Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Cp*Co^{III}-catalyzed formal [4 + 2] cycloaddition of 2-phenyl-1*H*-imidazoles to afford imidazo[1,2-*c*]quinazoline derivatives

Deyu Wu,[a,b] Zhengqiang Liu,[a,b] Yiting Chang,[a,b] Jiajing Chen,[a,b] Haixiang Qi,[a,b] Yi Dong,*[a,b,c] Heng Xu*[a,b]

[a] State Key Laboratory of Bioactive Substance and Function of Natural Medicines, Institute of Materia Medica, Chinese Academy of Medical Sciences and Peking Union Medical College, Beijing 100050, China

[b] Beijing Key Laboratory of Active Substances Discovery and DrugabilityEvaluation, Institute of Materia Medica, Chinese Academy of Medical Sciences and Peking Union Medical College, Beijing 100050, China

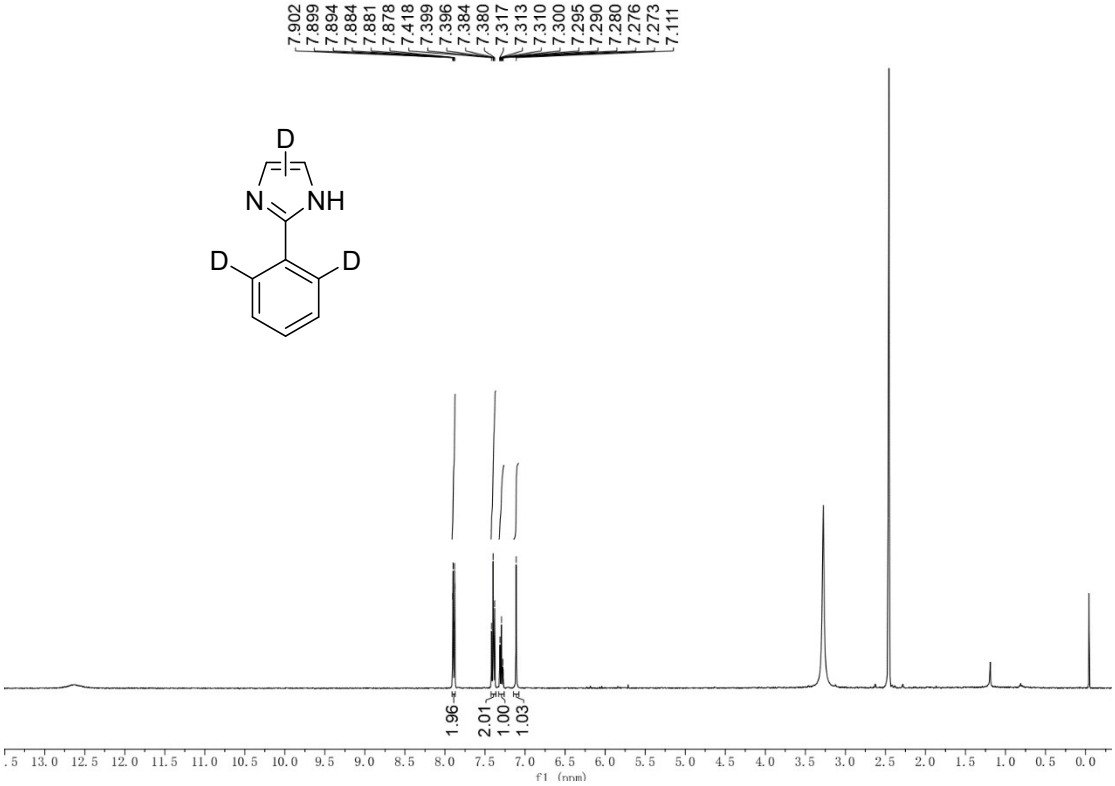
[c] State Key Laboratory of Functions and Applications of Medicinal Plants, Guizhou Medcial University, Guiyang 550014, China.

E-mail: dongyi@imm.ac.cn; xuheng@imm.ac.cn

Table of cotent

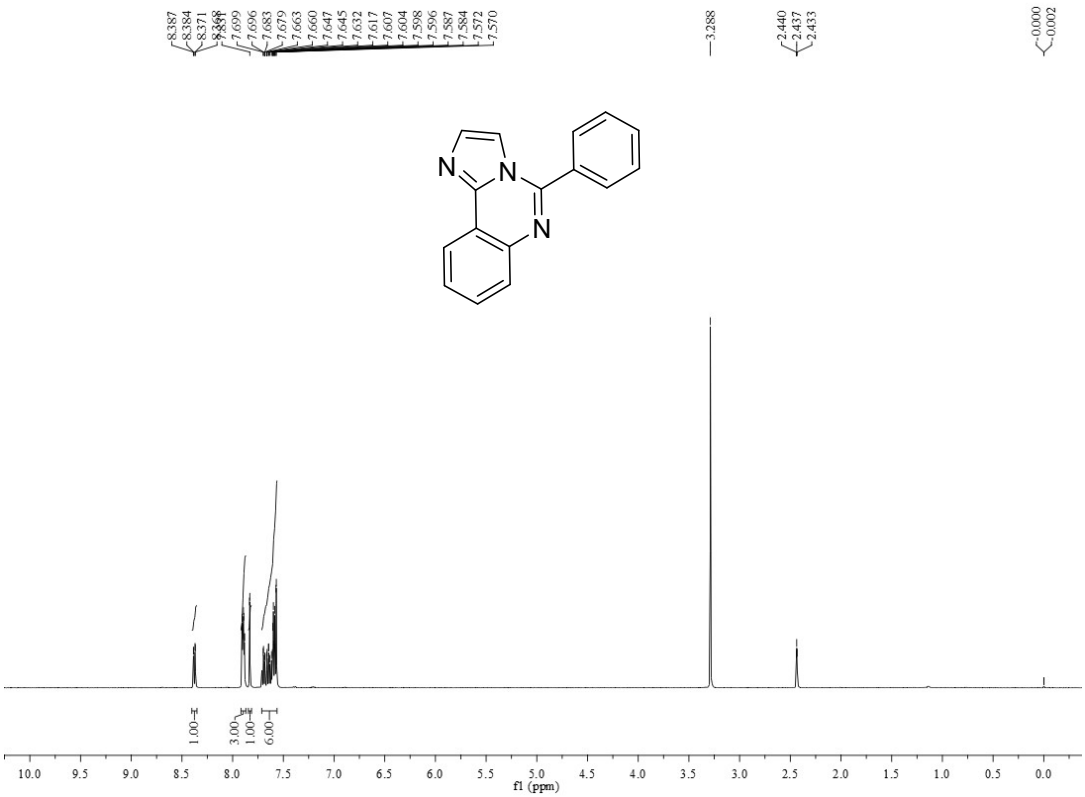
H/D exchange experiment

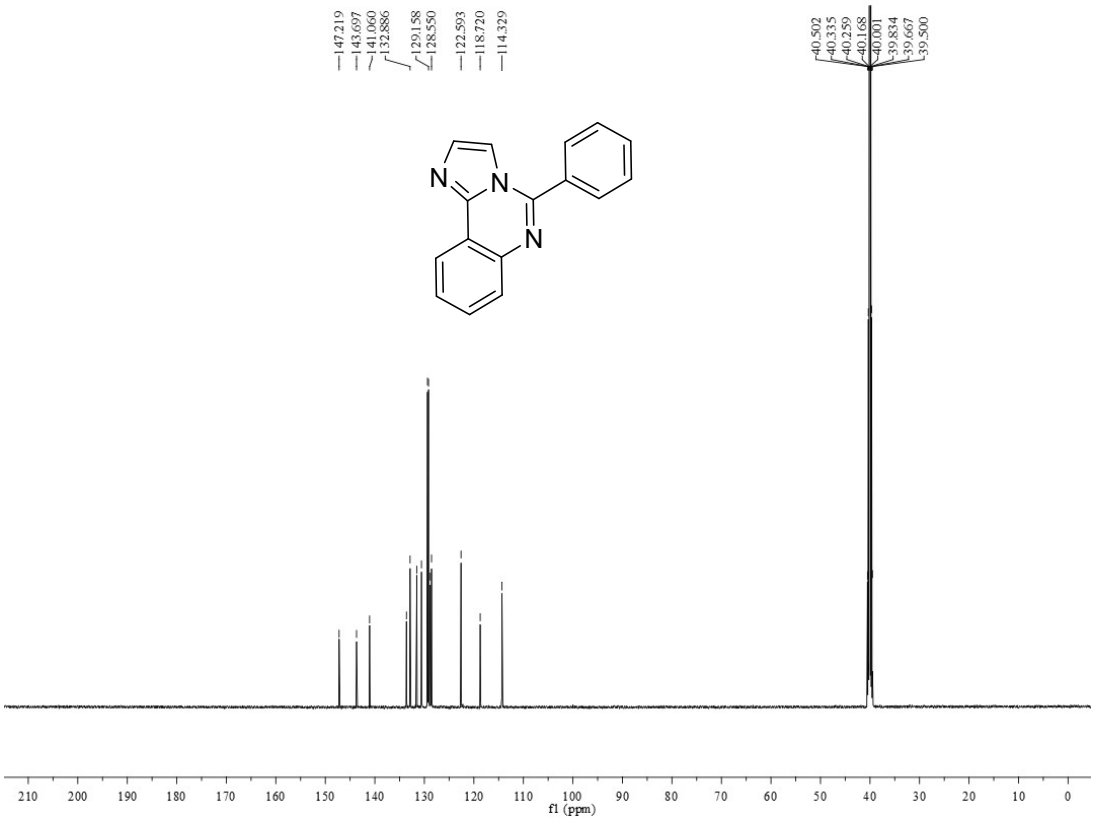
A mixture of [CoCp*(CO)I_2] (15.0 mol%), $AgSbF_6$ (30 mol%) and 2-phenyl-1*H*-imidazole **1a** (0.2 mmol) in 2.0 mL DCE and 0.5 mL [D_4]-MeOD was heated at 120°C, and stirred overnight. Then the reaction mixture was cooled to room temperature and filtered, the filtrate was concentrated and the residue was purified with preparative TLC to afford **1a/[D]-1a** (24 mg).

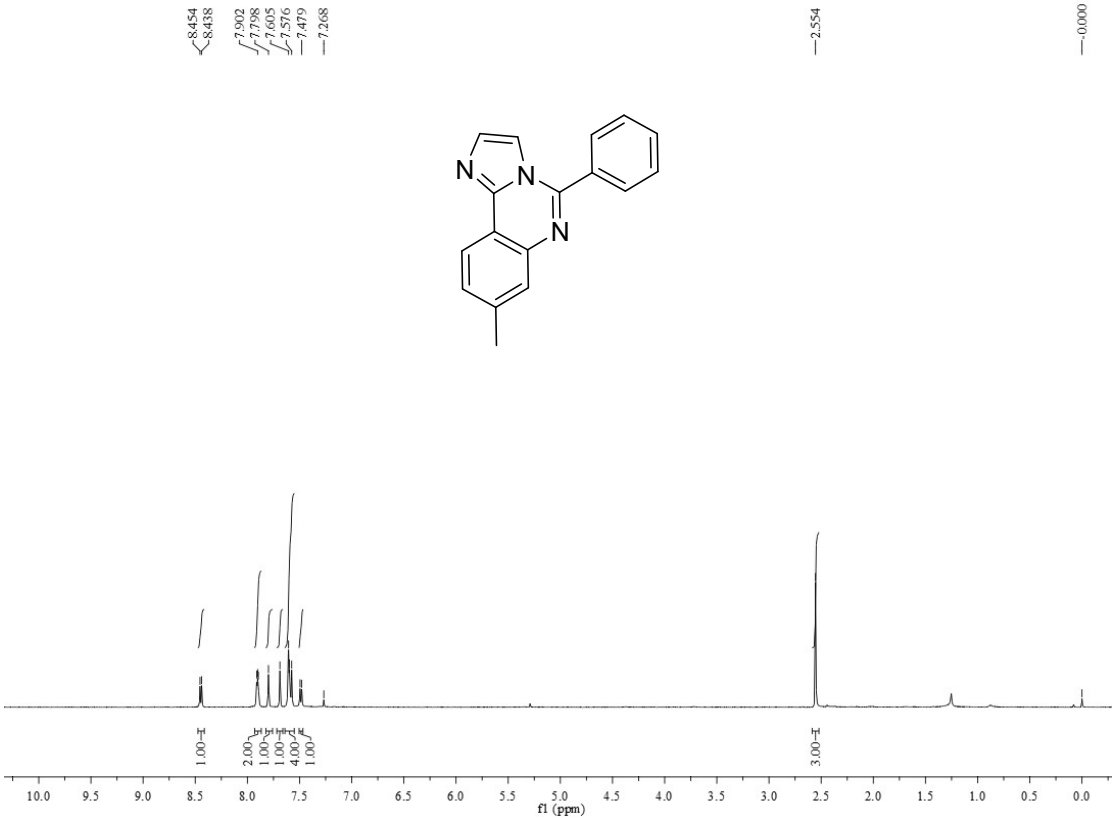


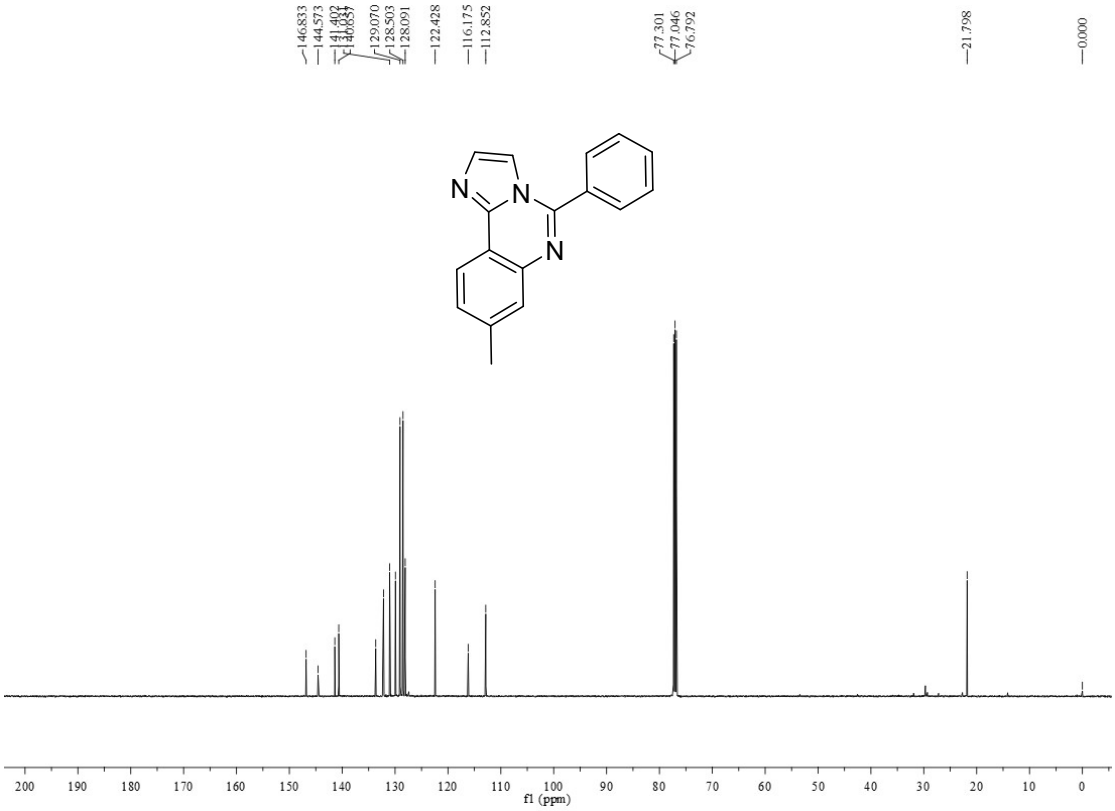
KIE experiment

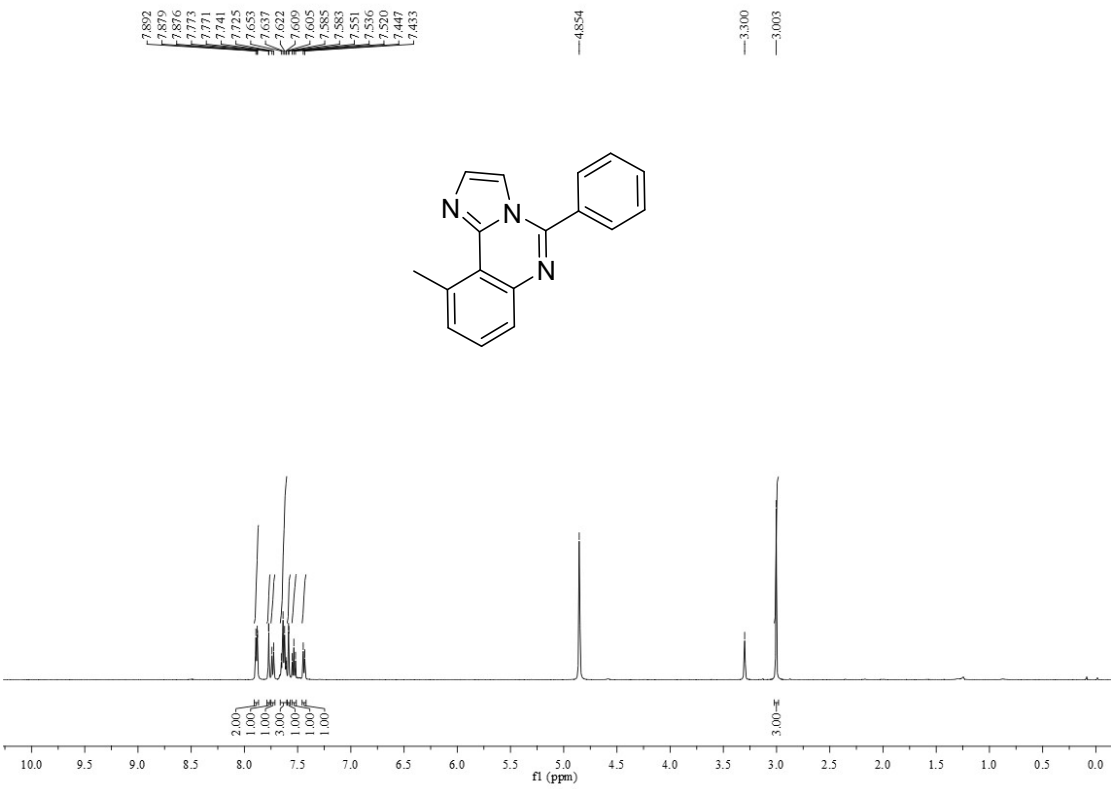
A mixture of [CoCp*(CO)I_2] (15.0 mol%), $AgSbF_6$ (30 mol%) and 2-phenyl-1*H*-imidazole **1a** (0.2 mmol) or deuterated **[D]-1a** (0.2 mmol) and 3-phenyl-1,4,2-dioxazol-5-one **2a** (0.3 mmol) in 2.0 mL DCE was heated at 120°C for 45 min. Then the reaction mixture was cooled to room temperature and filtered, the filtrate was concentrated and the residue was purified with preparative TLC to afford the desired product **3** (6.5 mg) or **[D]-3** (5 mg). KIE $\approx$ 1.3

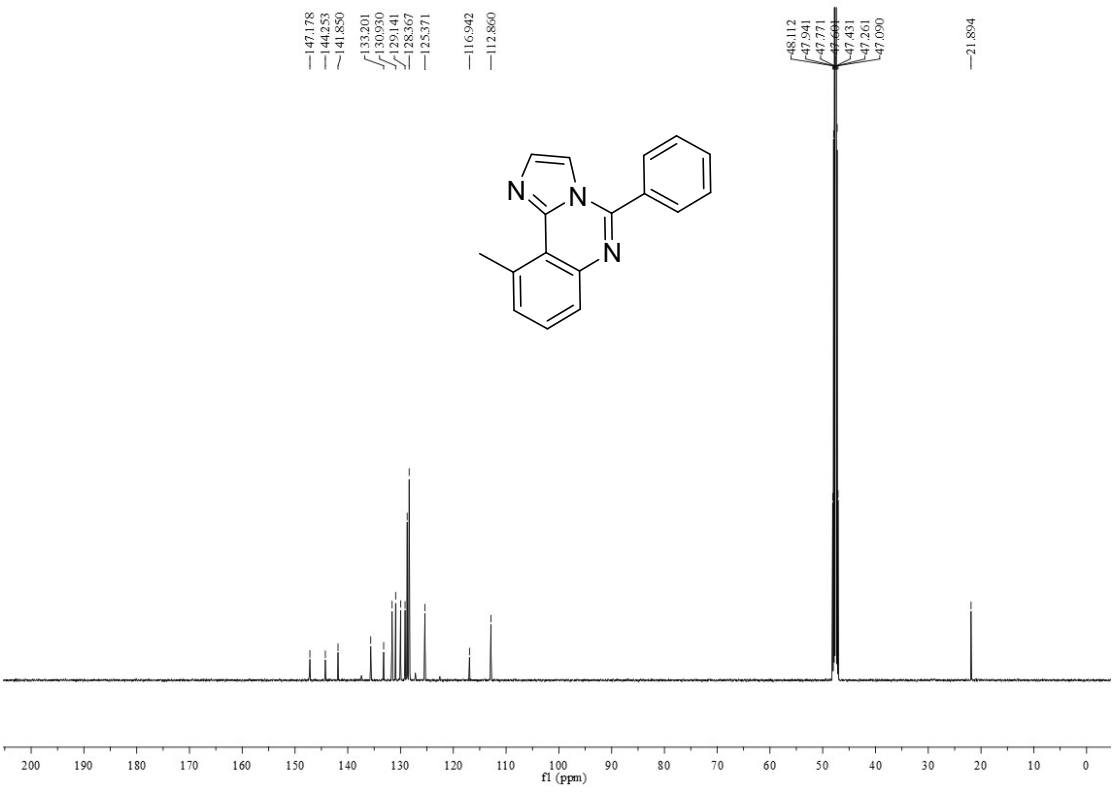

8.387
8.384
8.371
7.699
7.696
7.683
7.679
7.663
7.660
7.647
7.645
7.632
7.617
7.607
7.604
7.598
7.596
7.587
7.584
7.572
7.570
3.288
2.440
2.437
2.433
0.000
-0.002
1.00
3.00
1.00
6.00
f1 (ppm)

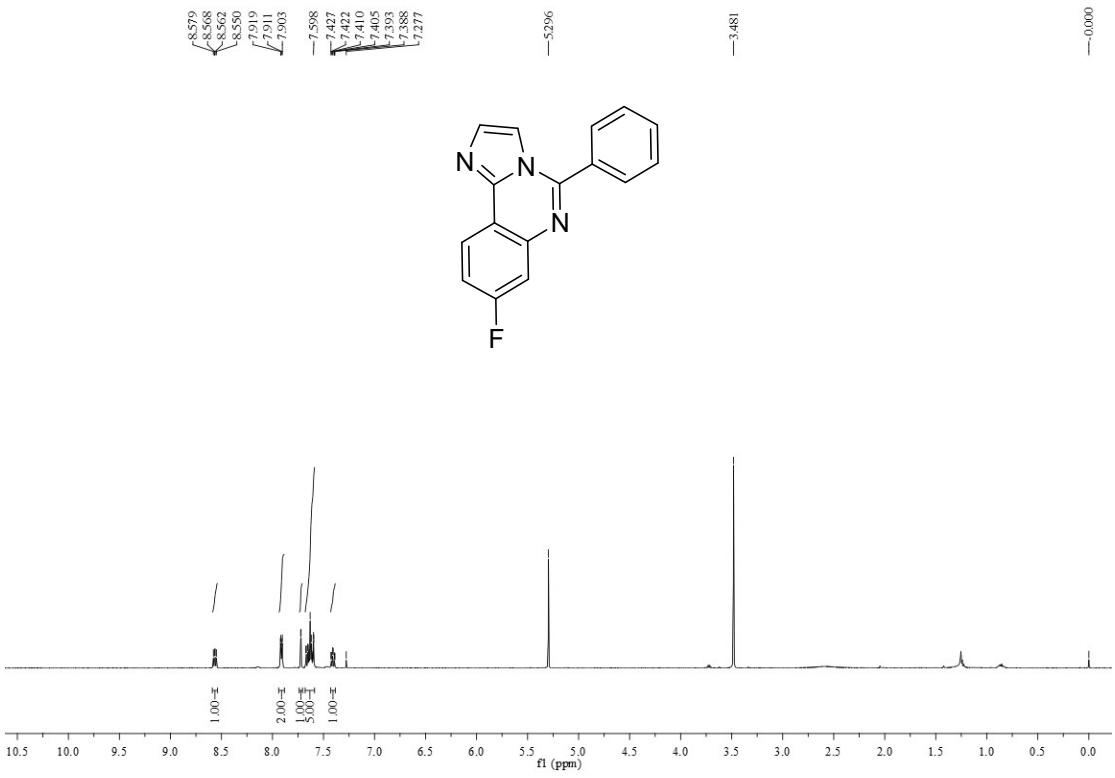

147.219
143.697
141.060
132.886
129.158
128.550
122.593
118.720
114.329
40.502
40.335
40.259
40.168
40.001
39.834
39.667
39.500
f1 (ppm)

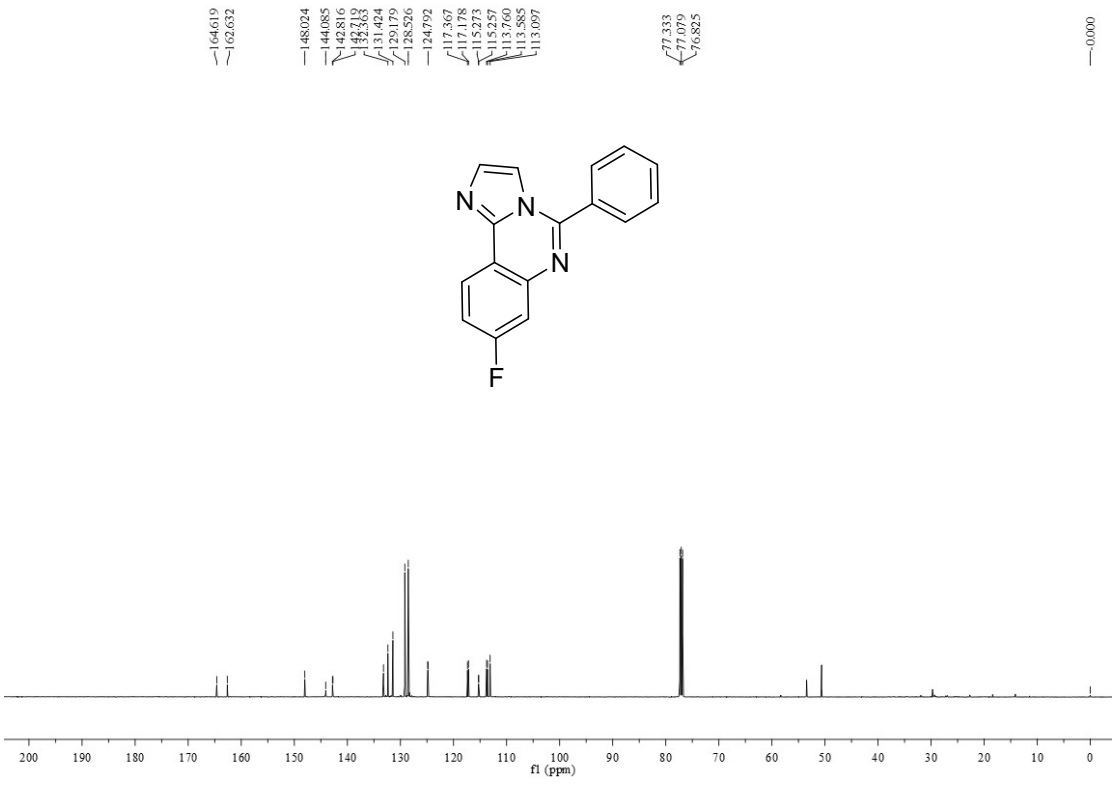

8.454
8.438
7.902
7.798
7.605
7.576
7.479
7.268
2.554
0.000
1.00
2.00
1.00
1.00
4.00
1.00
3.00
f1 (ppm)

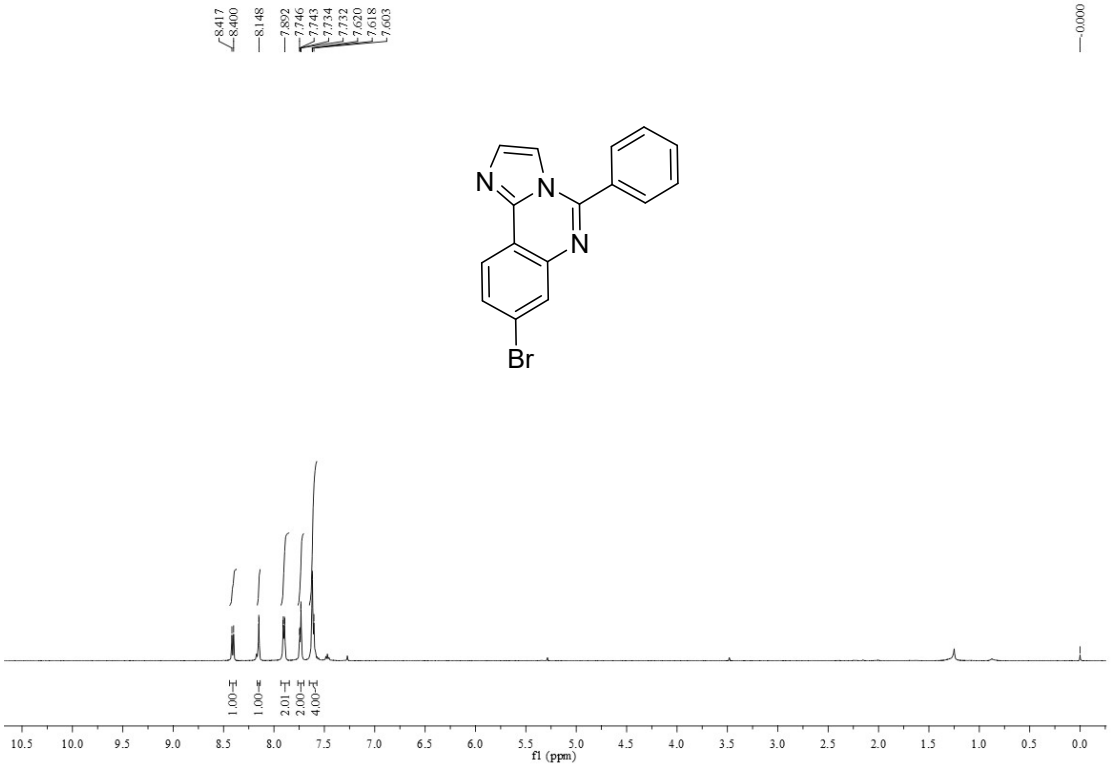

146.833
144.573
141.402
129.070
128.503
128.091
122.428
116.175
112.852
77.301
77.046
76.792
21.798
0.000
f1 (ppm)

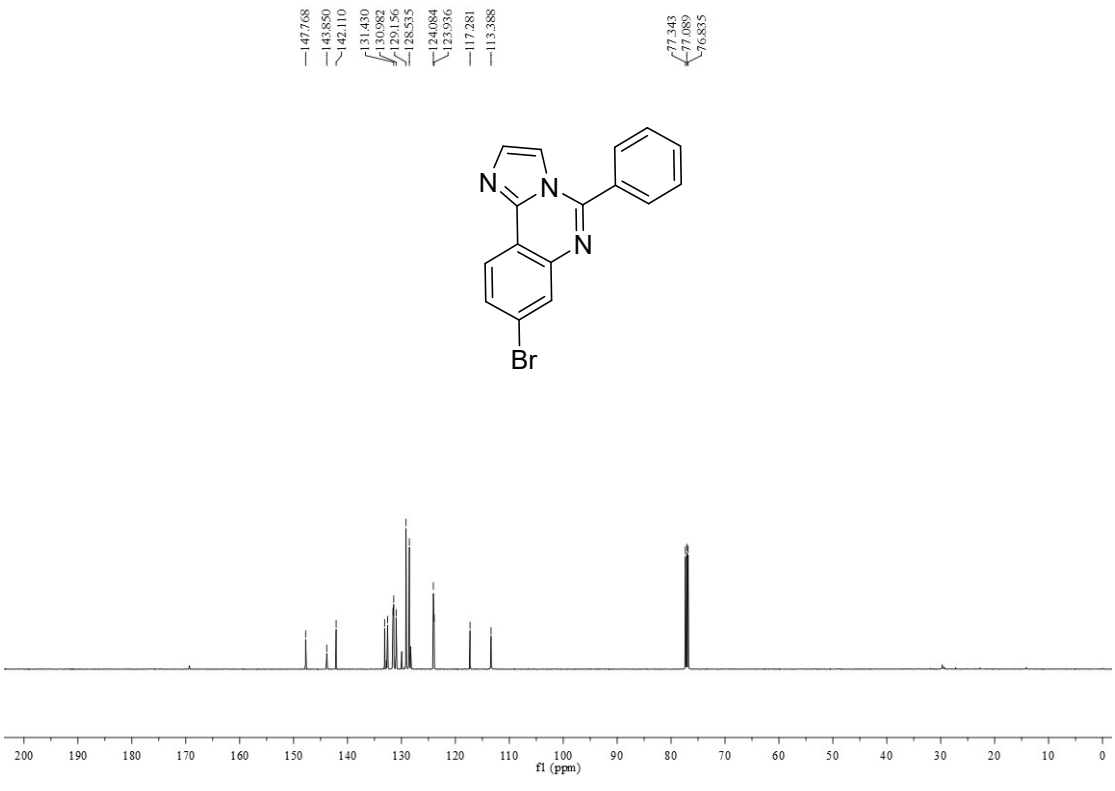

7.892
7.879
7.876
7.773
7.771
7.741
7.725
7.653
7.637
7.622
7.609
7.605
7.585
7.583
7.551
7.536
7.520
7.447
7.433
4.854
3.300
3.003
N
N
N
2.00
1.00
1.00
3.00
1.00
1.00
1.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

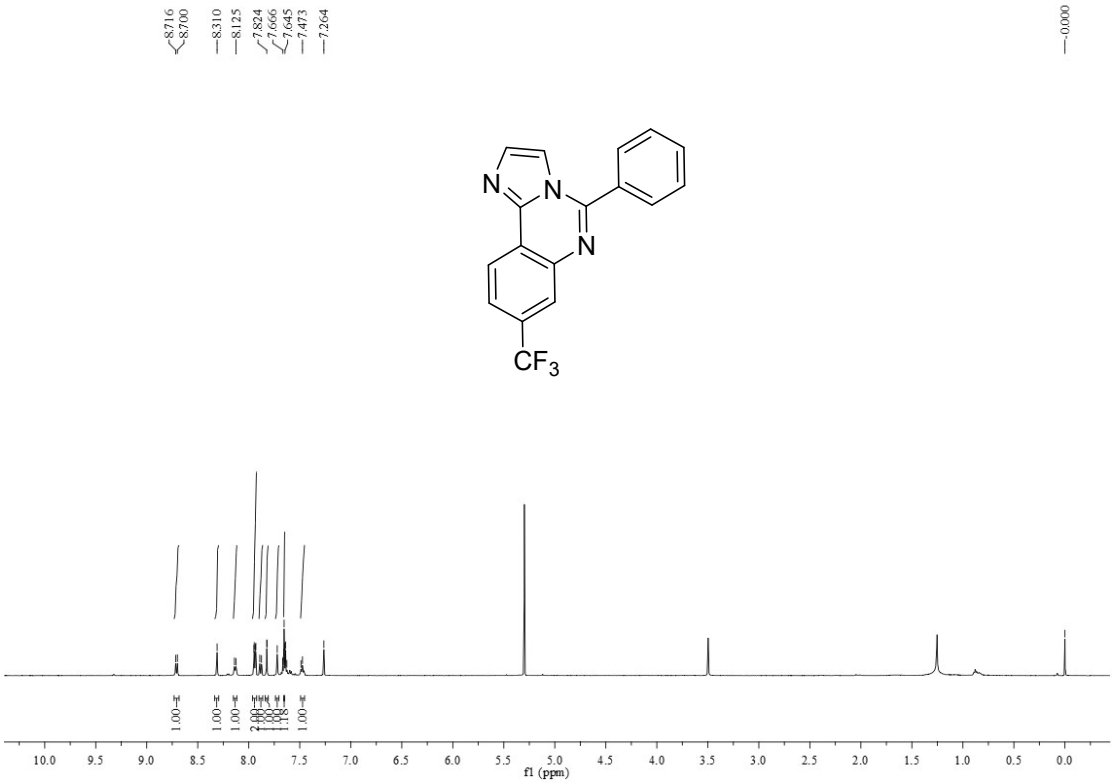

147.178
144.253
141.850
133.201
130.930
129.141
128.367
125.371
116.942
112.860
48.112
47.941
47.771
47.601
47.431
47.261
47.090
21.894
N
N
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

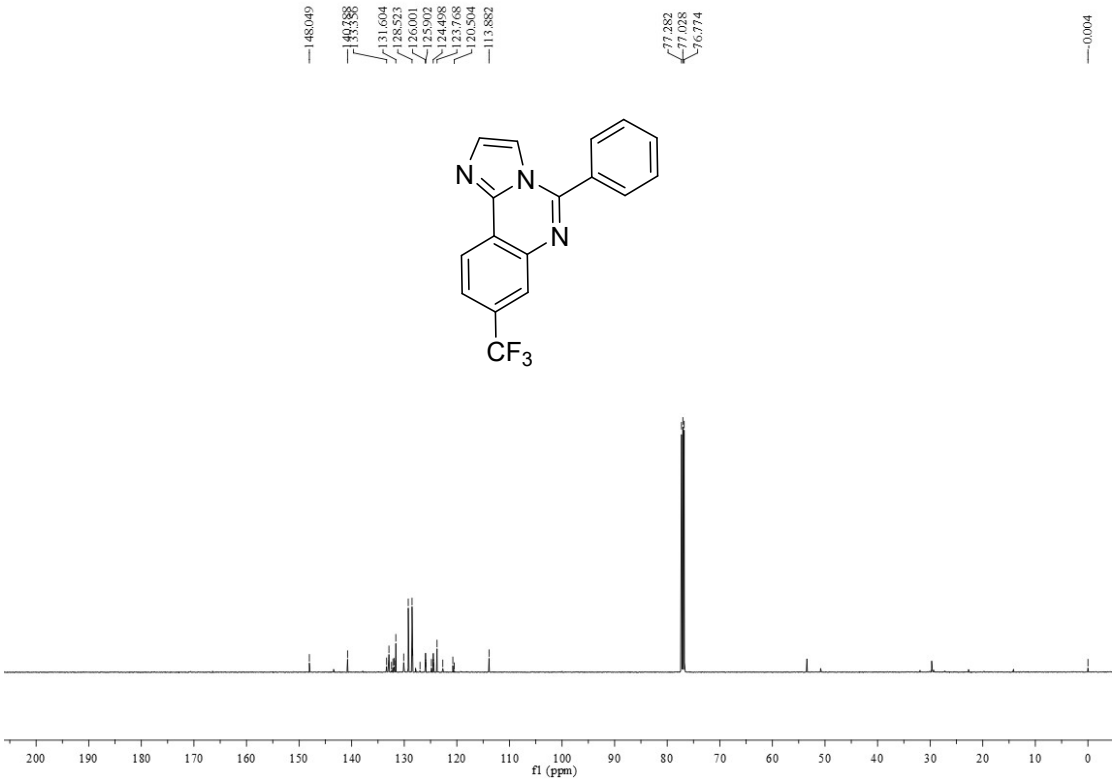

8.579
8.568
8.562
8.550
7.919
7.911
7.903
7.598
7.427
7.422
7.410
7.405
7.393
7.388
7.277
5.296
3.481
0.000
N
N
N
F
1.00
2.00
5.00
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

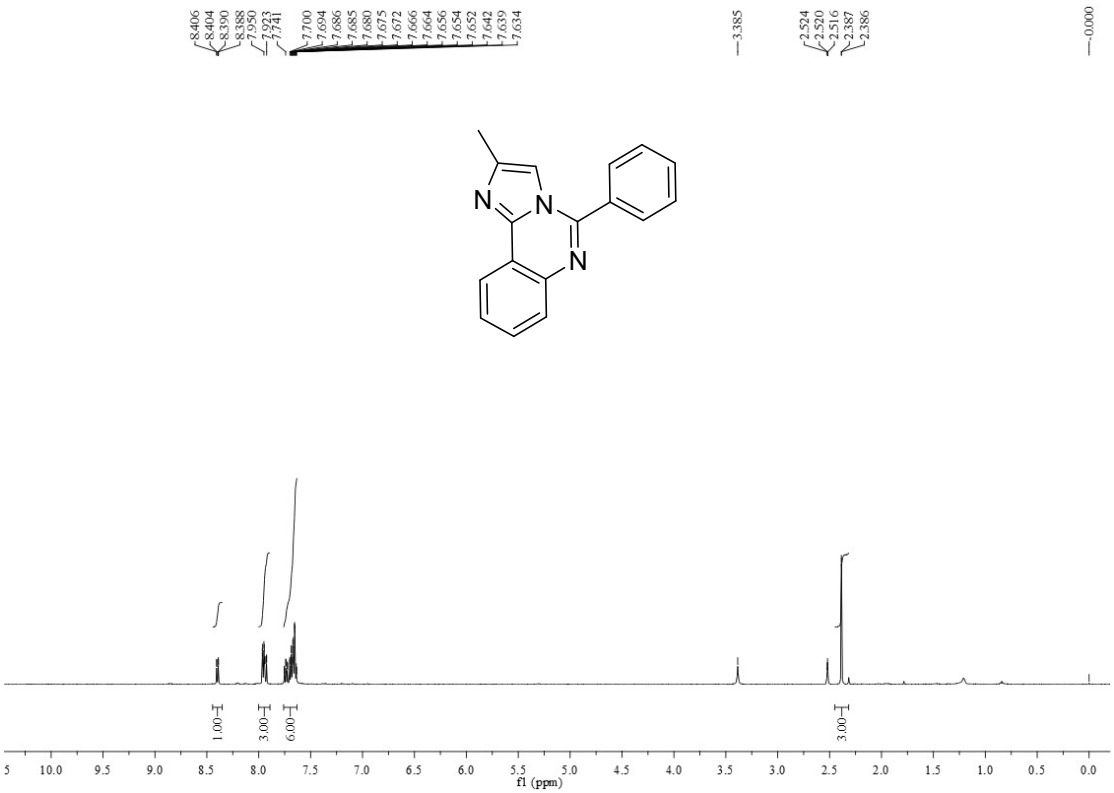

164.619
162.632
148.024
144.085
142.816
142.313
142.265
131.424
129.179
128.526
124.792
117.367
117.178
115.273
115.257
113.760
113.585
113.097
77.333
77.079
76.825
0.000
N
N
N
F
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

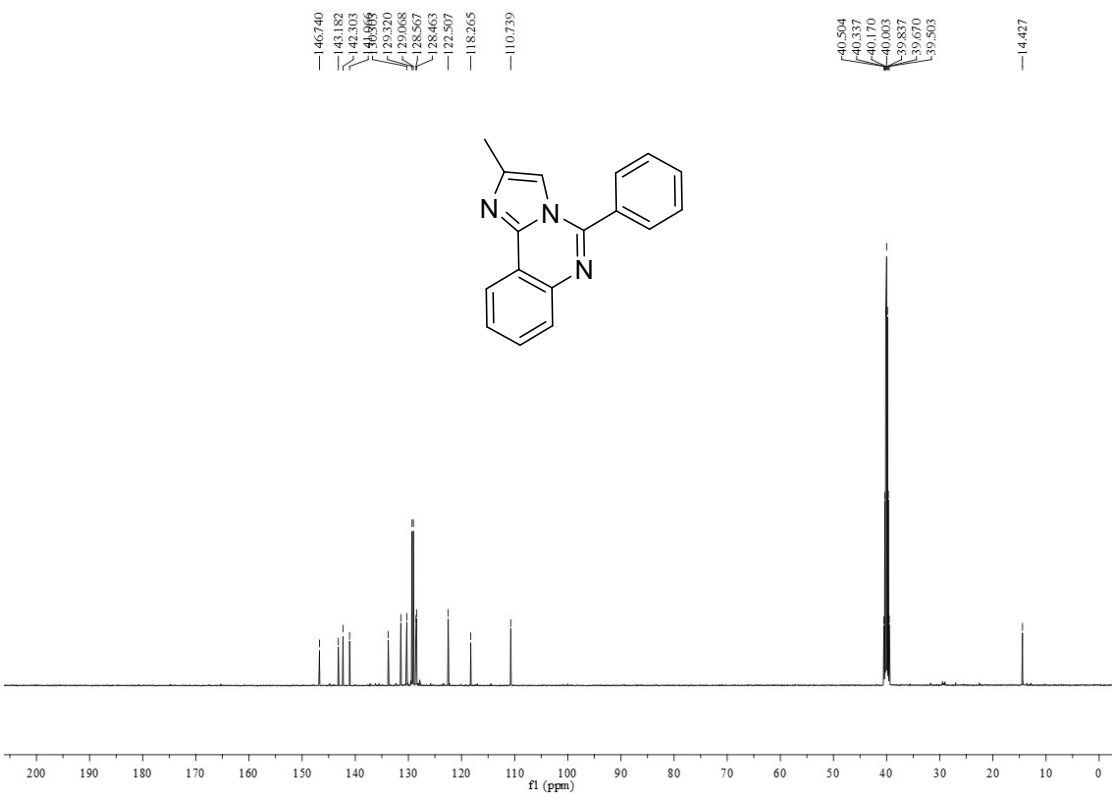

8.417
8.400
8.148
7.892
7.746
7.743
7.734
7.732
7.620
7.618
7.603
0.000
N
N
N
Br
1.00
1.00
2.01
2.00
4.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

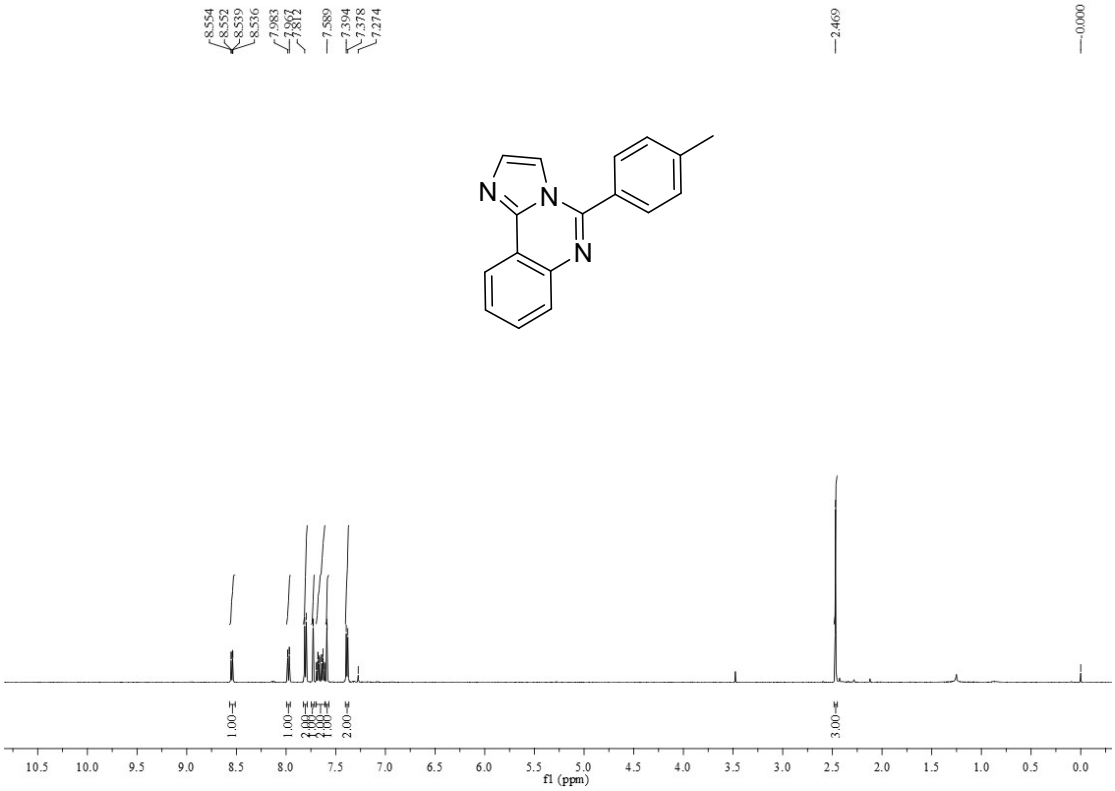

147.768
143.850
142.110
131.430
130.082
129.156
128.535
124.084
123.936
117.281
113.388
77.343
77.089
76.835
N
N
N
Br
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

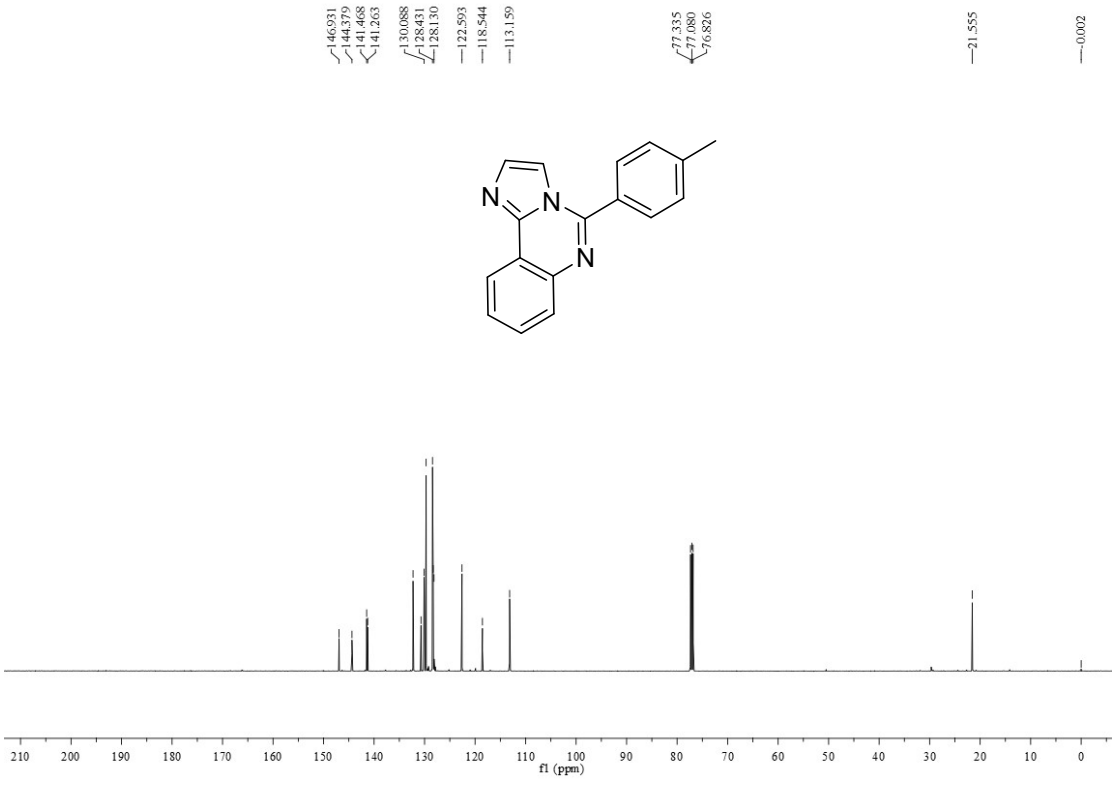

8.716
8.700
8.310
8.125
7.824
7.666
7.645
7.473
7.264
0.000
N
N
N
CF3
1.00
1.00
1.00
2.00
1.18
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

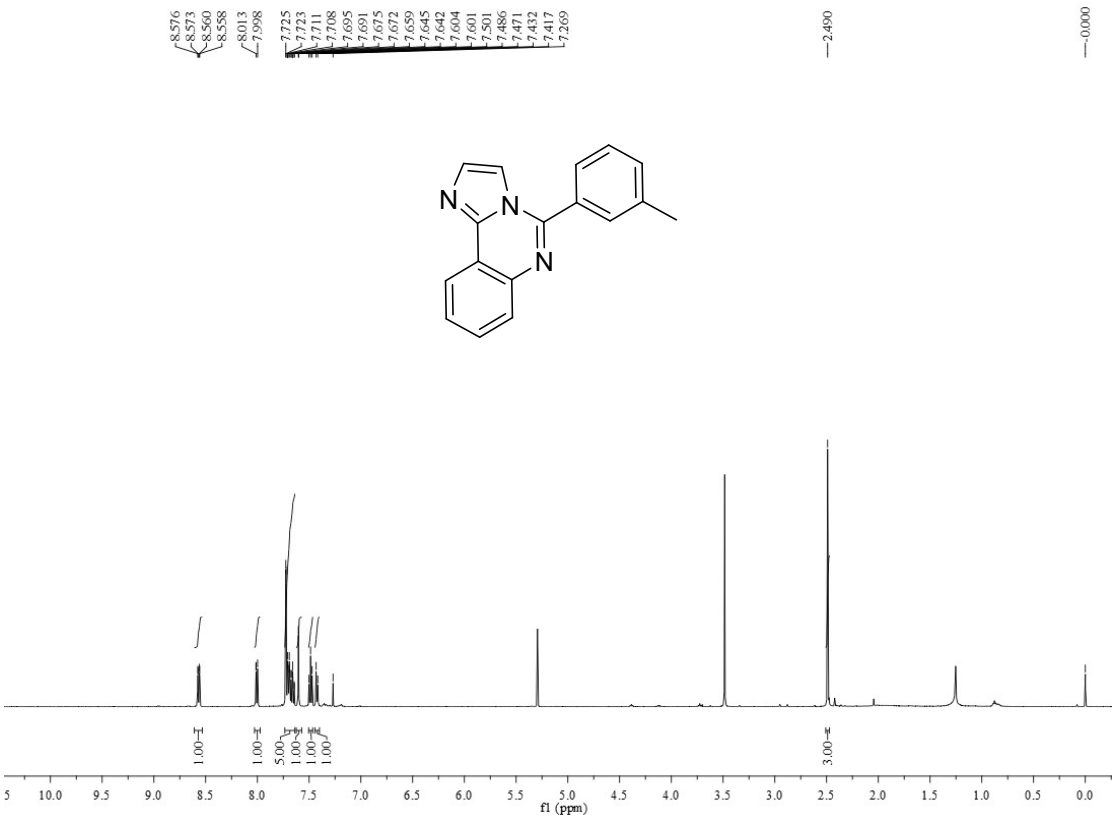

148.049
140.788
133.536
131.604
128.523
126.001
125.902
124.498
123.768
120.504
113.882
77.282
77.028
76.774
0.004
N
N
N
CF3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

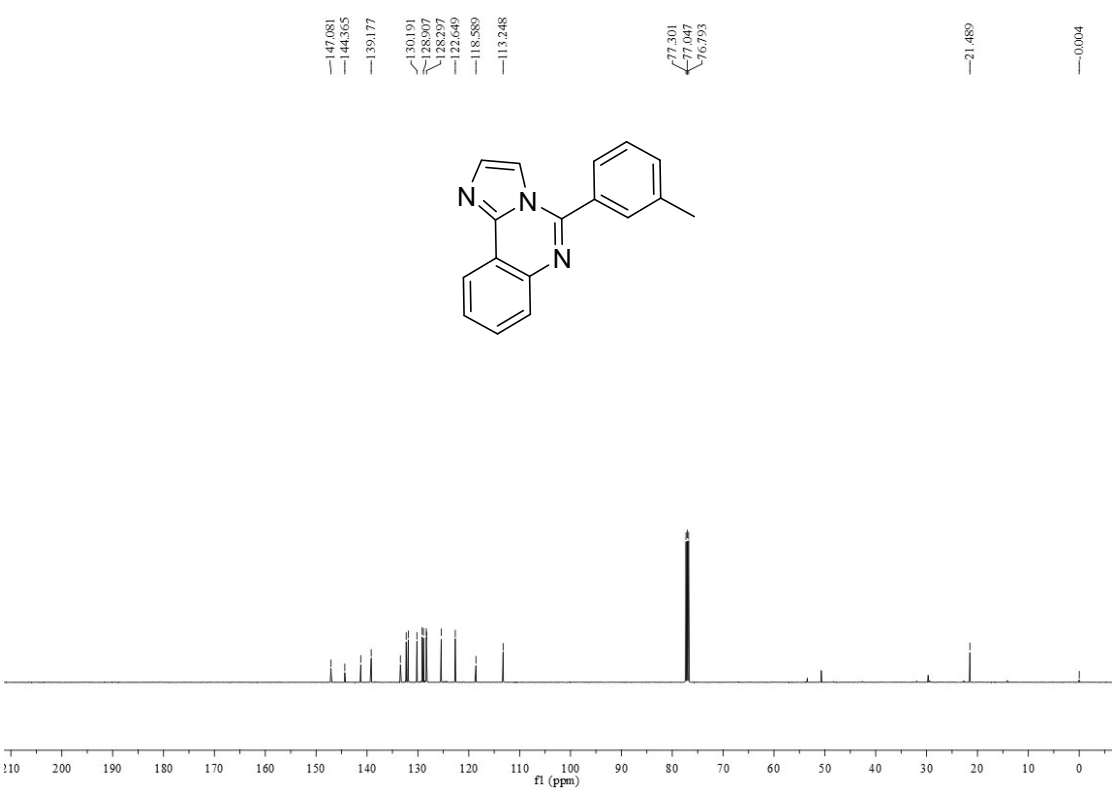

8.406
8.404
8.390
8.388
7.950
7.923
7.741
7.700
7.694
7.686
7.685
7.680
7.675
7.672
7.666
7.664
7.656
7.654
7.652
7.642
7.639
7.634
3.385
2.524
2.520
2.516
2.387
2.386
0.000
N
N
N
1.00
3.00
6.00
3.00
f1 (ppm)

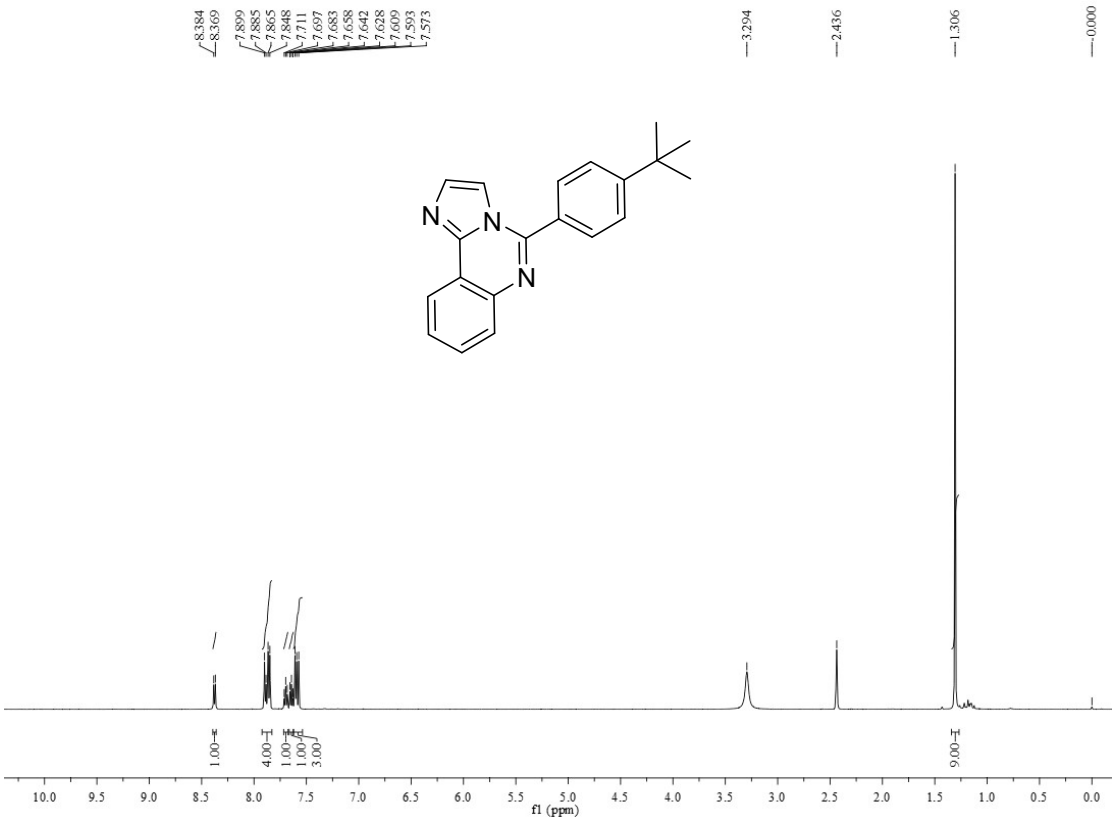

146.740
143.182
142.503
129.320
129.068
128.567
128.463
122.507
118.265
110.739
40.504
40.337
40.170
40.003
39.837
39.670
39.503
14.427
N
N
N
f1 (ppm)

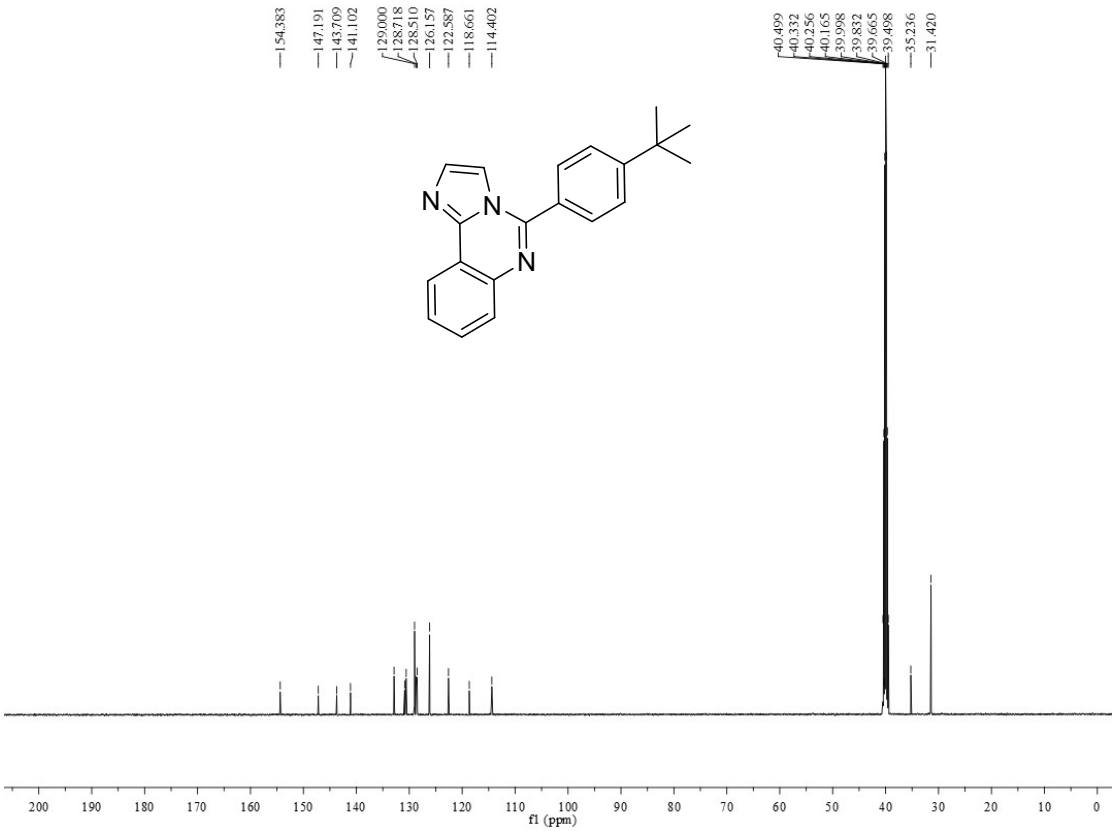

8.554
8.552
8.539
8.536
7.983
7.967
7.812
7.589
7.394
7.378
7.274
2.469
0.000
1.00
1.00
2.00
3.00
f1 (ppm)

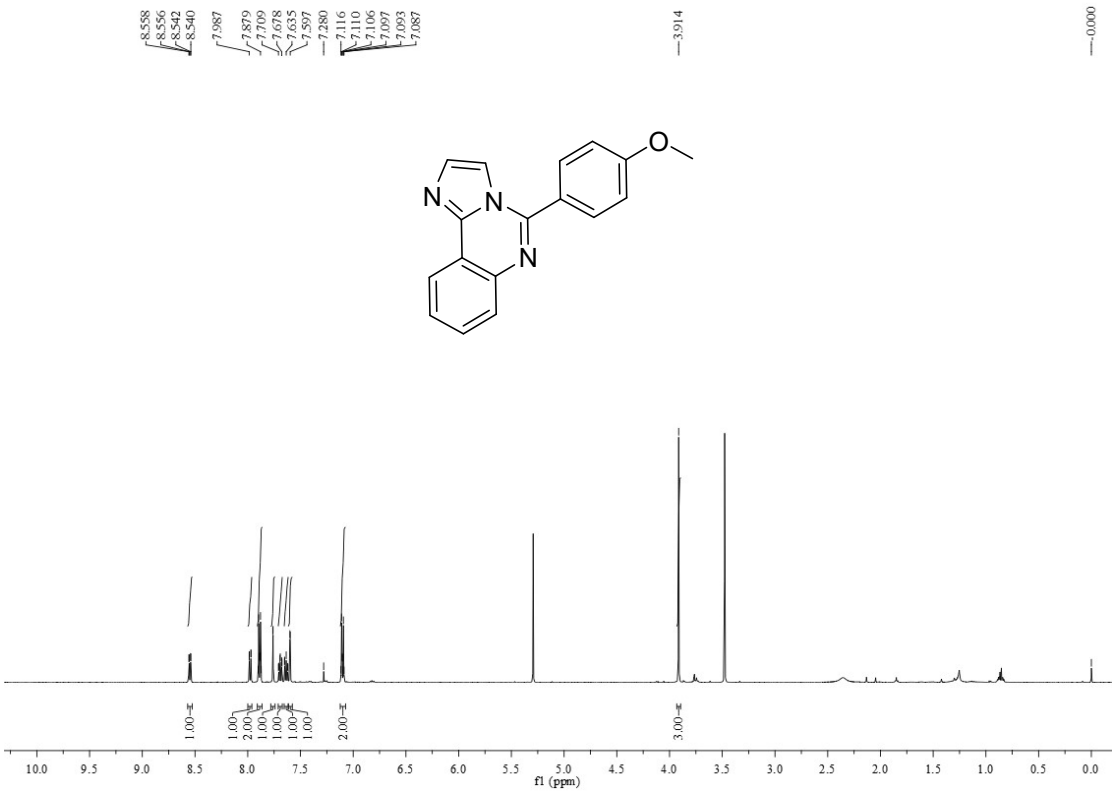

146.931
144.379
141.468
141.263
130.088
128.431
128.130
122.593
118.544
113.159
77.335
77.080
76.826
21.555
0.002
f1 (ppm)

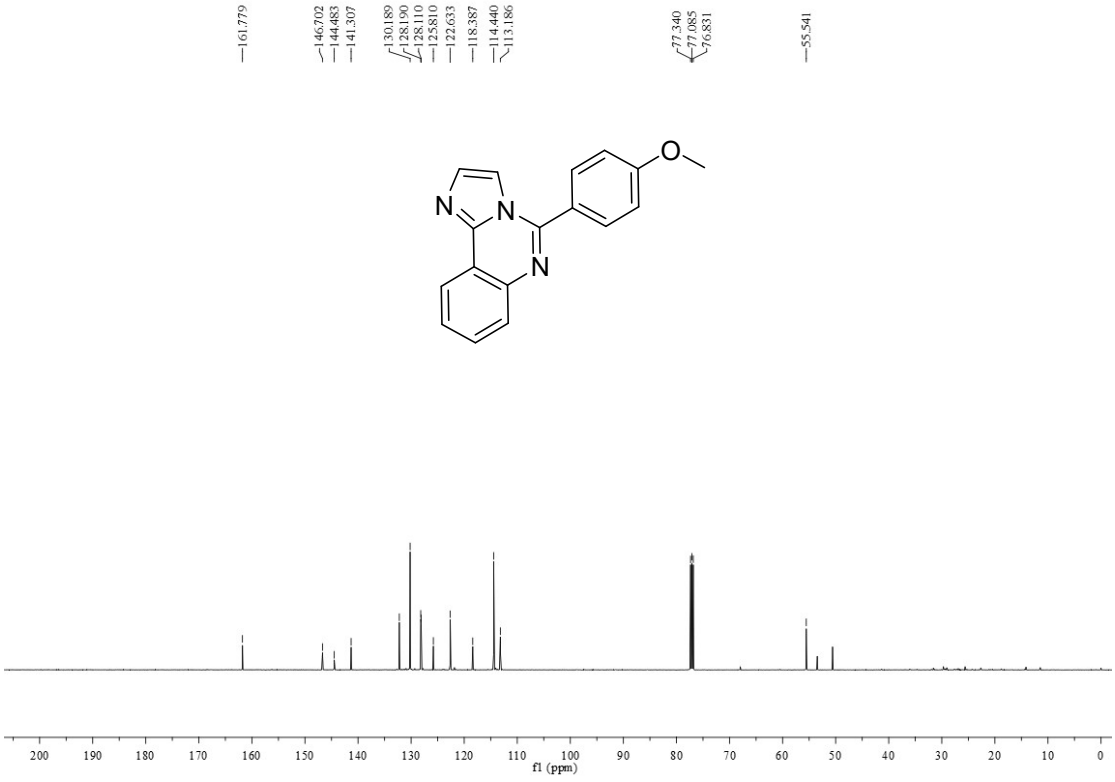

8.576
8.573
8.560
8.558
8.013
7.998
7.725
7.723
7.711
7.708
7.695
7.691
7.675
7.672
7.659
7.645
7.642
7.604
7.601
7.501
7.486
7.471
7.432
7.417
7.269
2.490
0.000
1.00
1.00
5.00
1.00
1.00
1.00
3.00
f1 (ppm)

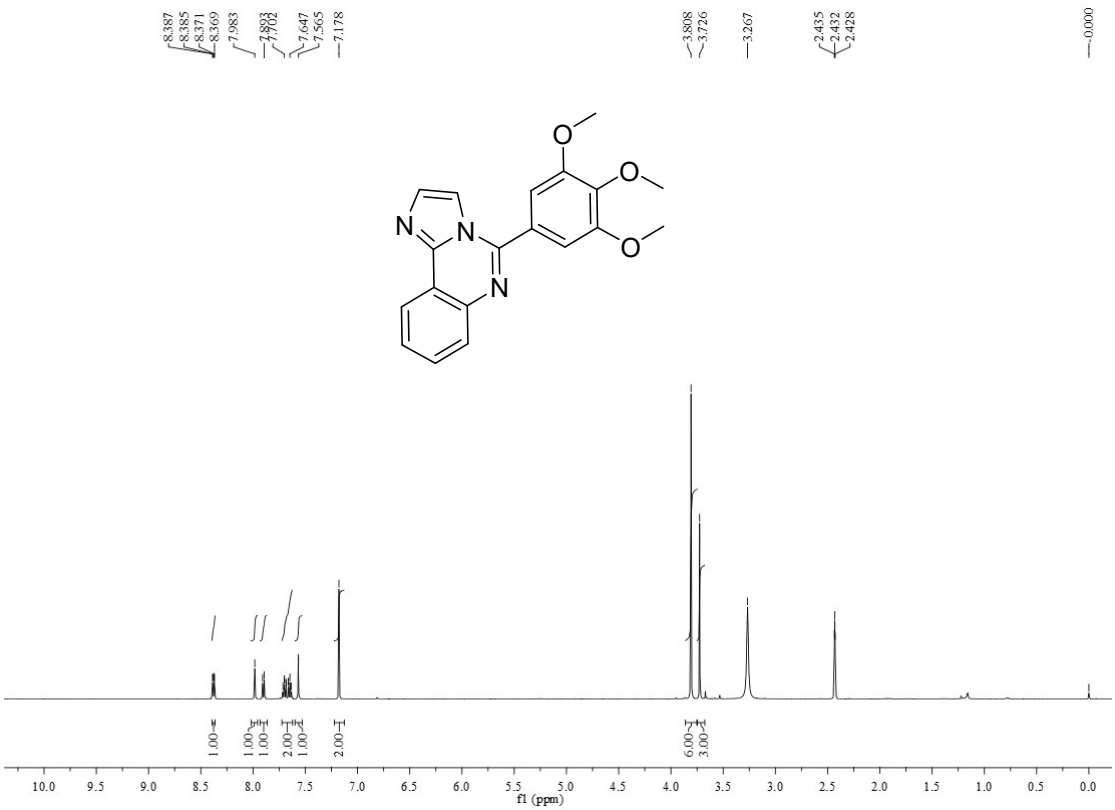

147.081
144.365
139.177
130.191
128.907
128.297
122.649
118.589
113.248
77.301
77.047
76.793
21.489
0.004
f1 (ppm)

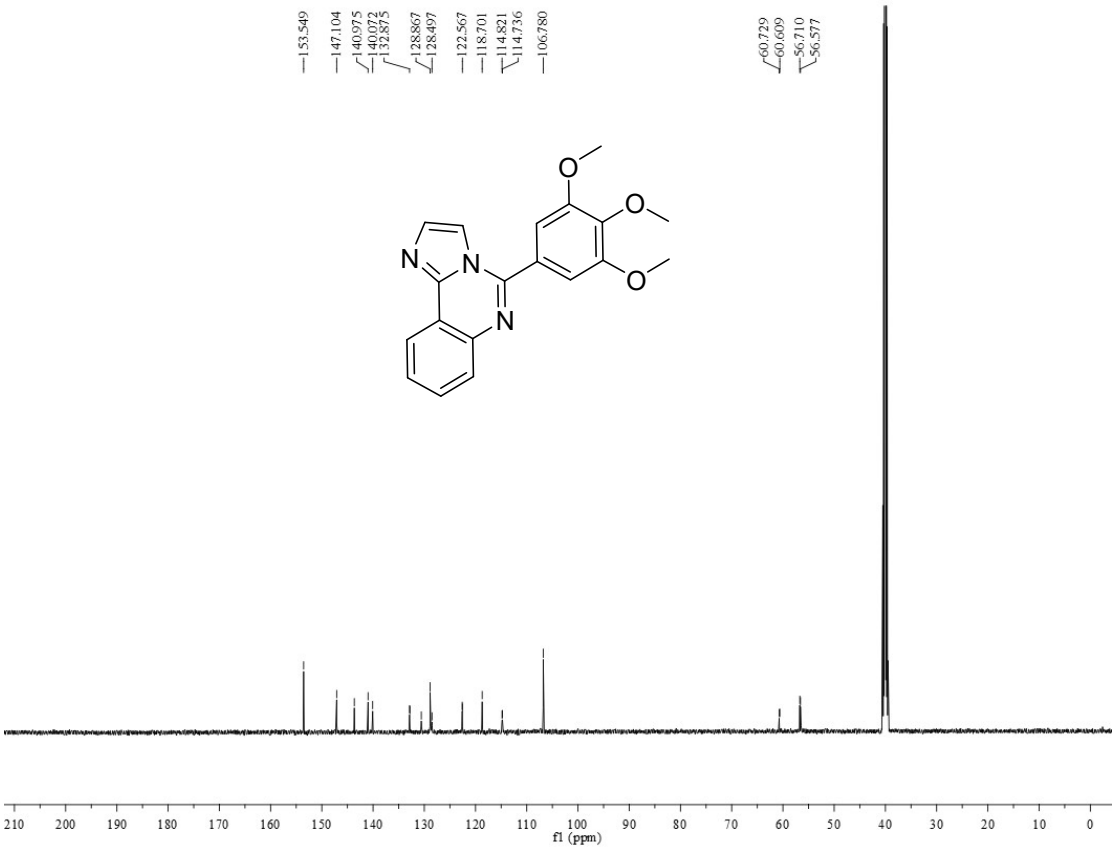

8.384
8.369
7.899
7.885
7.865
7.848
7.711
7.697
7.683
7.658
7.642
7.628
7.609
7.593
7.573
3.294
2.436
1.306
0.000
1.00
4.00
1.00
1.00
3.00
9.00
f1 (ppm)

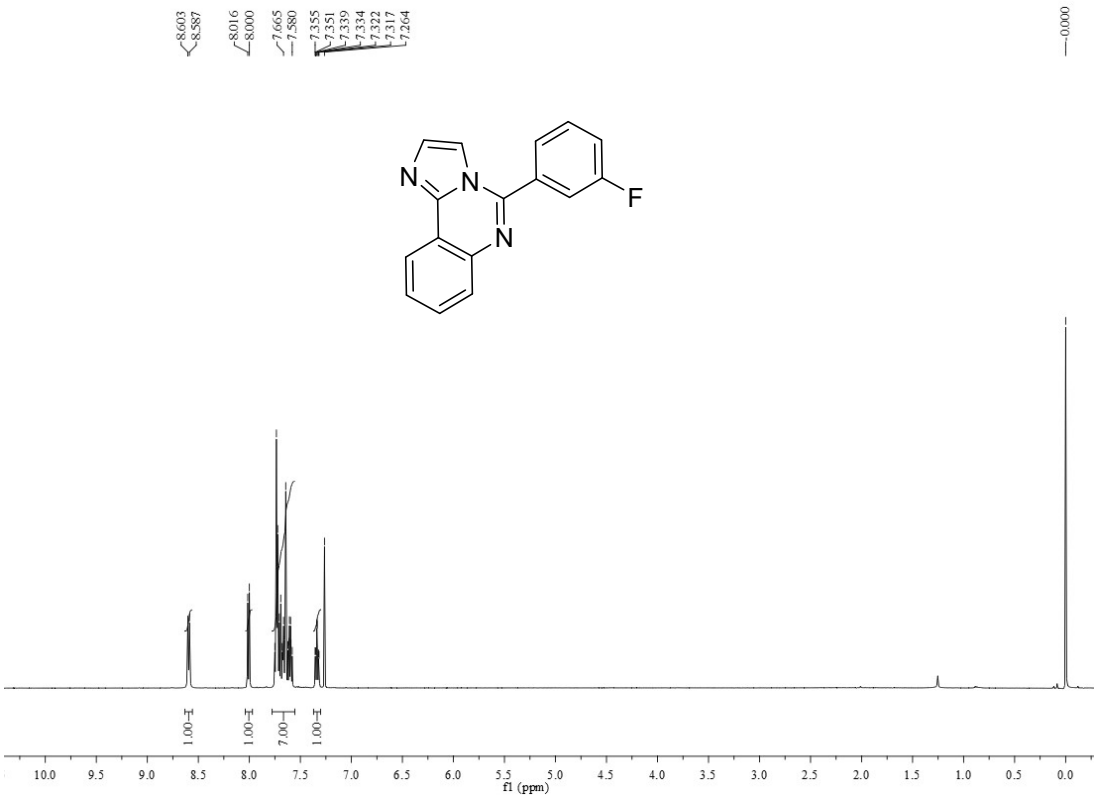

154.383
147.191
143.709
141.102
129.000
128.718
128.510
126.157
122.587
118.661
114.402
40.499
40.332
40.256
40.165
39.998
39.832
39.665
39.498
35.236
31.420
f1 (ppm)

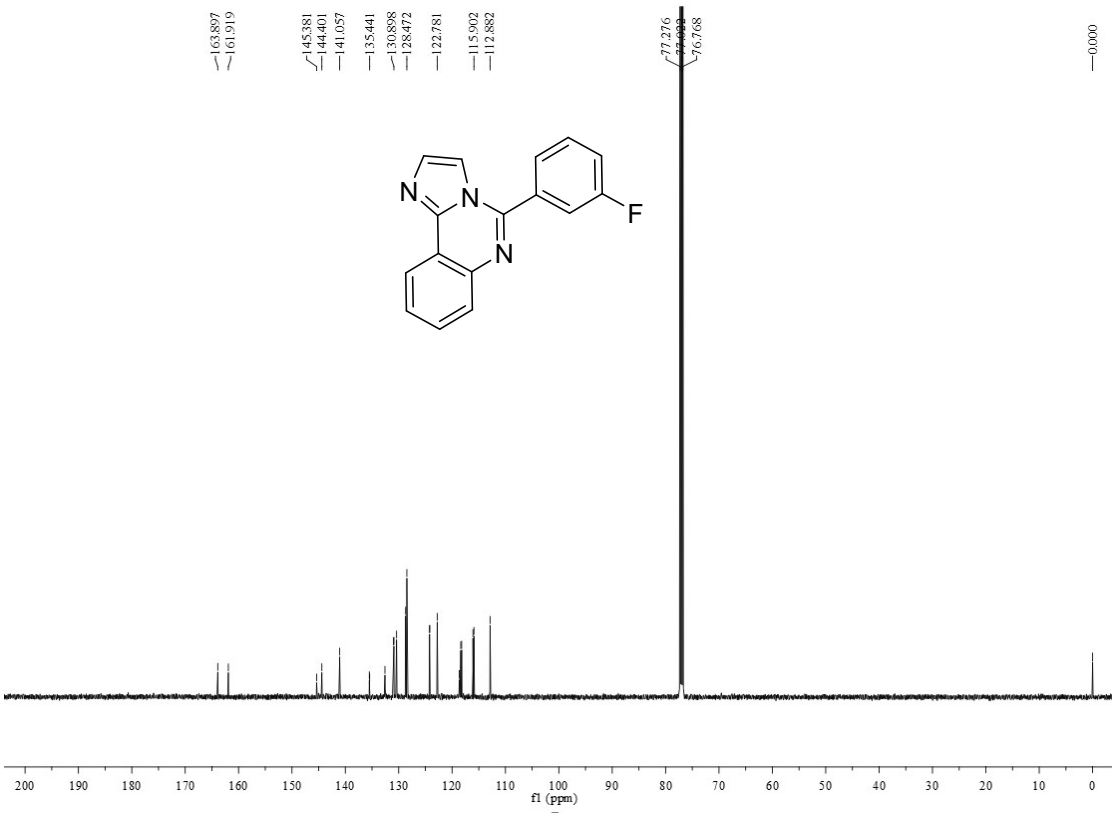

8.558
8.556
8.542
8.540
7.987
7.879
7.709
7.678
7.635
7.597
7.280
7.116
7.110
7.106
7.097
7.093
7.087
3.914
0.000
O
N
N
N
1.00
1.00
2.00
1.00
1.00
1.00
2.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

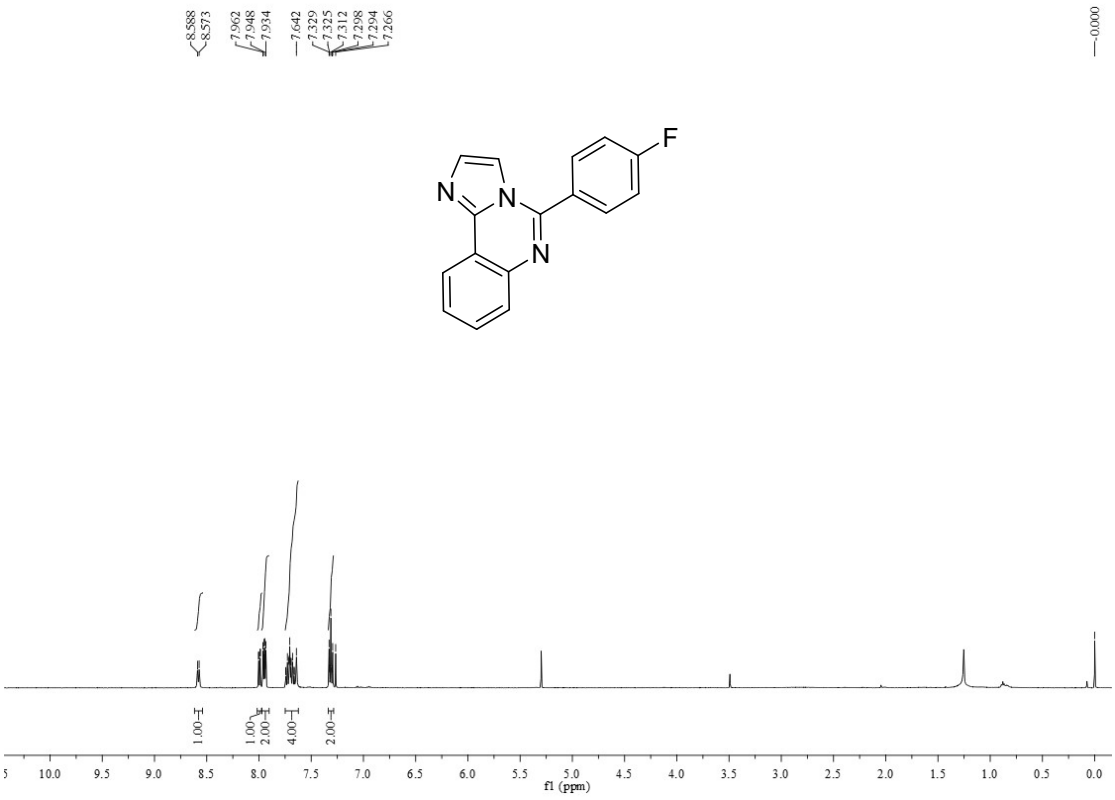

161.779
146.702
144.483
141.307
130.189
128.190
128.110
125.810
122.633
118.387
114.440
113.186
77.340
77.085
76.831
55.541
O
N
N
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

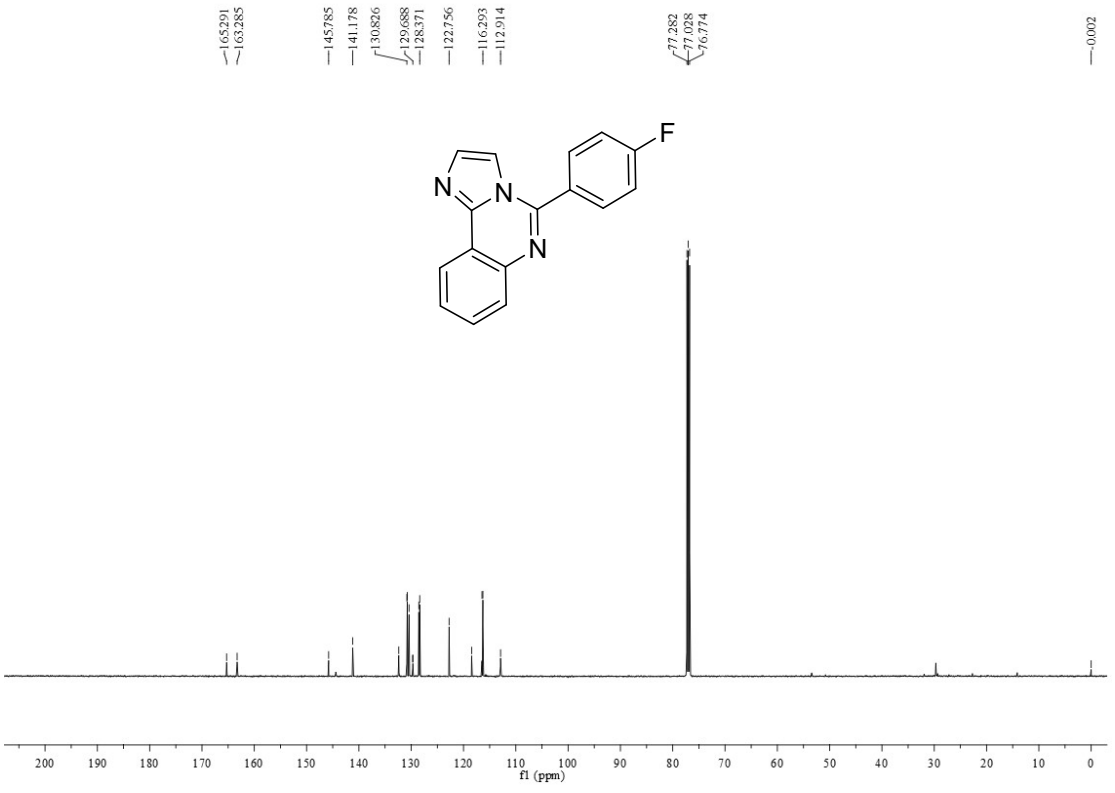

8.387
8.385
8.371
8.369
7.983
7.893
7.702
7.647
7.565
7.178
3.808
3.726
3.267
2.435
2.432
2.428
0.000
O
O
O
N
N
N
1.00
1.00
1.00
2.00
1.00
2.00
6.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

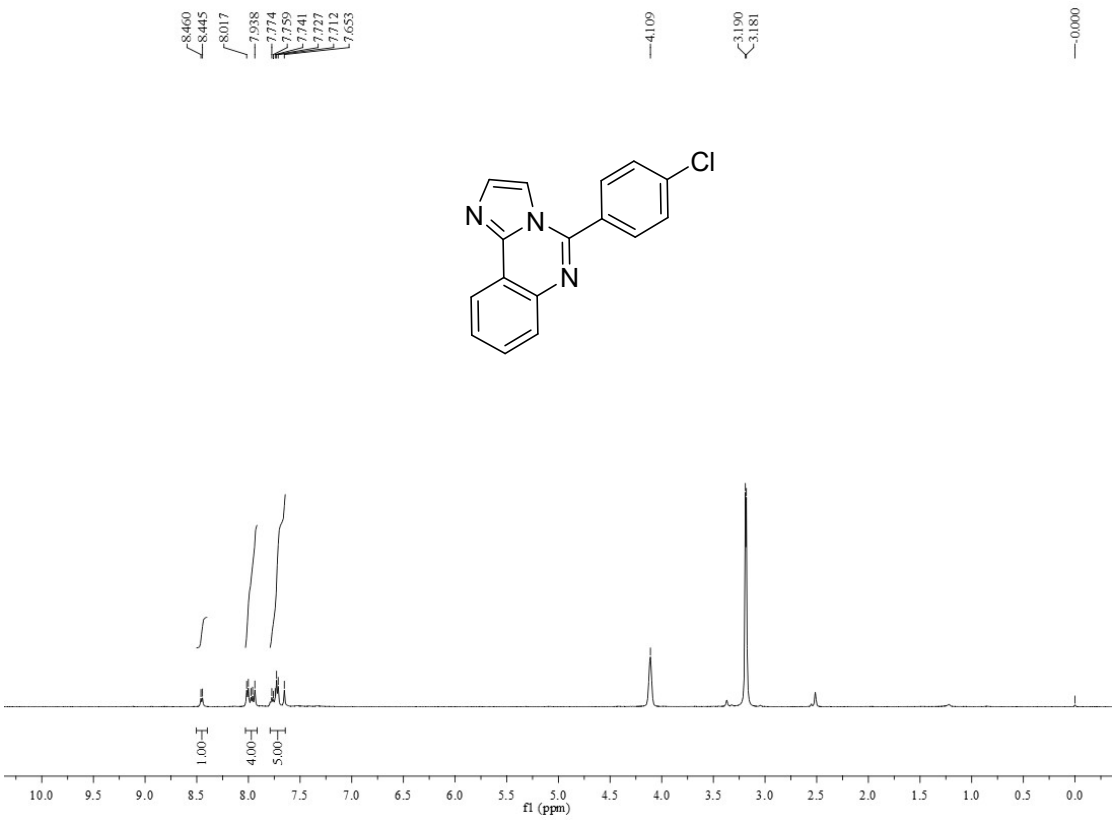

153.549
147.104
140.975
140.072
132.875
128.867
128.497
122.567
118.701
114.821
114.736
106.780
60.729
60.609
56.710
56.577
O
O
O
N
N
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

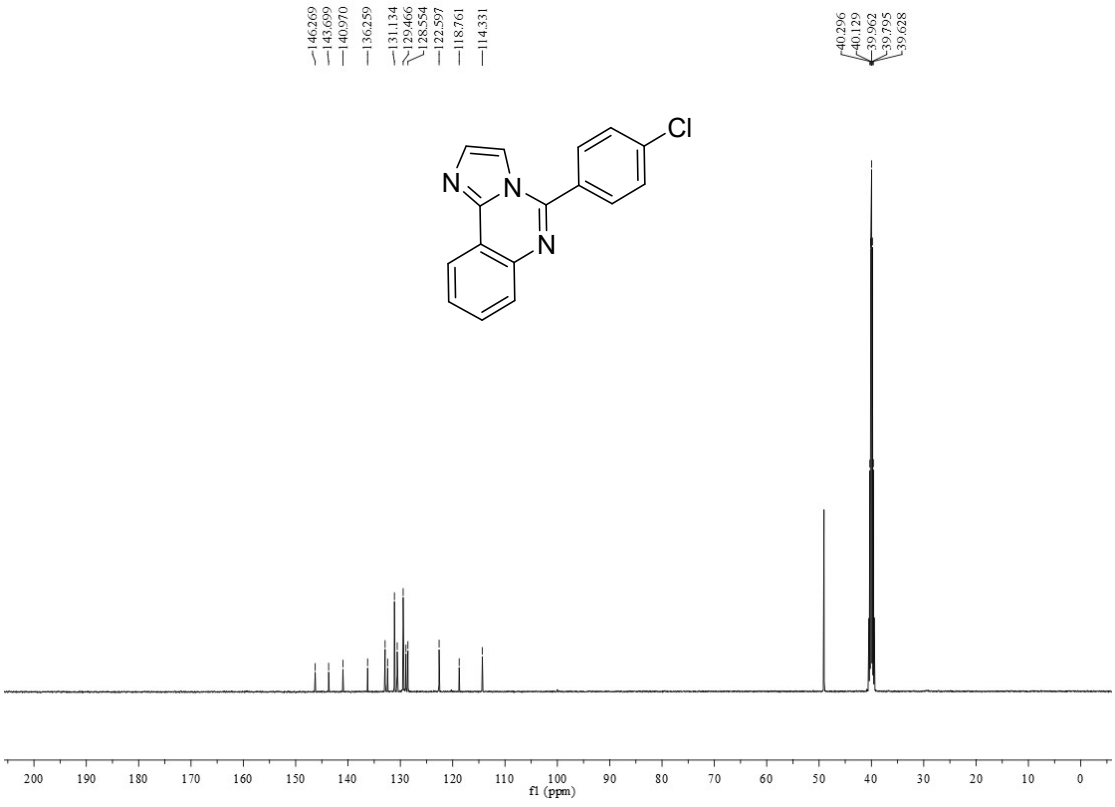

8.603
8.587
8.016
8.000
7.665
7.580
7.355
7.351
7.339
7.334
7.322
7.317
7.264
0.000
N
N
N
F
1.00
1.00
7.00
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

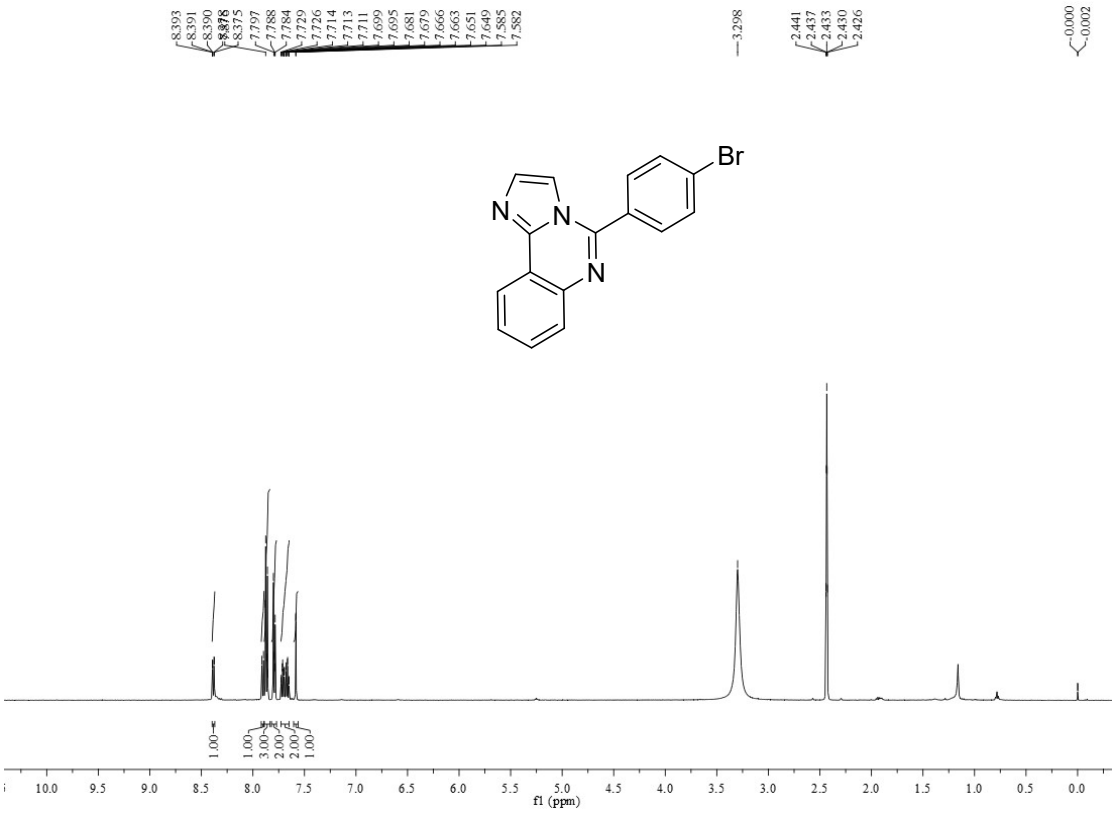

163.897
161.919
145.381
144.401
141.057
135.441
130.898
128.472
122.781
115.902
112.882
77.276
77.024
76.768
0.000
N
N
N
F
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

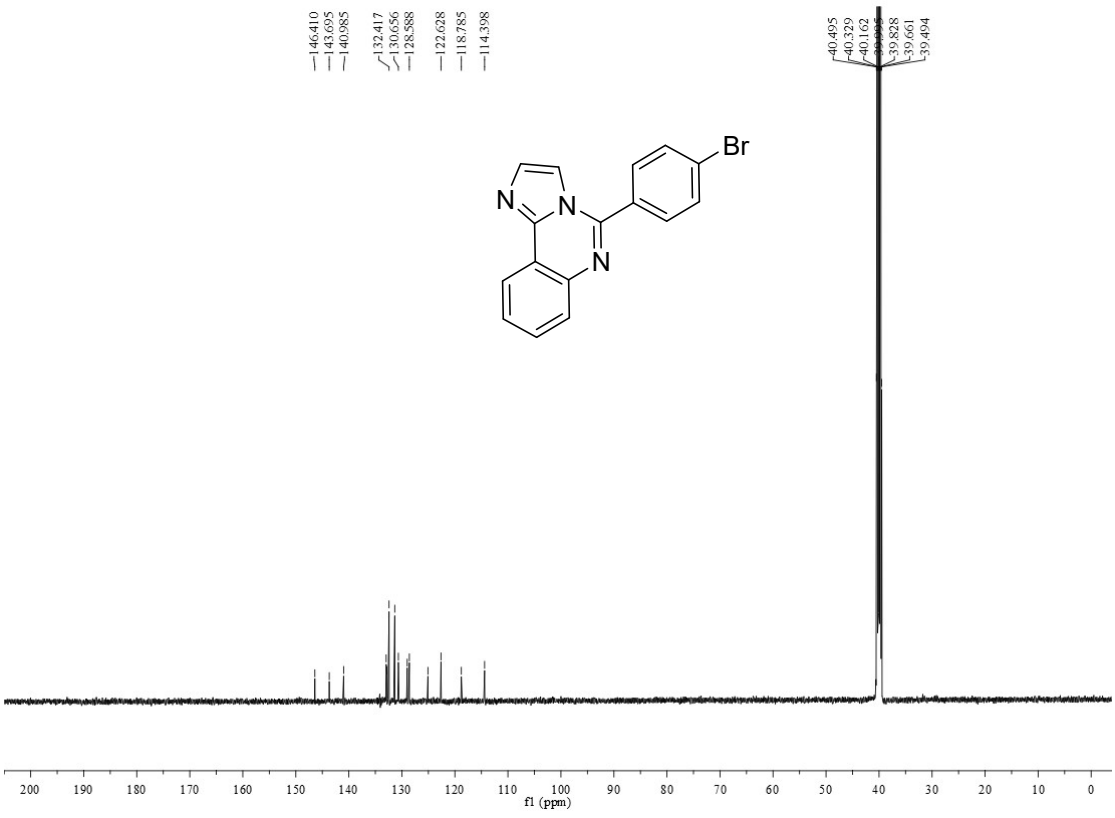

8.588
8.573
7.962
7.948
7.934
7.642
7.329
7.325
7.312
7.298
7.294
7.266
0.000
F
N
N
N
1.00
1.00
2.00
4.00
2.00
f1 (ppm)

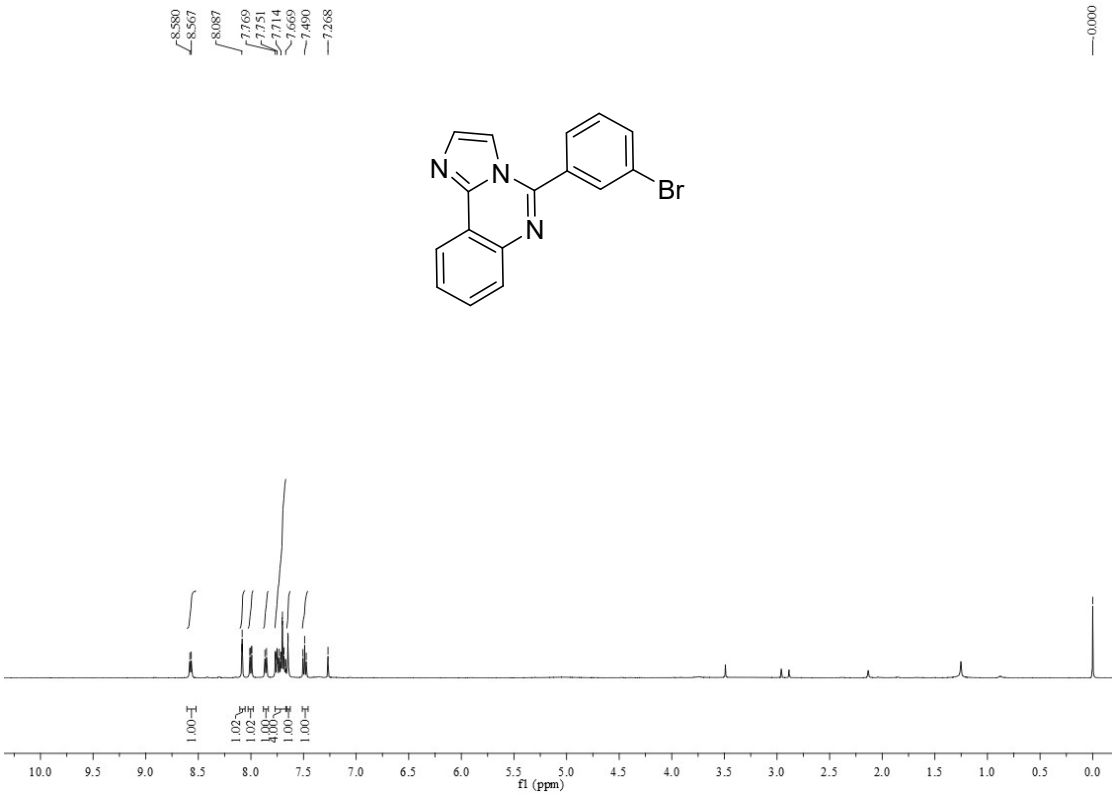

165.291
163.285
145.785
141.178
130.826
129.688
128.371
122.756
116.293
112.914
77.282
77.028
76.774
0.002
F
N
N
N
f1 (ppm)

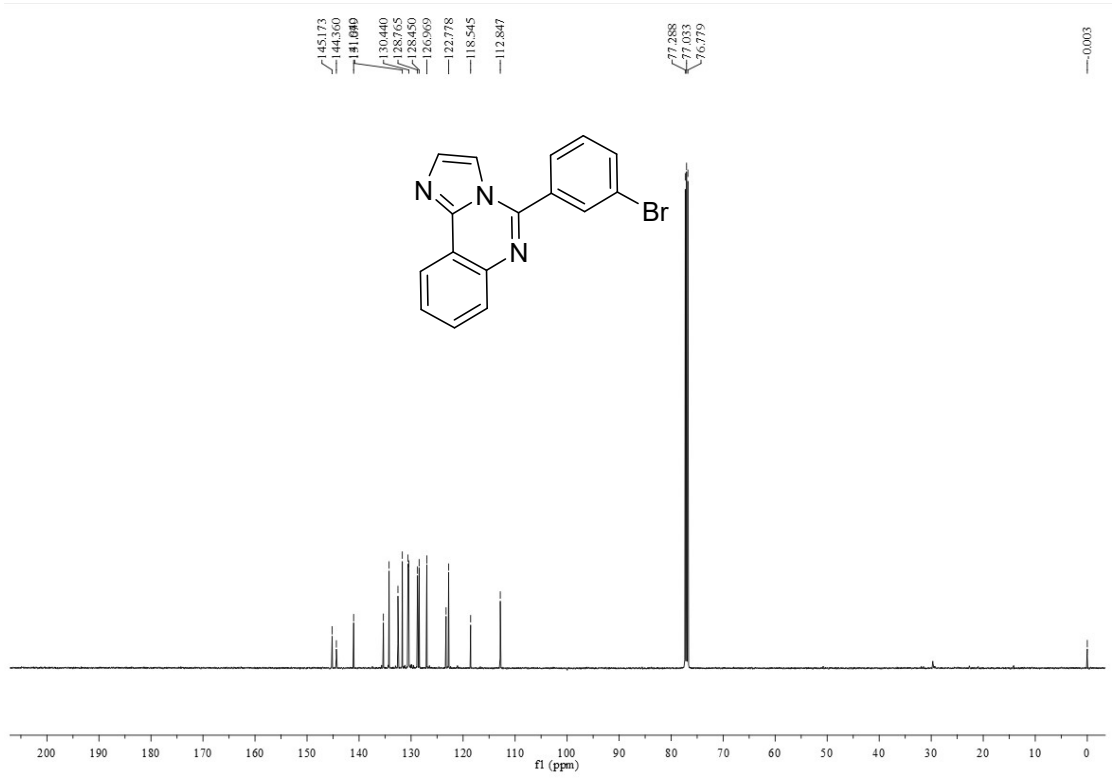

8.460
8.445
8.017
7.938
7.774
7.759
7.741
7.727
7.712
7.653
4.109
3.190
3.181
0.000
Cl
N
N
N
1.00
4.00
5.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

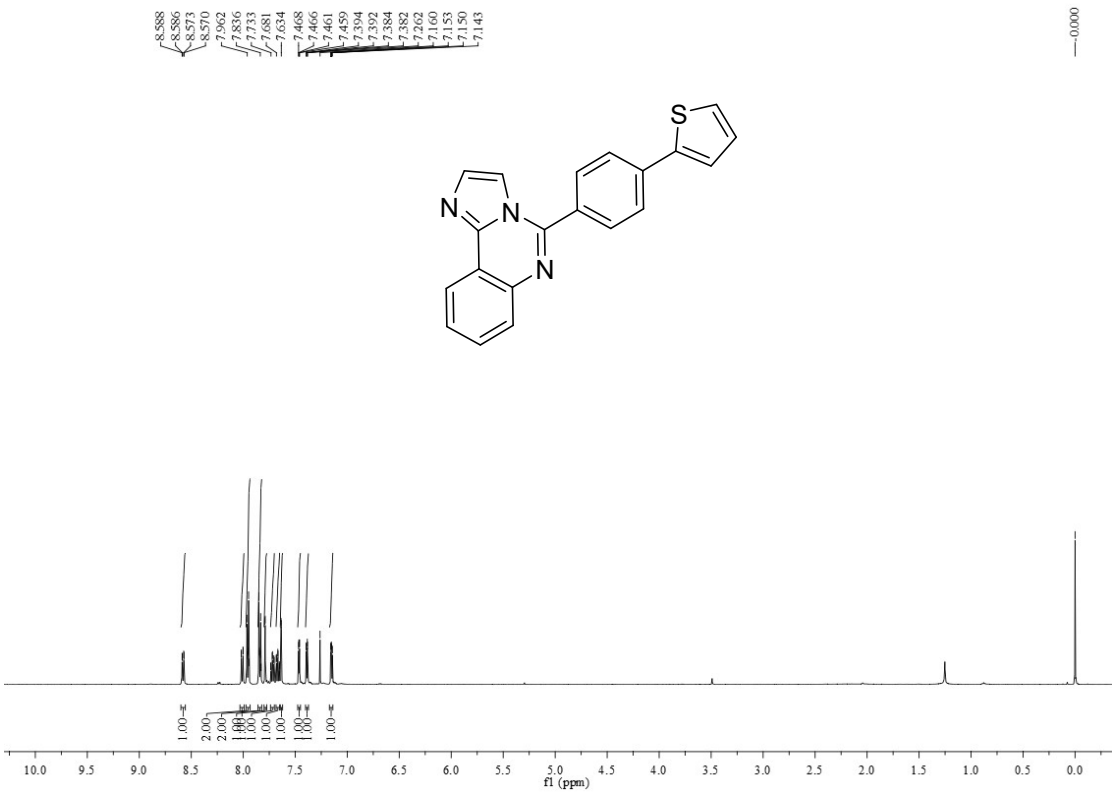

146.269
143.699
140.970
136.259
131.134
129.466
128.534
122.597
118.761
114.331
40.296
40.129
39.962
39.795
39.628
Cl
N
N
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

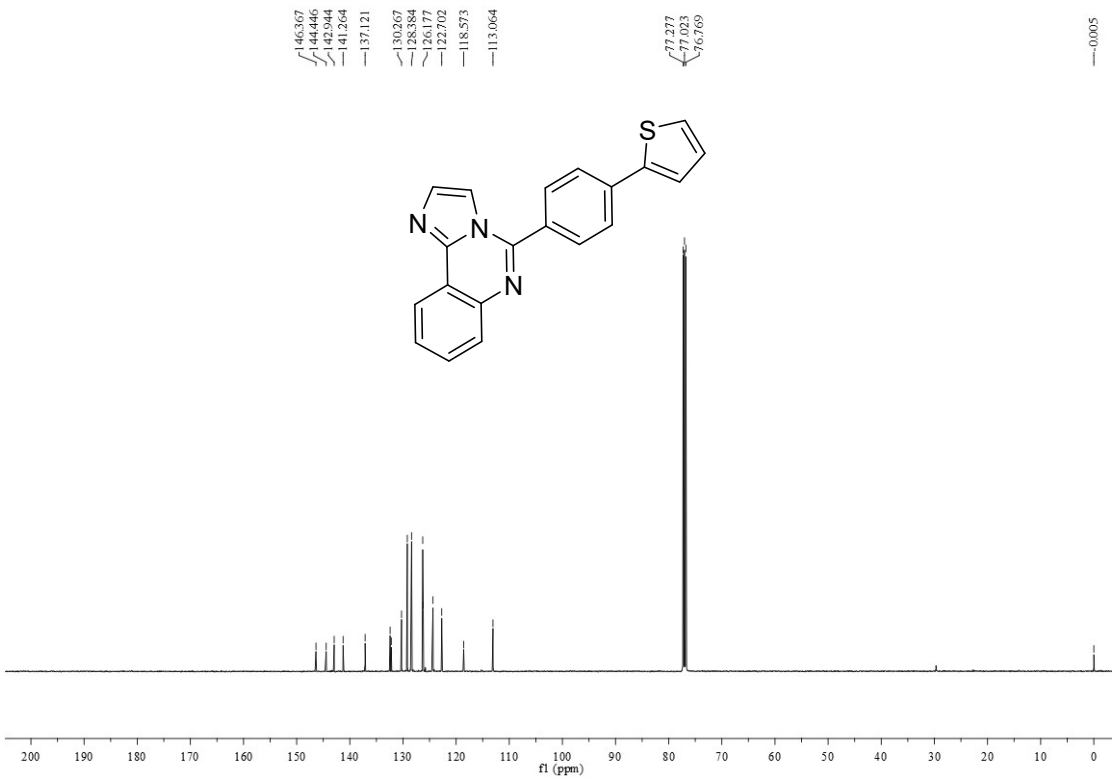

8.393
8.391
8.390
8.375
7.797
7.788
7.784
7.729
7.726
7.714
7.713
7.711
7.699
7.695
7.681
7.679
7.666
7.663
7.651
7.649
7.585
7.582
3.298
2.441
2.437
2.433
2.430
2.426
0.000
-0.002
Br
N
N
N
1.00
1.00
3.00
2.00
2.00
2.00
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

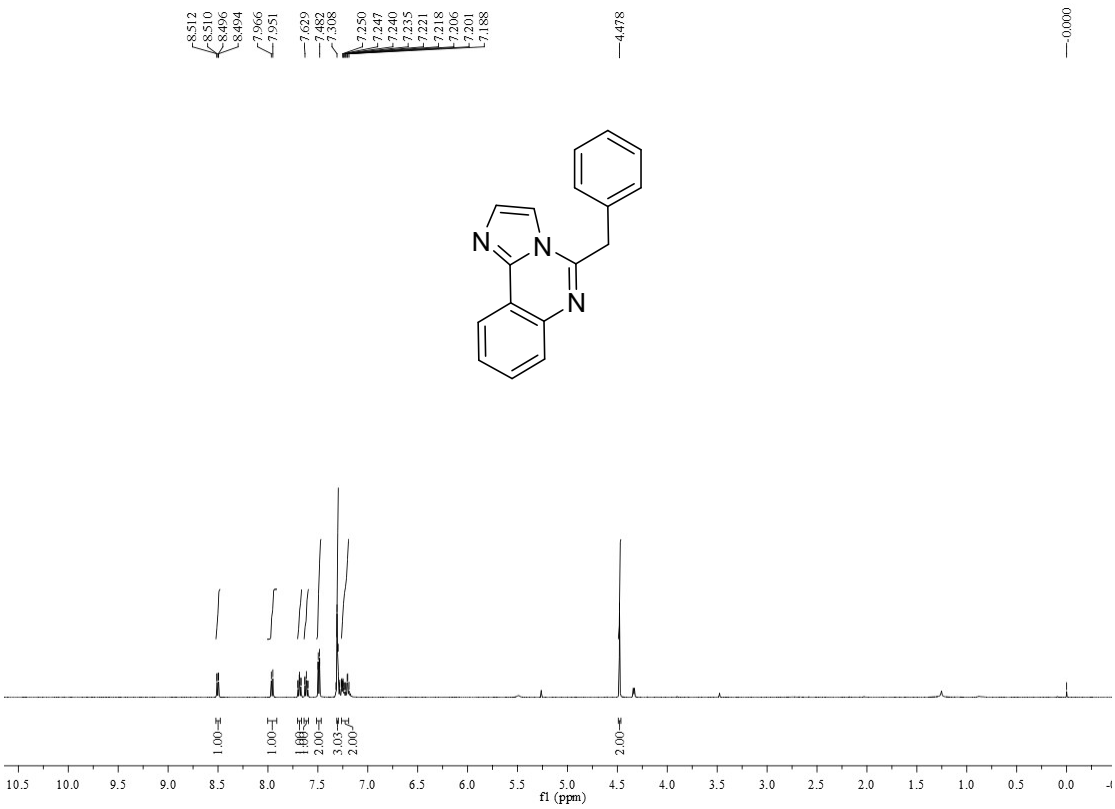

146.410
143.695
140.985
132.417
130.656
128.588
122.628
118.785
114.398
40.495
40.329
40.162
39.828
39.661
39.494
Br
N
N
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

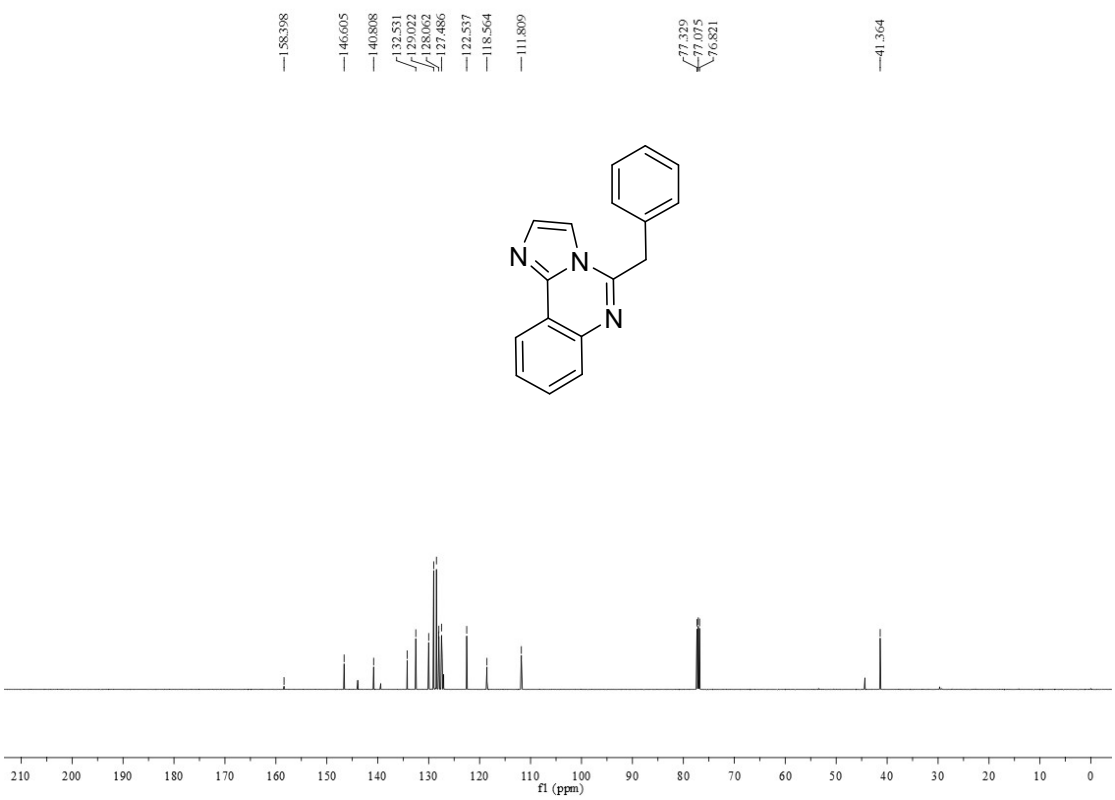

8.580
8.567
8.087
7.769
7.751
7.714
7.669
7.490
7.268
0.000
N
N
N
Br
1.00
1.02
1.02
1.00
4.00
1.00
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


145.173
144.360
141.040
130.440
128.765
128.450
126.969
122.778
118.545
112.847
77.288
77.033
76.779
0.003
N
N
N
Br
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.588
8.586
8.573
8.570
7.962
7.836
7.733
7.681
7.634
7.468
7.466
7.461
7.459
7.394
7.392
7.384
7.382
7.262
7.160
7.153
7.150
7.143
0.000
S
N
N
N
1.00
2.00
2.00
1.00
1.00
1.00
1.00
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


146.367
144.446
142.944
141.264
137.121
130.267
128.384
126.177
122.702
118.573
113.064
77.277
77.023
76.769
0.005
S
N
N
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.512
8.510
8.496
8.494
7.966
7.951
7.629
7.482
7.308
7.250
7.247
7.240
7.235
7.221
7.218
7.206
7.201
7.188
4.478
0.000
1.00
1.00
1.00
2.00
3.03
2.00
2.00
f1 (ppm)


158.398
146.605
140.808
132.531
129.022
128.062
127.486
122.537
118.564
111.809
77.329
77.075
76.821
41.364
f1 (ppm)