Supporting Information

Photoinitiated Decarboxylative C3-difluoroarylmethylation of Quinoxalin-2(1H)-ones with Potassium 2,2-Difluoro-2-arylacetates in water

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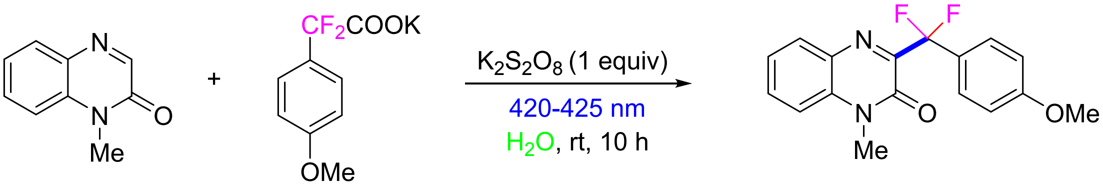
Table of Contents for Supporting Information

1. General considerations

All ^{1}H NMR and ^{13}C NMR spectra were recorded on 400 MHz or 600 MHz Bruker FT-NMR spectrometer (400 MHz or 100 MHz and 600 MHz or 150 MHz, respectively), and ^{19}F NMR spectra were recorded on a 400 MHz Bruker FT-NMR spectrometer (376 MHz). All chemical shifts are given as δ value (ppm) with reference to tetramethyl silane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in Hertz (Hz). High resolution mass spectroscopy data of the product were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI). Melting points (uncorrected) were obtained on WRS-1B digital melting point apparatus. The procedures for the synthesis of quinoxalin-2(1*H*)-ones are according to the reported method (See: S. Liu, Y. Huang, F.-L. Qing and X.-H. Xu. *Org. Lett.*, 2018, **20**, 5497). The preparation of potassium 2,2-difluoro-2-(4-methoxyphenyl)acetats is according to the reported procedure (See: W. Wan, G. Ma, J. Li, Y. Chen, Q. Hu, M. Li, H. Jiang, H. Deng and J. Hao. *Chem. Commun.*, 2016, **52**, 1598).

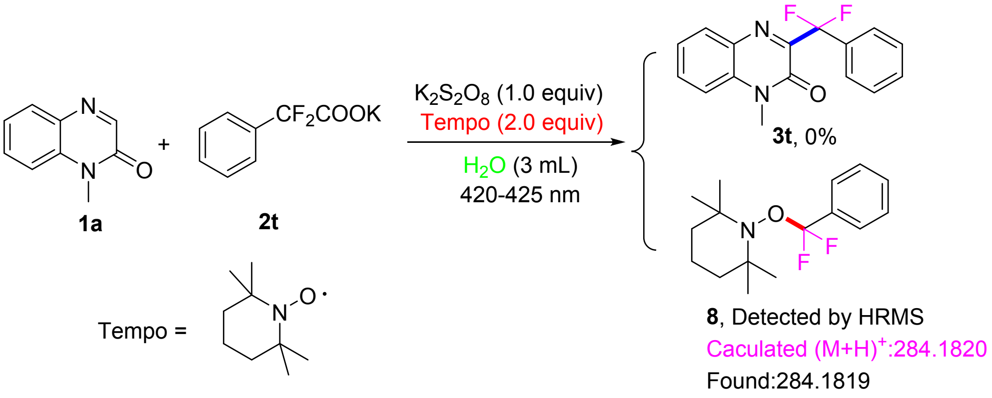
2. Representative procedure for the model reaction



A 5 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with *N*-methyl-quinoxalin-2(1*H*)-one (**1a**, 0.10 mmol), potassium 2,2-difluoro-2-(4-methoxyphenyl)acetate (**2a**, 0.20 mmol), $K_2S_2O_8$ (0.10 mmol) and H_2O (3.0 mL). The reaction vessel was exposed to a blue LED (420–425 nm, 1.5 W) irradiation at room temperature in air with stirring for 10 h. After completion of the reaction, the mixture was extracted with ethyl acetate and concentrated to yield the crude product, which was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 20:1 to 9:1) to give the desired product **3a**.

3. Mechanism investigation

A 5 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with *N*-methylquinoxalin-2(1*H*)-one (**1a**, 0.10 mmol), potassium 2,2-difluoro-2-phenylacetate (**2t**, 0.20 mmol), $K_2S_2O_8$ (1.0 eq.), TEMPO (2.5 eq.) and H_2O (3.0 mL), the reaction vessel was exposed to blue LED (420-425 nm, 1.5 W) irradiation in air at room temperature with stirring for 10 h. The reaction was completely inhibited, and an adduct (**8**) of TEMPO with a free radical was detected by HPLC/HRMS analysis of reaction mixture (Figure S1).



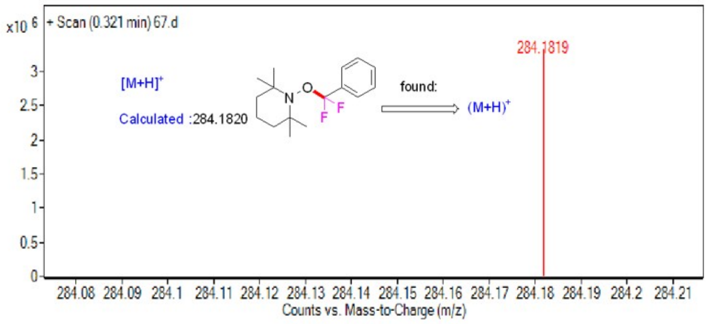
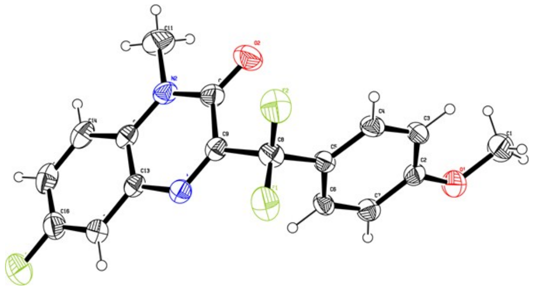
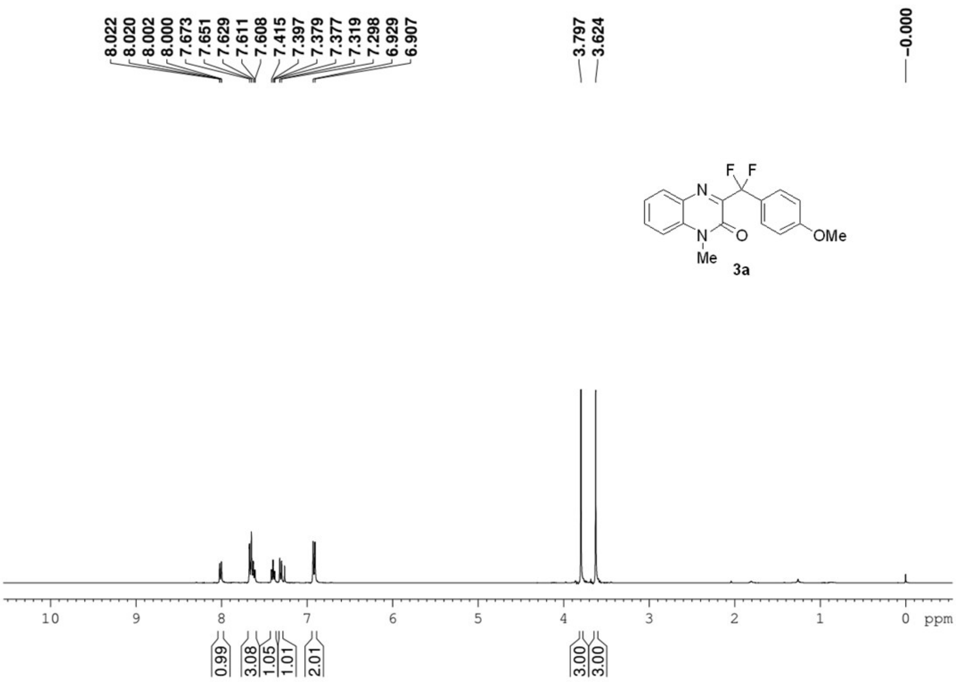


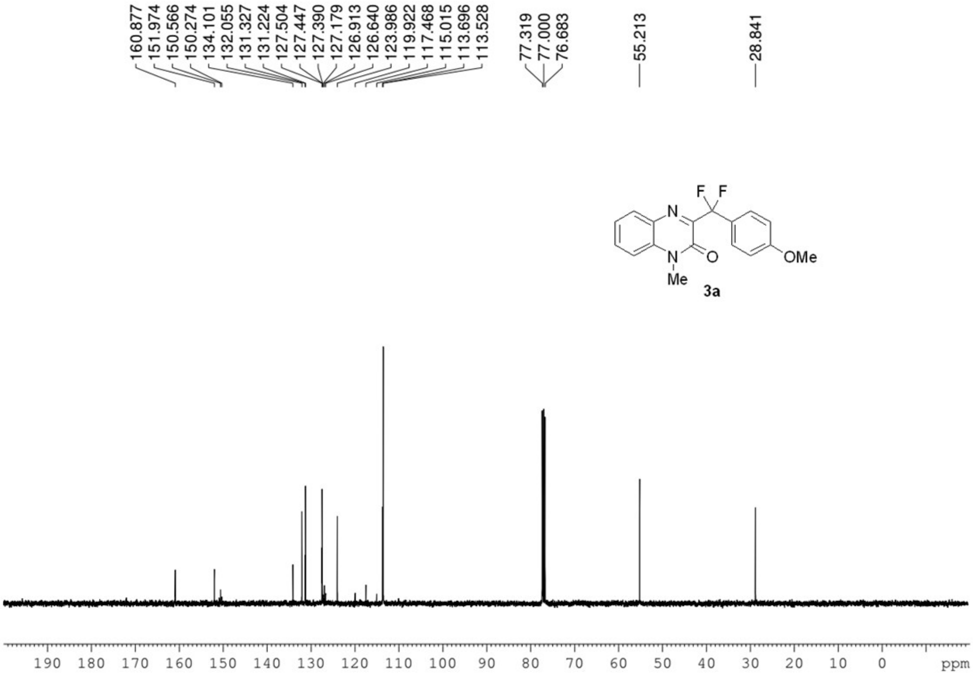
Figure S1. Analysis of reaction mixture by HRMS analysis

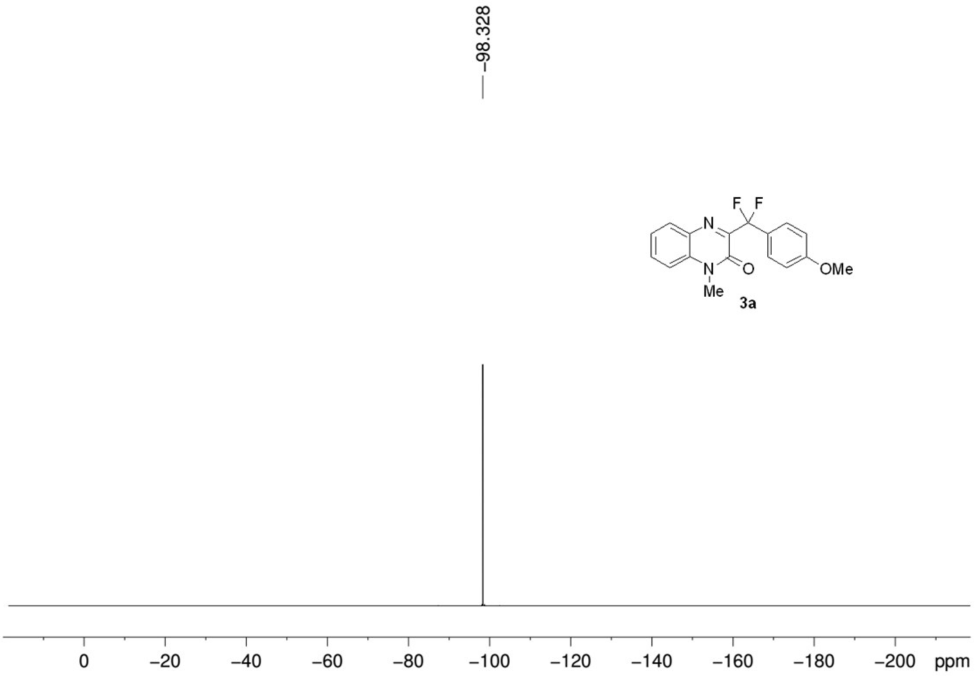
4. X-ray single crystal structure 3i (CCDC Number: 1961424)



5. ^{1}H, ^{13}C and ^{19}F NMR spectra of the products



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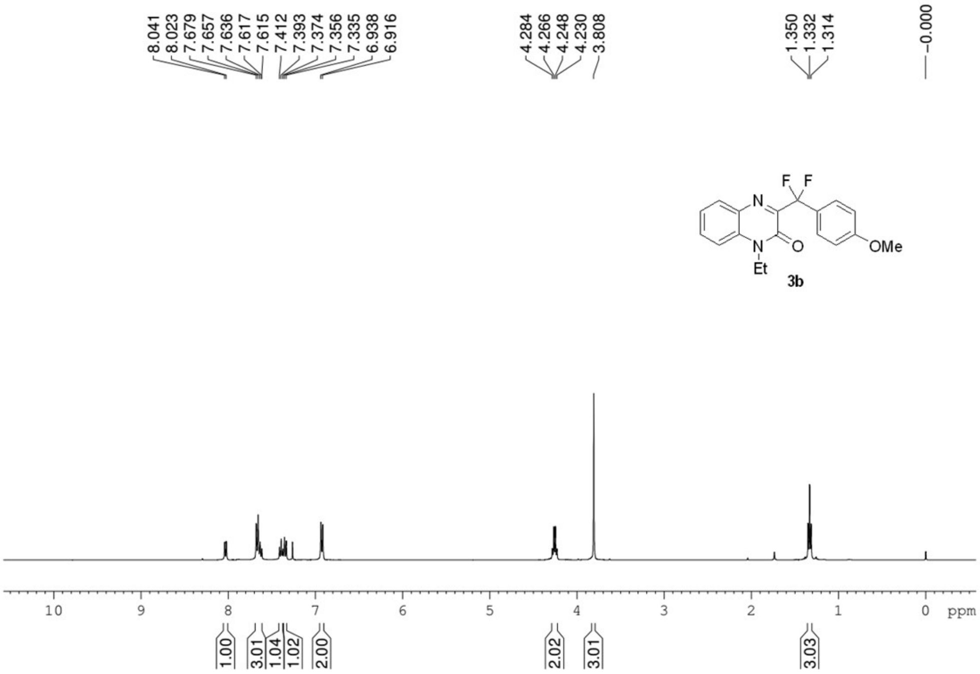
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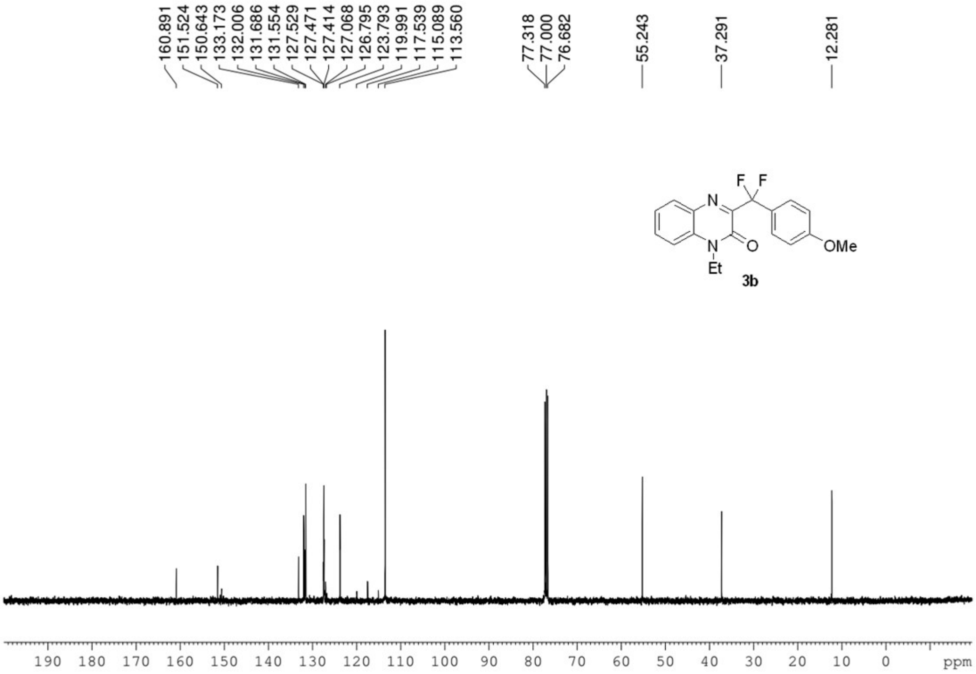
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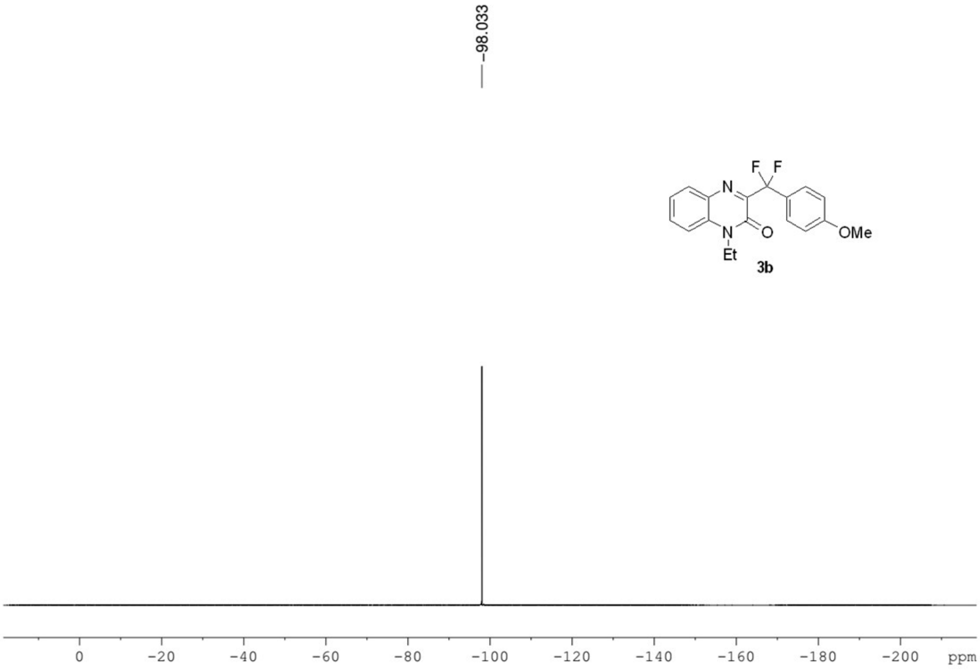
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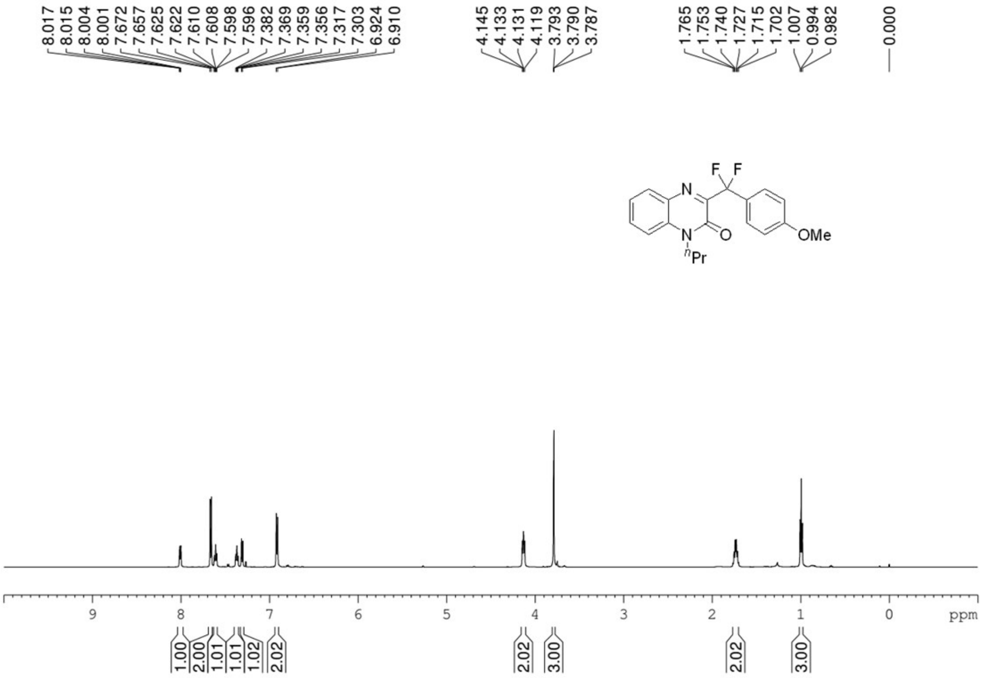
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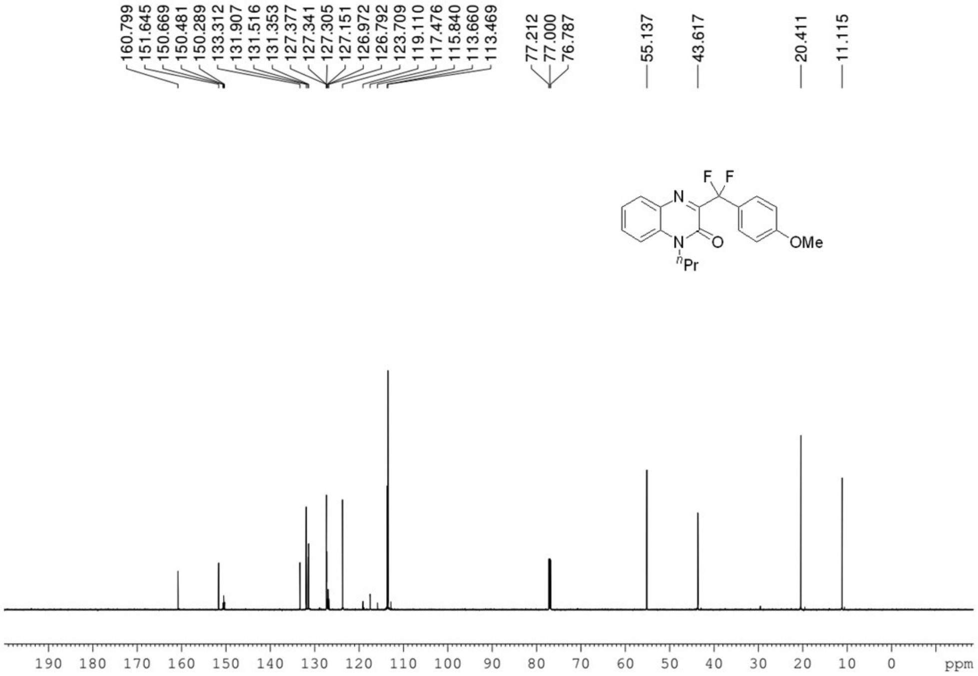
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OMe
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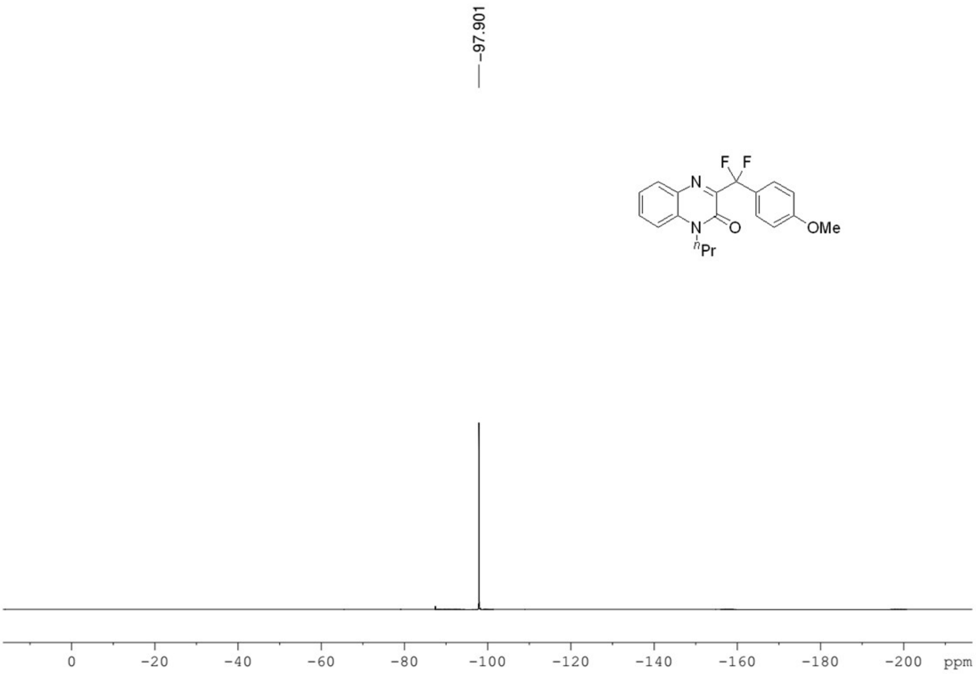
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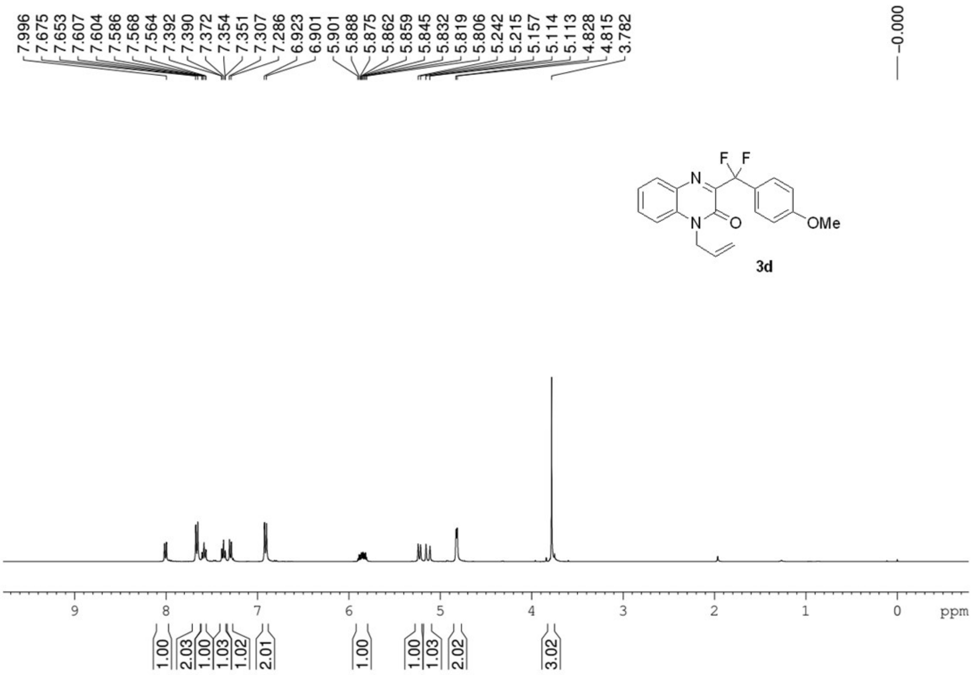
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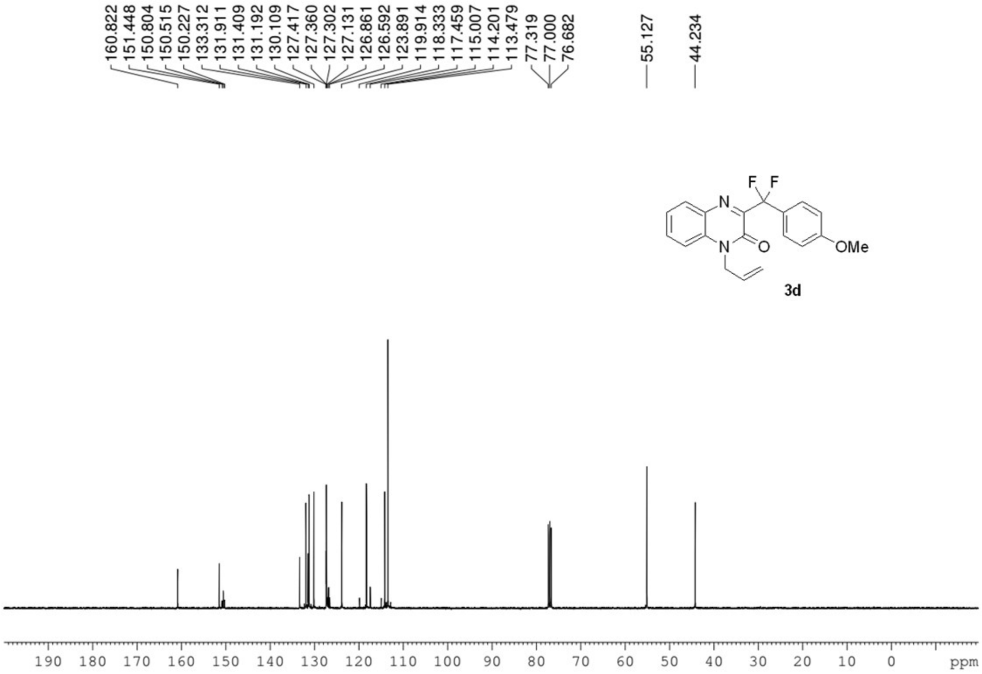
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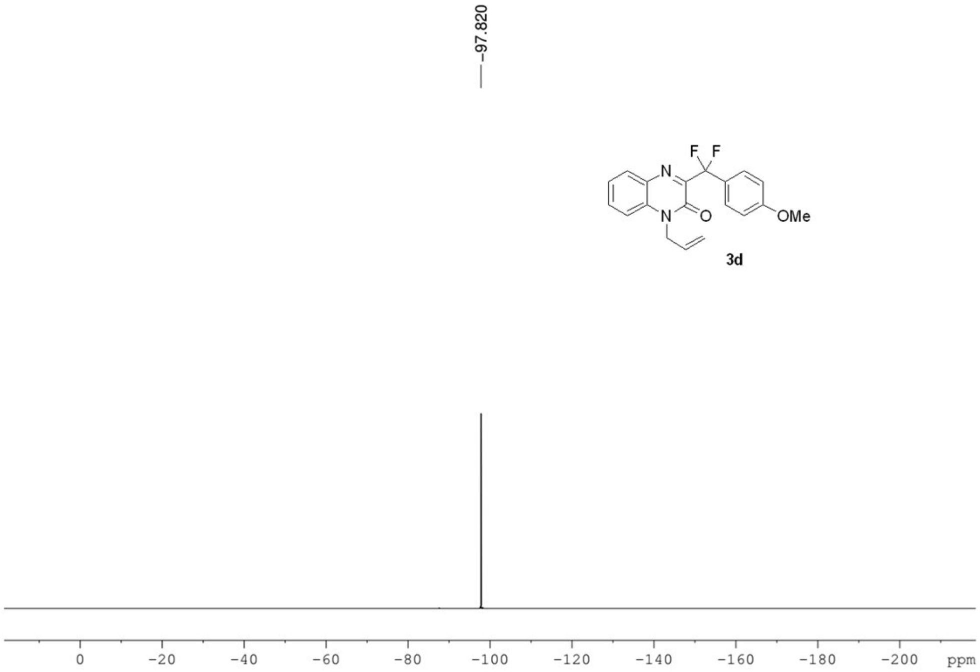
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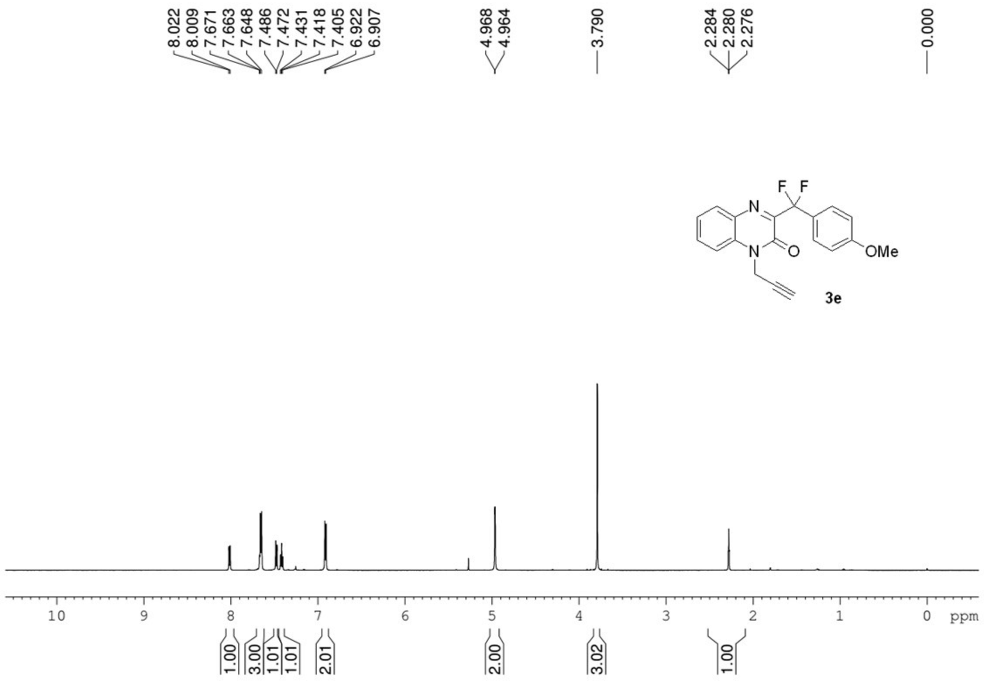
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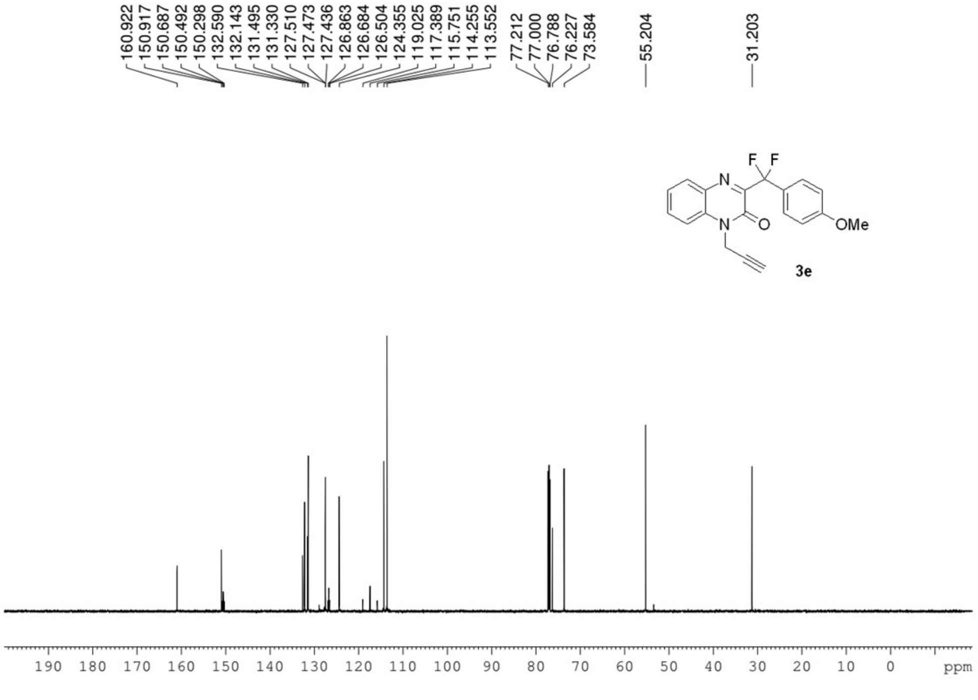
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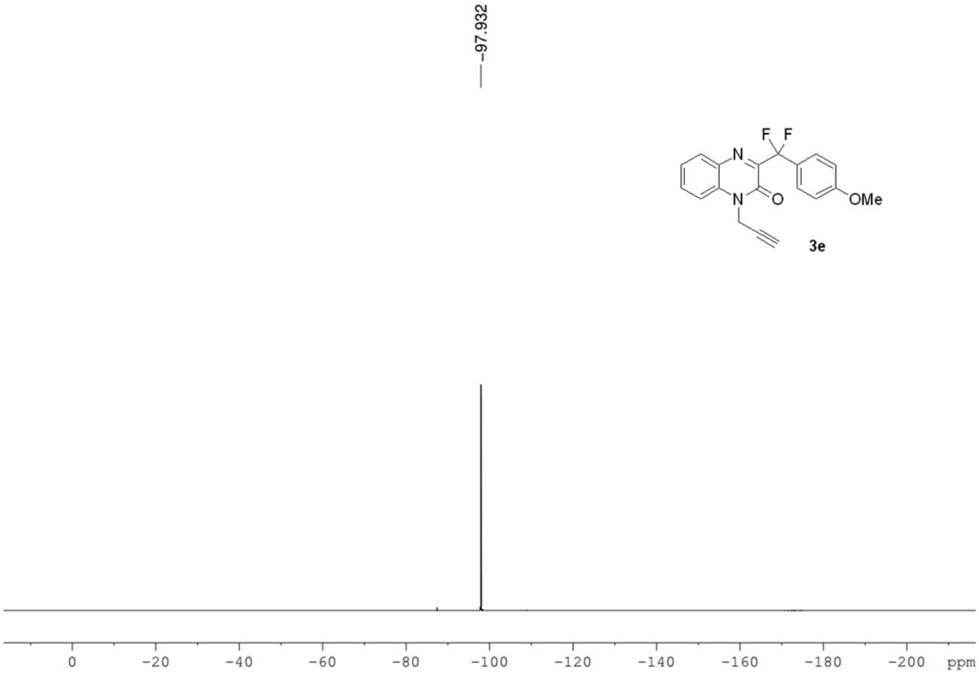
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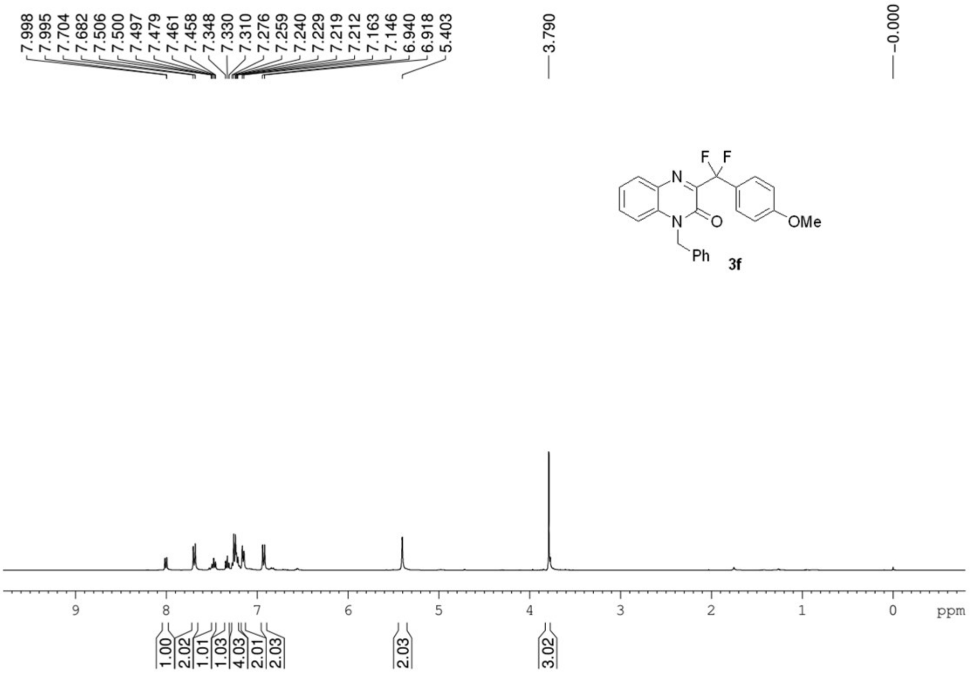
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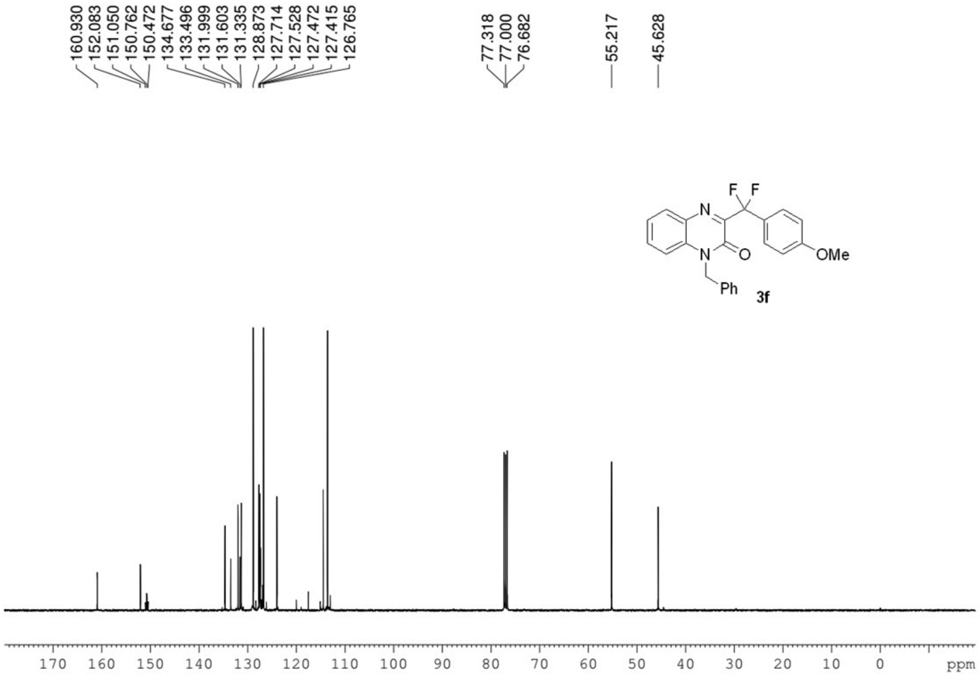
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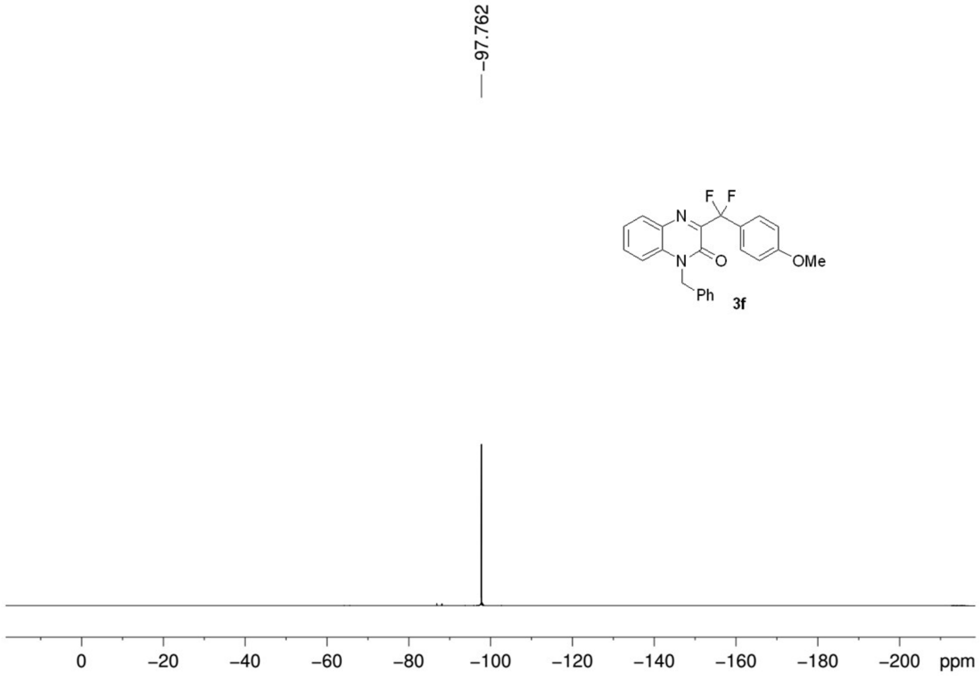
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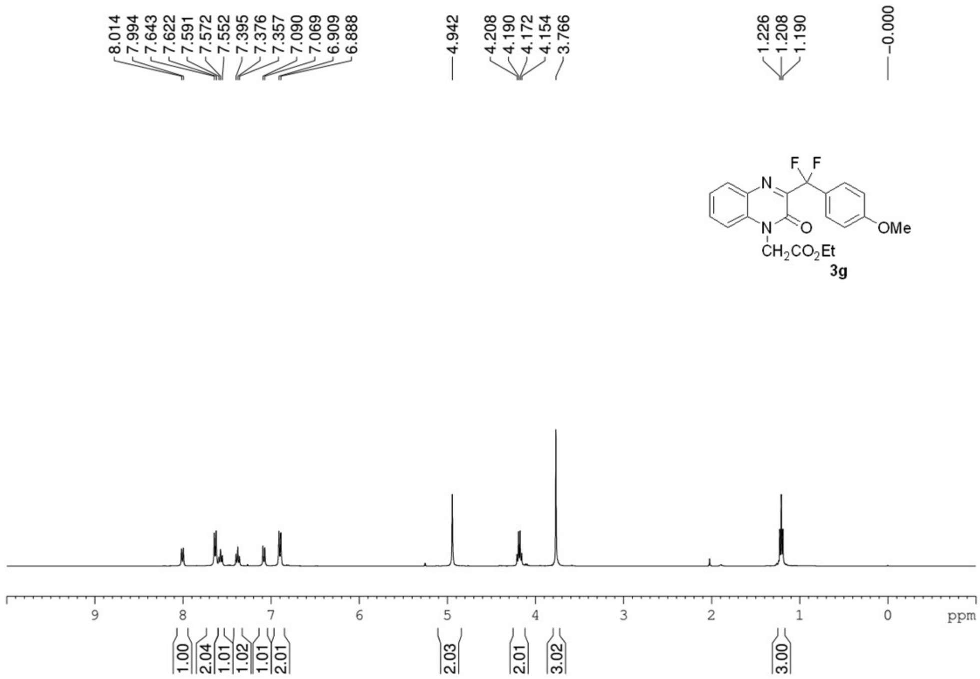
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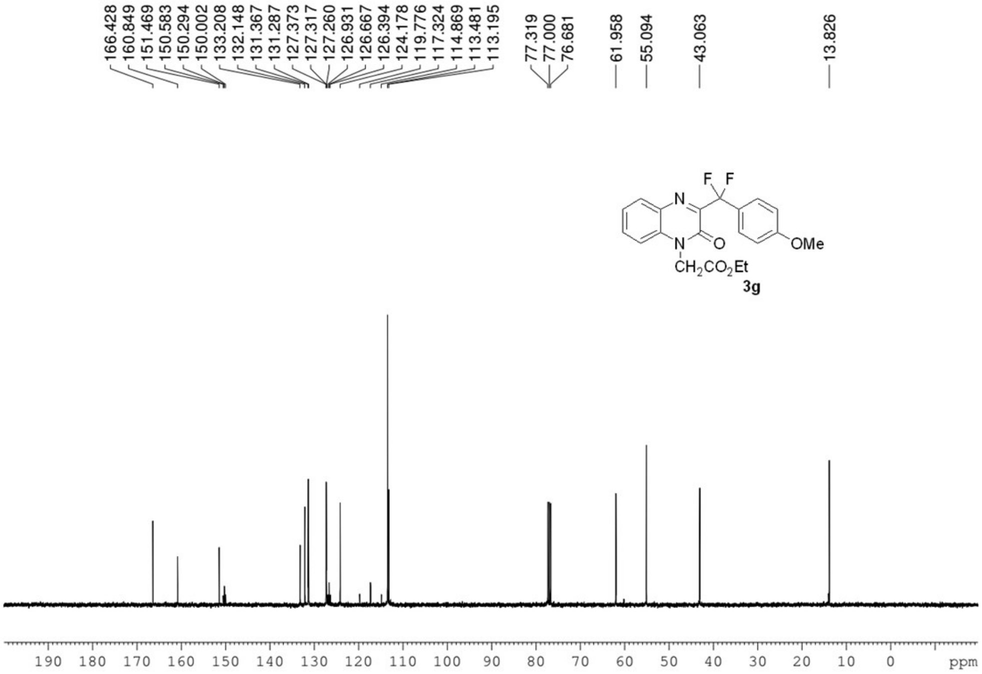
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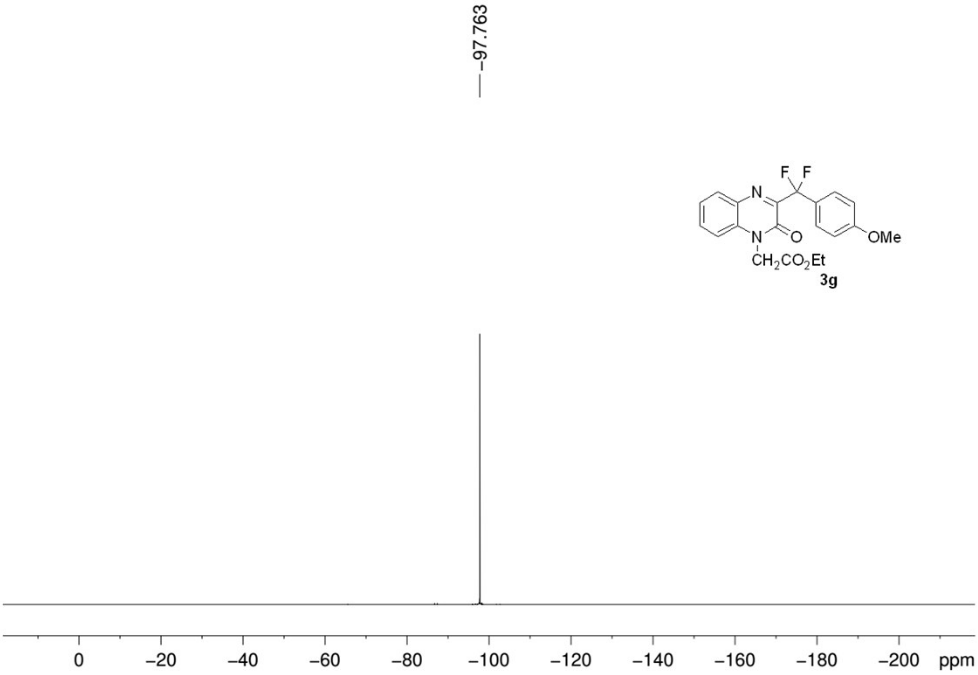
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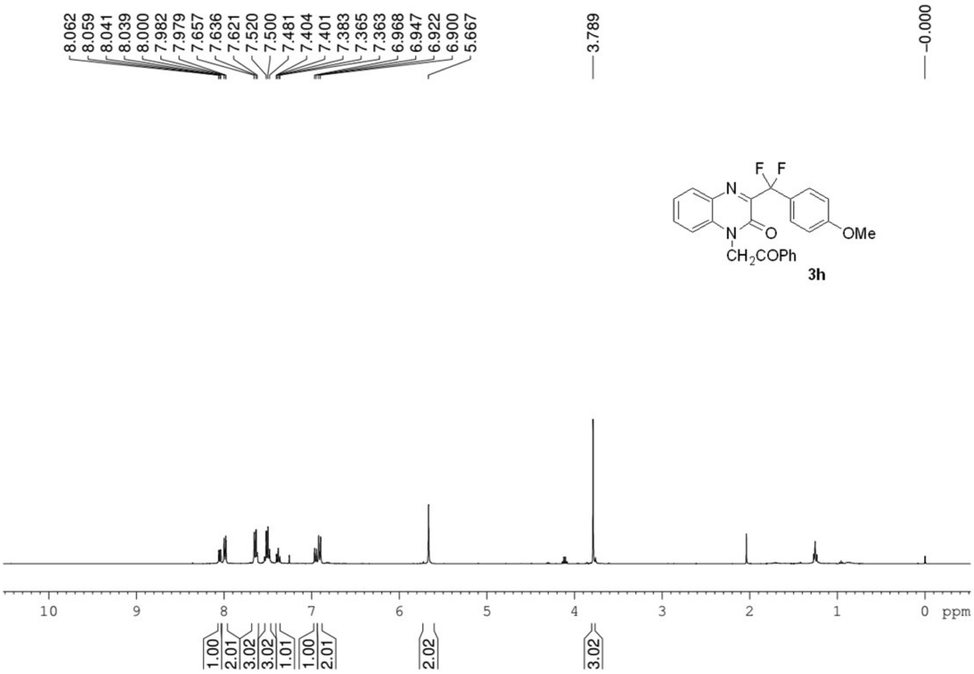
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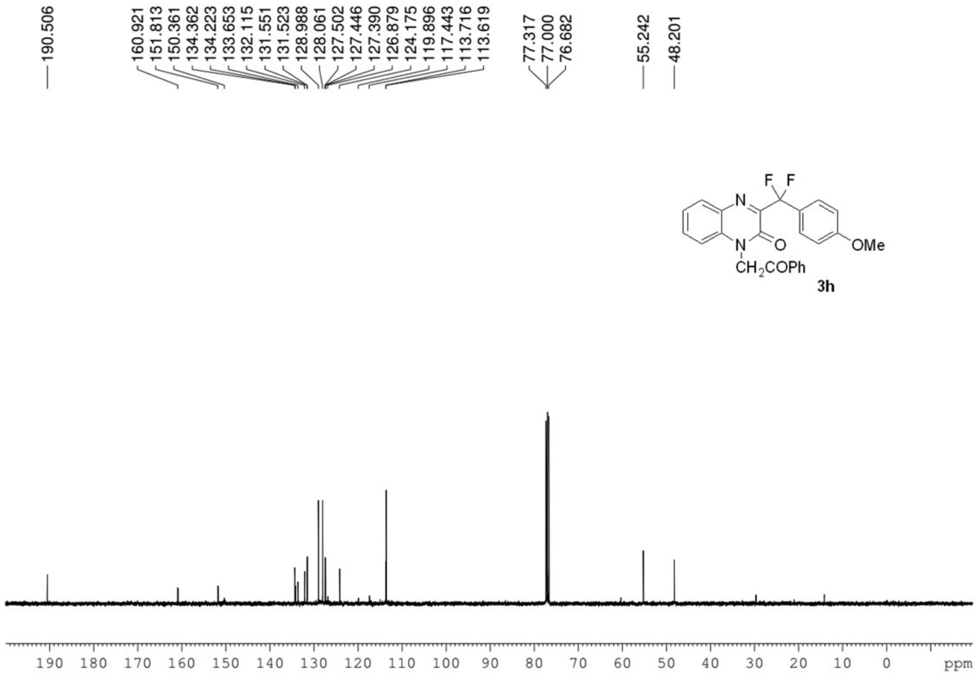
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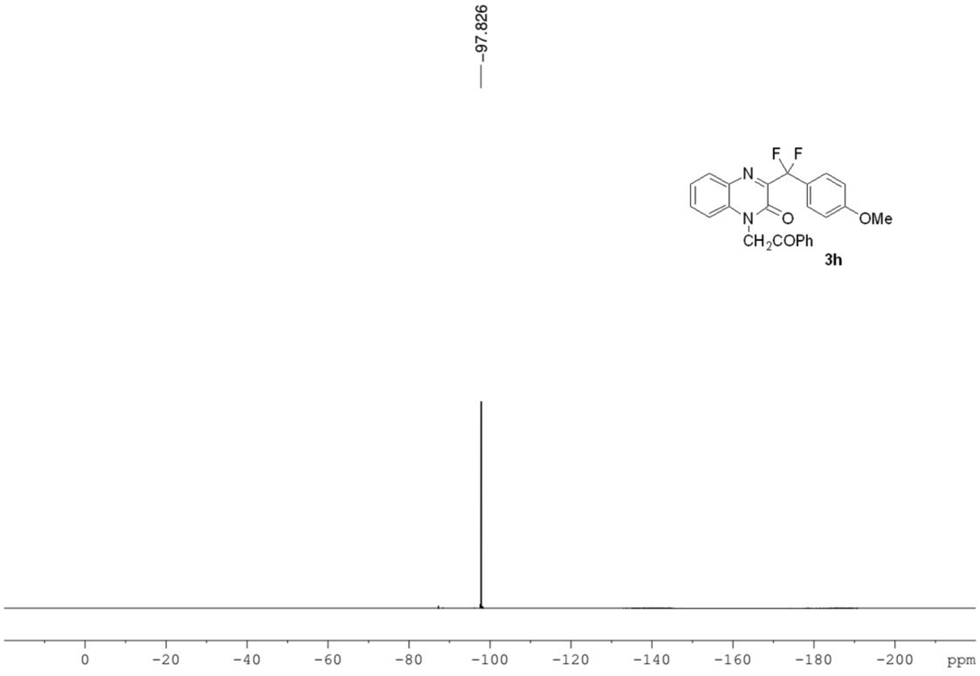
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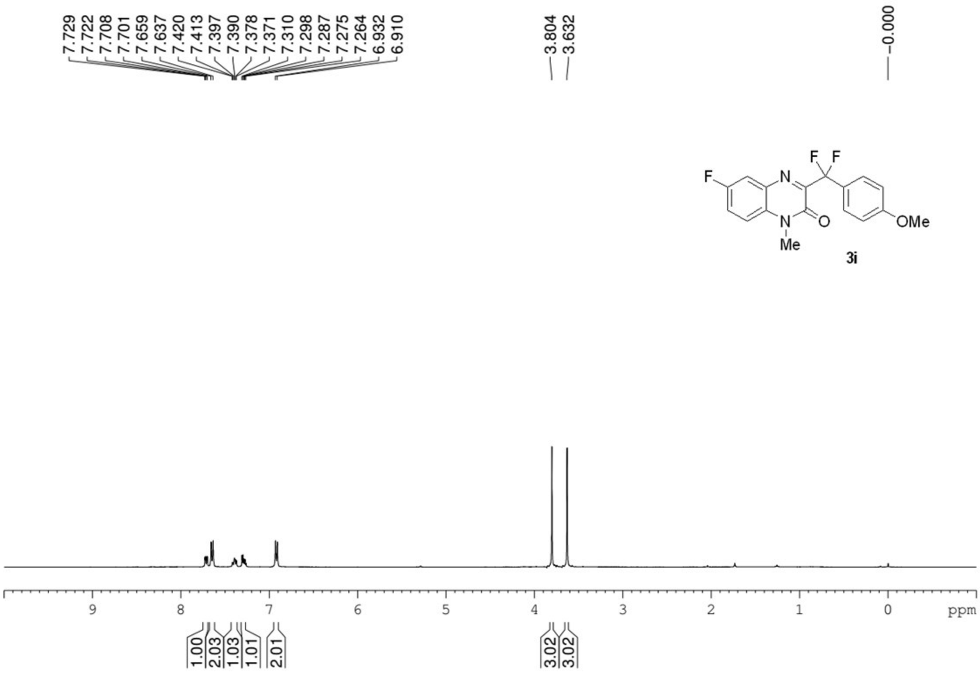
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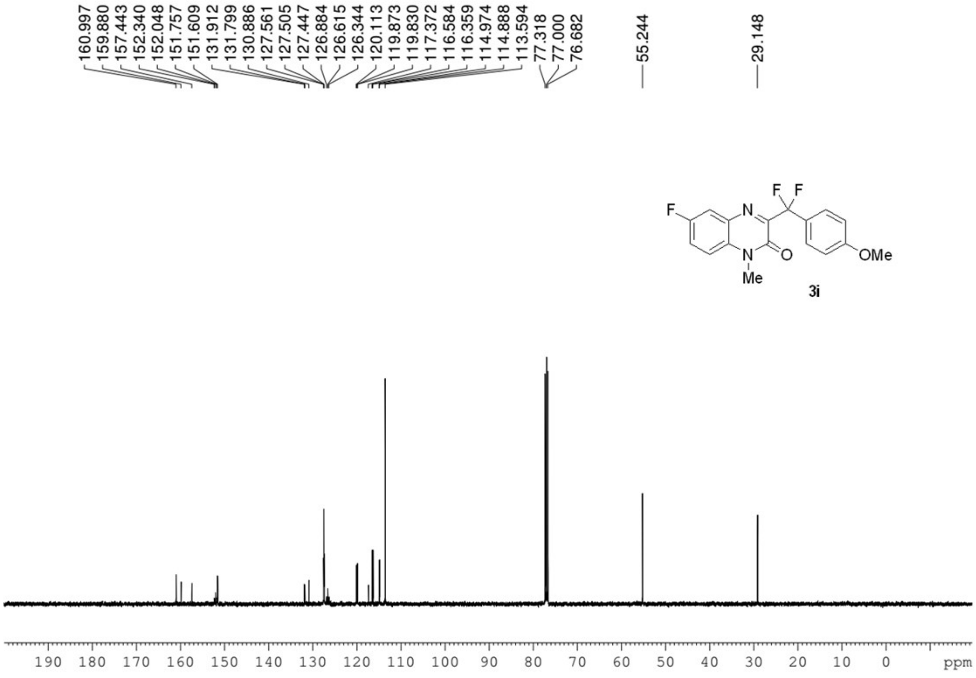
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126.344
120.113
119.873
119.830
117.372
116.584
116.359
114.974
114.888
113.594
77.318
77.000
76.682
55.244
29.148
F
N
F
F
N
O
OMe
Me
3i
190
180
170
160
150
140
130
120
110
100
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80
70
60
50
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20
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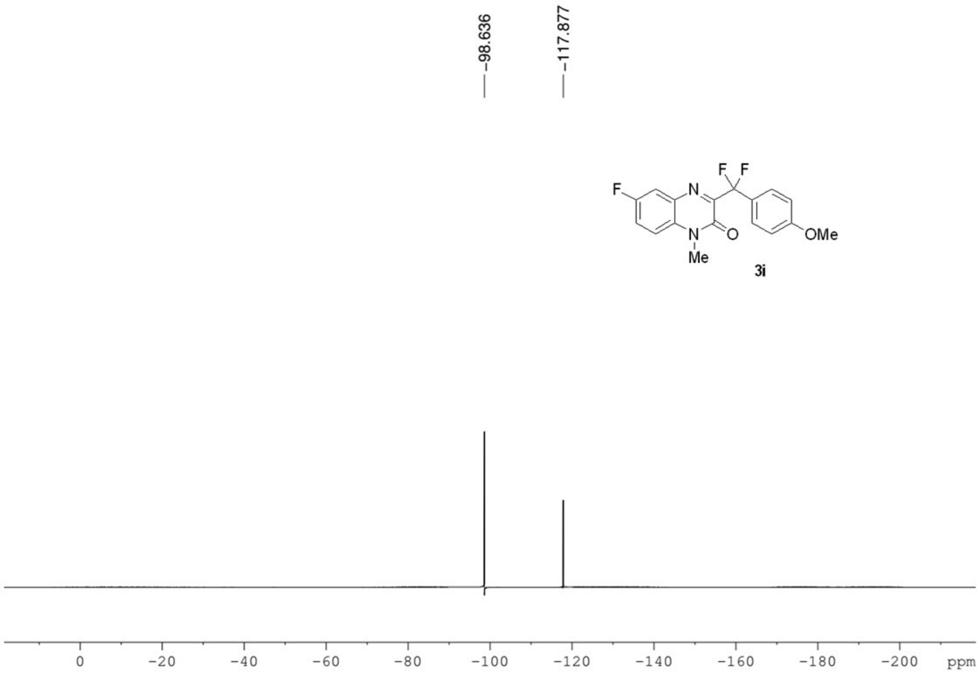
0
ppm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-117.877
F
N
F
F
N
O
Me
OMe
3i
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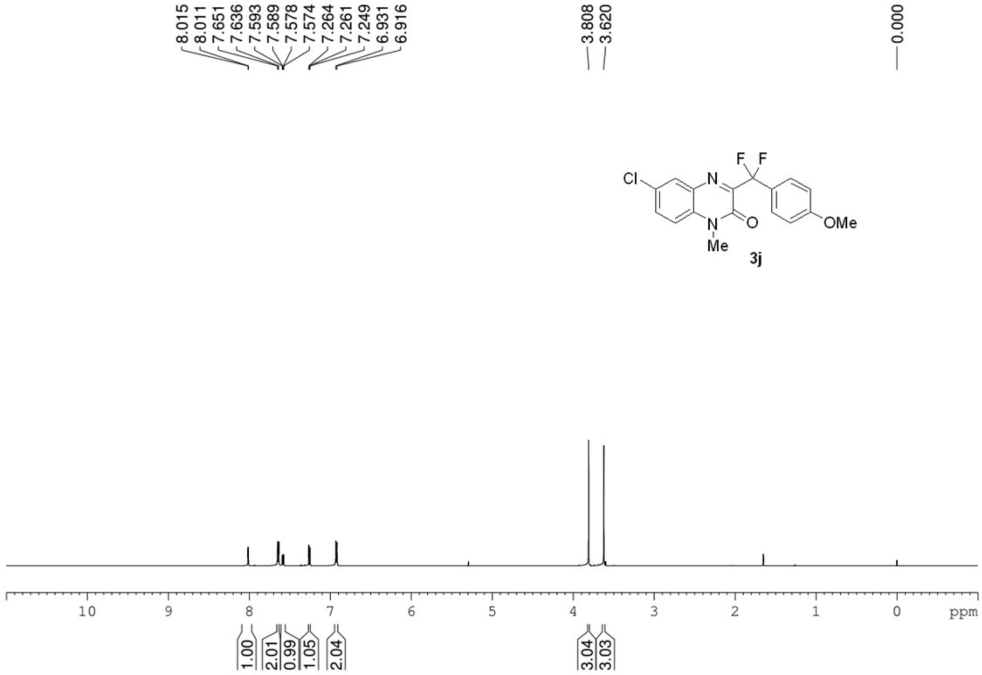
-80
-100
-120
-140
-160
-180
-200
ppm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8.011
7.651
7.636
7.593
7.589
7.578
7.574
7.264
7.261
7.249
6.931
6.916
3.808
3.620
0.000
Cl
N
F
F
N
O
Me
OMe
3j
10
9
8
7
6
5
4
3
2
1
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ppm
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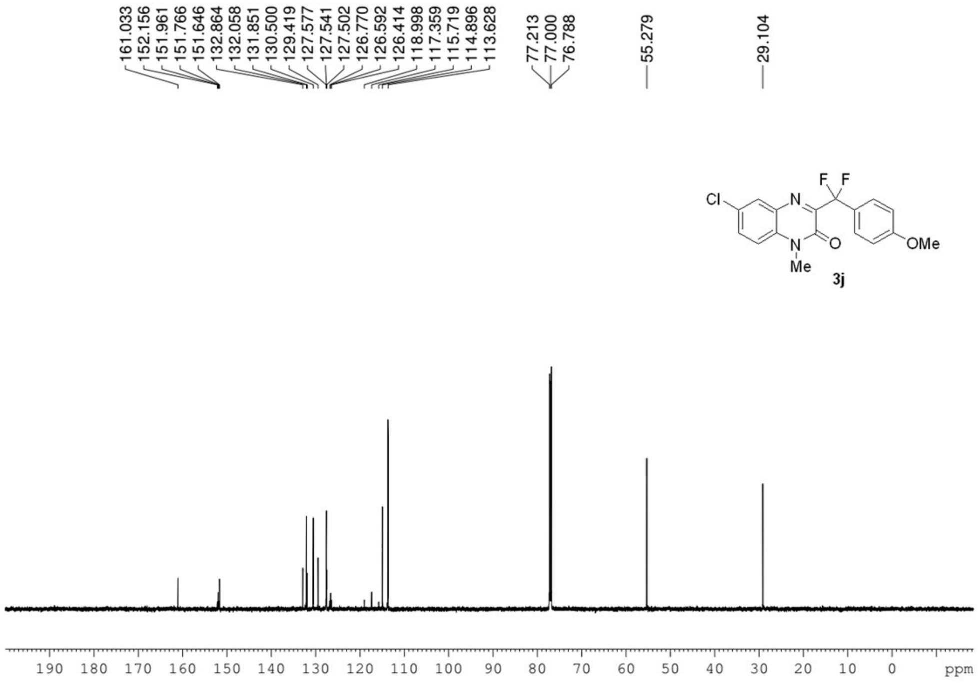
2.01
0.99
1.05
2.04
3.04
3.03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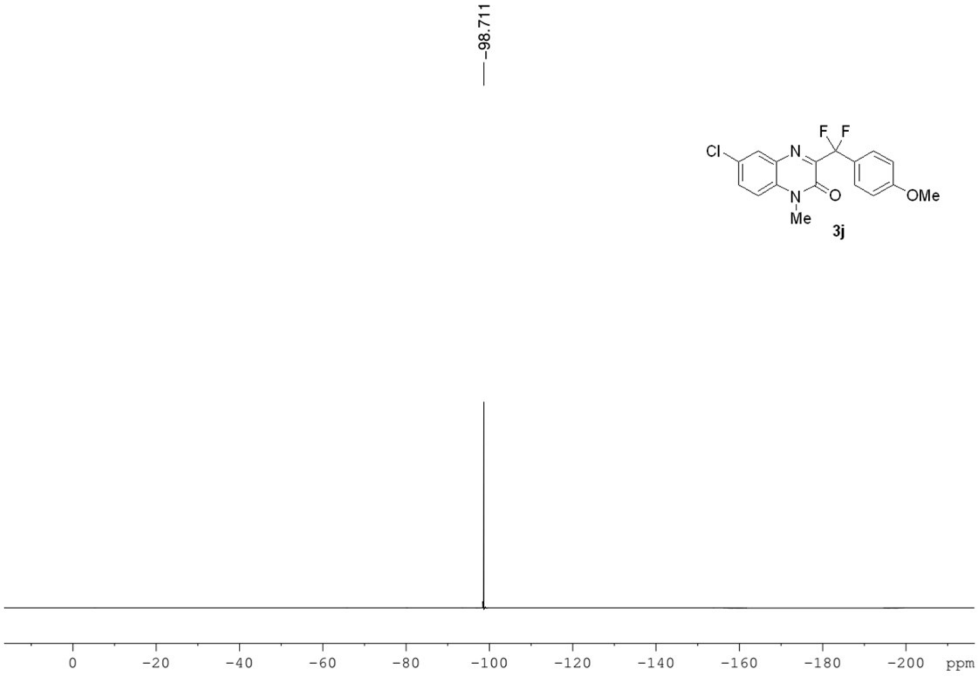
151.766
151.646
132.864
132.058
131.851
130.500
129.419
127.577
127.541
127.502
126.770
126.592
126.414
118.998
117.359
115.719
114.896
113.628
77.213
77.000
76.788
55.279
29.104
Cl
N
F F
N
O
OMe
Me
3j
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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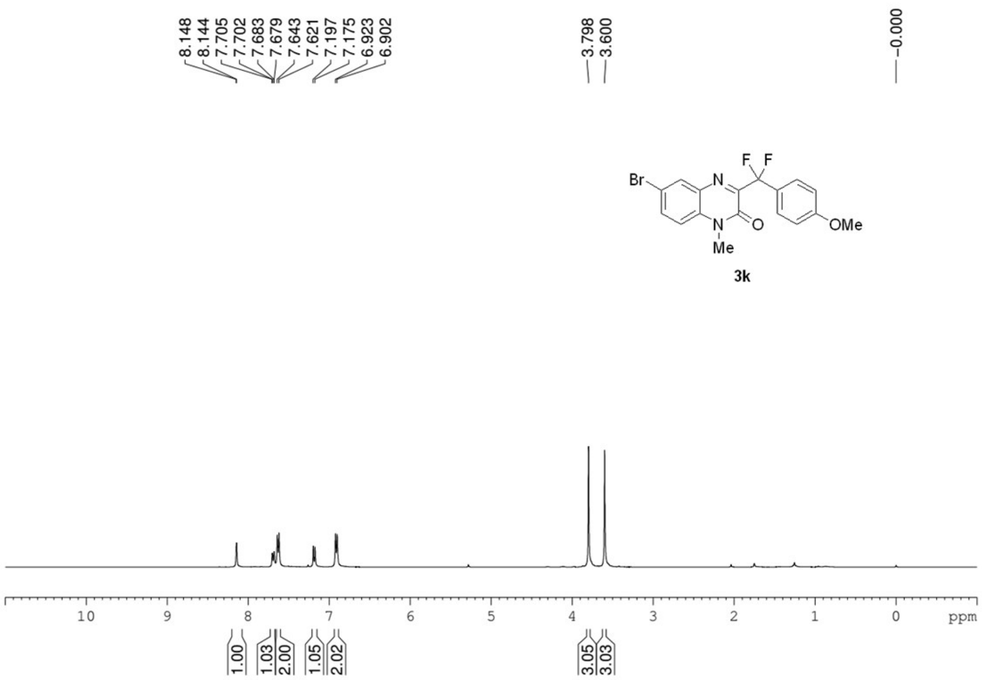
Cl
N
F F
N
O
OMe
Me
3j
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm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8.144
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7.702
7.683
7.679
7.643
7.621
7.197
7.175
6.923
6.902
3.798
3.600
0.000
Br
N
F
F
N
O
Me
OMe
3k
10
9
8
7
6
5
4
3
2
1
0
ppm
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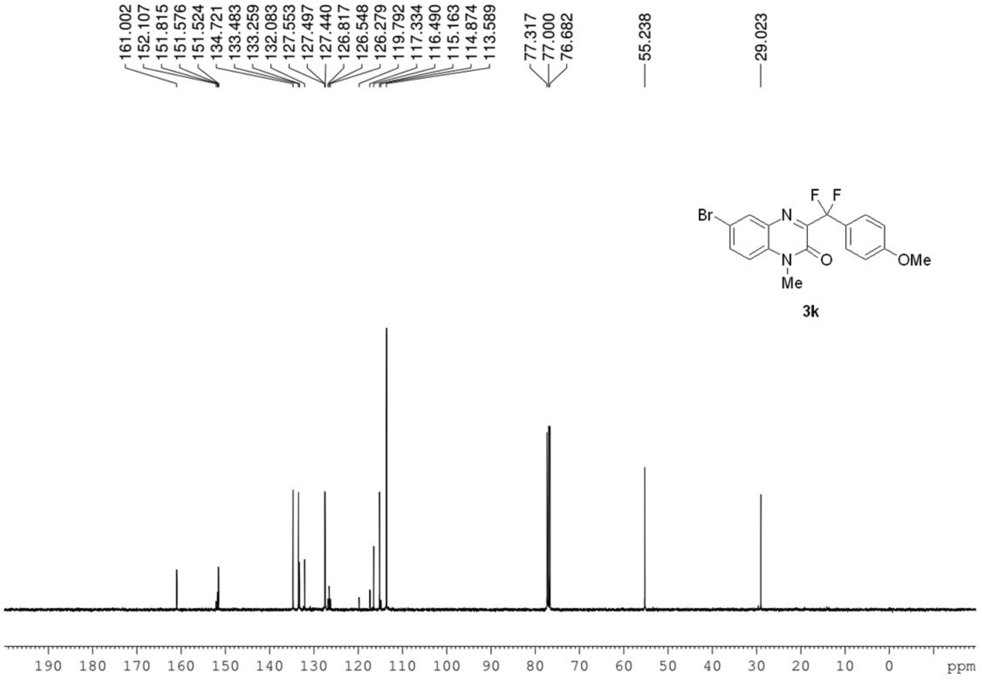
1.03
2.00
1.05
2.02
3.05
3.03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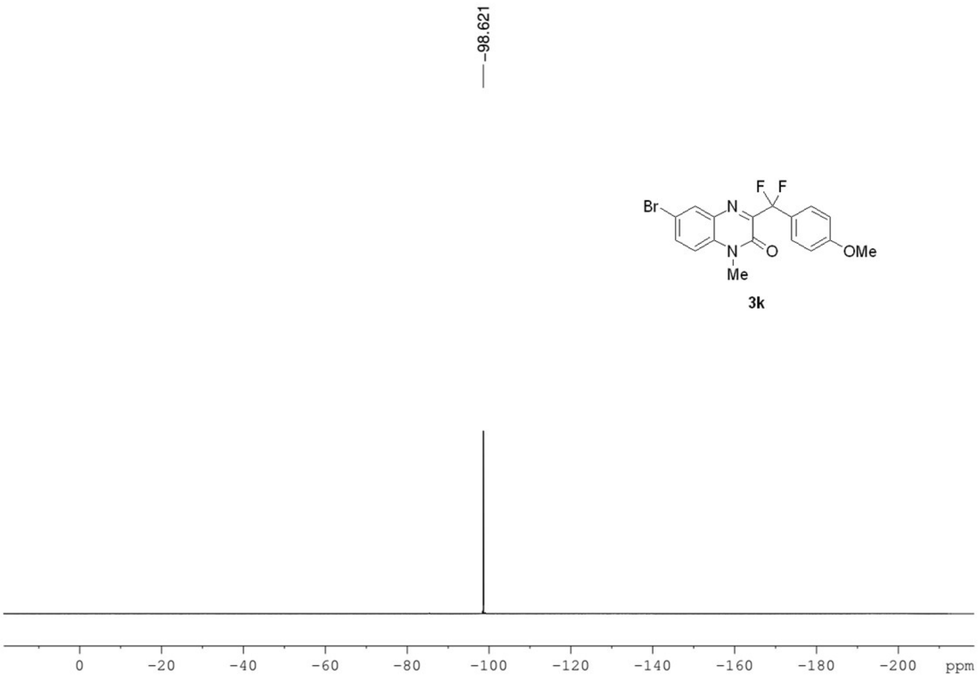
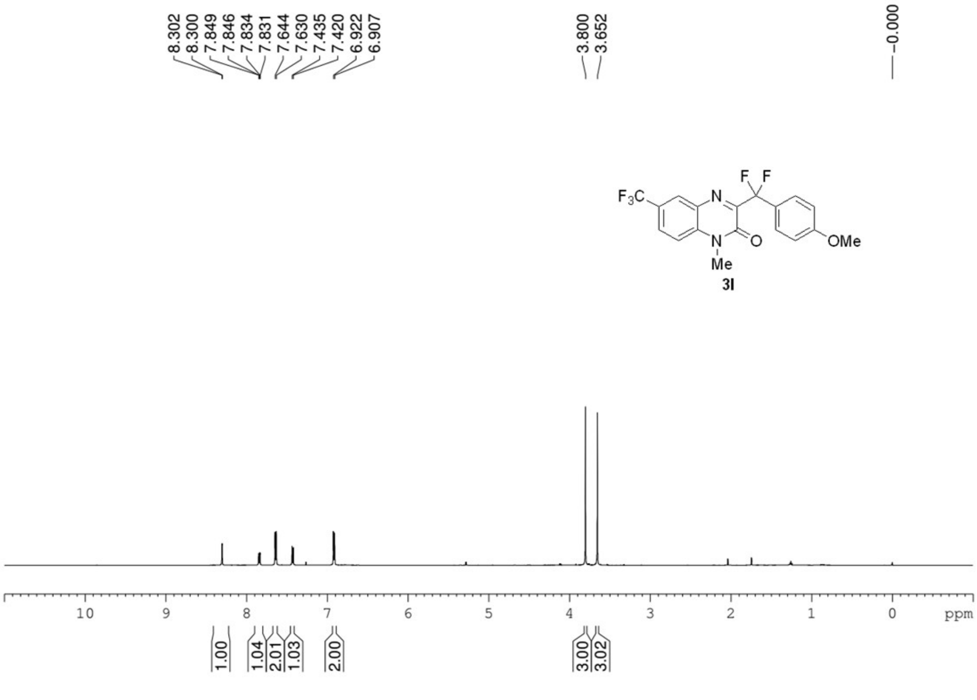
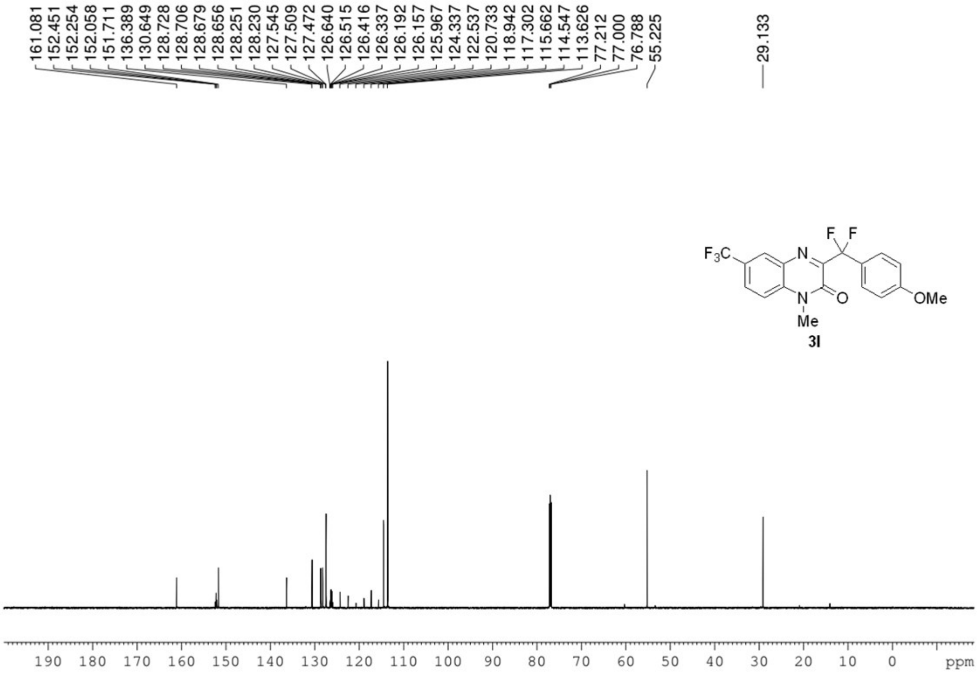
152.107
151.815
151.576
151.524
134.721
133.483
133.259
132.083
127.553
127.497
127.440
126.817
126.548
126.279
119.792
117.334
116.490
115.163
114.874
113.589
77.317
77.000
76.682
55.238
29.023
Br
N
F
F
N
O
Me
OMe
3k
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



-98.621
Br
N
F F
N
O
OMe
Me
3k
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm



8.302
8.300
7.849
7.846
7.834
7.831
7.644
7.630
7.435
7.420
6.922
6.907
3.800
3.652
-0.000
F₃C
N
F F
N
O
OMe
Me
3l
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.04
2.01
1.03
2.00
3.00
3.02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152.058
151.711
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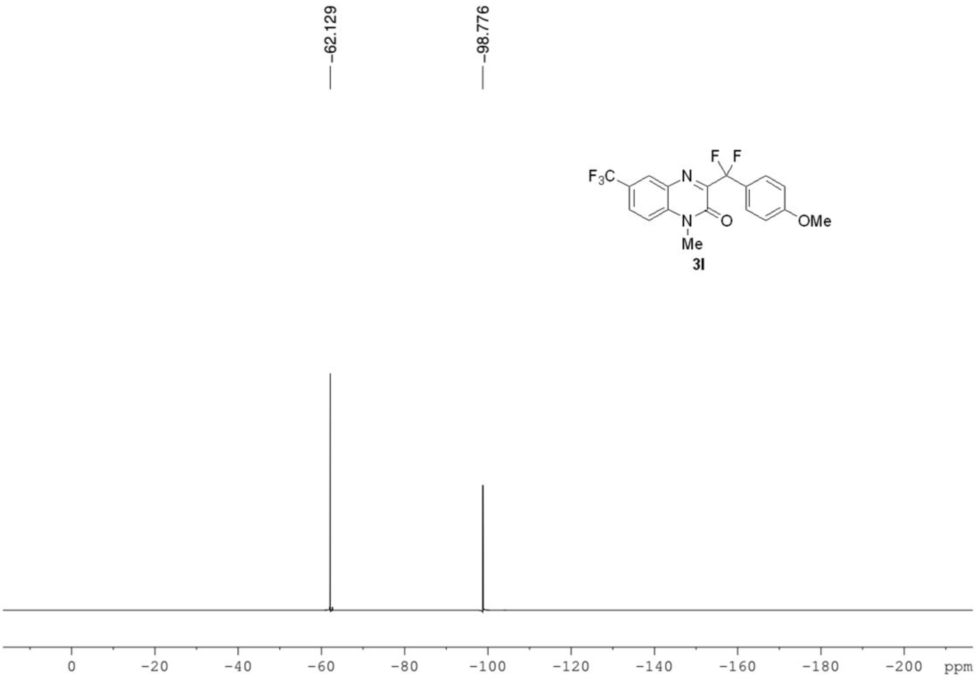
128.728
128.706
128.679
128.656
128.251
128.230
127.545
127.509
127.472
126.640
126.515
126.416
126.337
126.192
126.157
125.967
124.337
122.537
120.733
118.942
117.302
115.662
114.547
113.626
77.212
77.000
76.788
55.225
29.133
F
F
F_3C
N
N
O
Me
OMe
3l
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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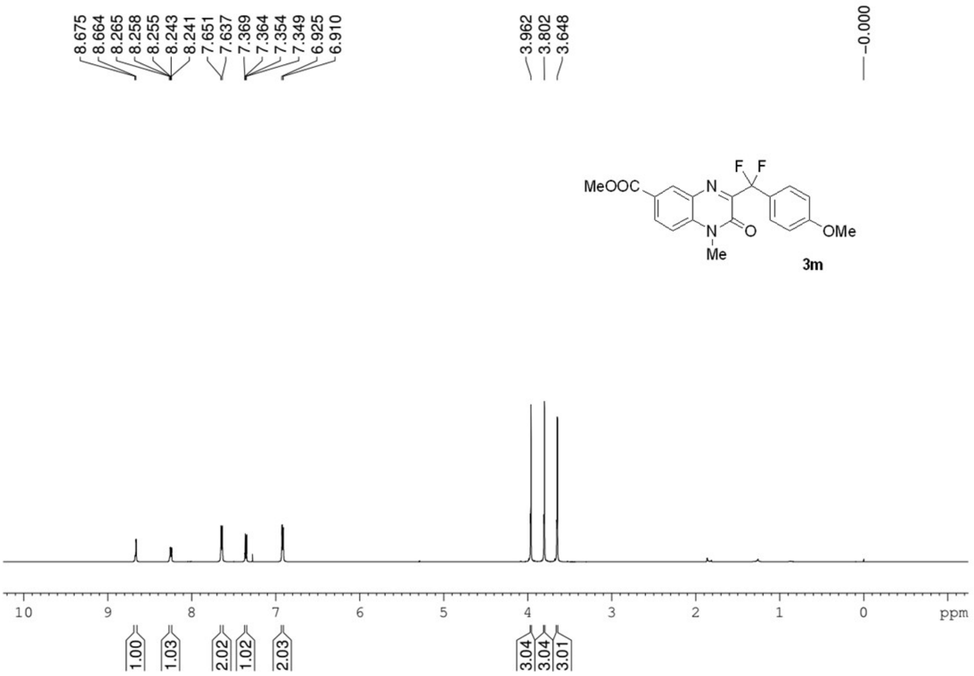
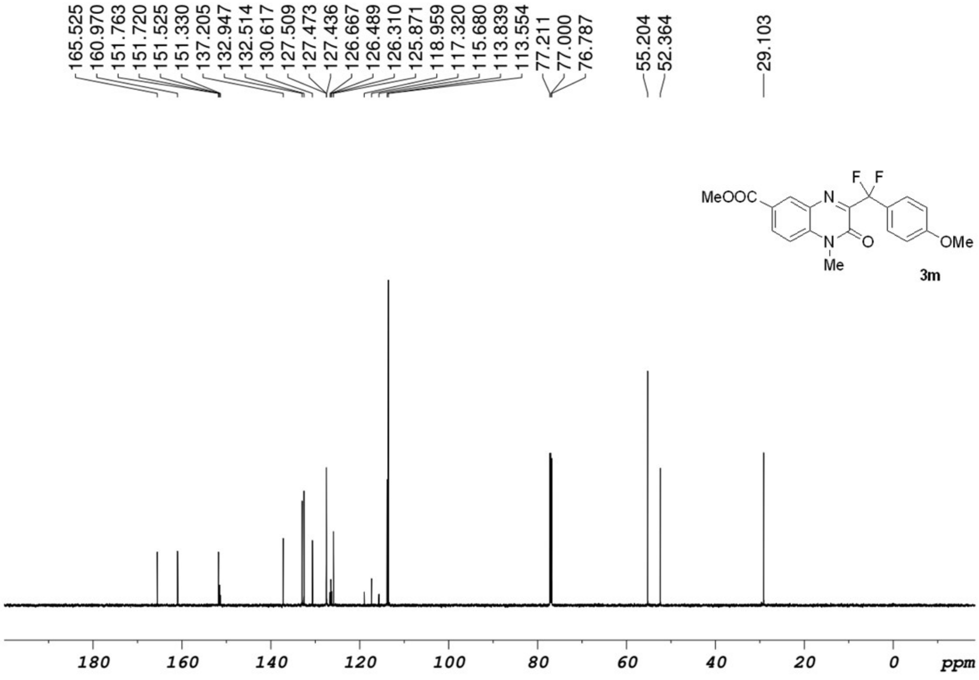
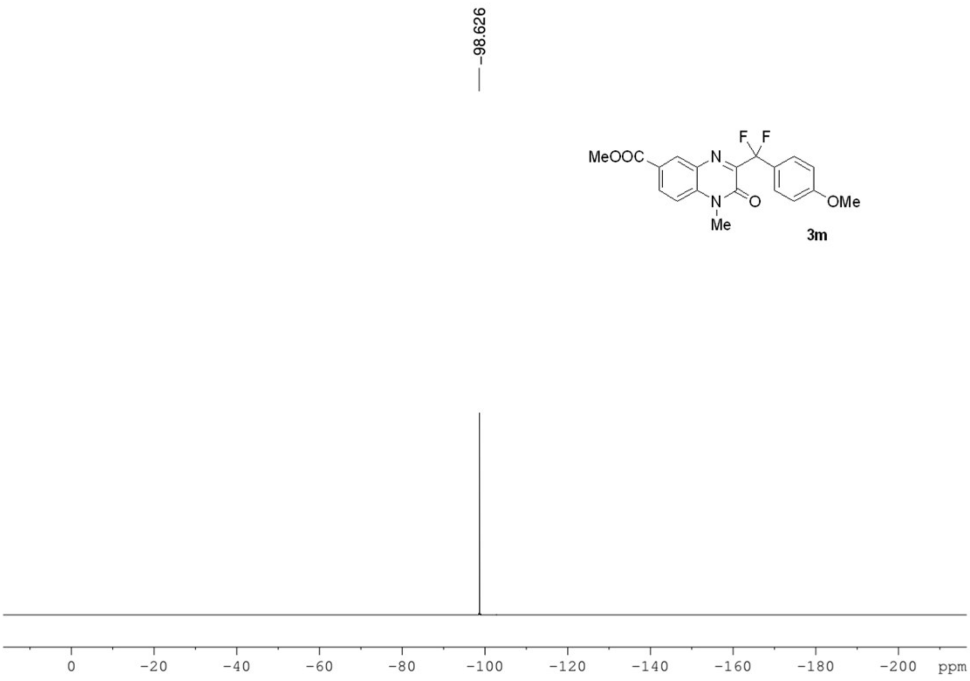
-98.776
F
F
F_3C
N
N
O
Me
OMe
3l
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
−200
ppm

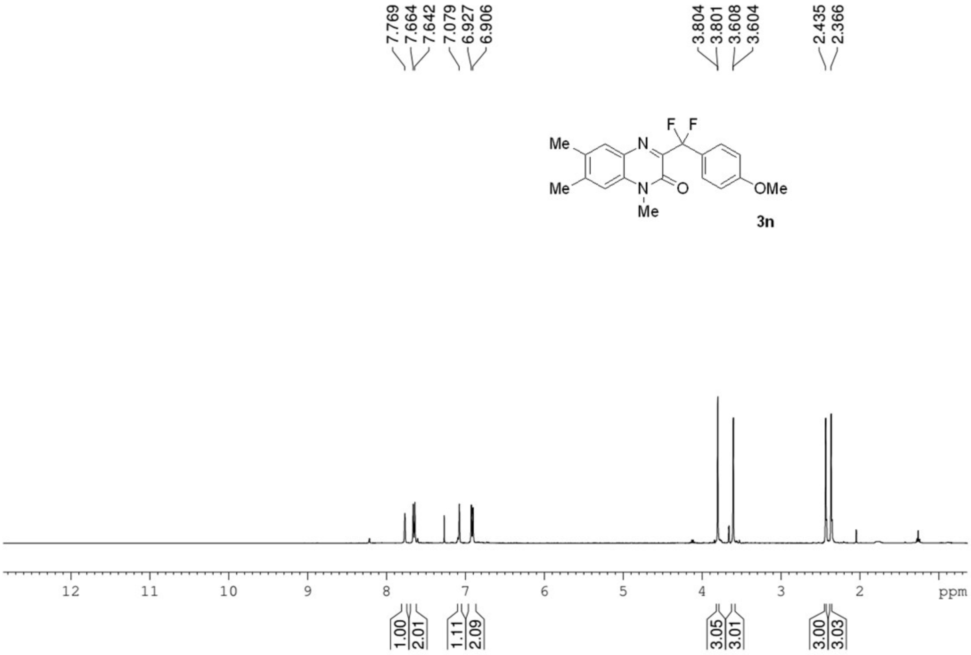

8.675
8.664
8.265
8.258
8.255
8.243
8.241
7.651
7.637
7.369
7.364
7.354
7.349
6.925
6.910
3.962
3.802
3.648
0.000
MeOOC
N
F
F
N
O
OMe
Me
3m
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.03
2.02
1.02
2.03
3.04
3.04
3.01


165.525
160.970
151.763
151.720
151.525
151.330
137.205
132.947
132.514
130.617
127.509
127.473
127.436
126.667
126.489
126.310
125.871
118.959
117.320
115.680
113.839
113.554
77.211
77.000
76.787
55.204
52.364
29.103
MeOOC
N
F
F
N
O
OMe
Me
3m
180
160
140
120
100
80
60
40
20
0
ppm



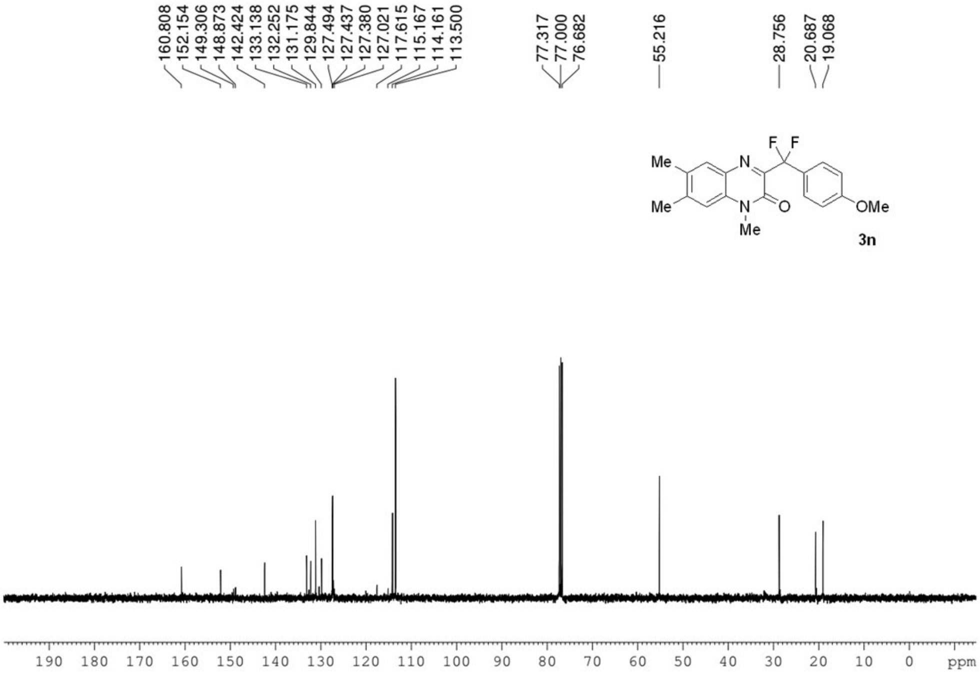
−98.626
MeOOC
N
F
F
O
OMe
N
Me
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
−200
ppm

3m



7.769
7.664
7.642
7.079
6.927
6.906
3.804
3.801
3.608
3.604
2.435
2.366
Me
Me
N
F
F
O
OMe
N
Me
12
11
10
9
8
7
6
5
4
3
2
ppm
1.00
2.01
1.11
2.09
3.05
3.01
3.00
3.03

3n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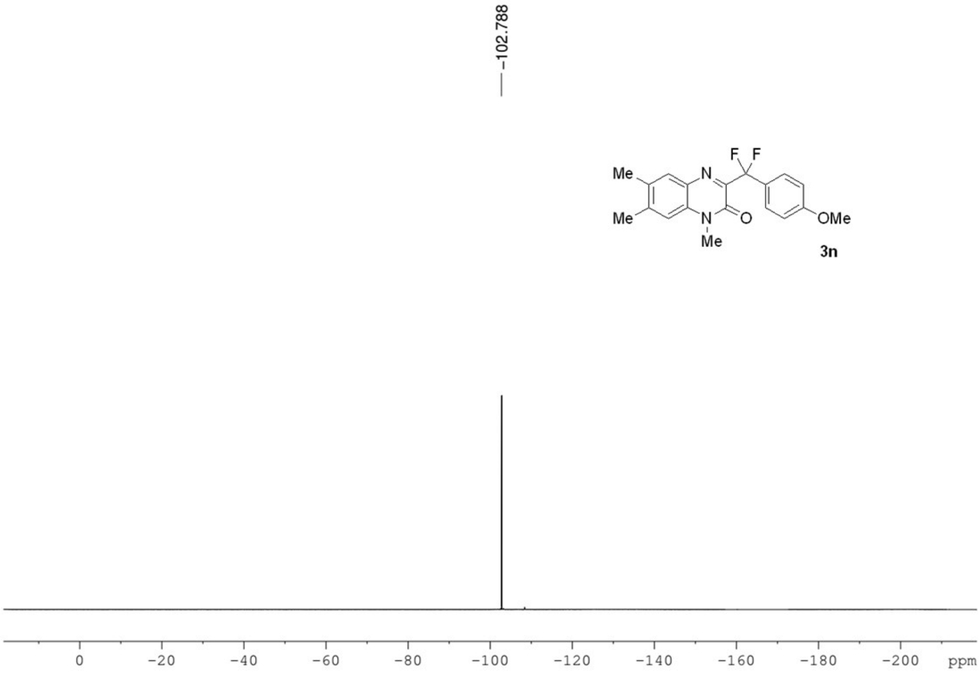
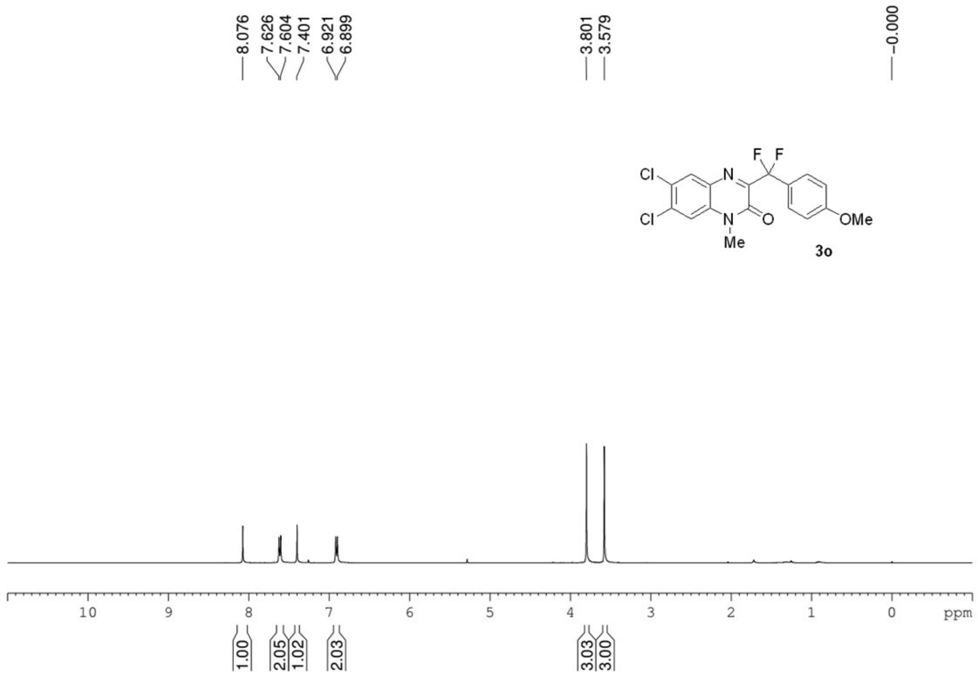
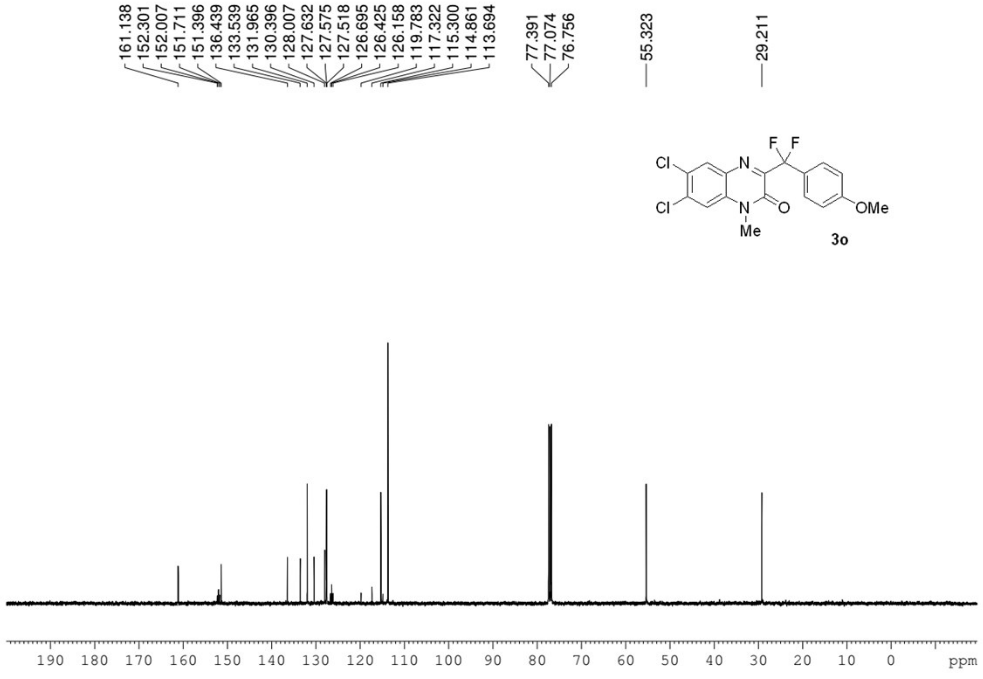
152.154
149.306
148.873
142.424
133.138
132.252
131.175
129.844
127.494
127.437
127.380
127.021
117.615
115.167
114.161
113.500
77.317
77.000
76.682
55.216
28.756
20.687
19.068
F F
Me
N
Me
N
O
Me
OMe
3n
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


-102.788
F F
Me
N
Me
N
O
Me
OMe
3n
0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 ppm


8.076
7.626
7.604
7.401
6.921
6.899
3.801
3.579
0.000
Cl
Cl
N
N
F
F
O
Me
OMe
3o
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
2.05
1.02
2.03
3.03
3.00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152.301
152.007
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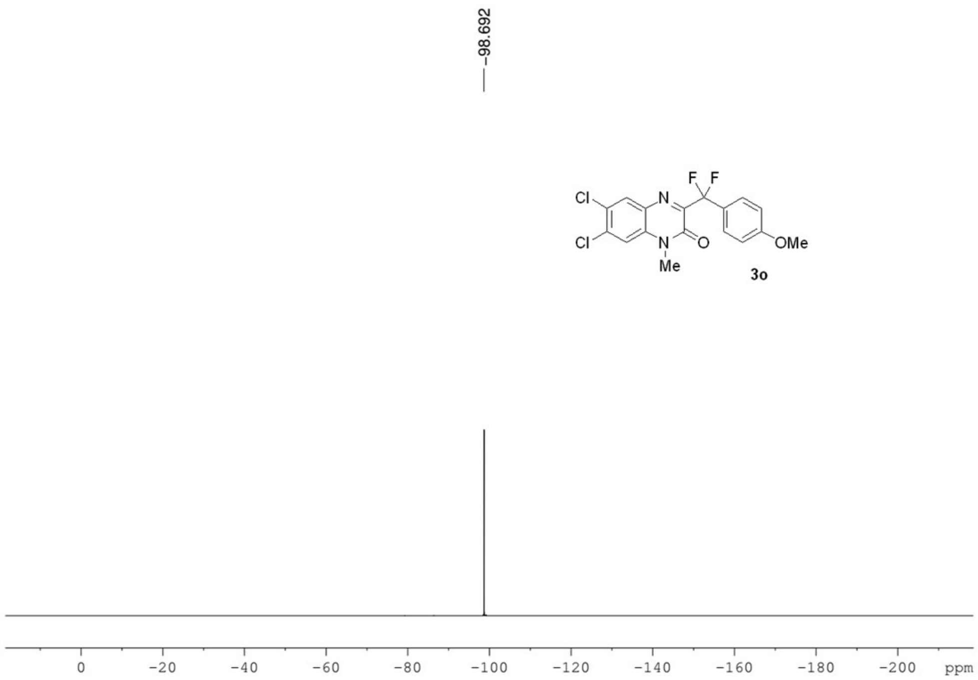
136.439
133.539
131.965
130.396
128.007
127.632
127.575
127.518
126.695
126.425
126.158
119.783
117.322
115.300
114.861
113.694
77.391
77.074
76.756
55.323
29.211
Cl
Cl
N
N
F
F
O
Me
OMe
3o
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


-98.692
F F
N
Cl
Cl
N
O
Me
OMe
3o
0
-20
-40
-60
-80
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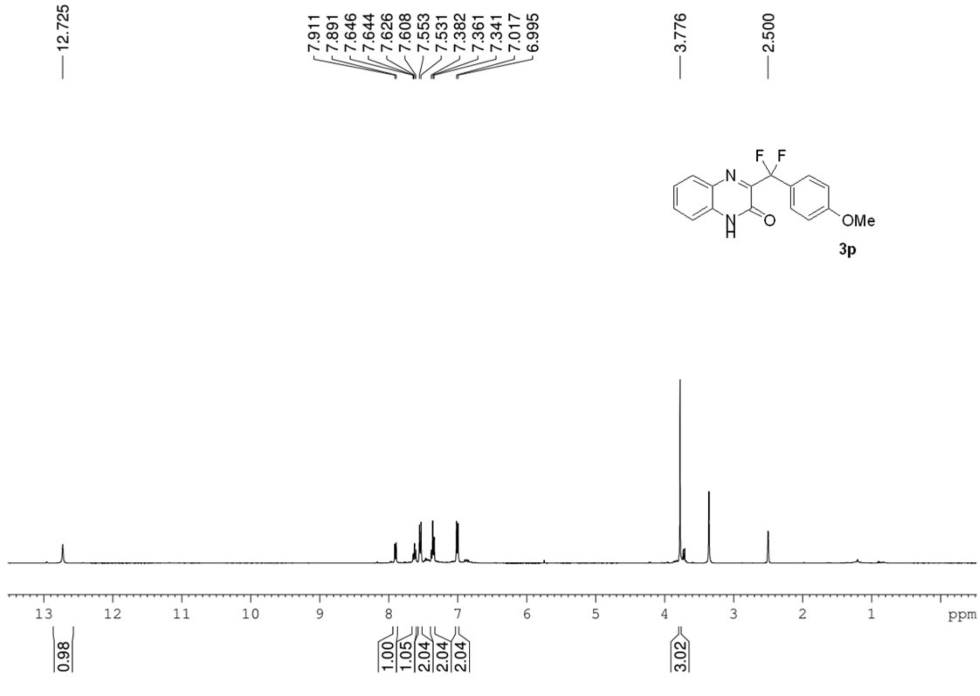
-120
-140
-160
-180
-200
ppm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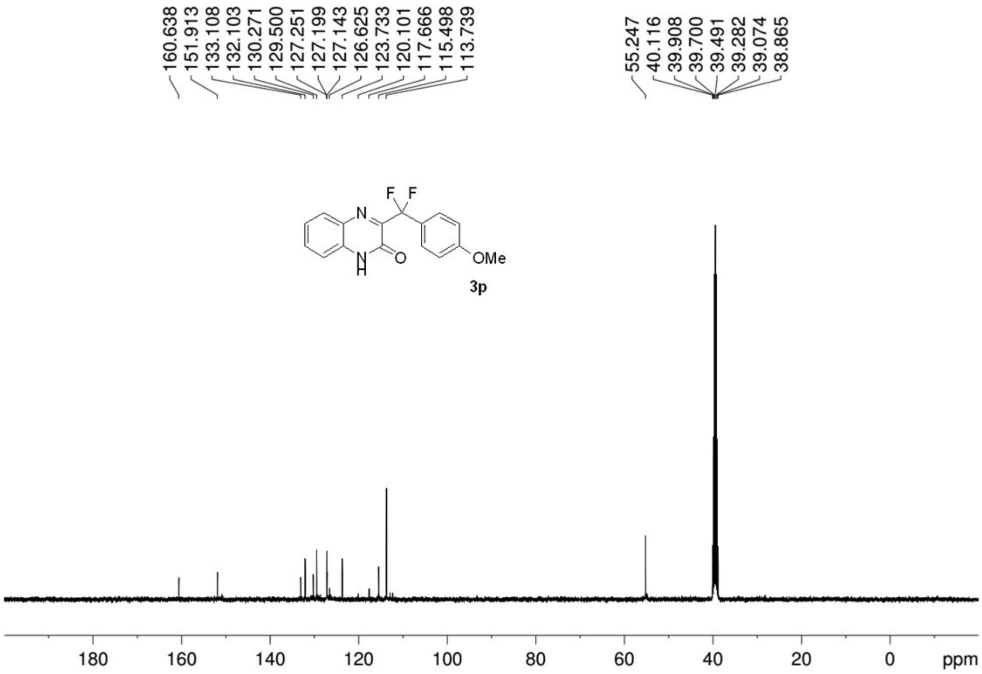
7.891
7.646
7.644
7.626
7.608
7.553
7.531
7.382
7.361
7.341
7.017
6.995
3.776
2.500
F F
N
N
H
O
OMe
3p
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.98
1.00
1.05
2.04
2.04
2.04
3.02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133.108
132.103
130.271
129.500
127.251
127.199
127.143
126.625
123.733
120.101
117.666
115.498
113.739
55.247
40.116
39.908
39.700
39.491
39.282
39.074
38.865
F
F
N
H
O
OMe
3p
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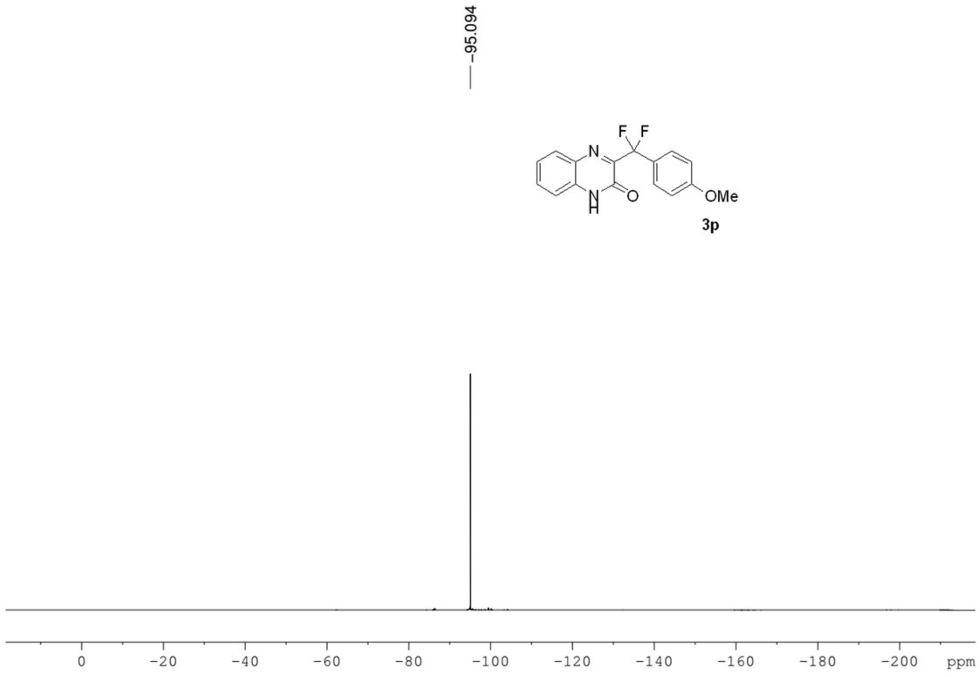
160
140
120
100
80
60
40
20
0
ppm


-95.094
F
F
N
H
O
OMe
3p
0
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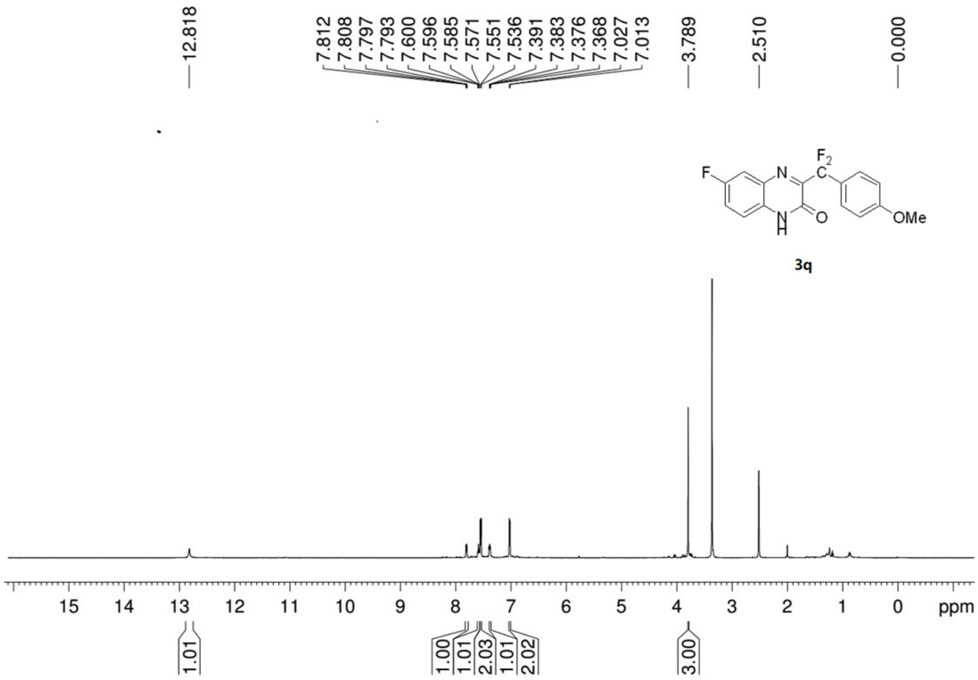
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm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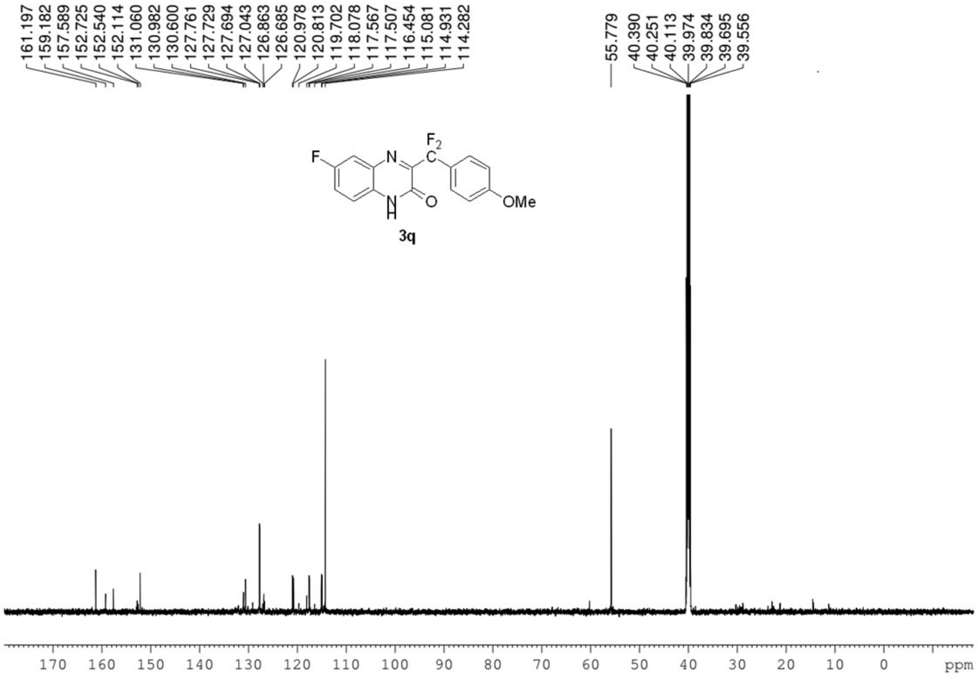
7.812
7.808
7.797
7.793
7.600
7.596
7.585
7.571
7.551
7.536
7.391
7.383
7.376
7.368
7.027
7.013
3.789
2.510
0.000
F
N
F2
C
N
H
O
OMe
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.01
1.00
1.01
2.03
1.01
2.02
3.00

3q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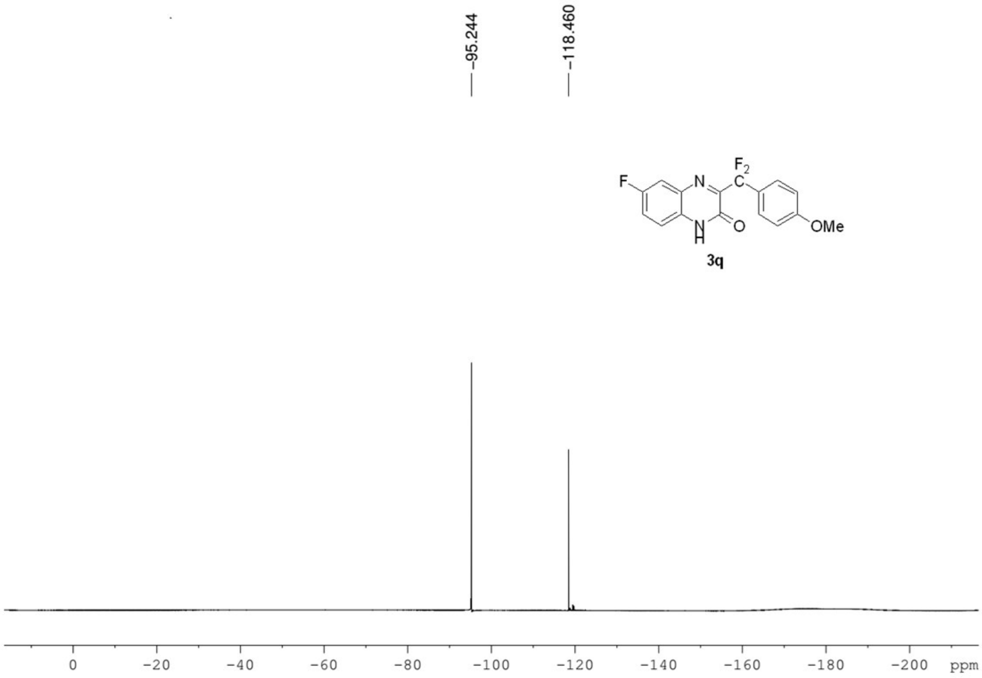
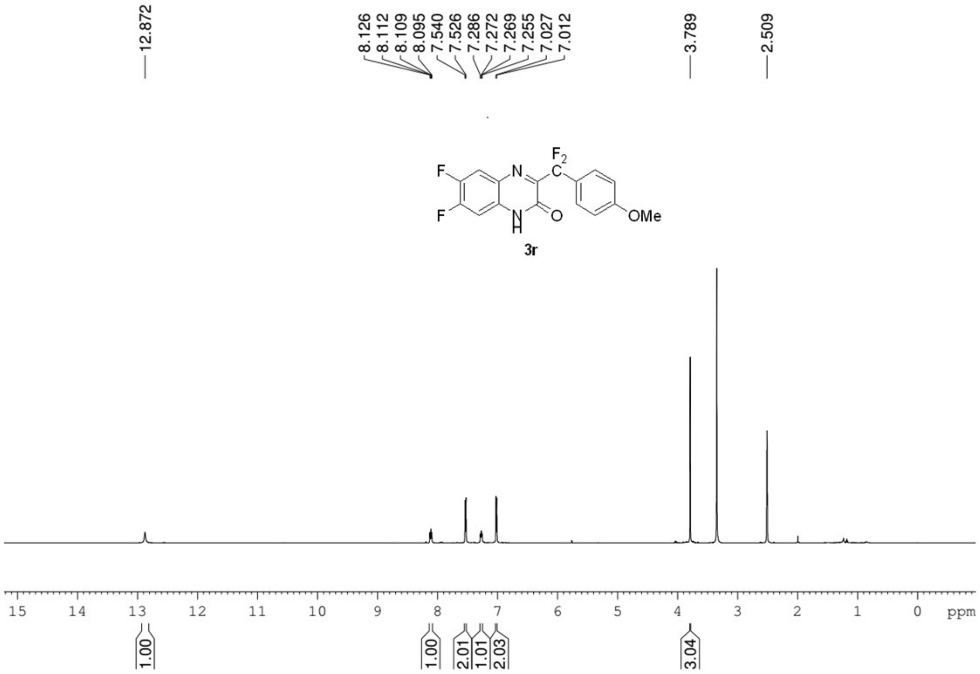
131.060
130.982
130.600
127.761
127.729
127.694
127.043
126.863
126.685
120.978
120.813
119.702
118.078
117.567
117.507
116.454
115.081
114.931
114.282
55.779
40.390
40.251
40.113
39.974
39.834
39.695
39.556
F
N
F2
C
N
H
O
OMe
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

3q



-95.244
-118.460
F
N
F2
C
N
H
O
OMe
3q
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm



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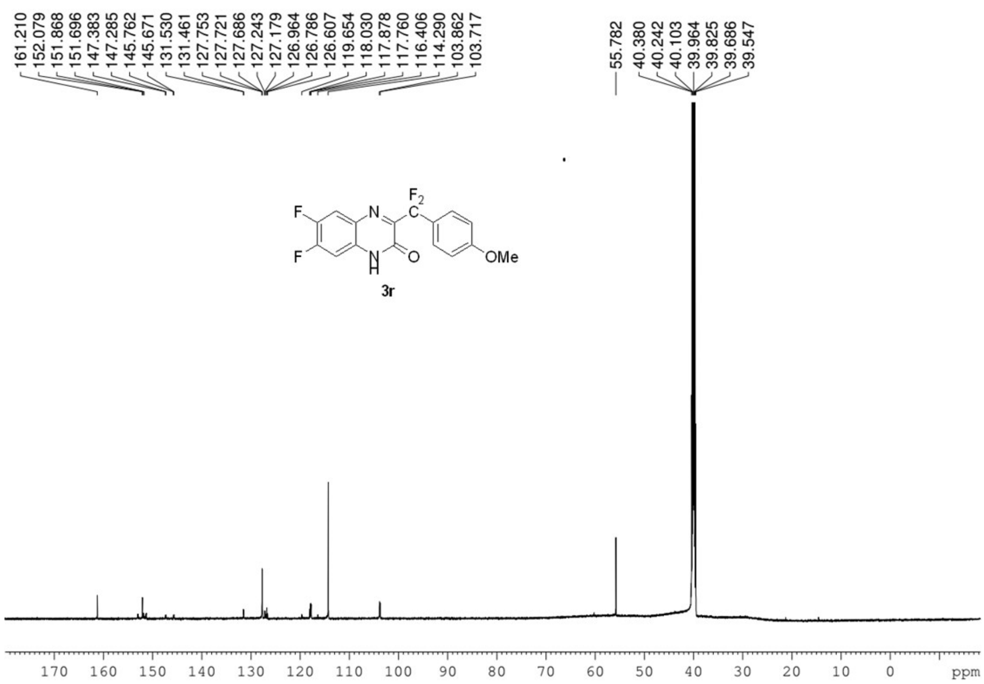
8.126
8.112
8.109
8.095
7.540
7.526
7.286
7.272
7.269
7.255
7.027
7.012
3.789
2.509
F
F
N
F2
C
N
H
O
OMe
3r
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
2.01
1.01
2.03
3.04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145.671
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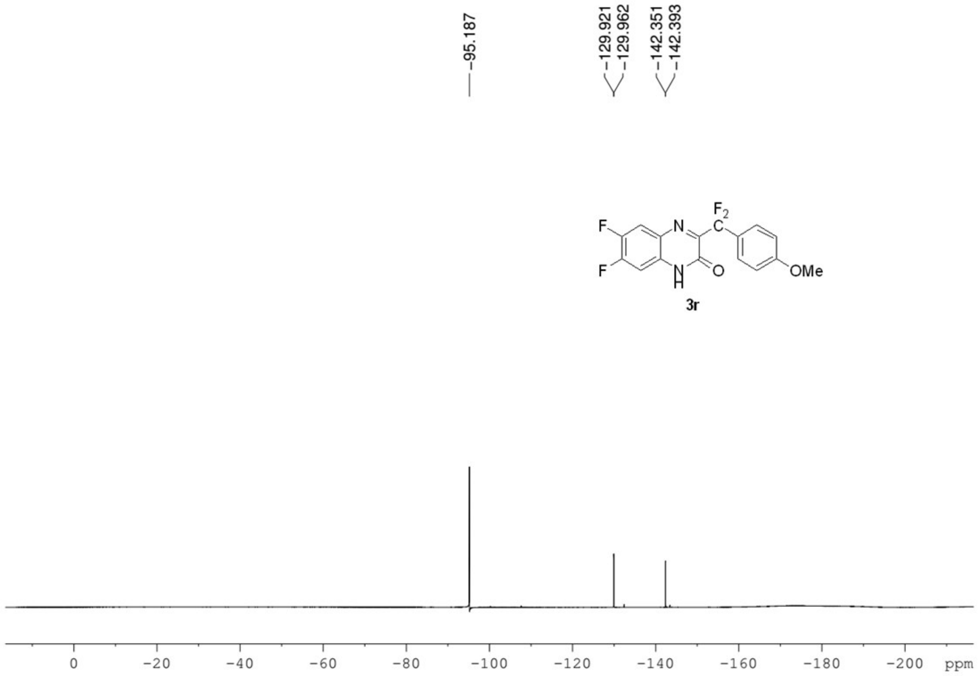
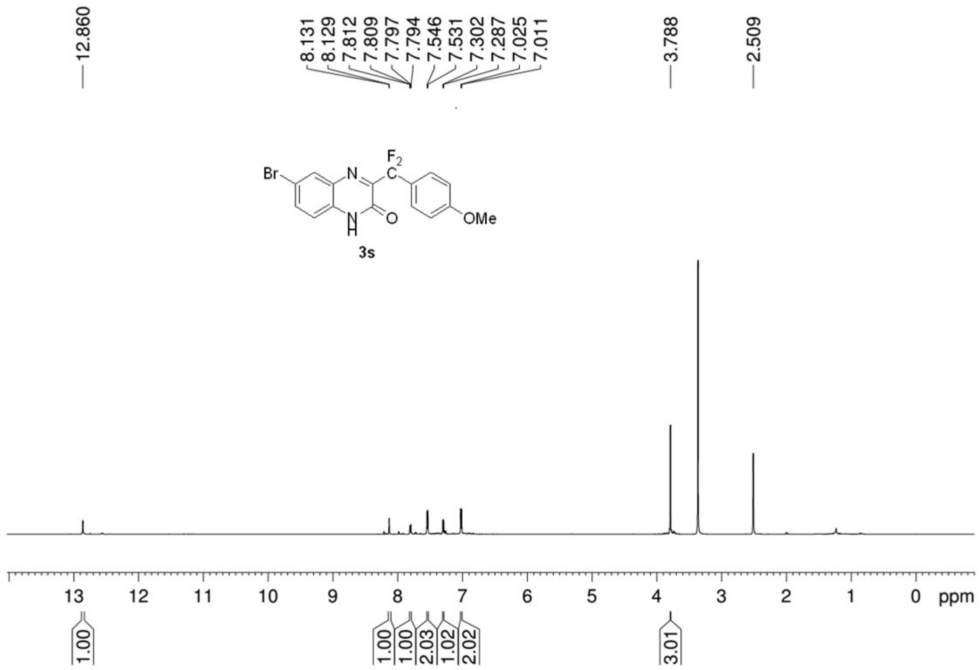
131.461
127.753
127.721
127.686
127.243
127.179
126.964
126.786
126.607
119.654
118.030
117.878
117.760
116.406
114.290
103.862
103.717
55.782
40.380
40.242
40.103
39.964
39.825
39.686
39.547
F
F
N
H
O
F_2
C
OMe
3r
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


-95.187
-129.921
-129.962
-142.351
-142.393
F
F
N
H
O
F_2
C
OMe
3r
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm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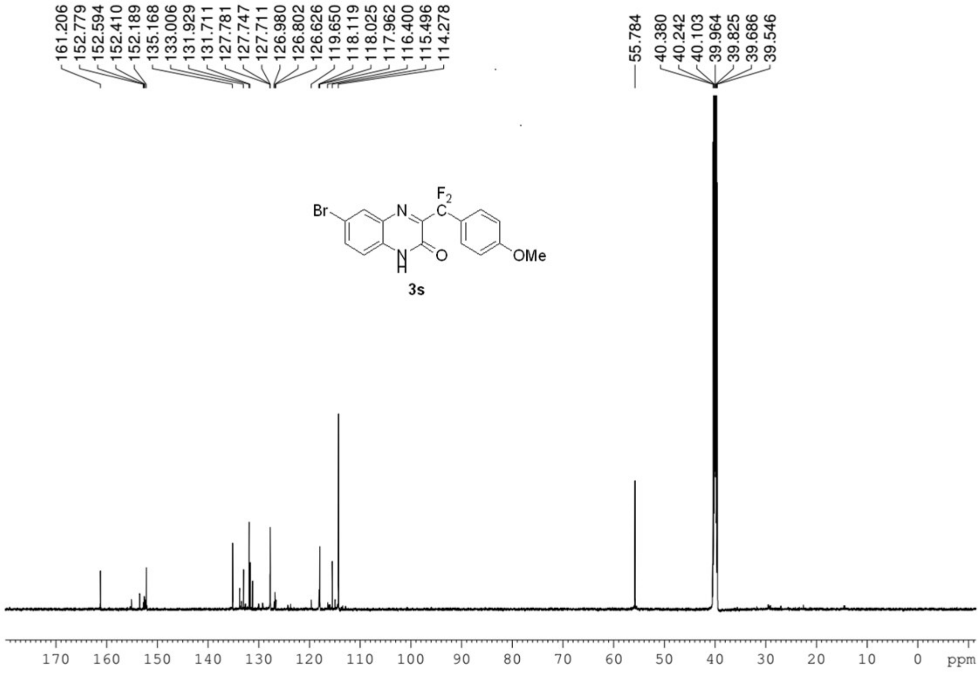
8.131
8.129
7.812
7.809
7.797
7.794
7.546
7.531
7.302
7.287
7.025
7.011
3.788
2.509
Br
N
F2
C
O
N
H
OMe
3s
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
1.00
2.03
1.02
2.02
3.01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152.410
152.189
135.168
133.006
131.929
131.711
127.781
127.747
127.711
126.980
126.802
126.626
119.650
118.119
118.025
117.962
116.400
115.496
114.278
55.784
40.380
40.242
40.103
39.964
39.825
39.686
39.546
Br
N
F2
C
O
N
H
OMe
3s
170
160
150
140
130
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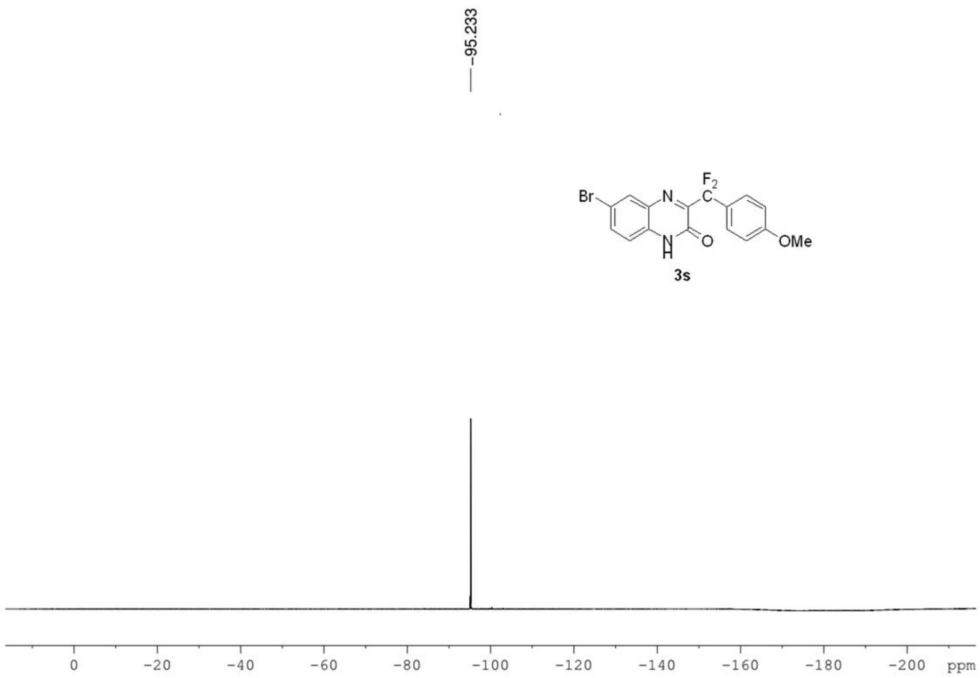
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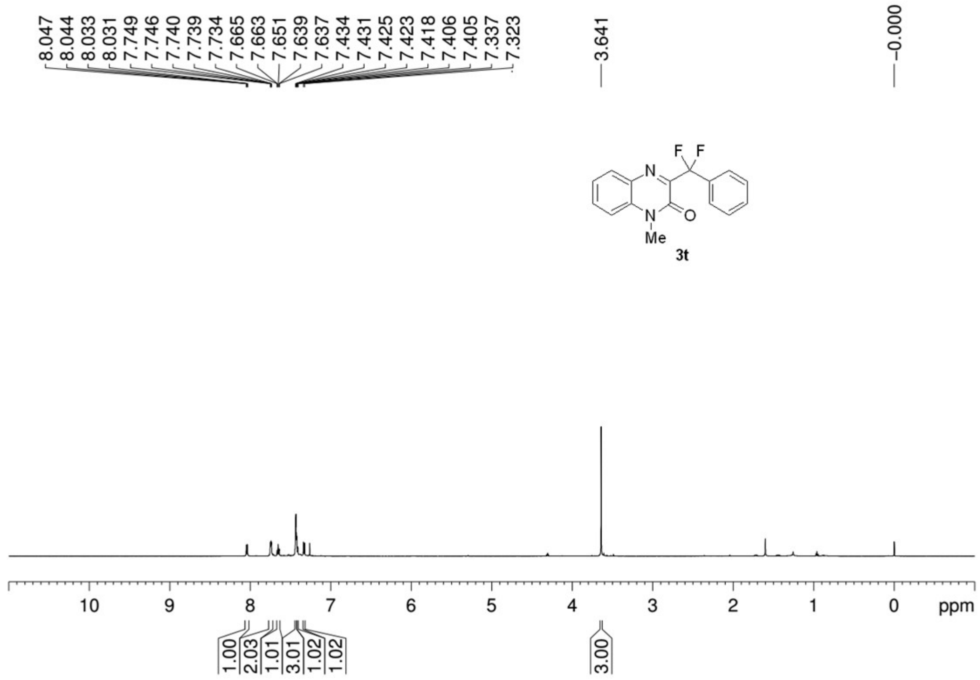
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7.651
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7.434
7.431
7.425
7.423
7.418
7.406
7.405
7.337
7.323
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N
F
F
N
O
Me
3t
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8
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1.01
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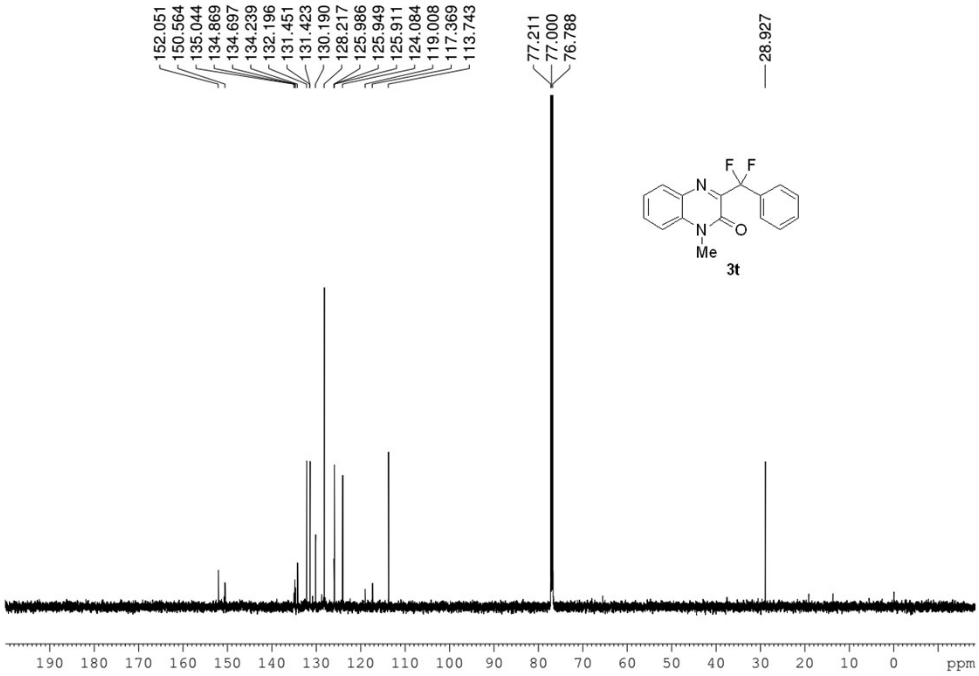
1.02
1.02
3.00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125.949
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119.008
117.369
113.743
77.211
77.000
76.788
28.927
F
F
N
N
O
Me
3t
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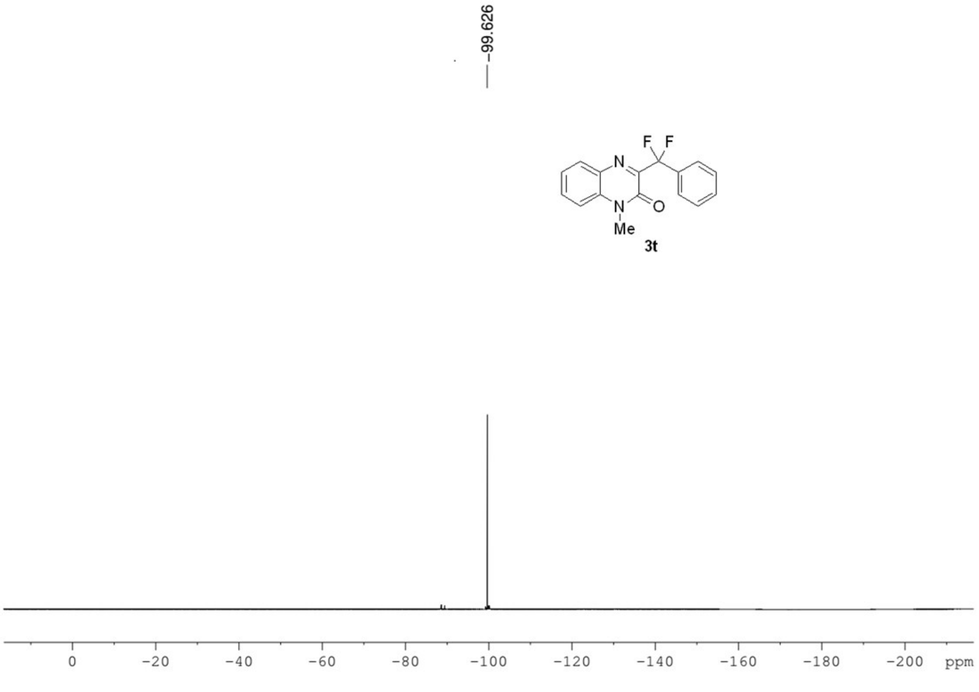
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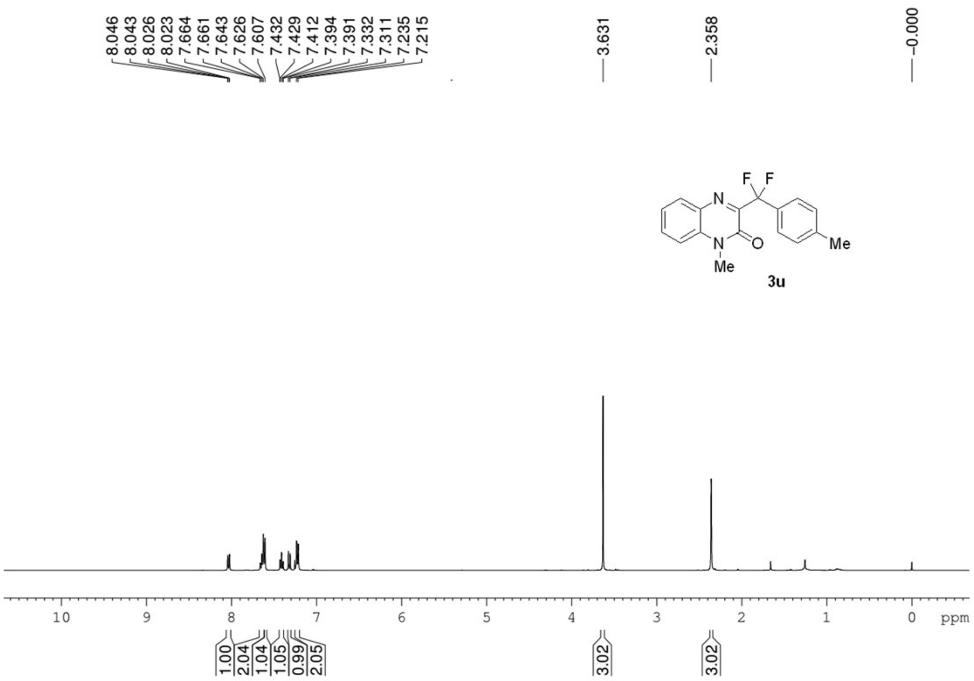
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7.626
7.607
7.432
7.429
7.412
7.394
7.391
7.332
7.311
7.235
7.215
3.631
2.358
-0.000
F
F
N
N
O
Me
Me
3u
10
9
8
7
6
5
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0
ppm
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1.05
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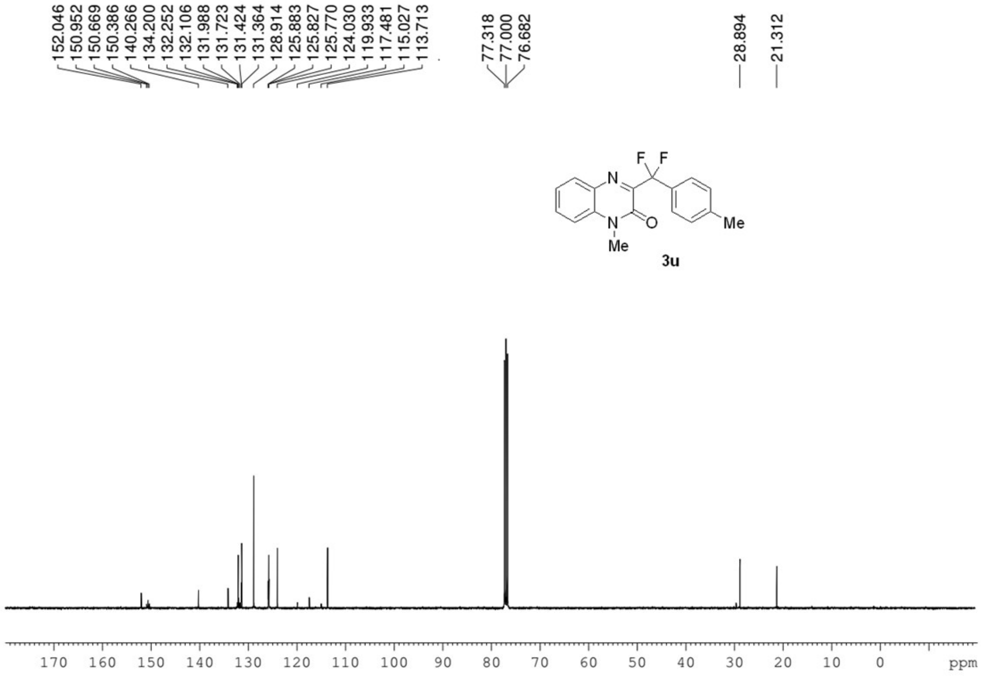
2.05
3.02
3.02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131.364
128.914
125.883
125.827
125.770
124.030
119.933
117.481
115.027
113.713
77.318
77.000
76.682
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21.312
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F
N
N
O
Me
Me
3u
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130
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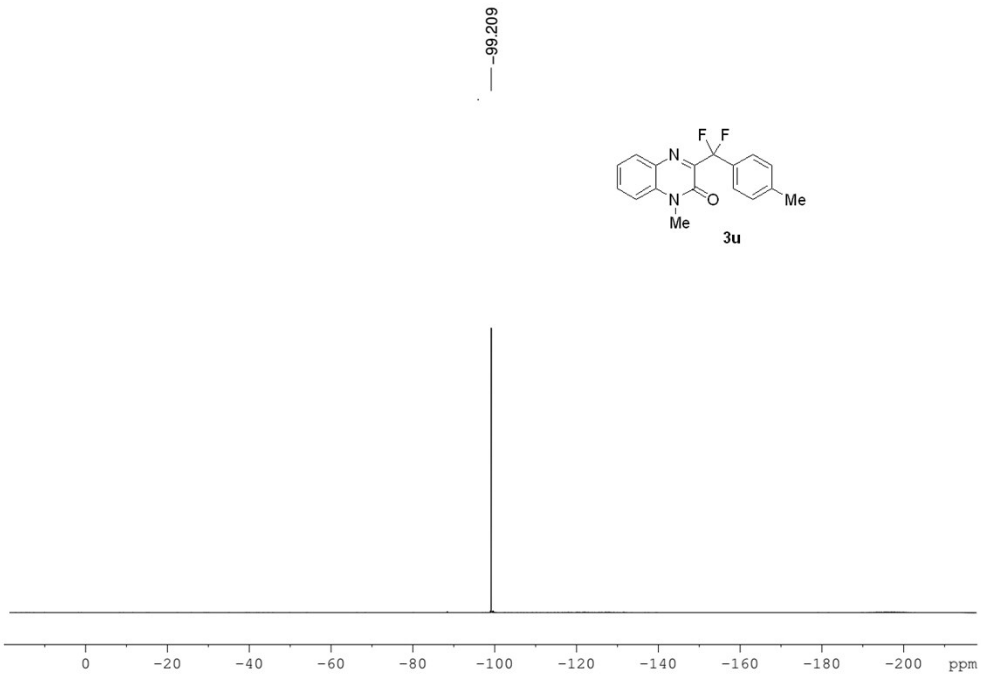
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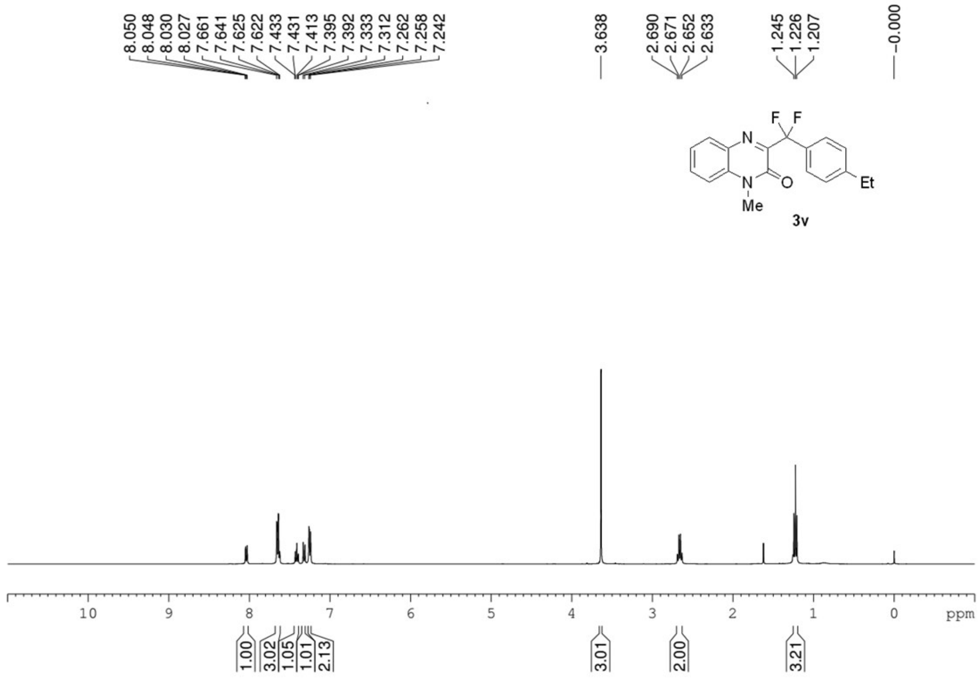
-200
ppm

3u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7.431
7.413
7.395
7.392
7.333
7.312
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7.258
7.242
3.638
2.690
2.671
2.652
2.633
1.245
1.226
1.207
-0.000
F
F
N
N
O
Me
Et
10
9
8
7
6
5
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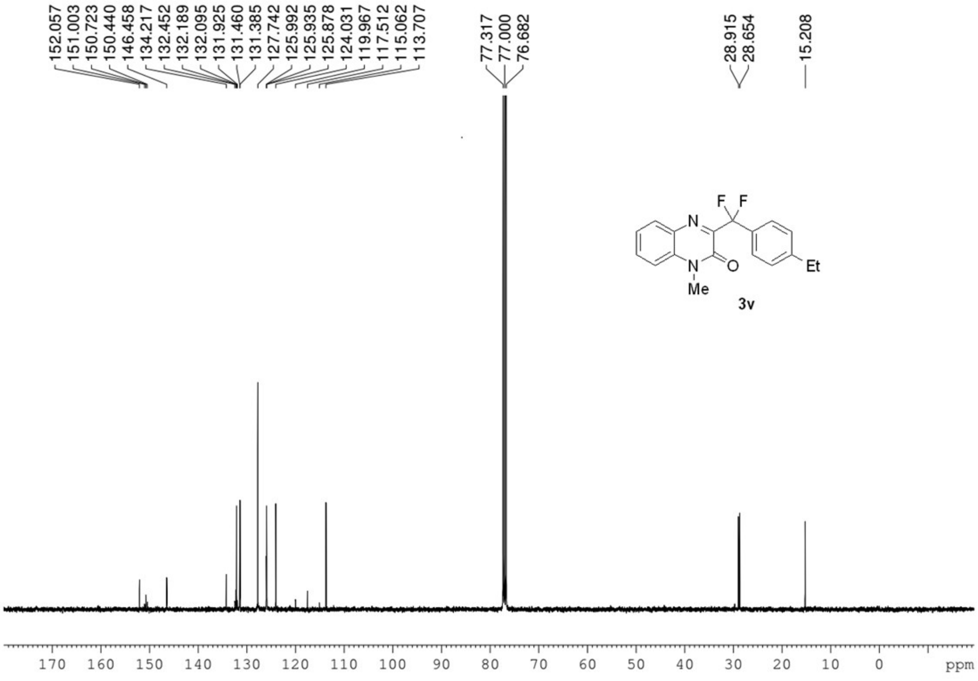
ppm
1.00
3.02
1.05
1.01
2.13
3.01
2.00
3.21

3v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134.217
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132.189
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131.925
131.460
131.385
127.742
125.992
125.935
125.878
124.031
119.967
117.512
115.062
113.707
77.317
77.000
76.682
28.915
28.654
15.208
F
F
N
N
O
Me
Et
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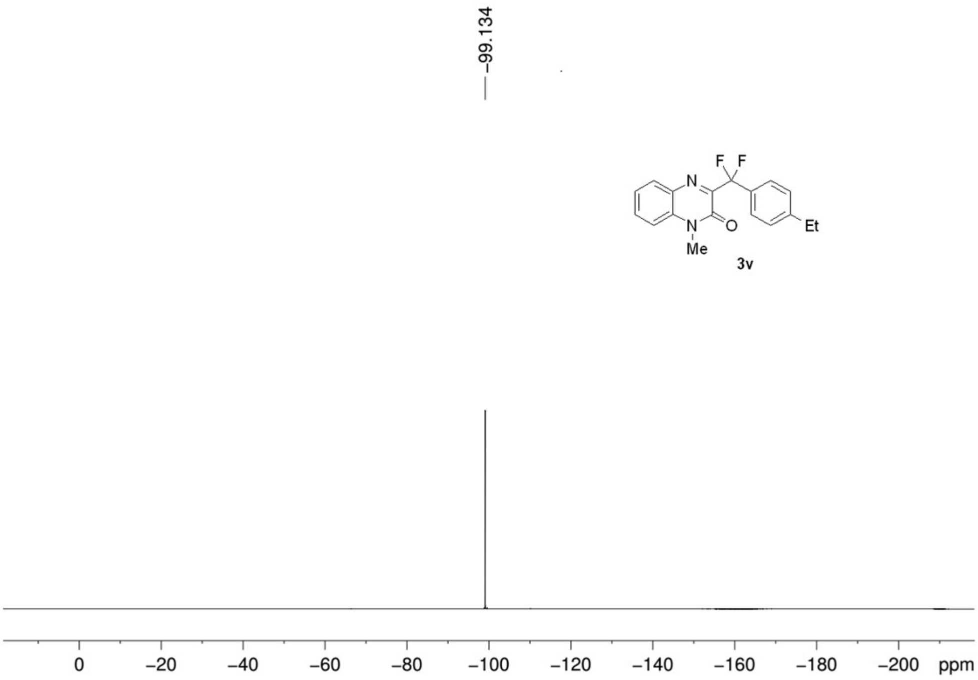
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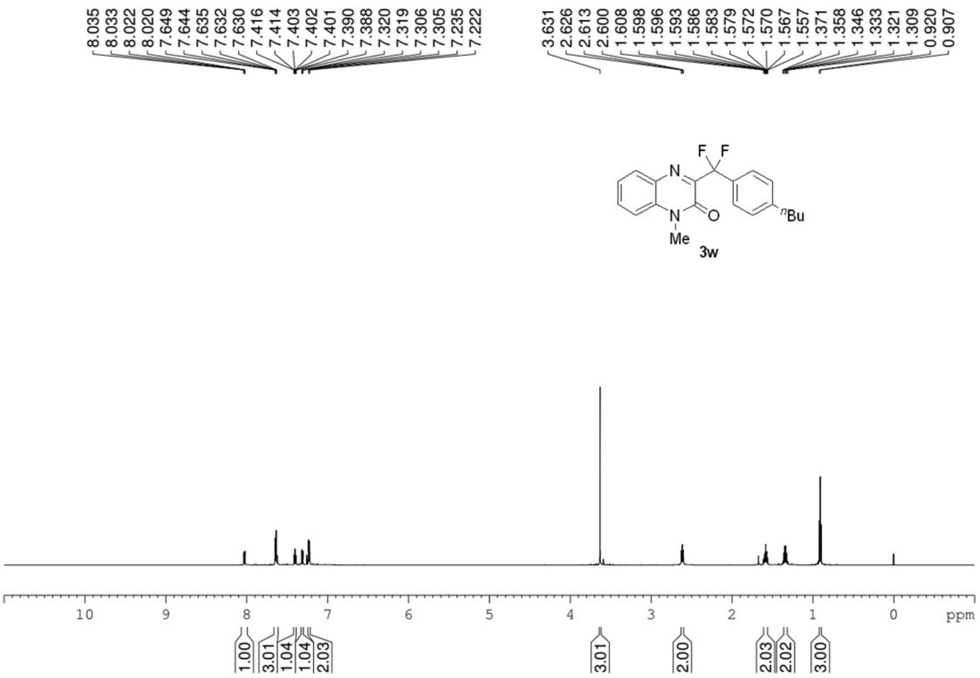
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7.402
7.401
7.390
7.388
7.320
7.319
7.306
7.305
7.235
7.222
3.631
2.626
2.613
2.600
1.608
1.598
1.596
1.593
1.586
1.583
1.579
1.572
1.570
1.567
1.557
1.371
1.358
1.346
1.333
1.321
1.309
0.920
0.907
F
F
N
N
O
Me
^{n}Bu
3w
10
9
8
7
6
5
4
3
2
1
0
ppm
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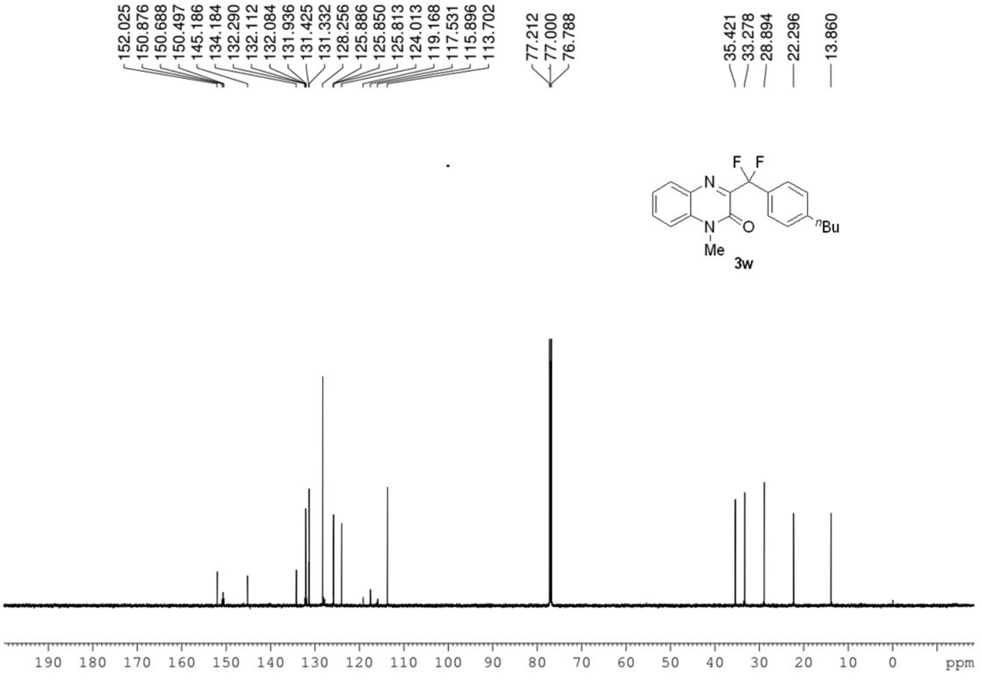
3.01
1.04
1.04
2.03
3.01
2.00
2.03
2.02
3.00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131.936
131.425
131.332
128.256
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125.850
125.813
124.013
119.168
117.531
115.896
113.702
77.212
77.000
76.788
35.421
33.278
28.894
22.296
13.860
F
F
N
N
O
Me
^{n}Bu
3w
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180
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140
130
120
110
100
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80
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60
50
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20
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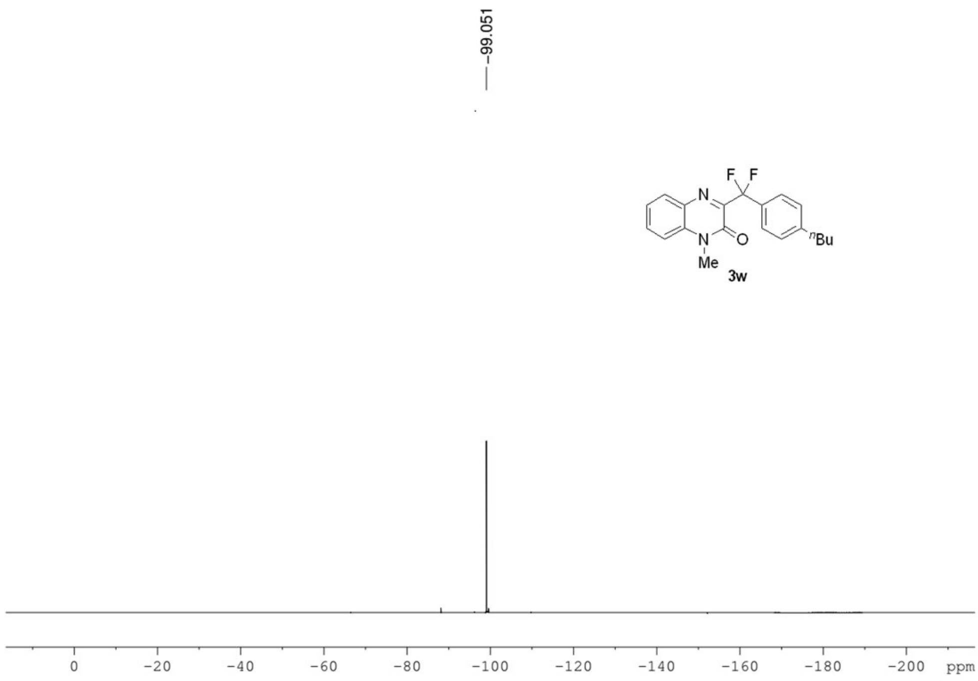
ppm


3w

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F
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ⁿBu
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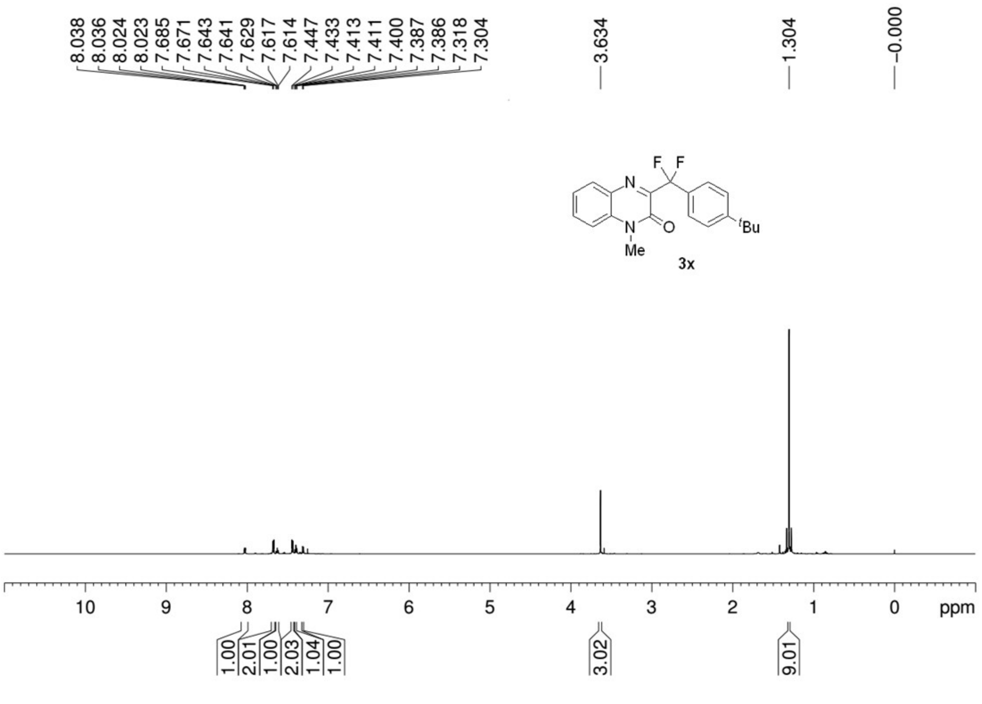
−180
−200
ppm


3x

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8.024
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7.617
7.614
7.447
7.433
7.413
7.411
7.400
7.387
7.386
7.318
7.304
3.634
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-0.000
F
F
N
N
O
Me
ᵗBu
10
9
8
7
6
5
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1
0
ppm
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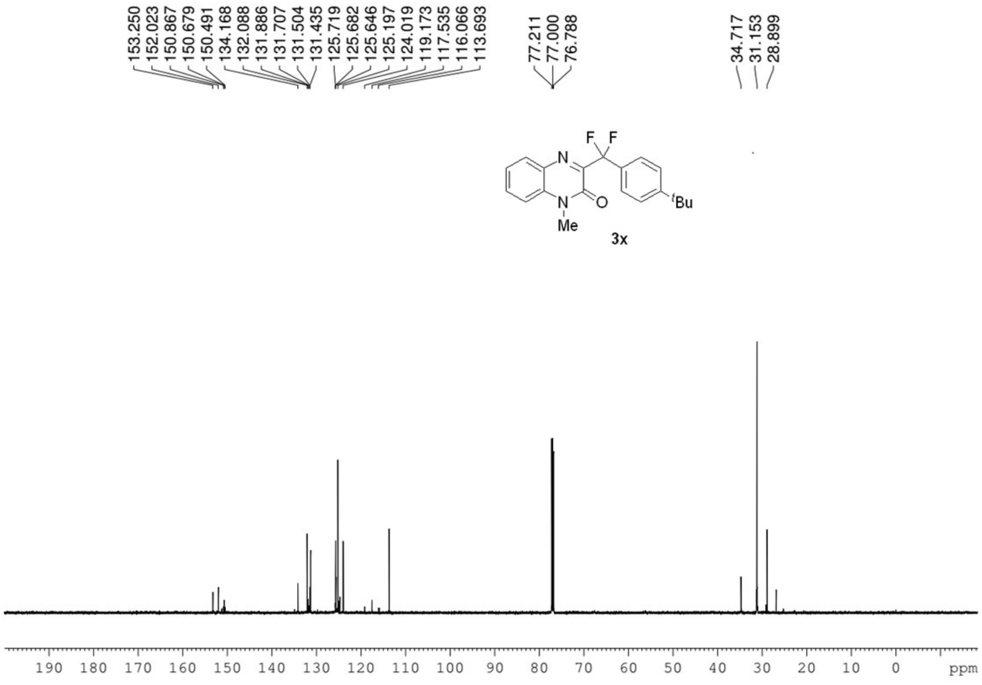
2.01
1.00
2.03
1.04
1.00
3.02
9.01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125.197
124.019
119.173
117.535
116.066
113.693
77.211
77.000
76.788
34.717
31.153
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F F
N
N
O
Me
ᵗBu
3x
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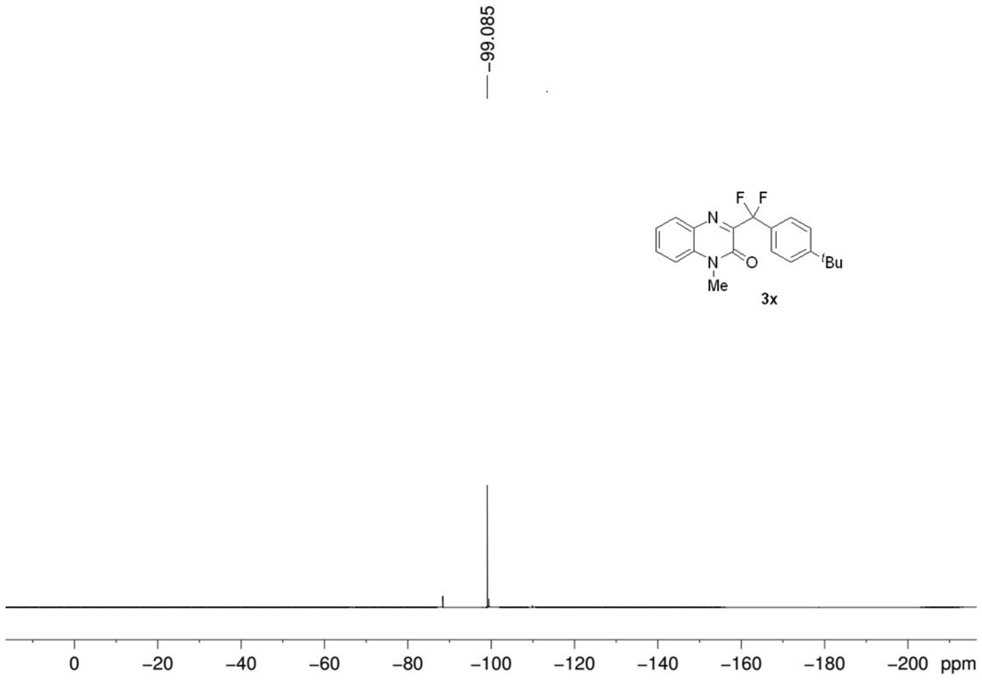
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F F
N
N
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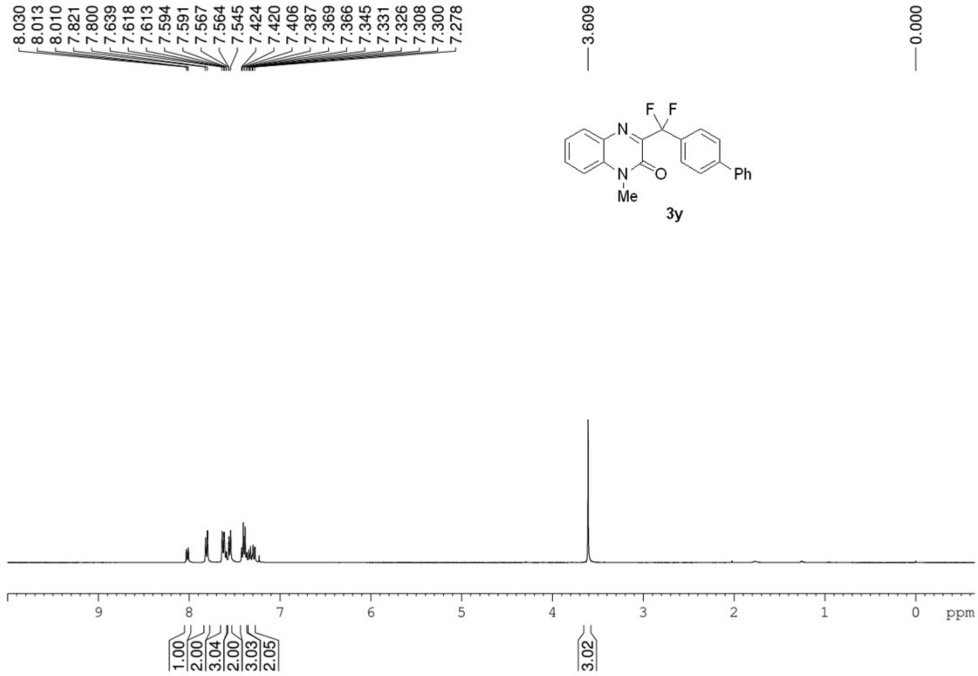
Me
ᵗBu
3x
0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 ppm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7.613
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7.591
7.567
7.564
7.545
7.424
7.420
7.406
7.387
7.369
7.366
7.345
7.331
7.326
7.308
7.300
7.278
3.609
0.000
F
F
N
O
N
Me
Ph
3y
9
8
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3.04
2.00
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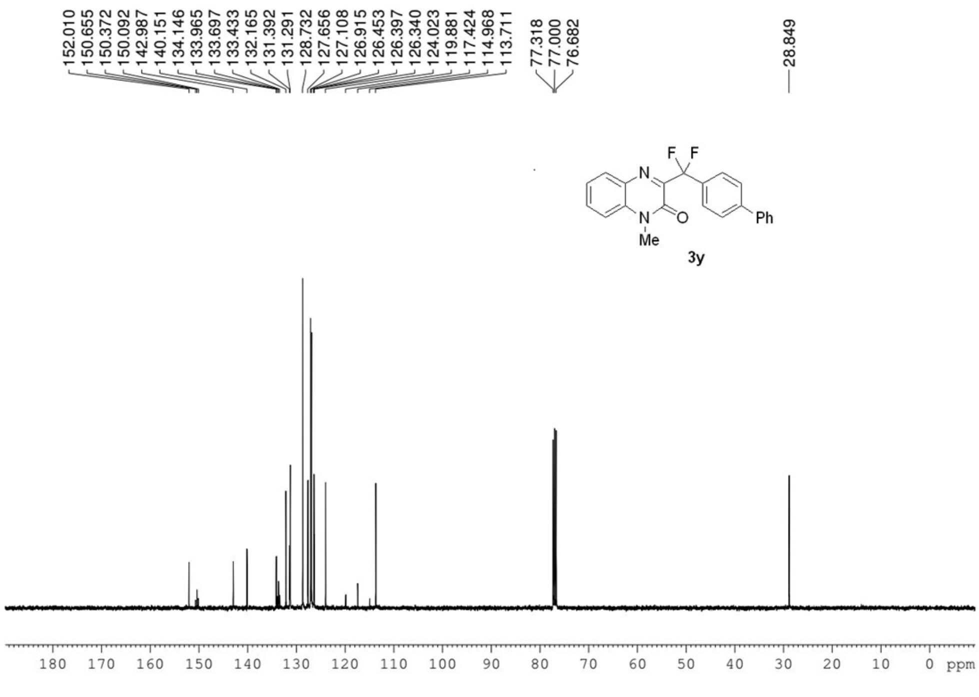
2.05
3.02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127.656
127.108
126.915
126.453
126.397
126.340
124.023
119.881
117.424
114.968
113.711
77.318
77.000
76.682
28.849
F
F
N
O
N
Me
Ph
3y
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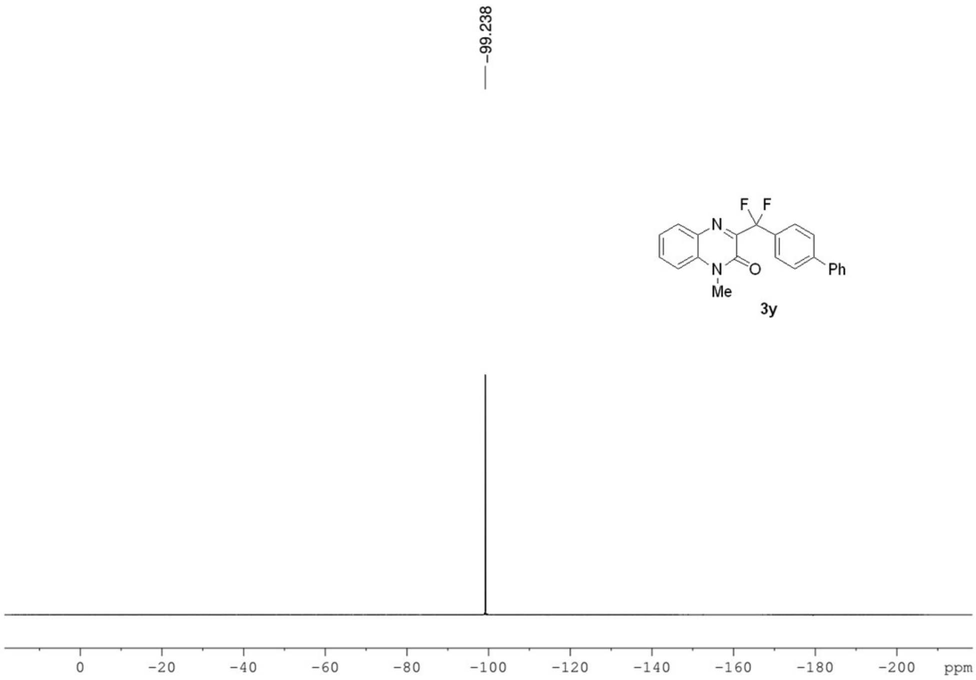
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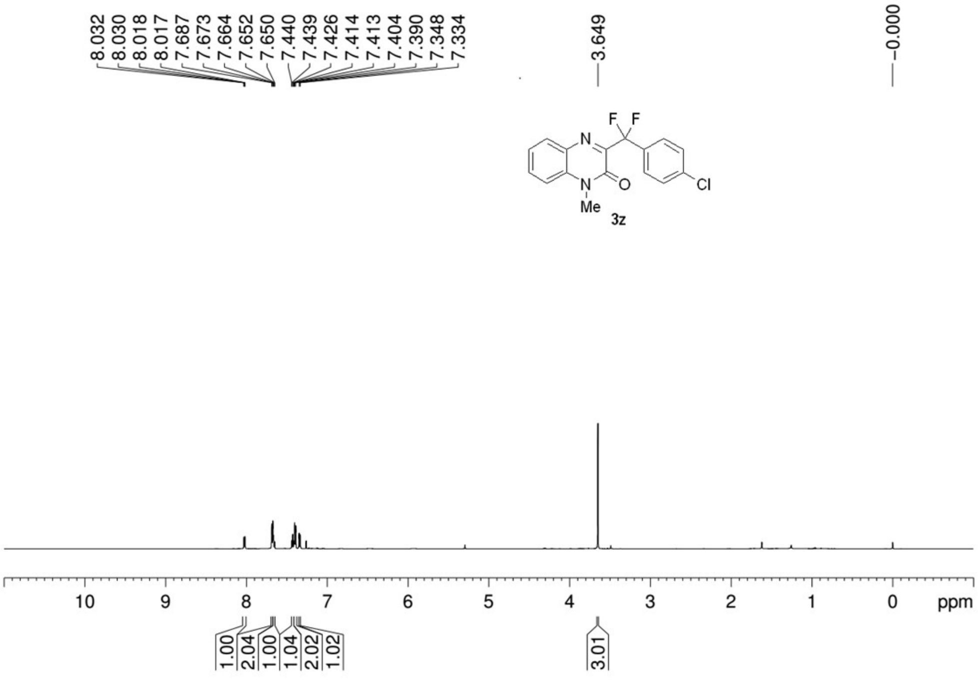
-200
ppm

3y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F
F
N
N
O
Me
Cl
10
9
8
7
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ppm
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1.04
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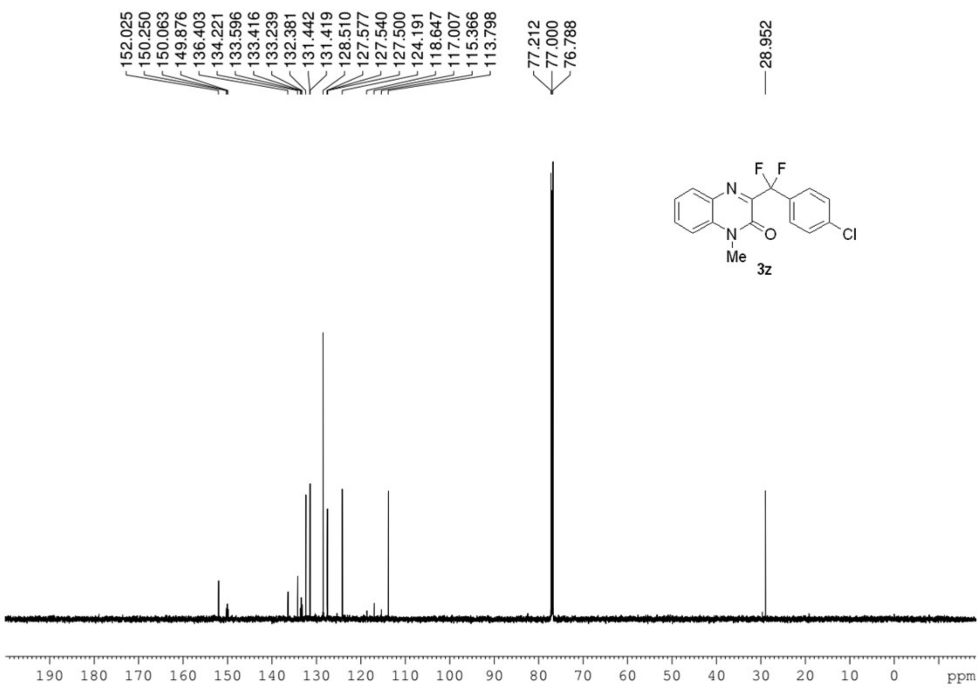
1.02
3.01

3z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132.381
131.442
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127.540
127.500
124.191
118.647
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115.366
113.798
77.212
77.000
76.788
28.952
F
F
N
N
O
Cl
Me
3z
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60
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20
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0
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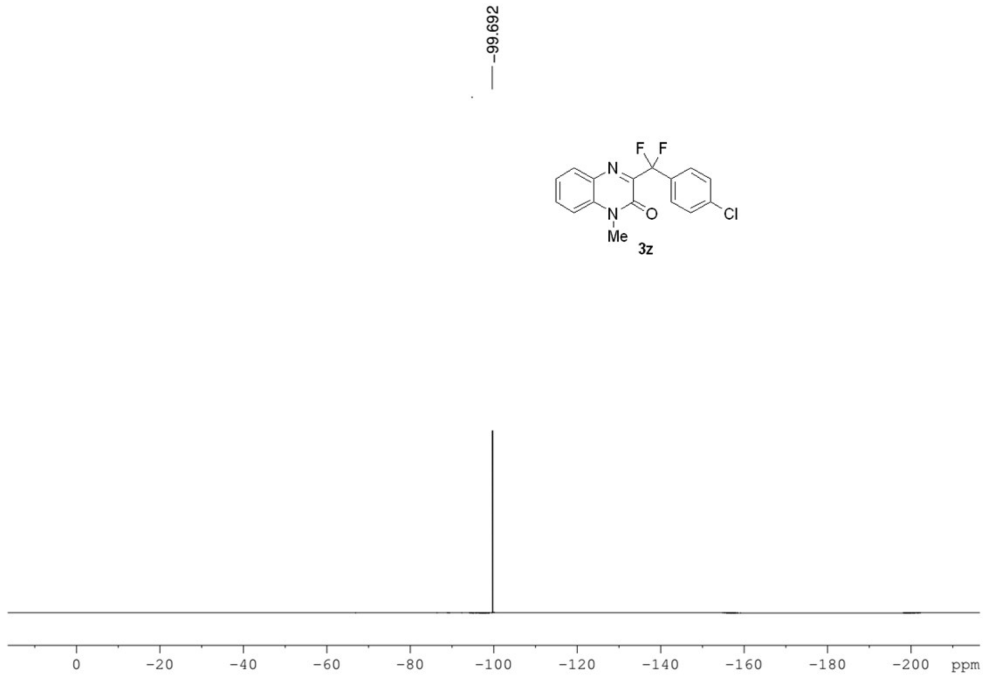
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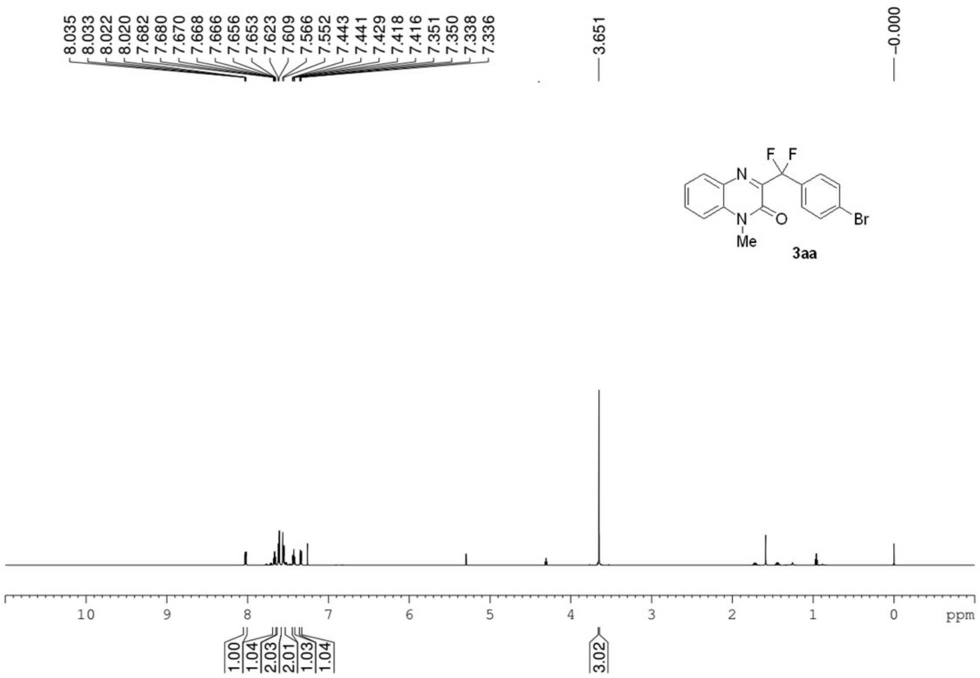
ppm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7.653
7.623
7.609
7.566
7.552
7.443
7.441
7.429
7.418
7.416
7.351
7.350
7.338
7.336
3.651
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F
F
N
N
O
Br
Me
3aa
10
9
8
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2
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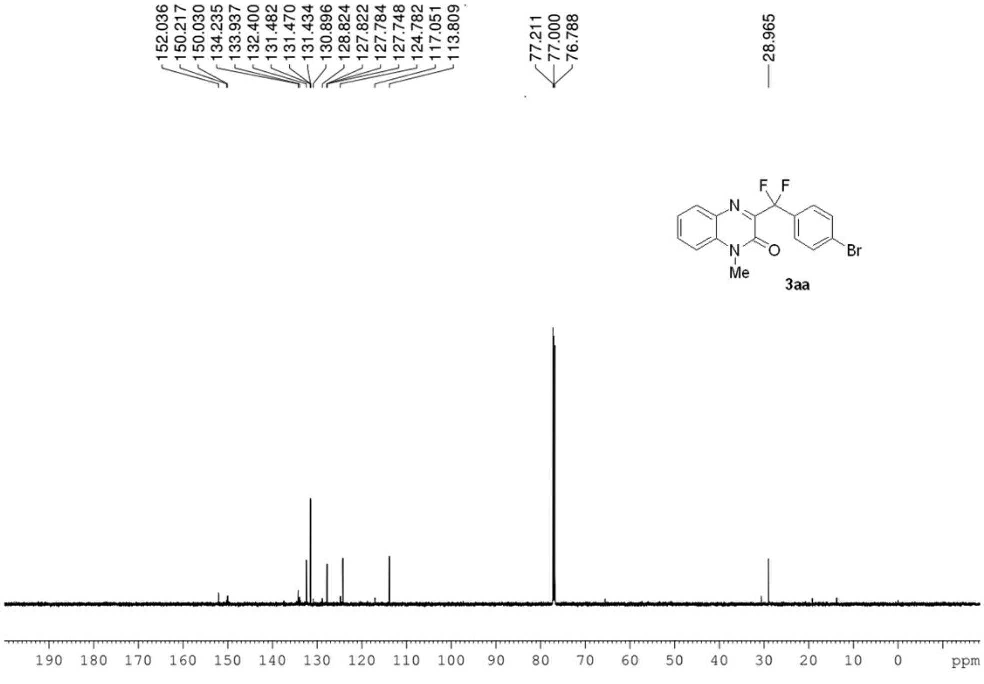
2.03
2.01
1.03
1.04
3.02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131.470
131.434
130.896
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127.822
127.784
127.748
124.782
117.051
113.809
77.211
77.000
76.788
28.965
F
F
N
N
O
Br
Me
3aa
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130
120
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100
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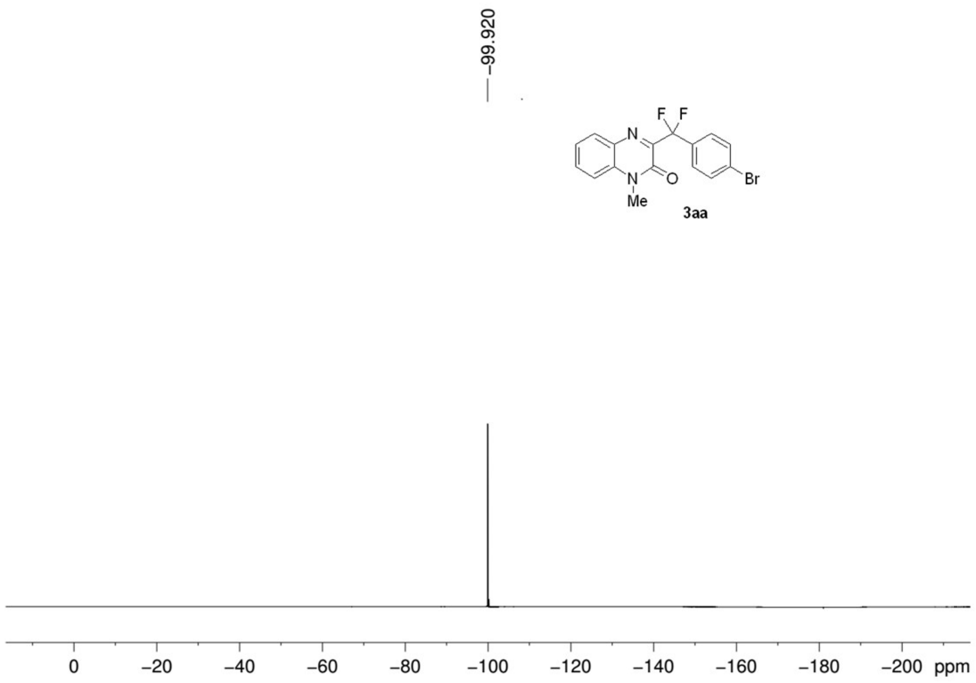

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N
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Br
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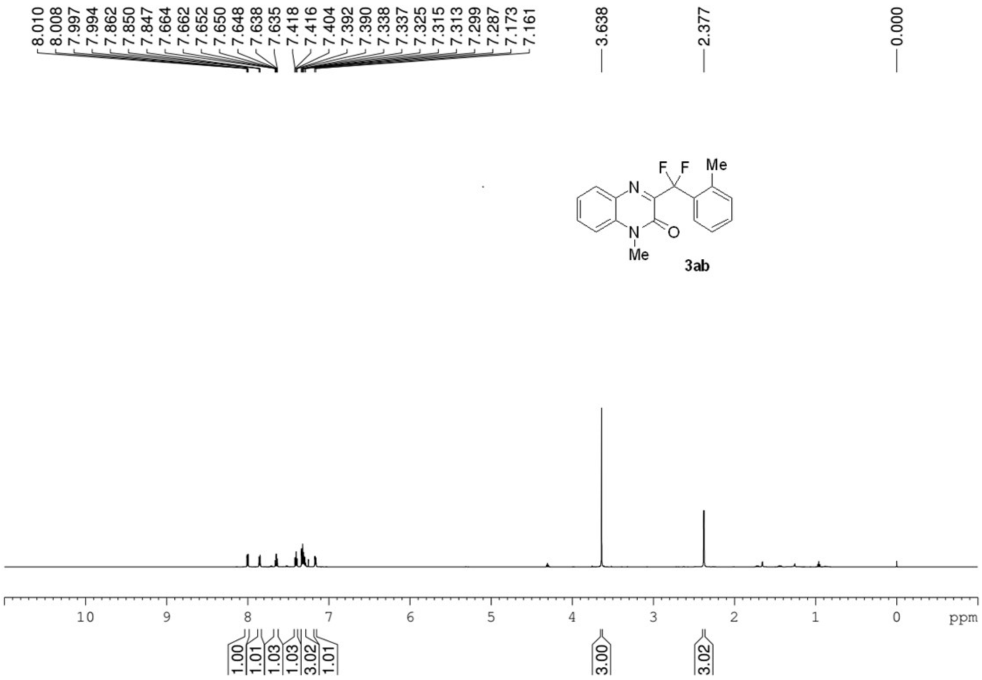
−200
ppm

3aa



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7.638
7.635
7.418
7.416
7.404
7.392
7.390
7.338
7.337
7.325
7.315
7.313
7.299
7.287
7.173
7.161
3.638
2.377
0.000
F
F
Me
N
N
O
Me
10
9
8
7
6
5
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ppm
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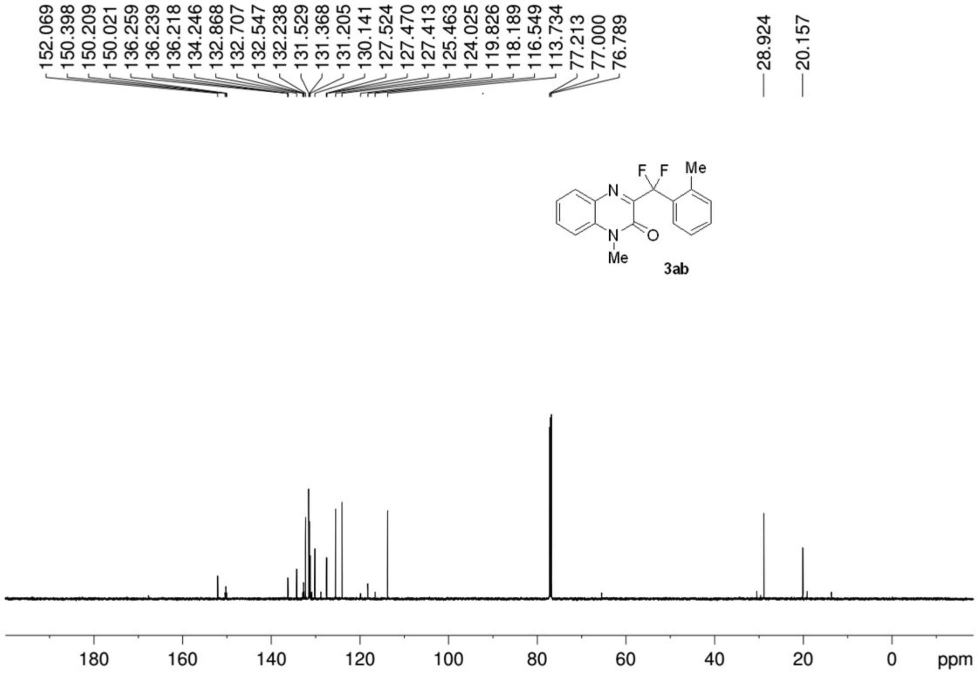
1.03
1.03
3.02
1.01
3.00
3.02

3ab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136.239
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134.246
132.868
132.707
132.547
132.238
131.529
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131.205
130.141
127.524
127.470
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125.463
124.025
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116.549
113.734
77.213
77.000
76.789
28.924
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O
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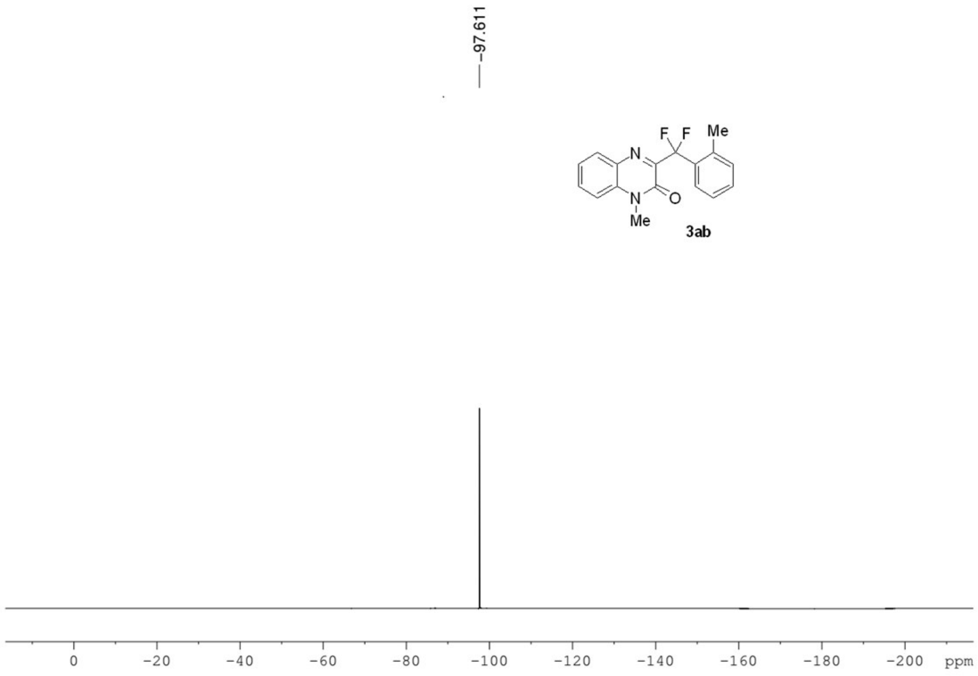
ppm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Me
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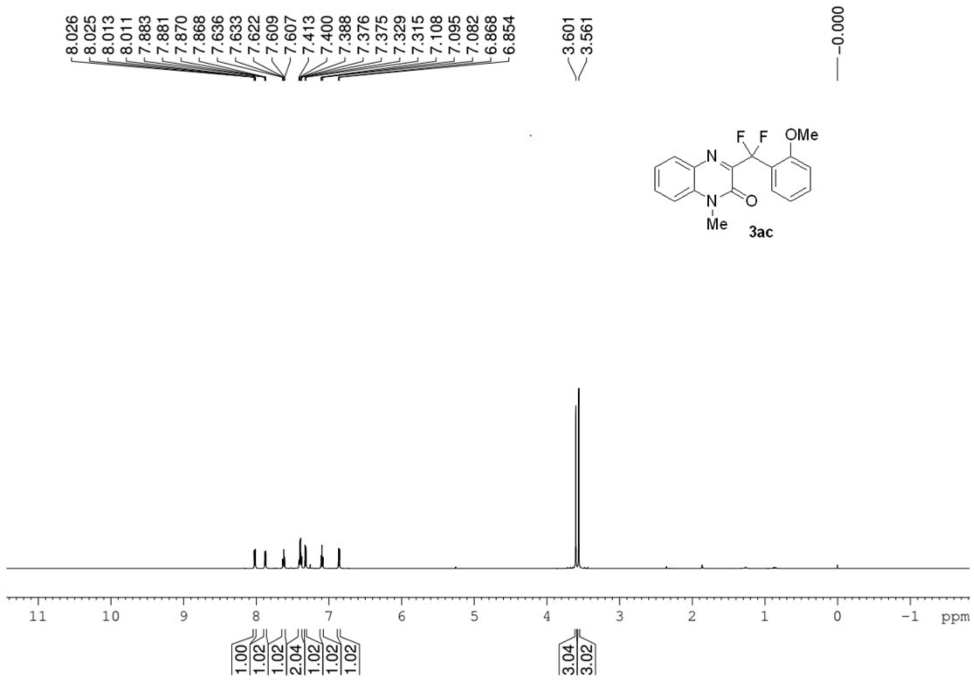
-200
ppm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7.633
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7.607
7.413
7.400
7.388
7.376
7.375
7.329
7.315
7.108
7.095
7.082
6.868
6.854
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3.561
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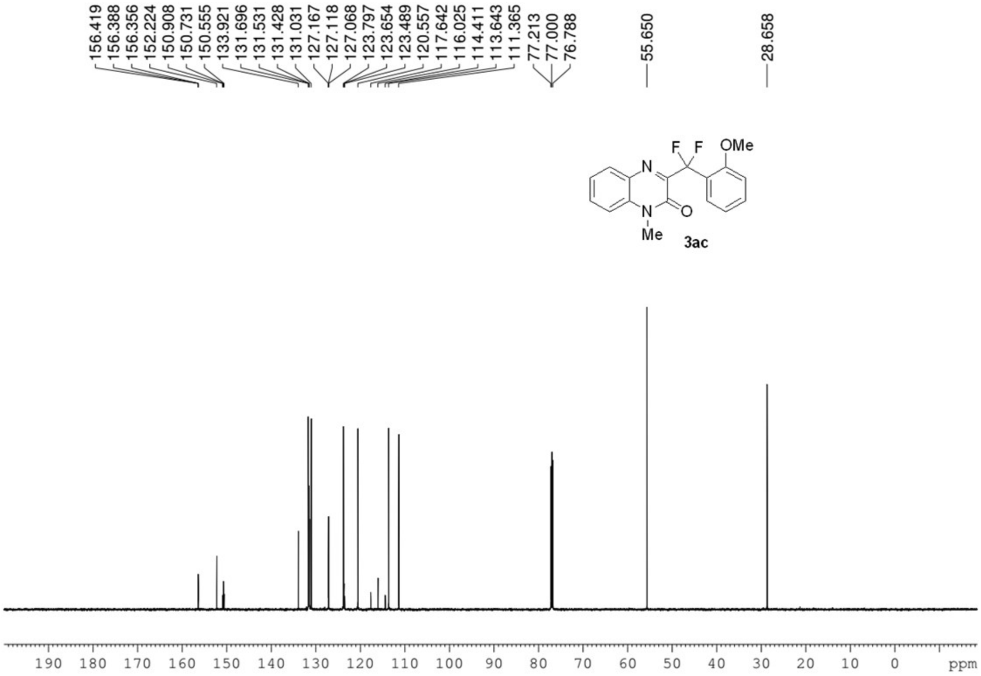
N
F
F
OMe
N
O
Me
3ac
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.00
1.02
1.02
1.02
2.04
1.02
1.02
1.02
1.02
3.04
3.02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156.356
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150.555
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131.031
127.167
127.118
127.068
123.797
123.654
123.489
120.557
117.642
116.025
114.411
113.643
111.365
77.213
77.000
76.788
55.650
28.658
N
F
F
OMe
N
O
Me
3ac
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
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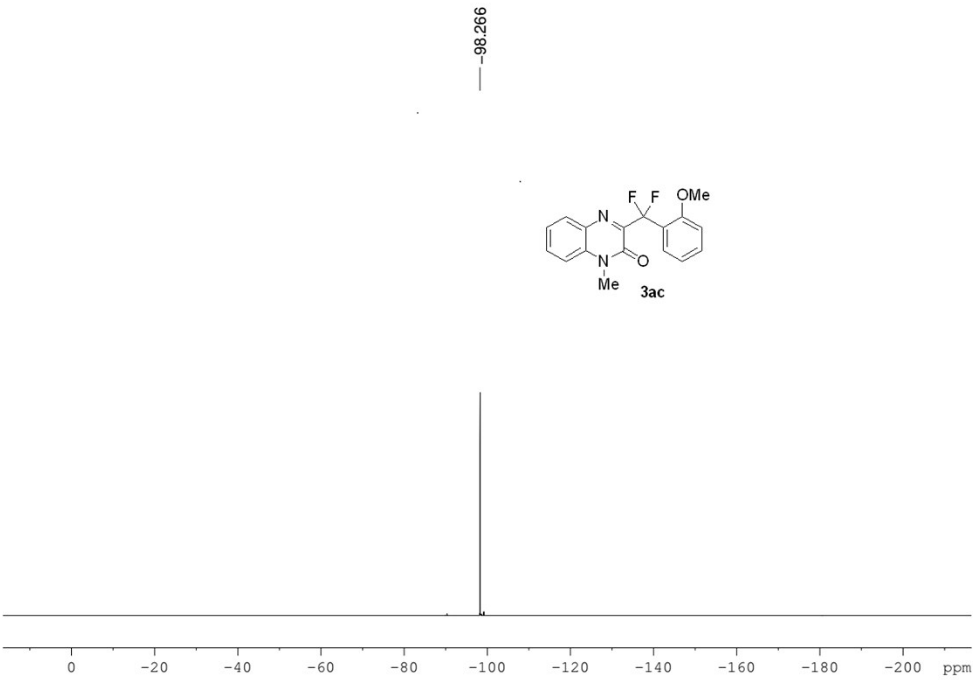
20
10
0
ppm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F F OMe
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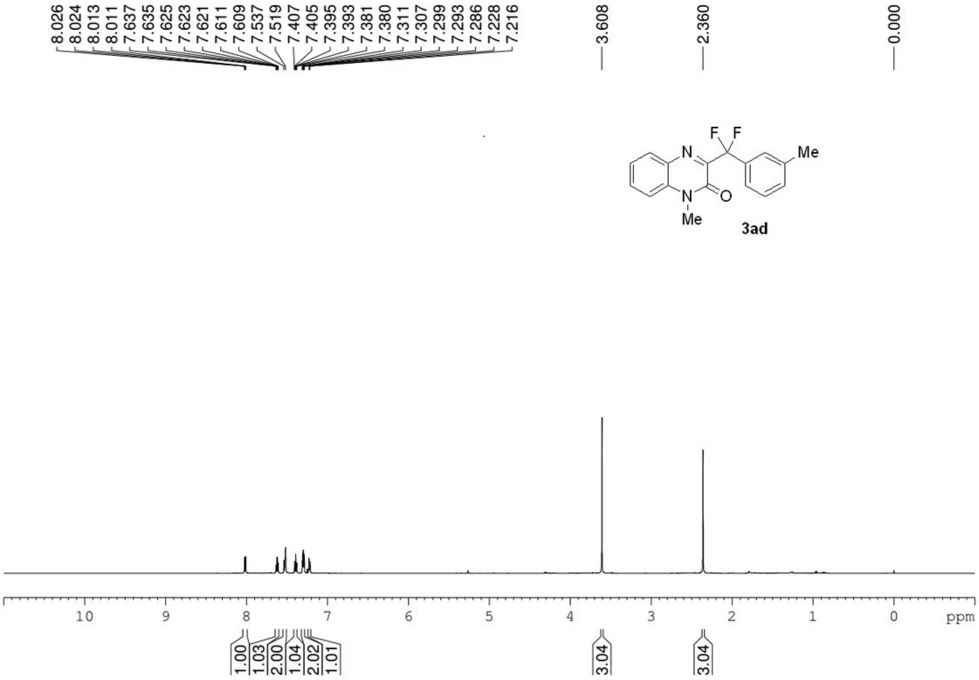
-180
-200
ppm

3ac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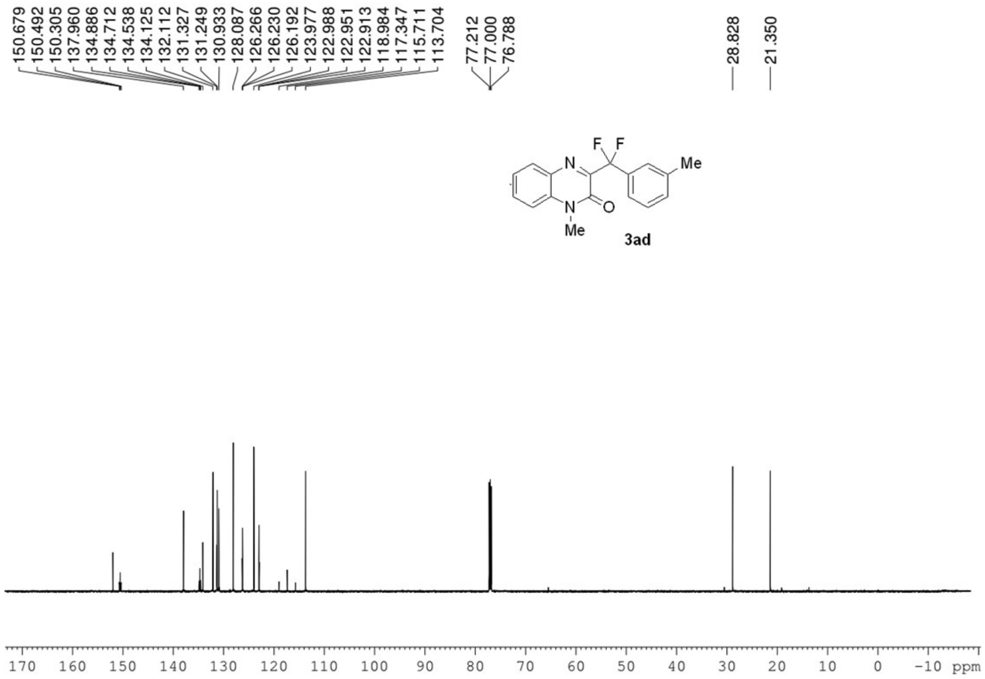
8.024
8.013
8.011
7.637
7.635
7.625
7.623
7.621
7.611
7.609
7.537
7.519
7.407
7.405
7.395
7.393
7.381
7.380
7.311
7.307
7.299
7.293
7.286
7.228
7.216
3.608
2.360
0.000
F F
Me
N
N
O
Me
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.03
2.00
1.04
2.02
1.01
3.04
3.04

3ad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150.492
150.305
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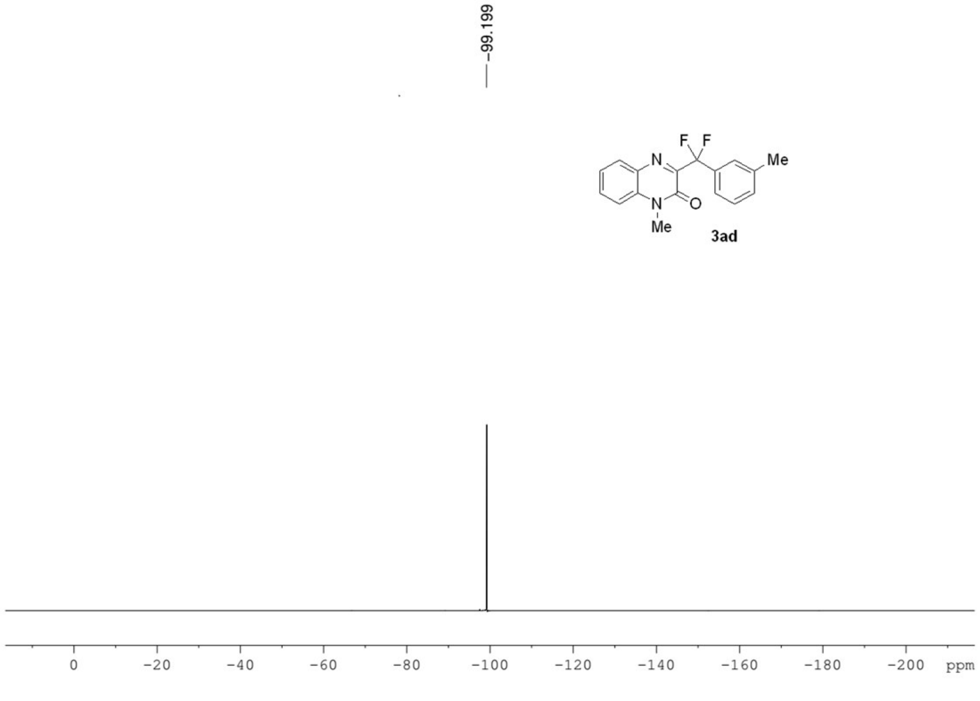
134.712
134.538
134.125
132.112
131.327
131.249
130.933
128.087
126.266
126.230
126.192
123.977
122.988
122.951
122.913
118.984
117.347
115.711
113.704
77.212
77.000
76.788
28.828
21.350
F
F
N
Me
N
O
Me
3ad
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 ppm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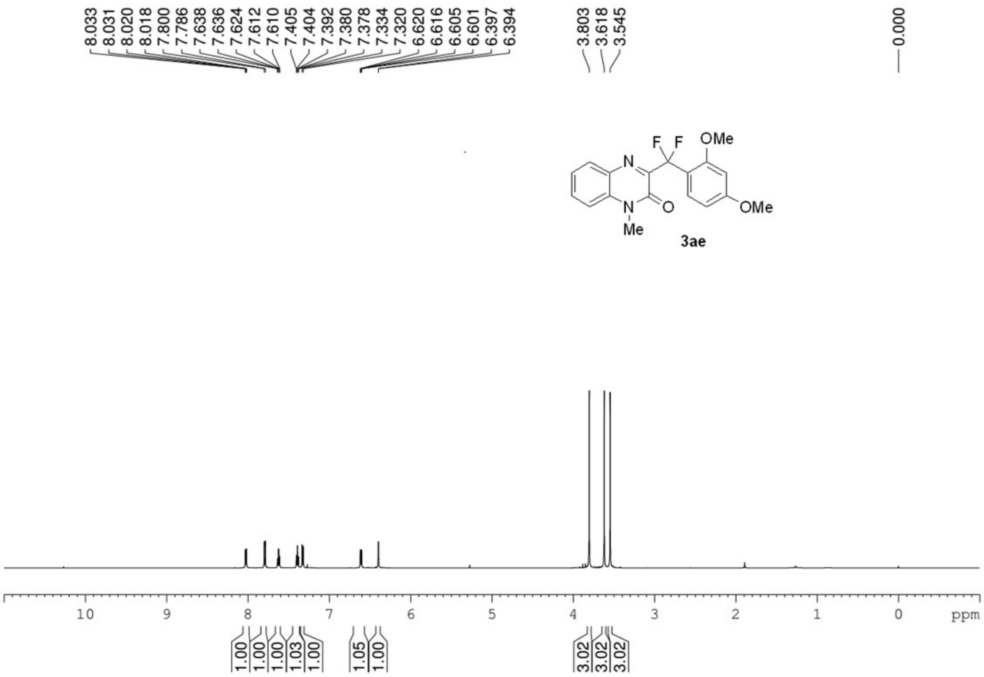
F
N
Me
N
O
Me
3ad
0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 ppm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8.031
8.020
8.018
7.800
7.786
7.638
7.636
7.624
7.612
7.610
7.405
7.404
7.392
7.380
7.378
7.334
7.320
6.620
6.616
6.605
6.601
6.397
6.394
3.803
3.618
3.545
0.000
F
F
OMe
N
N
O
Me
OMe
3ae
10
9
8
7
6
5
4
3
2
1
0
ppm
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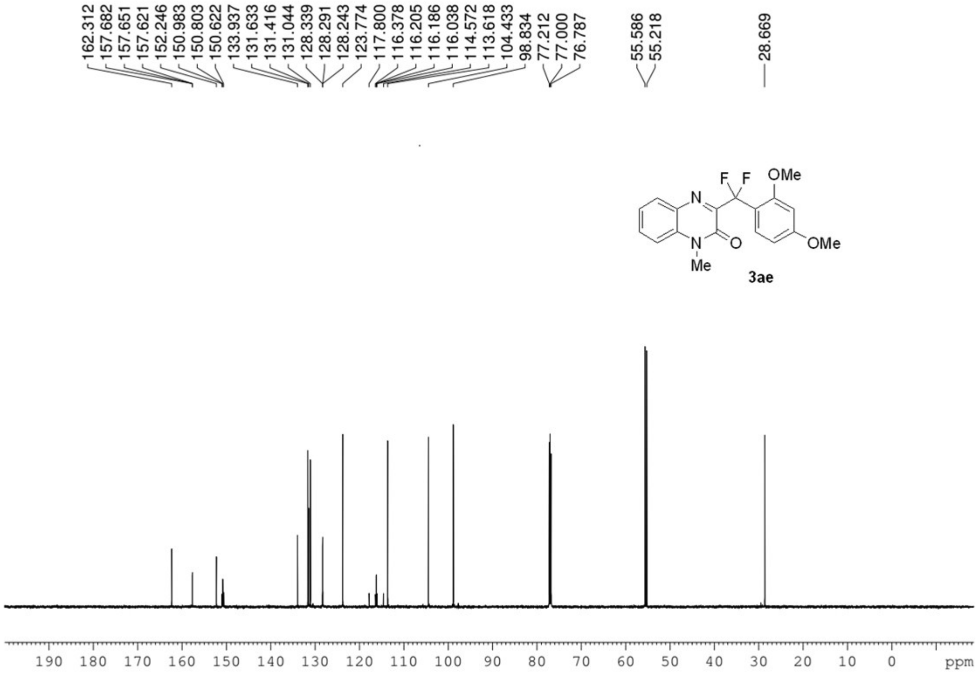
1.00
1.00
1.03
1.00
1.05
1.00
3.02
3.02
3.02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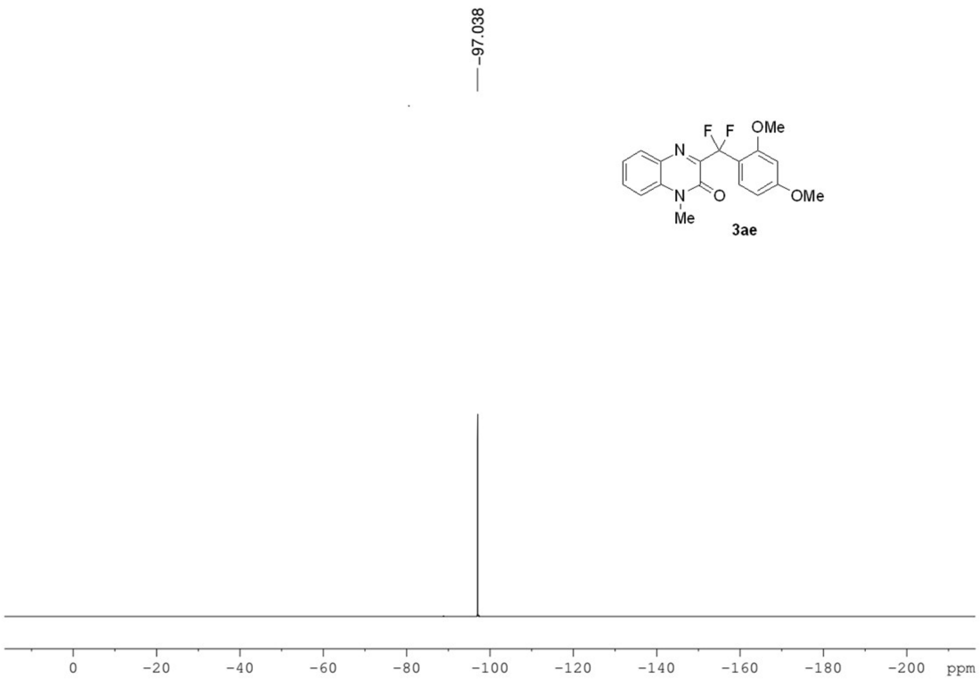
150.803
150.622
133.937
131.633
131.416
131.044
128.339
128.291
128.243
123.774
117.800
116.378
116.205
116.186
116.038
114.572
113.618
104.433
98.834
77.212
77.000
76.787
55.586
55.218
28.669
F
F
OMe
N
N
O
Me
OMe
3ae
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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F F
OMe
N
N
Me
O
OMe
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0
-20
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-60
-80
-100
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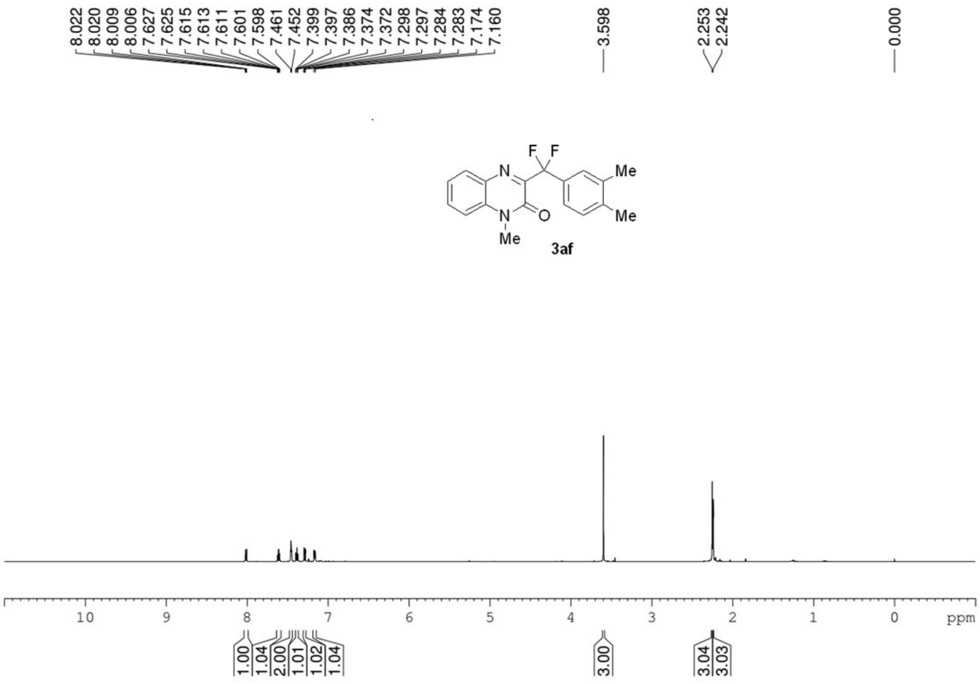
-140
-160
-180
-200
ppm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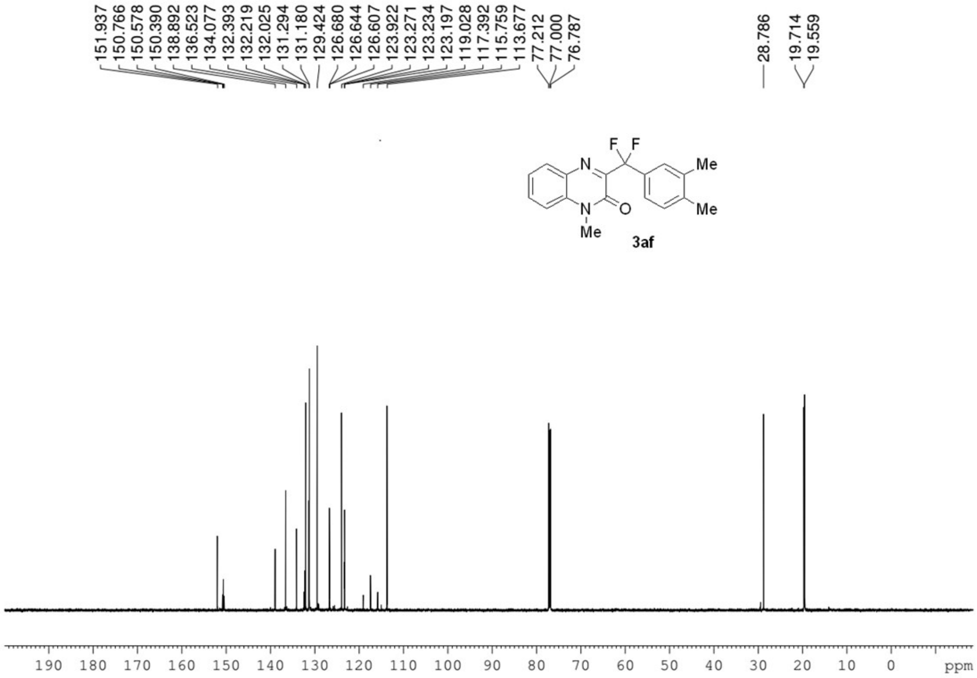
8.020
8.009
8.006
7.627
7.625
7.615
7.613
7.611
7.601
7.598
7.461
7.452
7.399
7.397
7.386
7.374
7.372
7.298
7.297
7.284
7.283
7.174
7.160
3.598
2.253
2.242
0.000
F F
Me
Me
N
N
Me
O
3af
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.04
2.00
1.01
1.02
1.04
3.00
3.04
3.03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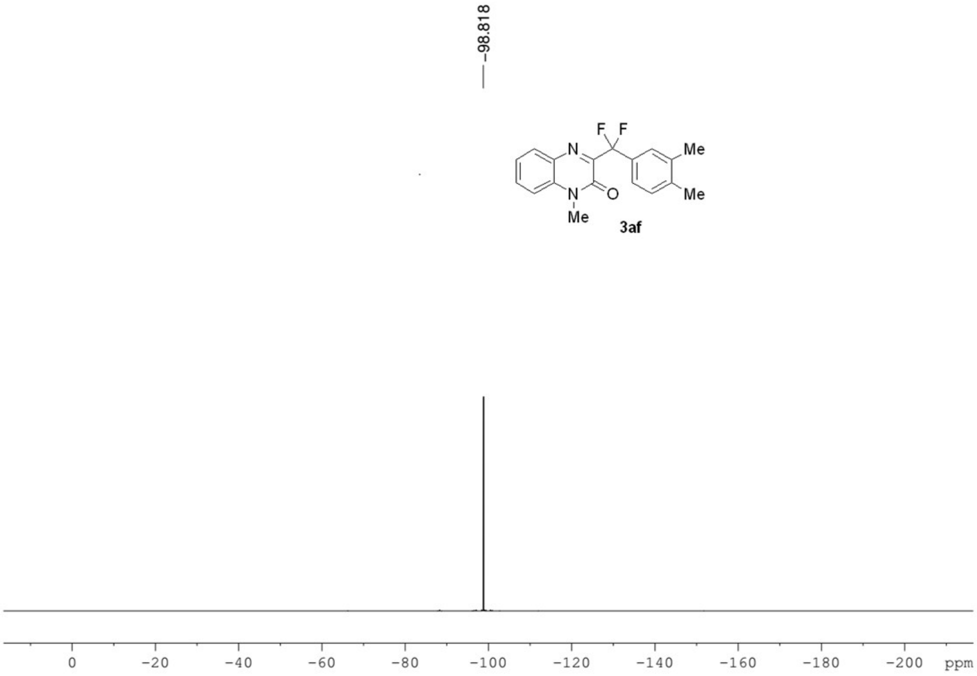
150.766
150.578
150.390
138.892
136.523
134.077
132.393
132.219
132.025
131.294
131.180
129.424
126.680
126.644
126.607
123.922
123.271
123.234
123.197
119.028
117.392
115.759
113.677
77.212
77.000
76.787
28.786
19.714
19.559
F
F
N
N
O
Me
Me
Me
3af
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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F
N
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O
Me
Me
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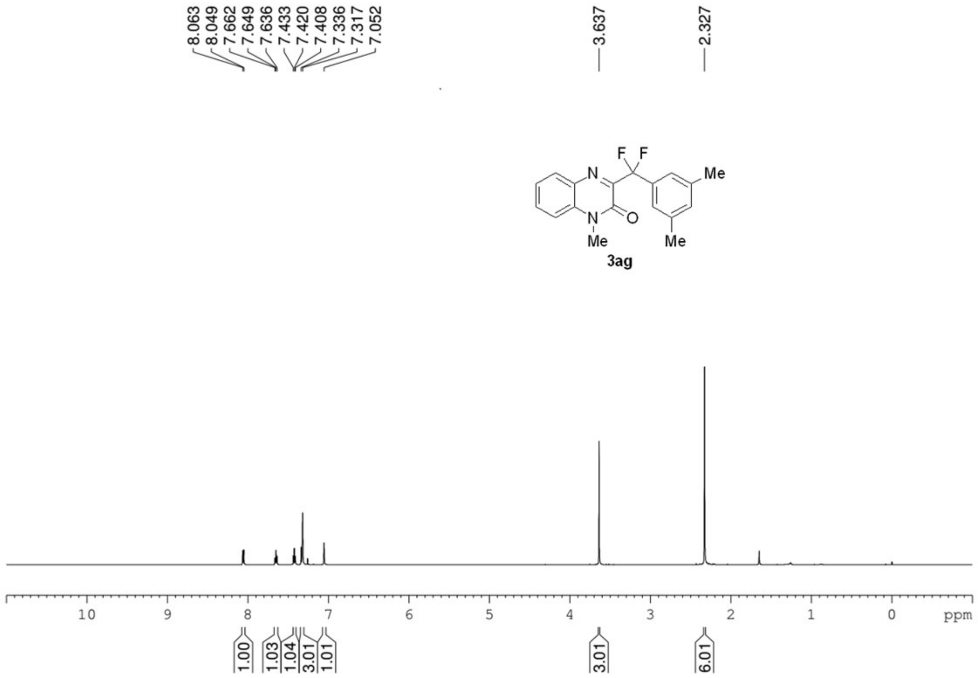
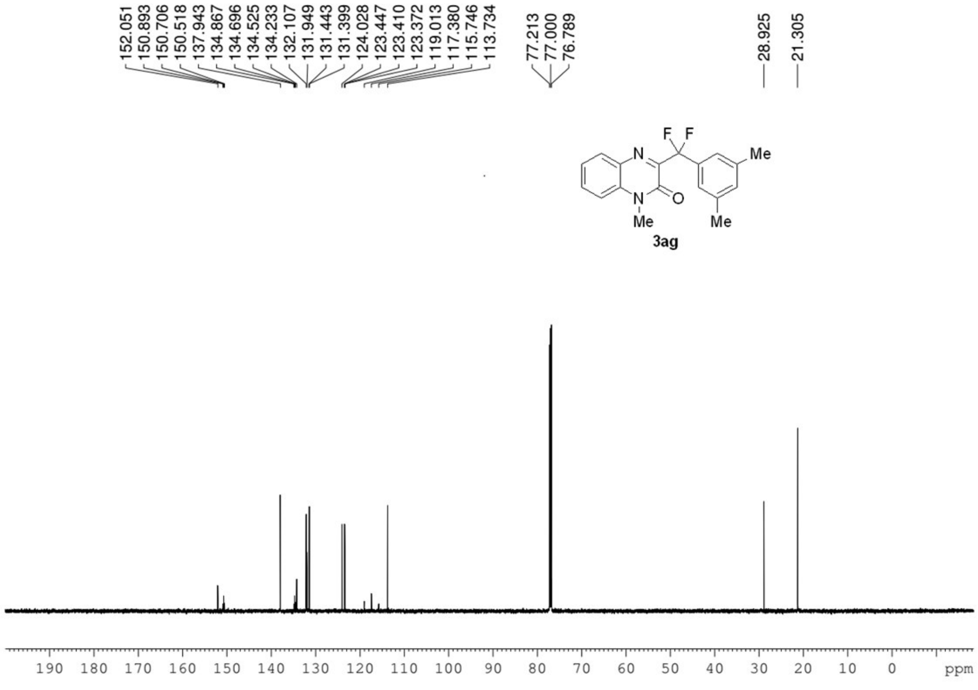
-180
-200
ppm


8.063
8.049
7.662
7.649
7.636
7.433
7.420
7.408
7.336
7.317
7.052
3.637
2.327
F
F
N
N
Me
O
Me
Me
3ag
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.03
1.04
3.01
1.01
3.01
6.01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150.893
150.706
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132.107
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131.443
131.399
124.028
123.447
123.410
123.372
119.013
117.380
115.746
113.734
77.213
77.000
76.789
28.925
21.305
F
F
N
N
Me
O
Me
Me
3ag
190
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170
160
150
140
130
120
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80
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50
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20
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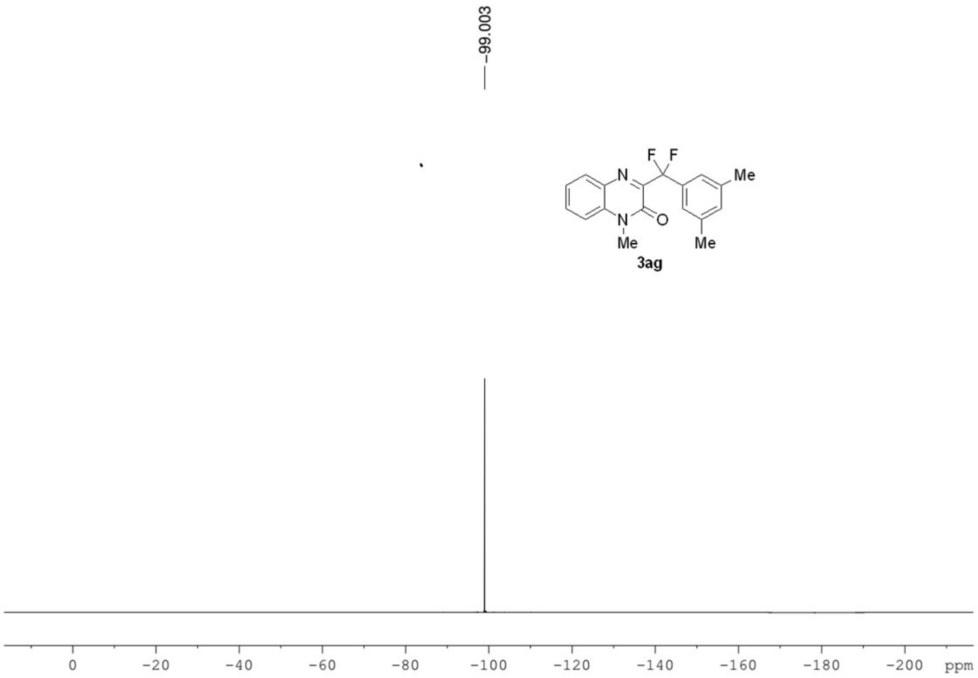
0
ppm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F
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N
N
O
Me
Me
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0
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−80
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−120
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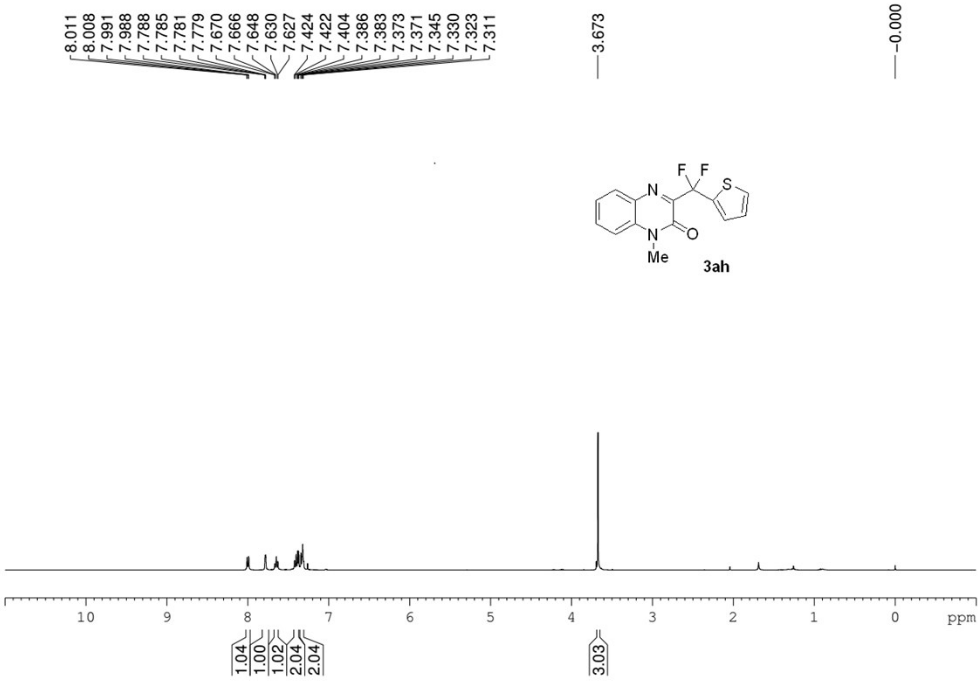
−180
−200
ppm


8.011
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7.988
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7.779
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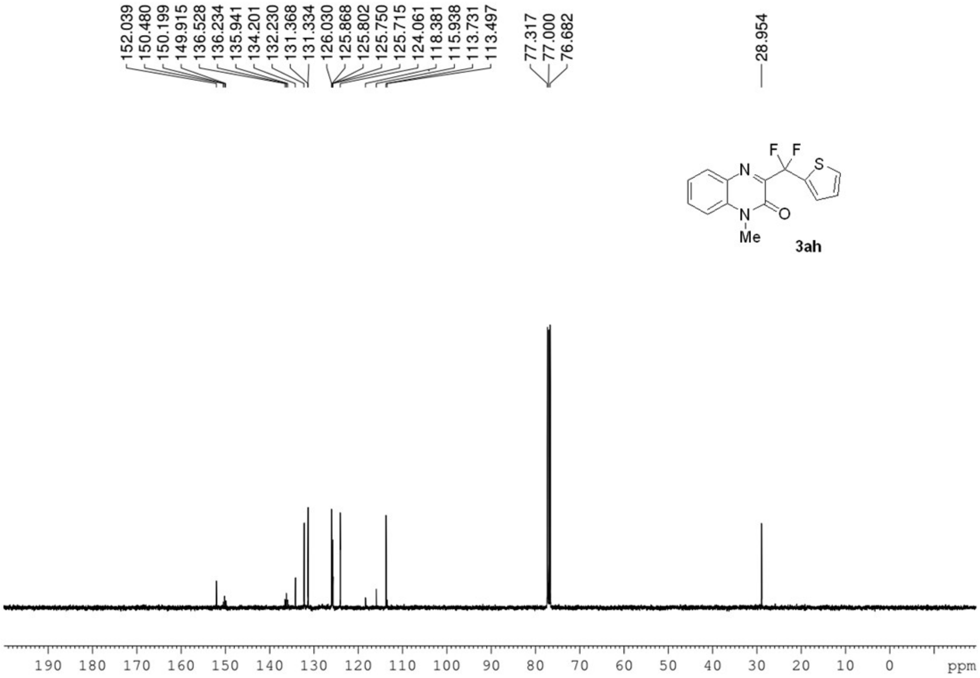
7.666
7.648
7.630
7.627
7.424
7.422
7.404
7.386
7.383
7.373
7.371
7.345
7.330
7.323
7.311
3.673
-0.000
F
F
N
S
N
O
Me
3ah
10
9
8
7
6
5
4
3
2
1
0
ppm
1.04
1.00
1.02
2.04
2.04
3.03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136.234
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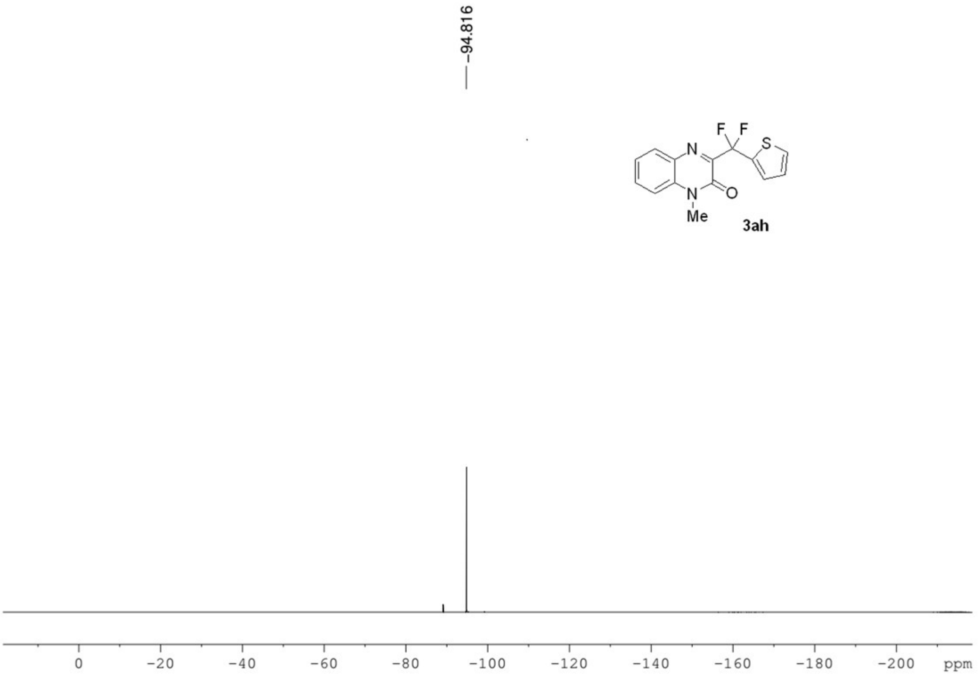
134.201
132.230
131.368
131.334
126.030
125.868
125.802
125.750
125.715
124.061
118.381
115.938
113.731
113.497
77.317
77.000
76.682
28.954
F
F
N
S
N
O
Me
3ah
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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S
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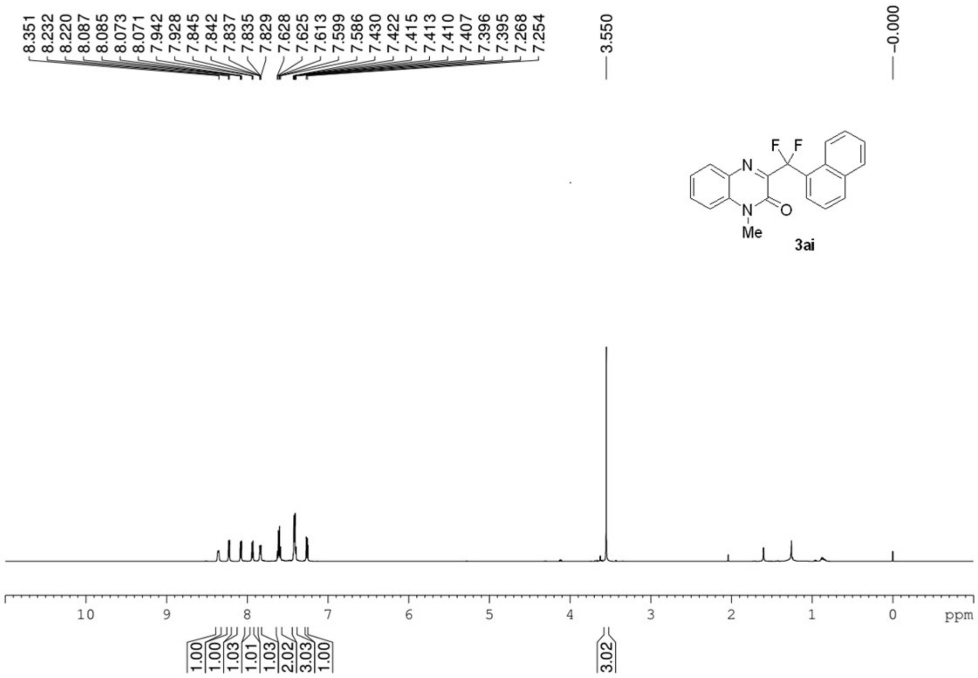
-180
-200
ppm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7.942
7.928
7.845
7.842
7.837
7.835
7.829
7.628
7.625
7.613
7.599
7.586
7.430
7.422
7.415
7.413
7.410
7.407
7.396
7.395
7.268
7.254
3.550
0.000
F
F
N
N
O
Me
3ai
10
9
8
7
6
5
4
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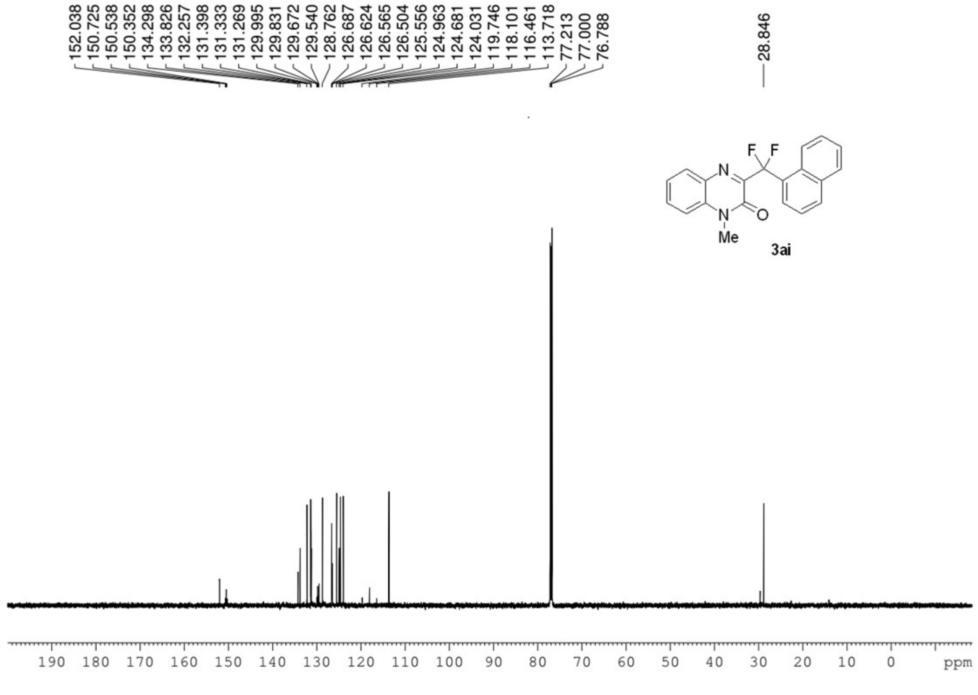
ppm
1.00
1.00
1.03
1.01
1.03
2.02
3.03
1.00
3.02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129.672
129.540
128.762
126.687
126.624
126.565
126.504
125.556
124.963
124.681
124.031
119.746
118.101
116.461
113.718
77.213
77.000
76.788
28.846
F
F
N
N
O
Me
3ai
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130
120
110
100
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60
50
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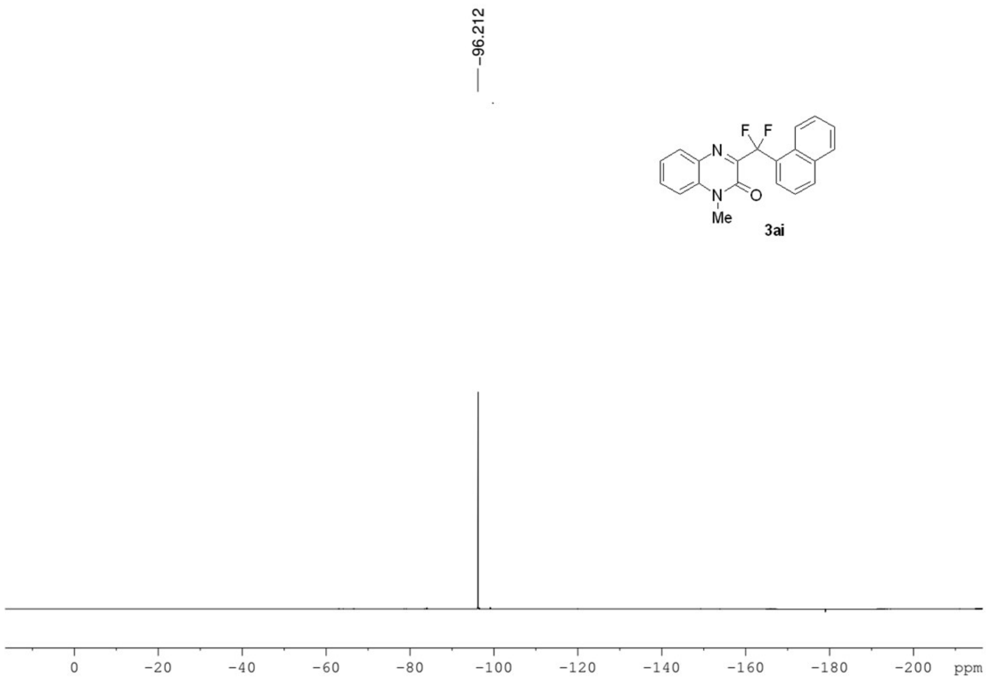
ppm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F
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O
Me
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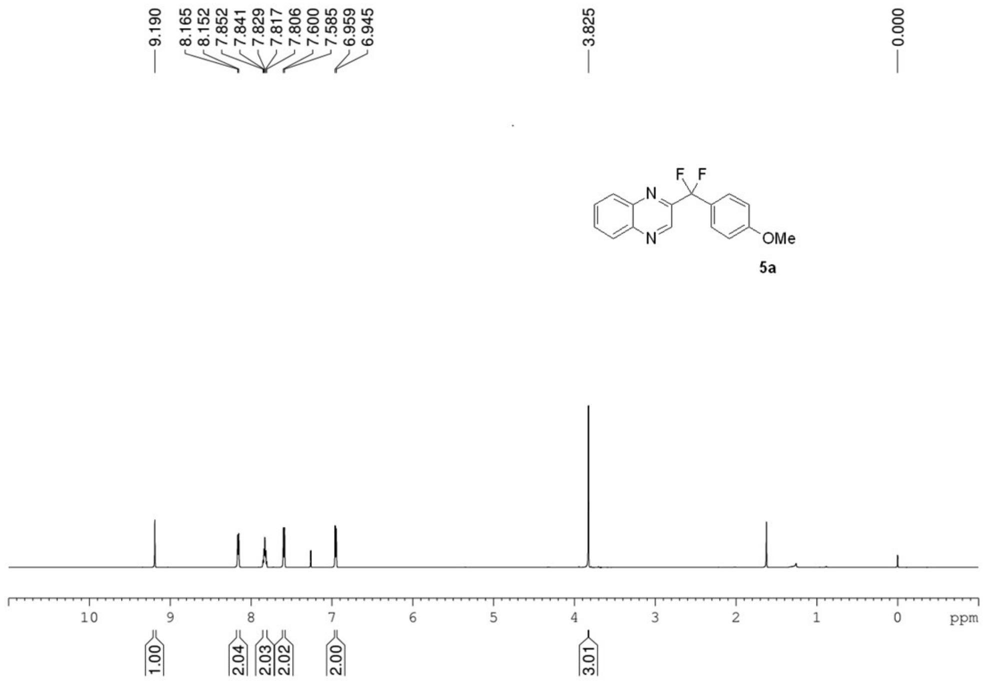
-180
-200
ppm

3ai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7.841
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7.817
7.806
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7.585
6.959
6.945
3.825
0.000
F
F
N
N
OMe
10
9
8
7
6
5
4
3
2
1
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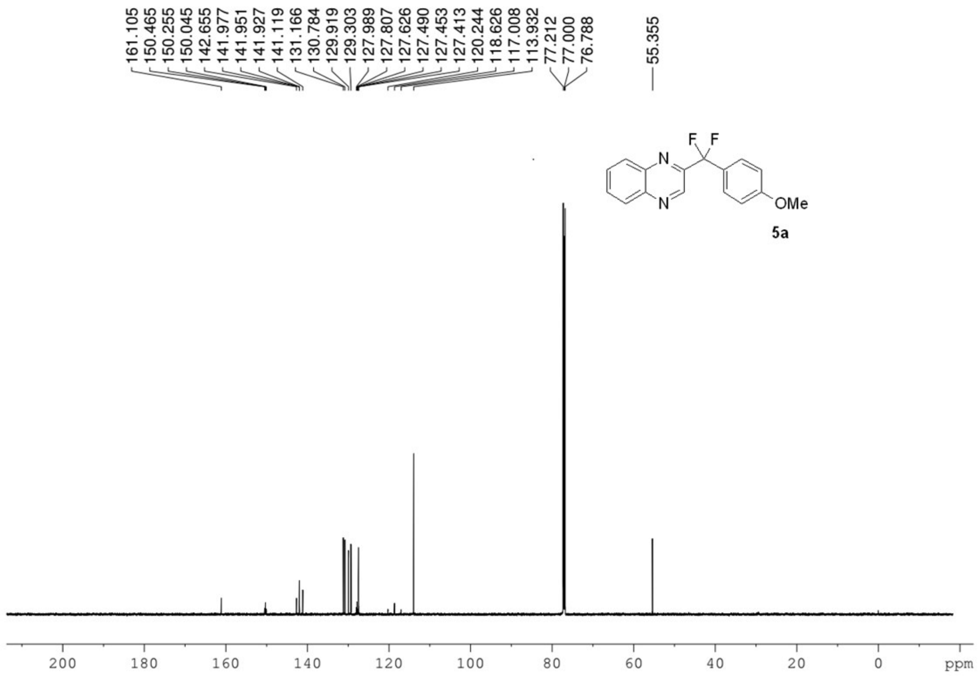
ppm
1.00
2.04
2.03
2.02
2.00
3.01

5a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141.927
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131.166
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129.919
129.303
127.989
127.807
127.626
127.490
127.453
127.413
120.244
118.626
117.008
113.932
77.212
77.000
76.788
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F F
N
N
OMe
5a
200
180
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120
100
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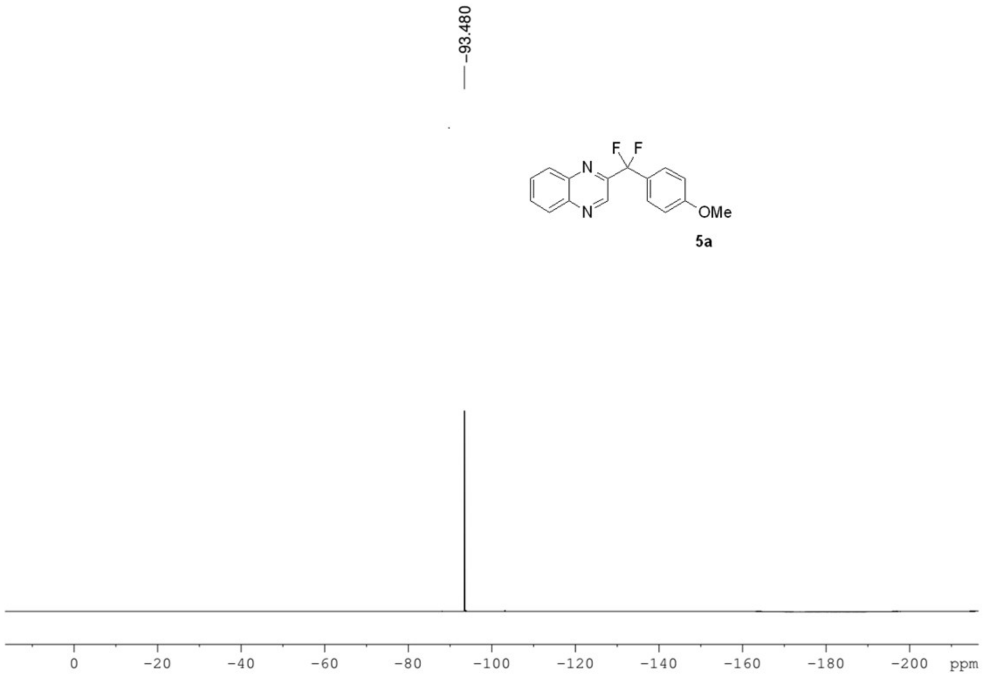
60
40
20
0
ppm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F F
N
N
OMe
5a
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm