Organic Chemistry Frontiers

One-pot three-component strategy for highly diastereoselective synthesis of spirocycloalkane fused pyrazolo[3,4-*b*]pyridine derivatives using recyclable solid acid as catalyst

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Electronic Supplementary Information (ESI)

Supplementary Information Available: complete product characterization data, analytical details.

Preparation and characterization of solid acid (C-SO_3H) catalyst

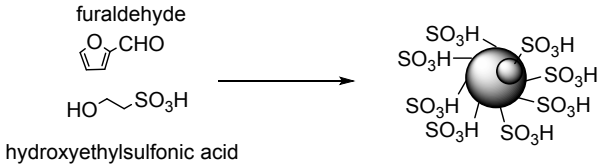


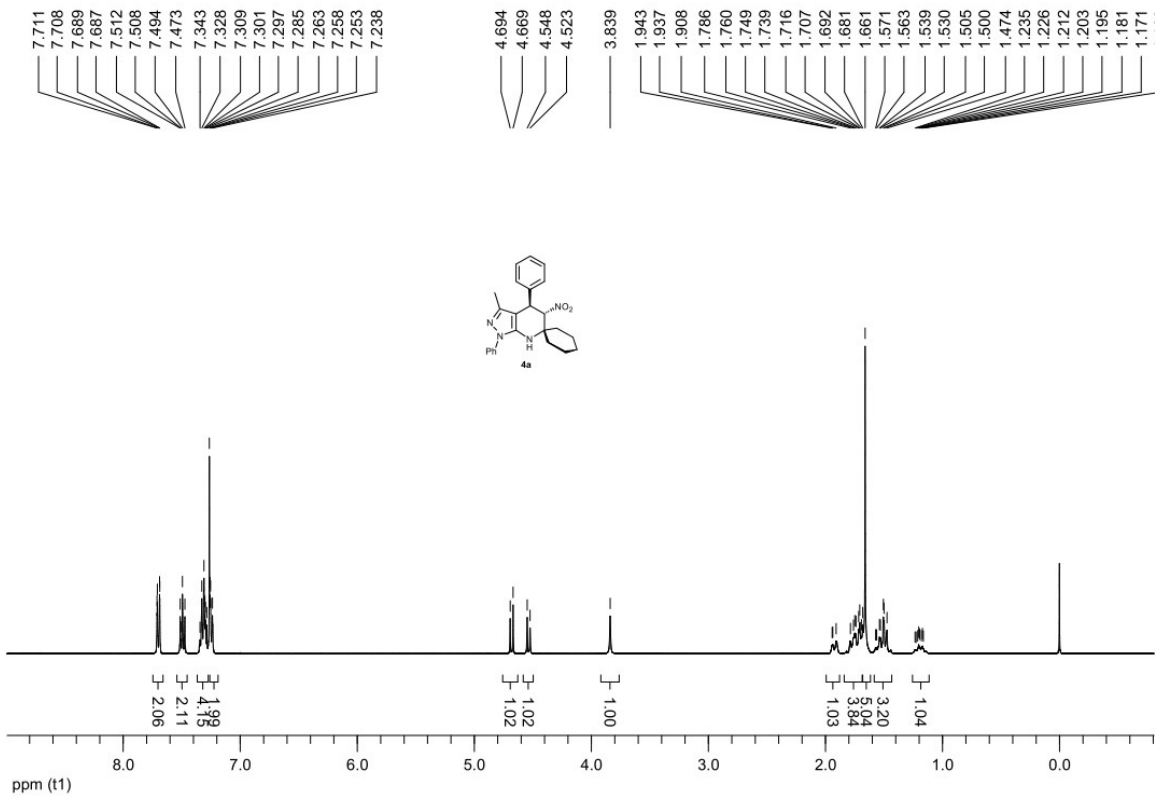
Fig. 1. The synthesis of solid acid with sulfonic acid groups

According to literature method,[1] the mixture of the 10 g furaldehyde, 5 g hydroxyethylsulfonic acid and 80 mL deionized water was placed in 100 mL Teflon-lined stainless steel autoclaves, which were heated in an oven at 200 °C for 5 h. The resulting products were filtered, washed with water and methanol, and dried in a vacuum oven at 110 °C for 5 h (Fig. 1). The acidity of the carbonaceous material was 2.4 mmol/g, which was determined through the neutralization titration. This carbonaceous material owned much higher acidity than that of the sulfonated carbonaceous materials, which were obtained via the sulfonation of the inactive carbon. The acid strength of the catalyst was determined by thermodesorption of chemisorbed ammonia (NH_3-TPD). The result showed that the catalyst had great acid strength in which ammonia was desorbed at 400 to 600 °C. IR(KBr) [cm^{-1}] = 3020 (Ar-H), 1704 (C=O), 1604 (C=C), 1204 (C-O), 1040 (S=O), 940 (S-O).

References:

1 X. Z. Liang, M. F. Zeng and C. Z. Qi, *Carbon*, 2010, **48**, 1844-1848.

^1H and ^{13}C NMR Spectra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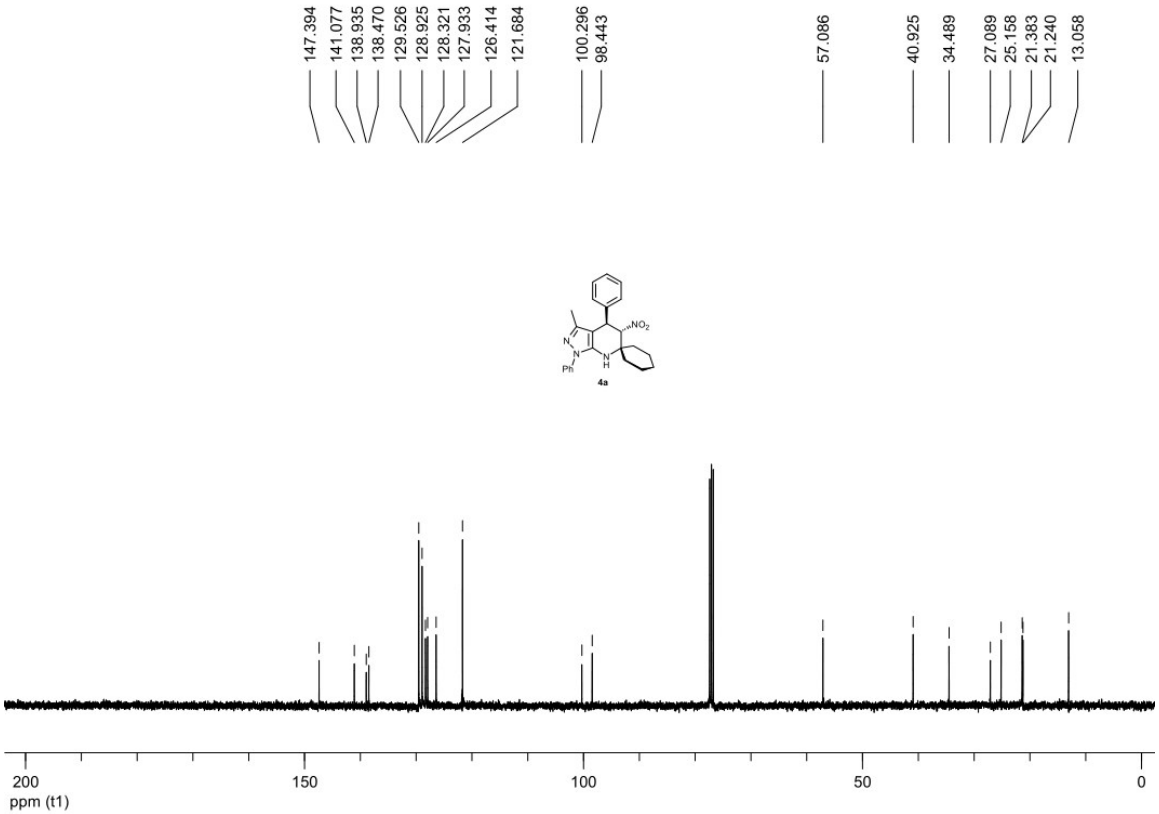
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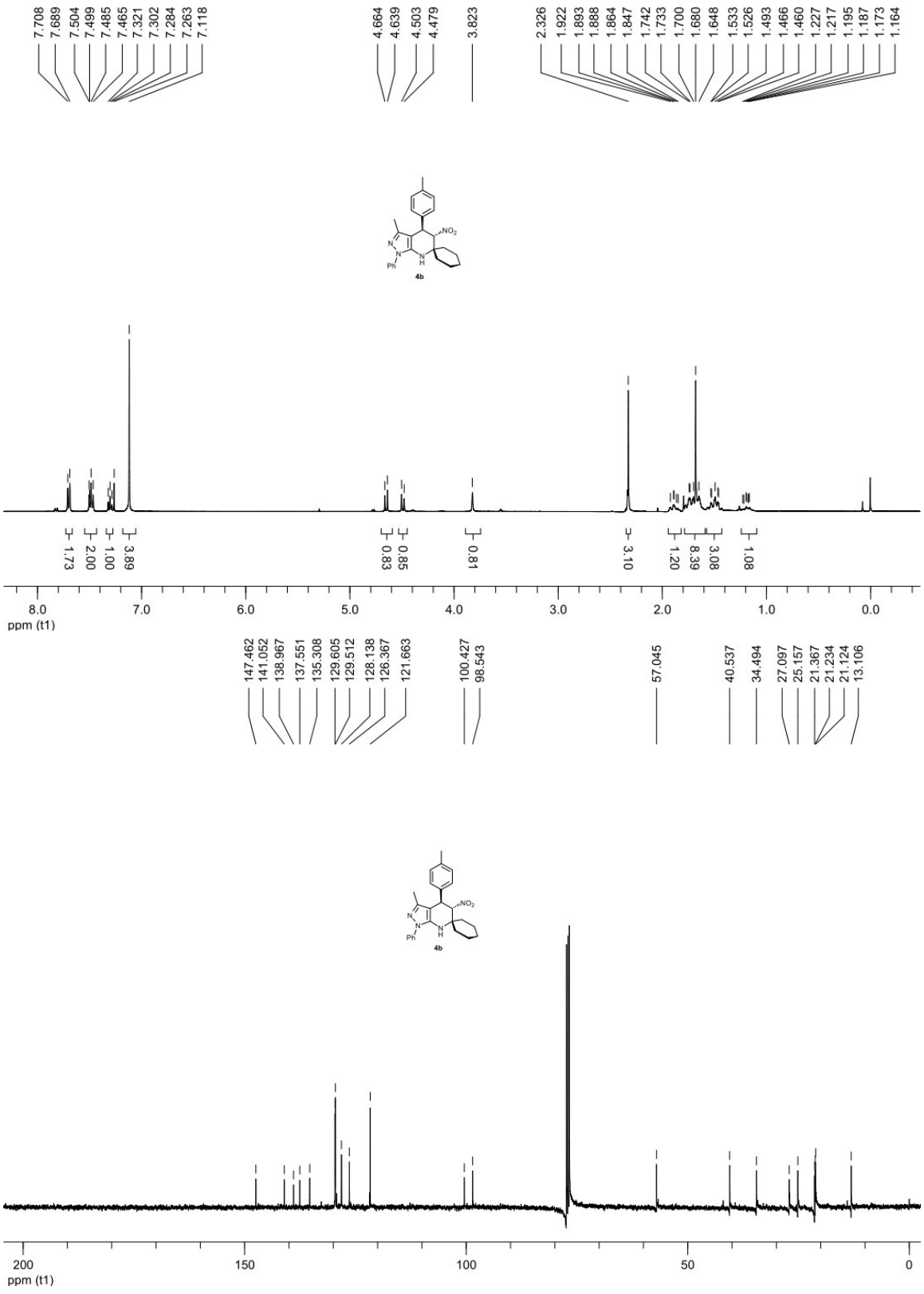
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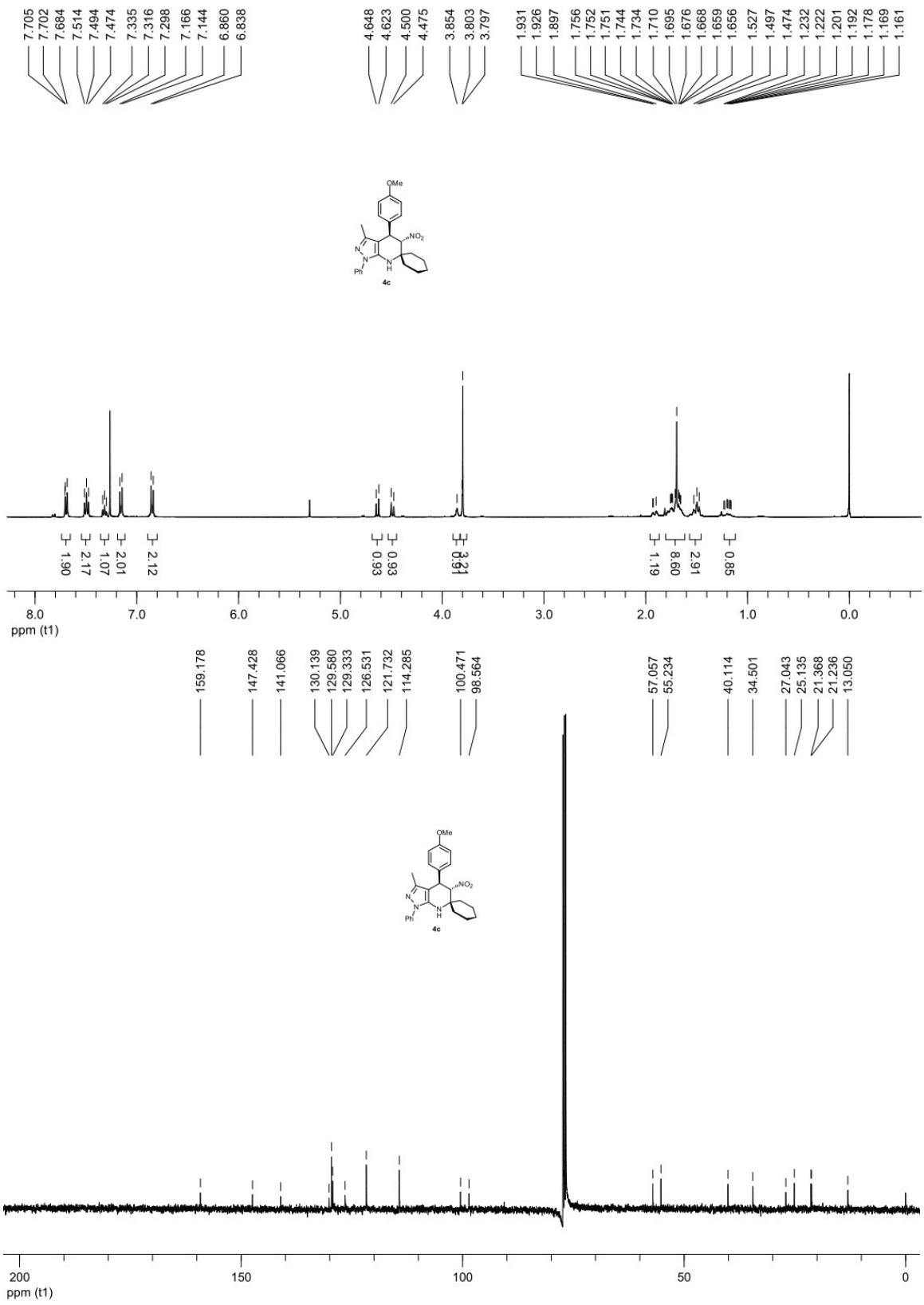
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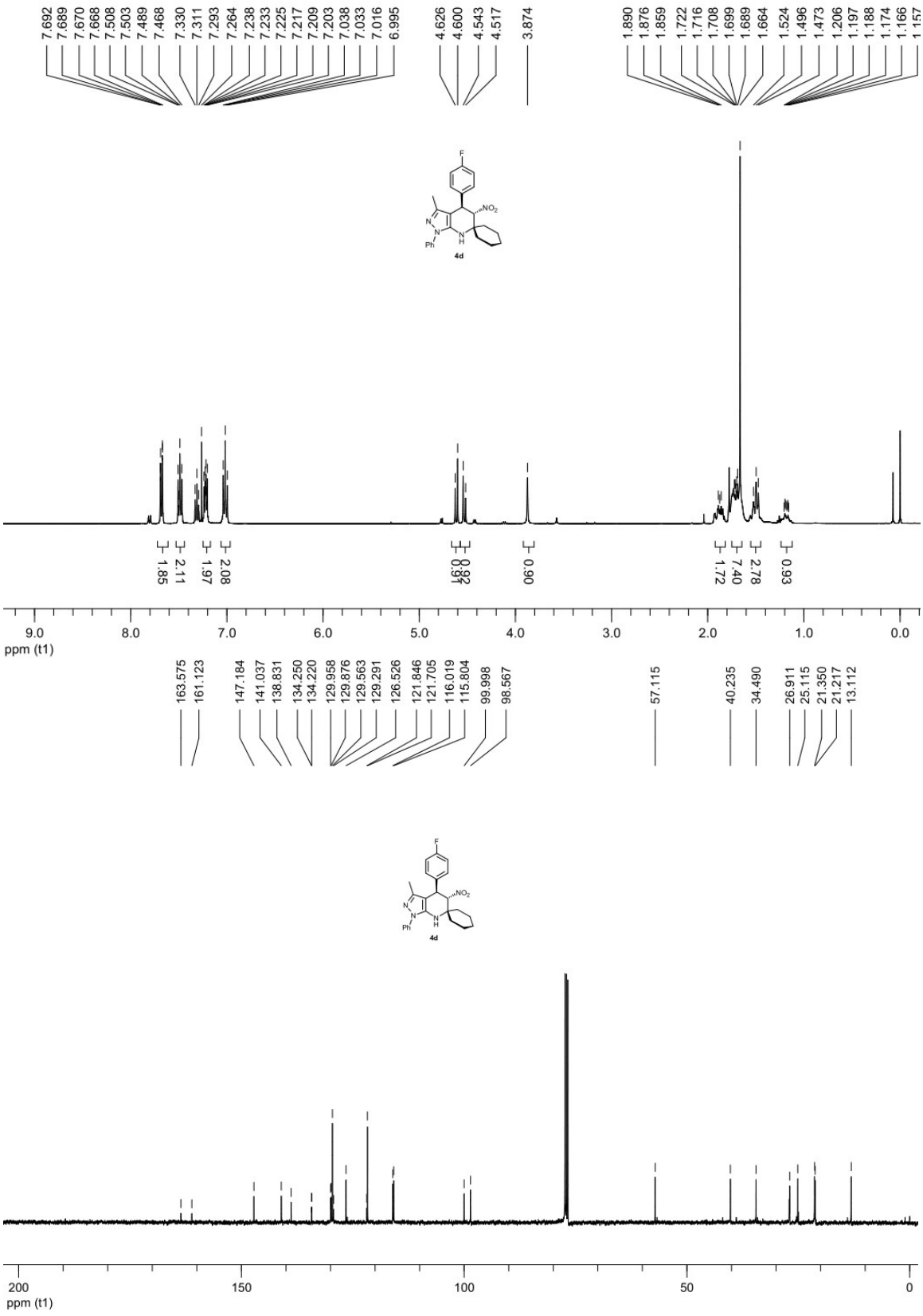
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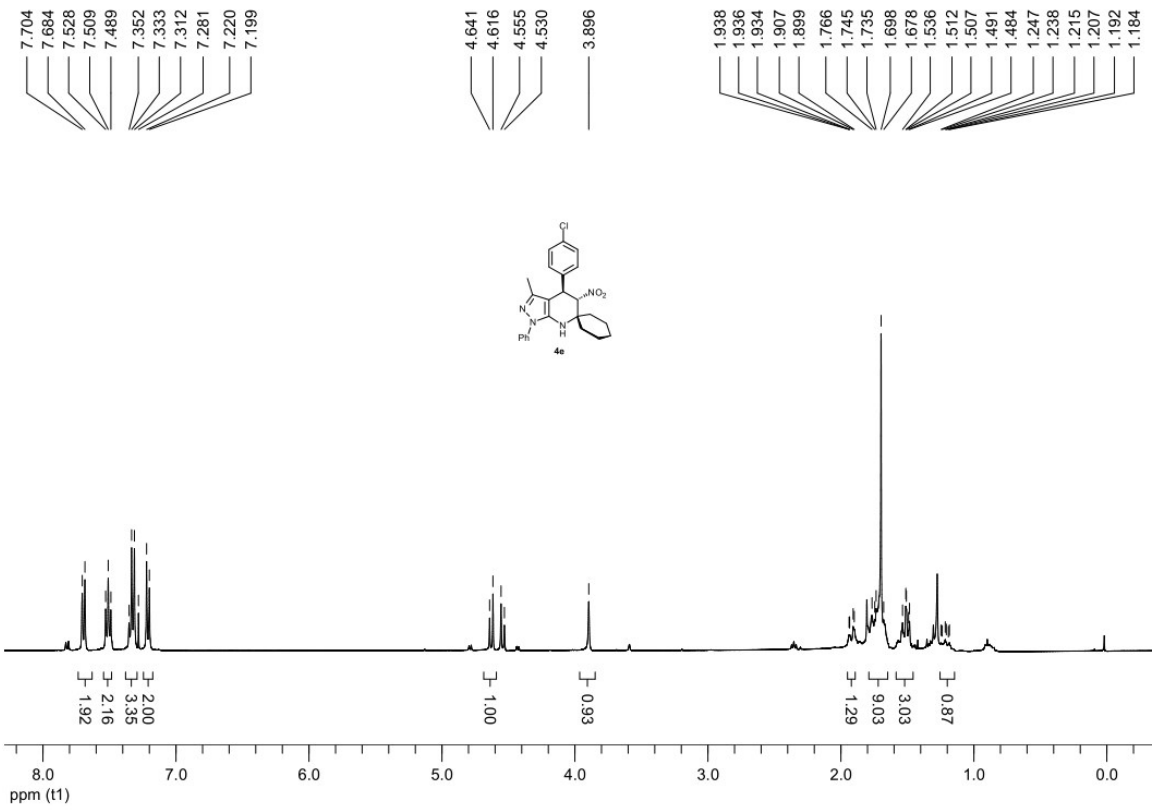
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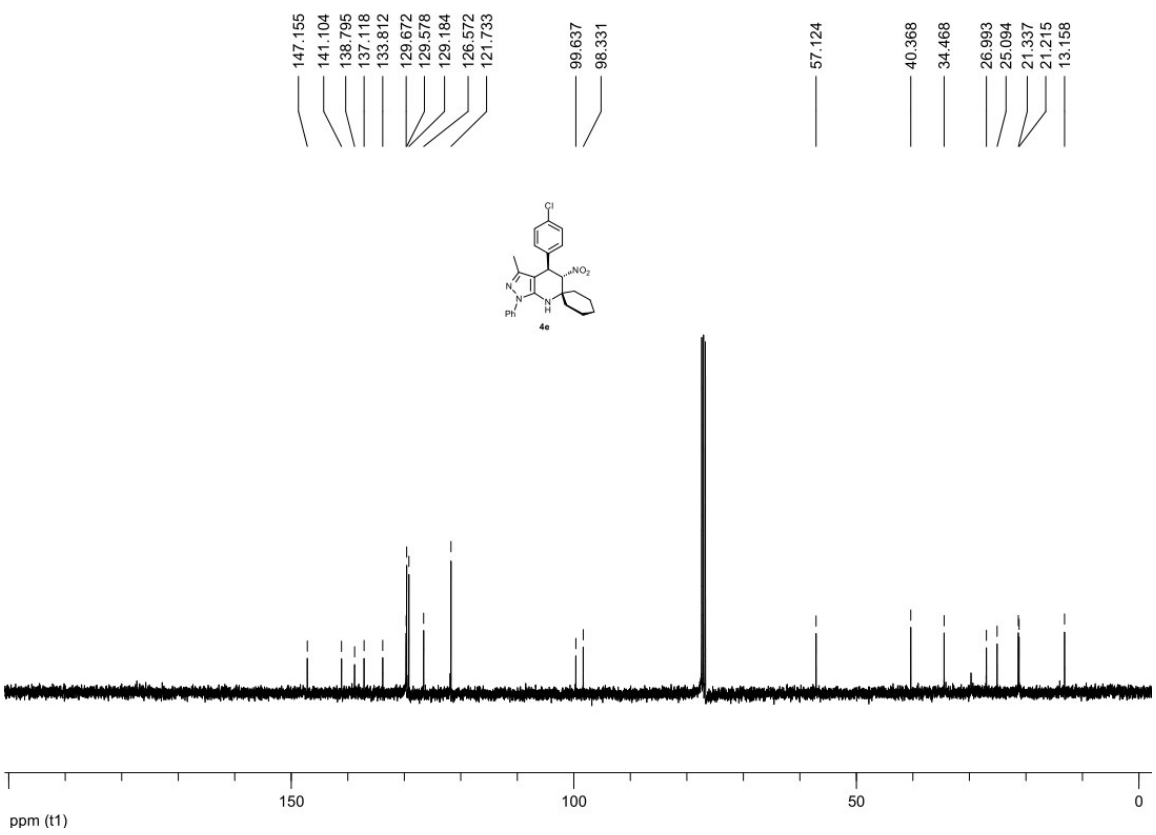
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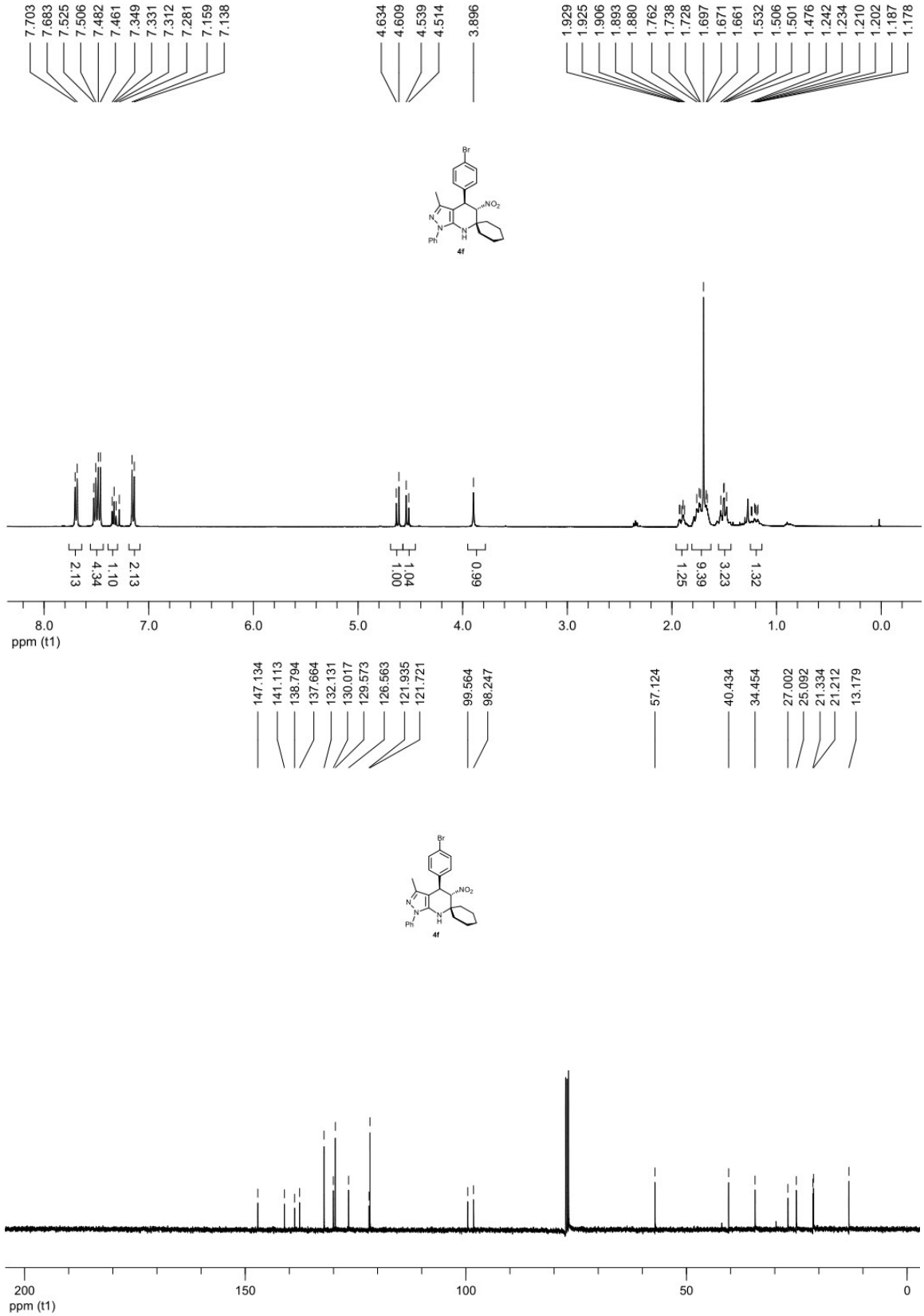
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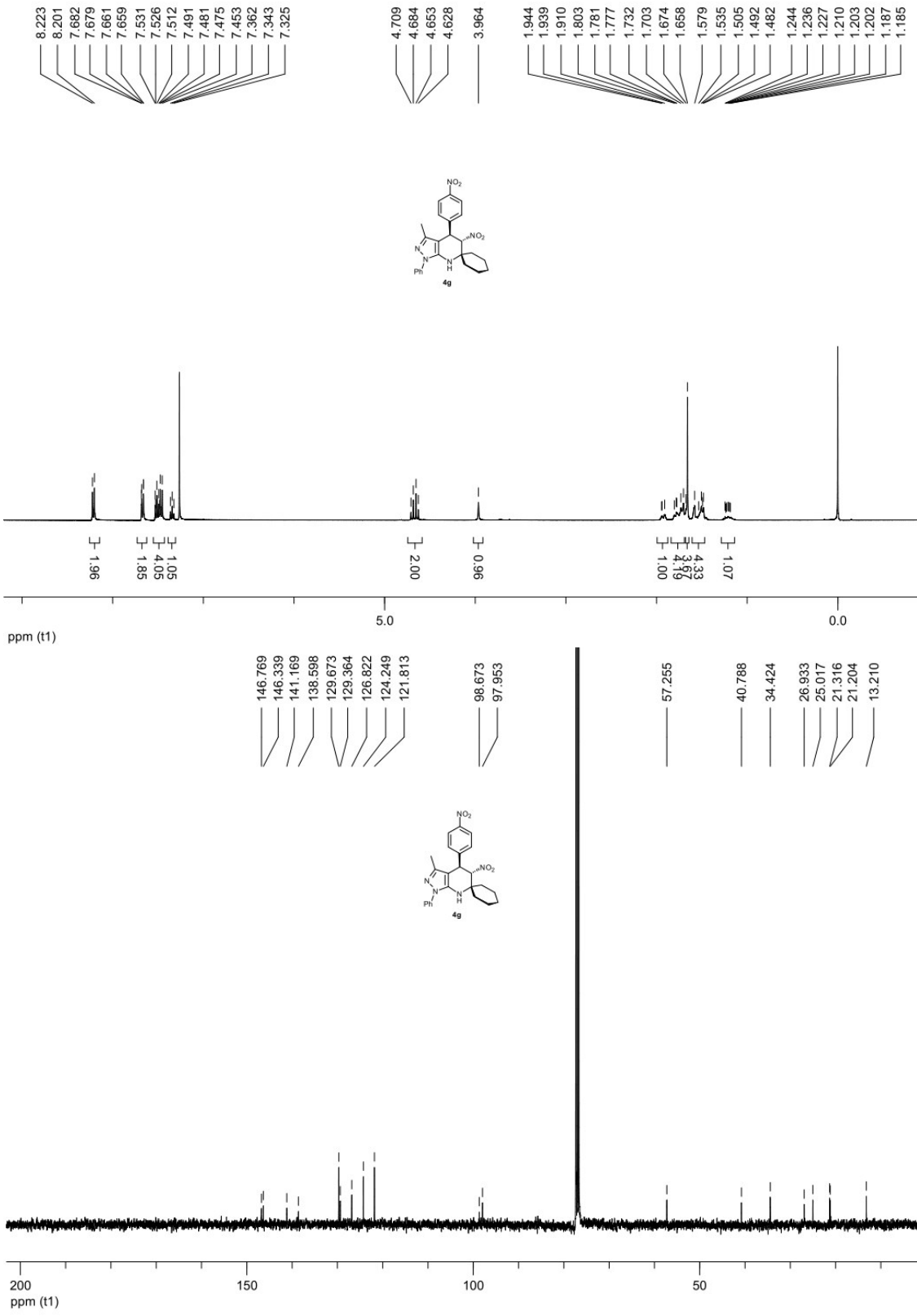
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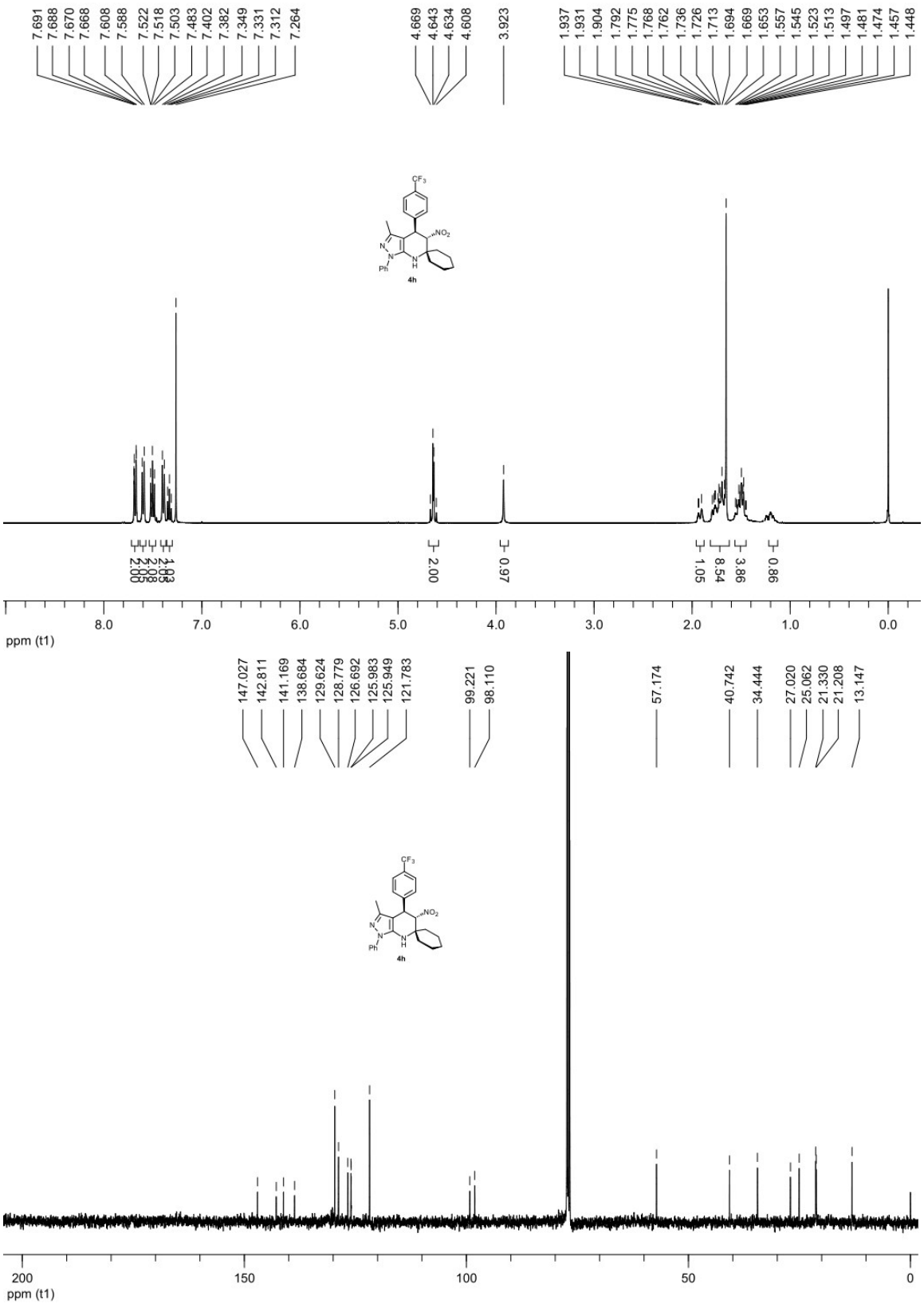
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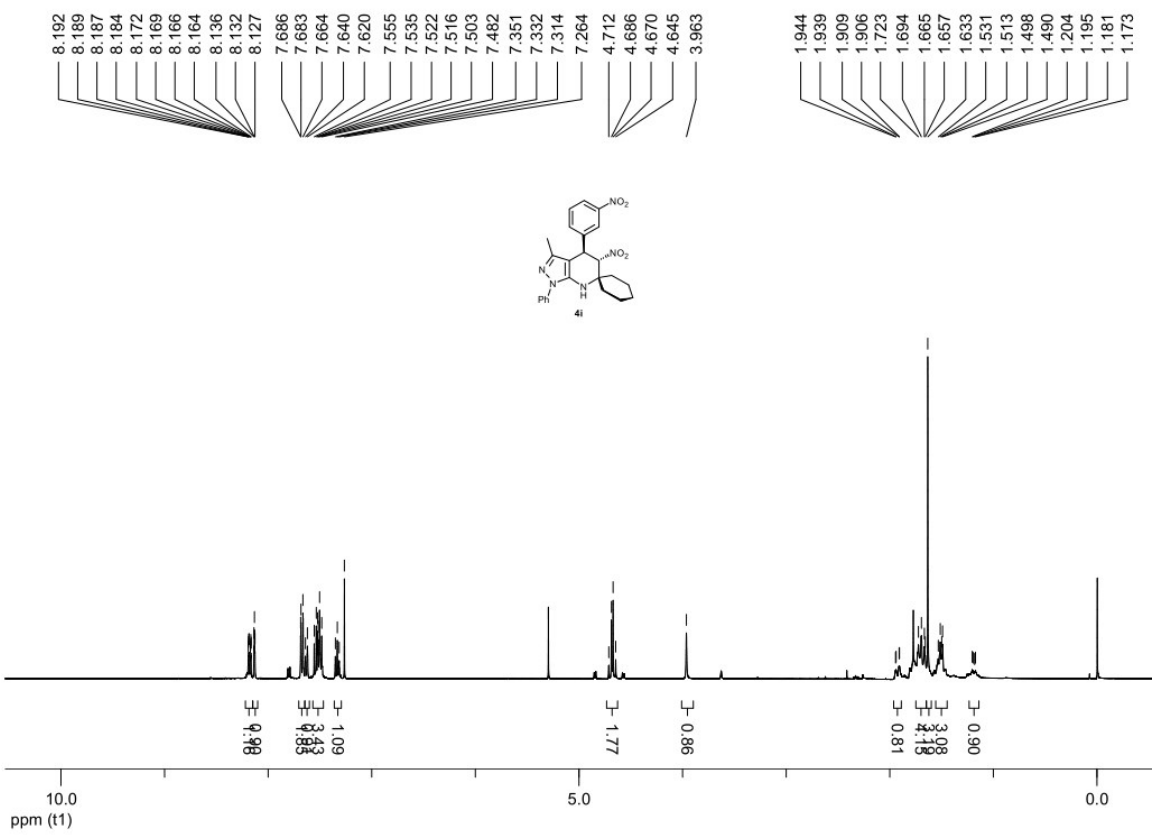
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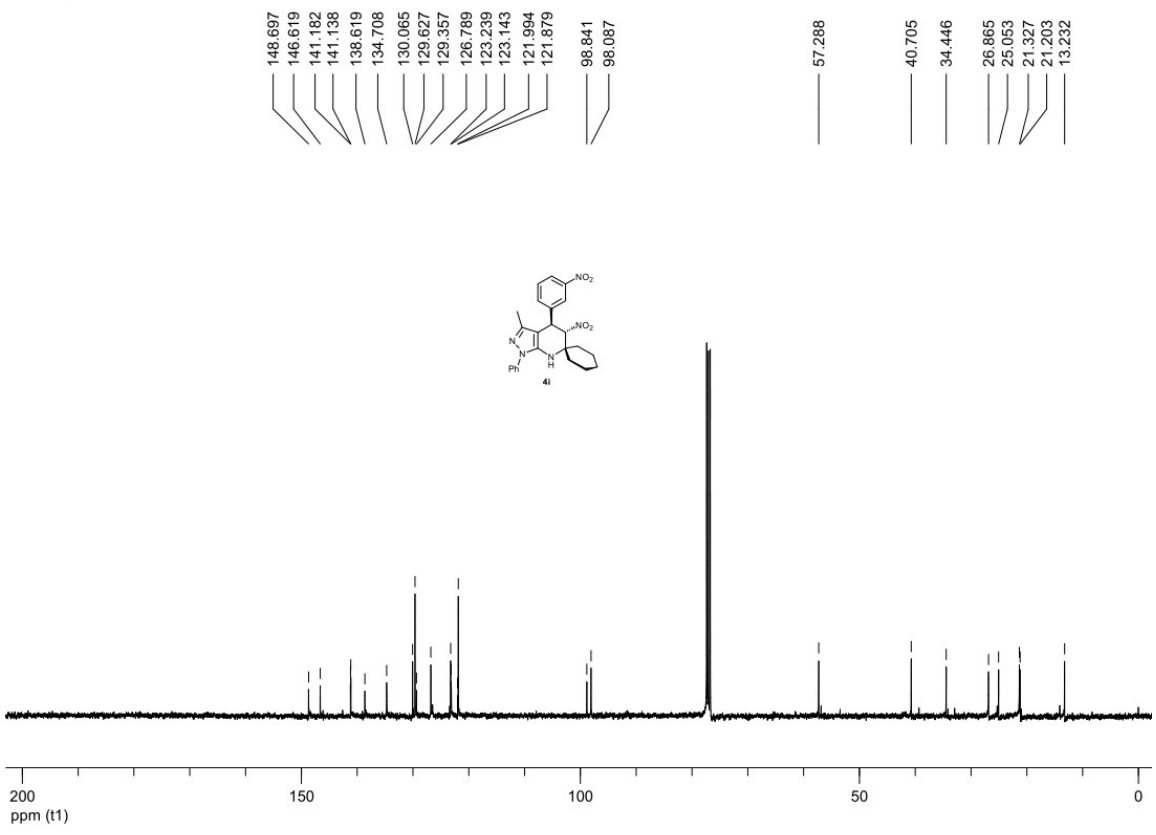
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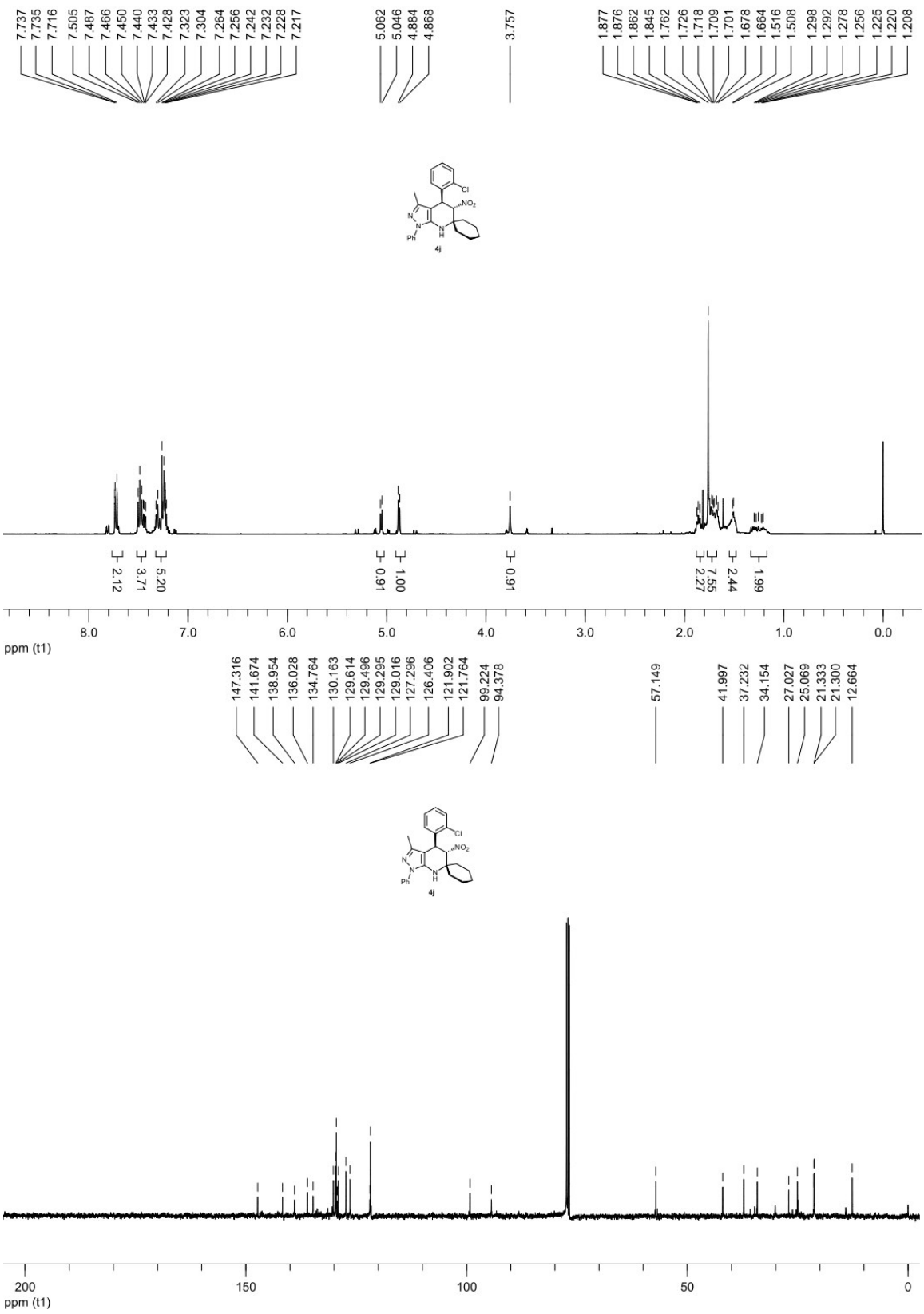
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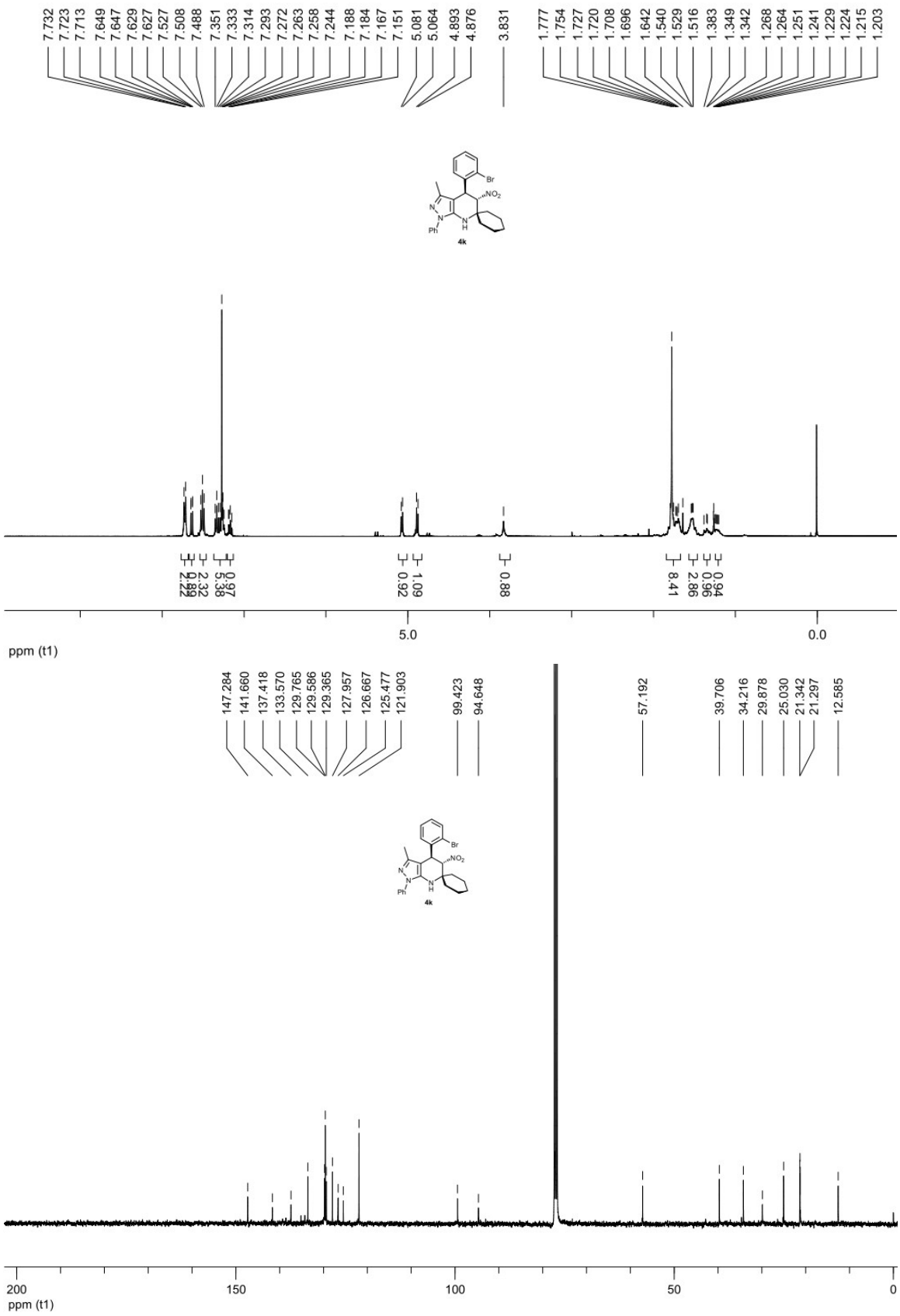
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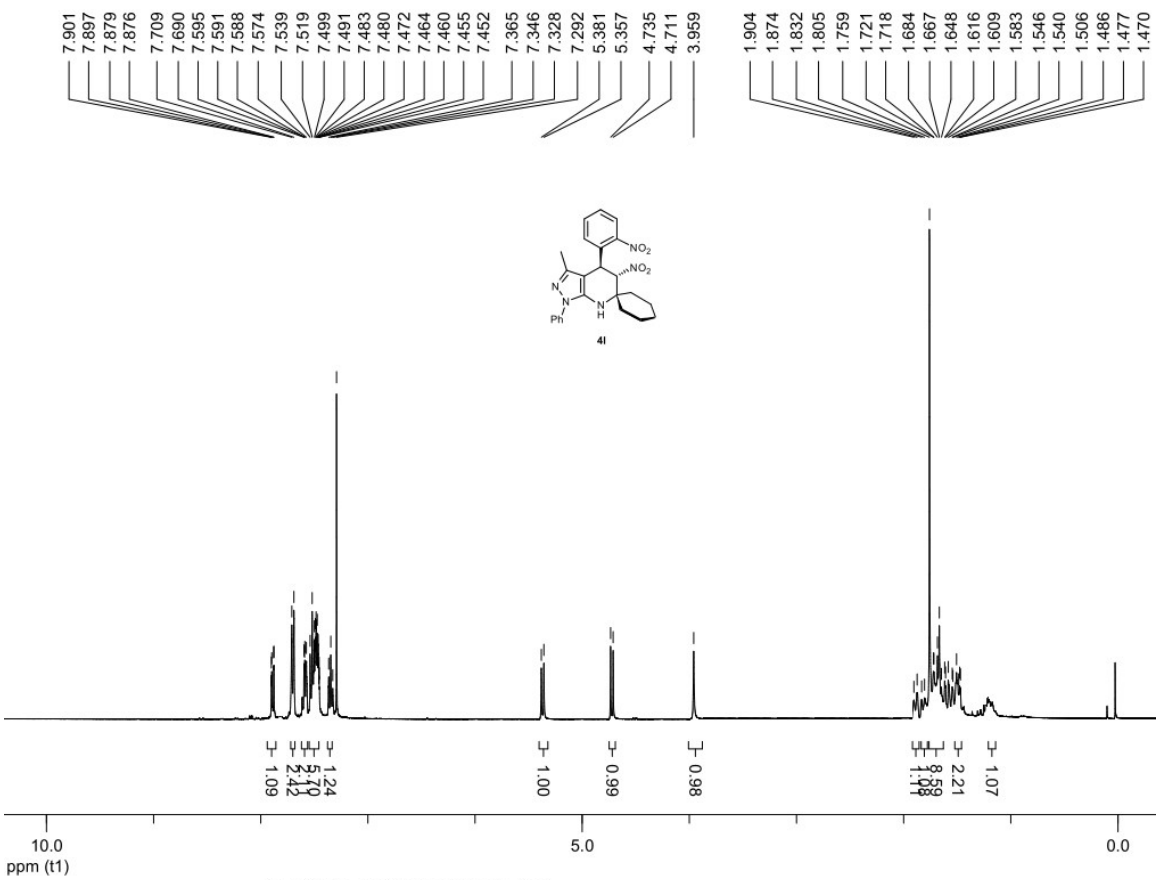
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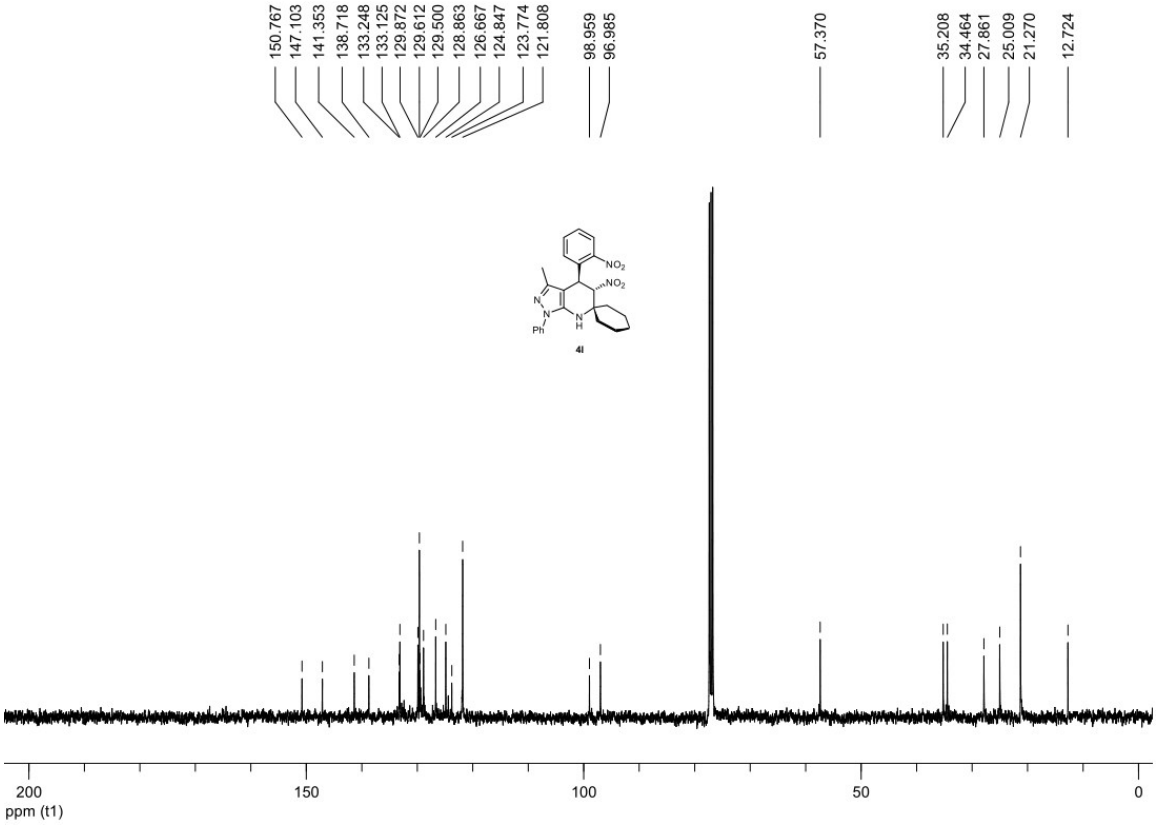
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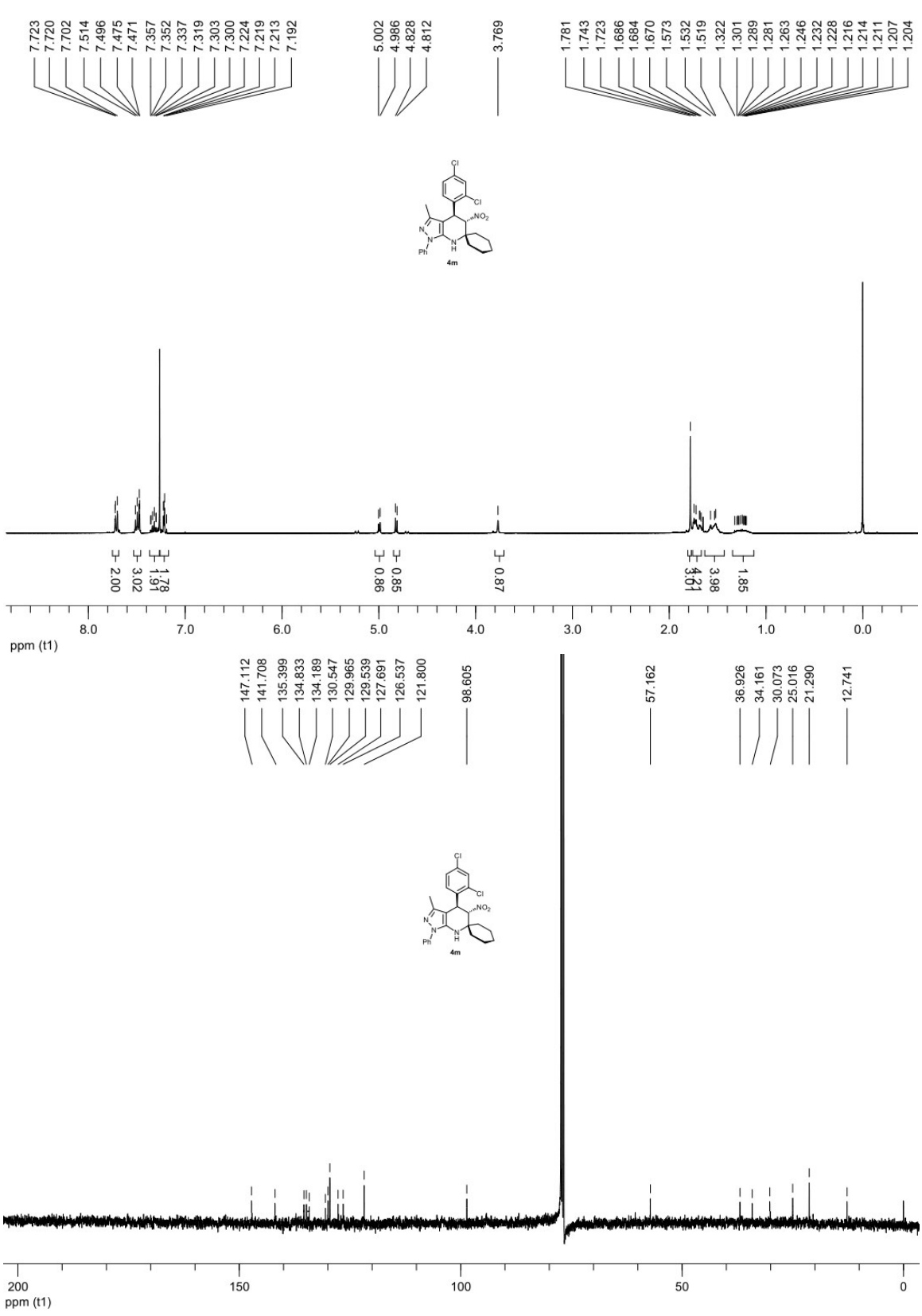
129.872
129.612
129.500
128.863
126.667
124.847
123.774
121.808
98.959
96.985
57.370
35.208
34.464
27.861
25.009
21.270
12.724
4l
200
150
100
50
0
ppm (t1)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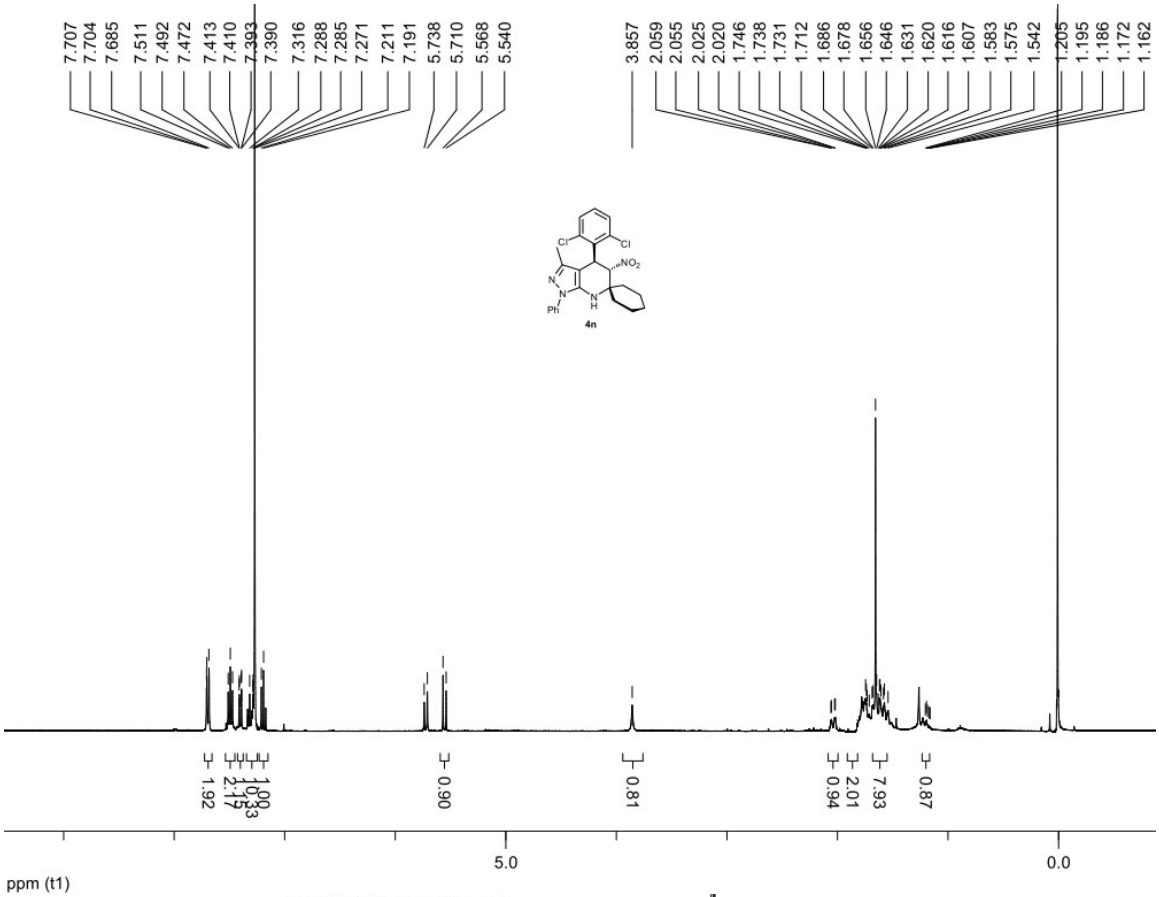
7.720
7.702
7.514
7.496
7.475
7.471
7.357
7.352
7.337
7.319
7.303
7.300
7.224
7.219
7.213
7.192
5.002
4.986
4.828
4.812
3.769
1.781
1.743
1.723
1.686
1.684
1.670
1.573
1.532
1.519
1.322
1.301
1.289
1.281
1.263
1.246
1.232
1.228
1.216
1.214
1.211
1.207
1.204
4m
2.00
3.02
1.91
1.78
0.86
0.85
0.87
3.01
4.21
3.98
1.85
ppm (t1)
147.112
141.708
135.399
134.833
134.189
130.547
129.965
129.539
127.691
126.537
121.800
98.605
57.162
36.926
34.161
30.073
25.016
21.290
12.741
4m
ppm (t1)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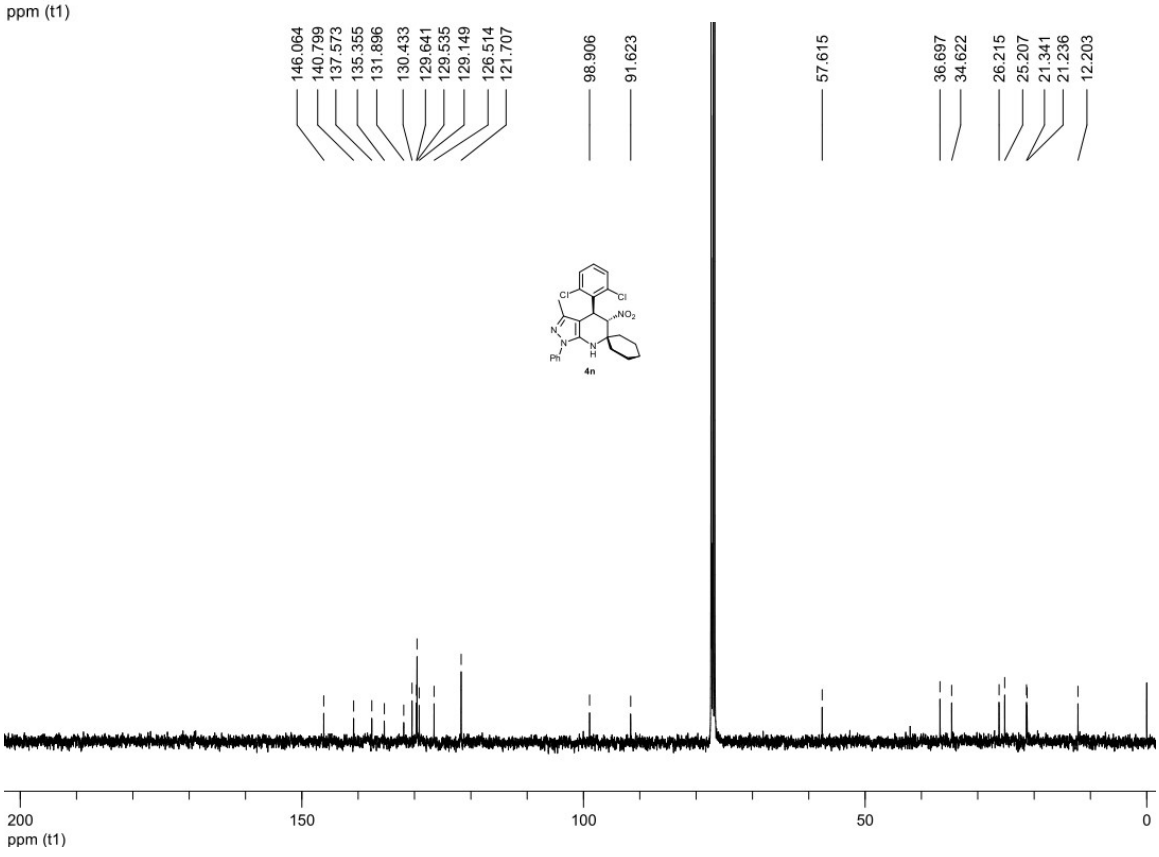
7.685
7.511
7.492
7.472
7.413
7.410
7.393
7.390
7.316
7.288
7.285
7.271
7.211
7.191
5.738
5.710
5.568
5.540
3.857
2.059
2.055
2.025
2.020
1.746
1.738
1.731
1.712
1.686
1.678
1.656
1.646
1.631
1.620
1.616
1.607
1.583
1.575
1.542
1.205
1.195
1.186
1.172
1.162
Cl
Cl
NO2
Ph
4n
1.92
2.17
1.83
1.00
0.90
0.81
0.94
2.01
7.93
0.87
5.0
0.0
ppm (t1)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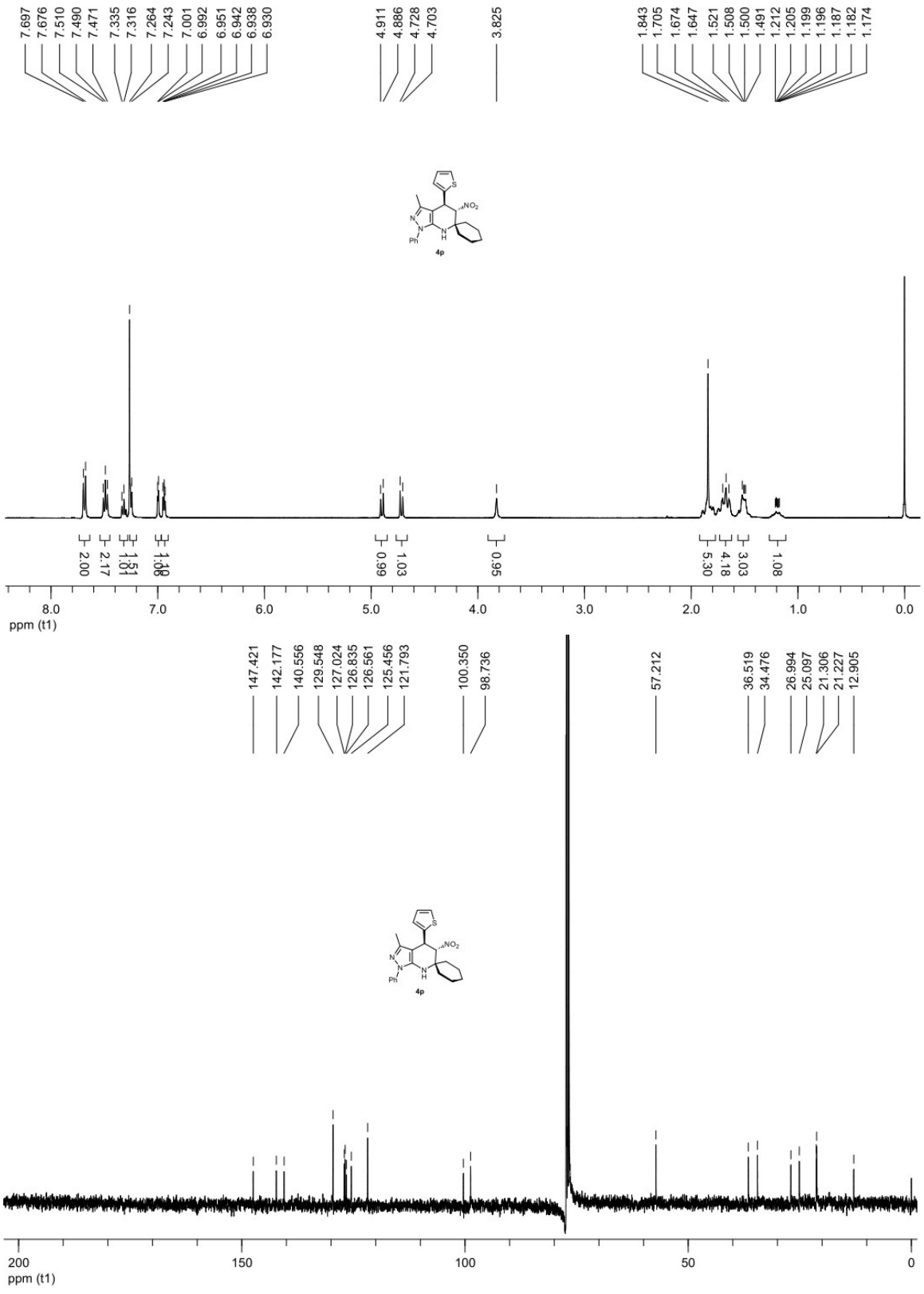
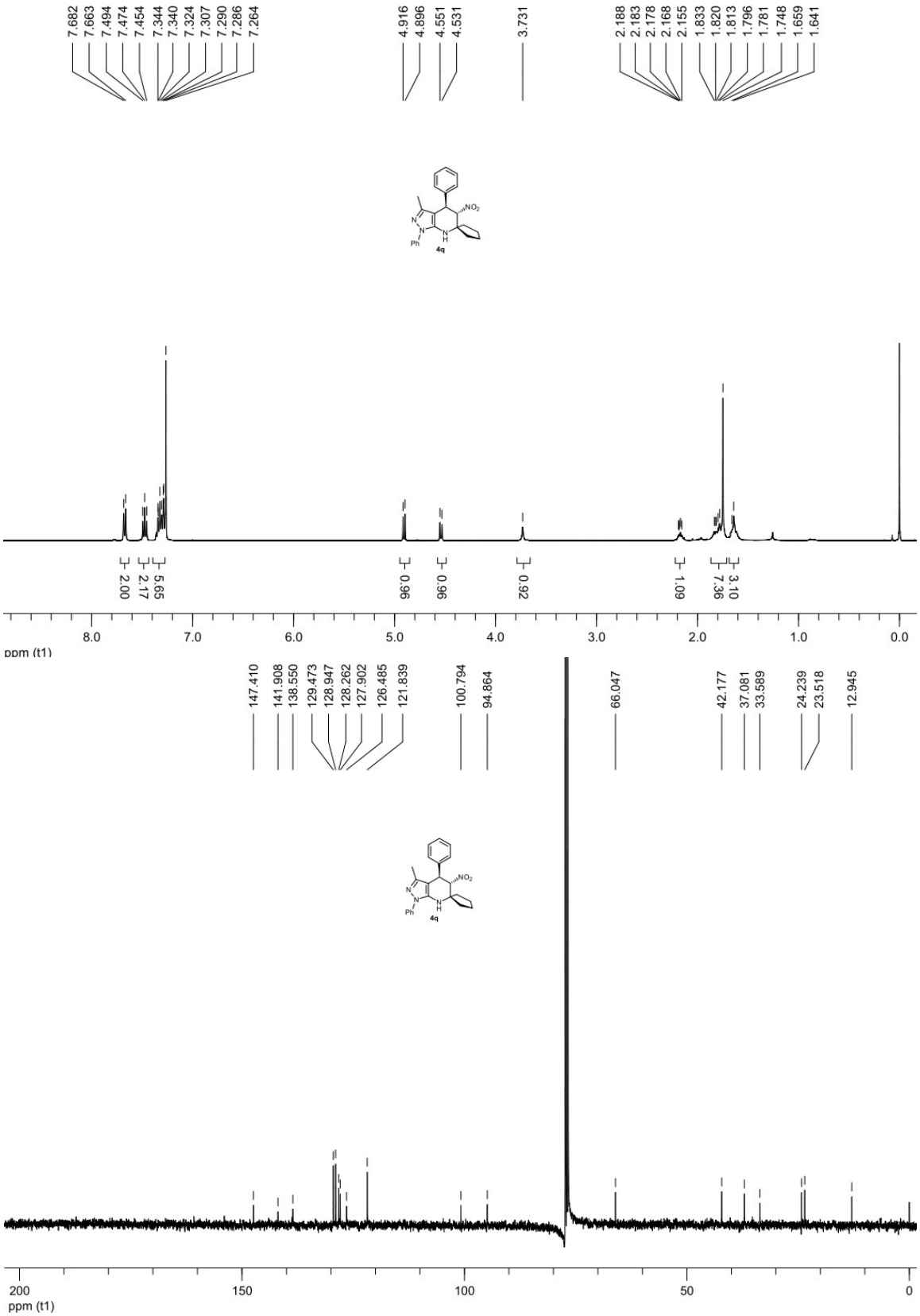
140.799
137.573
135.355
131.896
130.433
129.641
129.535
129.149
126.514
121.707
98.906
91.623
57.615
36.697
34.622
26.215
25.207
21.341
21.236
12.203
Cl
Cl
NO2
Ph
4n
200
150
100
50
0
ppm (t1)


7.697
7.676
7.510
7.490
7.471
7.335
7.316
7.264
7.243
7.001
6.992
6.951
6.942
6.938
6.930
4.911
4.886
4.728
4.703
3.825
1.843
1.705
1.674
1.647
1.521
1.508
1.500
1.491
1.212
1.205
1.199
1.196
1.187
1.182
1.174
4p
2.00
2.17
1.51
1.01
1.10
0.99
1.03
0.95
5.30
4.18
3.03
1.08
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
147.421
142.177
140.556
129.548
127.024
126.835
126.561
125.456
121.793
100.350
98.736
57.212
36.519
34.476
26.994
25.097
21.306
21.227
12.905
4p
200
150
100
50
0
ppm (t1)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7.663
7.494
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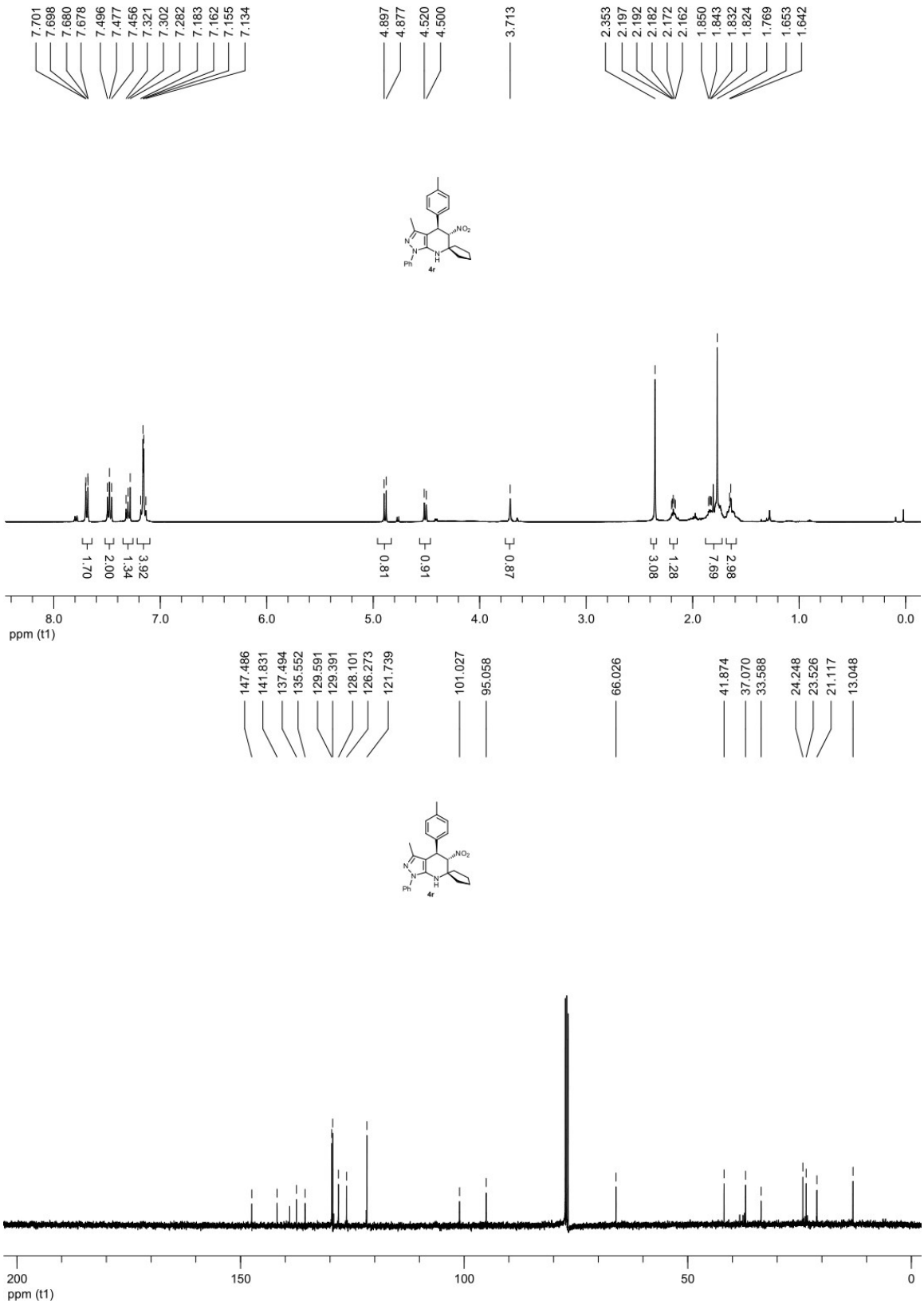
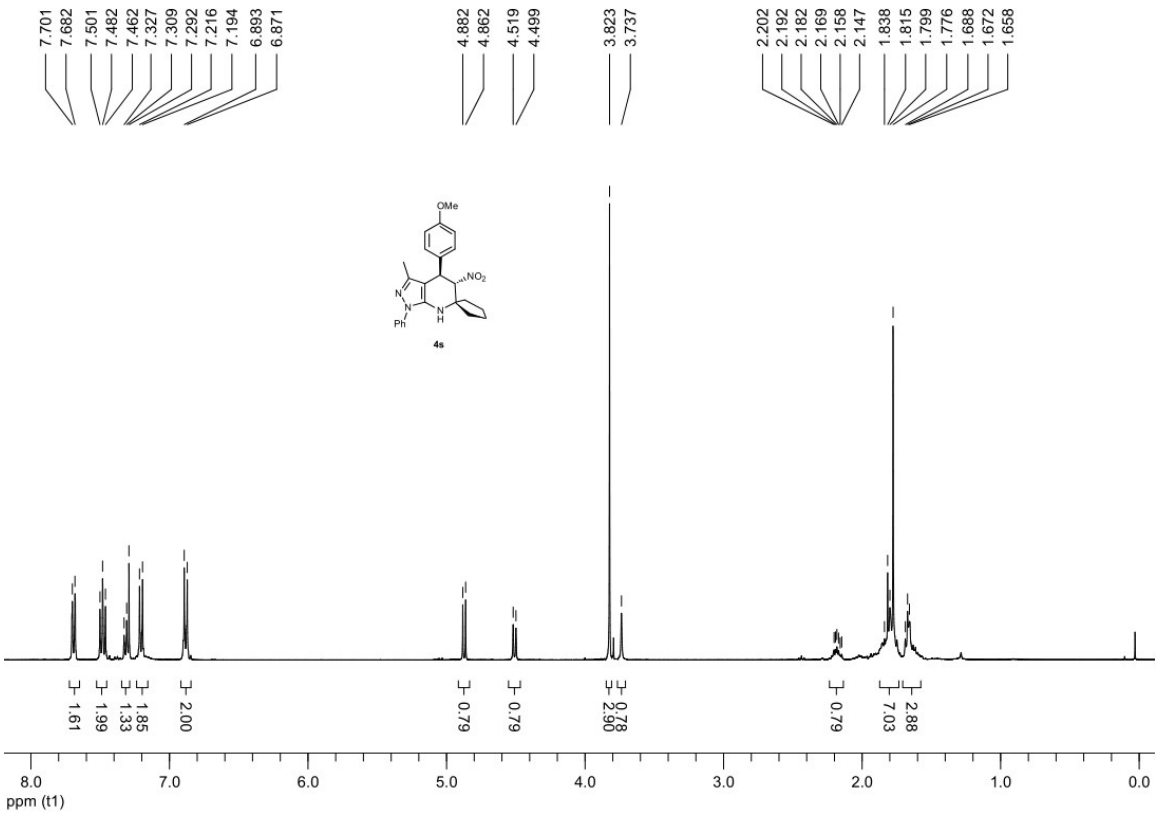
7.344
7.340
7.324
7.307
7.290
7.286
7.264
4.916
4.896
4.551
4.531
3.731
2.188
2.183
2.178
2.168
2.155
1.833
1.820
1.813
1.796
1.781
1.748
1.659
1.641
4q
2.00
2.17
5.65
0.96
0.96
0.92
1.09
7.36
3.10
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
147.410
141.908
138.550
129.473
128.947
128.262
127.902
126.485
121.839
100.794
94.864
66.047
42.177
37.081
33.589
24.239
23.518
12.945
4q
200
150
100
50
0
ppm (t1)


7.701
7.698
7.680
7.678
7.496
7.477
7.456
7.321
7.302
7.282
7.183
7.162
7.155
7.134
4.897
4.877
4.520
4.500
3.713
2.353
2.197
2.192
2.182
2.172
2.162
1.850
1.843
1.832
1.824
1.769
1.653
1.642
4r
1.70
2.00
1.34
3.92
0.81
0.91
0.87
3.08
1.28
7.69
2.98
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
147.486
141.831
137.494
135.552
129.591
129.391
128.101
126.273
121.739
101.027
95.058
66.026
41.874
37.070
33.588
24.248
23.526
21.117
13.048
4r
200
150
100
50
0
ppm (t1)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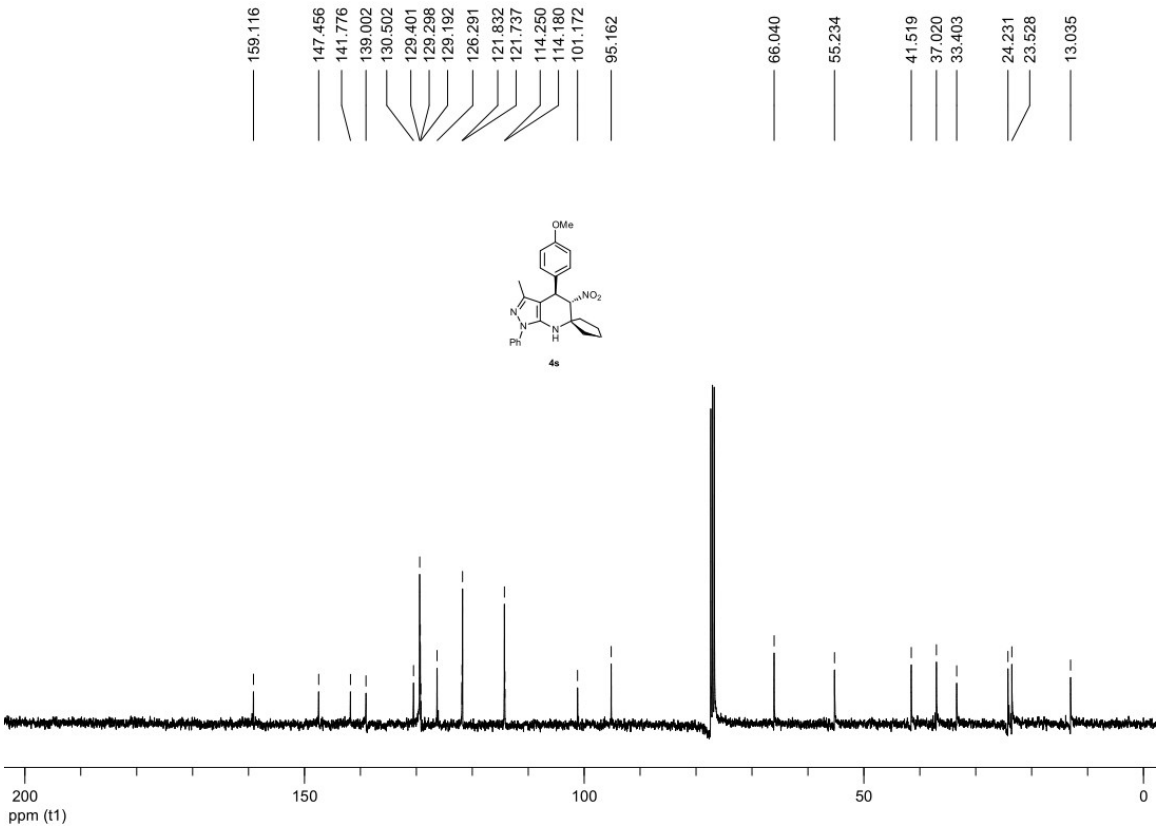
7.501
7.482
7.462
7.327
7.309
7.292
7.216
7.194
6.893
6.871
4.882
4.862
4.519
4.499
3.823
3.737
2.202
2.192
2.182
2.169
2.158
2.147
1.838
1.815
1.799
1.776
1.688
1.672
1.658
OMe
NO2
Ph
4s
1.61
1.69
1.33
1.85
2.00
0.79
0.79
2.90
0.78
0.79
7.03
2.88
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


159.116
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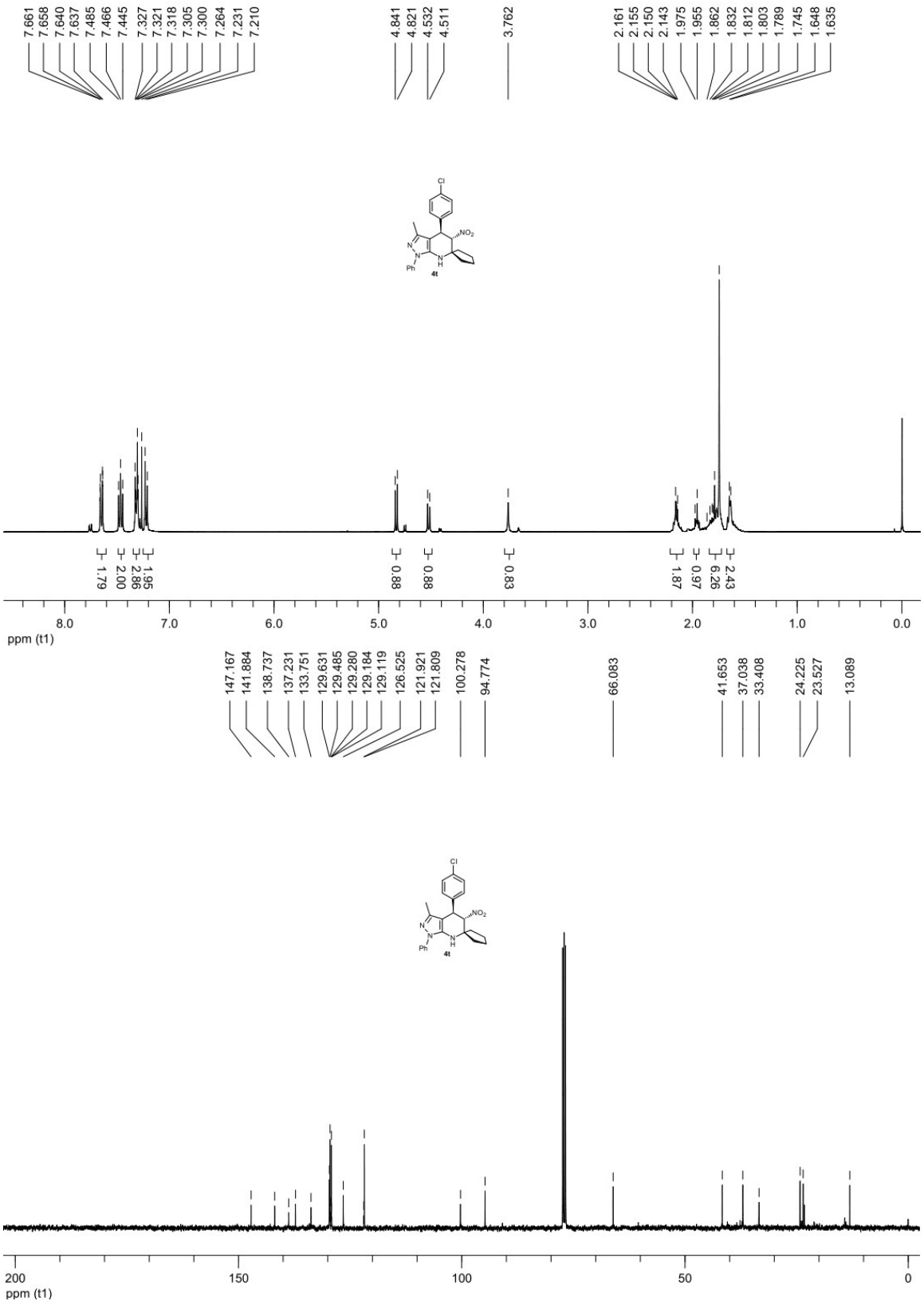
141.776
139.002
130.502
129.401
129.298
129.192
126.291
121.832
121.737
114.250
114.180
101.172
95.162
66.040
55.234
41.519
37.020
33.403
24.231
23.528
13.035
OMe
NO2
Ph
4s
200
150
100
50
0
ppm (t1)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7.658
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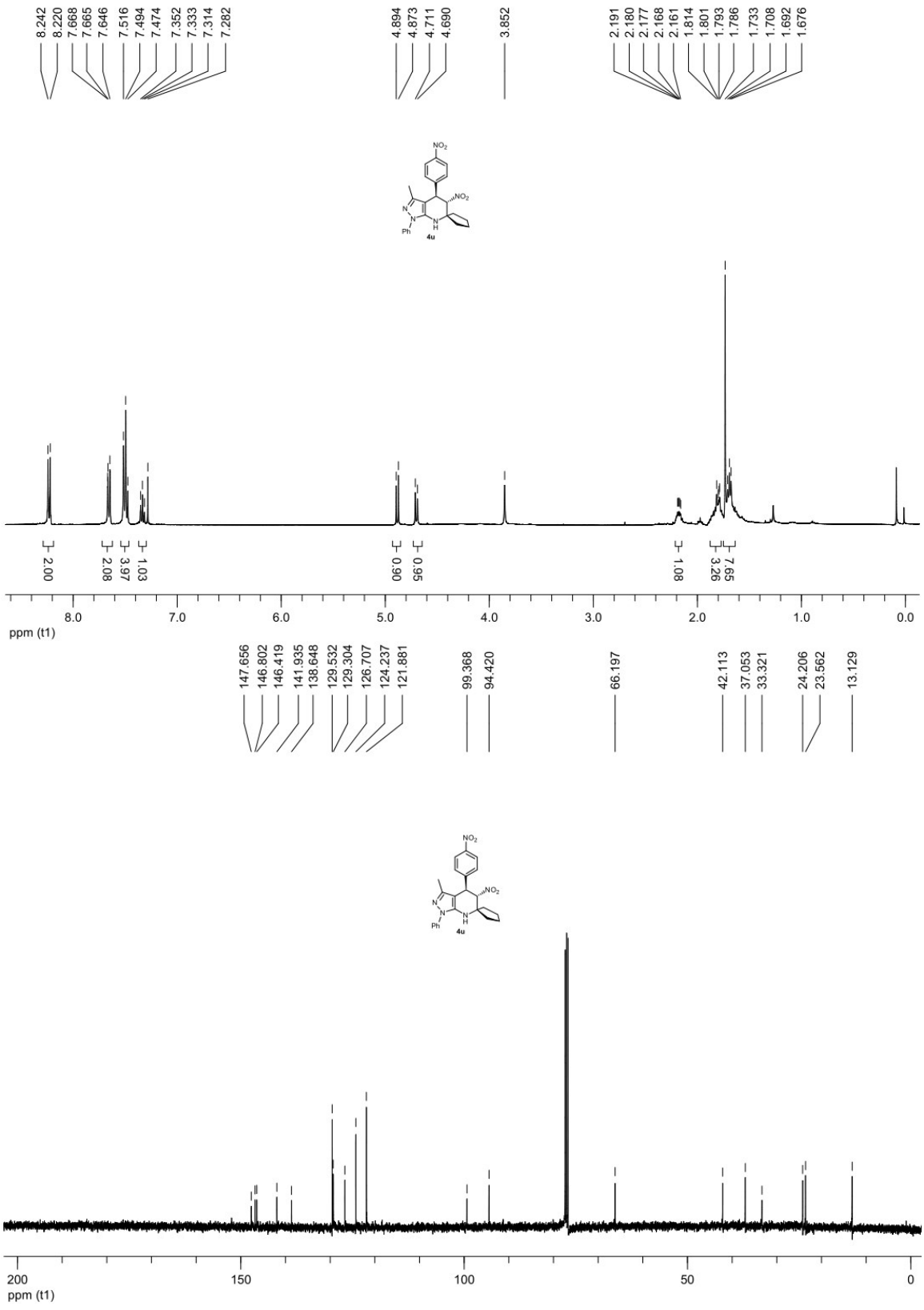
7.637
7.485
7.466
7.445
7.327
7.321
7.318
7.305
7.300
7.264
7.231
7.210
4.841
4.821
4.532
4.511
3.762
2.161
2.155
2.150
2.143
1.975
1.955
1.862
1.832
1.812
1.803
1.789
1.745
1.648
1.635
Cl
NO2
Ph
4t
1.79
2.00
2.86
1.96
0.88
0.88
0.83
1.87
0.97
6.26
2.43
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
147.167
141.884
138.737
137.231
133.751
129.631
129.485
129.280
129.184
129.119
126.525
121.921
121.809
100.278
94.774
66.083
41.653
37.038
33.408
24.225
23.527
13.089
200
150
100
50
0
ppm (t1)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7.474
7.352
7.333
7.314
7.282
4.894
4.873
4.711
4.690
3.852
2.191
2.180
2.177
2.168
2.161
1.814
1.801
1.793
1.786
1.733
1.708
1.692
1.676
4u
2.00
2.08
3.97
1.03
0.90
0.95
1.08
3.26
7.69
ppm (t1)
147.656
146.802
146.419
141.935
138.648
129.532
129.304
126.707
124.237
121.881
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66.197
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37.053
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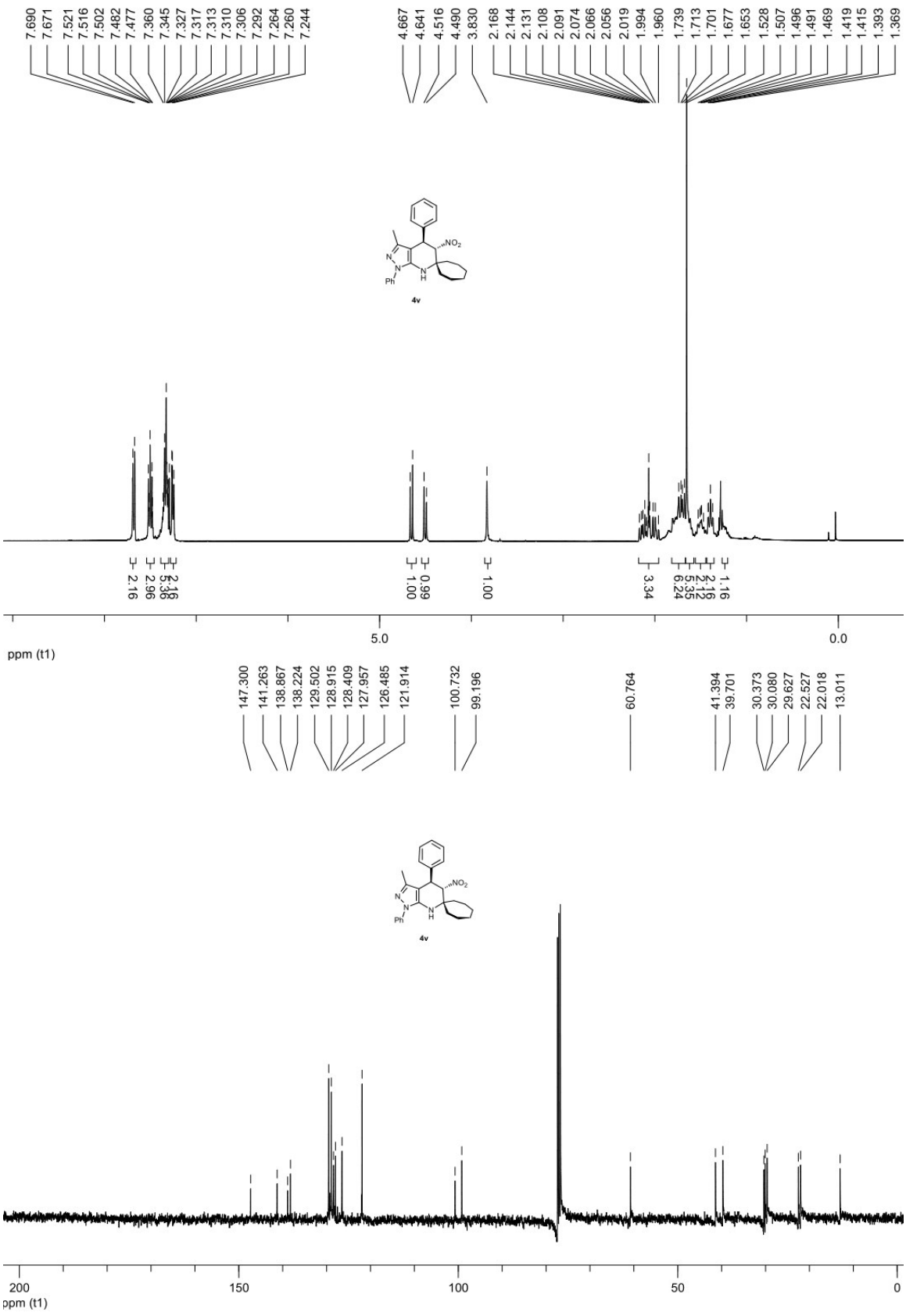
24.206
23.562
13.129
4u
ppm (t1)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7.482
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7.360
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7.317
7.313
7.310
7.306
7.292
7.264
7.260
7.244
4.667
4.641
4.516
4.490
3.830
2.168
2.144
2.131
2.108
2.091
2.074
2.066
2.056
2.019
1.994
1.960
1.739
1.713
1.701
1.677
1.653
1.528
1.507
1.496
1.491
1.469
1.419
1.415
1.393
1.369
4v
2.16
2.96
3.36
2.16
1.00
0.99
1.00
3.34
6.24
5.35
2.12
2.16
1.16
5.0
0.0
ppm (t1)
147.300
141.263
138.867
138.224
129.502
128.915
128.409
127.957
126.485
121.914
100.732
99.196
60.764
41.394
39.701
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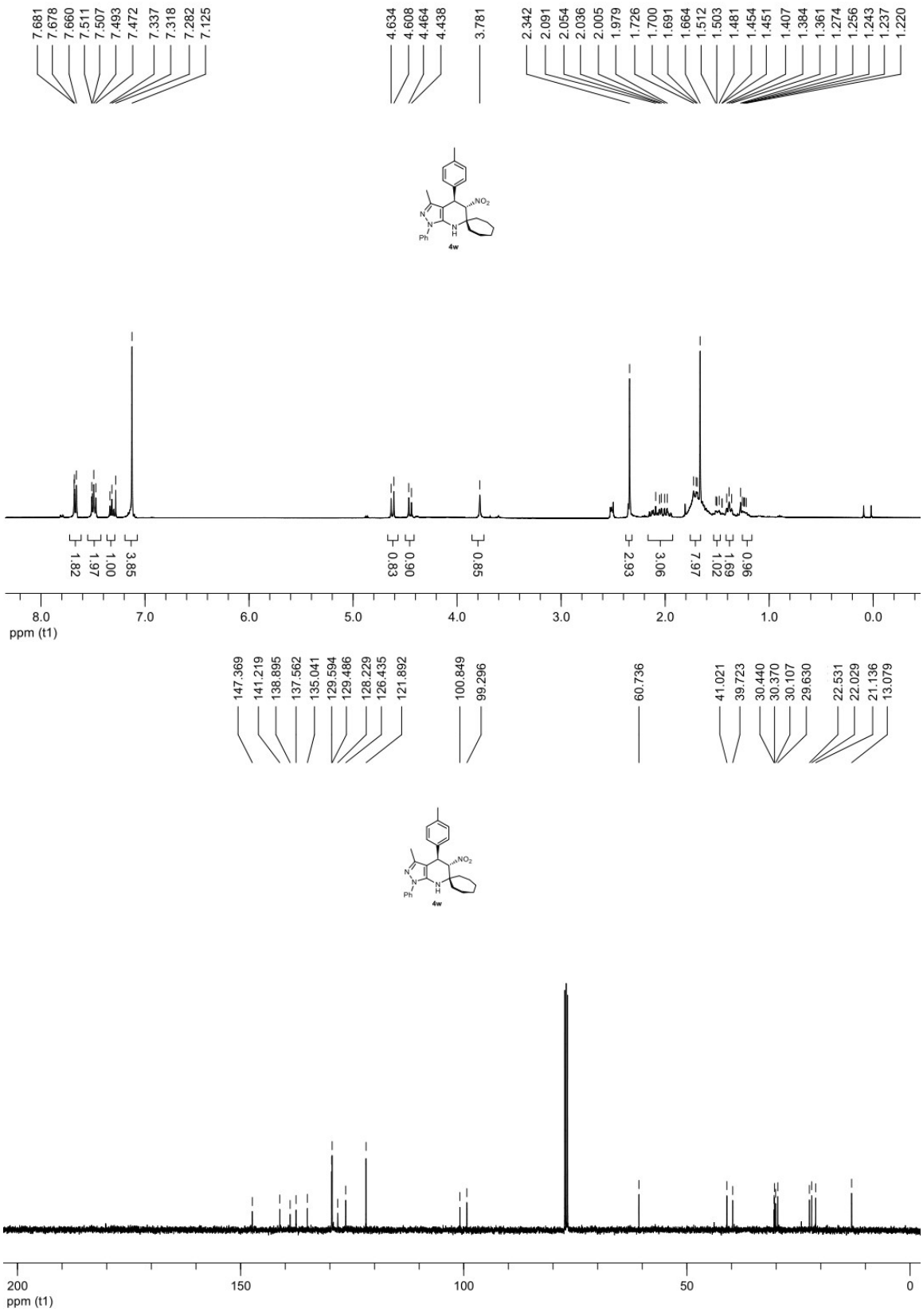
30.080
29.627
22.527
22.018
13.011
4v
200
150
100
50
0
ppm (t1)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7.493
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7.337
7.318
7.282
7.125
4.634
4.608
4.464
4.438
3.781
2.342
2.091
2.054
2.036
2.005
1.979
1.726
1.700
1.691
1.664
1.512
1.503
1.481
1.454
1.451
1.407
1.384
1.361
1.274
1.256
1.243
1.237
1.220
4w
1.82
1.97
1.00
3.85
0.83
0.90
0.85
2.33
3.06
7.97
1.02
1.69
0.96
ppm (t1)
147.369
141.219
138.895
137.562
135.041
129.594
129.486
128.229
126.435
121.892
100.849
99.296
60.736
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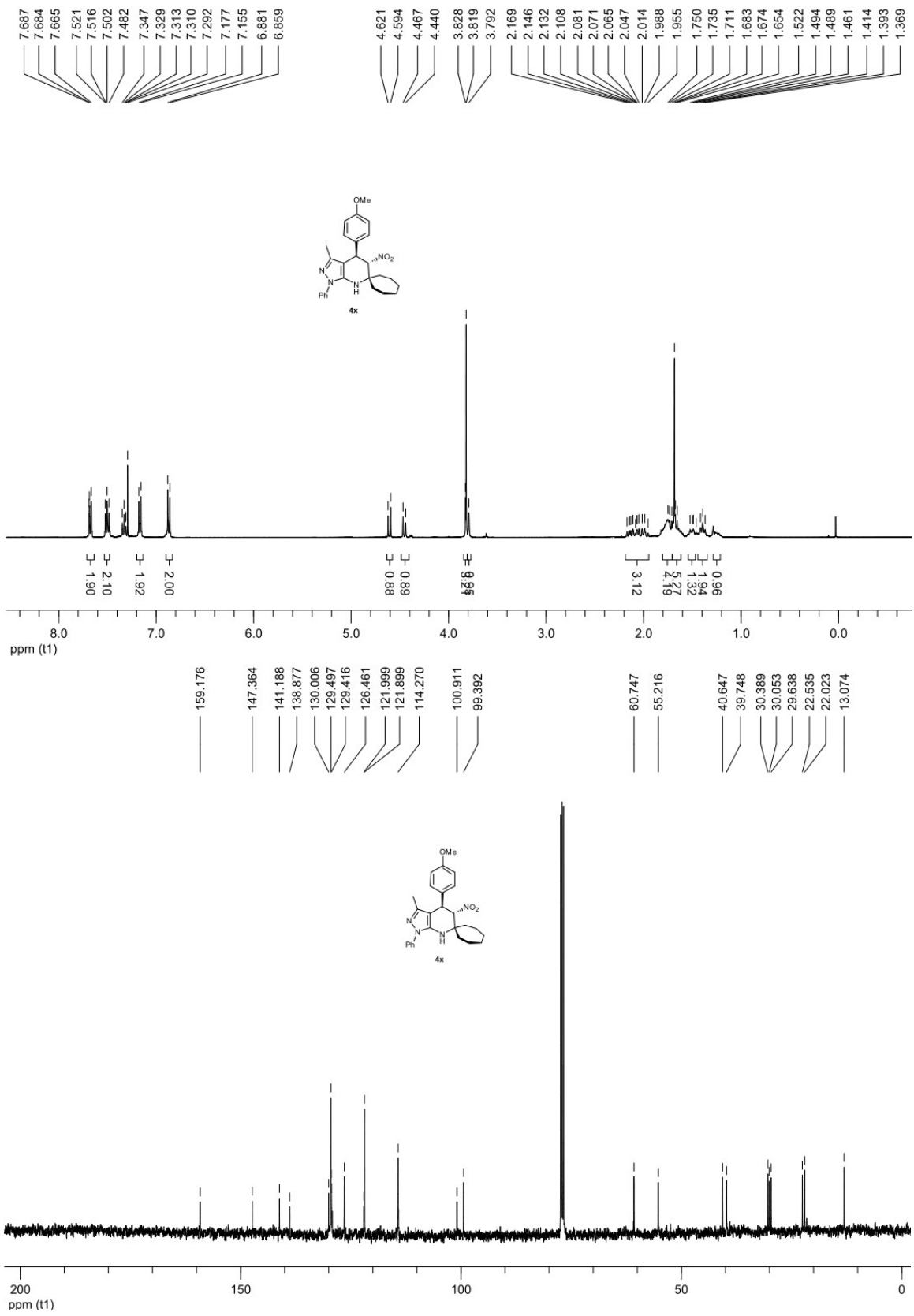
30.370
30.107
29.630
22.531
22.029
21.136
13.079
4w
ppm (t1)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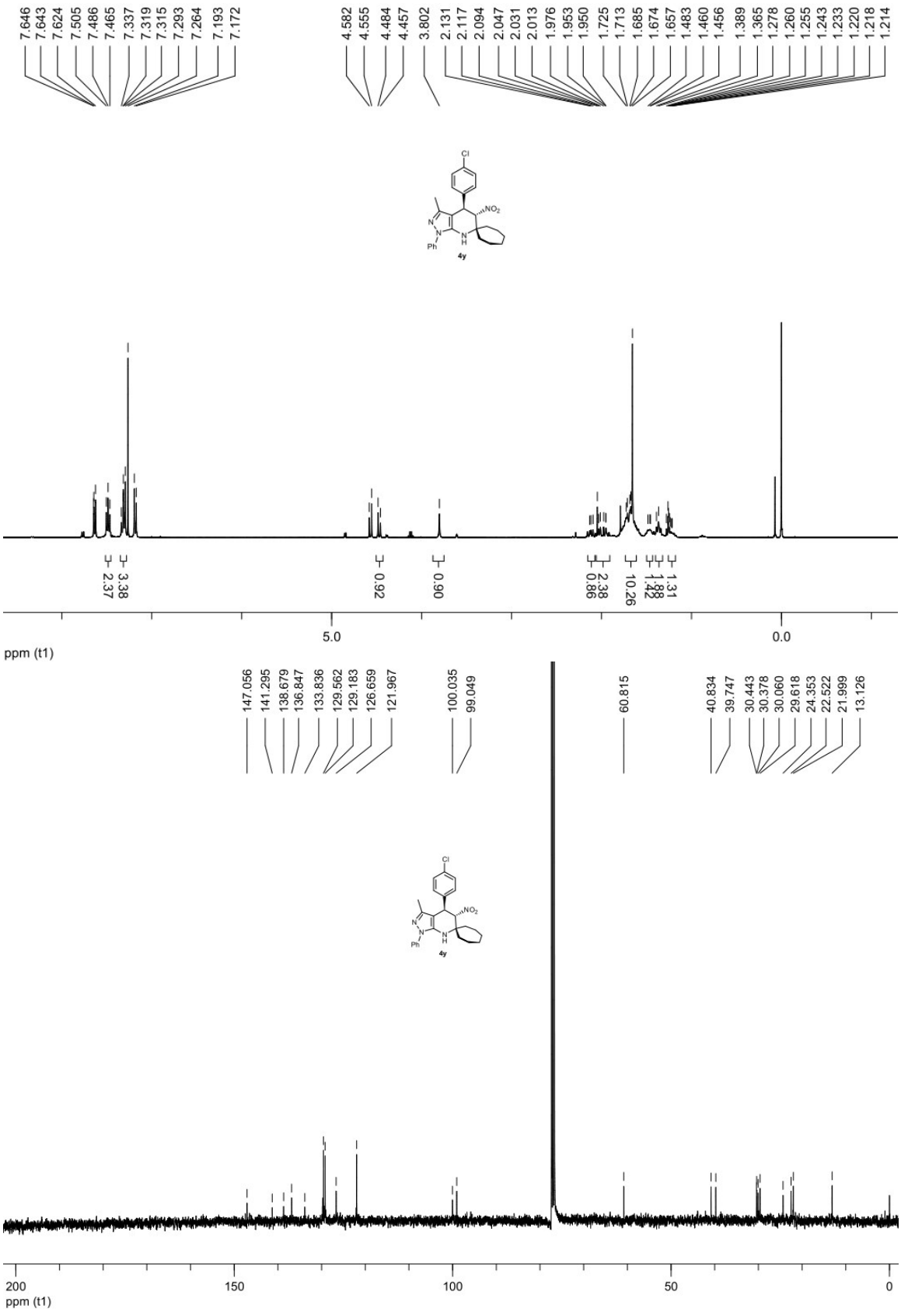
7.310
7.292
7.177
7.155
6.881
6.859
4.621
4.594
4.467
4.440
3.828
3.819
3.792
2.169
2.146
2.132
2.108
2.081
2.071
2.065
2.047
2.014
1.988
1.955
1.750
1.735
1.711
1.683
1.674
1.654
1.522
1.494
1.489
1.461
1.414
1.393
1.369
OMe
NO2
Ph
4x
1.90
2.10
1.92
2.00
0.88
0.89
3.12
5.27
4.19
1.94
1.32
0.96
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
159.176
147.364
141.188
138.877
130.006
129.497
129.416
126.461
121.999
121.899
114.270
100.911
99.392
60.747
55.216
40.647
39.748
30.389
30.053
29.638
22.535
22.023
13.074
200
150
100
50
0
ppm (t1)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7.465
7.337
7.319
7.315
7.293
7.264
7.193
7.172
4.582
4.555
4.484
4.457
3.802
2.131
2.117
2.094
2.047
2.031
2.013
1.976
1.953
1.950
1.725
1.713
1.685
1.674
1.657
1.483
1.460
1.456
1.389
1.365
1.278
1.260
1.255
1.243
1.233
1.220
1.218
1.214
Cl
NO2
N
N
Ph
H
4y
2.37
3.38
0.92
0.90
0.86
2.38
10.26
1.31
5.0
0.0
ppm (t1)
147.056
141.295
138.679
136.847
133.836
129.562
129.183
126.659
121.967
100.035
99.049
60.815
40.834
39.747
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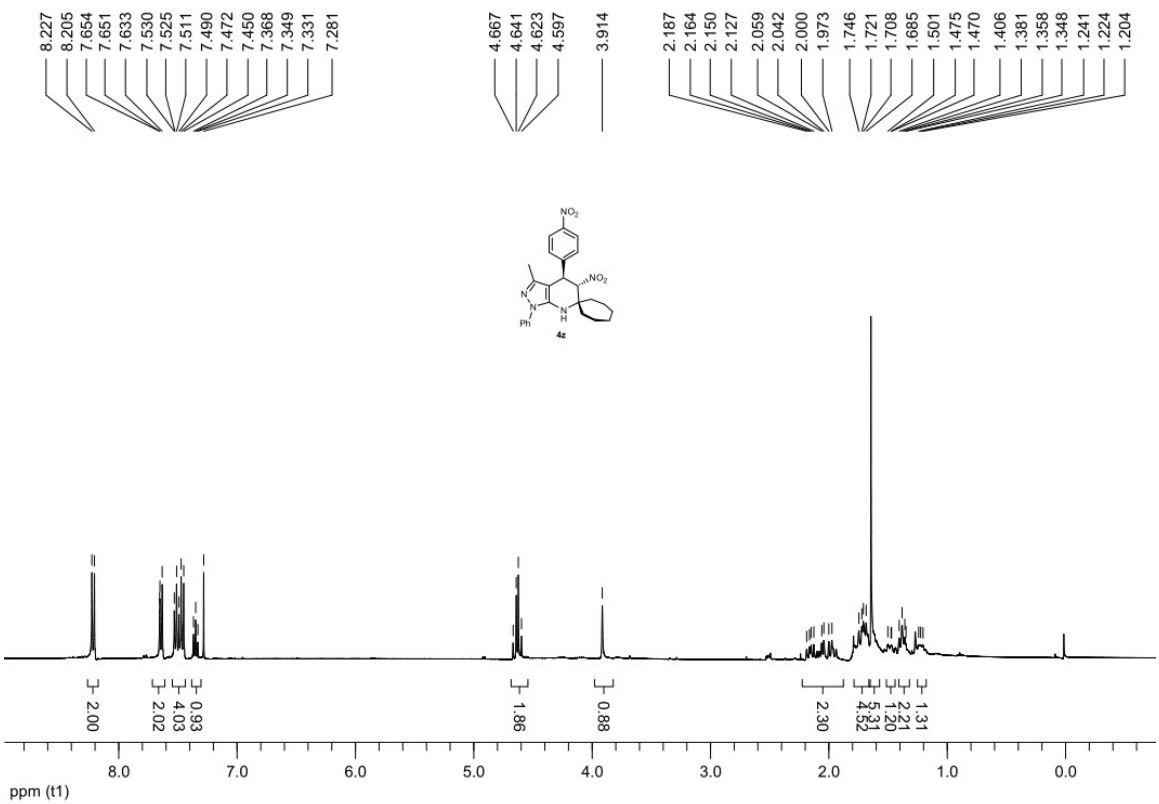
29.618
24.353
22.522
21.999
13.126
200
150
100
50
0
ppm (t1)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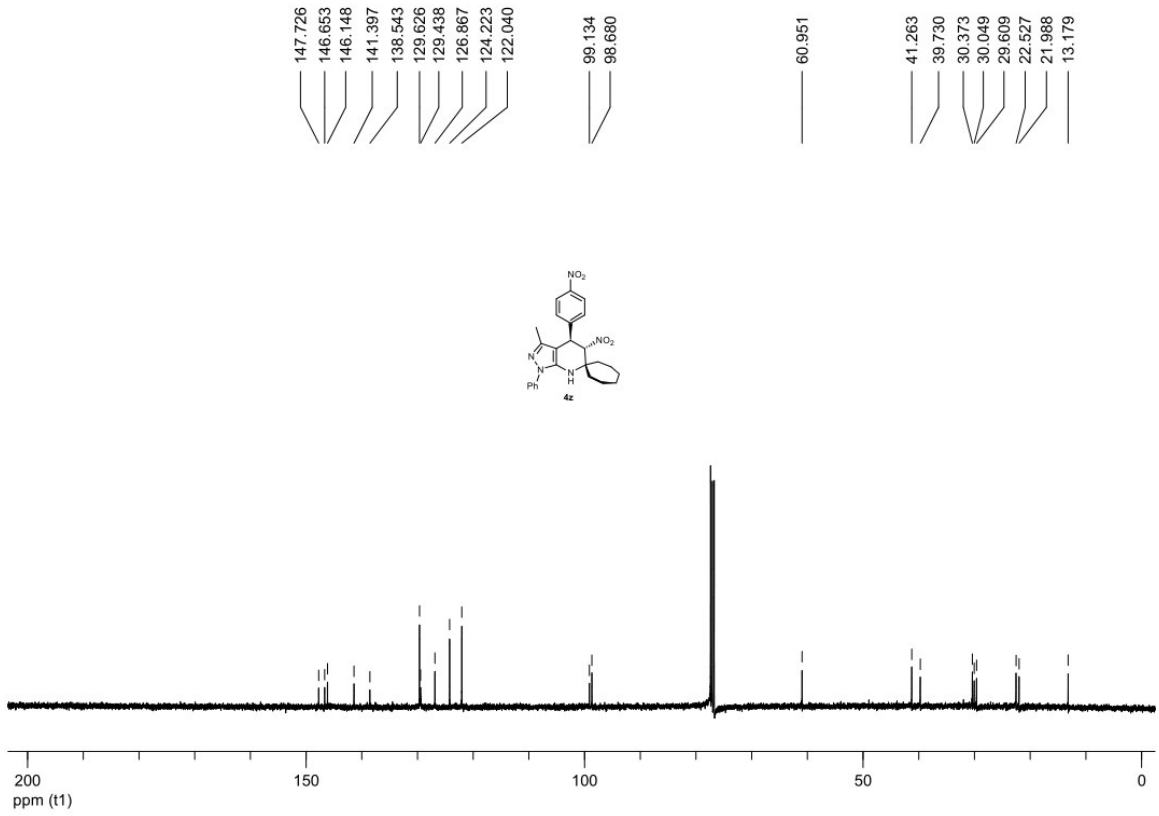
7.651
7.633
7.530
7.525
7.511
7.490
7.472
7.450
7.368
7.349
7.331
7.281
4.667
4.641
4.623
4.597
3.914
2.187
2.164
2.150
2.127
2.059
2.042
2.000
1.973
1.746
1.721
1.708
1.685
1.501
1.475
1.470
1.406
1.381
1.358
1.348
1.241
1.224
1.204
4z
2.00
2.02
4.03
0.93
1.86
0.88
2.30
4.52
5.31
1.20
2.21
1.31
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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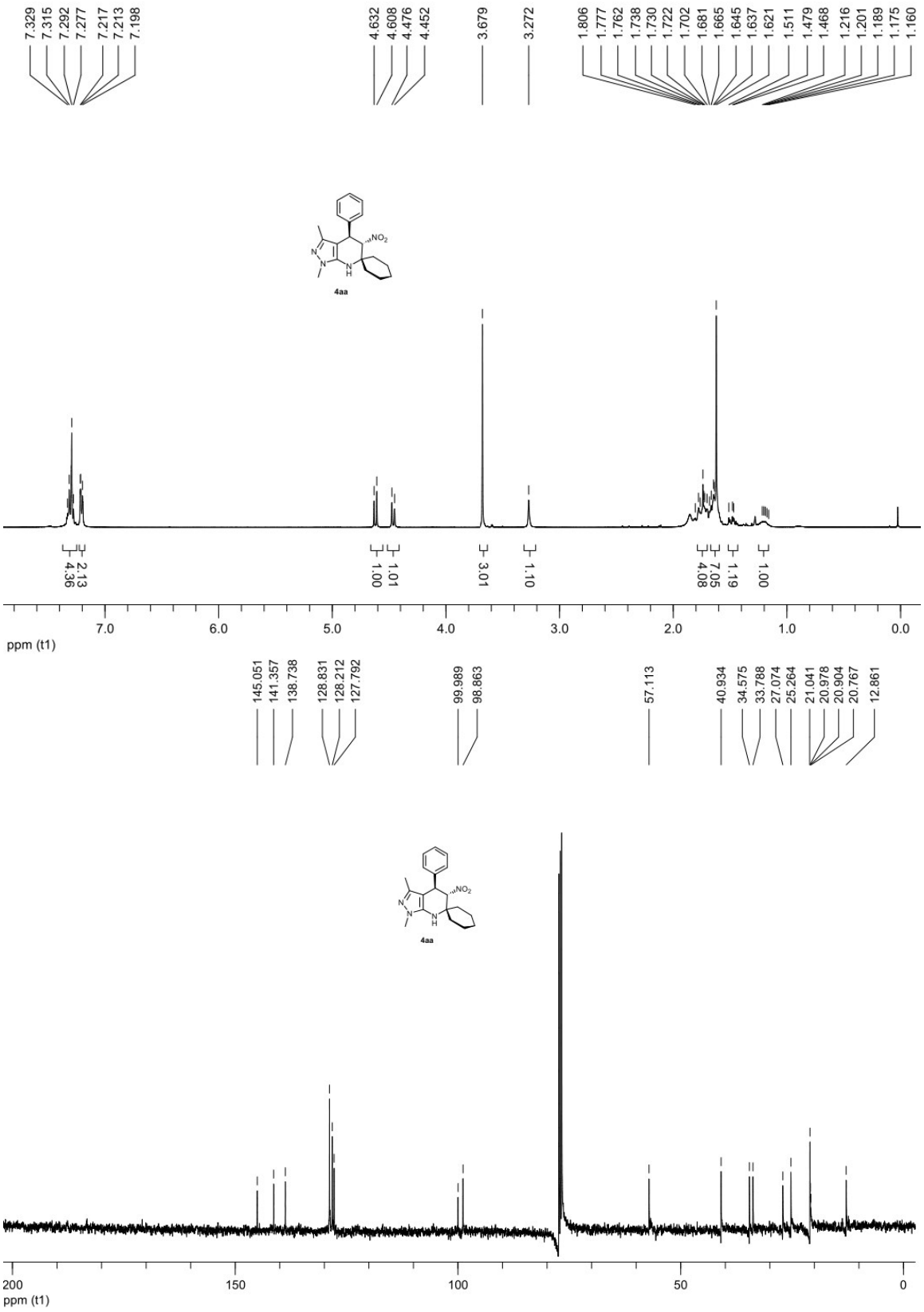
138.543
129.626
129.438
126.867
124.223
122.040
99.134
98.680
60.951
41.263
39.730
30.373
30.049
29.609
22.527
21.988
13.179
4z
200
150
100
50
0
ppm (t1)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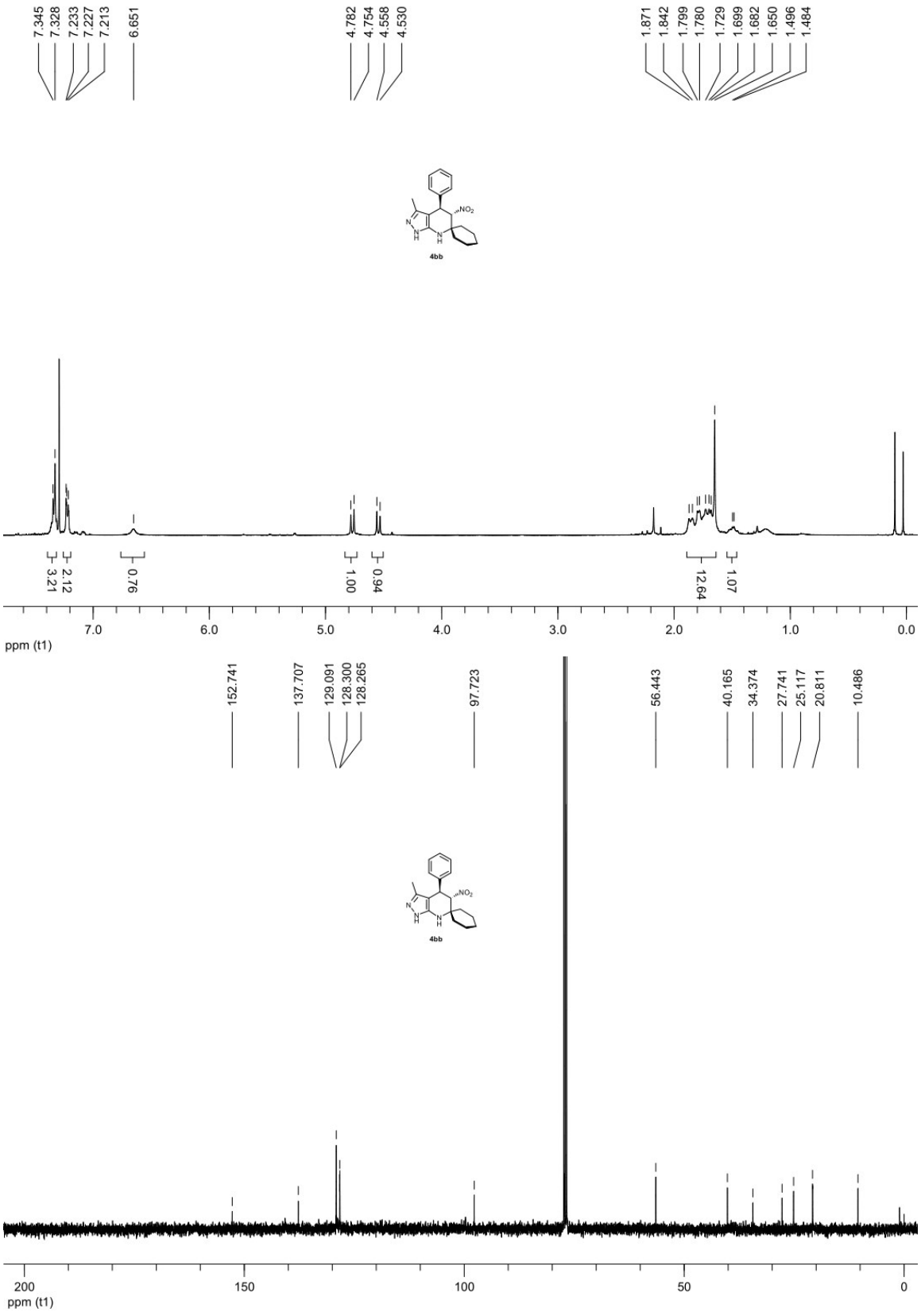
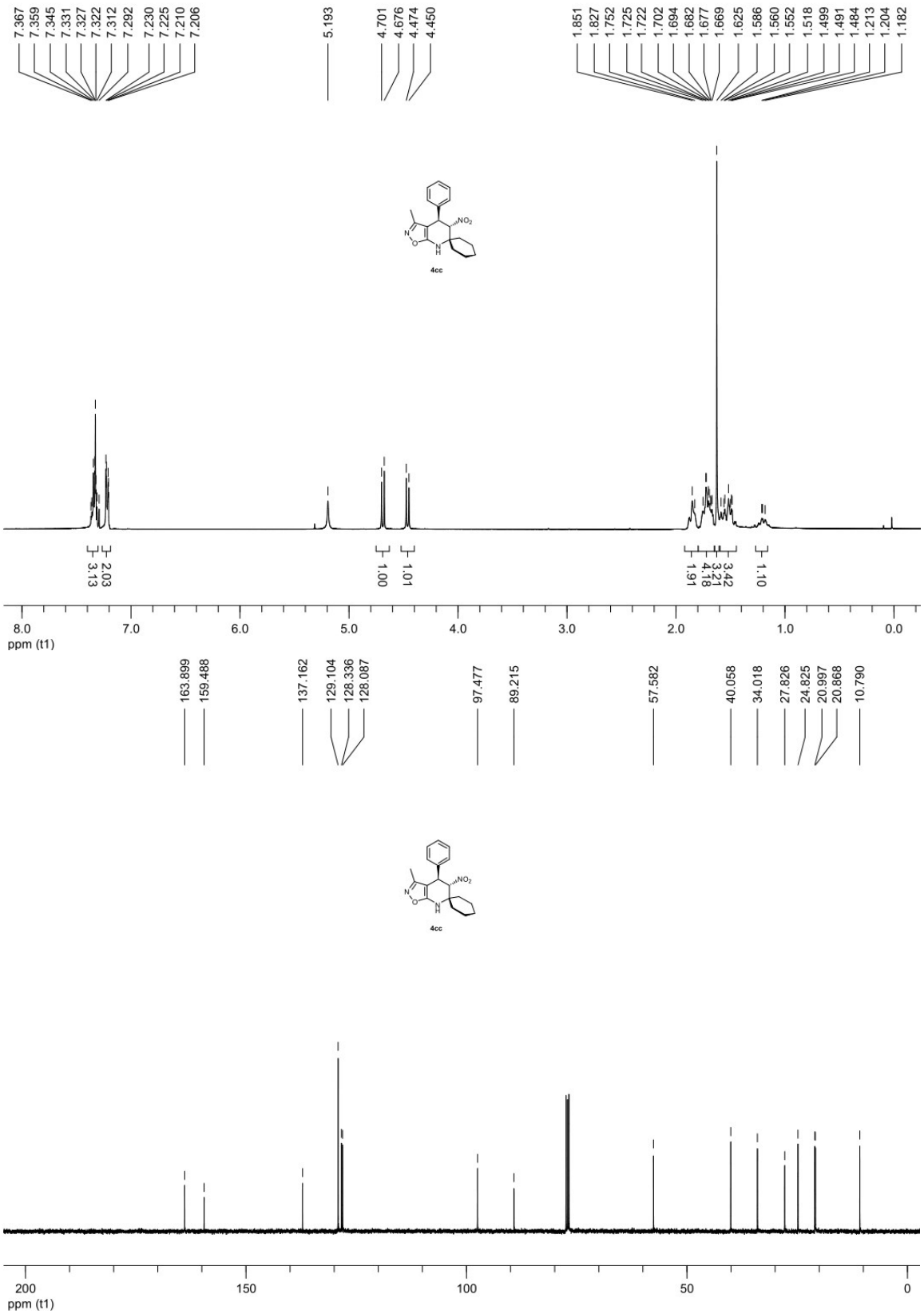
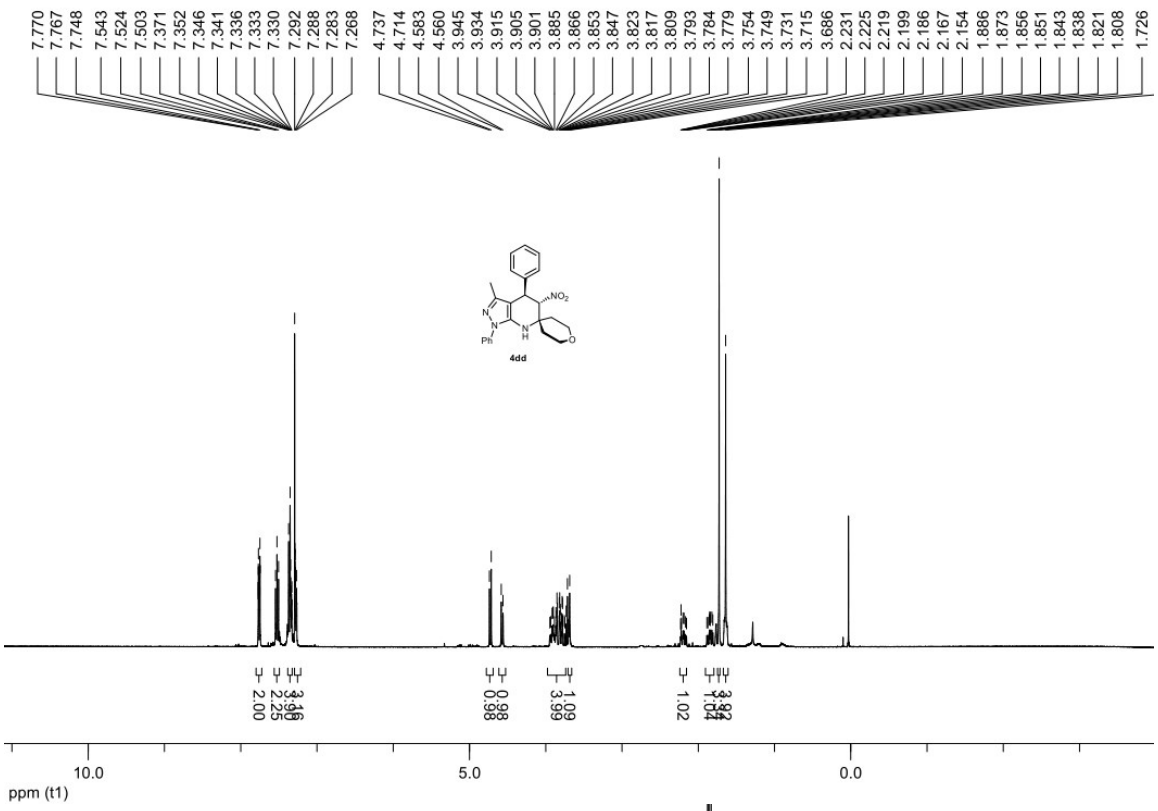
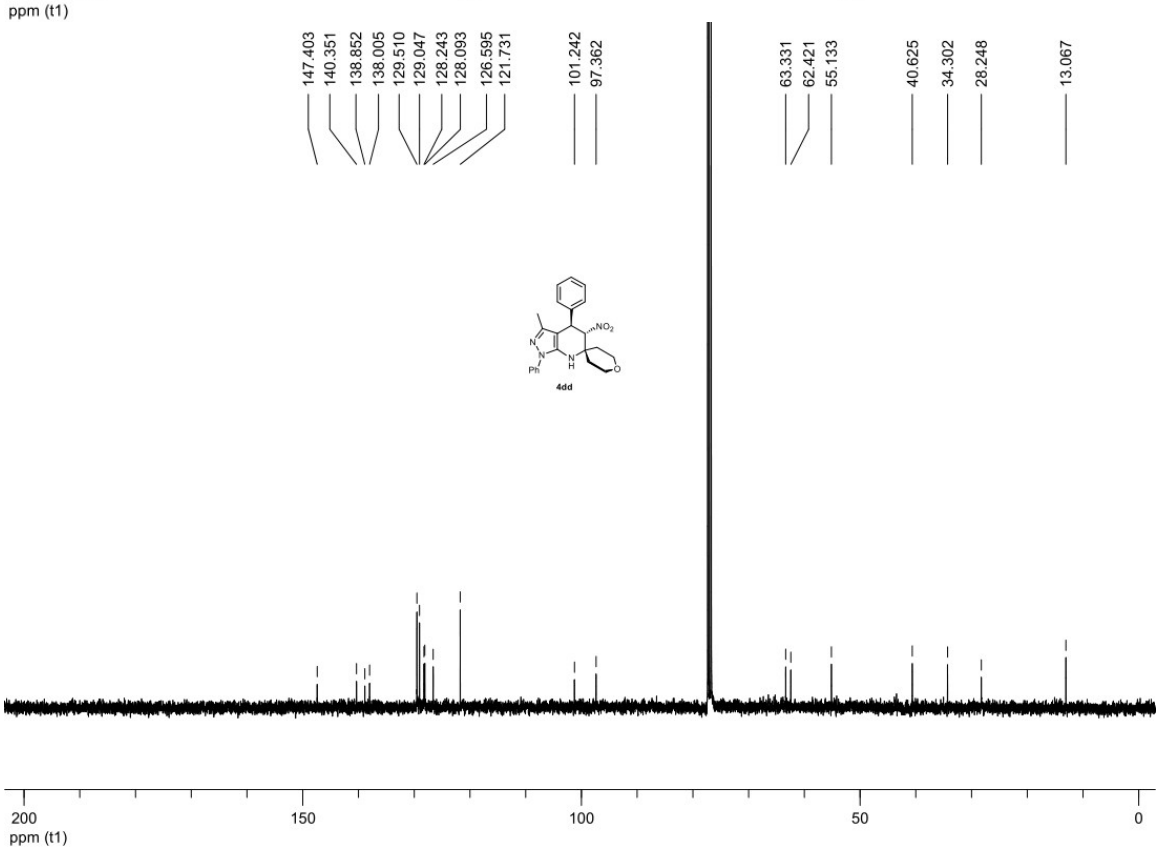
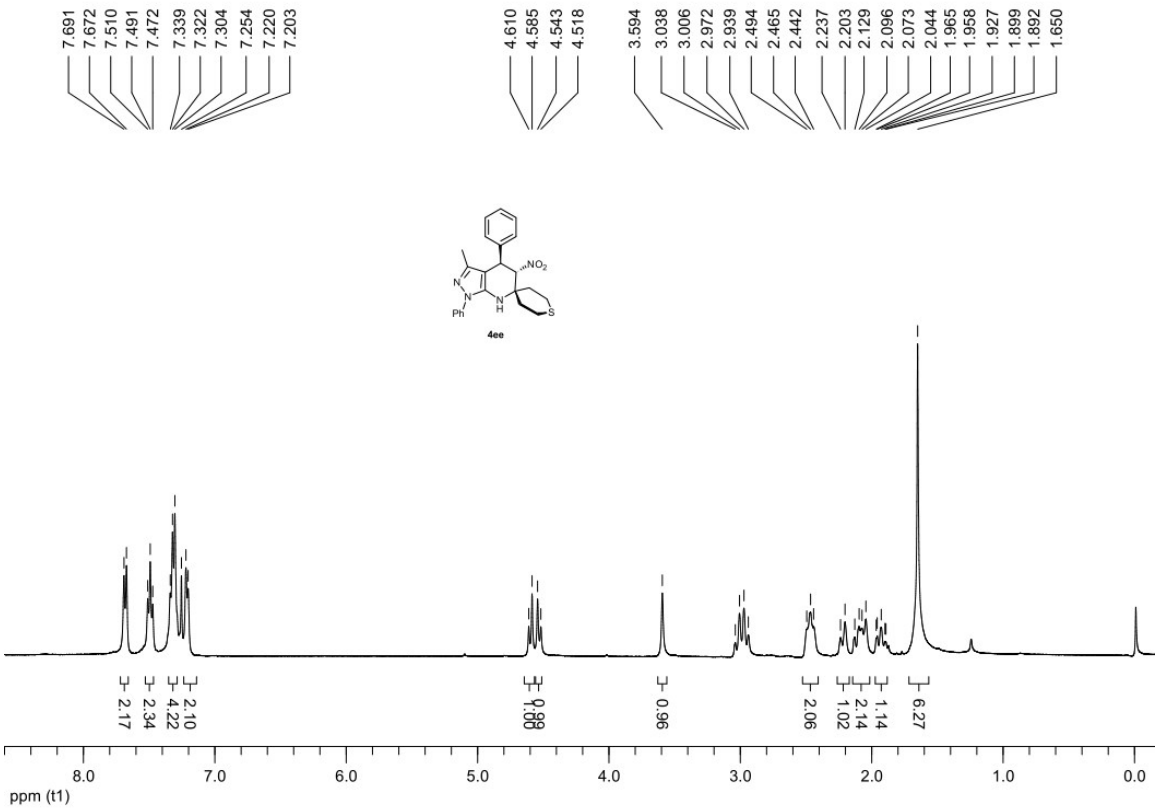
7.292
7.277
7.217
7.213
7.198
4.632
4.608
4.476
4.452
3.679
3.272
1.806
1.777
1.762
1.738
1.730
1.722
1.702
1.681
1.665
1.645
1.637
1.621
1.511
1.479
1.468
1.216
1.201
1.189
1.175
1.160
4aa
2.13
4.36
1.00
1.01
3.01
1.10
4.08
7.05
1.19
1.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
145.051
141.357
138.738
128.831
128.212
127.792
99.989
98.863
57.113
40.934
34.575
33.788
27.074
25.264
21.041
20.978
20.904
20.767
12.861
4aa
200
150
100
50
0
ppm (t1)

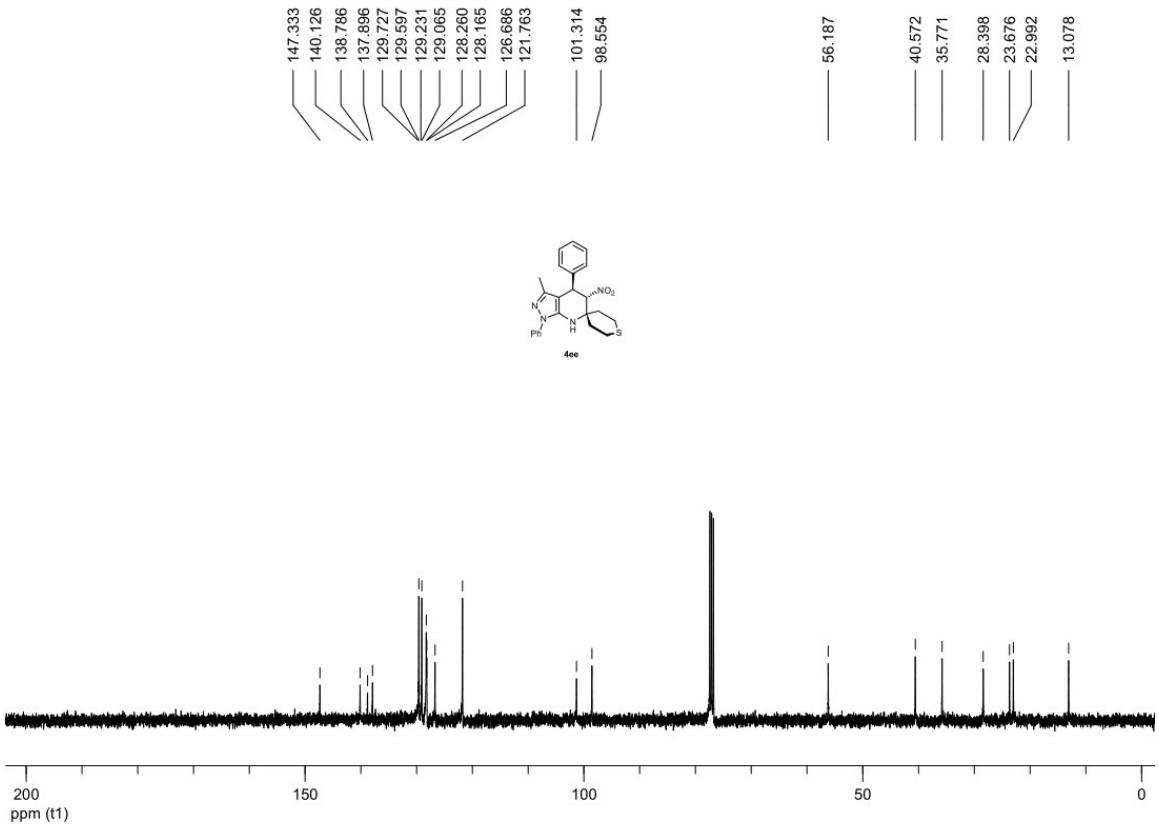

7.345
7.328
7.233
7.227
7.213
6.651
4.782
4.754
4.558
4.530
1.871
1.842
1.799
1.780
1.729
1.699
1.682
1.650
1.496
1.484
4bb
3.21
2.12
0.76
1.00
0.94
12.84
1.07
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
152.741
137.707
129.091
128.300
128.265
97.723
56.443
40.165
34.374
27.741
25.117
20.811
10.486
4bb
200
150
100
50
0
ppm (t1)

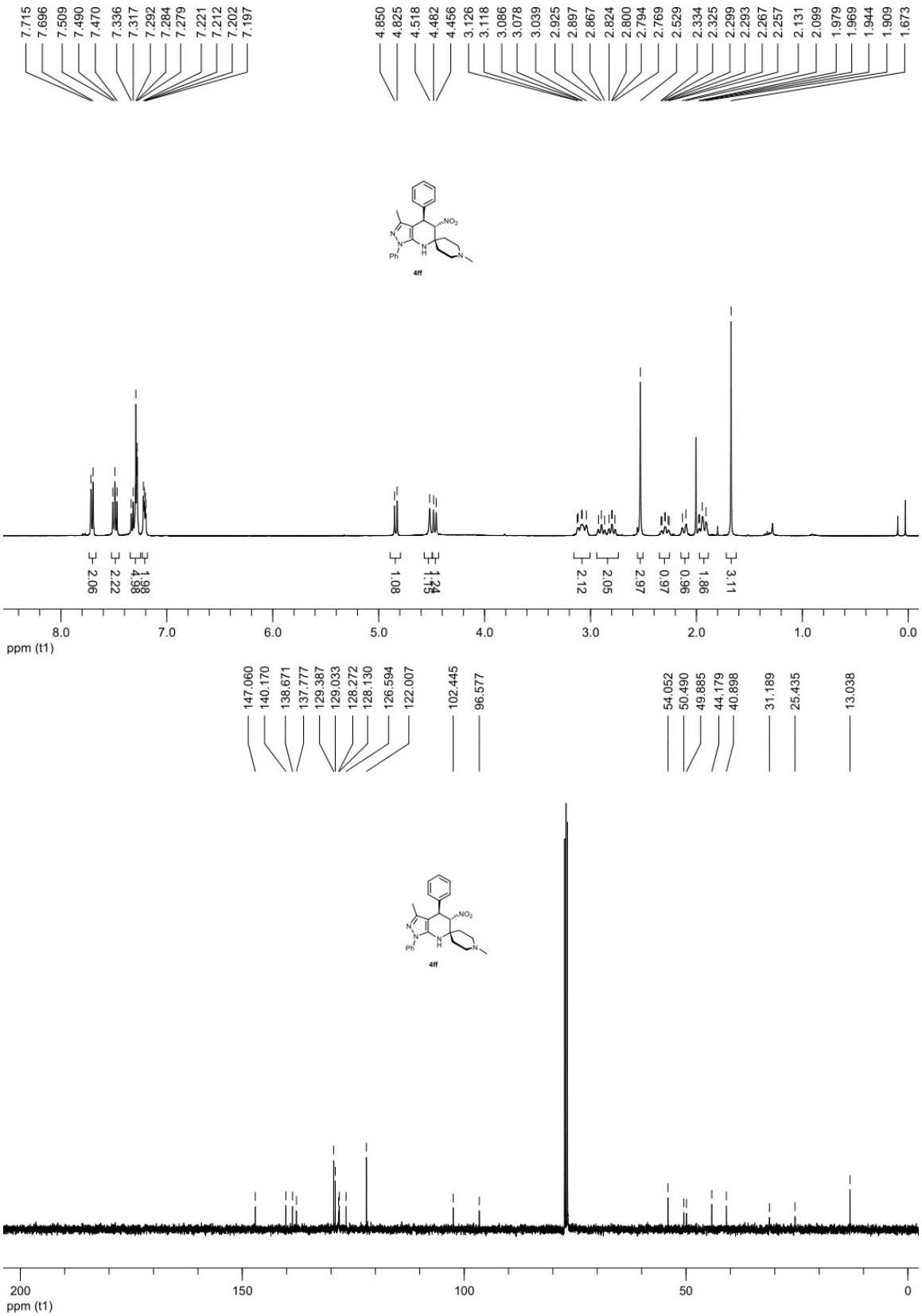

7.367
7.359
7.345
7.331
7.327
7.322
7.312
7.292
7.230
7.225
7.210
7.206
5.193
4.701
4.676
4.474
4.450
1.851
1.827
1.752
1.725
1.722
1.702
1.694
1.682
1.677
1.669
1.625
1.586
1.560
1.552
1.518
1.499
1.491
1.484
1.213
1.204
1.182
4cc
3.13
2.03
1.00
1.01
1.91
1.18
3.21
3.42
1.10
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
163.899
159.488
137.162
129.104
128.336
128.087
97.477
89.215
57.582
40.058
34.018
27.826
24.825
20.997
20.868
10.790
4cc
200
150
100
50
0
ppm (t1)

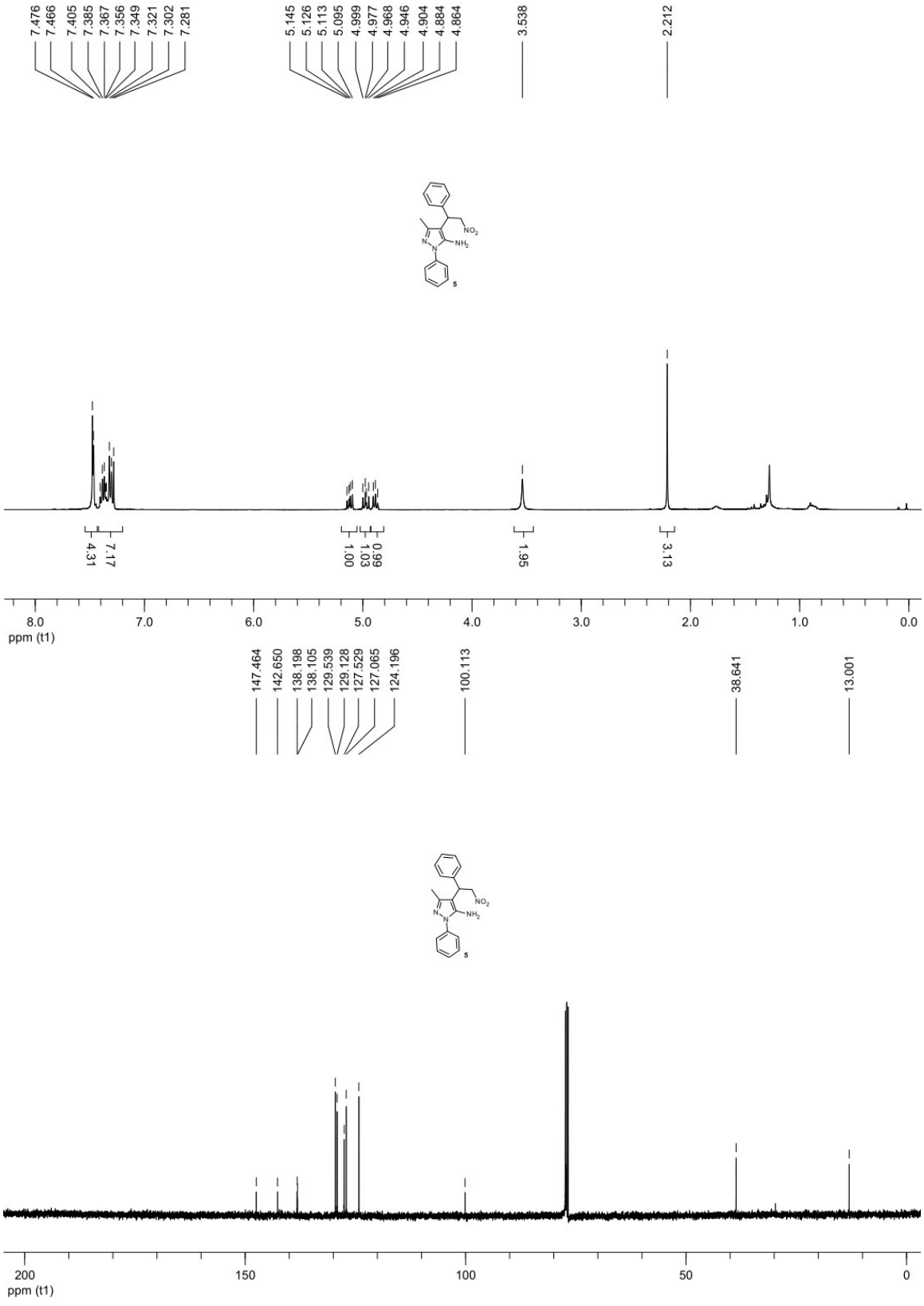

7.770
7.767
7.748
7.543
7.524
7.503
7.371
7.352
7.346
7.341
7.336
7.333
7.330
7.292
7.288
7.283
7.268
4.737
4.714
4.583
4.560
3.945
3.934
3.915
3.905
3.901
3.885
3.866
3.853
3.847
3.823
3.817
3.809
3.793
3.784
3.779
3.754
3.749
3.731
3.715
3.686
2.231
2.225
2.219
2.199
2.186
2.167
2.154
1.886
1.873
1.856
1.851
1.843
1.838
1.821
1.808
1.726
4dd
2.00
3.16
2.25
0.98
0.88
1.39
1.09
1.02
10.0
5.0
0.0
ppm (t1)


147.403
140.351
138.852
138.005
129.510
129.047
128.243
128.093
126.595
121.731
101.242
97.362
63.331
62.421
55.133
40.625
34.302
28.248
13.067
4dd
200
150
100
50
0
ppm (t1)


7.691
7.672
7.510
7.491
7.472
7.339
7.322
7.304
7.254
7.220
7.203
4.610
4.585
4.543
4.518
3.594
3.038
3.006
2.972
2.939
2.494
2.465
2.442
2.237
2.203
2.129
2.096
2.073
2.044
1.965
1.958
1.927
1.899
1.892
1.650
4ee
2.17
2.34
4.22
2.10
1.00
0.96
2.06
1.02
2.14
1.14
6.27
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


147.333
140.126
138.786
137.896
129.727
129.597
129.231
129.065
128.260
128.165
126.686
121.763
101.314
98.554
56.187
40.572
35.771
28.398
23.676
22.992
13.078
4ee
200
150
100
50
0
ppm (t1)


7.715
7.696
7.509
7.490
7.470
7.336
7.317
7.292
7.284
7.279
7.221
7.212
7.202
7.197
4.850
4.825
4.518
4.482
4.456
3.126
3.118
3.086
3.078
3.039
2.925
2.897
2.867
2.824
2.800
2.794
2.769
2.529
2.334
2.325
2.299
2.293
2.267
2.257
2.131
2.099
1.979
1.969
1.944
1.909
1.673
4ff
2.06
2.22
1.98
1.98
1.08
1.24
1.15
2.12
2.05
2.97
0.97
0.96
1.86
3.11
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
147.060
140.170
138.671
137.777
129.387
129.033
128.272
128.130
126.594
122.007
102.445
96.577
54.052
50.490
49.885
44.179
40.898
31.189
25.435
13.038
4ff
200
150
100
50
0
ppm (t1)


7.476
7.466
7.405
7.385
7.367
7.356
7.349
7.321
7.302
7.281
5.145
5.126
5.113
5.095
4.999
4.977
4.968
4.946
4.904
4.884
4.864
3.538
2.212
NO2
NH2
5
4.31
7.17
1.00
1.03
0.99
1.95
3.13
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
147.464
142.650
138.198
138.105
129.539
129.128
127.529
127.065
124.196
100.113
38.641
13.001
200
150
100
50
0
ppm (t1)