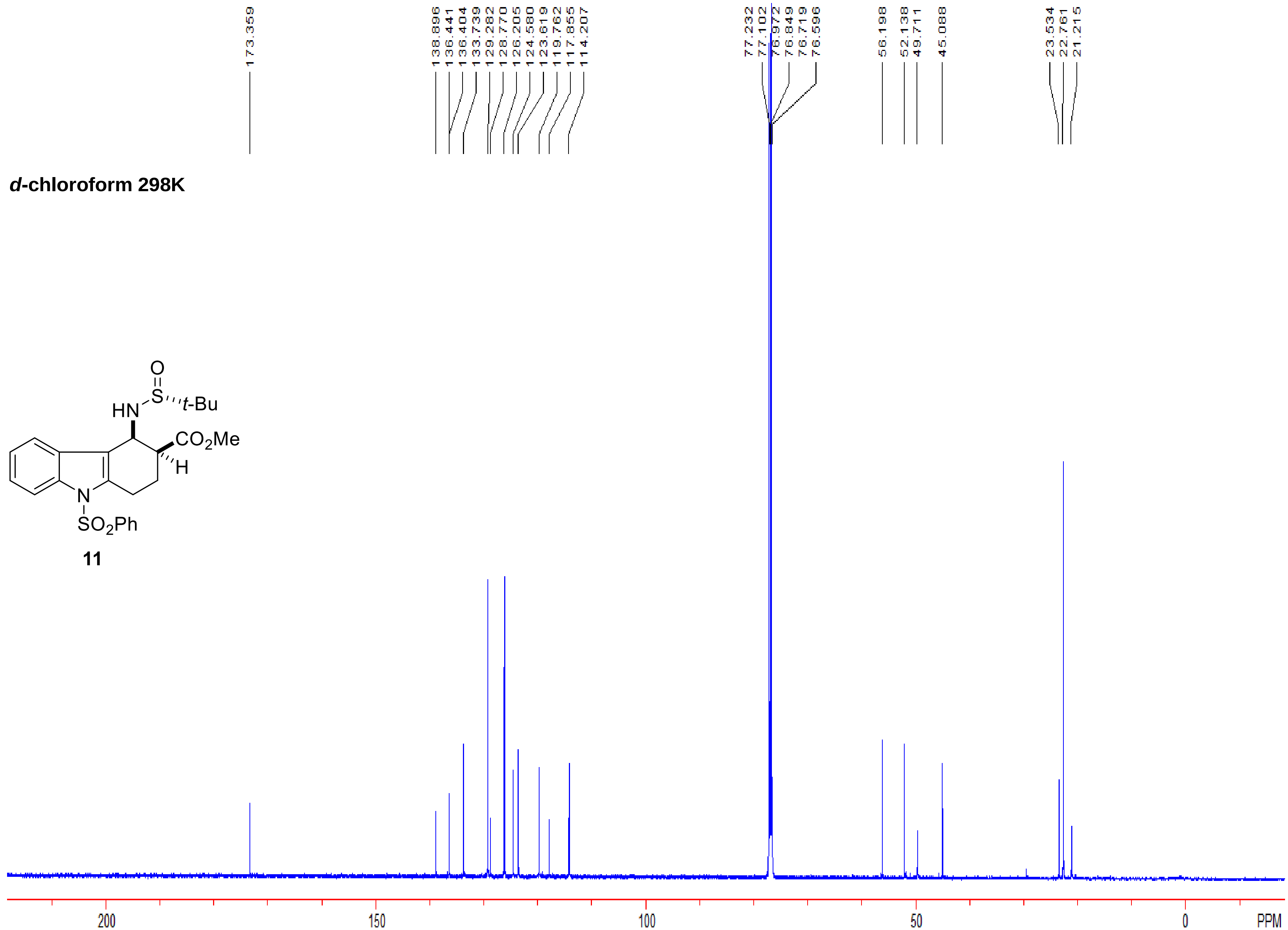
HN S O t-Bu CO2Me H N SO2Ph
11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N
SO2Ph
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123.619
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76.972
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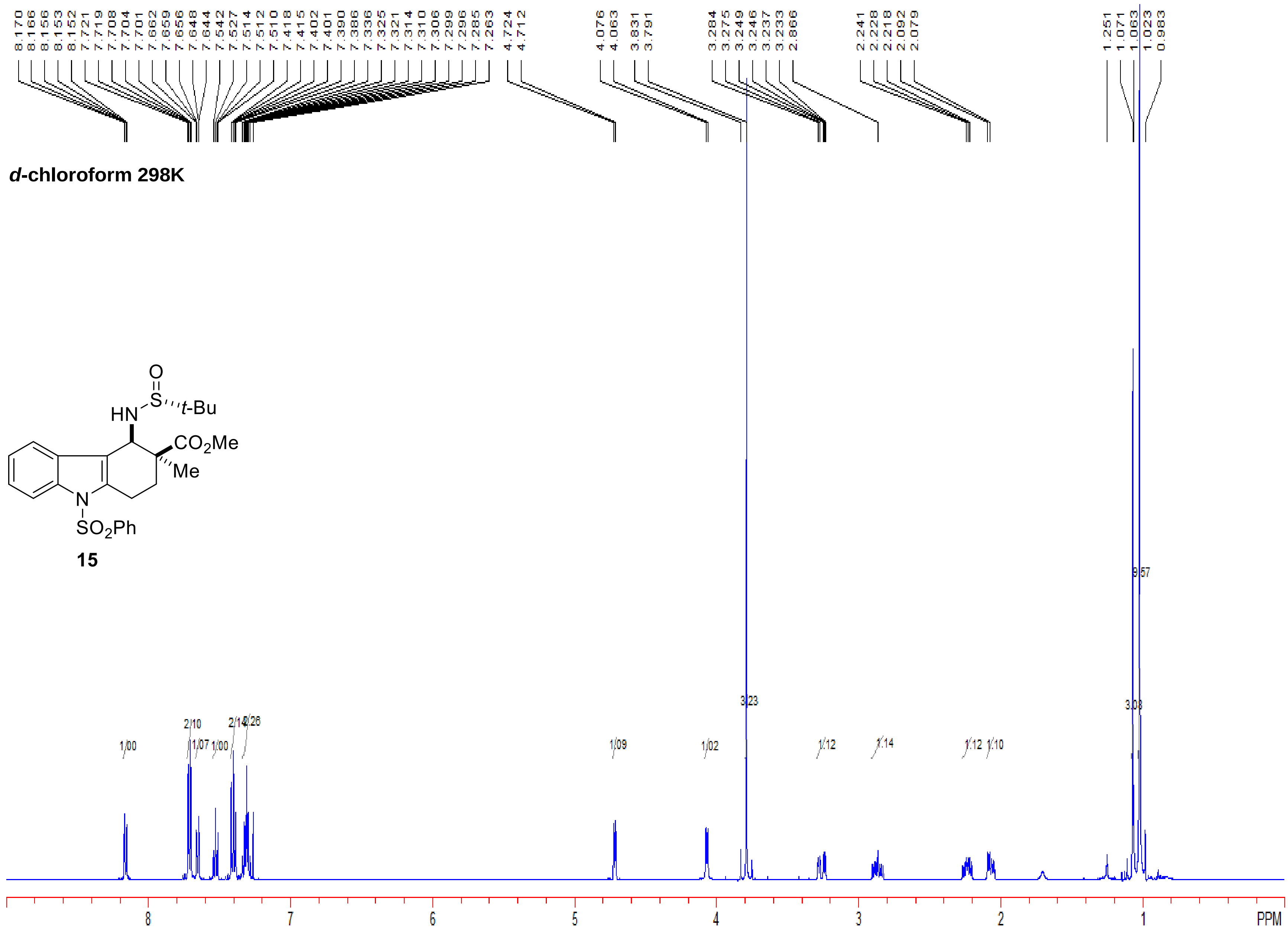
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7.527
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7.512
7.510
7.418
7.415
7.402
7.401
7.390
7.386
7.336
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7.321
7.314
7.310
7.306
7.299
7.296
7.285
7.263
4.724
4.712
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4.063
3.831
3.791
3.284
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3.237
3.233
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2.241
2.228
2.218
2.092
2.079
1.251
1.071
1.063
1.023
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O
S
t-Bu
HN
CO2Me
Me
N
SO2Ph
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2.10
1.07
1.00
2.14
2.26
1.09
1.02
3.23
1.12
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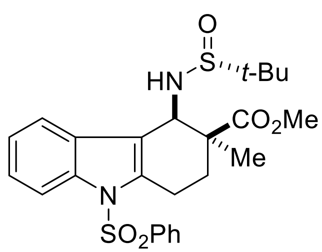
d-chloroform 298K



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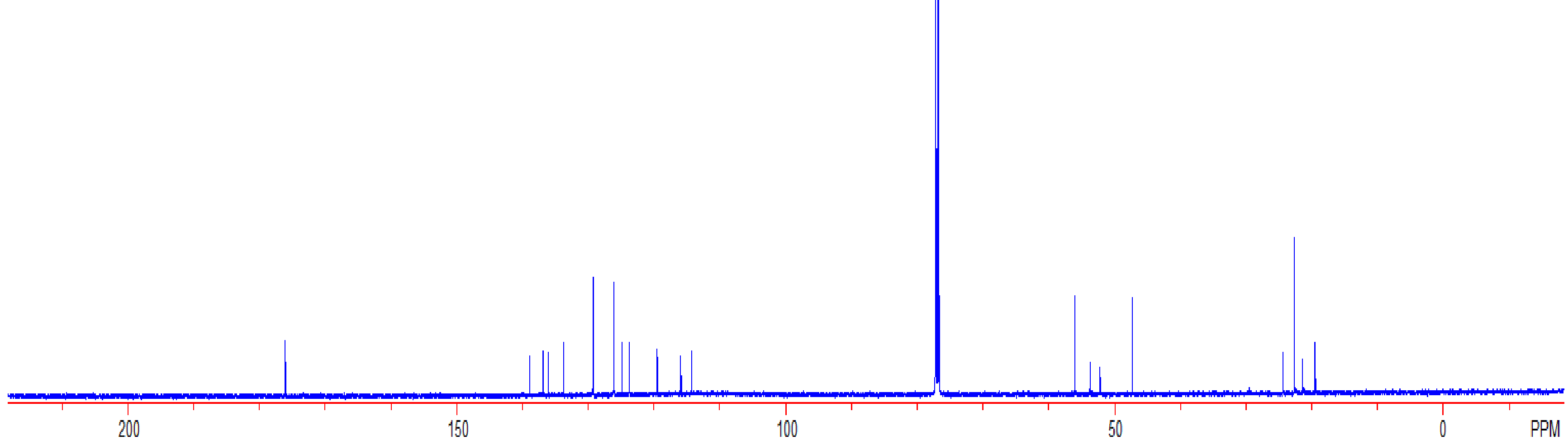

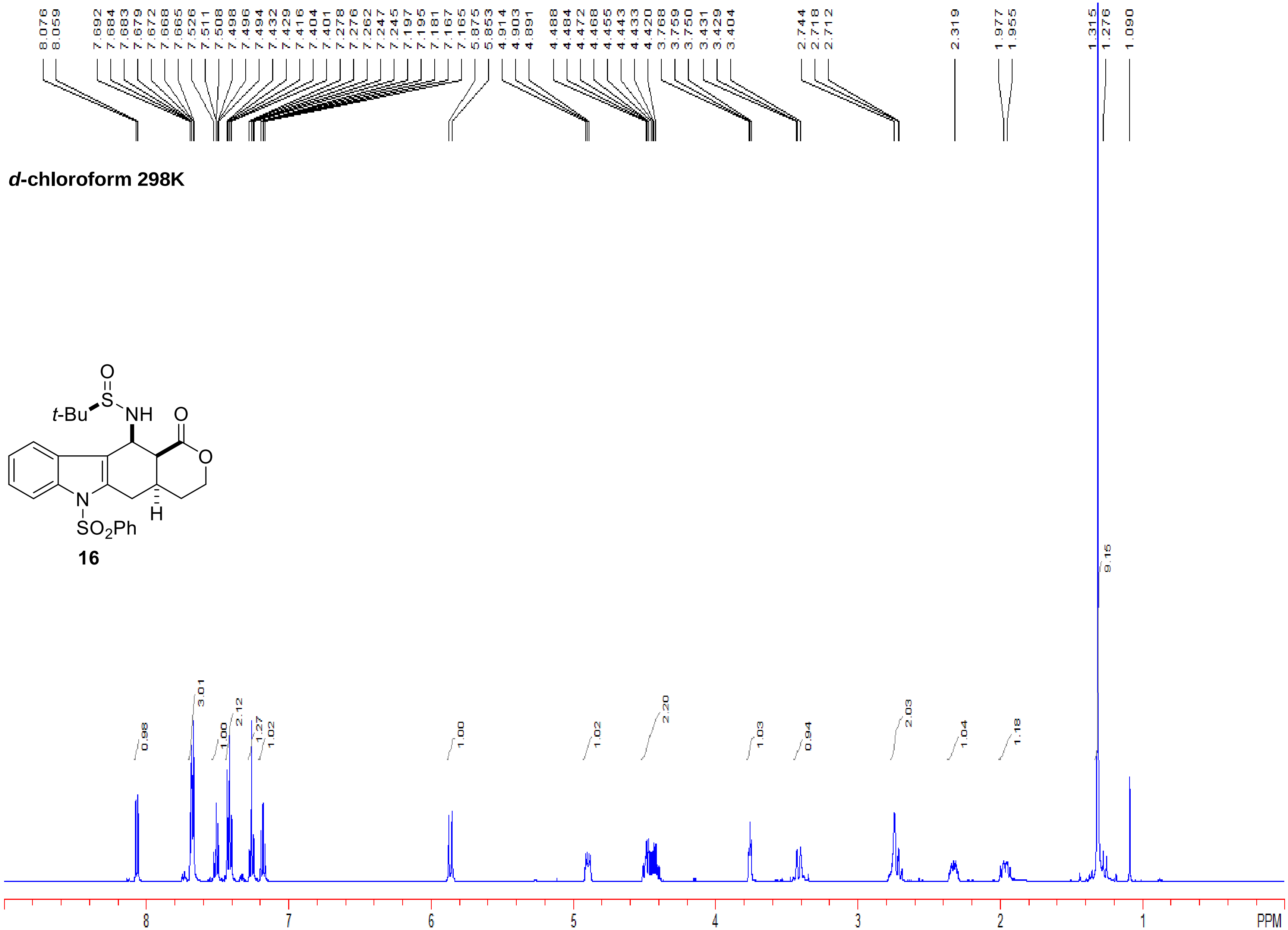
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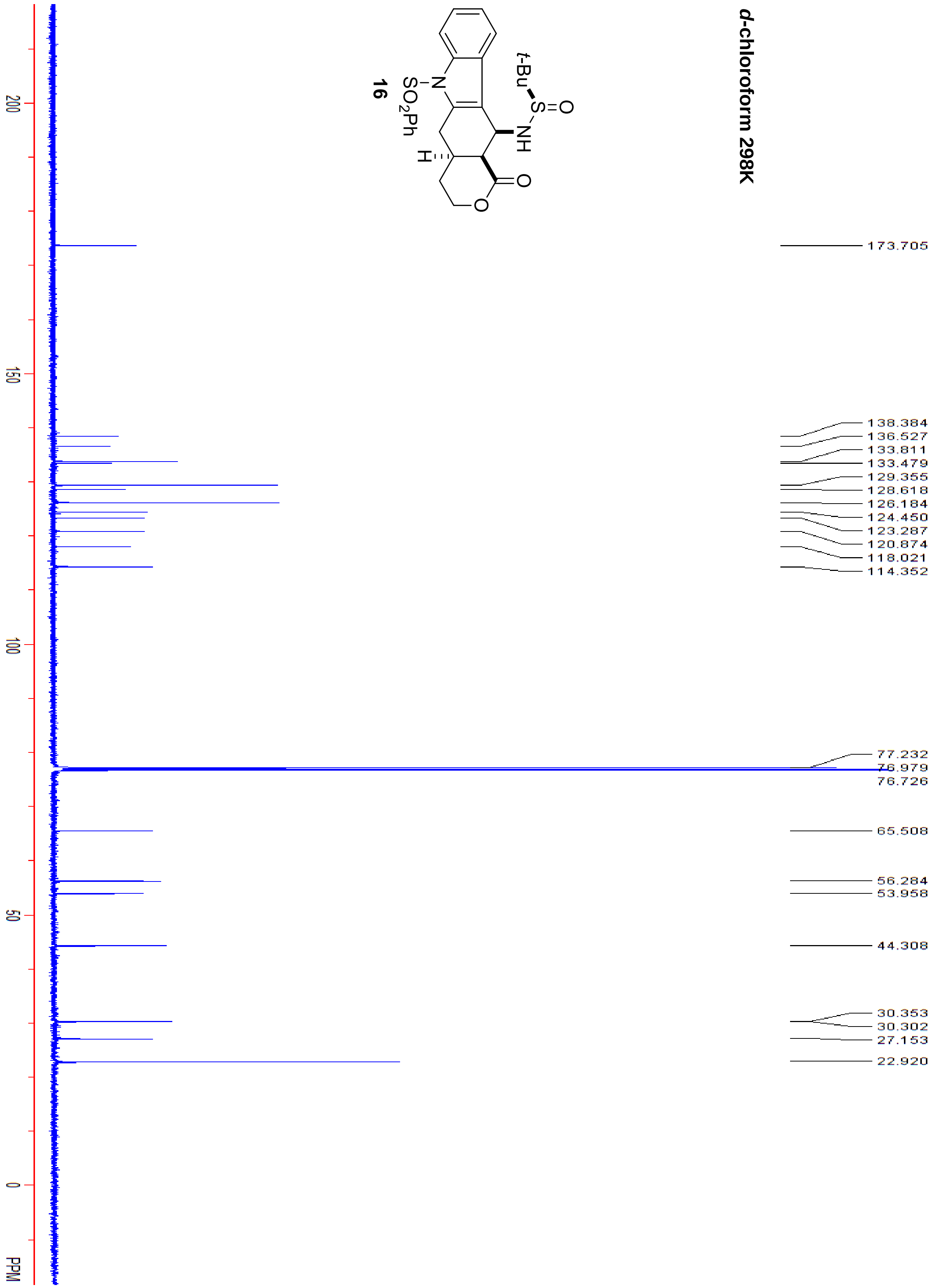
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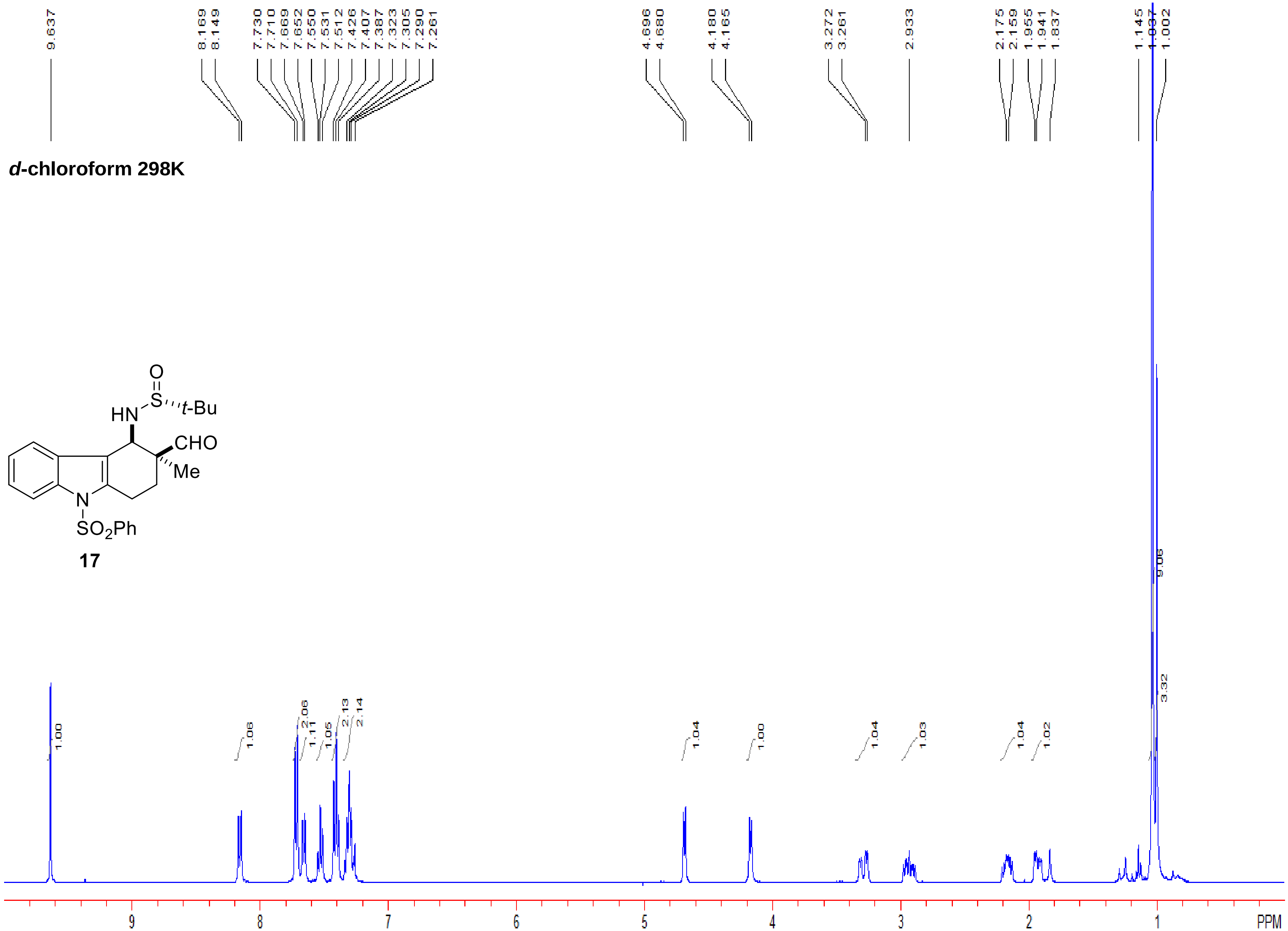
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7.387
7.323
7.305
7.290
7.261
4.696
4.680
4.180
4.165
3.272
3.261
2.933
2.175
2.159
1.955
1.941
1.837
1.145
1.037
1.002
d-chloroform 298K
HN
S
O
t-Bu
CHO
Me
N
SO2Ph
17
1.00
1.06
2.06
1.11
1.05
2.13
2.14
1.04
1.00
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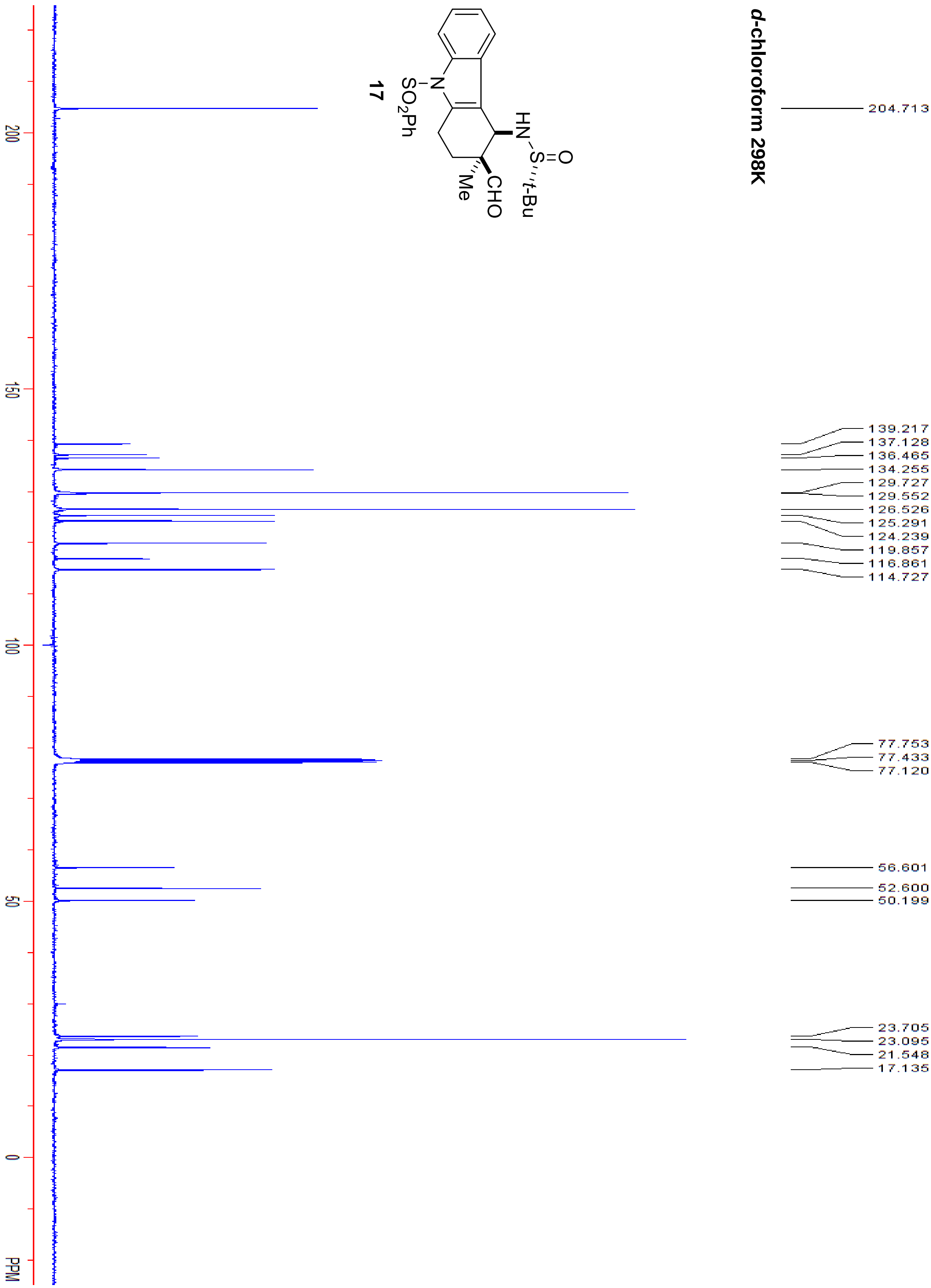
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119.857
116.861
114.727
77.753
77.433
77.120
56.601
52.600
50.199
23.705
23.095
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150
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50
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S
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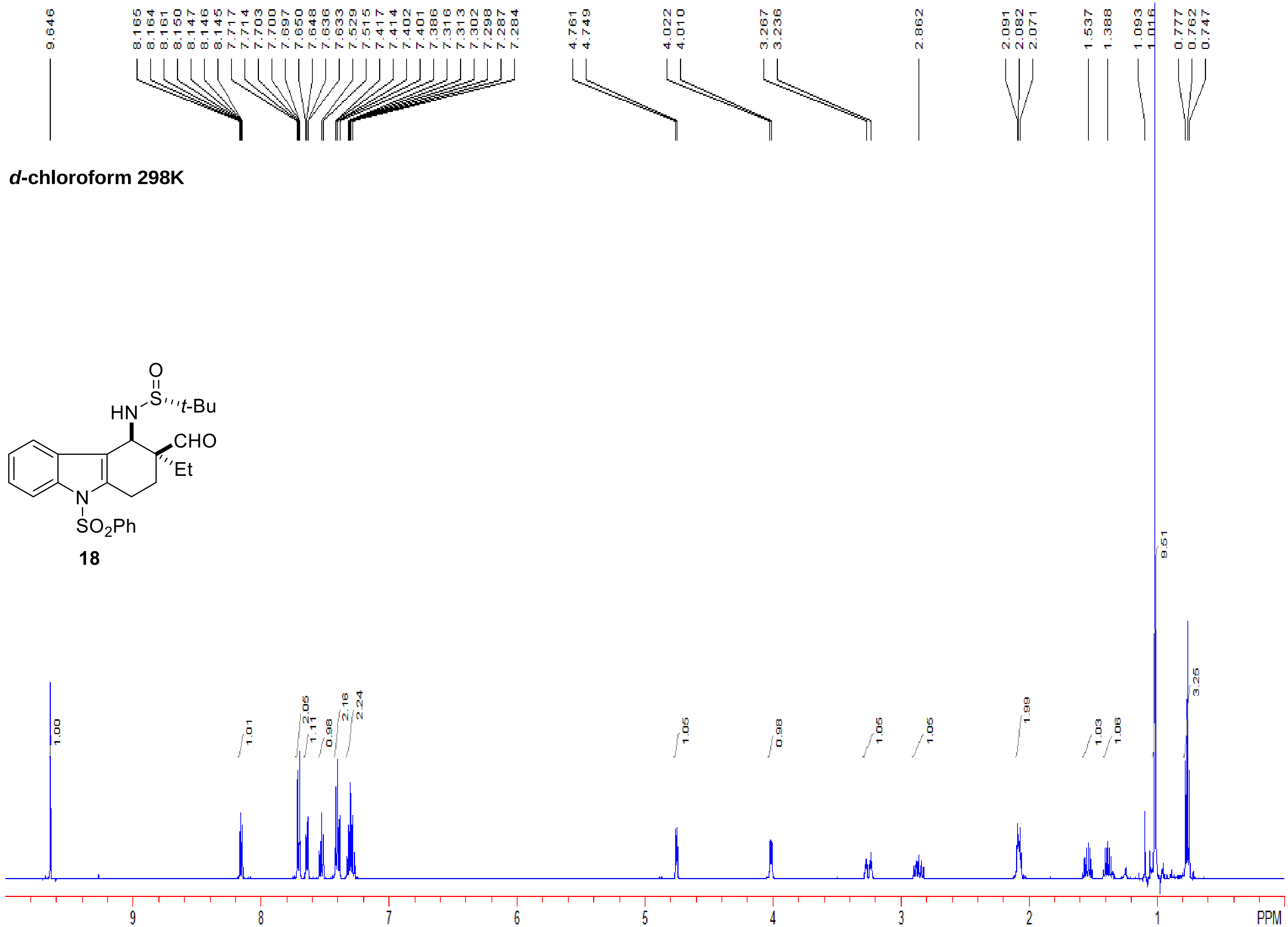
CHO
Me
N
SO2Ph

17



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7.714
7.703
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7.697
7.650
7.648
7.636
7.633
7.529
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7.417
7.414
7.402
7.401
7.386
7.316
7.313
7.302
7.298
7.287
7.284
4.761
4.749
4.022
4.010
3.267
3.236
2.862
2.091
2.082
2.071
1.537
1.388
1.093
1.016
0.777
0.762
0.747
d-chloroform 298K
HN
S
O
t-Bu
CHO
Et
N
SO_2Ph
18
1.00
1.01
2.05
1.11
0.98
2.16
2.24
1.05
0.98
1.05
1.05
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6
5
4
3
2
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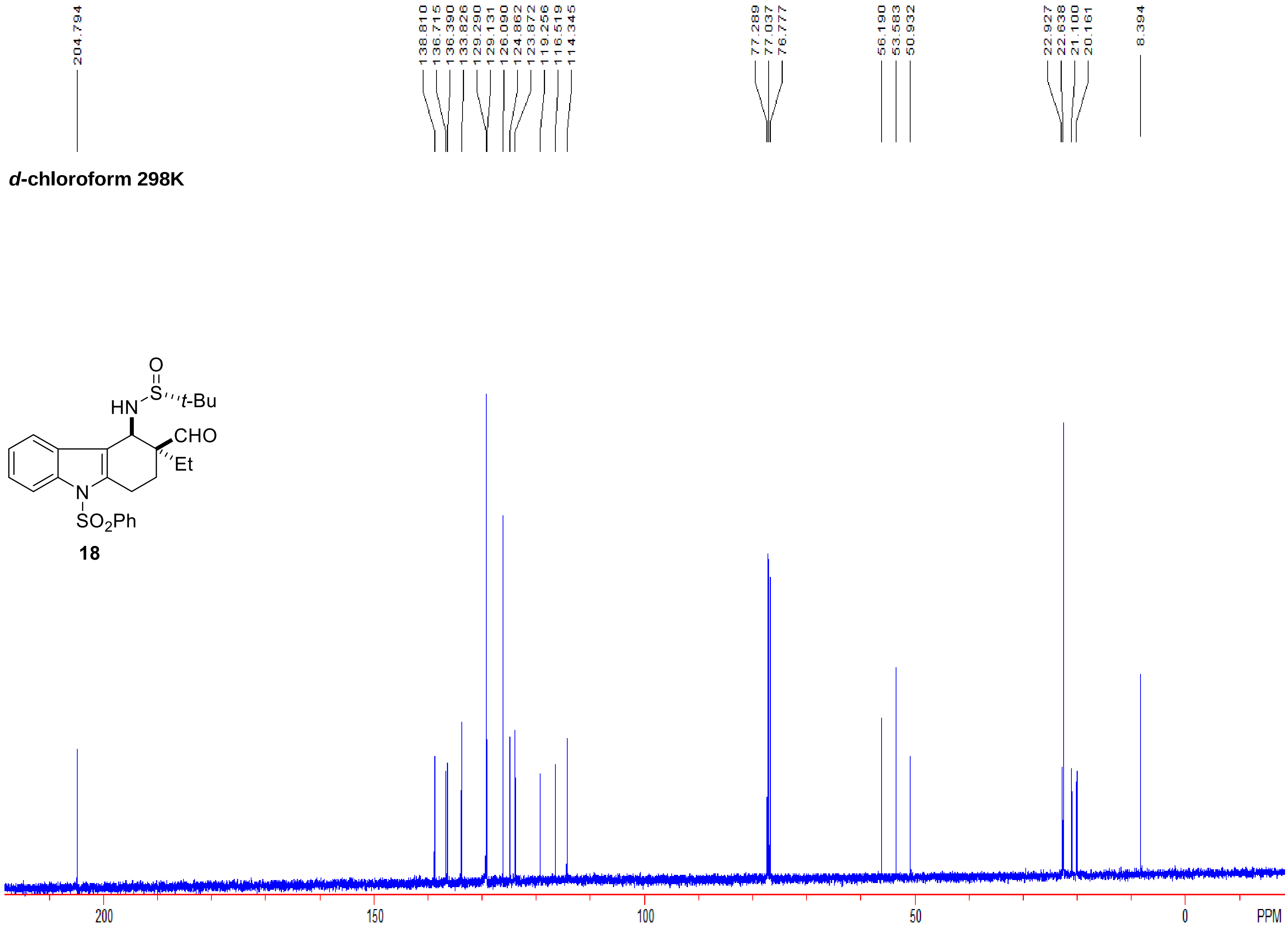
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114.345
77.289
77.037
76.777
56.190
53.583
50.932
22.927
22.638
21.100
20.161
8.394
d-chloroform 298K
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S
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HN
CHO
Et
N
SO2Ph
200
150
100
50
0
PPM

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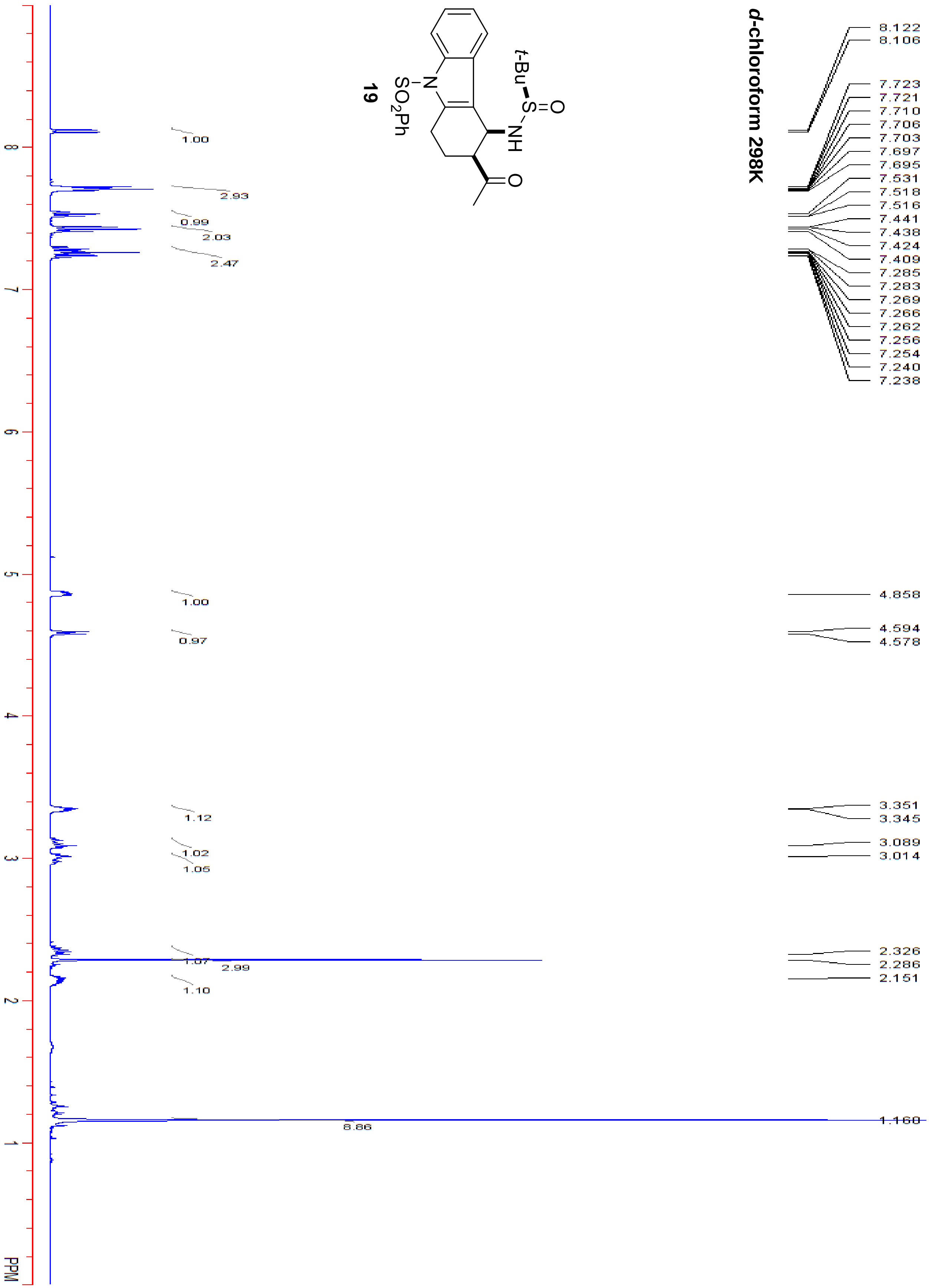
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O
N
SO2Ph
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7.706
7.703
7.697
7.695
7.531
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7.516
7.441
7.438
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7.283
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7.262
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7.240
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4.578
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3.014
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2.286
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0.97
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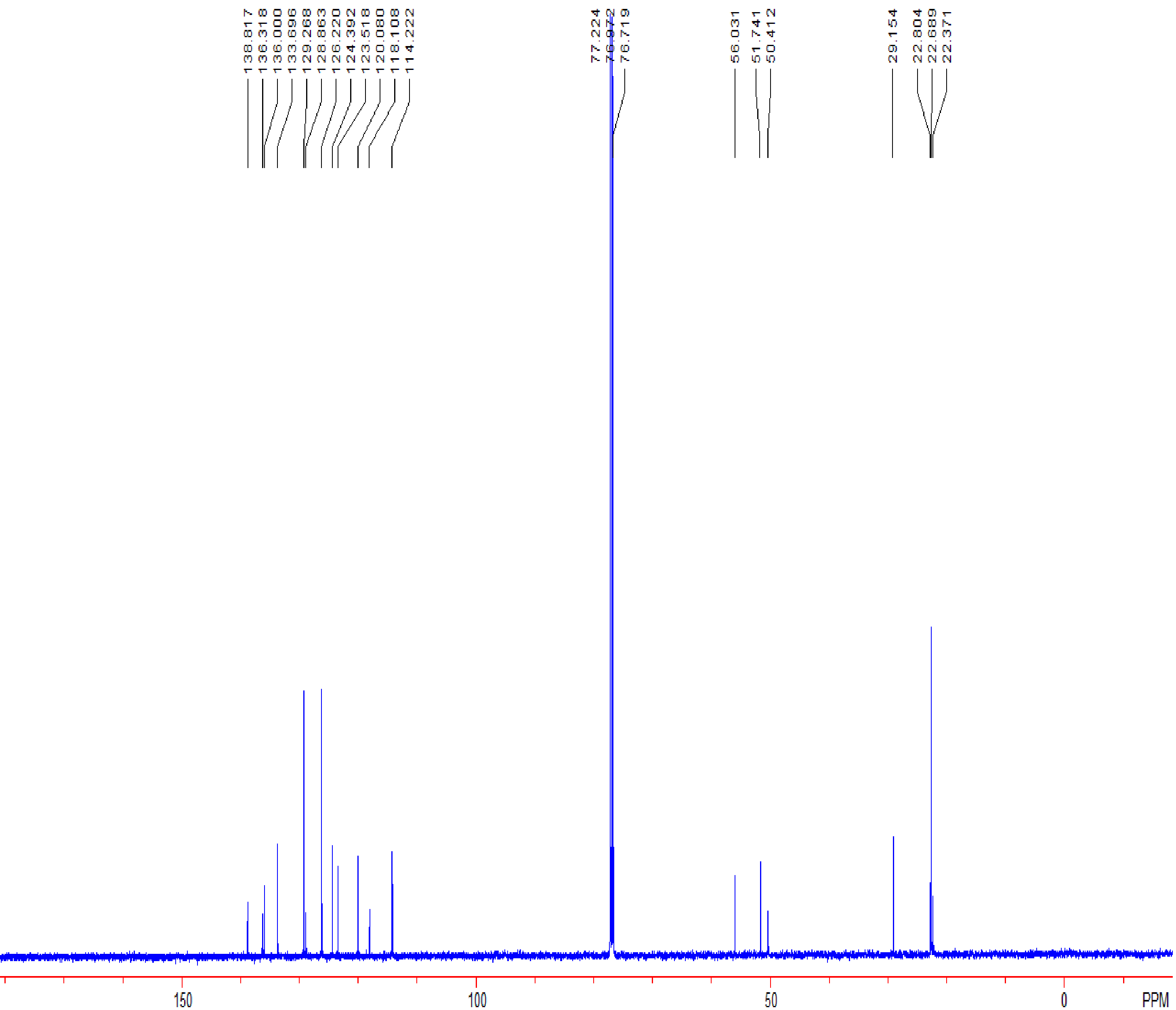
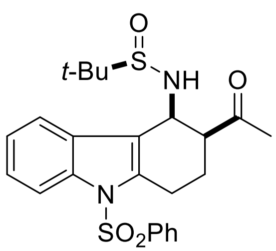


d-chloroform 298K



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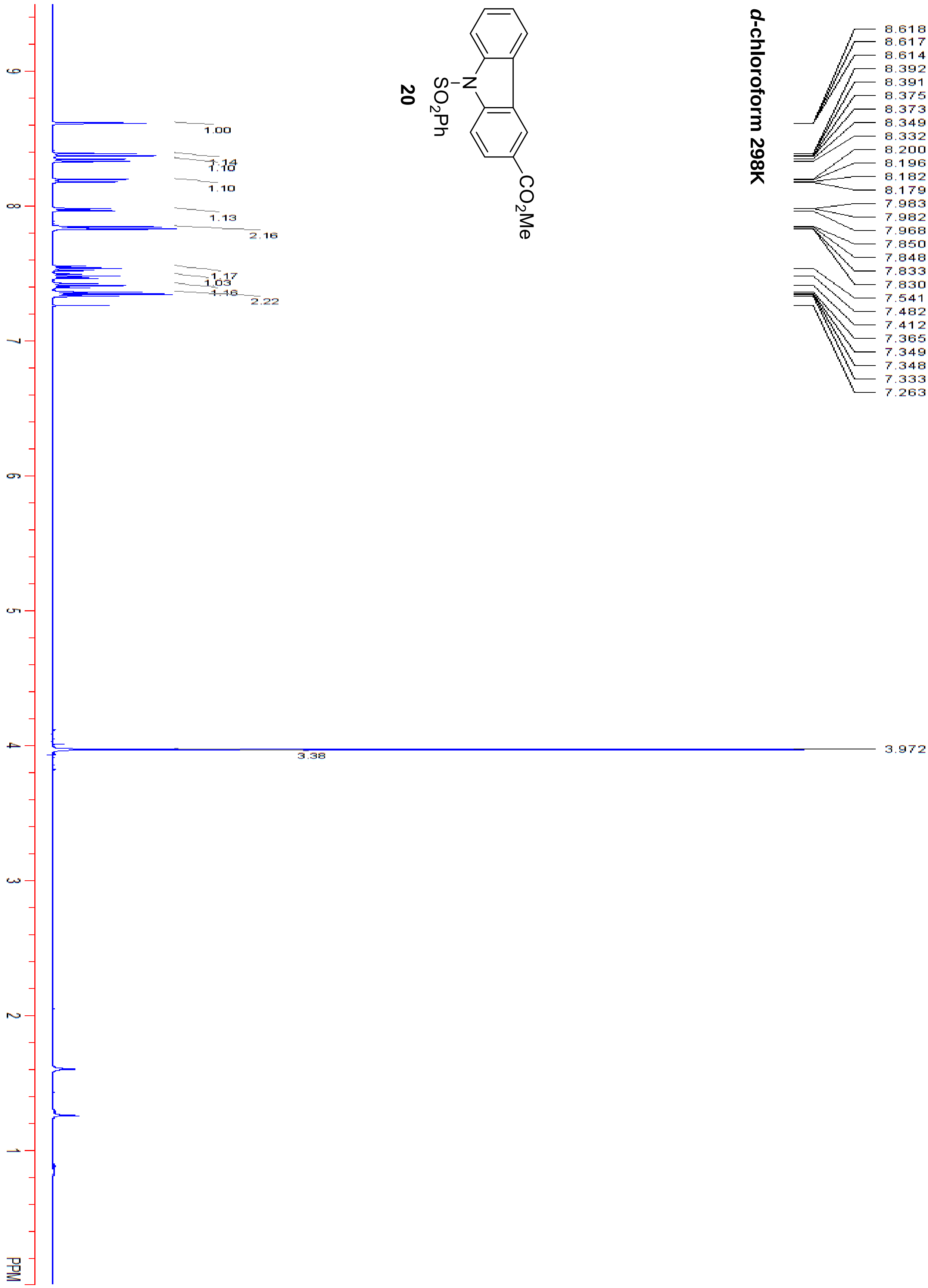
d-chloroform 298K
N
SO2Ph
CO2Me
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8.349
8.332
8.200
8.196
8.182
8.179
7.983
7.982
7.968
7.850
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7.830
7.541
7.482
7.412
7.365
7.349
7.348
7.333
7.263
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1.14
1.10
1.10
1.13
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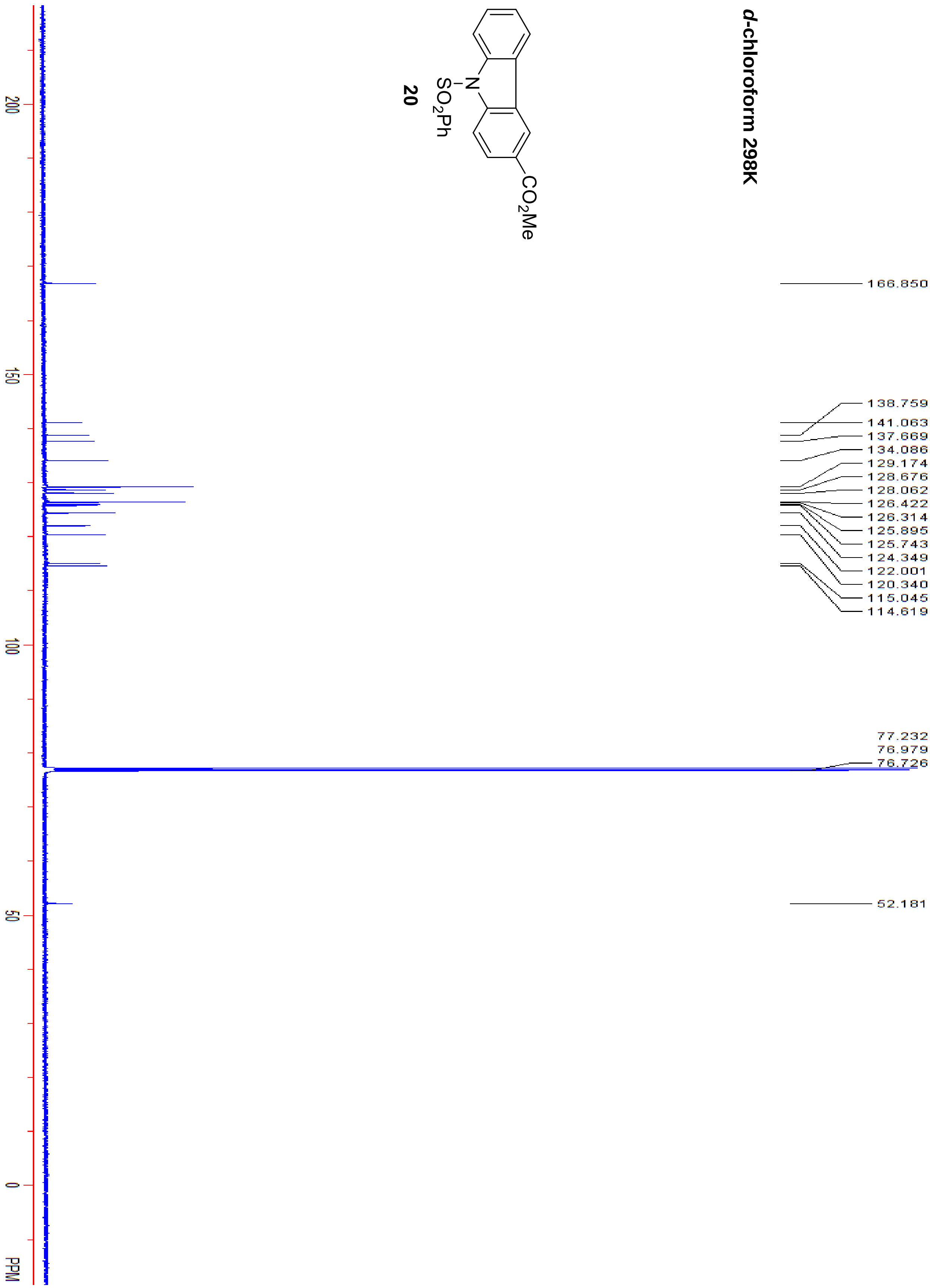
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124.349
122.001
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76.726
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150
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50
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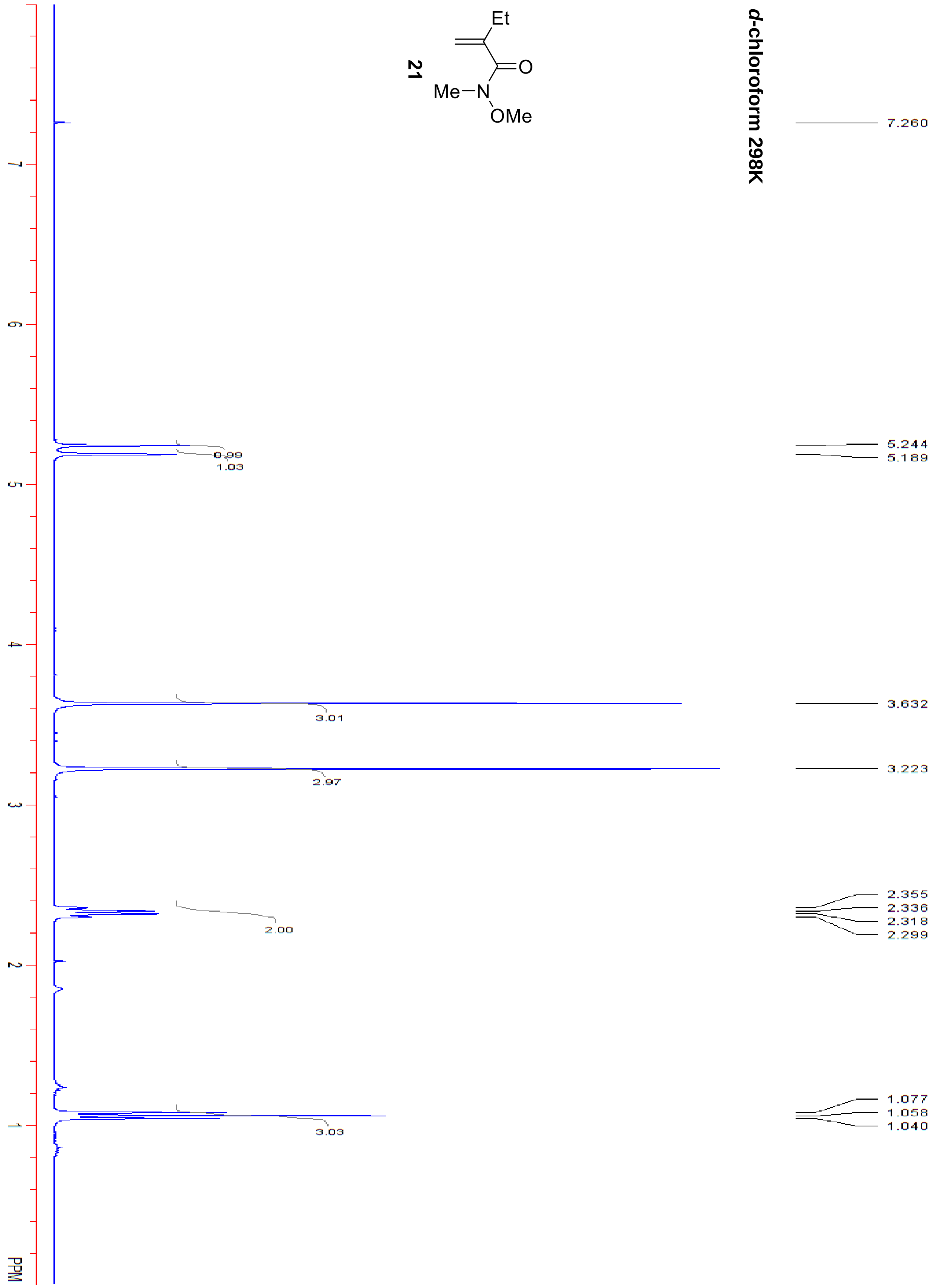
PPM



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Me
N
OMe
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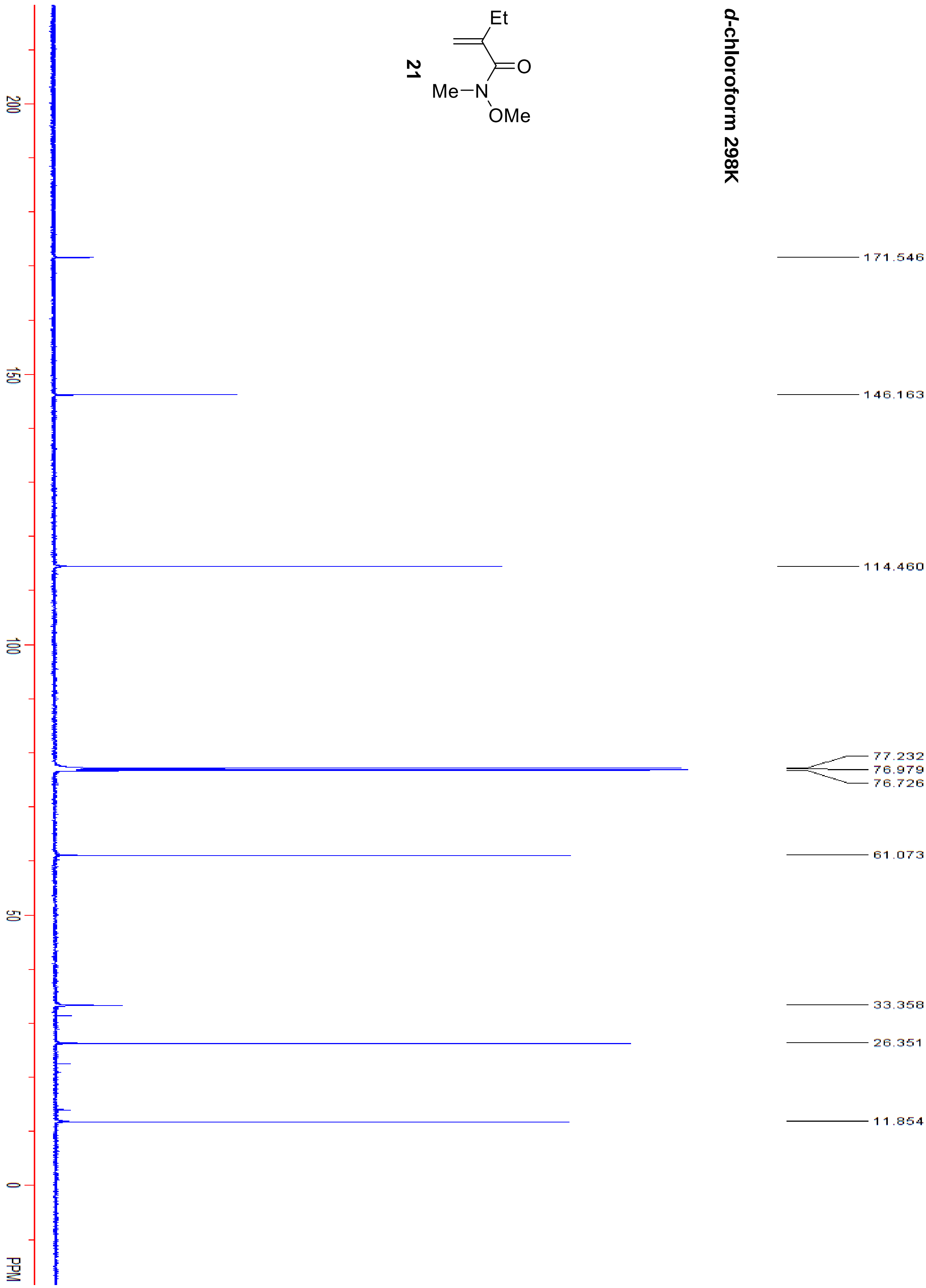
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O
Me−N
OMe
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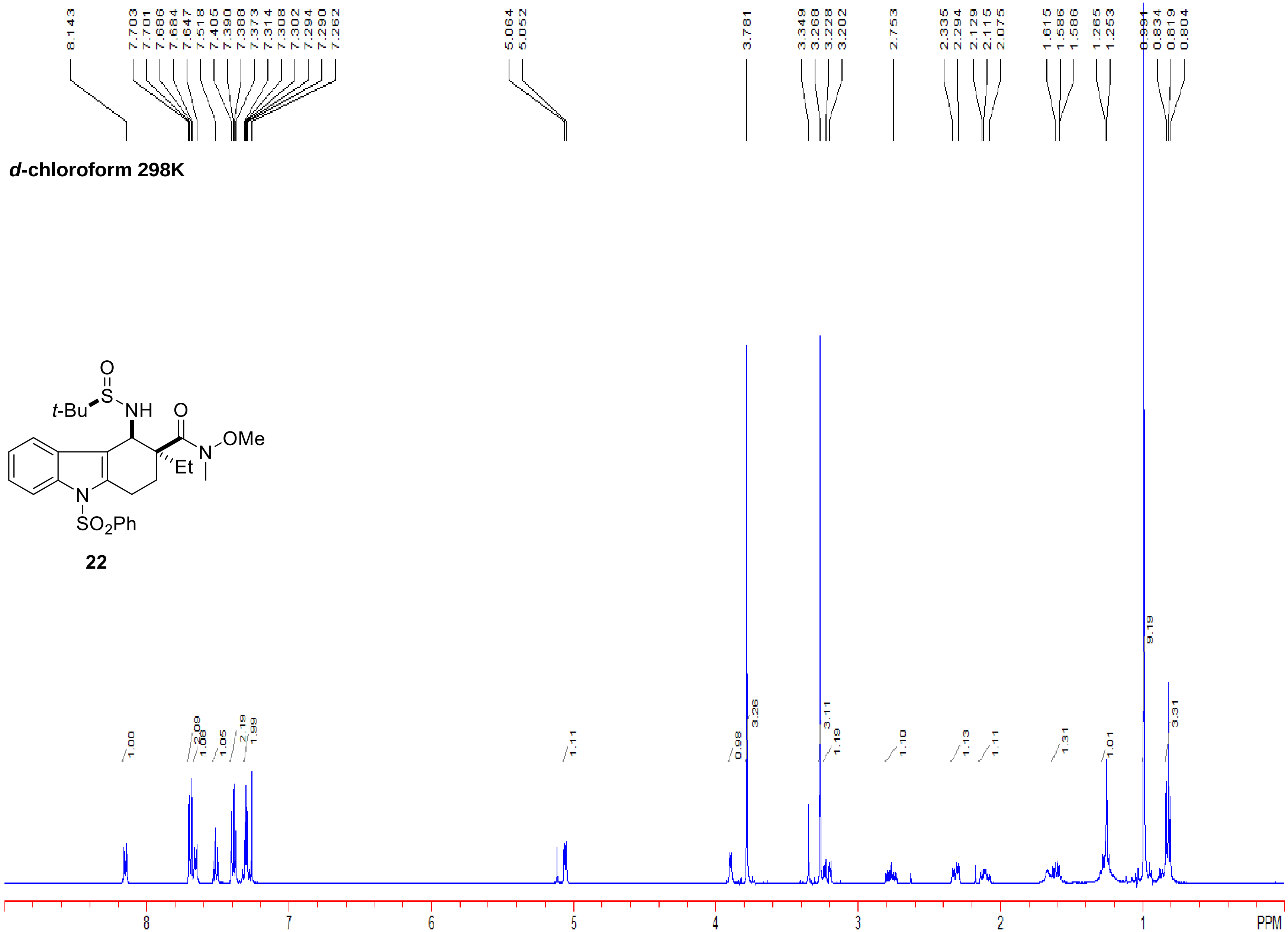

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5.052
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3.228
3.202
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2.335
2.294
2.129
2.115
2.075
1.615
1.586
1.586
1.265
1.253
0.991
0.834
0.819
0.804
d-chloroform 298K
t-Bu
S
O
NH
O
N
OMe
Et
N
SO2Ph
22
1.00
2.09
1.08
1.05
2.19
1.99
1.11
0.98
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1.19
1.10
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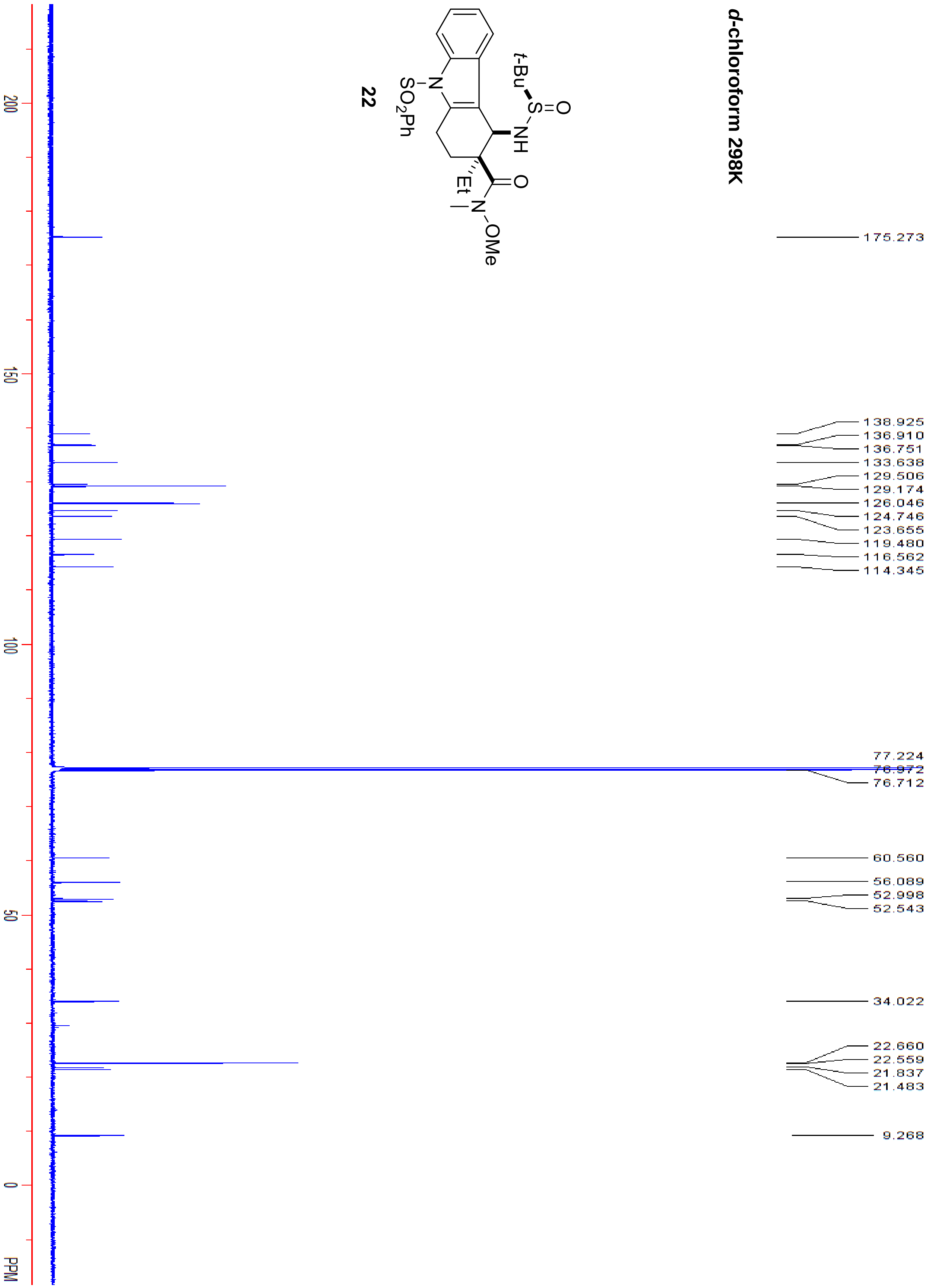
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S=O
NH
O
N
OMe
Et
N
SO2Ph
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136.751
133.638
129.506
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126.046
124.746
123.655
119.480
116.562
114.345
77.224
76.972
76.712
60.560
56.089
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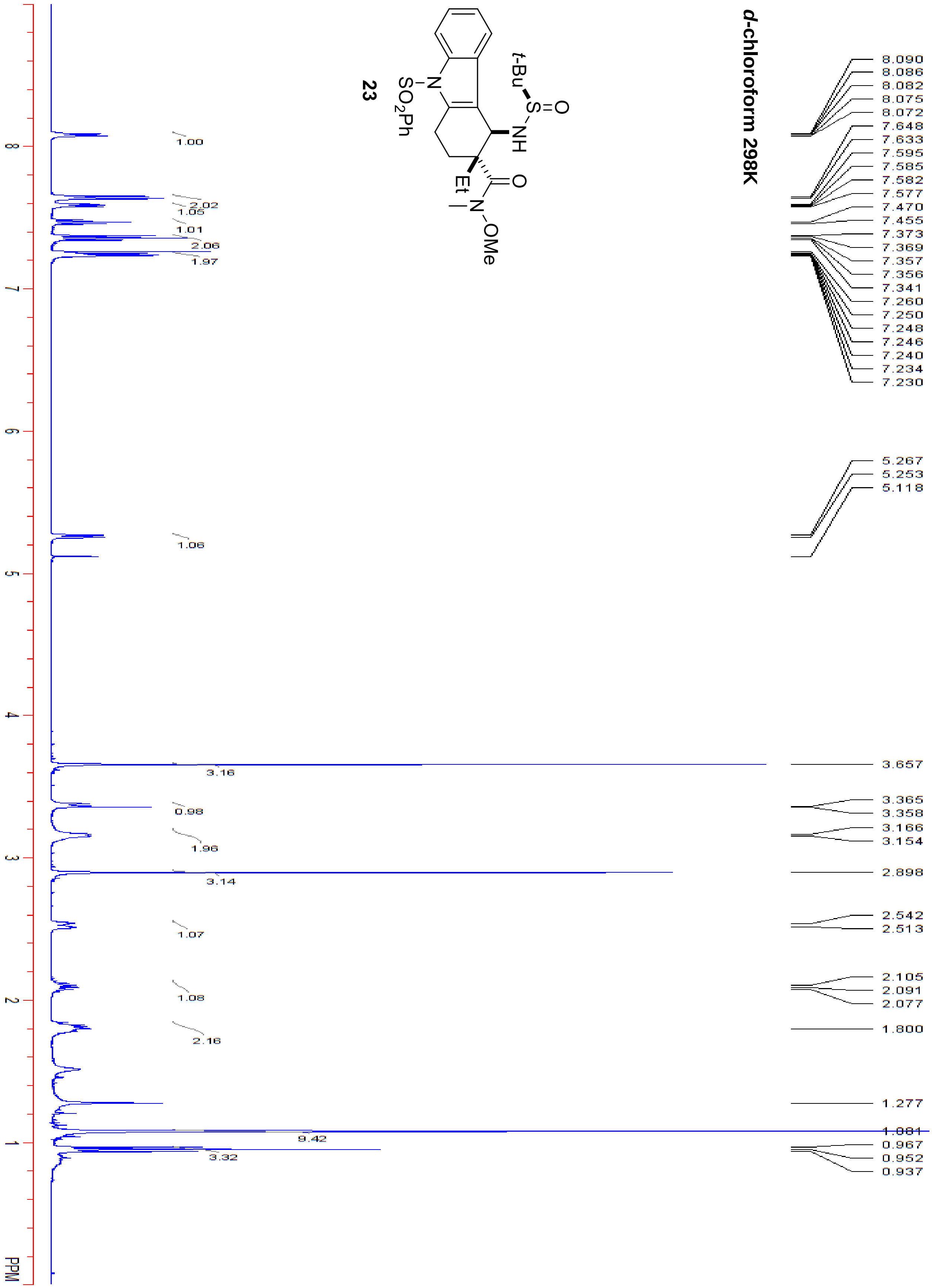
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7.260
7.250
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7.230
5.267
5.253
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2.513
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0.952
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1.01
2.06
1.97
1.06
3.16
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1.96
3.14
1.07
1.08
2.16
9.42
3.32
8
7
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O
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OMe
Et
N
SO2Ph
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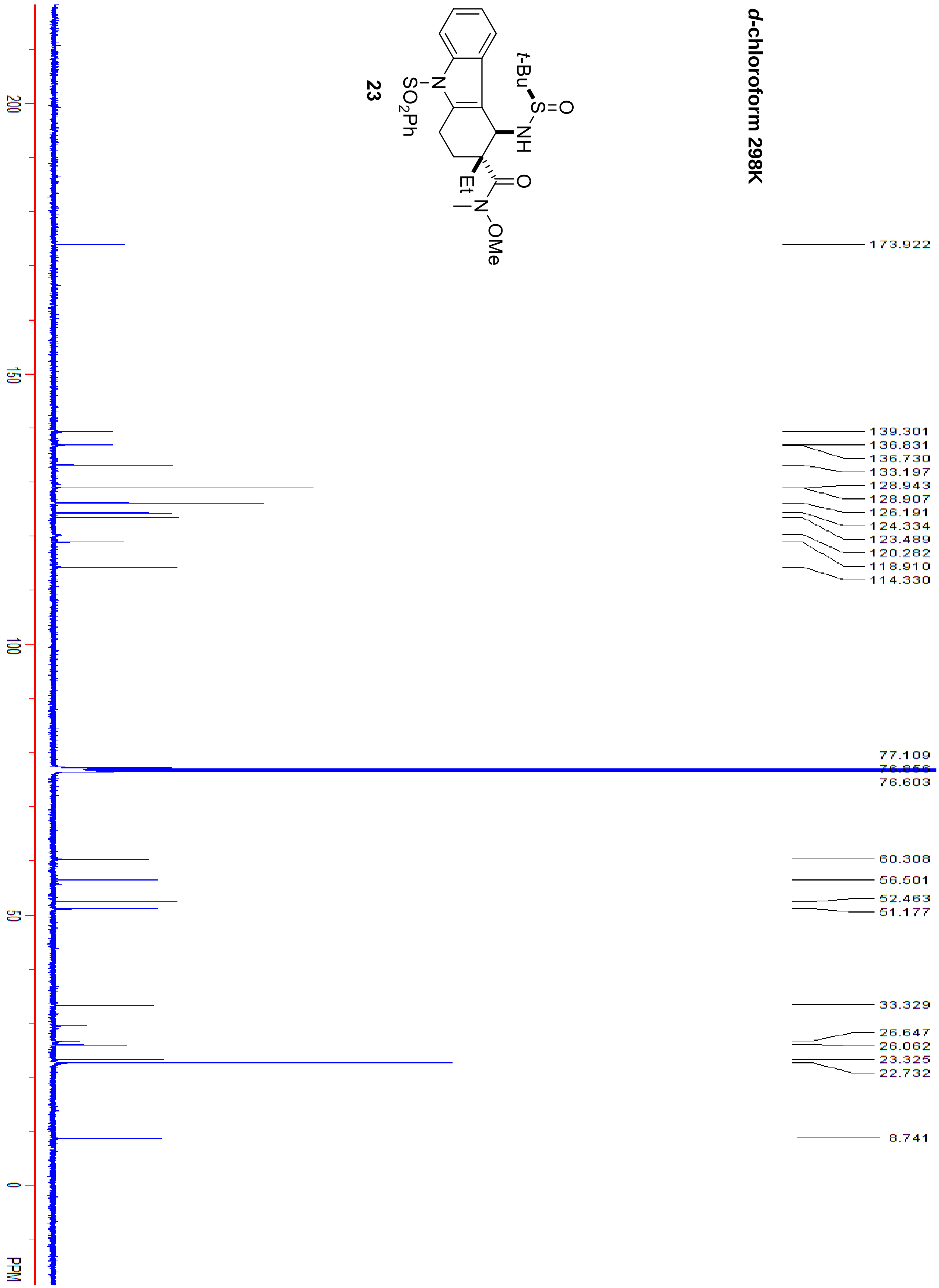
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OMe
Et
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136.730
133.197
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128.907
126.191
124.334
123.489
120.282
118.910
114.330
77.109
76.856
76.603
60.308
56.501
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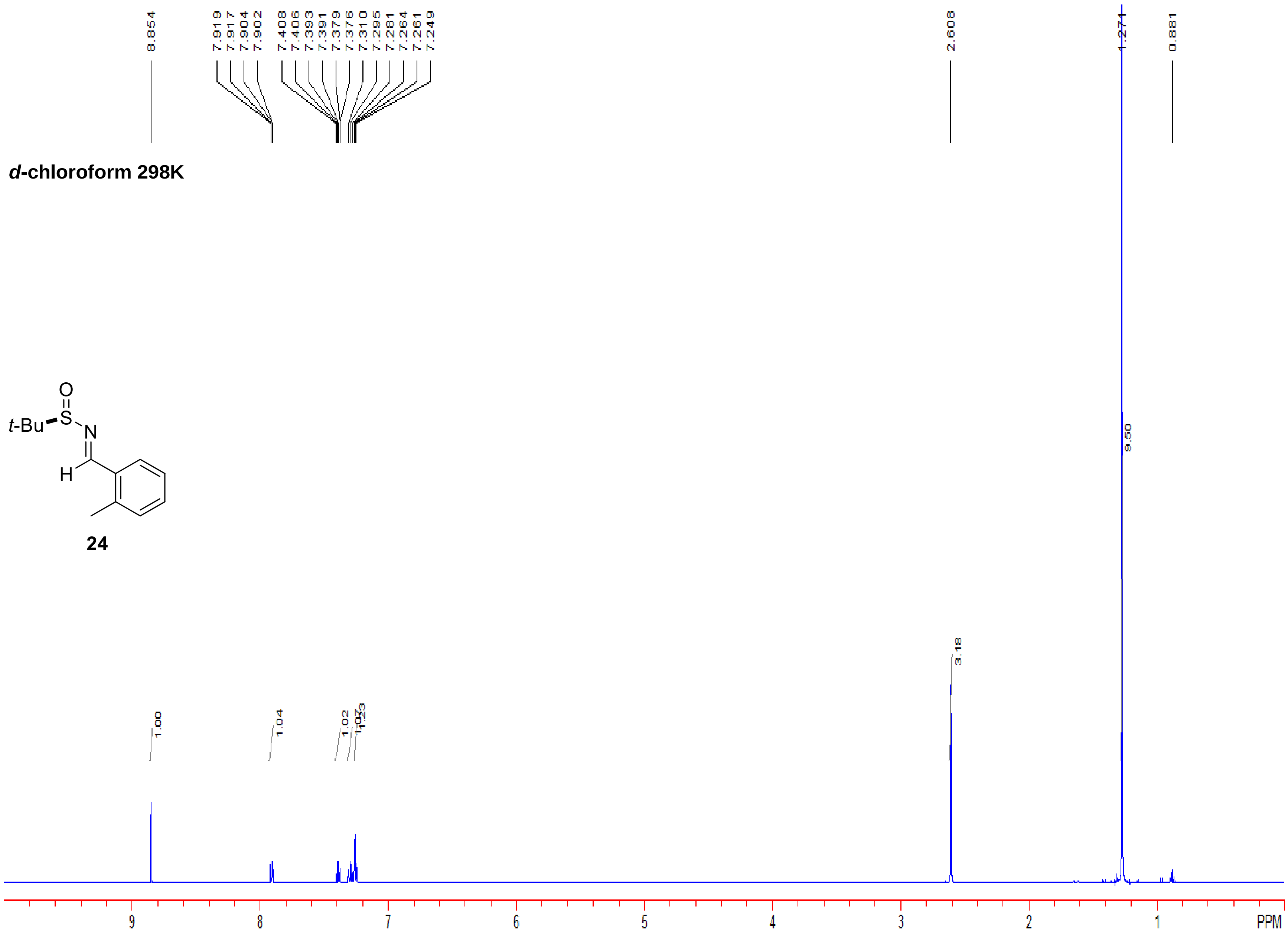
PPM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7.376
7.310
7.295
7.281
7.264
7.261
7.249
2.608
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0.881
O
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S
N
H
24
1.00
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1
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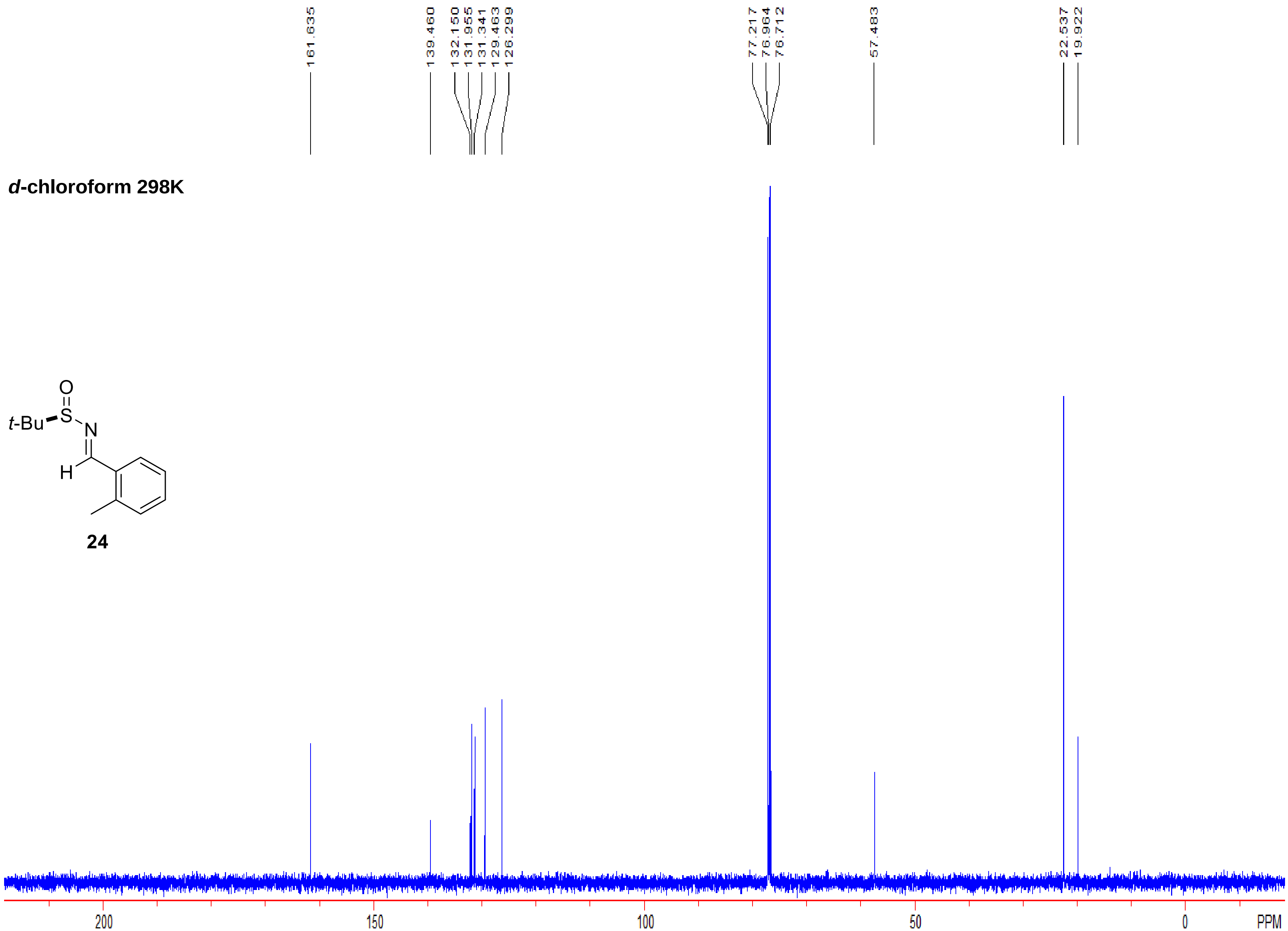
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d-chloroform 298K
t-Bu
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O
N
H
24
200
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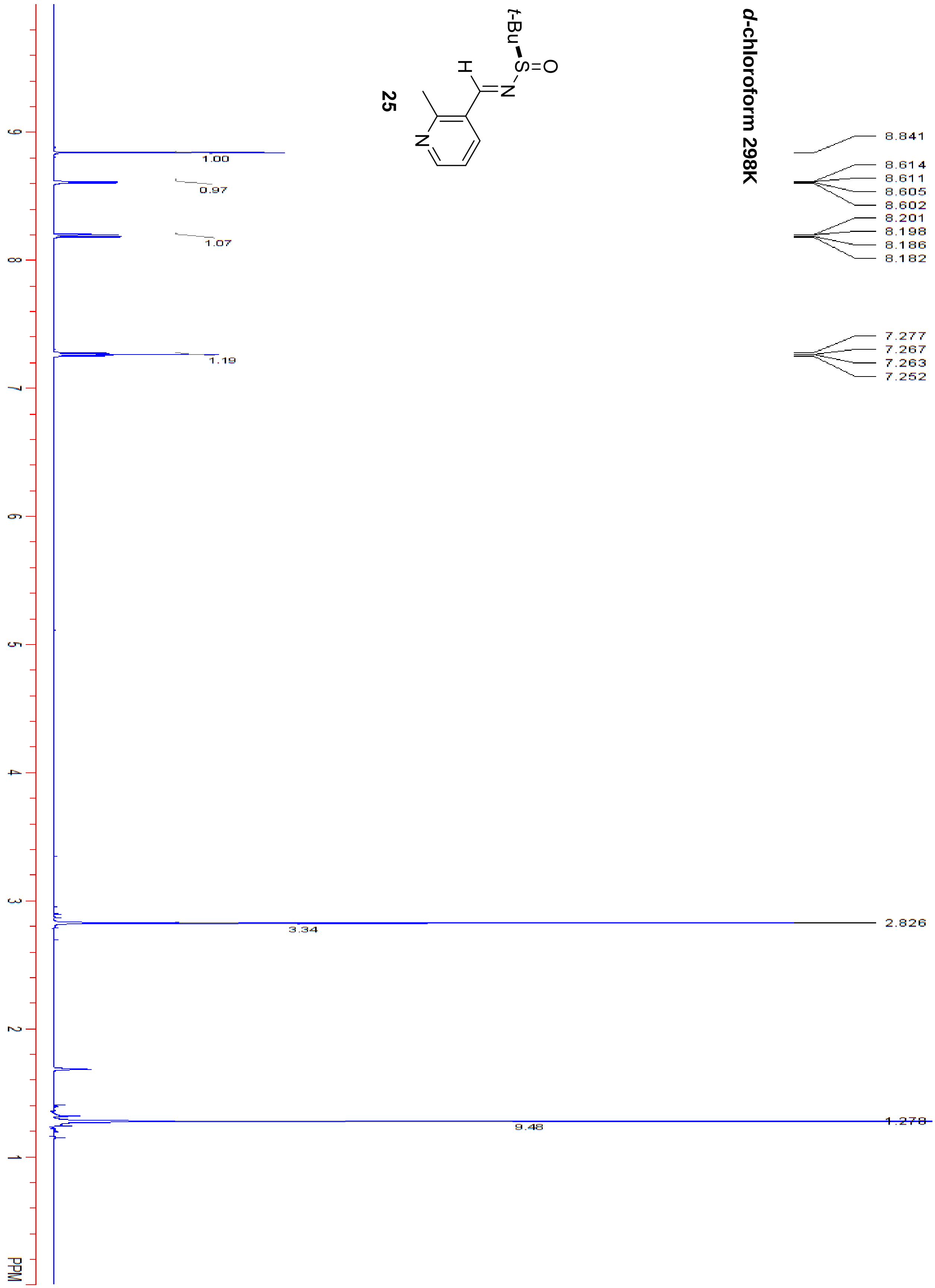
PPM



d-chloroform 298K
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H
N
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1.278
1.00
0.97
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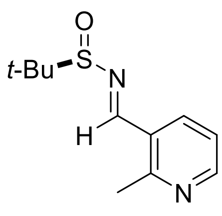
d-chloroform 298K



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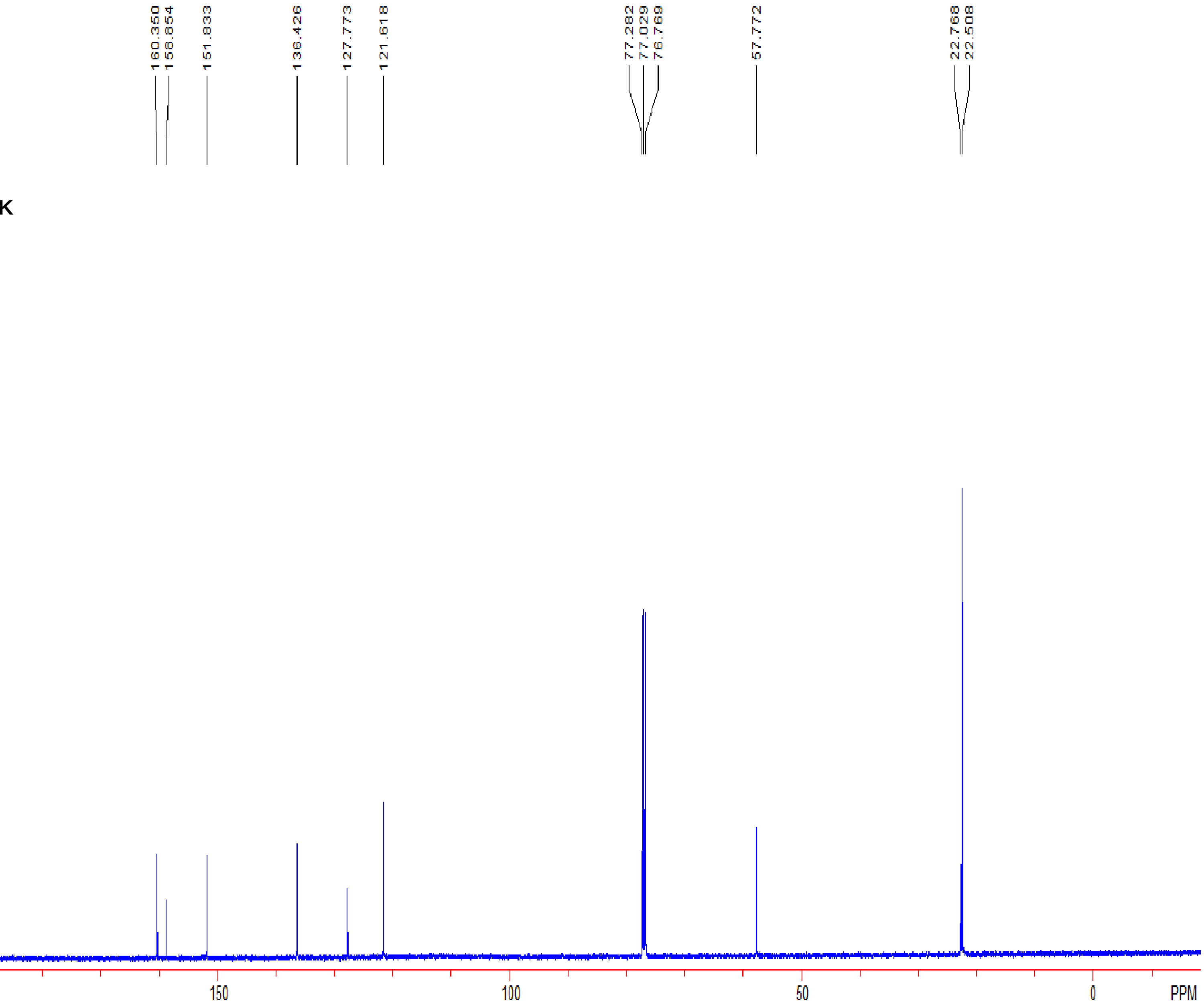
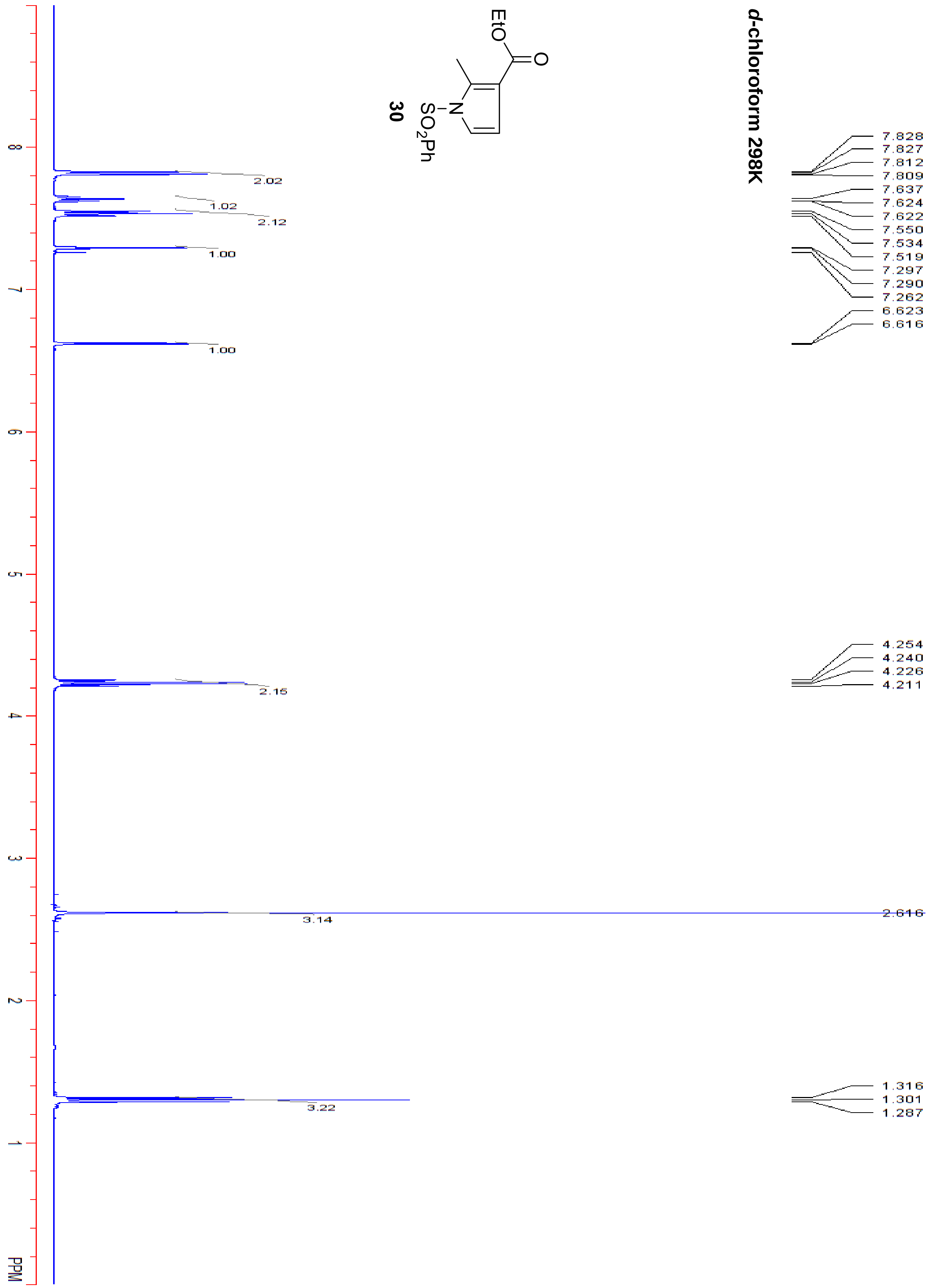
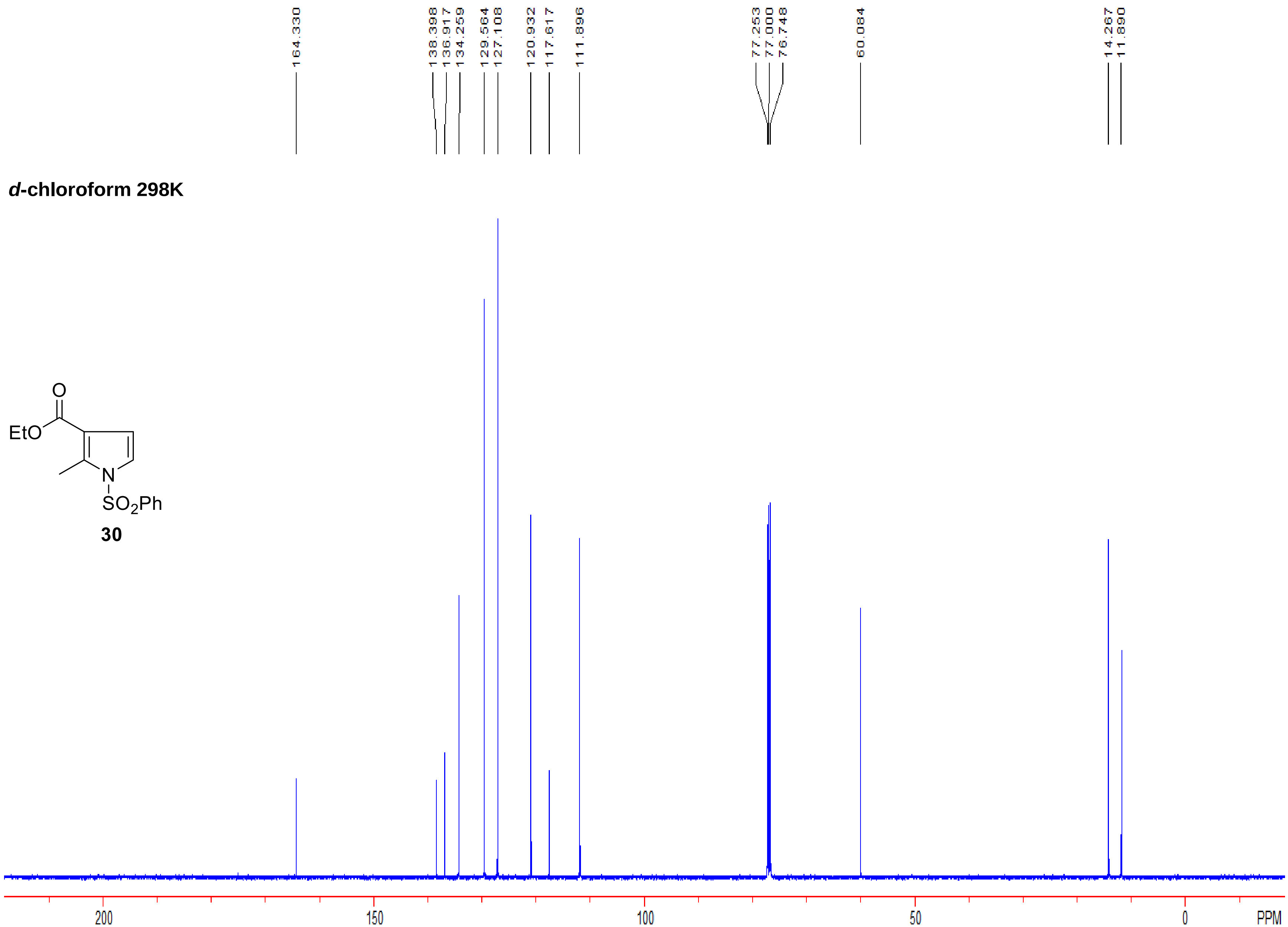
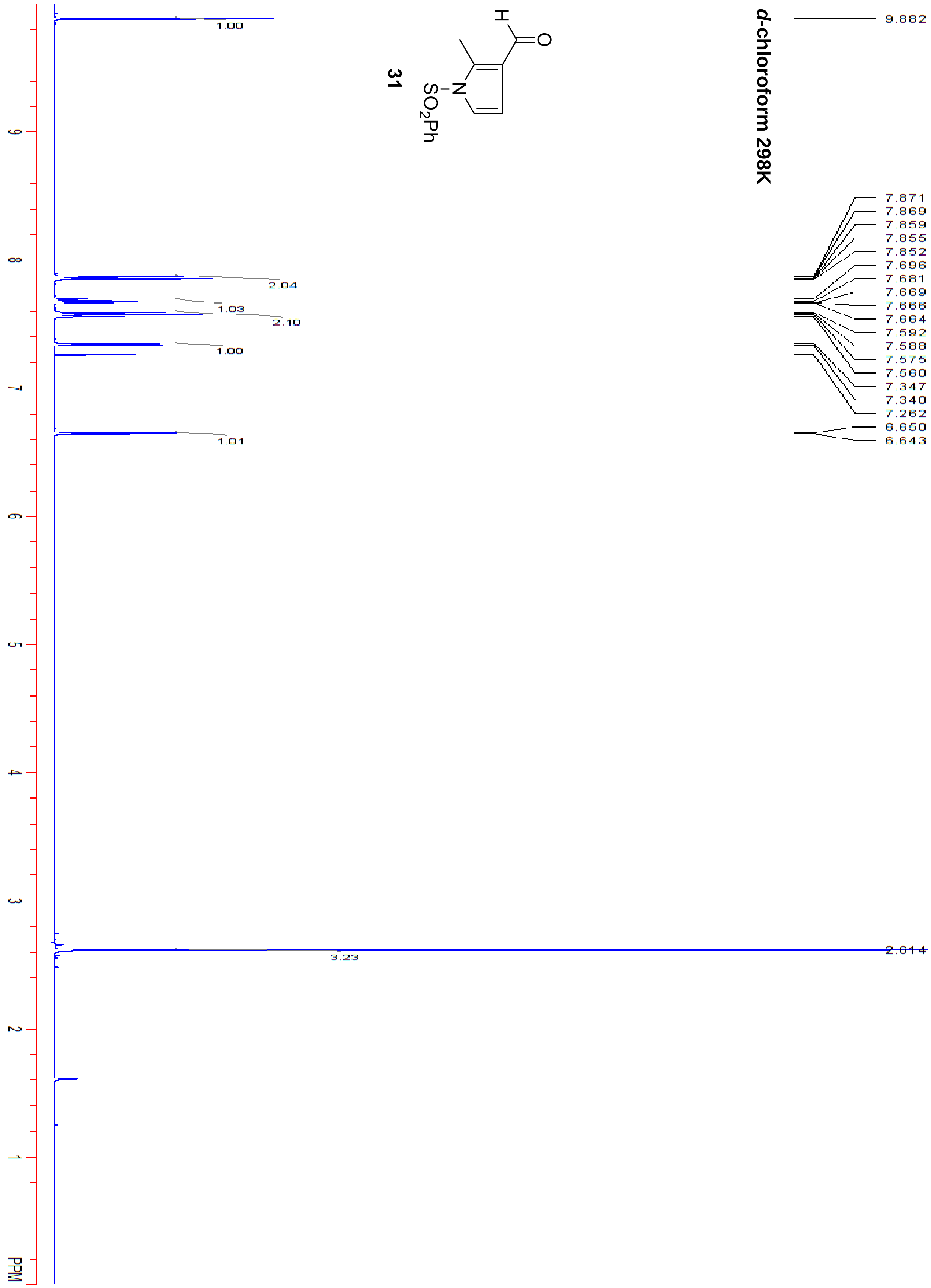



d-chloroform 298K
EtO
O
N
SO2Ph
30
7.828
7.827
7.812
7.809
7.637
7.624
7.622
7.550
7.534
7.519
7.297
7.290
7.262
6.623
6.616
4.254
4.240
4.226
4.211
2.616
1.316
1.301
1.287
2.02
1.02
2.12
1.00
1.00
2.15
3.14
3.22
8
7
6
5
4
3
2
1
PPM


d-chloroform 298K
164.330
138.398
136.917
134.259
129.564
127.108
120.932
117.617
111.896
77.253
77.000
76.748
60.084
14.267
11.890
EtO
O
N
SO2Ph
30
200
150
100
50
0
PPM



d-chloroform 298K
9.882
7.871
7.869
7.859
7.855
7.852
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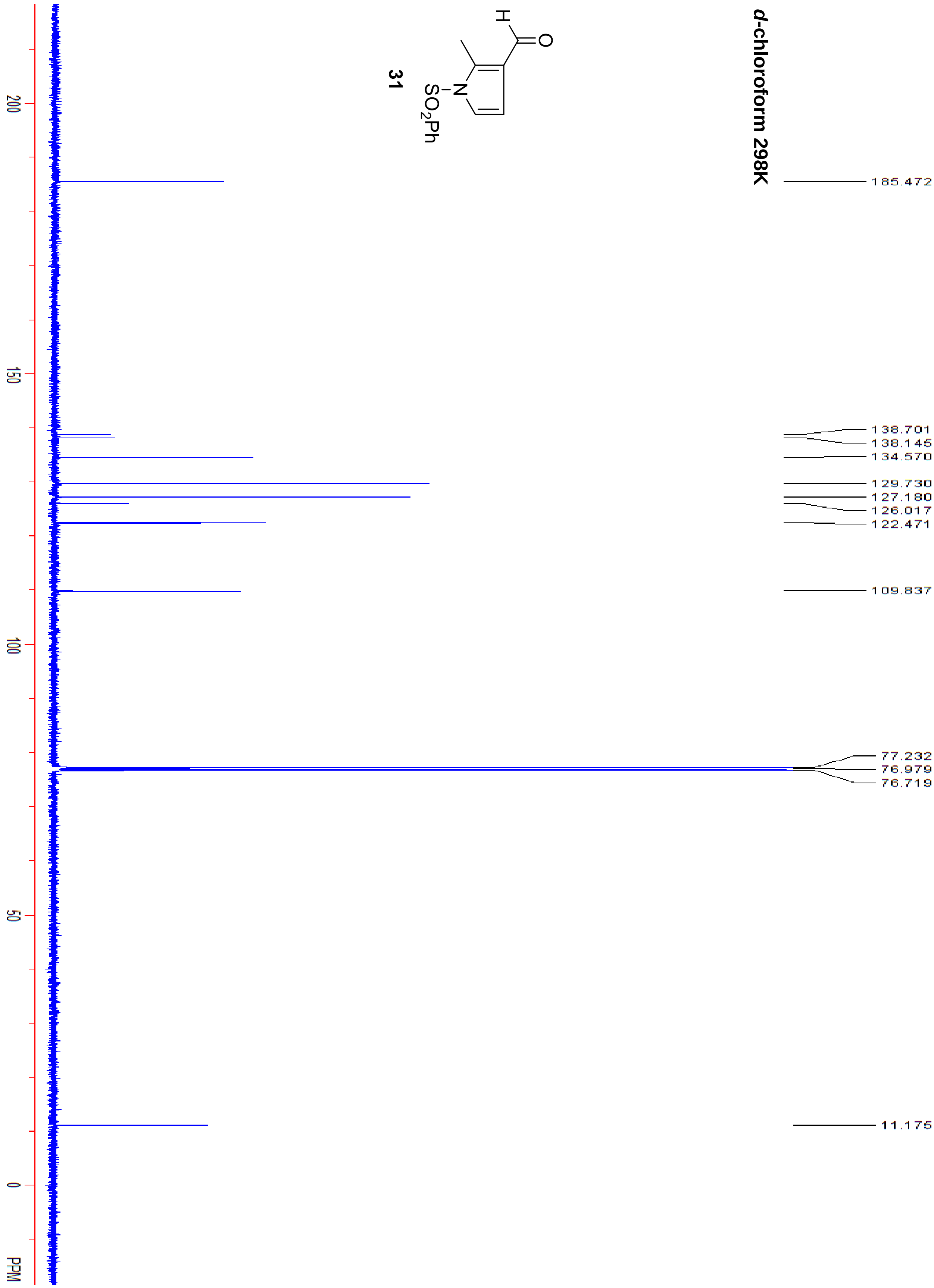
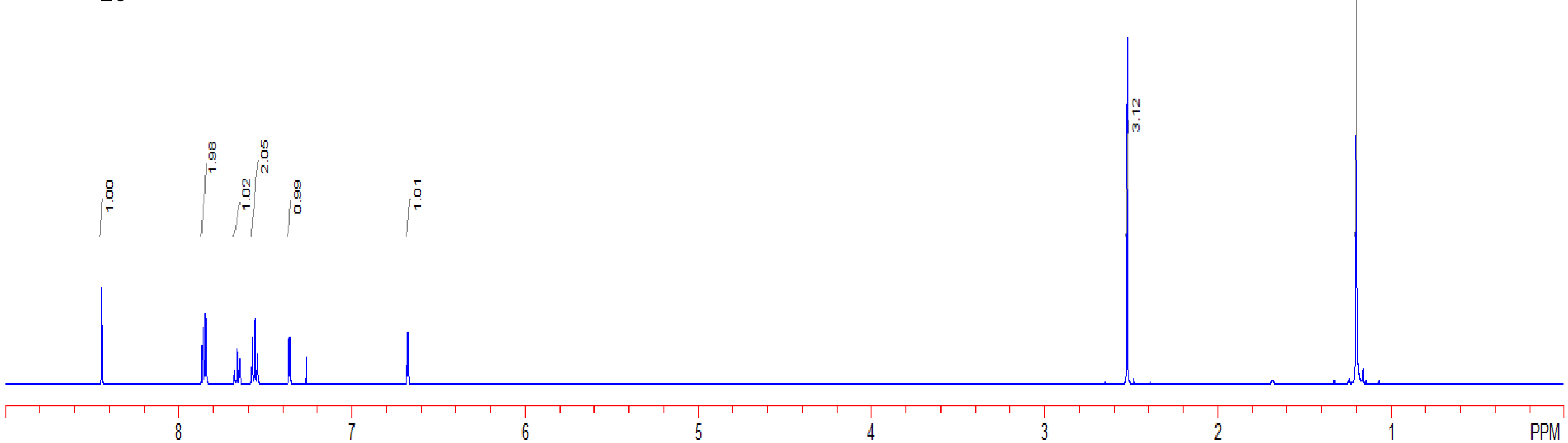
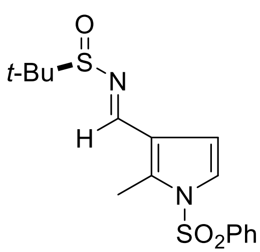
7.681
7.669
7.666
7.664
7.592
7.588
7.575
7.560
7.347
7.340
7.262
6.650
6.643
2.614
1.00
2.04
1.03
2.10
1.00
1.01
3.23
O
H
N
SO2Ph
31
9
8
7
6
5
4
3
2
1
PPM

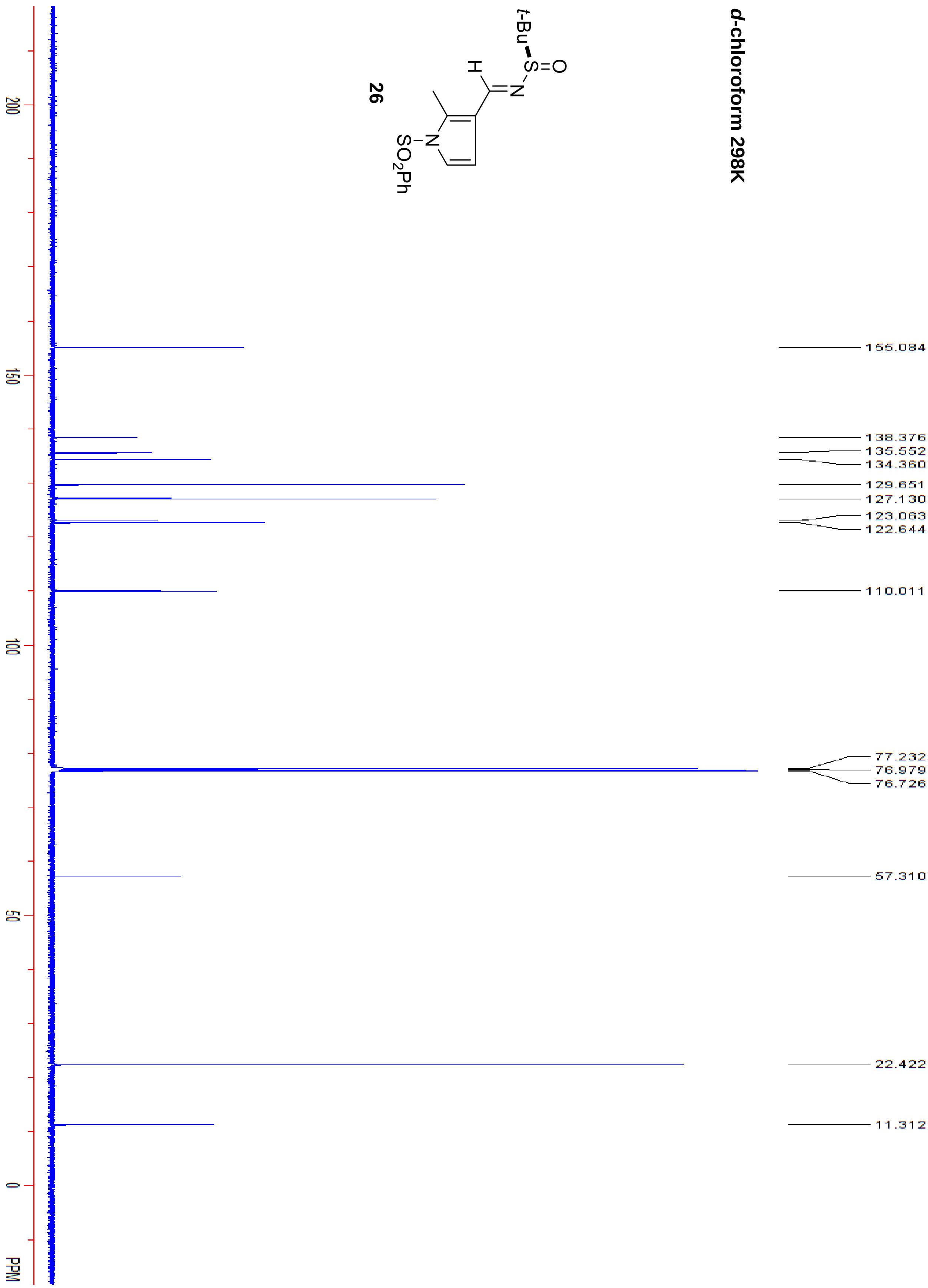

d-chloroform 298K
185.472
138.701
138.145
134.570
129.730
127.180
126.017
122.471
109.837
77.232
76.979
76.719
11.175
31
200
150
100
50
0
PPM

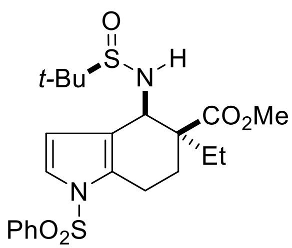


***d*-chloroform 298K**

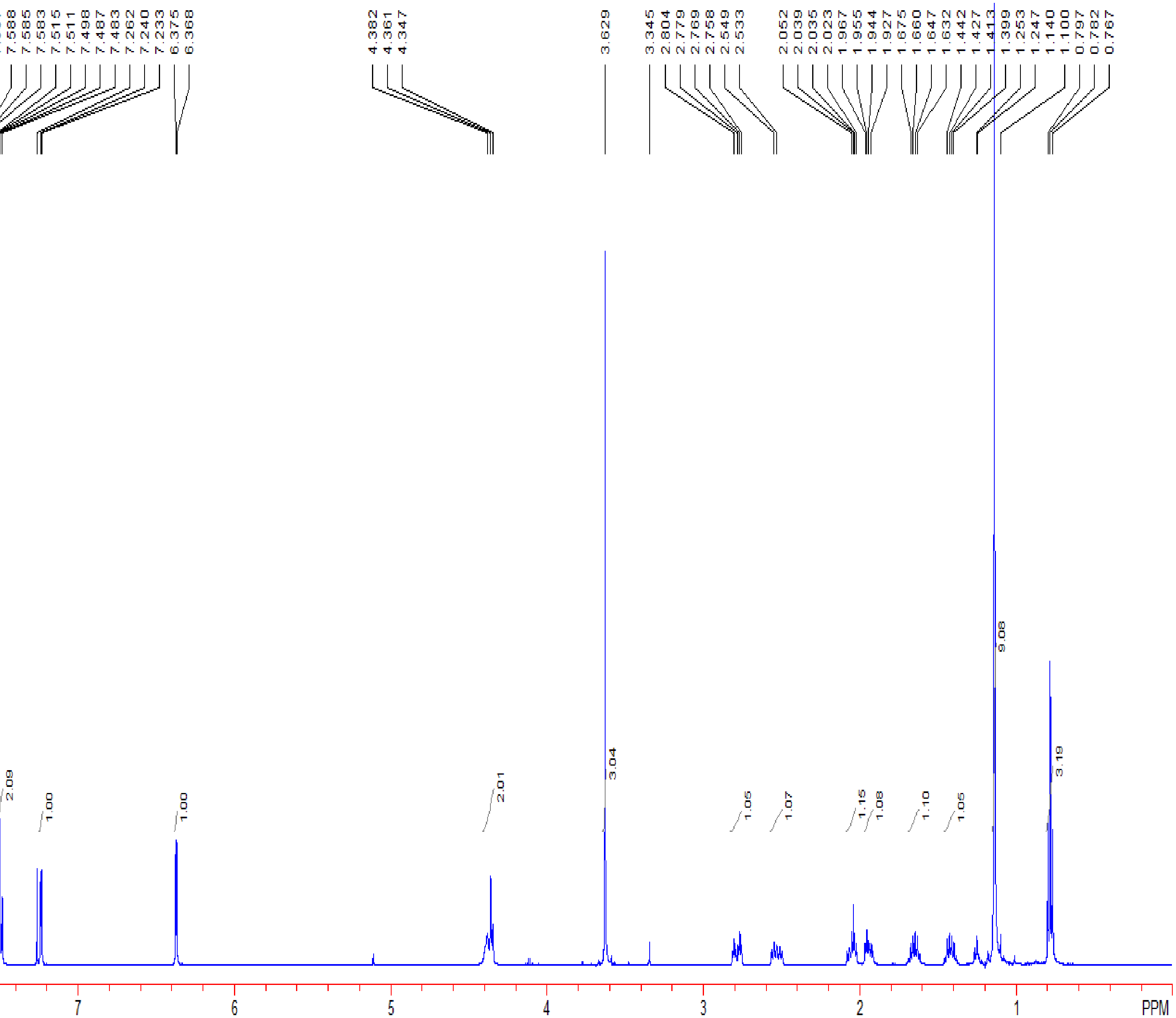


26

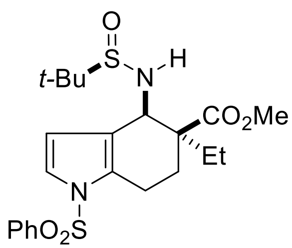

d-chloroform 298K
t-Bu
S
O
N
H
N
SO2Ph
26
155.084
138.376
135.552
134.360
129.651
127.130
123.063
122.644
110.011
77.232
76.979
76.726
57.310
22.422
11.312
200
150
100
50
0
PPM



34

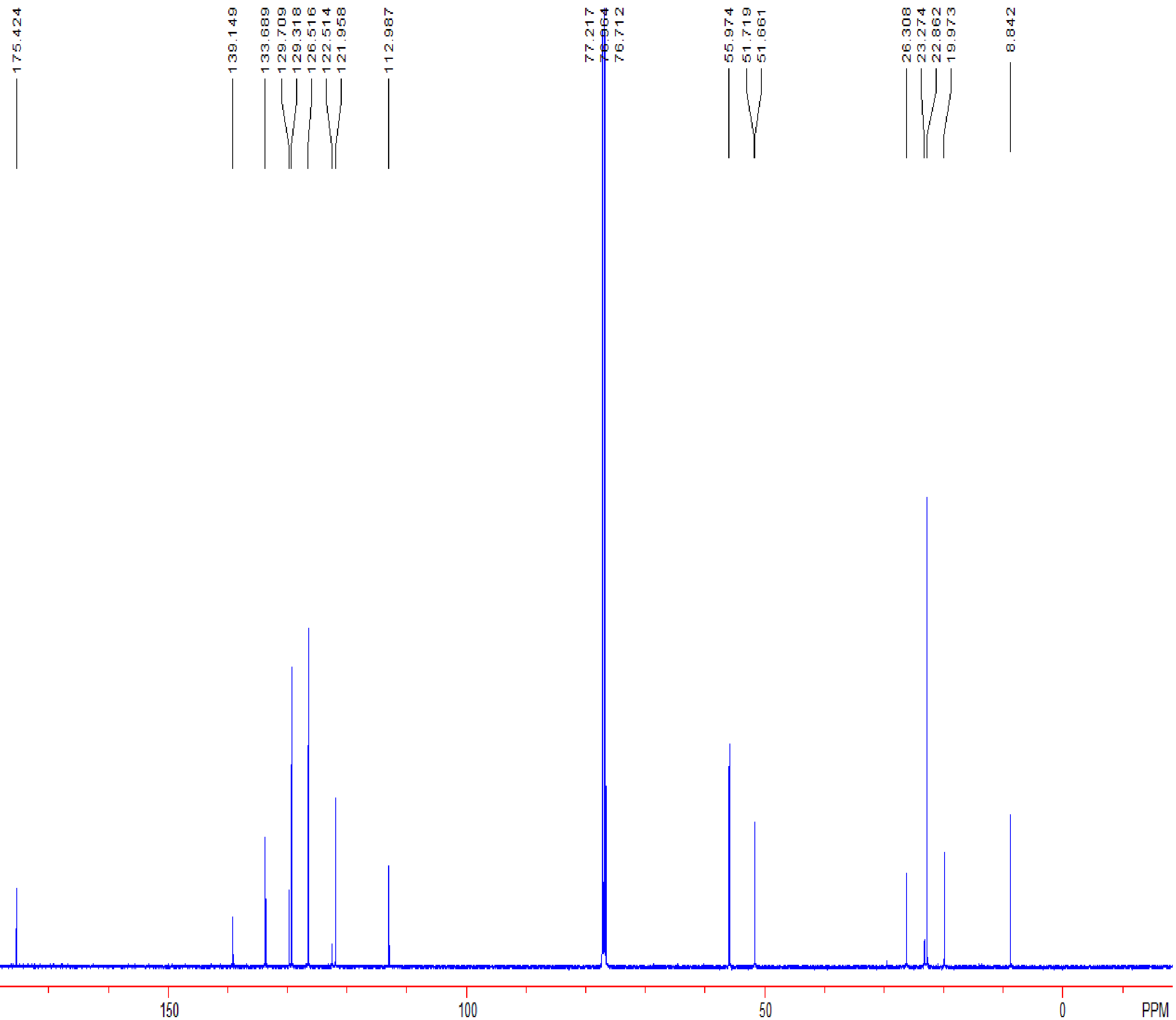


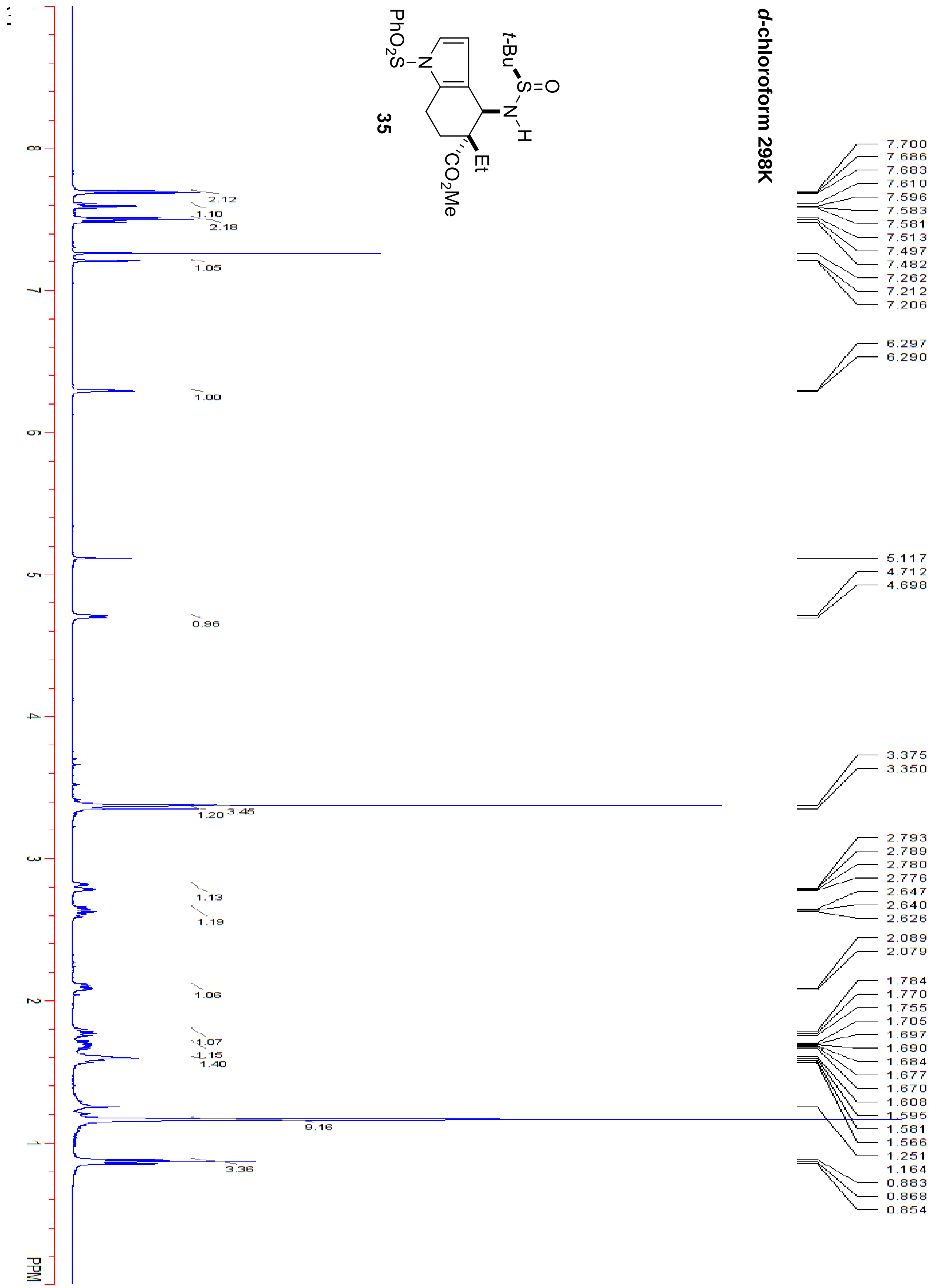
7.731
7.729
7.718
7.714
7.712
7.617
7.615
7.613
7.604
7.600
7.597
7.588
7.585
7.583
7.515
7.511
7.498
7.487
7.483
7.262
7.240
7.233
6.375
6.368
4.382
4.361
4.347
3.629
3.345
2.804
2.779
2.769
2.758
2.549
2.533
2.052
2.039
2.035
2.023
1.967
1.955
1.944
1.927
1.675
1.660
1.647
1.632
1.442
1.427
1.413
1.399
1.253
1.247
1.140
1.100
0.797
0.782
0.767
d-chloroform 298K
2.03
1.03
2.09
1.00
1.00
2.01
3.04
1.05
1.07
1.15
1.08
1.10
1.05
9.08
3.19
8
7
6
5
4
3
2
1
PPM

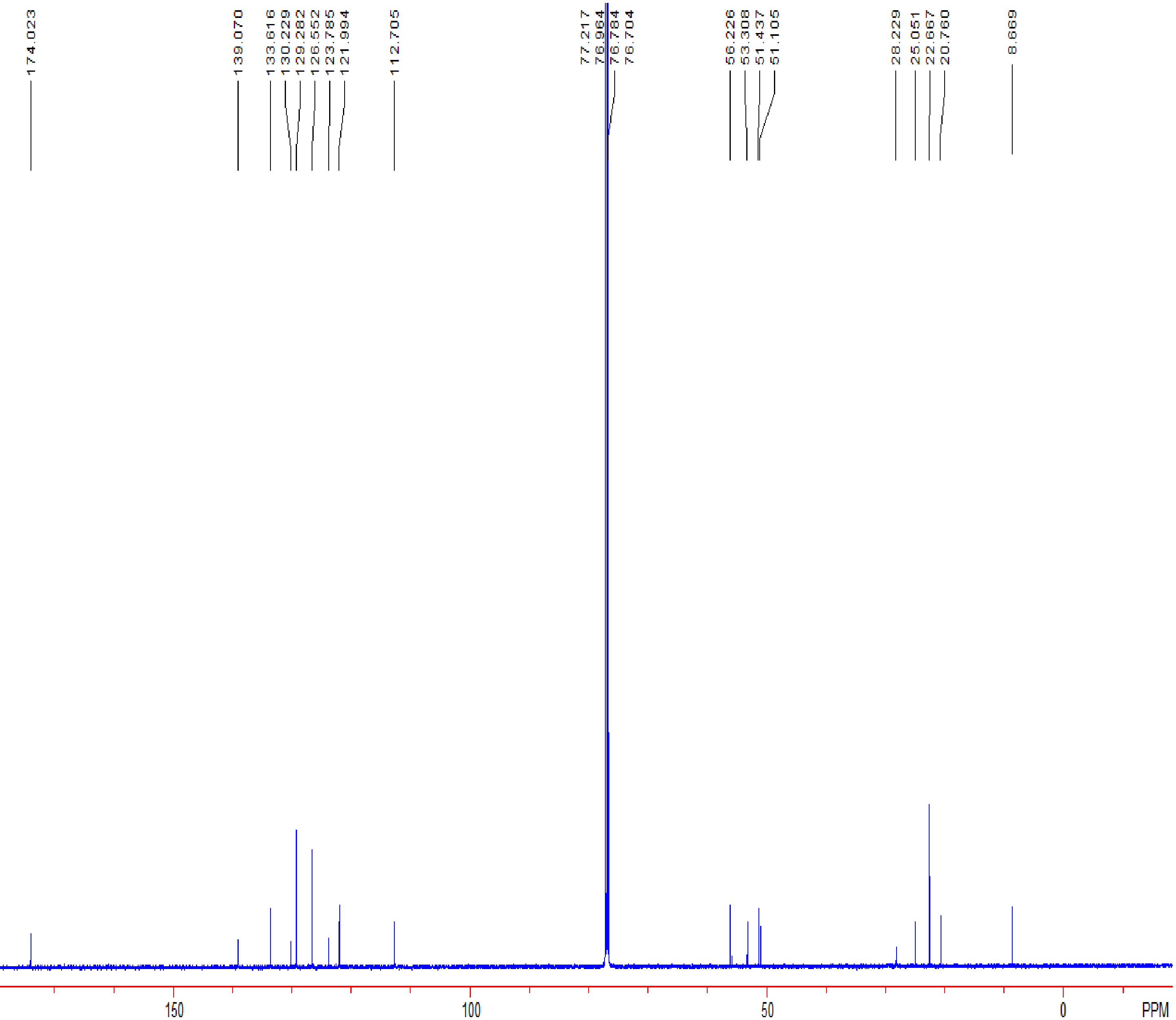


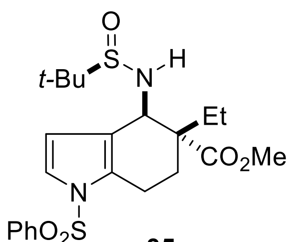
34

***d*-chloroform 298K**




d-chloroform 298K
35
7.700
7.686
7.683
7.610
7.596
7.583
7.581
7.513
7.497
7.482
7.262
7.212
7.206
6.297
6.290
5.117
4.712
4.698
3.375
3.350
2.793
2.789
2.780
2.776
2.647
2.640
2.626
2.089
2.079
1.784
1.770
1.755
1.705
1.697
1.690
1.684
1.677
1.670
1.608
1.595
1.581
1.566
1.251
1.164
0.883
0.868
0.854
PPM


d-chloroform 298K
174.023
139.070
133.616
130.229
129.282
126.552
123.785
121.994
112.705
77.217
76.964
76.784
76.704
56.226
53.308
51.437
51.105
28.229
25.051
22.667
20.760
8.669
200
150
100
50
0
PPM


O
S
t-Bu
N
H
Et
CO2Me
N
PhO2S

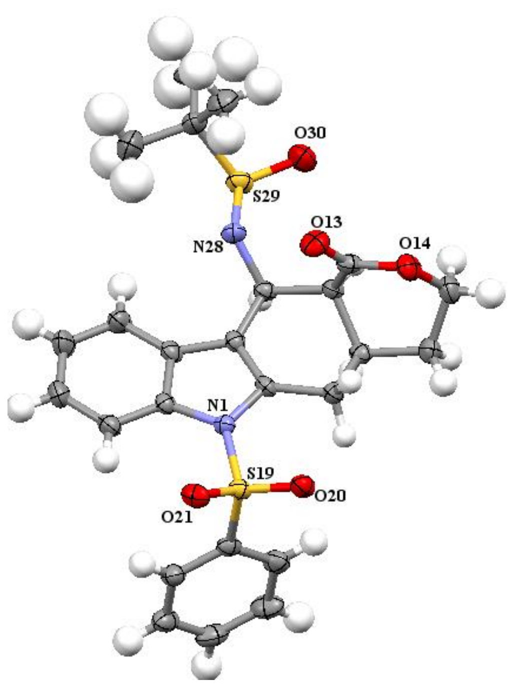
35

Crystal Structure Report 16

A specimen of $C_{25}H_{27}N_2O_5S_2$, approximate dimensions 0.046 mm x 0.164 mm x 0.622 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The total exposure time was 9.75 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 11005 reflections to a maximum θ angle of 27.86° (0.76 Å resolution), of which 5677 were independent (average redundancy 1.939, completeness = 98.5%, R_{int} = 3.17%) and 4354 (76.70%) were greater than $2\sigma(F^2)$. The final cell constants of a = 16.865(7) Å, b = 24.087(10) Å, c = 6.115(3) Å, volume = 2484.1(18) $Å^3$, are based upon the refinement of the XYZ-centroids of 4100 reflections above 20 σ(I) with 5.111° < 2θ < 55.43°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.764. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7637 and 1.0000.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 21 21 2, with Z = 4 for the formula unit, $C_{25}H_{27}N_2O_5S_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 307 variables converged at R1 = 4.50%, for the observed data and wR2 = 11.60% for all data. The goodness-of-fit was 1.059. The largest peak in the final difference electron density synthesis was 0.419 $e^-/Å^3$ and the largest hole was -0.548 $e^-/Å^3$ with an RMS deviation of 0.068 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.336 g/cm^3 and F(000), 1052 e^-.



Ellipsoid contour percent probability level for Compound 16 = 50%

Table 1. Sample and crystal data.

Chemical formula	$C_{25}H_{27}N_2O_5S_2$	
Formula weight	499.60	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal size	0.046 x 0.164 x 0.622 mm	
Crystal system	orthorhombic	
Space group	P 21 21 2	
Unit cell dimensions	a = 16.865(7) Å	α = 90°
	b = 24.087(10) Å	β = 90°
	c = 6.115(3) Å	γ = 90°
Volume	2484.1(18) $Å^3$	
Z	4	
Density (calculated)	1.336 g/cm^3	
Absorption coefficient	0.253 mm^{-1}	
F(000)	1052	

Table 2. Data collection and structure refinement.

Theta range for data collection	1.69 to 27.86°	
Index ranges	-18<=h<=22, -31<=k<=28, -8<=l<=8	
Reflections collected	11005	
Independent reflections	5677 [R(int) = 0.0317]	
Coverage of independent reflections	98.5%	
Absorption correction	multi-scan	
Max. and min. transmission	1.0000 and 0.7637	
Structure solution technique	direct methods	
Structure solution program	SHELXL-2013 (Sheldrick, 2013)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2013 (Sheldrick, 2013)	
Function minimized	Σ w(F_o^2 - F_c^2)^2	
Data / restraints / parameters	5677 / 0 / 307	
Goodness-of-fit on F^2	1.059	
Δ/σ_{max}	0.001	
Final R indices	4354 data; I>2σ(I)	R1 = 0.0450, wR2 = 0.1004
	all data	R1 = 0.0742, wR2 = 0.1160
Weighting scheme	w=1/[σ^2(F_o^2)+(0.0483P)^2+0.9848P] where P=(F_o^2+2F_c^2)/3	
Absolute structure parameter	-0.0(0)	
Largest diff. peak and hole	0.419 and -0.548 eÅ^{-3}	
R.M.S. deviation from mean	0.068 eÅ^{-3}	

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å²).

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
C2	0.3238(2)	0.74807(14)	0.2689(7)	0.0231(8)
C3	0.3513(2)	0.80094(14)	0.2903(7)	0.0245(8)
C4	0.4128(2)	0.80987(15)	0.1290(8)	0.0286(9)
C5	0.4634(2)	0.85483(16)	0.0816(9)	0.0377(11)
C6	0.5168(2)	0.84977(18)	0.9098(10)	0.0450(12)
C7	0.5206(2)	0.80155(17)	0.7854(9)	0.0384(11)
C8	0.4722(2)	0.75600(16)	0.8287(8)	0.0320(9)
C9	0.41907(19)	0.76079(13)	0.0018(8)	0.0252(8)
C10	0.3208(2)	0.84099(13)	0.4606(7)	0.0261(8)
C11	0.2428(2)	0.81934(14)	0.5637(7)	0.0249(8)
C12	0.1701(2)	0.82542(14)	0.4196(7)	0.0270(9)
C15	0.1072(2)	0.77826(18)	0.7209(9)	0.0407(11)
C16	0.1752(2)	0.73689(16)	0.7452(8)	0.0349(10)
C17	0.2495(2)	0.75642(15)	0.6179(7)	0.0265(8)
C18	0.2610(2)	0.72189(15)	0.4106(7)	0.0271(8)
C22	0.4323(2)	0.62006(14)	0.1341(7)	0.0273(9)
C23	0.5034(2)	0.61287(14)	0.0226(9)	0.0326(10)
C24	0.5649(2)	0.58421(16)	0.1266(10)	0.0415(12)
C25	0.5541(3)	0.56406(16)	0.3376(10)	0.0430(12)
C26	0.4829(3)	0.57148(17)	0.4459(9)	0.0438(12)
C27	0.4208(3)	0.59950(16)	0.3451(8)	0.0354(10)
C31	0.3111(3)	0.00739(16)	0.3527(9)	0.0404(11)
C32	0.3192(4)	0.05939(17)	0.4966(13)	0.0734(19)
C33	0.2300(3)	0.00632(19)	0.2410(10)	0.0528(14)
C34	0.3772(3)	0.0052(2)	0.1807(12)	0.0693(19)
N1	0.36269(18)	0.72243(11)	0.0884(6)	0.0241(7)
N28	0.31357(19)	0.89746(12)	0.3644(6)	0.0298(8)
O13	0.16761(16)	0.84661(12)	0.2410(6)	0.0387(7)
O14	0.10335(14)	0.80164(11)	0.5011(6)	0.0366(7)
O20	0.27938(15)	0.63700(11)	0.0913(5)	0.0328(7)
O30	0.25070(19)	0.95174(13)	0.6937(6)	0.0481(9)
S19	0.35392(5)	0.65606(3)	0.00720(18)	0.0258(2)
S29	0.32166(6)	0.94906(4)	0.5474(2)	0.0353(3)

	x/a	y/b	z/c	U(eq)
O21	0.36812(16)	0.65612(11)	0.7759(5)	0.0330(6)

Table 4. Bond lengths (Å).

C2-C3	1.362(5)	C2-N1	1.425(5)
C2-C18	1.506(5)	C3-C4	1.448(6)
C3-C10	1.510(5)	C4-C5	1.409(5)
C4-C9	1.419(5)	C5-C6	1.389(7)
C5-H5A	0.95	C6-C7	1.390(6)
C6-H6A	0.95	C7-C8	1.393(6)
C7-H7A	0.95	C8-C9	1.391(6)
C8-H8A	0.95	C9-N1	1.428(5)
C10-N28	1.487(5)	C10-C11	1.550(5)
C10-H10A	1.0	C11-C12	1.518(5)
C11-C17	1.555(5)	C11-H11A	1.0
C12-O13	1.206(5)	C12-O14	1.358(5)
C15-O14	1.458(6)	C15-C16	1.526(6)
C15-H15A	0.99	C15-H15B	0.99
C16-C17	1.548(5)	C16-H16A	0.99
C16-H16B	0.99	C17-C18	1.528(6)
C17-H17A	1.0	C18-H18A	0.99
C18-H18B	0.99	C22-C23	1.391(6)
C22-C27	1.395(6)	C22-S19	1.761(4)
C23-C24	1.398(6)	C23-H23A	0.95
C24-C25	1.390(8)	C24-H24A	0.95
C25-C26	1.384(7)	C25-H25A	0.95
C26-C27	1.391(6)	C26-H26A	0.95
C27-H27A	0.95	C31-C33	1.529(7)
C31-C34	1.534(7)	C31-C32	1.537(7)
C31-S29	1.850(5)	C32-H32A	0.98
C32-H32B	0.98	C32-H32C	0.98
C33-H33A	0.98	C33-H33B	0.98
C33-H33C	0.98	C34-H34A	0.98
C34-H34B	0.98	C34-H34C	0.98
N1-S19	1.680(3)	N28-S29	1.678(3)
O20-S19	1.434(3)	O30-S29	1.496(3)
S19-O21	1.434(3)		

Table 5. Bond angles (°).

C3-C2-N1	108.8(3)	C3-C2-C18	125.2(3)
N1-C2-C18	126.0(3)	C2-C3-C4	108.6(3)
C2-C3-C10	123.2(3)	C4-C3-C10	128.2(3)
C5-C4-C9	118.9(4)	C5-C4-C3	133.5(4)
C9-C4-C3	107.6(3)	C6-C5-C4	118.7(4)
C6-C5-H5A	120.6	C4-C5-H5A	120.6
C5-C6-C7	121.2(4)	C5-C6-H6A	119.4
C7-C6-H6A	119.4	C6-C7-C8	121.8(4)
C6-C7-H7A	119.1	C8-C7-H7A	119.1
C9-C8-C7	117.2(4)	C9-C8-H8A	121.4
C7-C8-H8A	121.4	C8-C9-C4	122.2(3)
C8-C9-N1	131.1(3)	C4-C9-N1	106.6(3)
N28-C10-C3	109.9(3)	N28-C10-C11	113.5(3)
C3-C10-C11	110.8(3)	N28-C10-H10A	107.5
C3-C10-H10A	107.5	C11-C10-H10A	107.5
C12-C11-C10	114.7(3)	C12-C11-C17	106.0(3)
C10-C11-C17	110.7(3)	C12-C11-H11A	108.4
C10-C11-H11A	108.4	C17-C11-H11A	108.4
O13-C12-O14	118.9(3)	O13-C12-C11	126.5(4)
O14-C12-C11	114.6(4)	O14-C15-C16	112.1(4)
O14-C15-H15A	109.2	C16-C15-H15A	109.2
O14-C15-H15B	109.2	C16-C15-H15B	109.2
H15A-C15-H15B	107.9	C15-C16-C17	111.1(3)
C15-C16-H16A	109.4	C17-C16-H16A	109.4
C15-C16-H16B	109.4	C17-C16-H16B	109.4
H16A-C16-H16B	108.0	C18-C17-C16	110.8(3)
C18-C17-C11	111.3(3)	C16-C17-C11	110.2(3)
C18-C17-H17A	108.2	C16-C17-H17A	108.2
C11-C17-H17A	108.2	C2-C18-C17	109.8(3)
C2-C18-H18A	109.7	C17-C18-H18A	109.7
C2-C18-H18B	109.7	C17-C18-H18B	109.7
H18A-C18-H18B	108.2	C23-C22-C27	121.9(4)
C23-C22-S19	119.5(3)	C27-C22-S19	118.6(3)
C22-C23-C24	118.6(5)	C22-C23-H23A	120.7
C24-C23-H23A	120.7	C25-C24-C23	119.8(4)

C25-C24-H24A	120.1	C23-C24-H24A	120.1
C26-C25-C24	120.8(4)	C26-C25-H25A	119.6
C24-C25-H25A	119.6	C25-C26-C27	120.3(5)
C25-C26-H26A	119.8	C27-C26-H26A	119.8
C26-C27-C22	118.5(4)	C26-C27-H27A	120.7
C22-C27-H27A	120.7	C33-C31-C34	110.1(5)
C33-C31-C32	110.4(4)	C34-C31-C32	110.9(4)
C33-C31-S29	111.2(3)	C34-C31-S29	110.2(3)
C32-C31-S29	104.0(4)	C31-C32-H32A	109.5
C31-C32-H32B	109.5	H32A-C32-H32B	109.5
C31-C32-H32C	109.5	H32A-C32-H32C	109.5
H32B-C32-H32C	109.5	C31-C33-H33A	109.5
C31-C33-H33B	109.5	H33A-C33-H33B	109.5
C31-C33-H33C	109.5	H33A-C33-H33C	109.5
H33B-C33-H33C	109.5	C31-C34-H34A	109.5
C31-C34-H34B	109.5	H34A-C34-H34B	109.5
C31-C34-H34C	109.5	H34A-C34-H34C	109.5
H34B-C34-H34C	109.5	C2-N1-C9	108.3(3)
C2-N1-S19	126.9(3)	C9-N1-S19	124.4(3)
C10-N28-S29	114.0(3)	C12-O14-C15	117.7(3)
O20-S19-O21	120.03(18)	O20-S19-N1	106.01(16)
O21-S19-N1	106.01(17)	O20-S19-C22	110.00(19)
O21-S19-C22	108.05(19)	N1-S19-C22	105.79(16)
O30-S29-N28	111.47(18)	O30-S29-C31	105.9(2)
N28-S29-C31	97.2(2)		

Table 6. Torsion angles (°).

N1-C2-C3-C4	-3.1(4)	C18-C2-C3-C4	178.2(4)
N1-C2-C3-C10	177.8(3)	C18-C2-C3-C10	-0.9(6)
C2-C3-C4-C5	-177.1(5)	C10-C3-C4-C5	1.9(7)
C2-C3-C4-C9	2.6(4)	C10-C3-C4-C9	-178.4(4)
C9-C4-C5-C6	0.9(7)	C3-C4-C5-C6	-179.5(5)
C4-C5-C6-C7	0.2(7)	C5-C6-C7-C8	-0.9(8)
C6-C7-C8-C9	0.4(7)	C7-C8-C9-C4	0.8(6)
C7-C8-C9-N1	-179.5(4)	C5-C4-C9-C8	-1.4(6)
C3-C4-C9-C8	178.8(4)	C5-C4-C9-N1	178.8(4)
C3-C4-C9-N1	-0.9(4)	C2-C3-C10-N28	-140.0(4)

C4-C3-C10-N28	41.1(5)	C2-C3-C10-C11	-13.8(5)
C4-C3-C10-C11	167.3(4)	N28-C10-C11-C12	48.6(4)
C3-C10-C11-C12	-75.6(4)	N28-C10-C11-C17	168.5(3)
C3-C10-C11-C17	44.3(4)	C10-C11-C12-O13	-2.6(5)
C17-C11-C12-O13	-125.0(4)	C10-C11-C12-O14	173.9(3)
C17-C11-C12-O14	51.5(4)	O14-C15-C16-C17	38.1(5)
C15-C16-C17-C18	-106.1(4)	C15-C16-C17-C11	17.5(5)
C12-C11-C17-C18	61.6(4)	C10-C11-C17-C18	-63.4(4)
C12-C11-C17-C16	-61.7(4)	C10-C11-C17-C16	173.3(3)
C3-C2-C18-C17	-15.8(5)	N1-C2-C18-C17	165.7(3)
C16-C17-C18-C2	169.5(3)	C11-C17-C18-C2	46.6(4)
C27-C22-C23-C24	-0.1(6)	S19-C22-C23-C24	179.9(3)
C22-C23-C24-C25	-0.5(6)	C23-C24-C25-C26	0.7(6)
C24-C25-C26-C27	-0.2(7)	C25-C26-C27-C22	-0.4(6)
C23-C22-C27-C26	0.6(6)	S19-C22-C27-C26	-179.5(3)
C3-C2-N1-C9	2.6(4)	C18-C2-N1-C9	-178.8(3)
C3-C2-N1-S19	175.3(3)	C18-C2-N1-S19	-6.1(5)
C8-C9-N1-C2	179.3(4)	C4-C9-N1-C2	-0.9(4)
C8-C9-N1-S19	6.4(6)	C4-C9-N1-S19	-173.8(3)
C3-C10-N28-S29	-153.3(2)	C11-C10-N28-S29	82.1(3)
O13-C12-O14-C15	-177.7(4)	C11-C12-O14-C15	5.6(5)
C16-C15-O14-C12	-53.7(5)	C2-N1-S19-O20	22.8(4)
C9-N1-S19-O20	-165.6(3)	C2-N1-S19-O21	151.4(3)
C9-N1-S19-O21	-37.0(3)	C2-N1-S19-C22	-94.0(3)
C9-N1-S19-C22	77.6(3)	C23-C22-S19-O20	152.3(3)
C27-C22-S19-O20	-27.7(4)	C23-C22-S19-O21	19.5(3)
C27-C22-S19-O21	-160.4(3)	C23-C22-S19-N1	-93.6(3)
C27-C22-S19-N1	86.4(3)	C10-N28-S29-O30	-70.8(3)
C10-N28-S29-C31	178.9(3)	C33-C31-S29-O30	-52.4(4)
C34-C31-S29-O30	-174.7(4)	C32-C31-S29-O30	66.4(4)
C33-C31-S29-N28	62.4(4)	C34-C31-S29-N28	-59.9(4)
C32-C31-S29-N28	-178.7(3)		

Table 7. Anisotropic atomic displacement parameters (Å^2).

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C2	0.0189(15)	0.0266(16)	0.024(2)	-0.0031(15)	0.0009(16)	0.0040(14)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C3	0.0188(15)	0.0262(17)	0.029(2)	0.0000(15)	-0.0003(17)	0.0017(14)
C4	0.0191(17)	0.0300(18)	0.037(3)	-0.0020(18)	0.0007(17)	0.0029(14)
C5	0.031(2)	0.0274(19)	0.055(3)	-0.007(2)	0.007(2)	-0.0052(15)
C6	0.032(2)	0.039(2)	0.064(4)	-0.005(2)	0.016(2)	-0.0071(18)
C7	0.030(2)	0.040(2)	0.046(3)	0.003(2)	0.012(2)	0.0017(17)
C8	0.0277(19)	0.0324(19)	0.036(3)	-0.0031(19)	0.0039(19)	0.0048(16)
C9	0.0199(15)	0.0259(16)	0.030(2)	0.0005(18)	-0.0007(18)	0.0015(12)
C10	0.0212(15)	0.0231(15)	0.034(2)	-0.0039(17)	-0.0020(17)	0.0013(13)
C11	0.0230(17)	0.0235(16)	0.028(2)	-0.0020(16)	0.0000(16)	0.0032(13)
C12	0.0244(18)	0.0229(16)	0.034(3)	-0.0030(16)	-0.0058(17)	0.0029(13)
C15	0.031(2)	0.043(2)	0.049(3)	-0.002(2)	0.012(2)	-0.0019(18)
C16	0.038(2)	0.033(2)	0.033(3)	0.0037(19)	0.008(2)	-0.0001(17)
C17	0.0247(18)	0.0263(17)	0.028(2)	0.0006(16)	-0.0007(16)	0.0033(14)
C18	0.0249(18)	0.0243(16)	0.032(2)	-0.0002(16)	0.0010(17)	-0.0004(13)
C22	0.0274(18)	0.0198(16)	0.035(3)	-0.0046(16)	-0.0032(18)	-0.0008(14)
C23	0.0291(18)	0.0253(17)	0.043(3)	0.0017(19)	0.000(2)	0.0010(14)
C24	0.026(2)	0.030(2)	0.068(4)	0.004(2)	-0.001(2)	0.0017(16)
C25	0.041(2)	0.0270(19)	0.061(4)	0.004(2)	-0.016(2)	0.0027(17)
C26	0.058(3)	0.036(2)	0.037(3)	0.003(2)	-0.011(2)	0.0080(19)
C27	0.042(2)	0.031(2)	0.034(3)	-0.0048(19)	0.003(2)	0.0053(17)
C31	0.040(2)	0.0241(18)	0.058(3)	-0.004(2)	0.011(2)	-0.0021(17)
C32	0.098(4)	0.024(2)	0.099(5)	-0.016(3)	0.009(5)	-0.005(2)
C33	0.057(3)	0.040(2)	0.061(4)	0.015(3)	0.003(3)	0.005(2)
C34	0.066(3)	0.046(3)	0.096(6)	0.010(3)	0.034(4)	-0.006(2)
N1	0.0245(15)	0.0218(13)	0.0259(18)	-0.0012(13)	0.0008(14)	0.0016(11)
N28	0.0341(17)	0.0215(14)	0.034(2)	-0.0052(14)	0.0030(16)	-0.0002(13)
O13	0.0363(15)	0.0394(15)	0.040(2)	0.0073(15)	-0.0109(14)	0.0005(12)
O14	0.0210(12)	0.0398(14)	0.049(2)	-0.0008(16)	-0.0025(15)	-0.0003(10)
O20	0.0279(13)	0.0275(12)	0.043(2)	-0.0067(13)	0.0009(13)	-0.0018(10)
O30	0.056(2)	0.0441(17)	0.045(2)	-0.0101(17)	0.0162(17)	0.0039(15)
S19	0.0250(4)	0.0226(4)	0.0297(5)	-0.0043(4)	-0.0021(4)	0.0014(3)
S29	0.0328(5)	0.0266(4)	0.0465(8)	-0.0104(5)	0.0004(5)	-0.0011(4)
O21	0.0405(15)	0.0353(14)	0.0231(16)	-0.0055(13)	-0.0047(13)	0.0067(12)