Supporting Information

Visible-light induced decarboxylative C2-alkylation of benzothiazoles with carboxylic acids under metal-free conditions

Bin Wang,[†] Pinhua Li,*[,†] Tao Miao,[†] Long Zou,[†] and Lei Wang*[,†,‡]

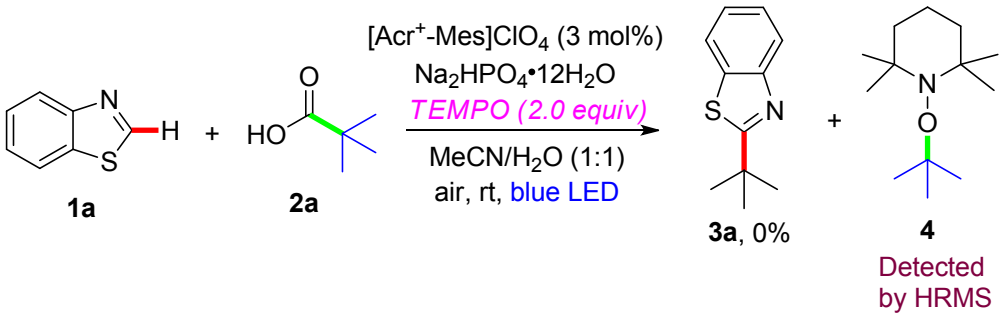
[†] Department of Chemistry, Huaibei Normal University, Huaibei, Anhui 235000, P. R. China

[‡] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, P. R. China

E-mail: pphuali@126.com; leiwang@chnu.edu.cn

Table of Contents

1. The free radical trapping experiment



A tubed vessel containing a stir bar was charged with benzothiazole (**1a**, 0.50 mmol), pivalic acid (**2a**, 1.5 mmol), [Acr$^+$-Mes]ClO_4 (3 mol%), $Na_2HPO_4 \cdot 12H_2O$ (1.5 mmol), 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, a radical-trapping reagent, 1.0 mmol) and CH_3CN/H_2O (1:1, 3.0 mL). The reaction vessel was exposed to blue LED (410–415 nm, 1.5 W) at room temperature for 36 h. Upon completion of the reaction, the mixture was diluted with water (3 mL) and extracted with ethyl acetate (10 mL × 3). The organic layer was combined, dried over anhydrous Na_2SO_4, and filtered. The crude reaction mixture was directly detected by HPLC-HRMS analysis, a *tert*-butyl radical adduct **4** with radical scavenger (TEMPO) was detected, as shown in Figure S1.

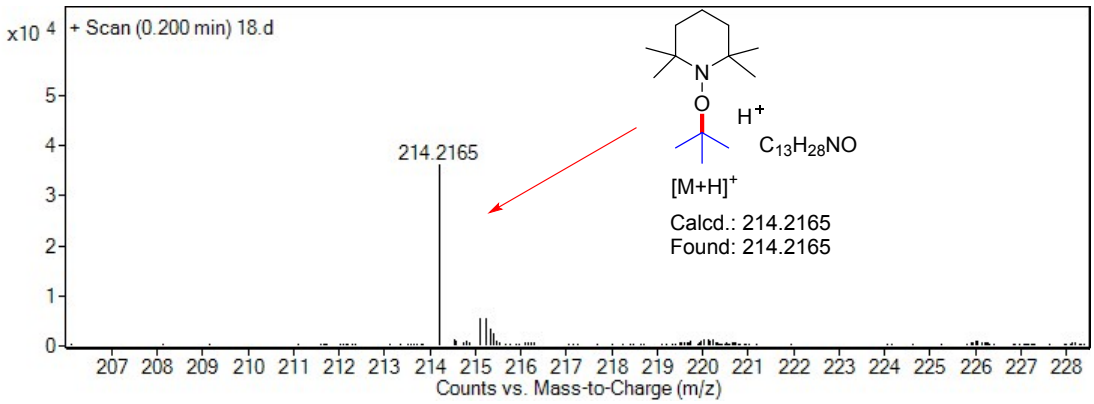
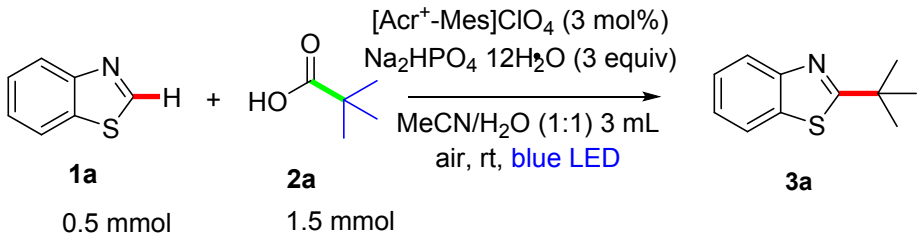


Figure S1. HRMS analysis of the adduct **4** of *tert*-butyl radical with TEMPO

2. Light/Dark experiments



The conversion of **1a** was determined by NMR analysis with CH_2Br_2 as an internal standard.

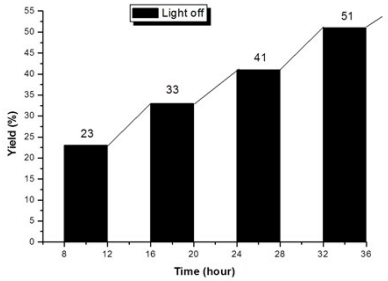
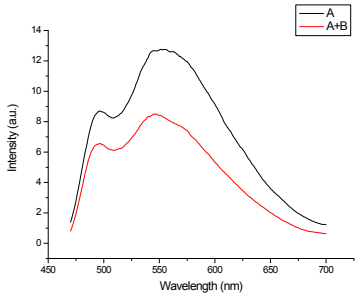


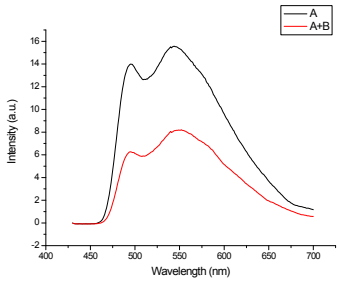
Figure S2. Light/Dark experiments

3. Fluorescence quenching experiment

A: [Acr$^+$-Mes]ClO_4, 3 mol%], 0.015 mmol; B: benzothiazole 0.5 mmol; Solvent: CH_3CN/H_2O (1:1, 3 mL).

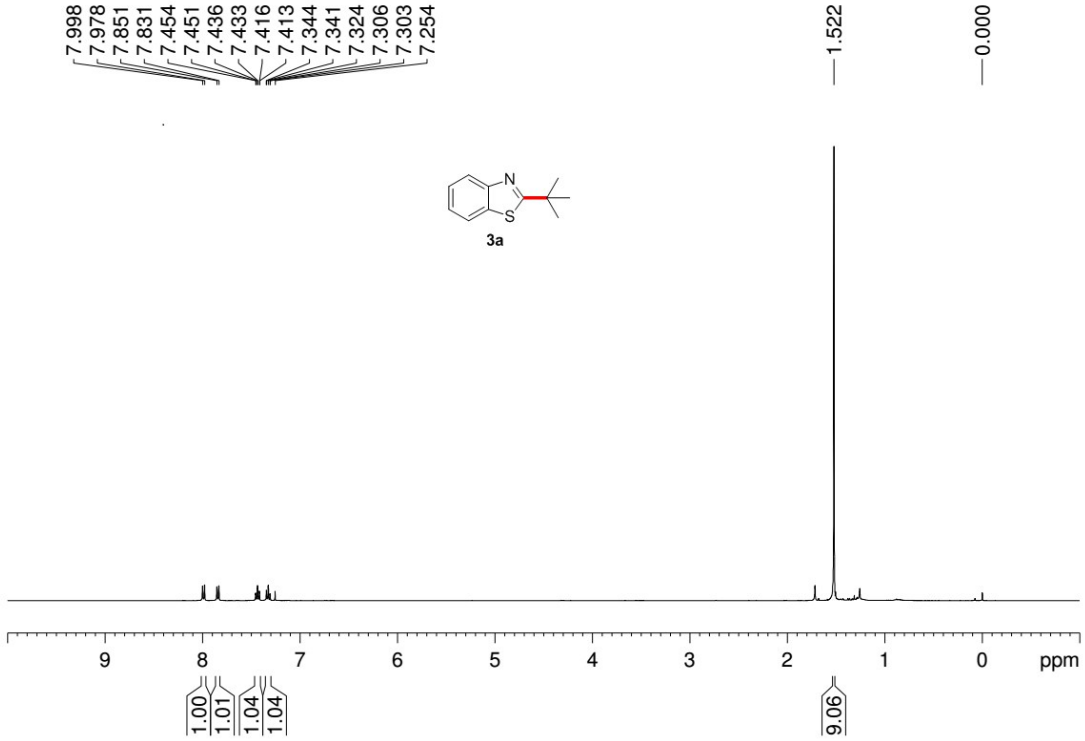


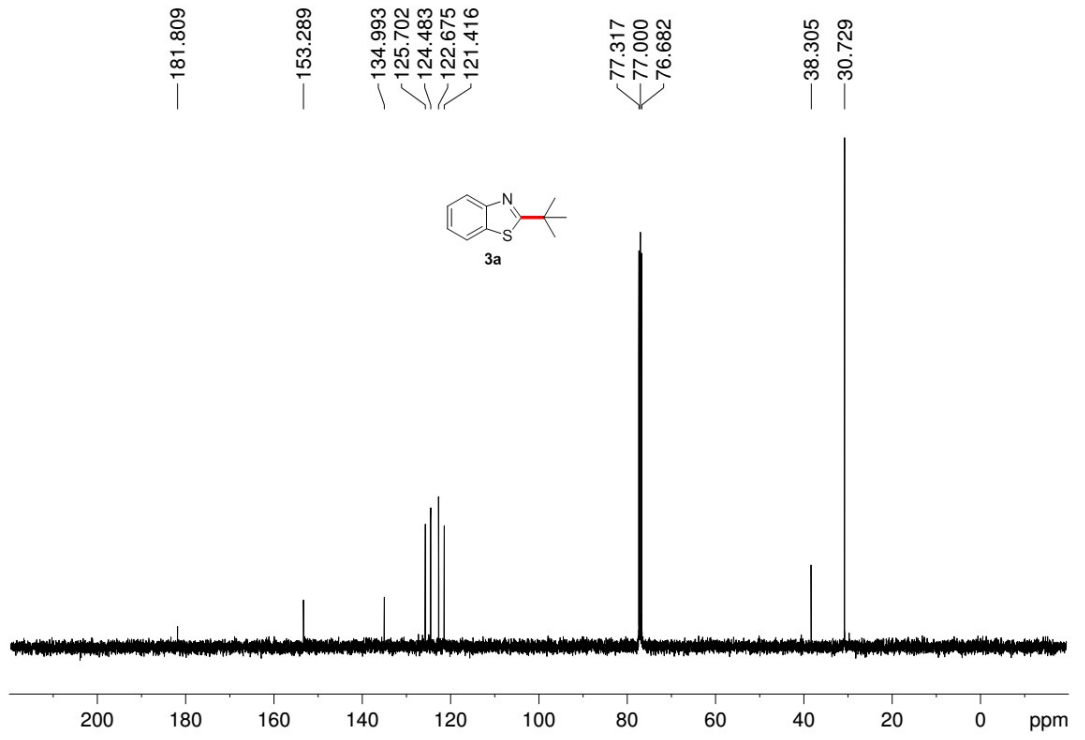
450 nm excitation wavelength

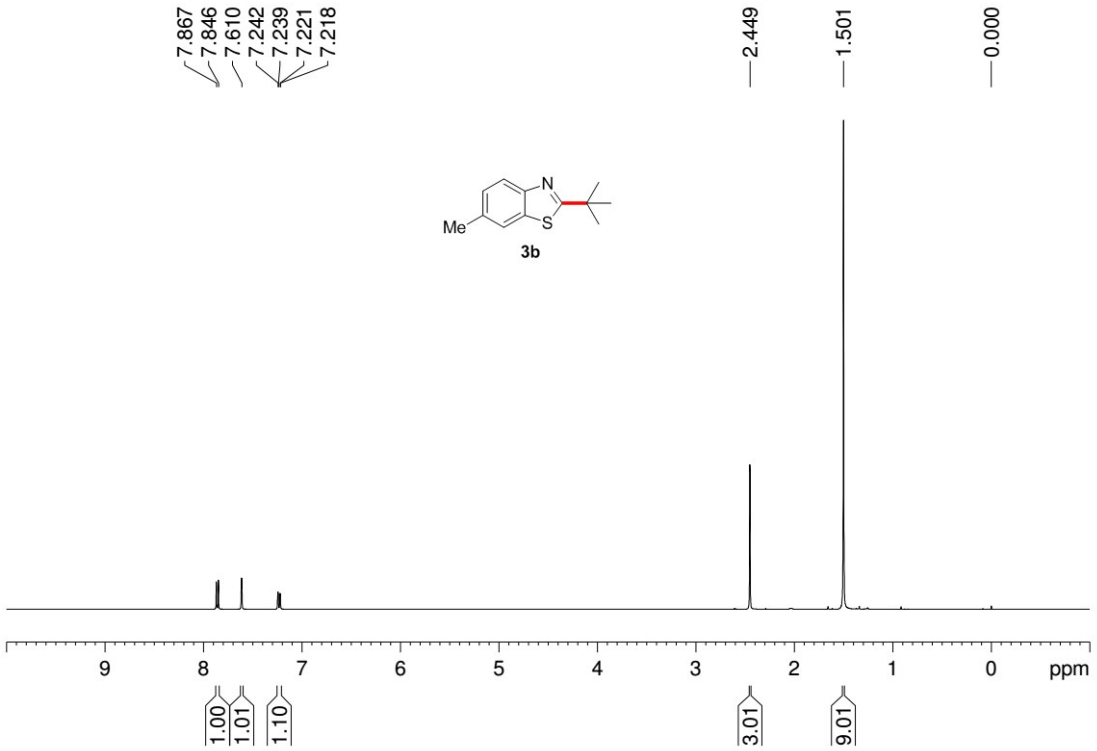


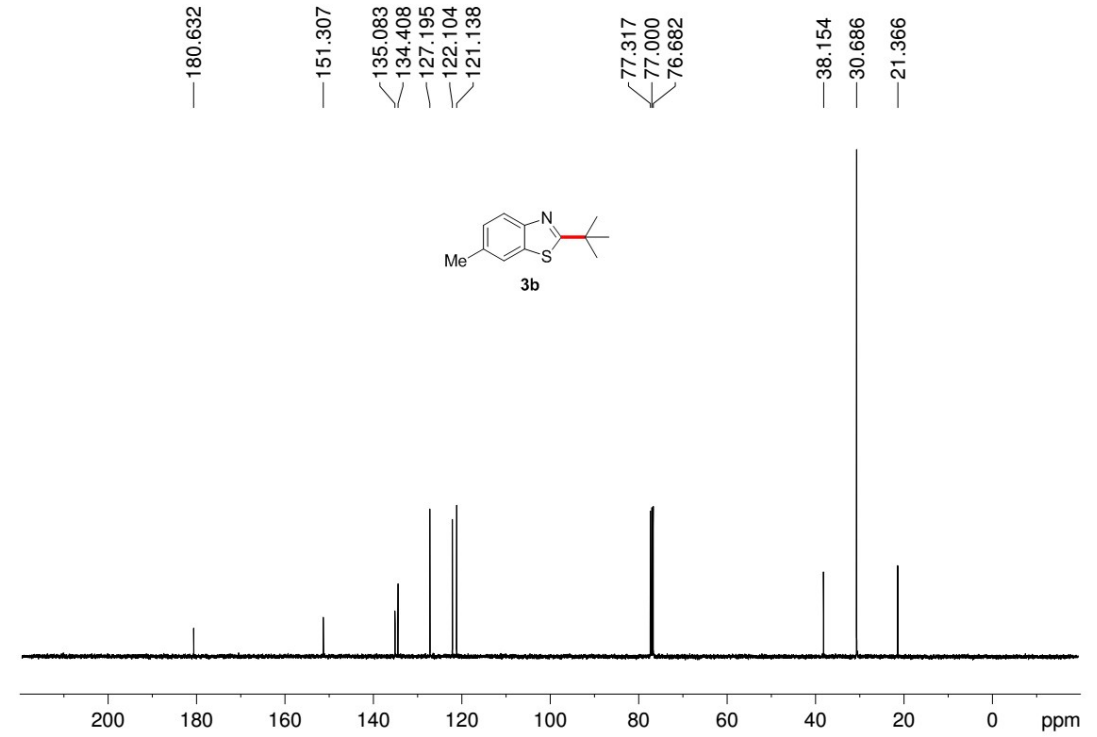
415 nm excitation wavelength

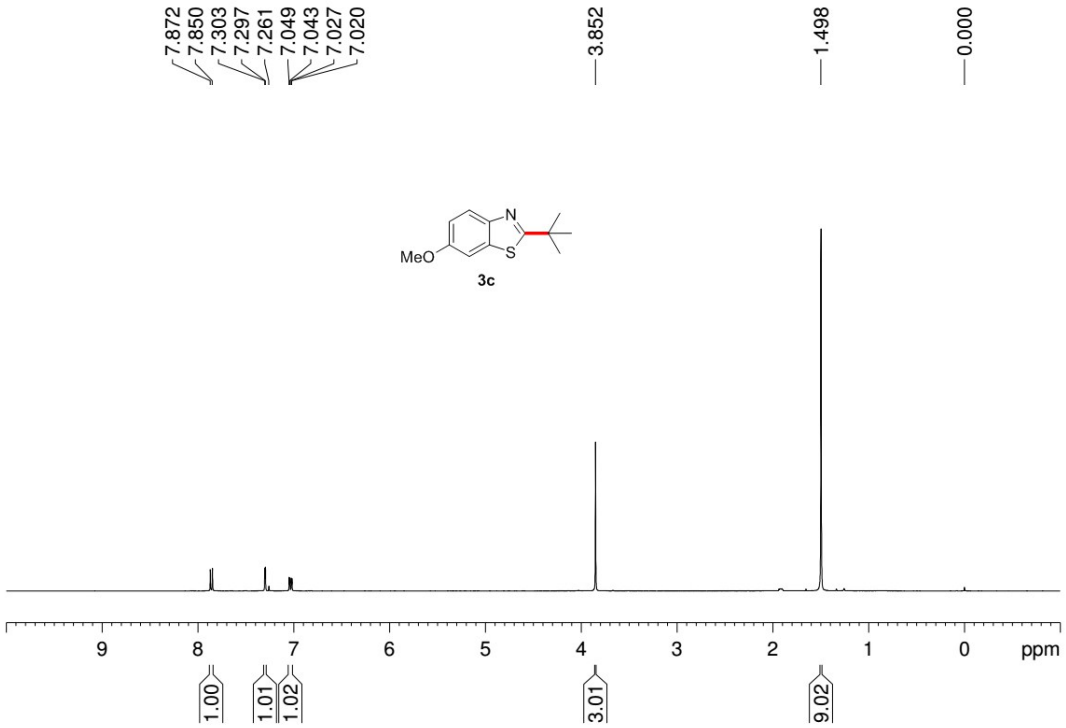
4. ^{1}H and ^{13}C NMR spectra of the products

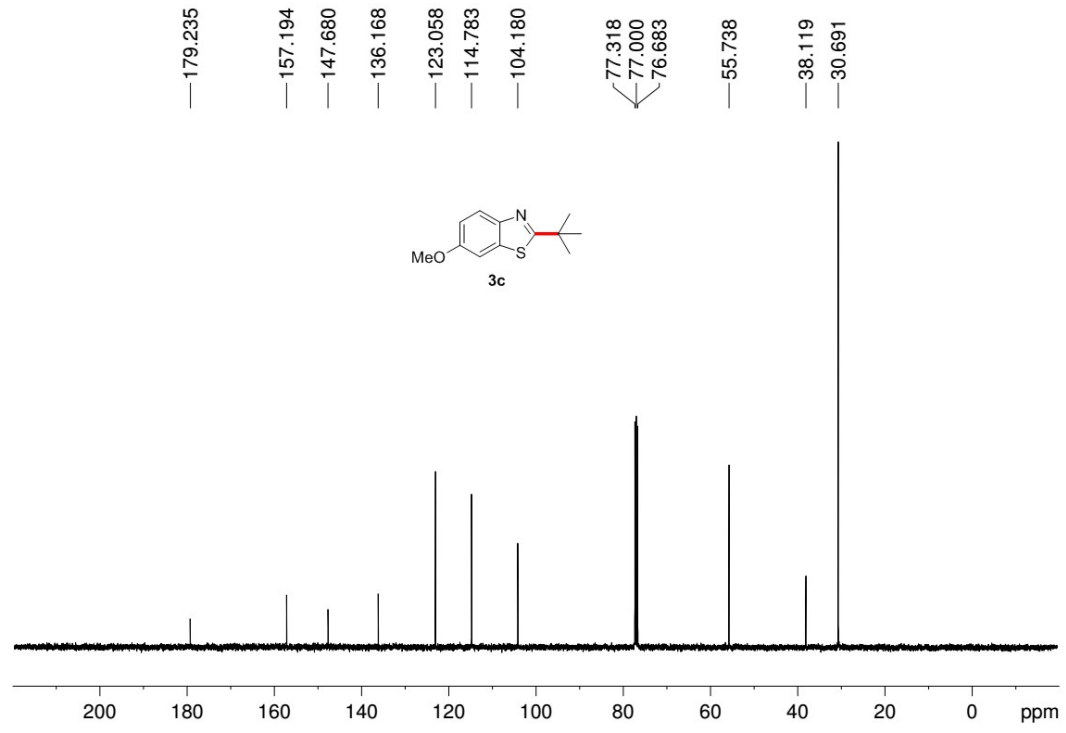


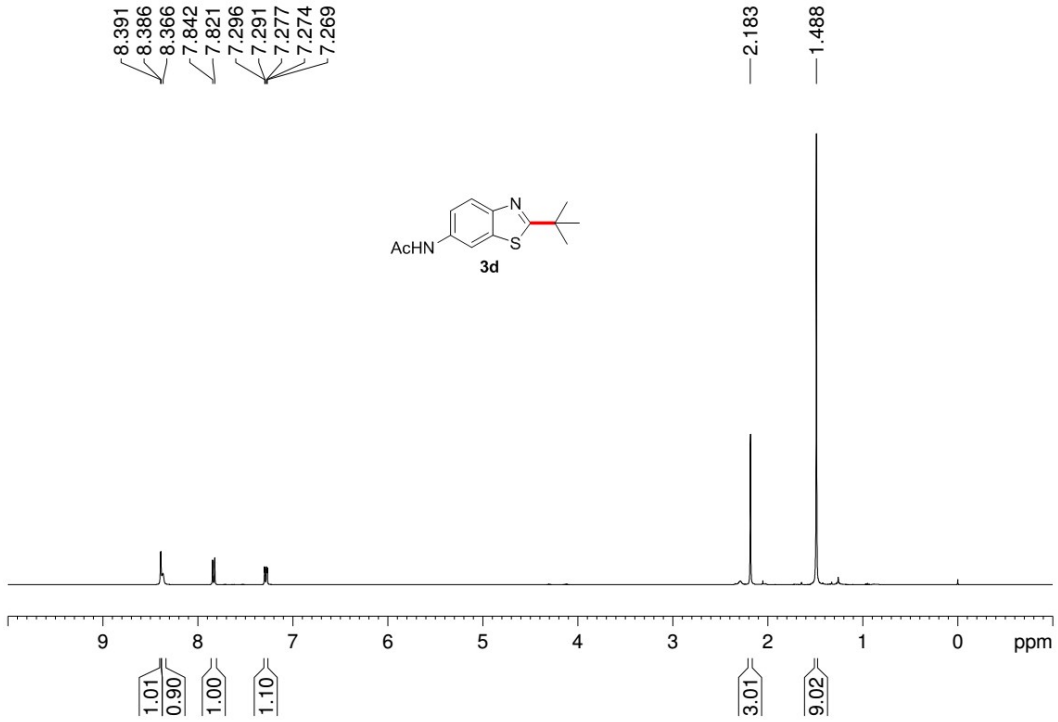


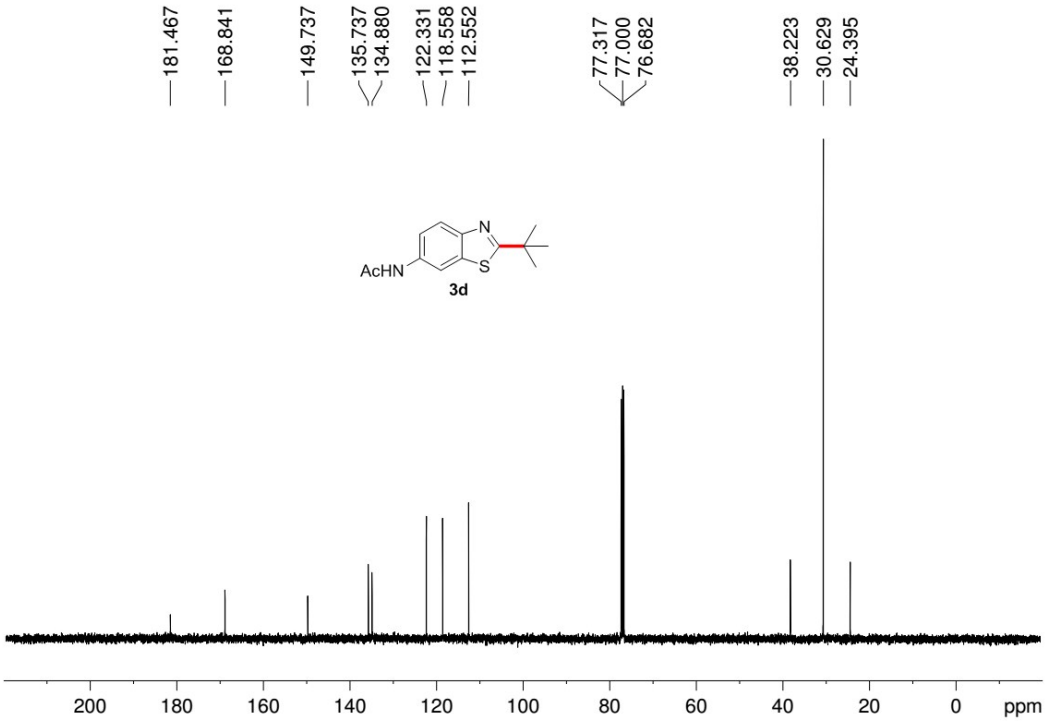

7.867
7.846
7.610
7.242
7.239
7.221
7.218
2.449
1.501
0.000
N
S
Me
3b
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
1.10
3.01
9.01

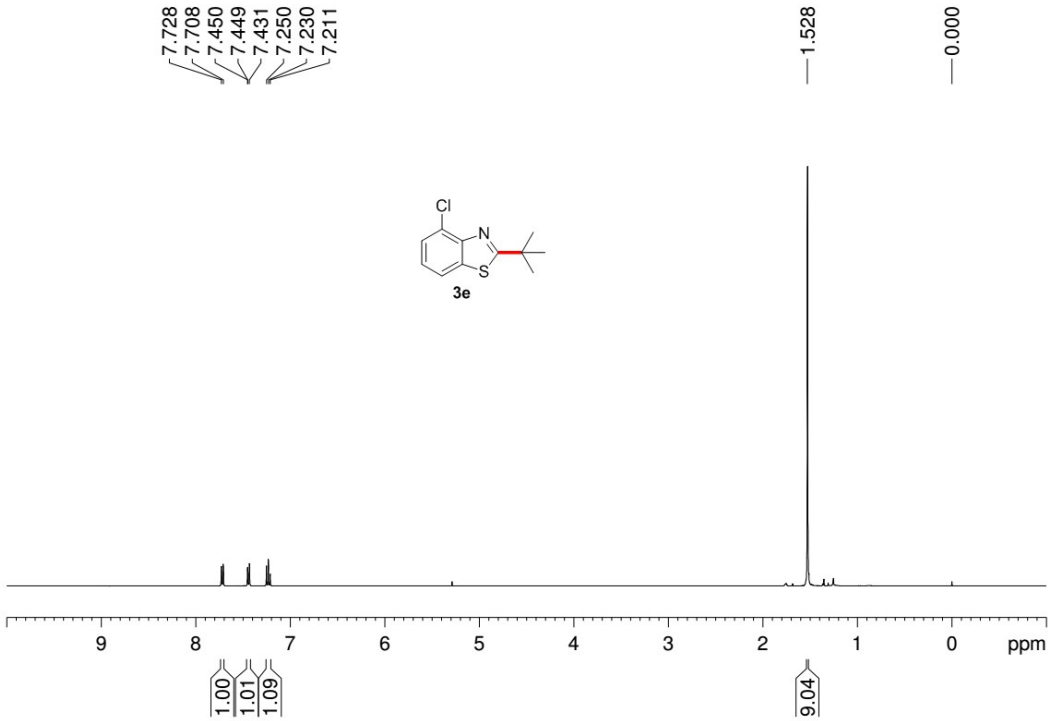

180.632
151.307
135.083
134.408
127.195
122.104
121.138
77.317
77.000
76.682
38.154
30.686
21.366
N
S
Me
3b
200
180
160
140
120
100
80
60
40
20
0
ppm

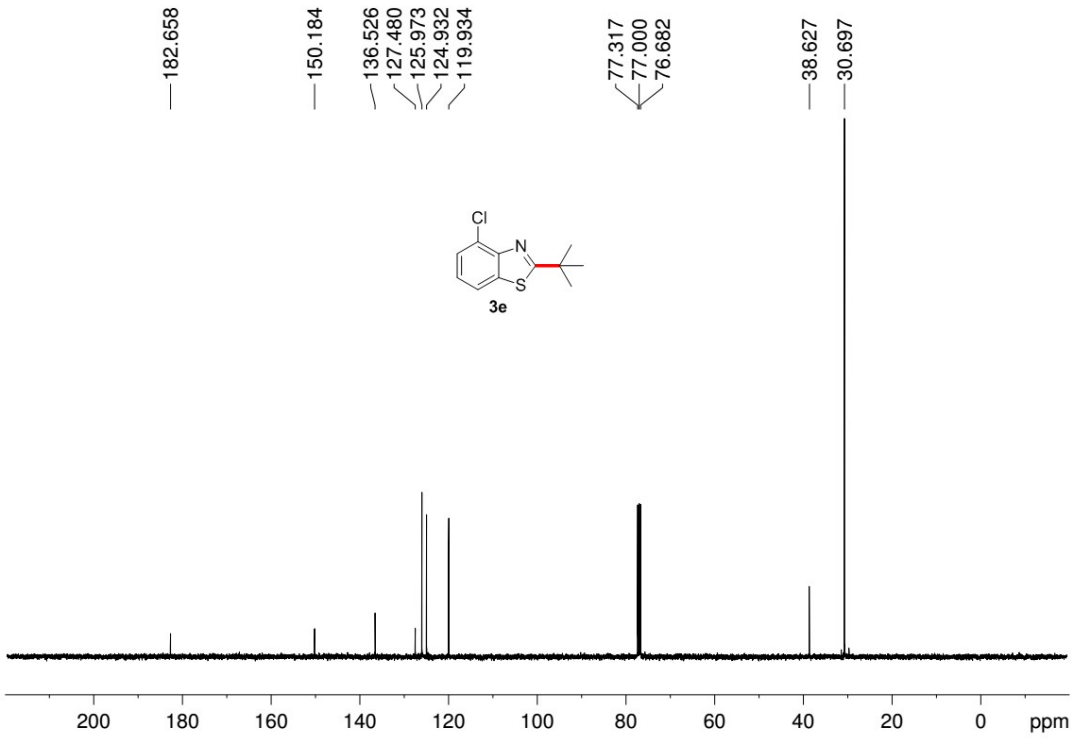

7.872
7.850
7.303
7.297
7.261
7.049
7.043
7.027
7.020
3.852
1.498
0.000
MeO
3c
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
1.02
3.01
9.02

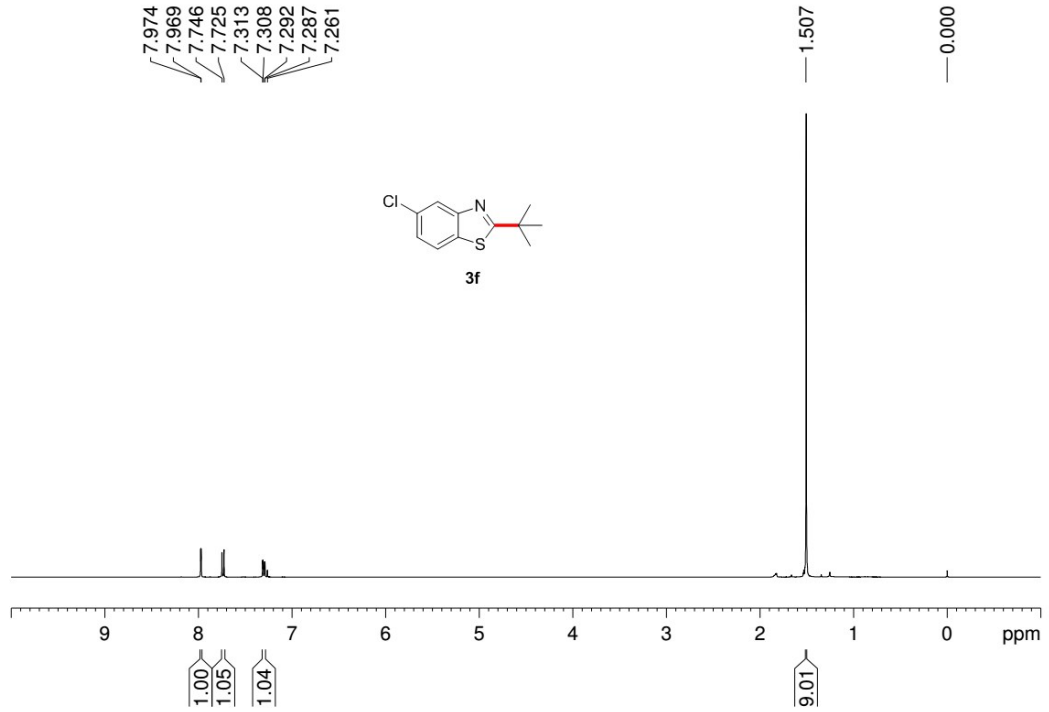

179.235
157.194
147.680
136.168
123.058
114.783
104.180
77.318
77.000
76.683
55.738
38.119
30.691
MeO
3c
200
180
160
140
120
100
80
60
40
20
0
ppm

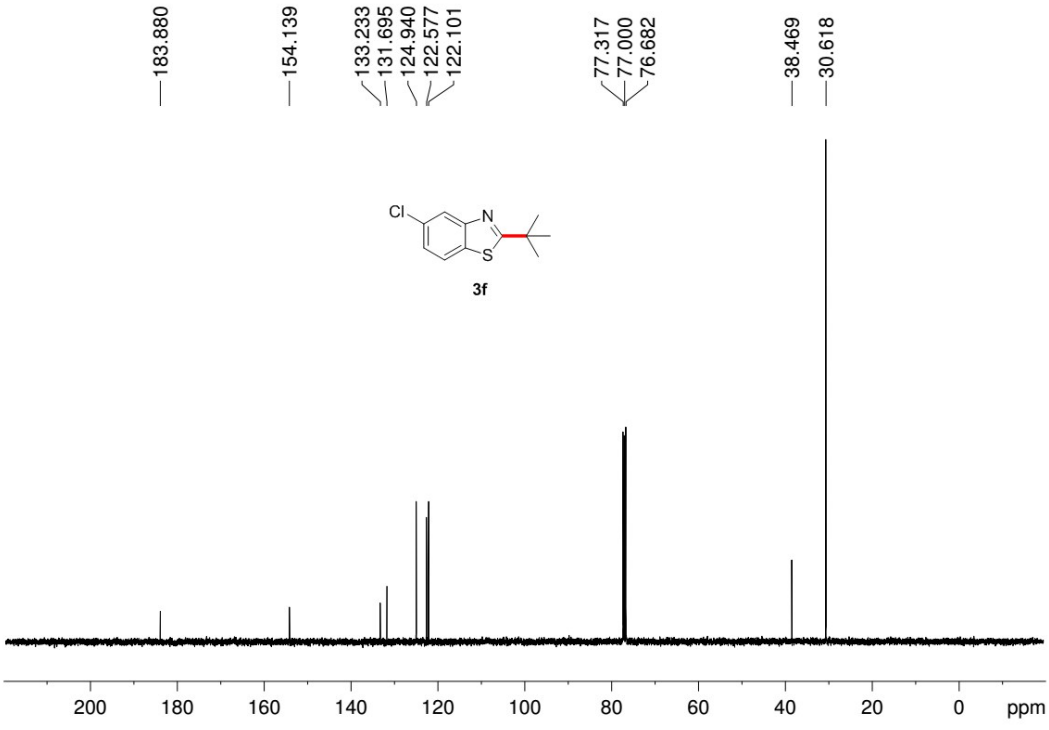

8.391
8.386
8.366
7.842
7.821
7.296
7.291
7.277
7.274
7.269
2.183
1.488
AcHN
N
S
3d
9
8
7
6
5
4
3
2
1
0
ppm
1.01
0.90
1.00
1.10
3.01
9.02

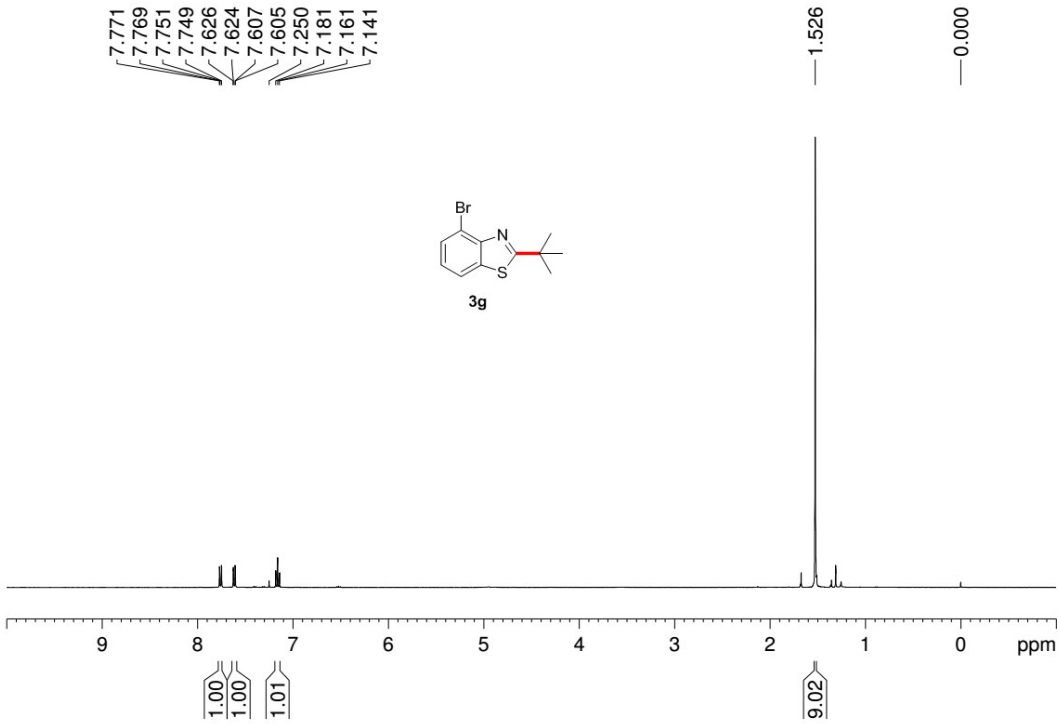

181.467
168.841
149.737
135.737
134.880
122.331
118.558
112.552
77.317
77.000
76.682
38.223
30.629
24.395
AcHN
N
S
3d
200
180
160
140
120
100
80
60
40
20
0
ppm

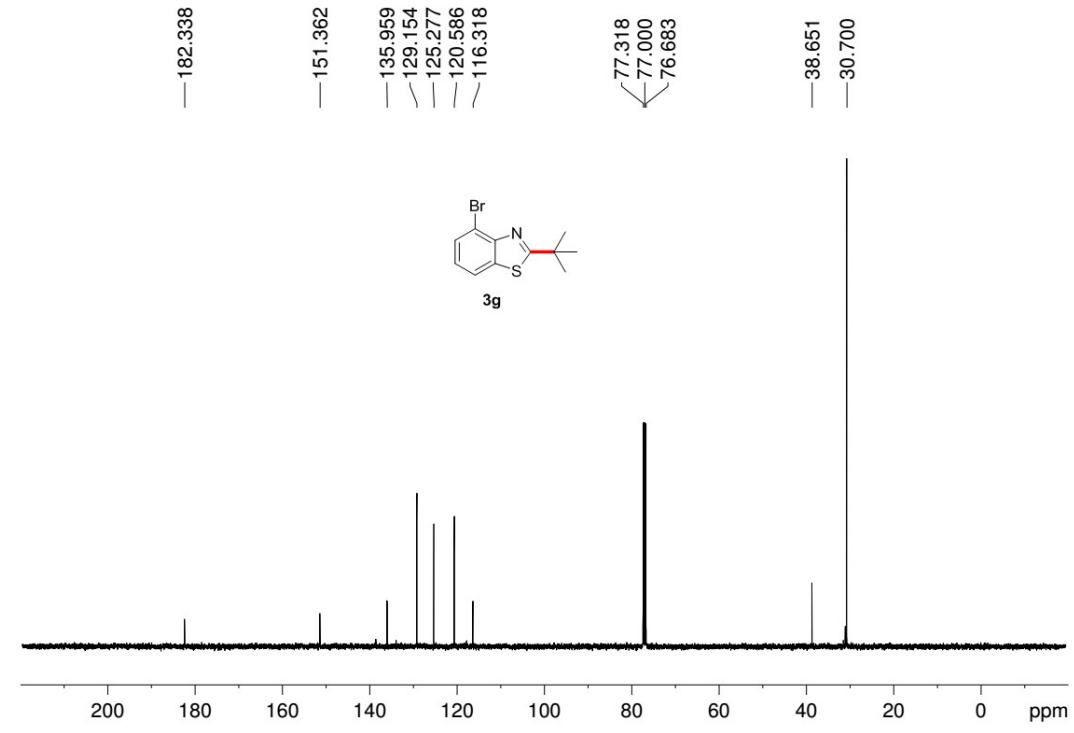

7.728
7.708
7.450
7.449
7.431
7.250
7.230
7.211
1.528
0.000
Cl
N
S
3e
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
1.09
9.04

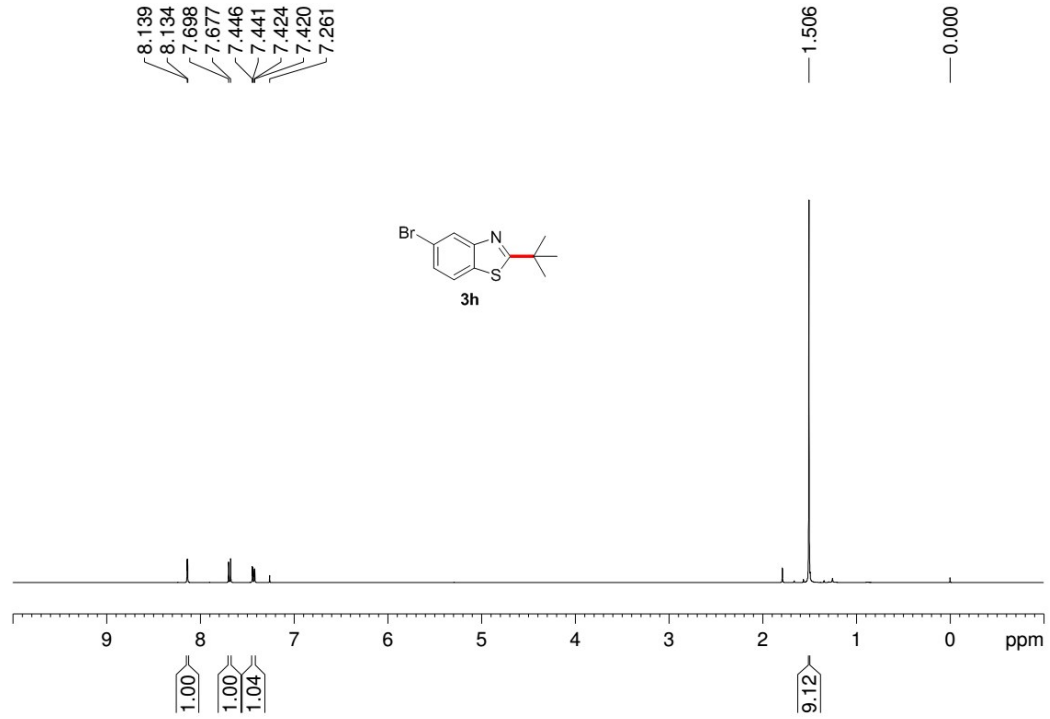

182.658
150.184
136.526
127.480
125.973
124.932
119.934
77.317
77.000
76.682
38.627
30.697
Cl
N
S
3e
200
180
160
140
120
100
80
60
40
20
0
ppm

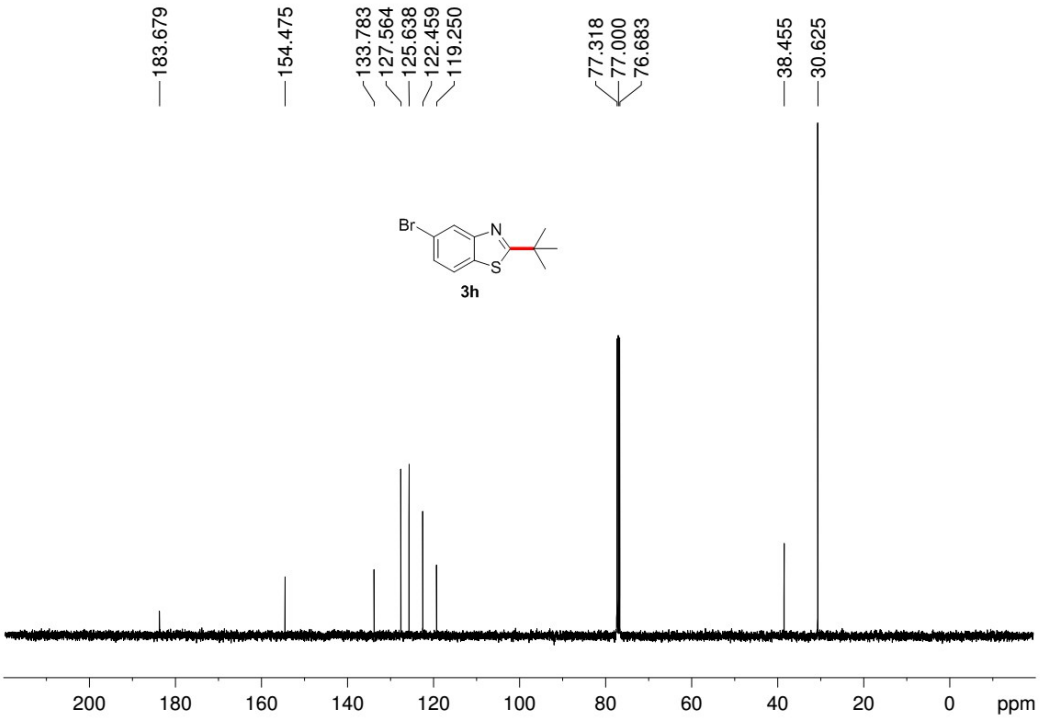

7.974
7.969
7.746
7.725
7.313
7.308
7.292
7.287
7.261
1.507
0.000
Cl
N
S
3f
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.05
1.04
9.01

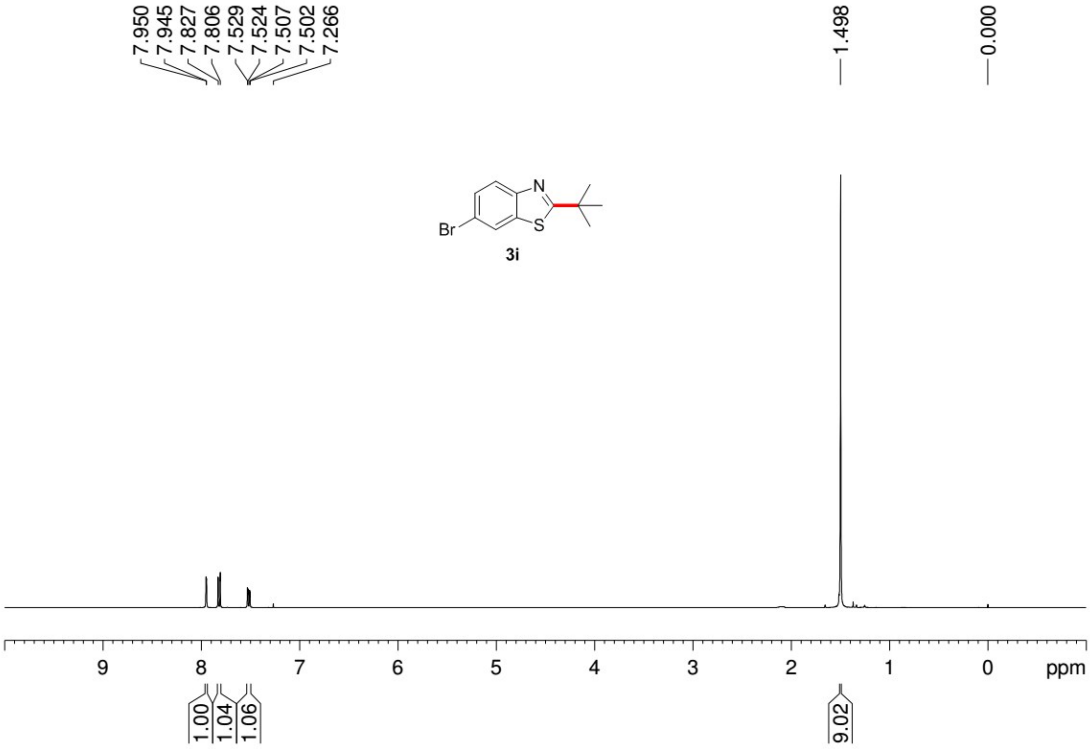

183.880
154.139
133.233
131.695
124.940
122.577
122.101
77.317
77.000
76.682
38.469
30.618
Cl
N
S
3f
200
180
160
140
120
100
80
60
40
20
0
ppm

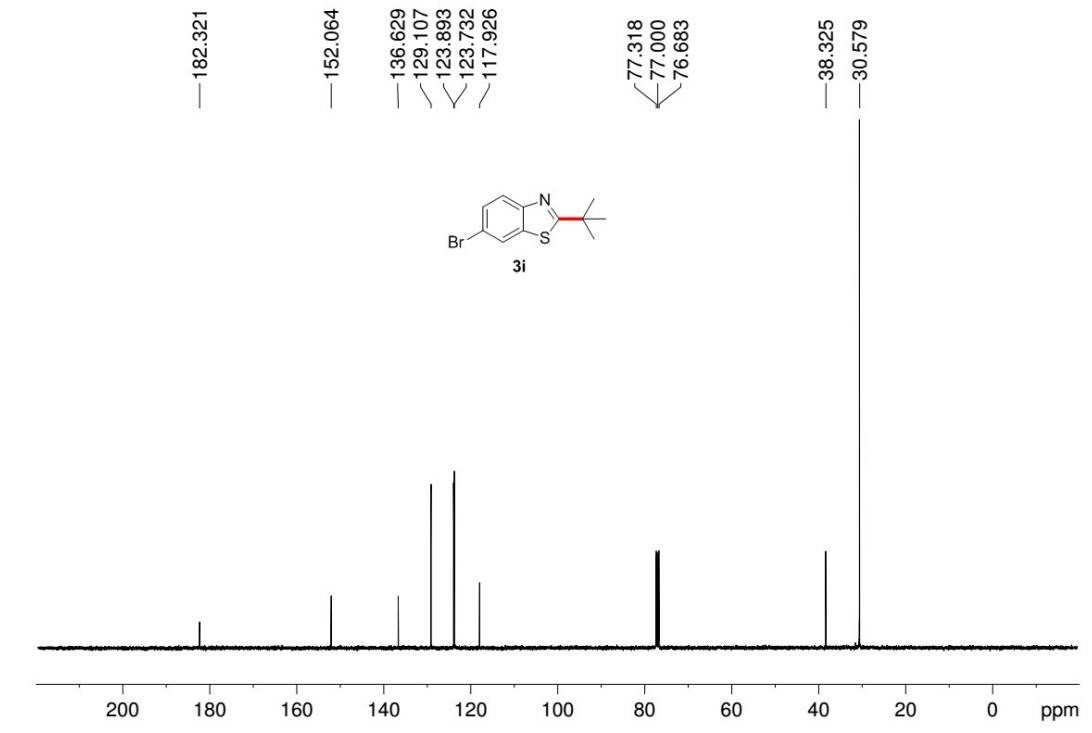

7.771
7.769
7.751
7.749
7.626
7.624
7.607
7.605
7.250
7.181
7.161
7.141
1.526
0.000
Br
N
S
3g
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
1.01
9.02

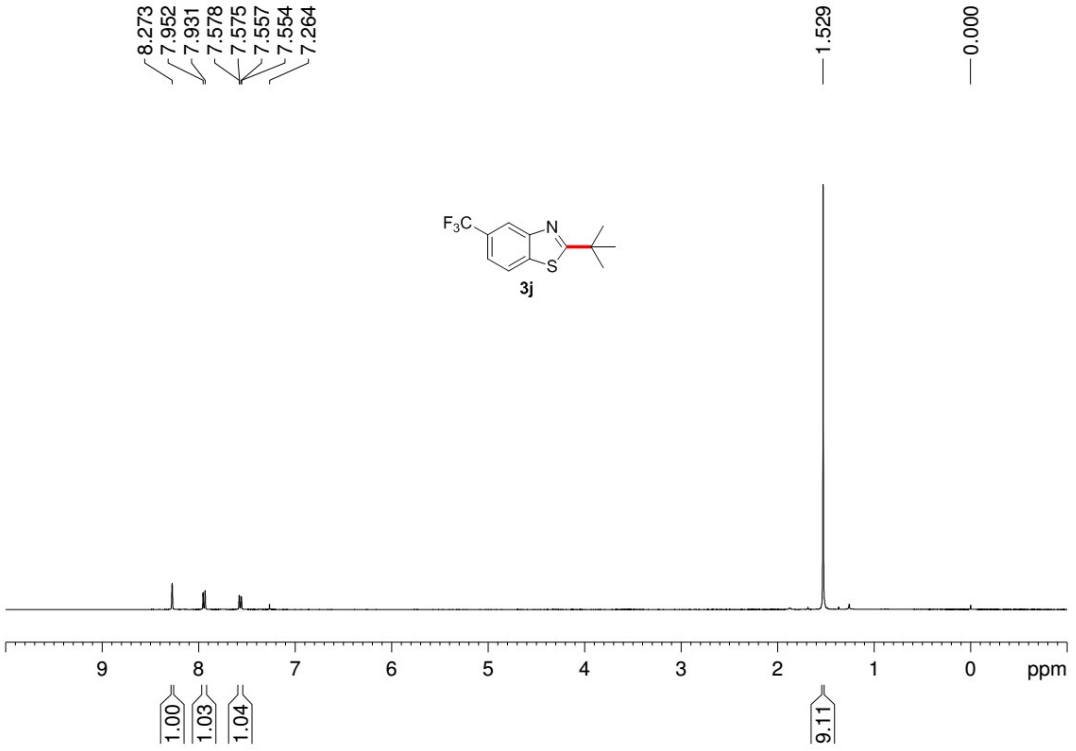

182.338
151.362
135.959
129.154
125.277
120.586
116.318
77.318
77.000
76.683
38.651
30.700
Br
N
S
3g
200
180
160
140
120
100
80
60
40
20
0
ppm

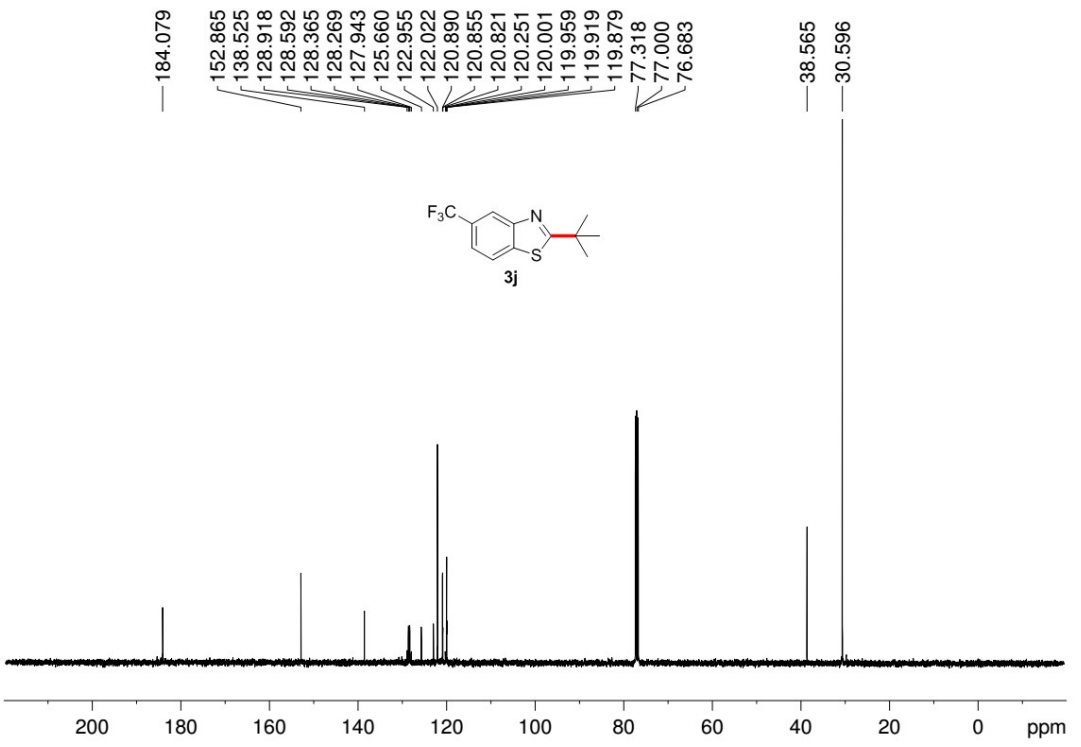

8.139
8.134
7.698
7.677
7.446
7.441
7.424
7.420
7.261
1.506
0.000
Br
N
S
3h
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
1.04
9.12

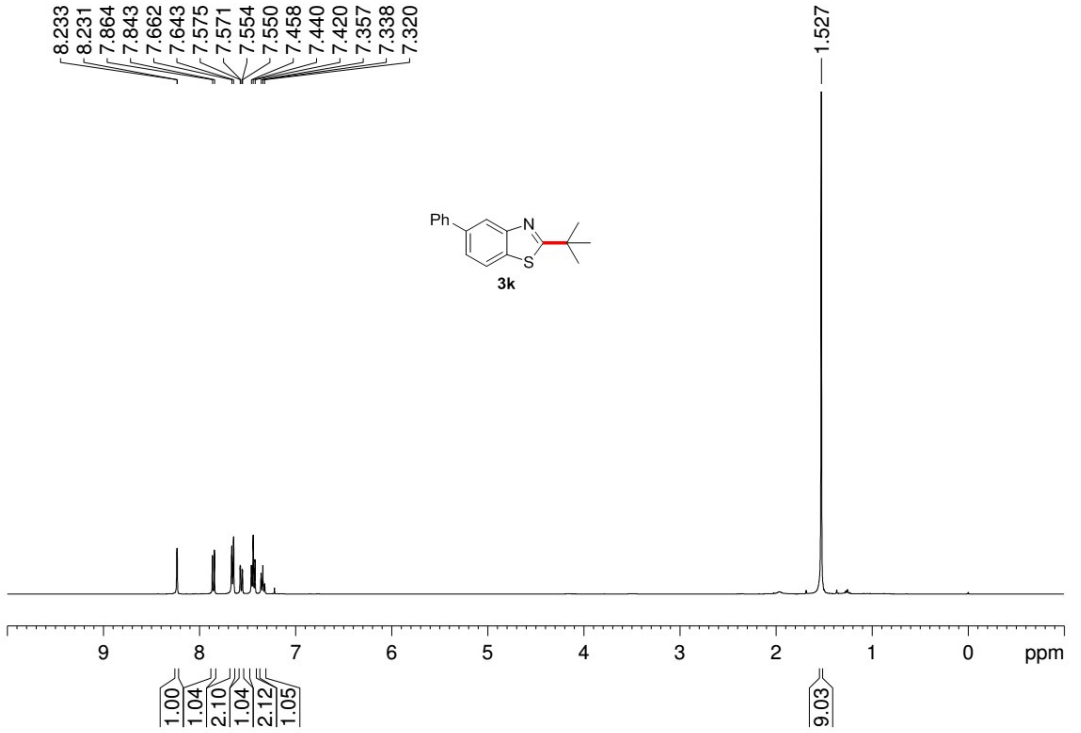

183.679
154.475
133.783
127.564
125.638
122.459
119.250
77.318
77.000
76.683
38.455
30.625
Br
N
S
3h
200
180
160
140
120
100
80
60
40
20
0
ppm

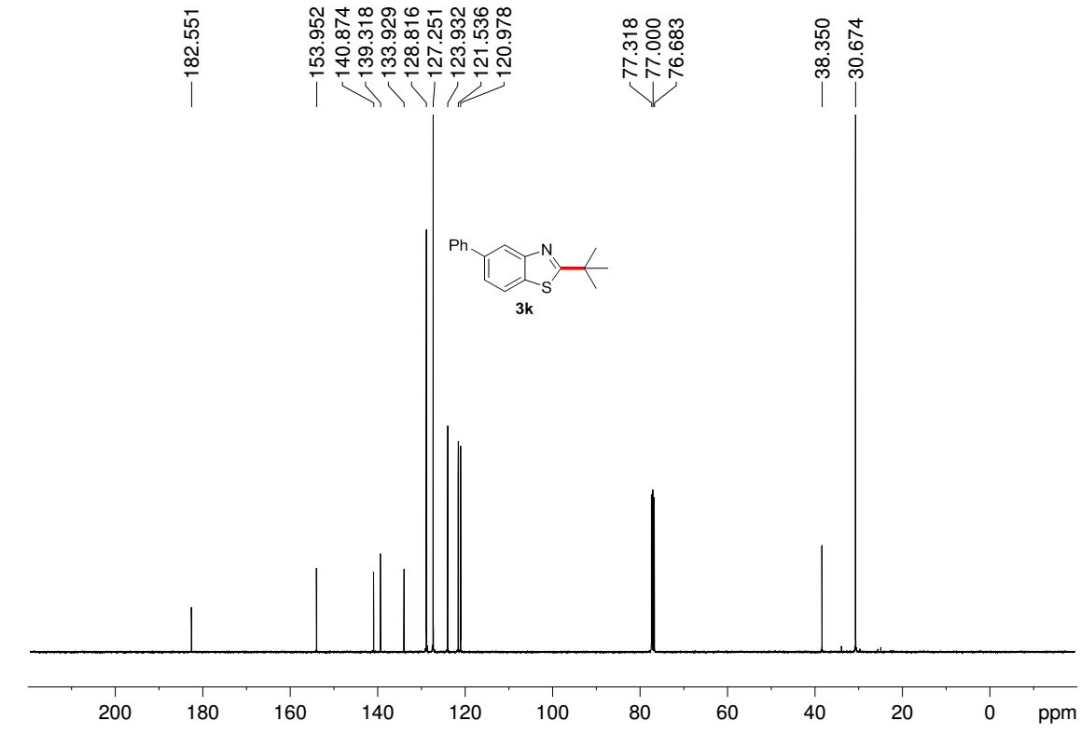

7.950
7.945
7.827
7.806
7.529
7.524
7.507
7.502
7.266
1.498
0.000
Br
N
S
3i
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.04
1.06
9.02

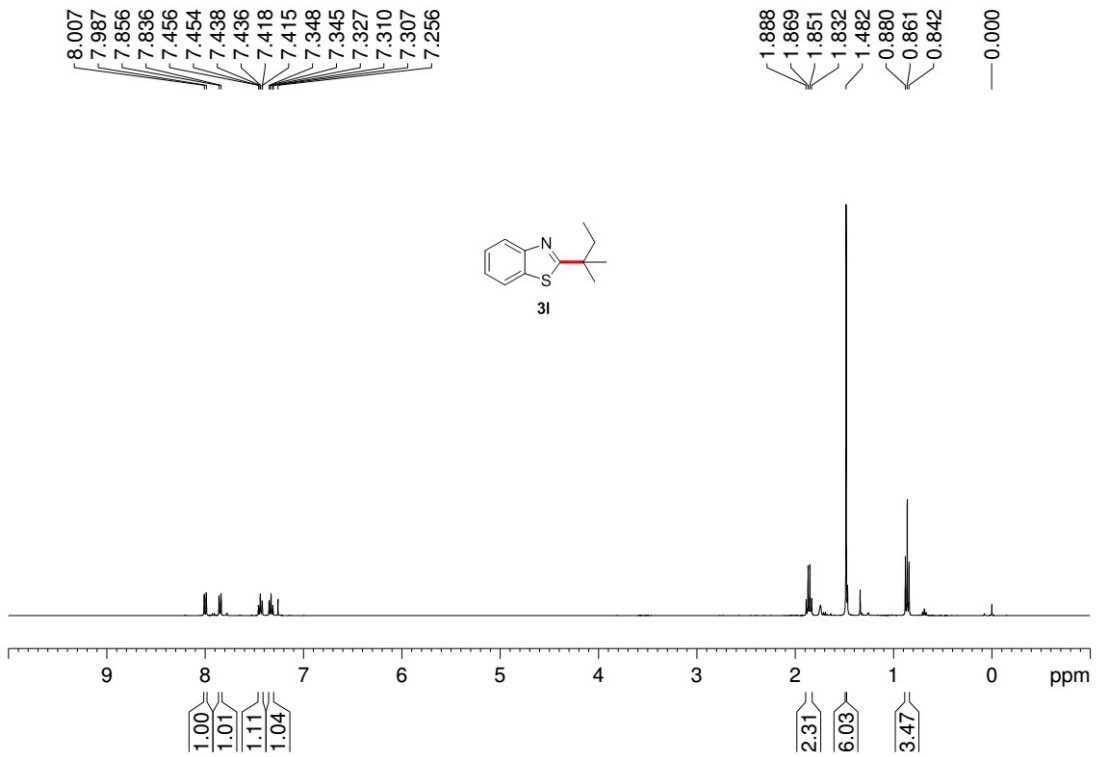

182.321
152.064
136.629
129.107
123.893
123.732
117.926
77.318
77.000
76.683
38.325
30.579
Br
N
S
3i
200
180
160
140
120
100
80
60
40
20
0
ppm

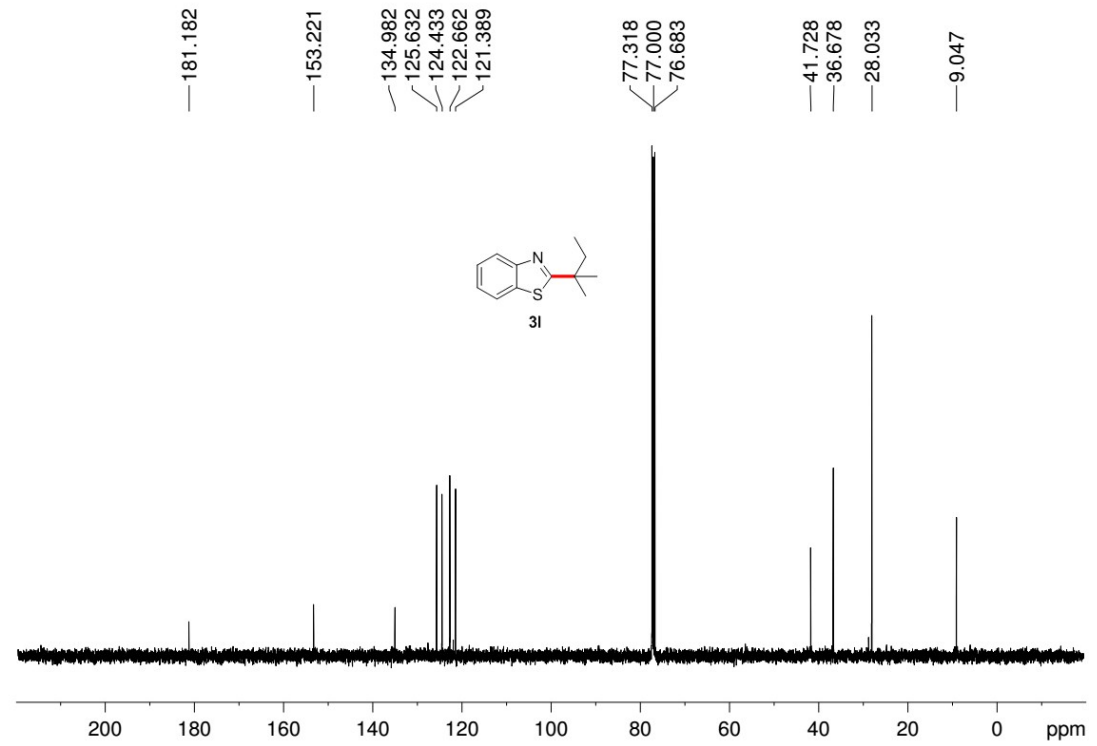

8.273
7.952
7.931
7.578
7.575
7.557
7.554
7.264
1.529
0.000
F3C
N
S
3j
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.03
1.04
9.11

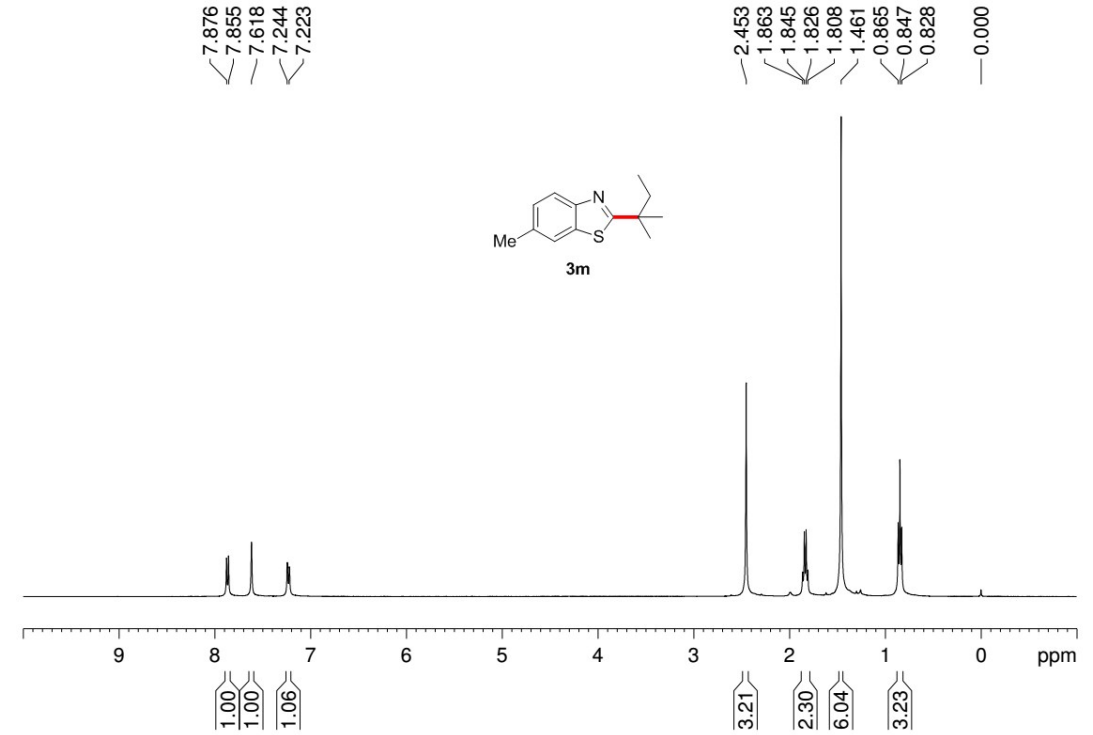

184.079
152.865
138.525
128.918
128.592
128.365
128.269
127.943
125.660
122.955
122.022
120.890
120.855
120.821
120.251
120.001
119.959
119.919
119.879
77.318
77.000
76.683
38.565
30.596
F3C
N
S
3j
200
180
160
140
120
100
80
60
40
20
0
ppm

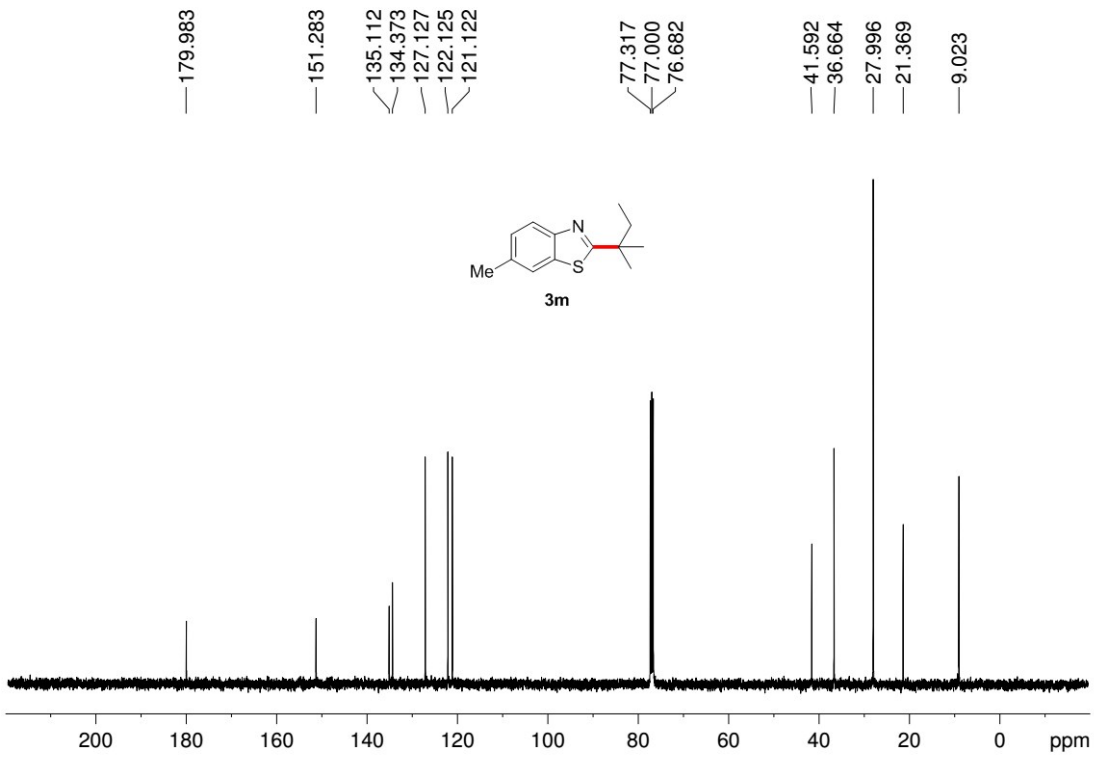

8.233
8.231
7.864
7.843
7.662
7.643
7.575
7.571
7.554
7.550
7.458
7.440
7.420
7.357
7.338
7.320
1.527
Ph
N
S
3k
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.04
2.10
1.04
2.12
1.05
9.03

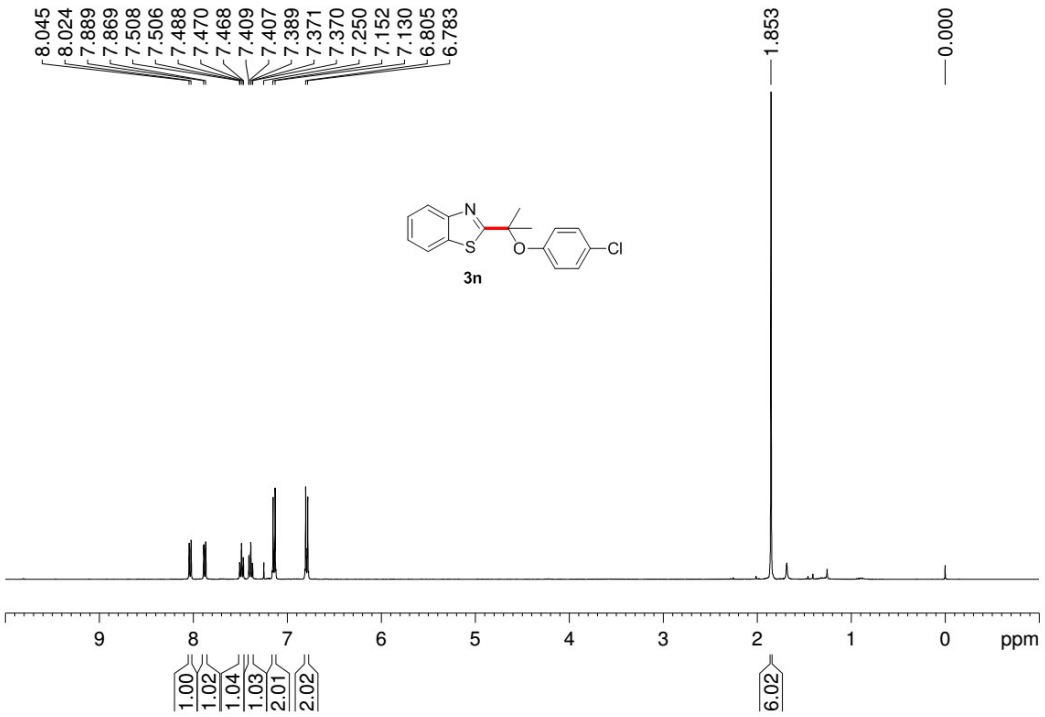

182.551
153.952
140.874
139.318
133.929
128.816
127.251
123.932
121.536
120.978
77.318
77.000
76.683
38.350
30.674
Ph
N
S
3k
200
180
160
140
120
100
80
60
40
20
0
ppm

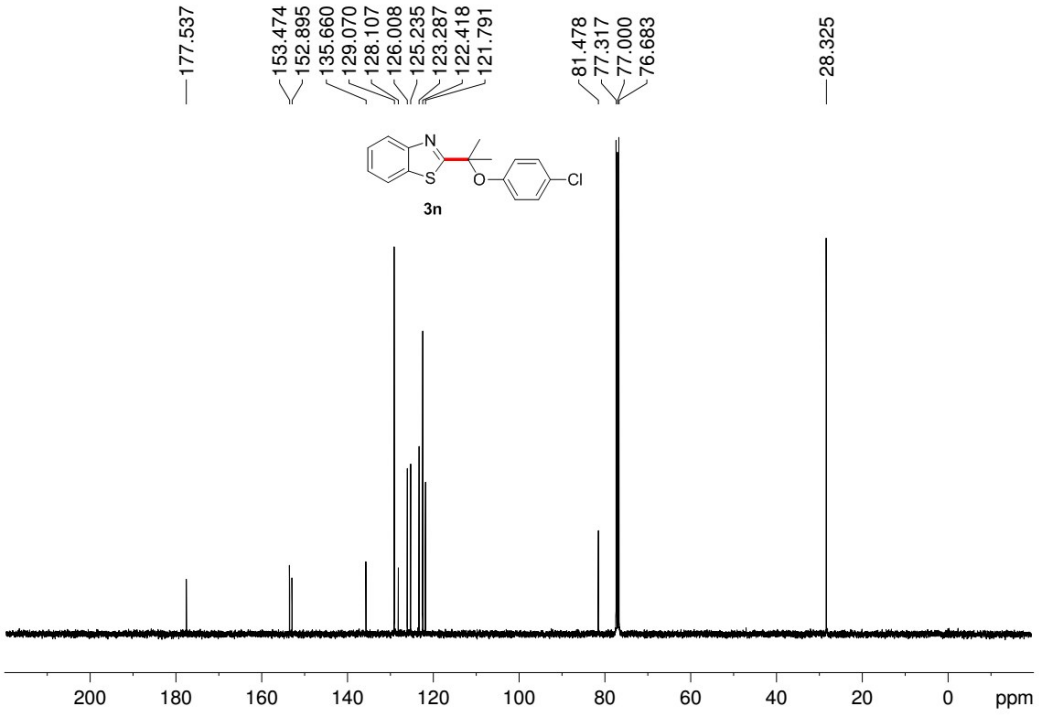

8.007
7.987
7.856
7.836
7.456
7.454
7.438
7.436
7.418
7.415
7.348
7.345
7.327
7.310
7.307
7.256
1.888
1.869
1.851
1.832
1.482
0.880
0.861
0.842
0.000
3l
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
1.11
1.04
2.31
6.03
3.47

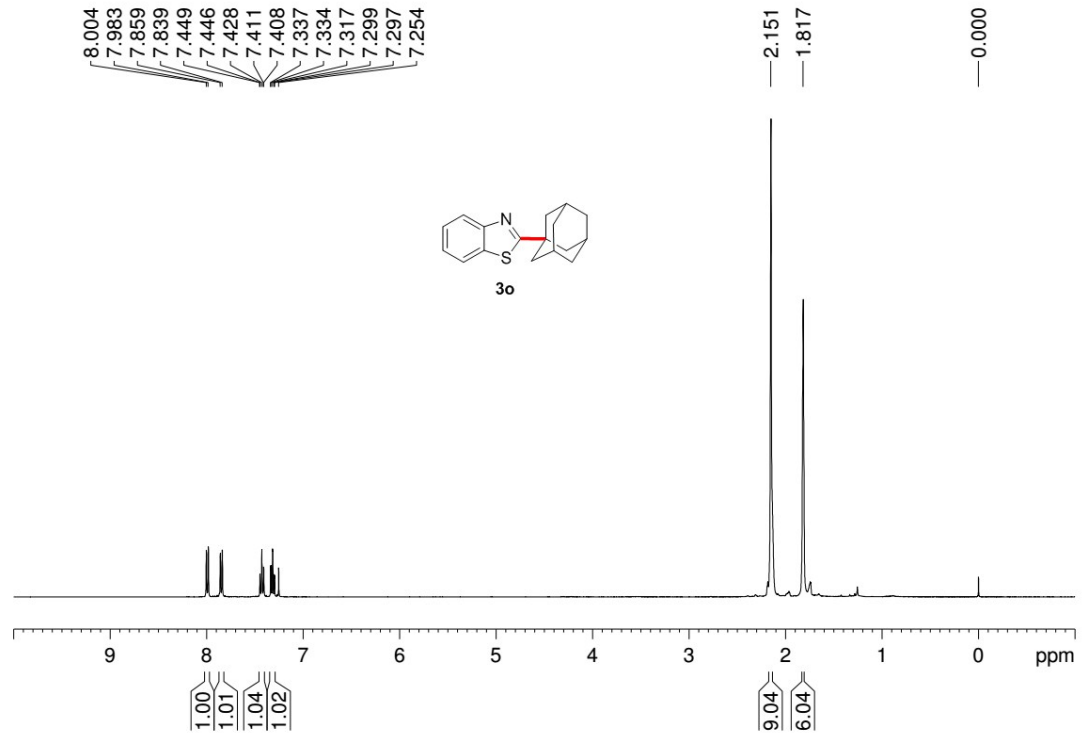

181.182
153.221
134.982
125.632
124.433
122.662
121.389
77.318
77.000
76.683
41.728
36.678
28.033
9.047
3l
200
180
160
140
120
100
80
60
40
20
0
ppm

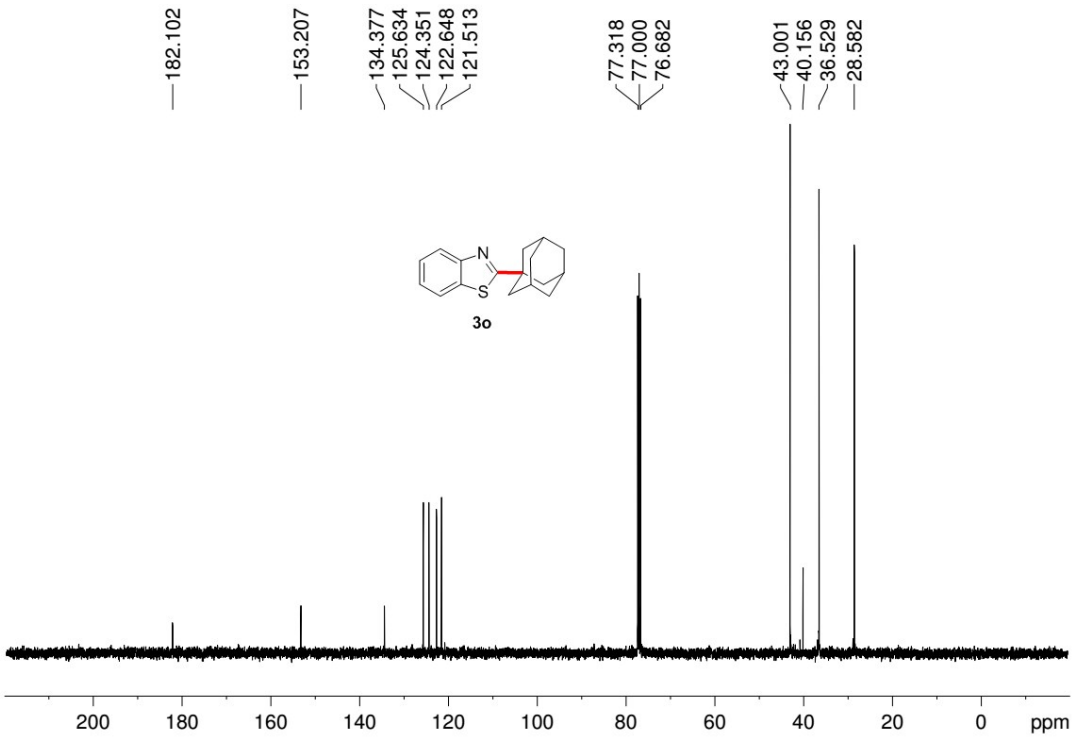

7.876
7.855
7.618
7.244
7.223
2.453
1.863
1.845
1.826
1.808
1.461
0.865
0.847
0.828
0.000
N
S
Me
3m
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
1.06
3.21
2.30
6.04
3.23

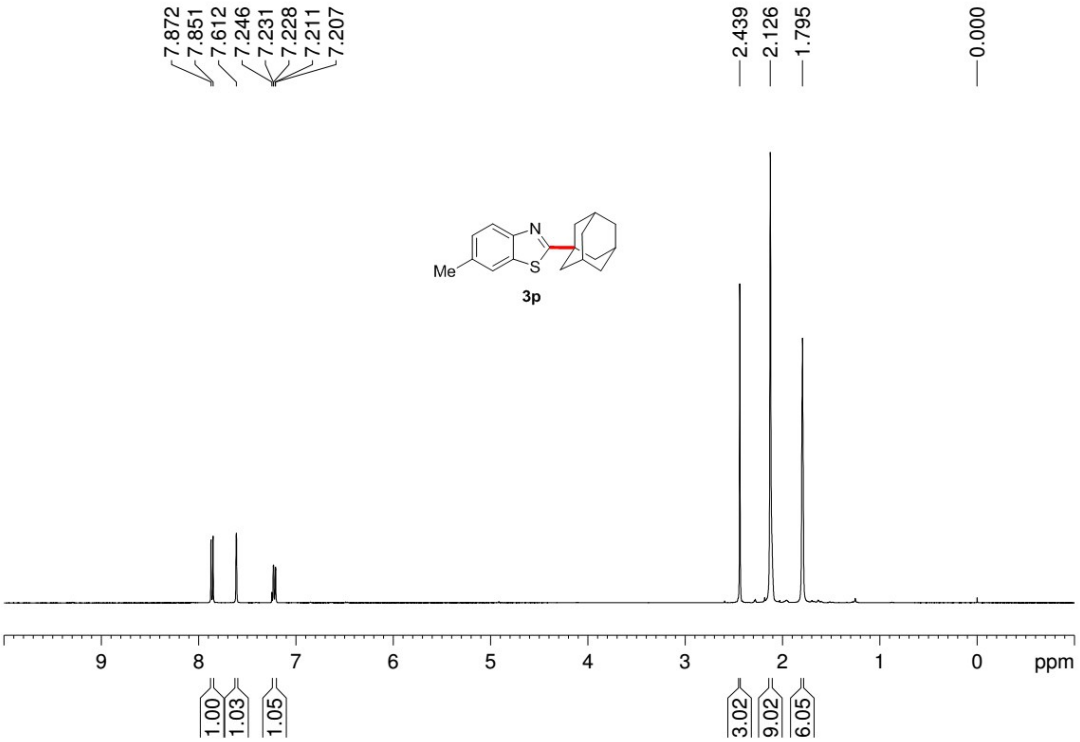

179.983
151.283
135.112
134.373
127.127
122.125
121.122
77.317
77.000
76.682
41.592
36.664
27.996
21.369
9.023
N
S
Me
3m
200
180
160
140
120
100
80
60
40
20
0
ppm

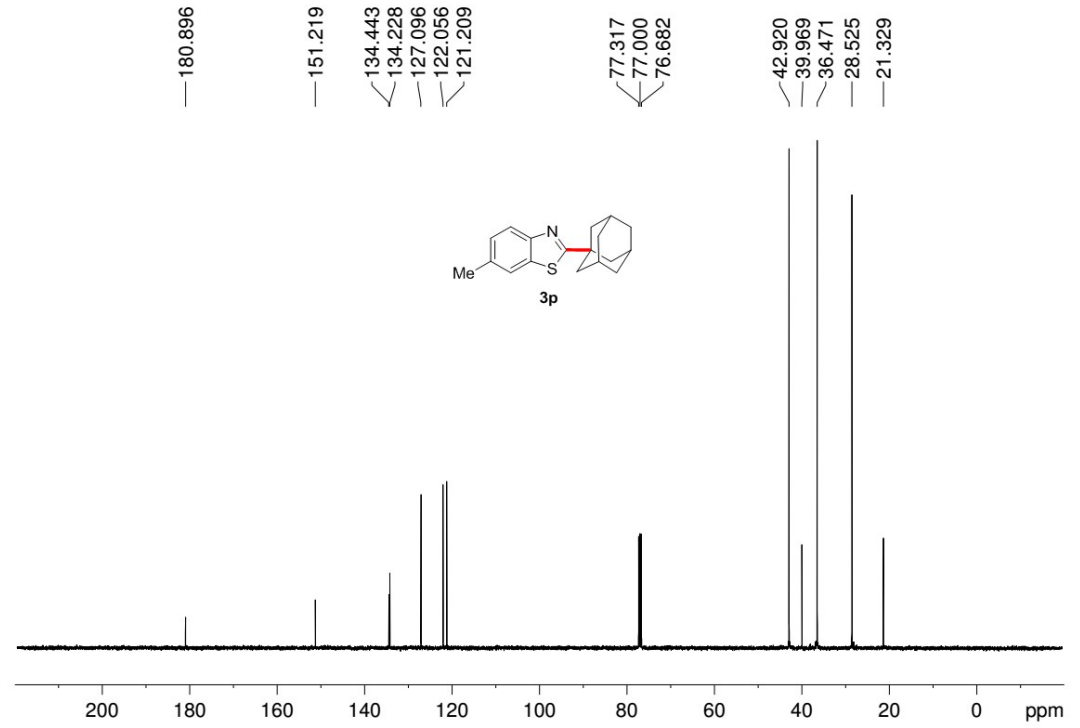

8.045
8.024
7.889
7.869
7.508
7.506
7.488
7.470
7.468
7.409
7.407
7.389
7.371
7.370
7.250
7.152
7.130
6.805
6.783
1.853
0.000
N
S
O
Cl
3n
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.02
1.04
1.03
2.01
2.02
6.02

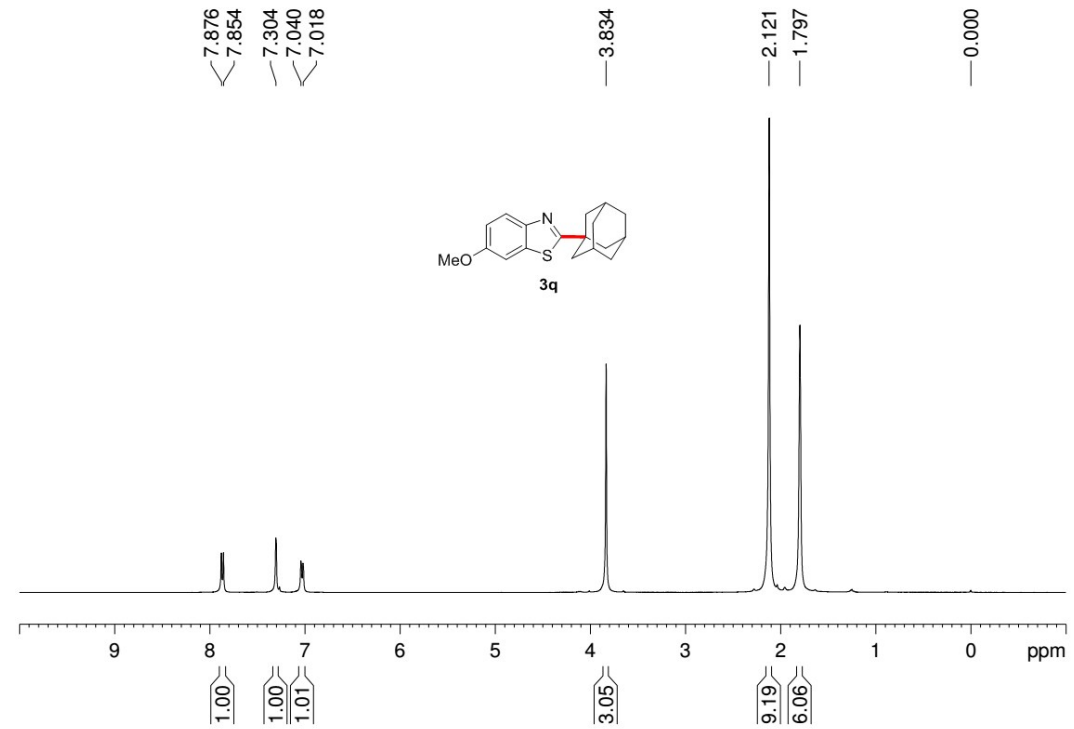

177.537
153.474
152.895
135.660
129.070
128.107
126.008
125.235
123.287
122.418
121.791
81.478
77.317
77.000
76.683
28.325
N
S
O
Cl
3n
200
180
160
140
120
100
80
60
40
20
0
ppm

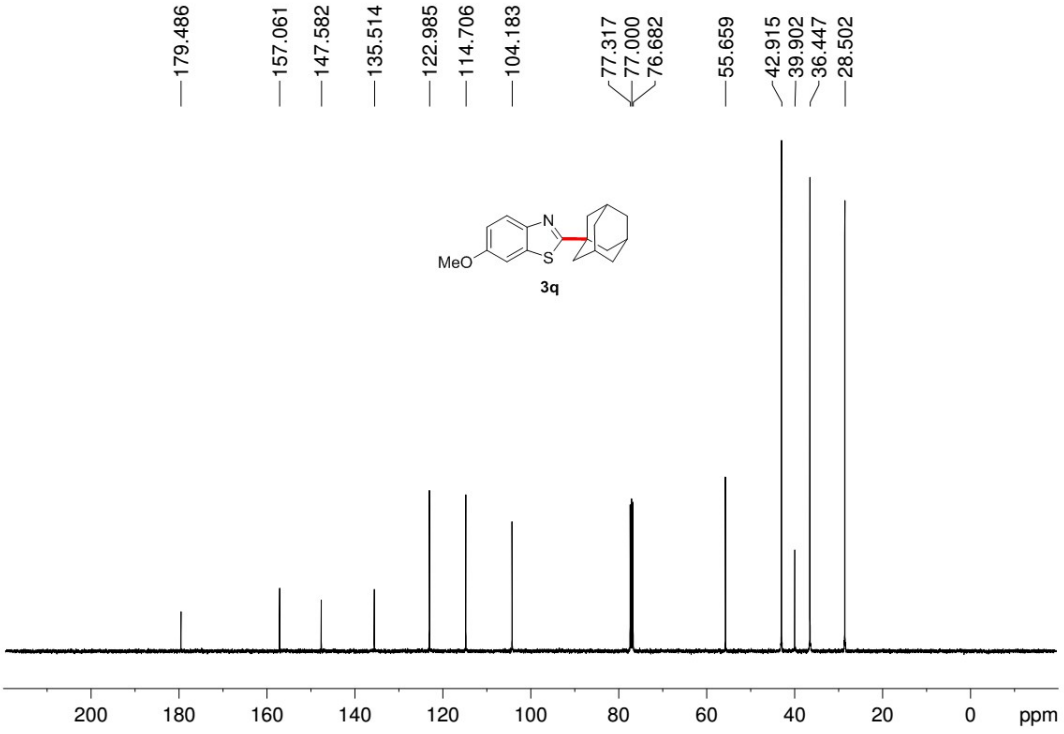

8.004
7.983
7.859
7.839
7.449
7.446
7.428
7.411
7.408
7.337
7.334
7.317
7.299
7.297
7.254
2.151
1.817
0.000
3o
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
1.04
1.02
9.04
6.04

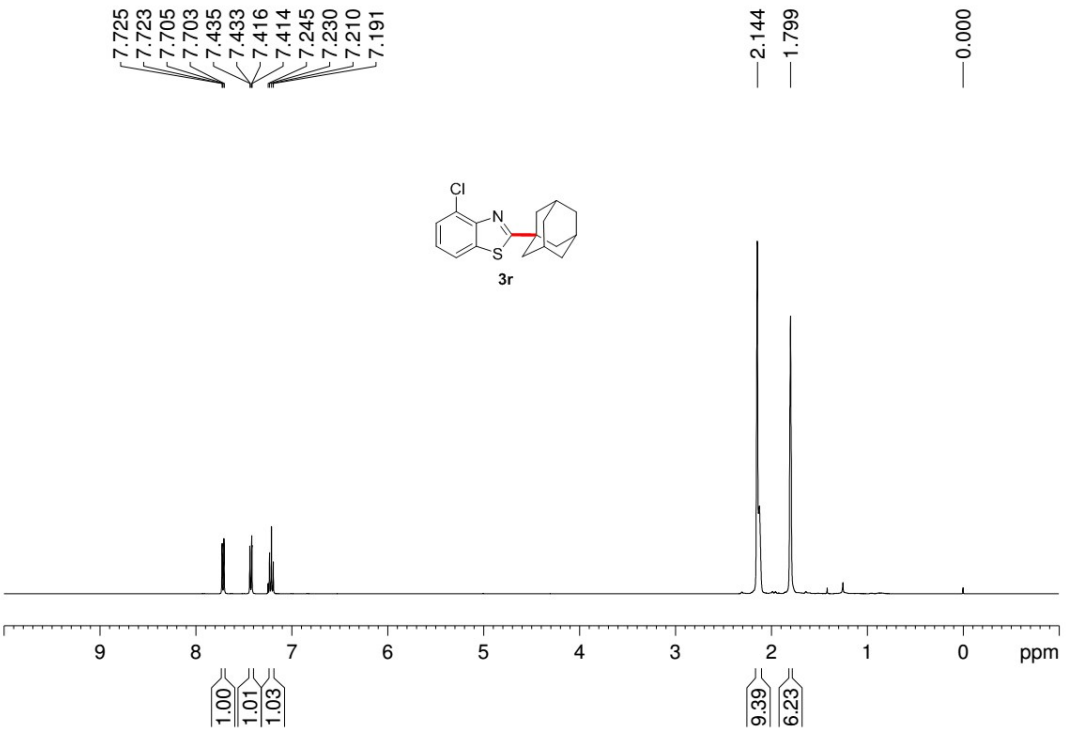

182.102
153.207
134.377
125.634
124.351
122.648
121.513
77.318
77.000
76.682
43.001
40.156
36.529
28.582
3o
200
180
160
140
120
100
80
60
40
20
0
ppm

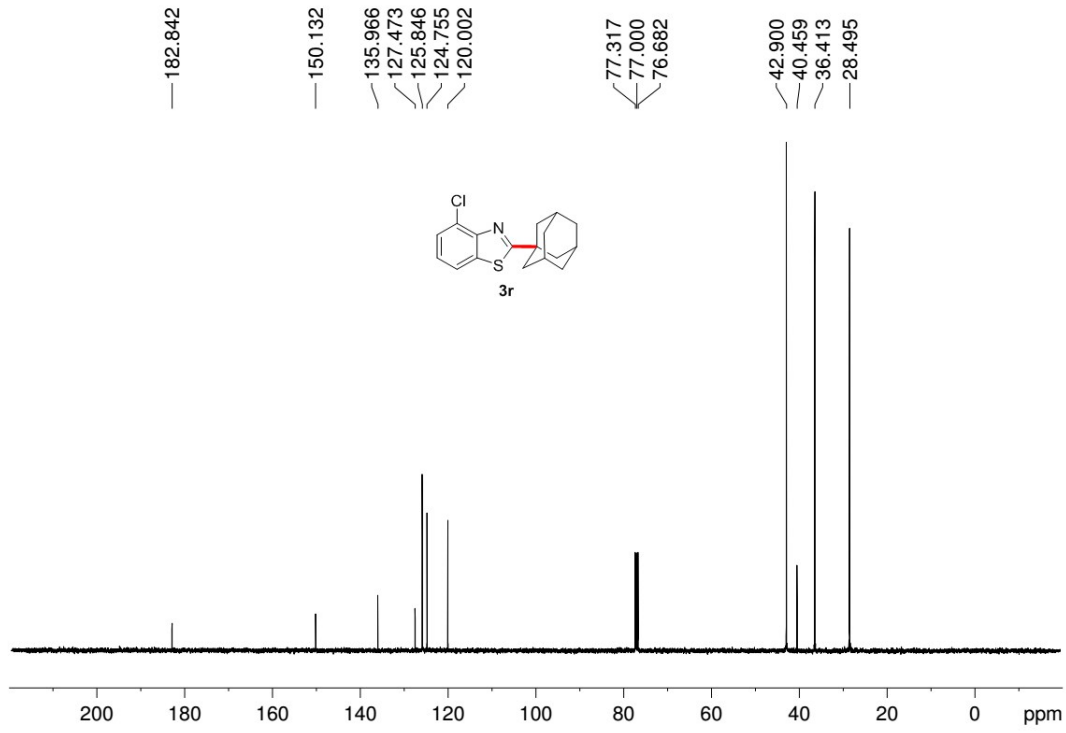

7.872
7.851
7.612
7.246
7.231
7.228
7.211
7.207
2.439
2.126
1.795
0.000
N
S
Me
3p
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.03
1.05
3.02
9.02
6.05

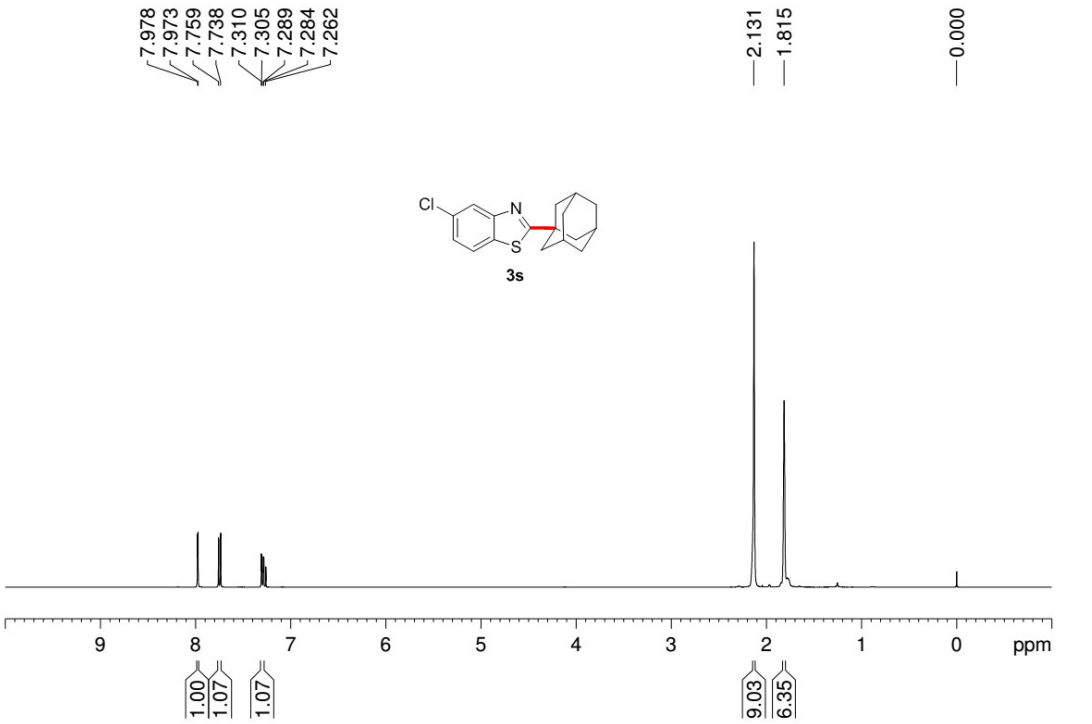

180.896
151.219
134.443
134.228
127.096
122.056
121.209
77.317
77.000
76.682
42.920
39.969
36.471
28.525
21.329
N
S
Me
3p
200
180
160
140
120
100
80
60
40
20
0
ppm

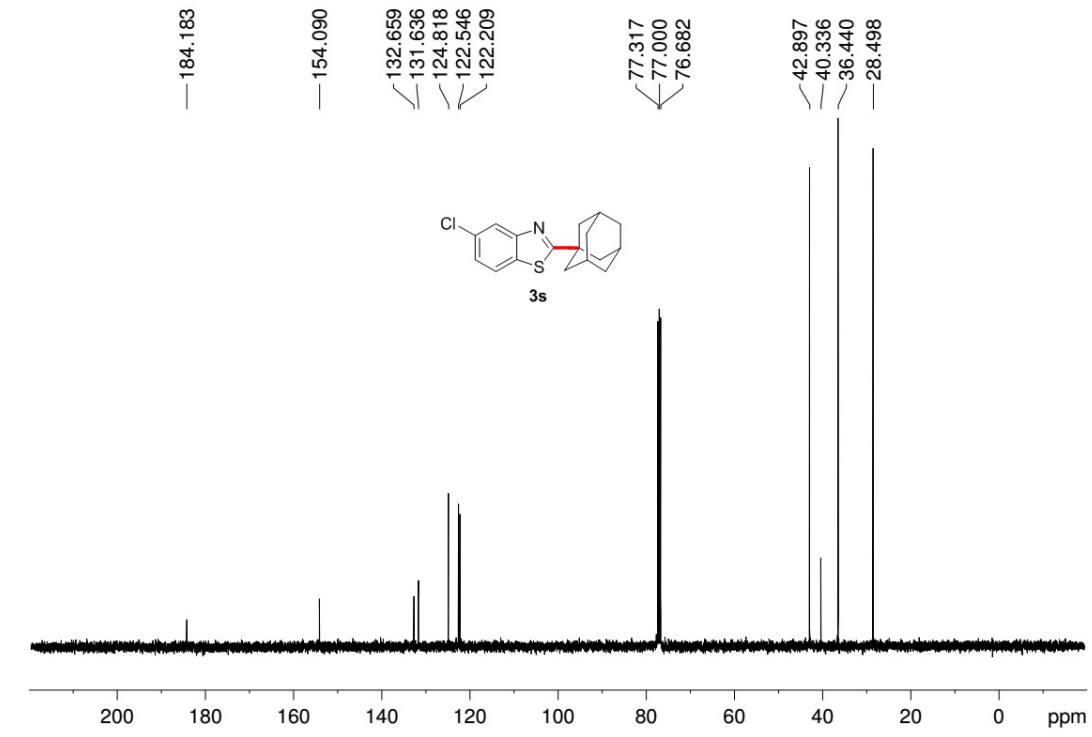

7.876
7.854
7.304
7.040
7.018
3.834
2.121
1.797
0.000
MeO
N
S
3q
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
1.01
3.05
9.19
6.06

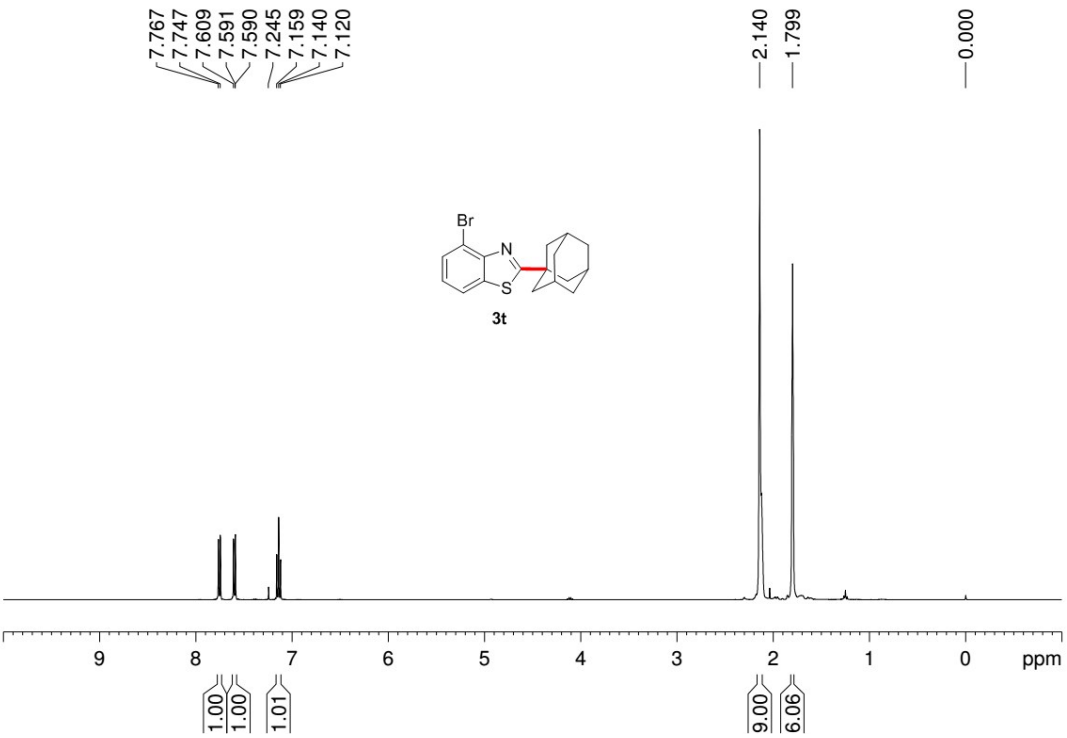

179.486
157.061
147.582
135.514
122.985
114.706
104.183
77.317
77.000
76.682
55.659
42.915
39.902
36.447
28.502
MeO
N
S
3q
200
180
160
140
120
100
80
60
40
20
0
ppm

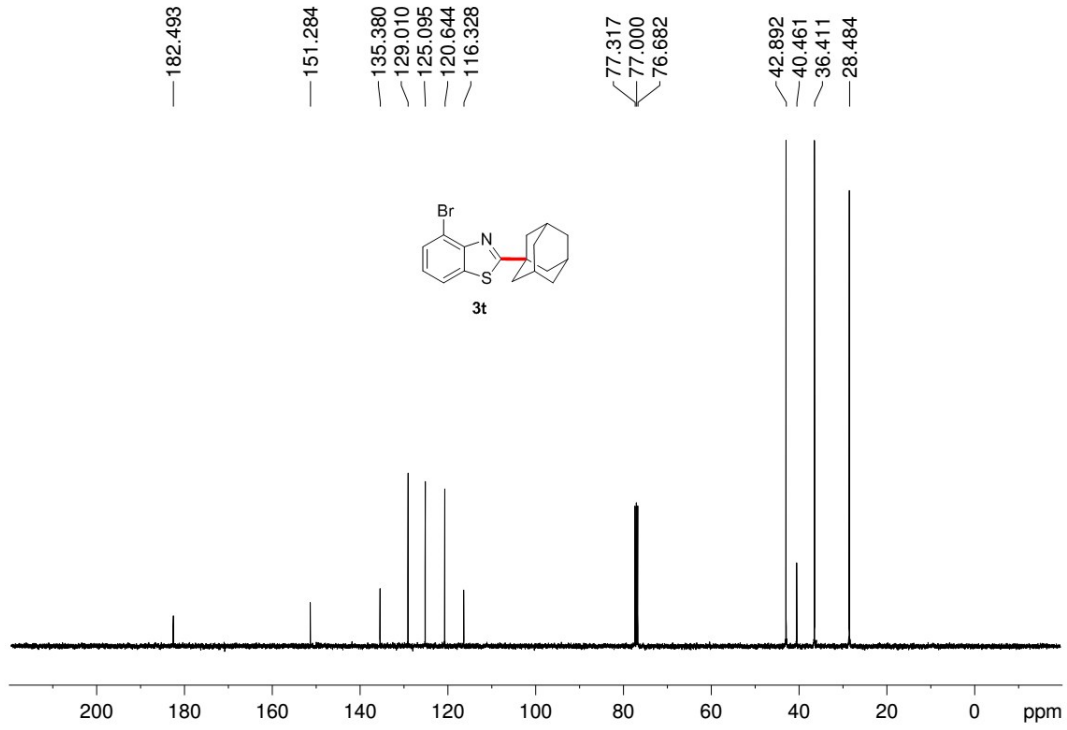

7.725
7.723
7.705
7.703
7.435
7.433
7.416
7.414
7.245
7.230
7.210
7.191
2.144
1.799
0.000
Cl
N
S
3r
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
1.03
9.39
6.23

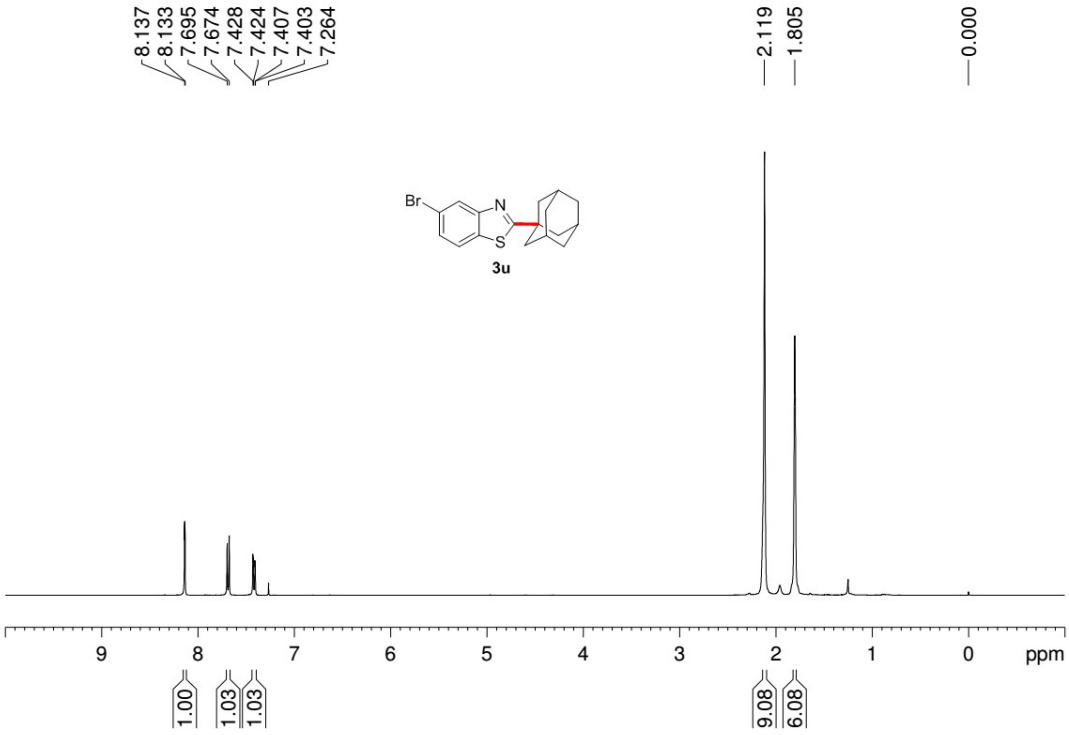

182.842
150.132
135.966
127.473
125.846
124.755
120.002
77.317
77.000
76.682
42.900
40.459
36.413
28.495
Cl
N
S
3r
200
180
160
140
120
100
80
60
40
20
0
ppm

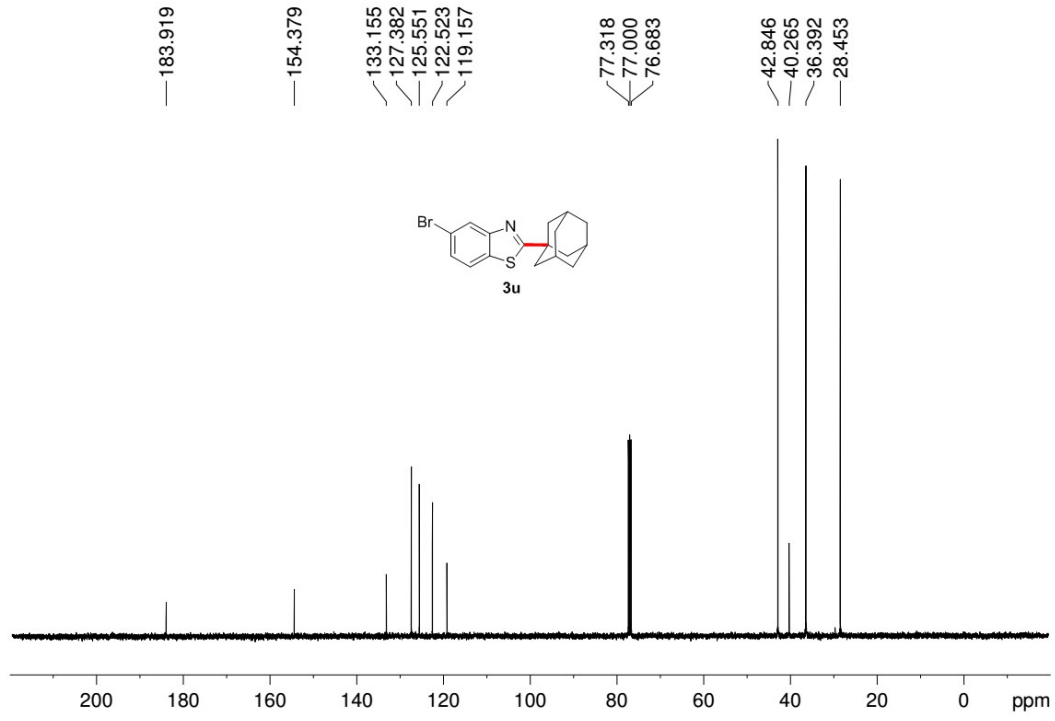

7.978
7.973
7.759
7.738
7.310
7.305
7.289
7.284
7.262
2.131
1.815
0.000
Cl
N
S
3s
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.07
1.07
9.03
6.35

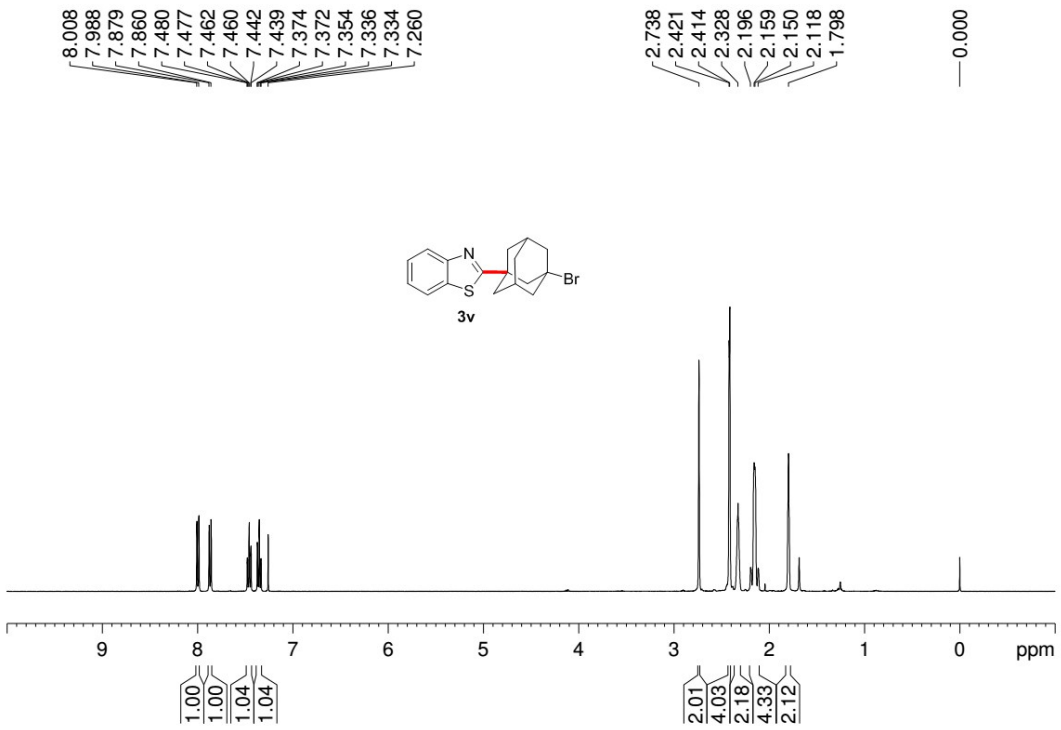

184.183
154.090
132.659
131.636
124.818
122.546
122.209
77.317
77.000
76.682
42.897
40.336
36.440
28.498
Cl
N
S
3s
200
180
160
140
120
100
80
60
40
20
0
ppm

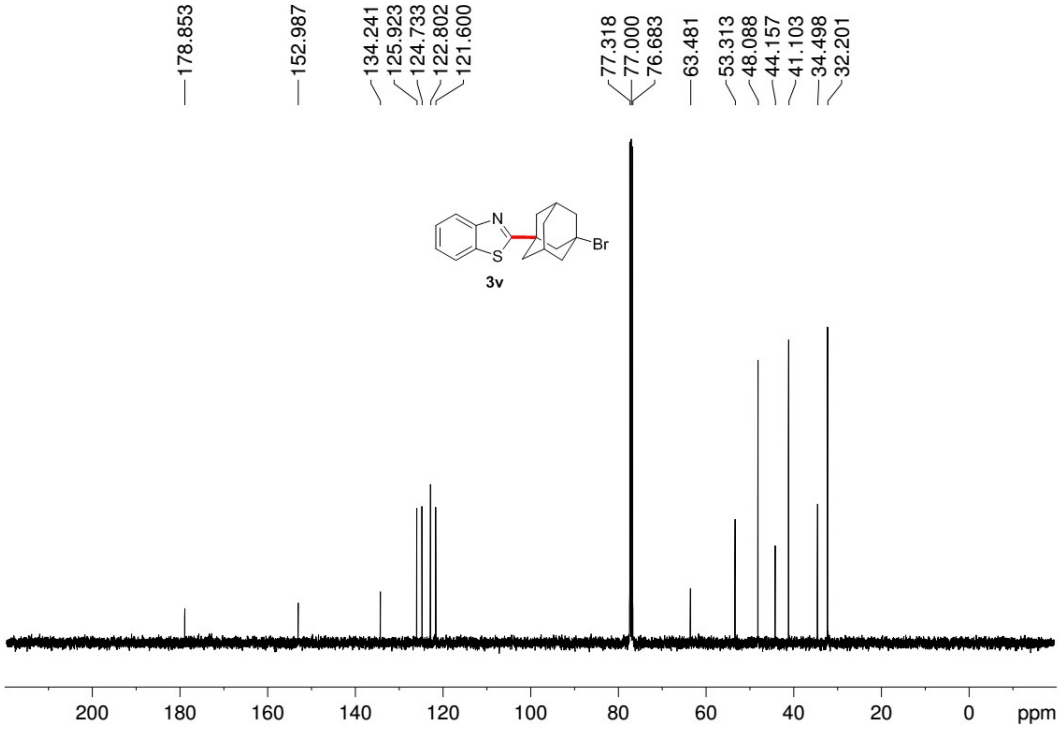

7.767
7.747
7.609
7.591
7.590
7.245
7.159
7.140
7.120
2.140
1.799
0.000
Br
N
S
3t
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
1.01
9.00
6.06

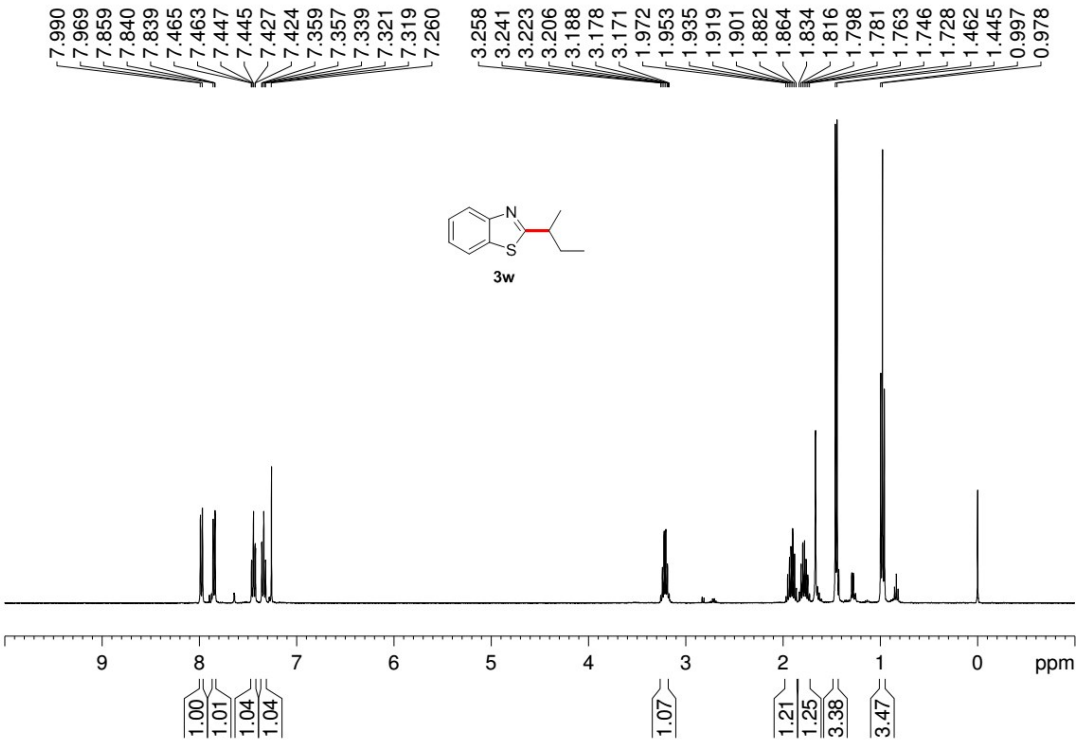

182.493
151.284
135.380
129.010
125.095
120.644
116.328
77.317
77.000
76.682
42.892
40.461
36.411
28.484
Br
N
S
3t
200
180
160
140
120
100
80
60
40
20
0
ppm

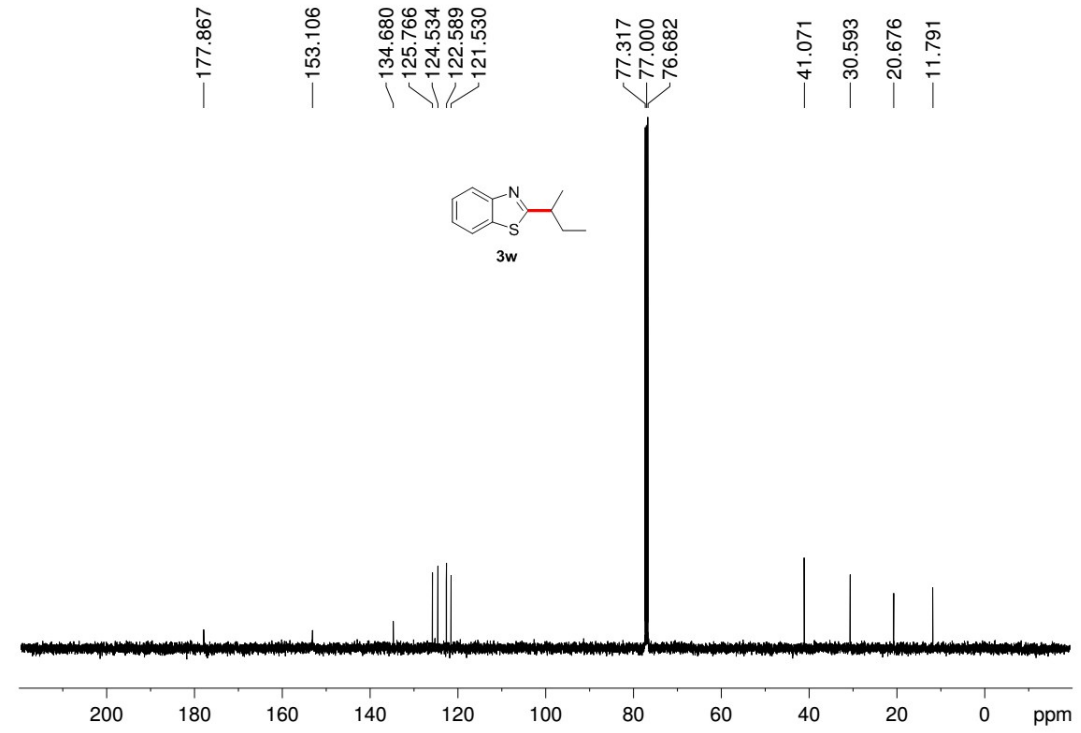

8.137
8.133
7.695
7.674
7.428
7.424
7.407
7.403
7.264
2.119
1.805
0.000
Br
N
S
3u
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.03
1.03
9.08
6.08

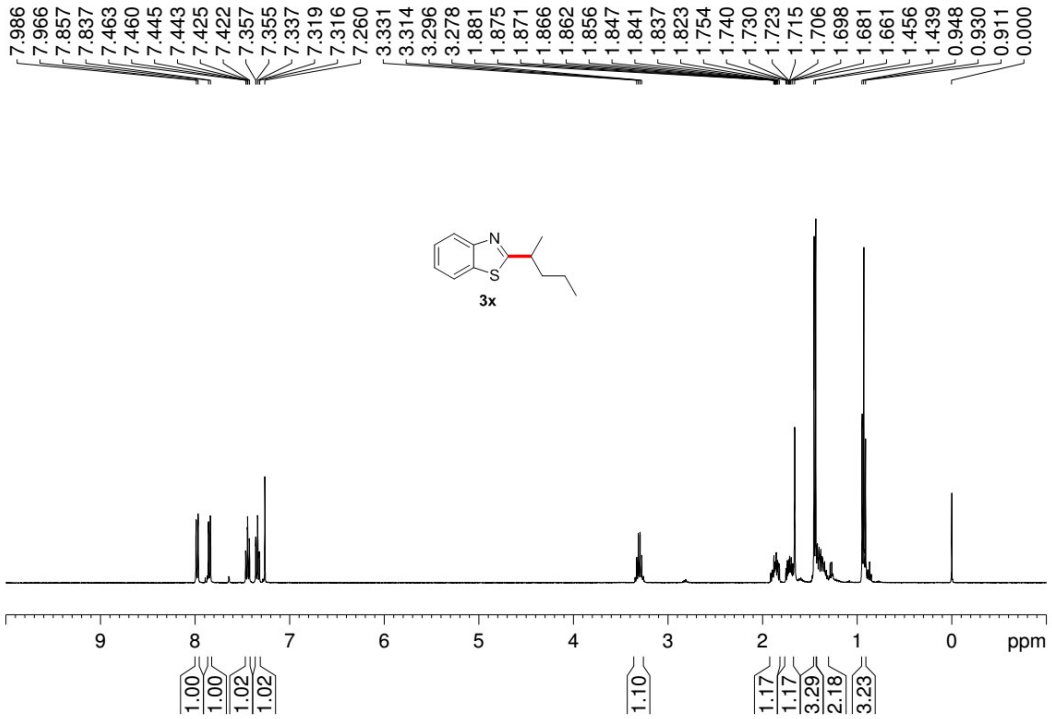

183.919
154.379
133.155
127.382
125.551
122.523
119.157
77.318
77.000
76.683
42.846
40.265
36.392
28.453
Br
N
S
3u
200
180
160
140
120
100
80
60
40
20
0
ppm

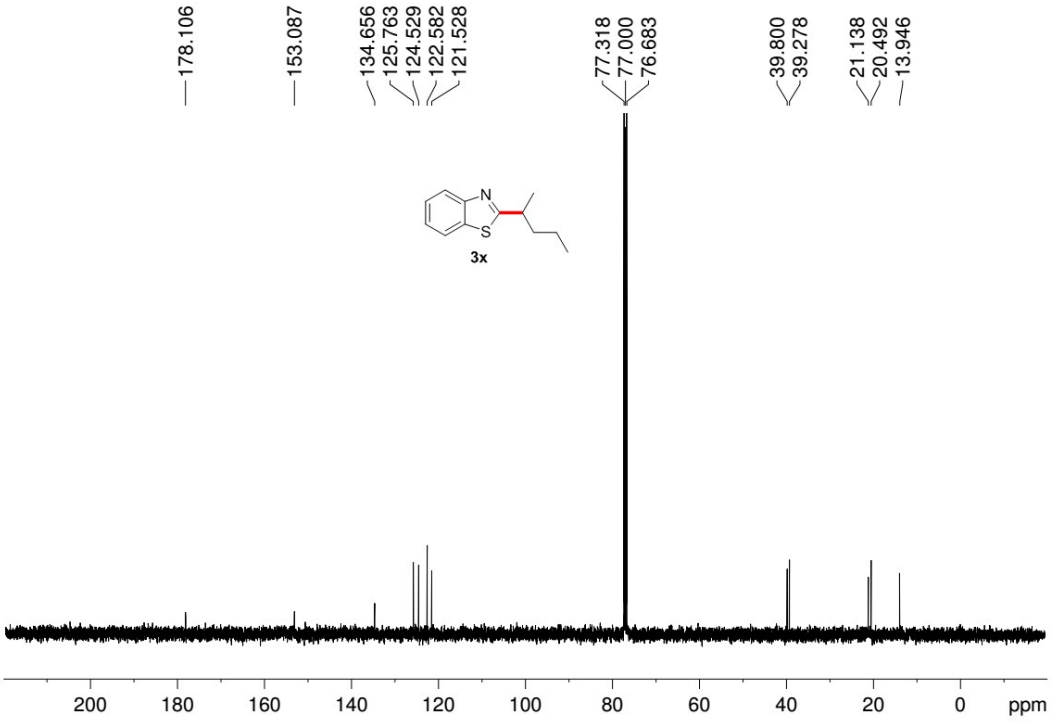

8.008
7.988
7.879
7.860
7.480
7.477
7.462
7.460
7.442
7.439
7.374
7.372
7.354
7.336
7.334
7.260
2.738
2.421
2.414
2.328
2.196
2.159
2.150
2.118
1.798
0.000
N
S
Br
3v
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
1.04
1.04
2.01
4.03
2.18
4.33
2.12

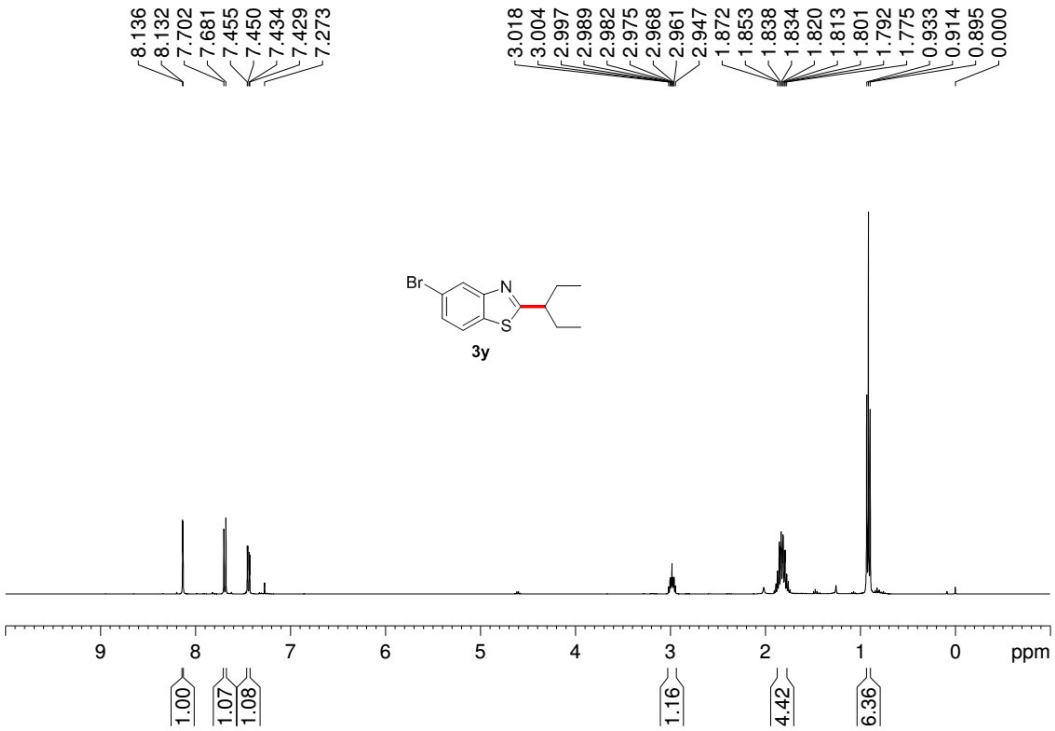

178.853
152.987
134.241
125.923
124.733
122.802
121.600
77.318
77.000
76.683
63.481
53.313
48.088
44.157
41.103
34.498
32.201
N
S
Br
3v
200
180
160
140
120
100
80
60
40
20
0
ppm

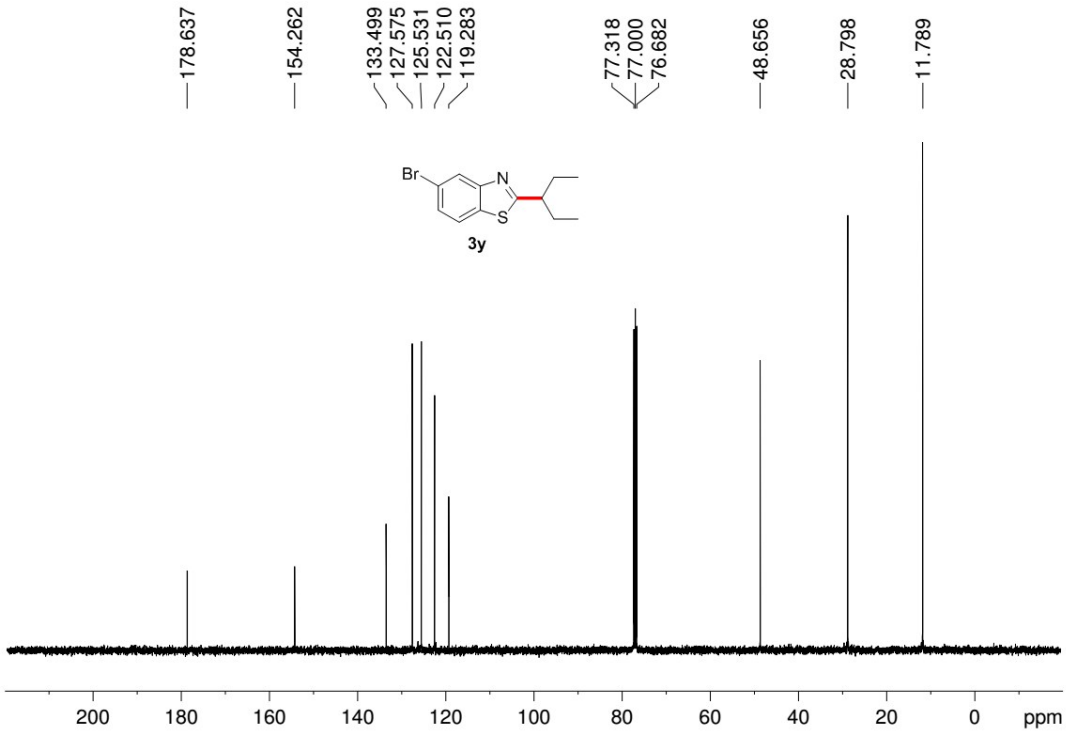

7.990
7.969
7.859
7.840
7.839
7.465
7.463
7.447
7.445
7.427
7.424
7.359
7.357
7.339
7.321
7.319
7.260
3.258
3.241
3.223
3.206
3.188
3.178
3.171
1.972
1.953
1.935
1.919
1.901
1.882
1.864
1.834
1.816
1.798
1.781
1.763
1.746
1.728
1.462
1.445
0.997
0.978
3w
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
1.04
1.04
1.07
1.21
1.25
3.38
3.47

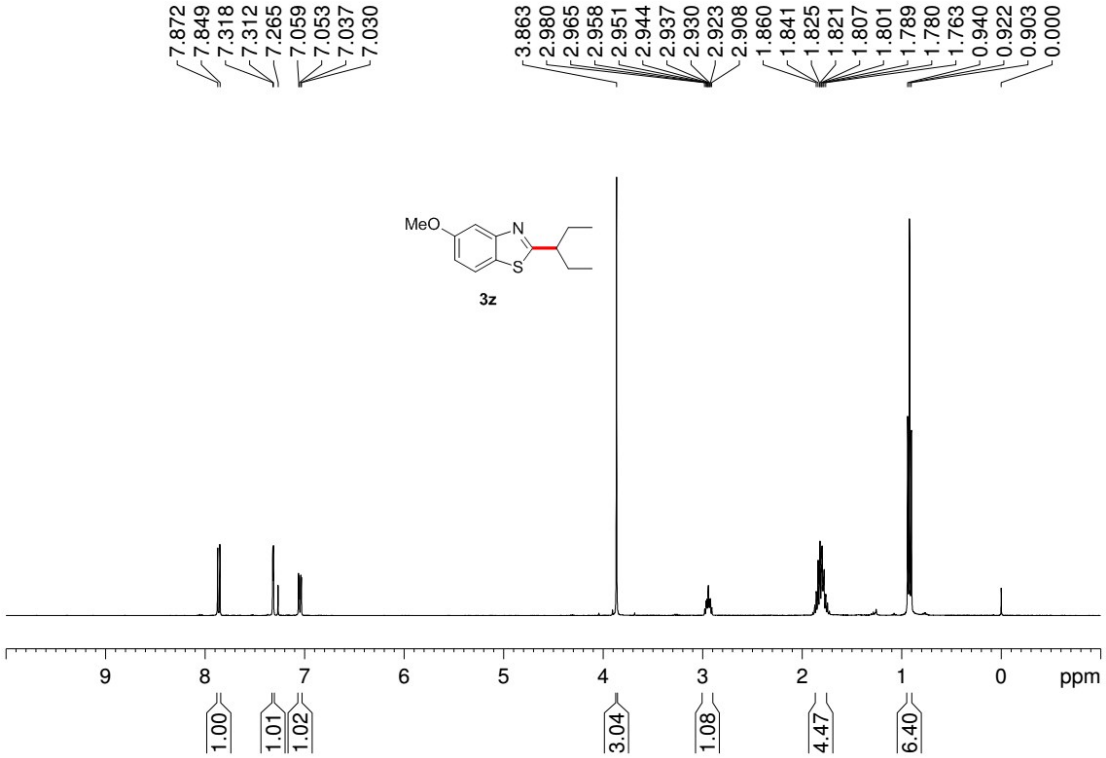

177.867
153.106
134.680
125.766
124.534
122.589
121.530
77.317
77.000
76.682
41.071
30.593
20.676
11.791
3w
200
180
160
140
120
100
80
60
40
20
0
ppm

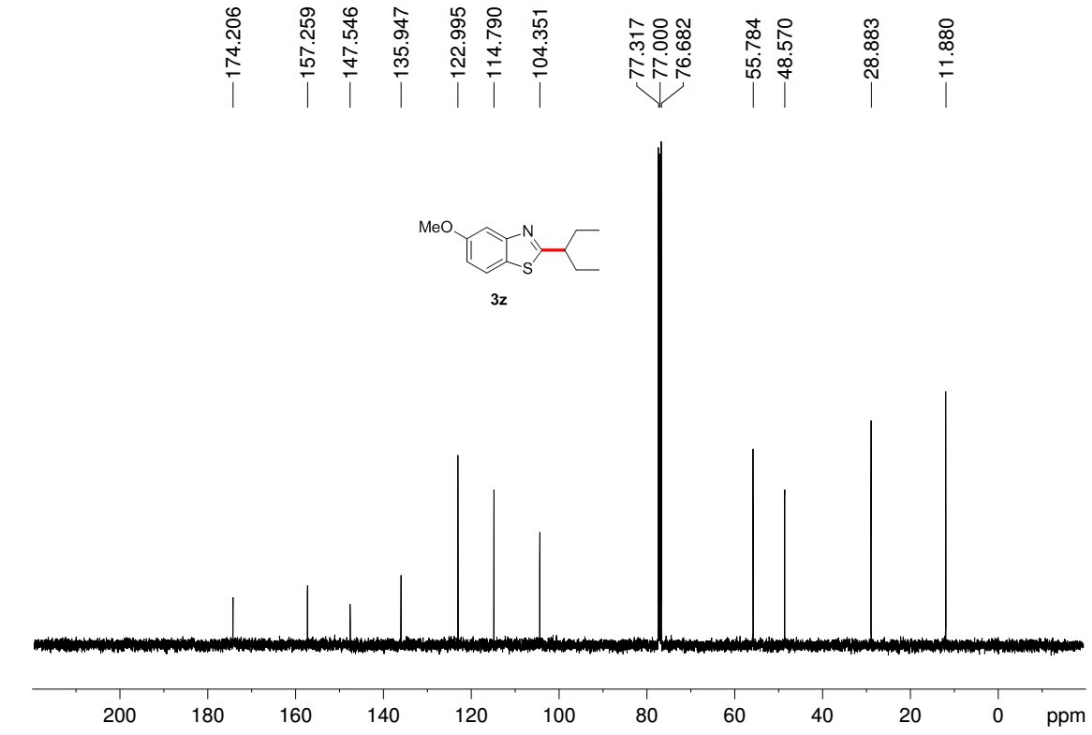

7.986
7.966
7.857
7.837
7.463
7.460
7.445
7.443
7.425
7.422
7.357
7.355
7.337
7.319
7.316
7.260
3.331
3.314
3.296
3.278
1.881
1.875
1.871
1.866
1.862
1.856
1.847
1.841
1.837
1.823
1.754
1.740
1.730
1.723
1.715
1.706
1.698
1.681
1.661
1.456
1.439
0.948
0.930
0.911
0.000
3x
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
1.02
1.02
1.10
1.17
1.17
3.29
2.18
3.23

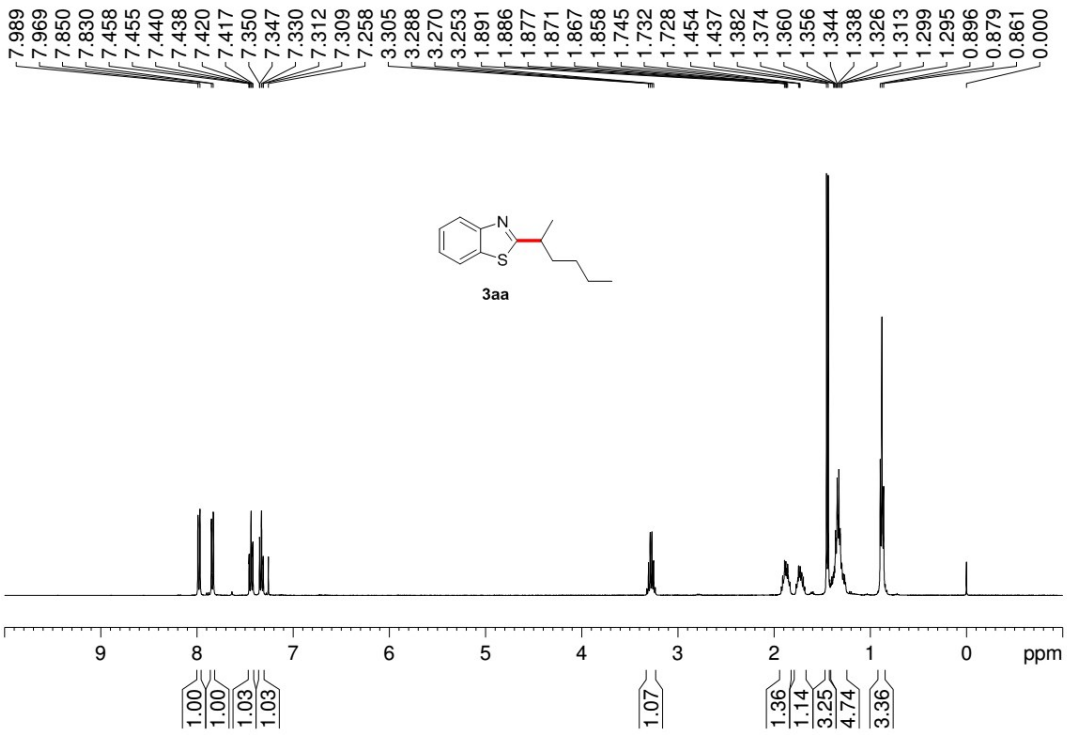

178.106
153.087
134.656
125.763
124.529
122.582
121.528
77.318
77.000
76.683
39.800
39.278
21.138
20.492
13.946
3x
200
180
160
140
120
100
80
60
40
20
0
ppm

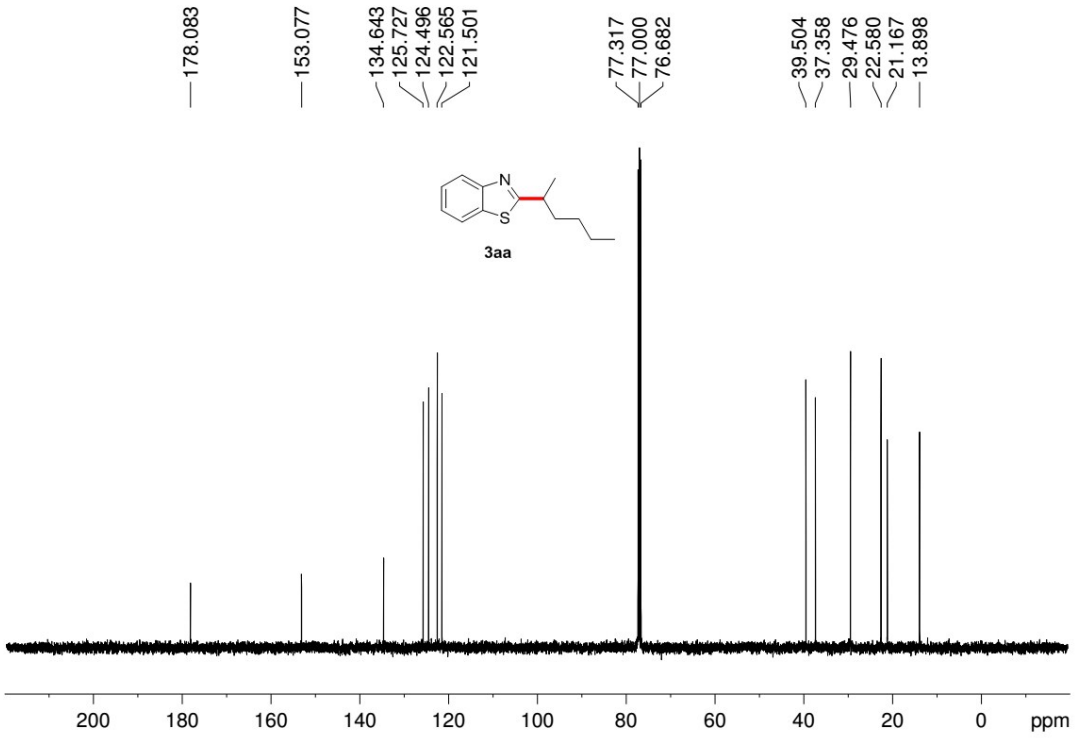

8.136
8.132
7.702
7.681
7.455
7.450
7.434
7.429
7.273
3.018
3.004
2.997
2.989
2.982
2.975
2.968
2.961
2.947
1.872
1.853
1.838
1.834
1.820
1.813
1.801
1.792
1.775
0.933
0.914
0.895
0.000
Br
N
S
3y
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.07
1.08
1.16
4.42
6.36

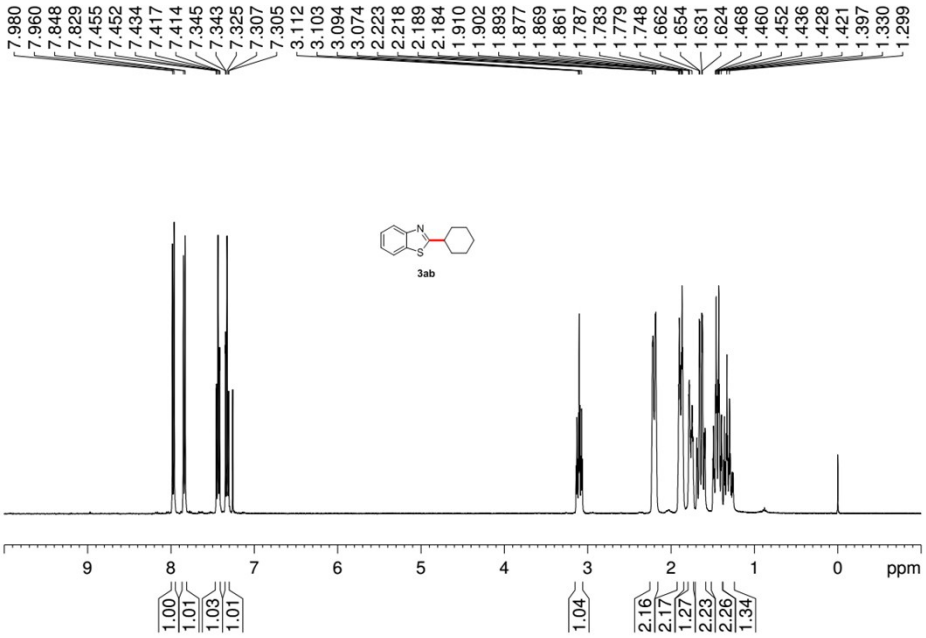

178.637
154.262
133.499
127.575
125.531
122.510
119.283
77.318
77.000
76.682
48.656
28.798
11.789
Br
N
S
3y
200
180
160
140
120
100
80
60
40
20
0
ppm

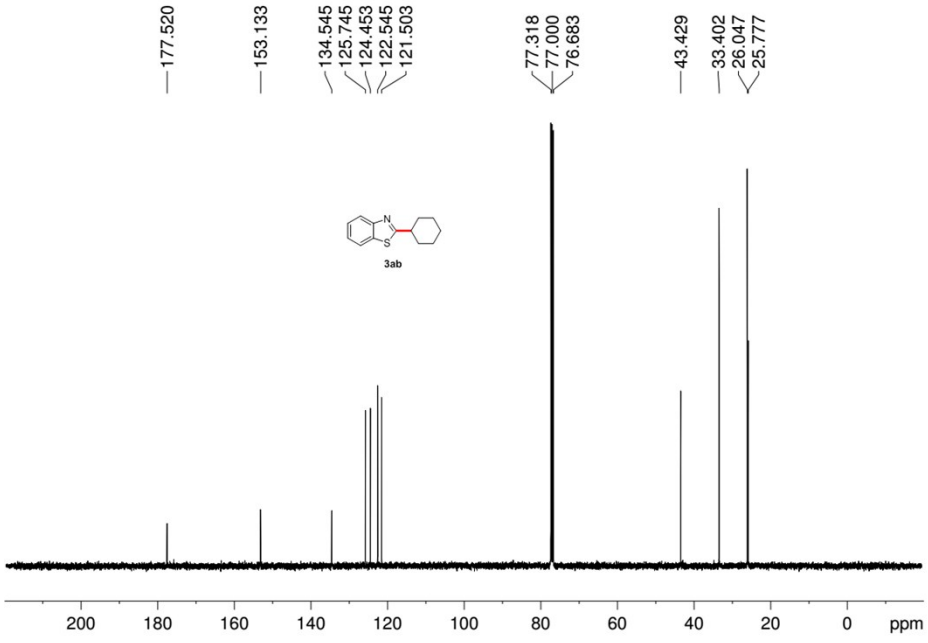

7.872
7.849
7.318
7.312
7.265
7.059
7.053
7.037
7.030
3.863
2.980
2.965
2.958
2.951
2.944
2.937
2.930
2.923
2.908
1.860
1.841
1.825
1.821
1.807
1.801
1.789
1.780
1.763
0.940
0.922
0.903
0.000
MeO
N
S
3z
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
1.02
3.04
1.08
4.47
6.40


174.206
157.259
147.546
135.947
122.995
114.790
104.351
77.317
77.000
76.682
55.784
48.570
28.883
11.880
MeO
N
S
3z
200
180
160
140
120
100
80
60
40
20
0
ppm


7.989
7.969
7.850
7.830
7.458
7.455
7.440
7.438
7.420
7.417
7.350
7.347
7.330
7.312
7.309
7.258
3.305
3.288
3.270
3.253
1.891
1.886
1.877
1.871
1.867
1.858
1.745
1.732
1.728
1.454
1.437
1.382
1.374
1.360
1.356
1.344
1.338
1.326
1.313
1.299
1.295
0.896
0.879
0.861
0.000
3aa
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
1.03
1.03
1.07
1.36
1.14
3.25
4.74
3.36


178.083
153.077
134.643
125.727
124.496
122.565
121.501
77.317
77.000
76.682
39.504
37.358
29.476
22.580
21.167
13.898
3aa
200
180
160
140
120
100
80
60
40
20
0
ppm


7.980
7.960
7.848
7.829
7.455
7.452
7.434
7.417
7.414
7.345
7.343
7.325
7.307
7.305
3.112
3.103
3.094
3.074
2.223
2.218
2.189
2.184
1.910
1.902
1.893
1.877
1.869
1.861
1.787
1.783
1.779
1.748
1.662
1.654
1.631
1.624
1.468
1.460
1.452
1.436
1.428
1.421
1.397
1.330
1.299
3ab
ppm
1.00
1.01
1.03
1.01
1.04
2.16
2.17
1.27
2.23
2.26
1.34


177.520
153.133
134.545
125.745
124.453
122.545
121.503
77.318
77.000
76.683
43.429
33.402
26.047
25.777
3ab
ppm