t-BuOK-Mediated Oxidative Dehydrogenative C(sp^3)-H Arylation of Alkylazaarenes with Nitroarenes

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Supporting Information

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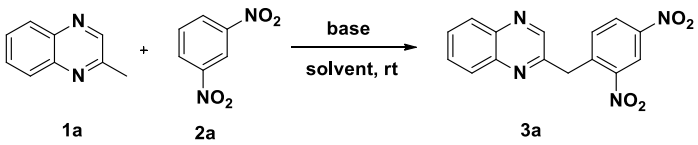
1. Control Experiments[a]



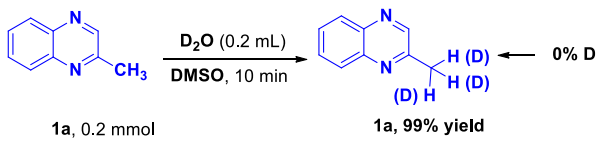
entry	base	solvent	additive	time (h)	yield (%)[b]
1	*t*-BuOK	Dioxane	--	12	NR
2	*t*-BuOK	Dioxane/ DMSO = 3:2	--	12	60
3	*t*-BuOK	Dioxane	DMSO [30 equiv.]	12	53
4	*t*-BuOK	Dioxane	DMSO [20 equiv.]	12	47
5	*t*-BuOK	Dioxane	DMSO [10 equiv.]	12	8
6[c]	*t*-BuOK	DMSO	--	12	65

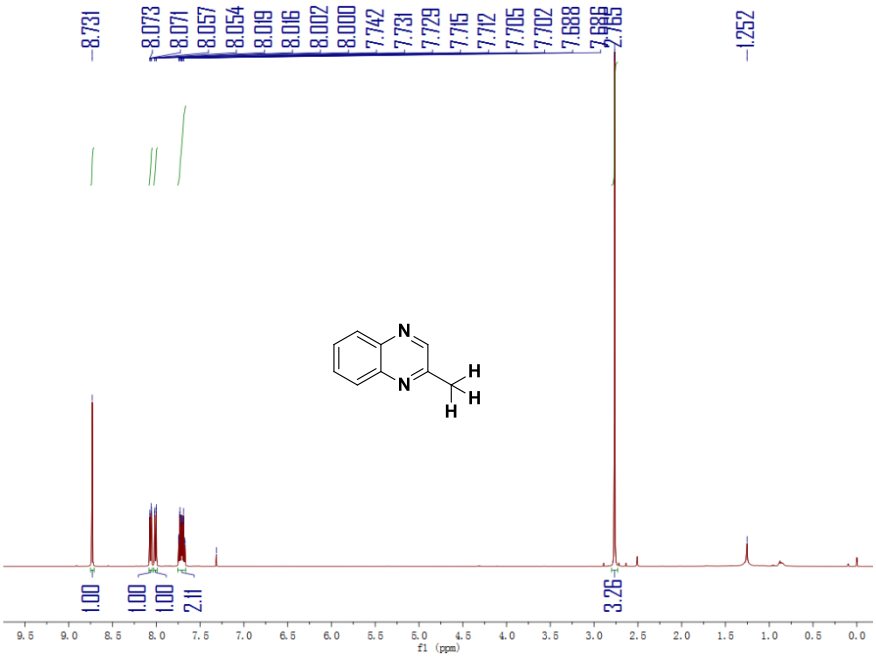
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), *t*-BuOK (2.0 equiv.) in 2 mL solvent at room temperature under air. [b] Isolated yield after column chromatography. [c] N_2 atmosphere.

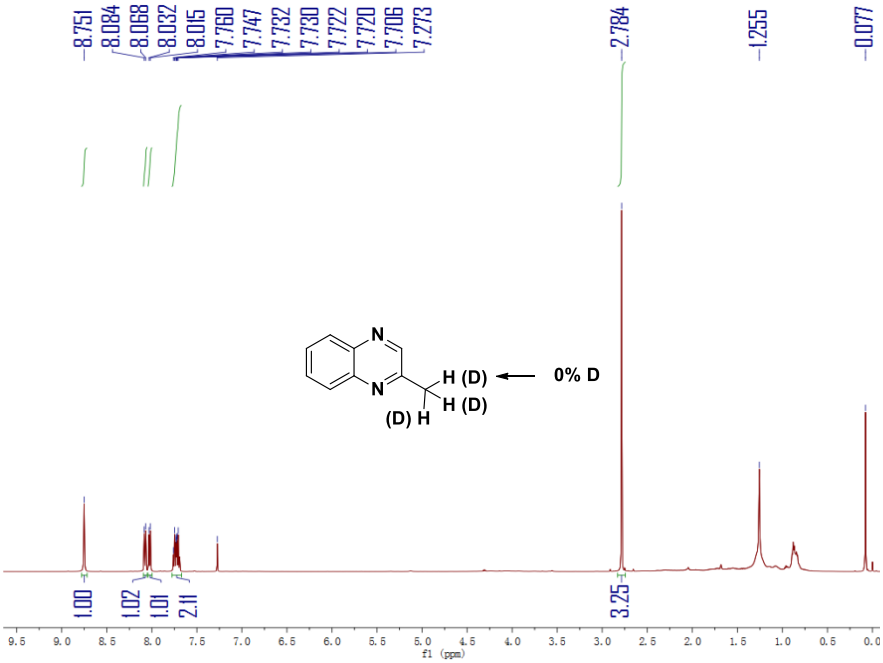
2. Deuterium Experiments

To investigate the mechanism of this reaction, deuterium experiments and a kinetic isotope effect (KIE) study were conducted.

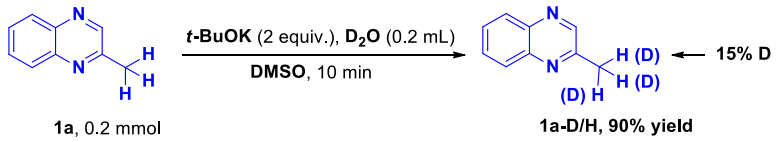
a.





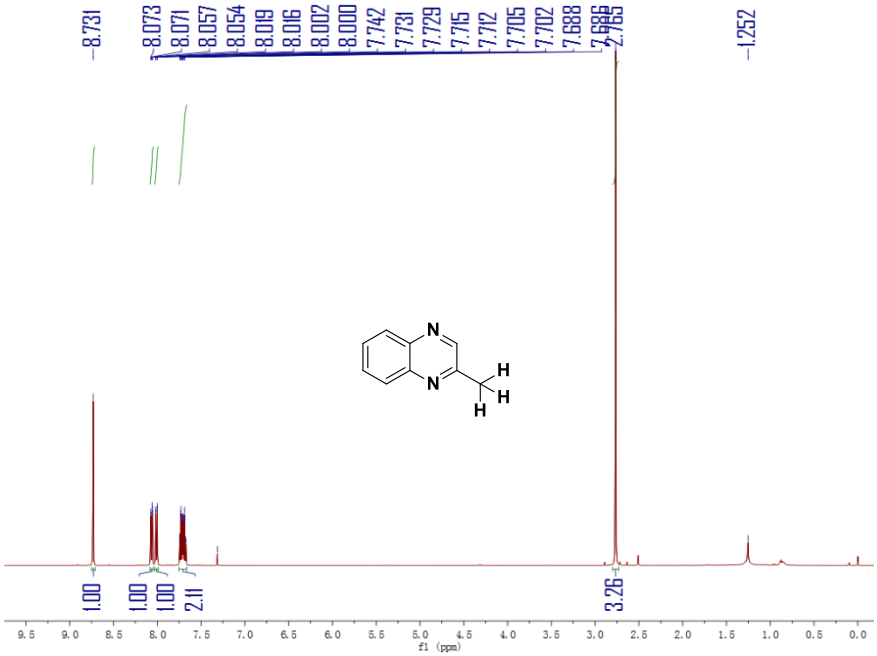


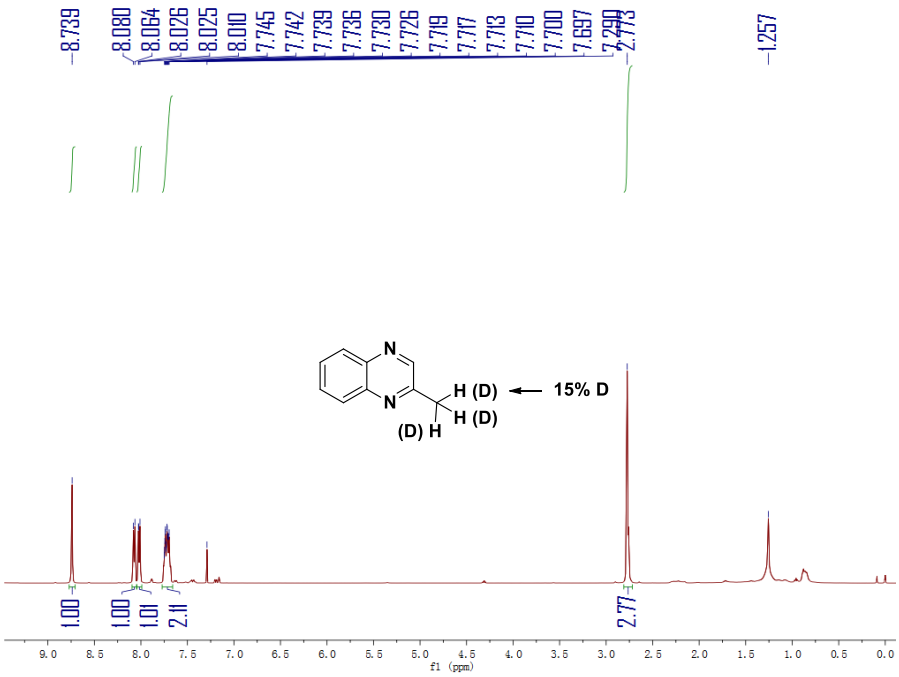
b.



1a, 0.2 mmol

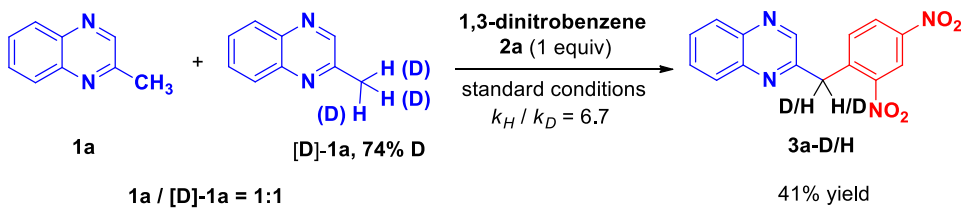
1a-D/H, 90% yield

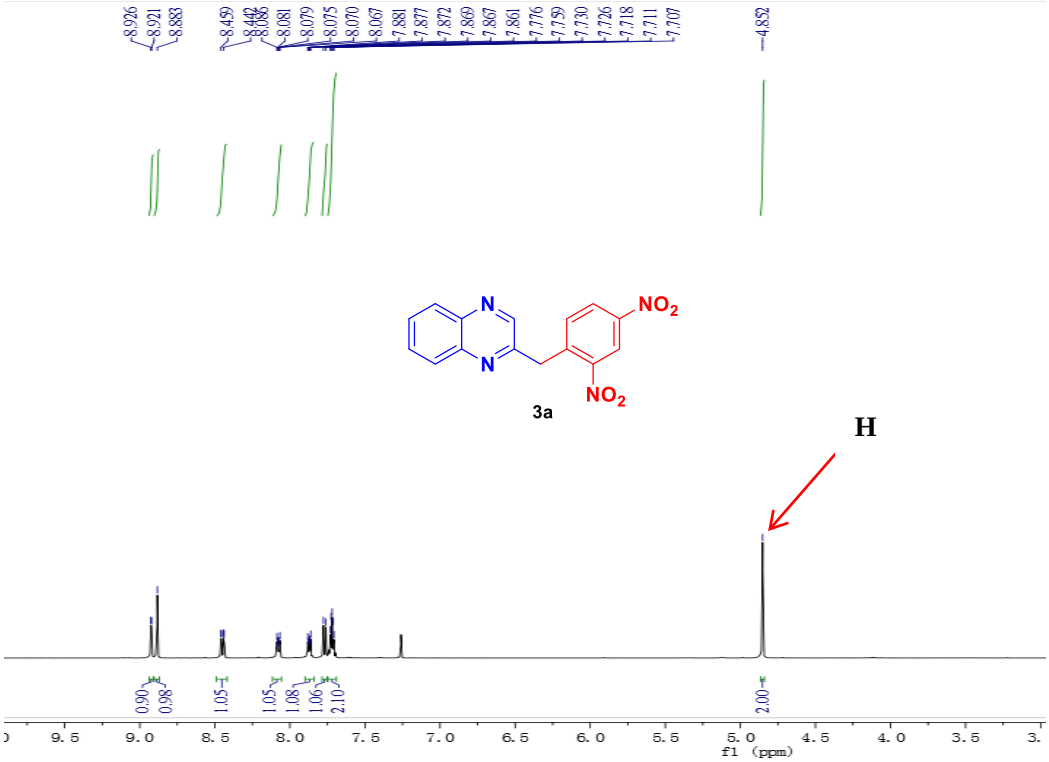




c. KIE Experiment

The deuterium kinetic isotopic effects were determined to be 6.7, thus indicates that the cleavage of C−H bond in methyl group might be involved in the rate-determining step.

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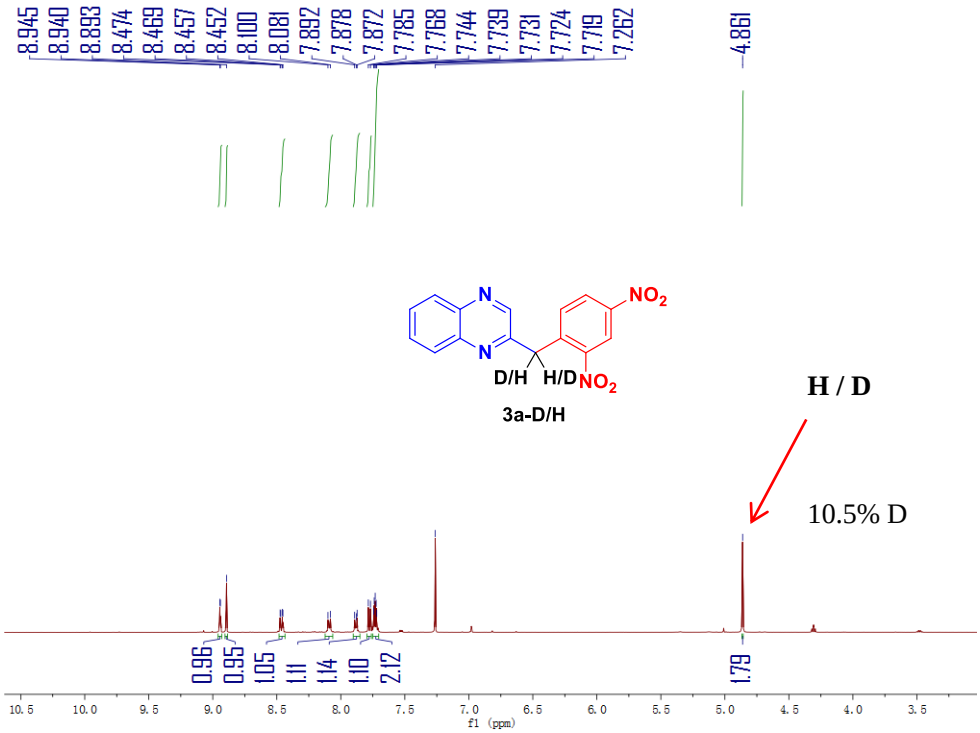
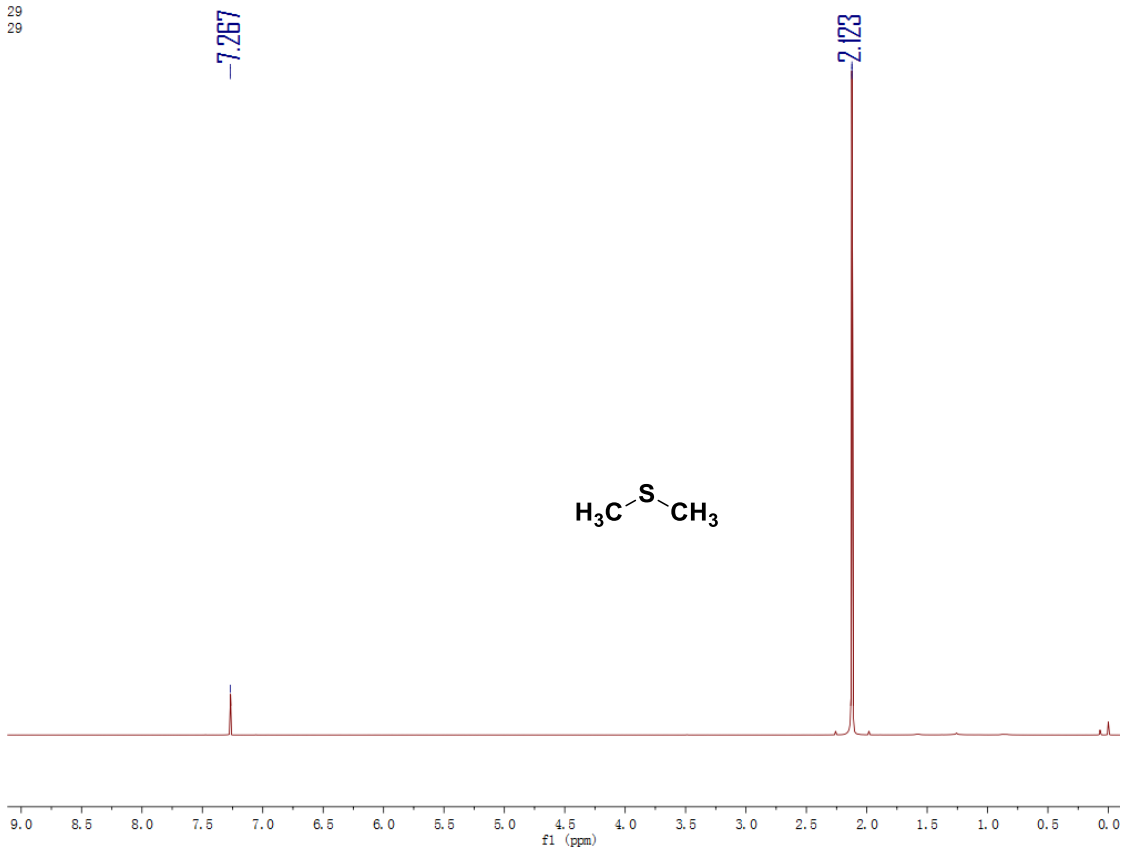
8.921
8.883
8.459
8.081
8.079
8.075
8.070
8.067
7.881
7.877
7.872
7.869
7.867
7.861
7.776
7.759
7.730
7.726
7.718
7.711
7.707
4.852
N
N
NO2
NO2
3a
H
0.90
0.98
1.05
1.05
1.08
1.06
2.10
2.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
f1 (ppm)

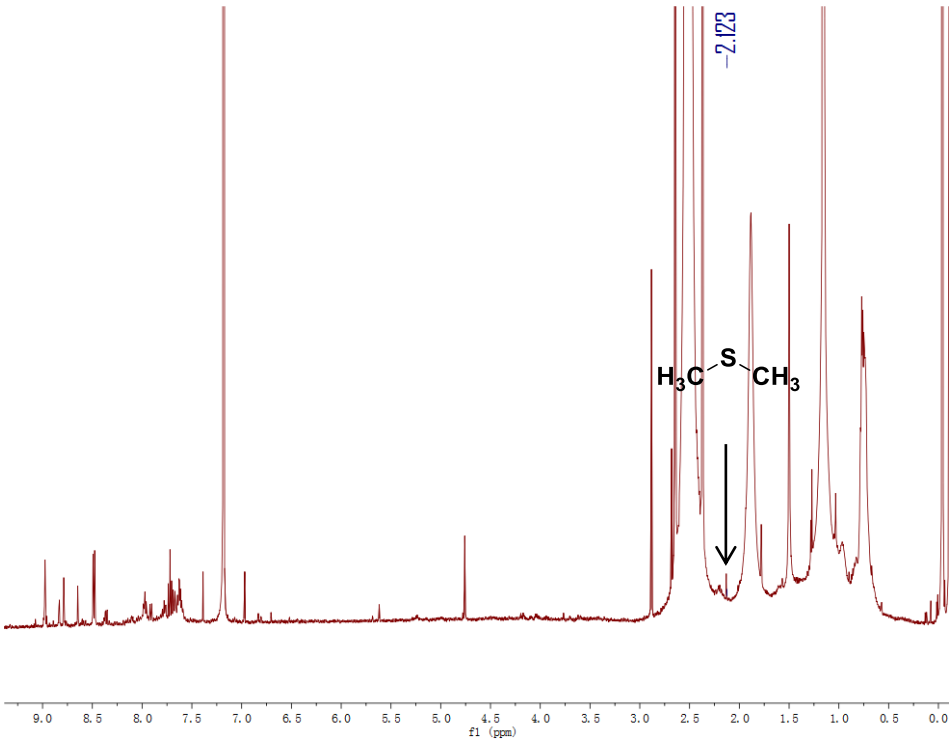

8.945
8.940
8.893
8.474
8.469
8.457
8.452
8.100
8.081
7.892
7.878
7.872
7.785
7.768
7.744
7.739
7.731
7.724
7.719
7.262
4.861
N
N
NO2
NO2
D/H
H/D
3a-D/H
H / D
10.5% D
0.96
0.95
1.05
1.11
1.14
1.10
2.12
1.79
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
f1 (ppm)

3. Detection of Dimethyl Sulfide

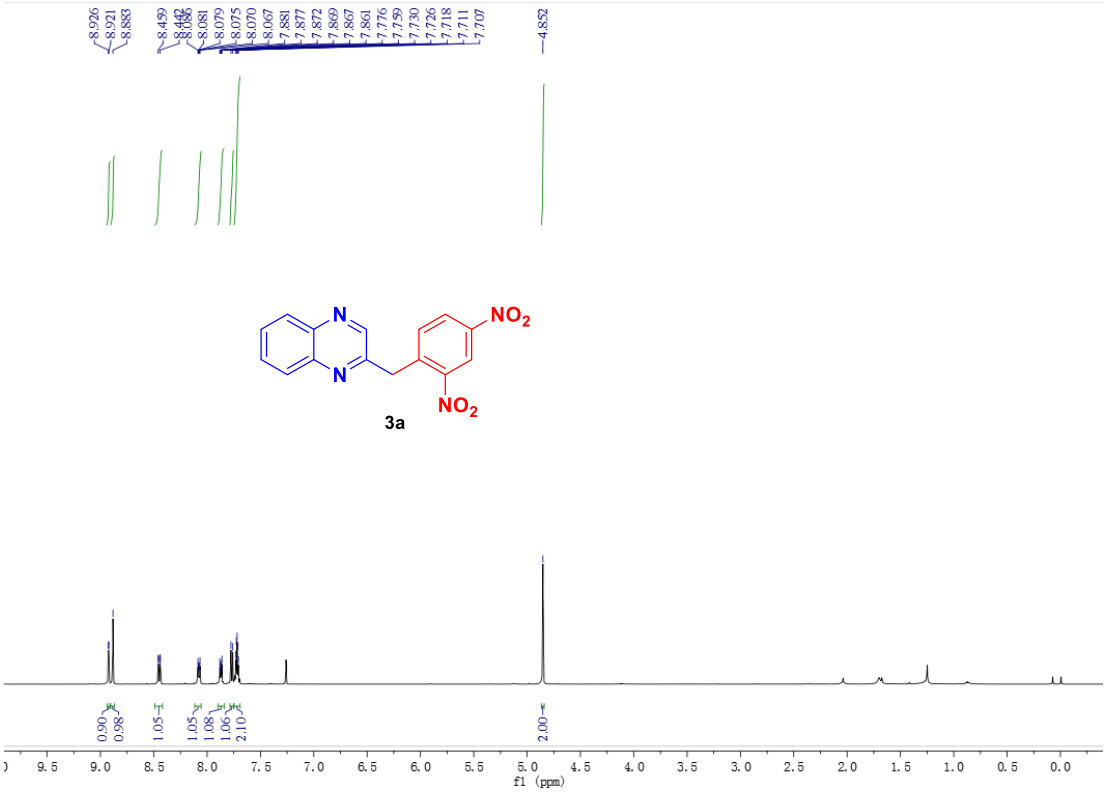
^{1}H NMR of dimethyl sulfide

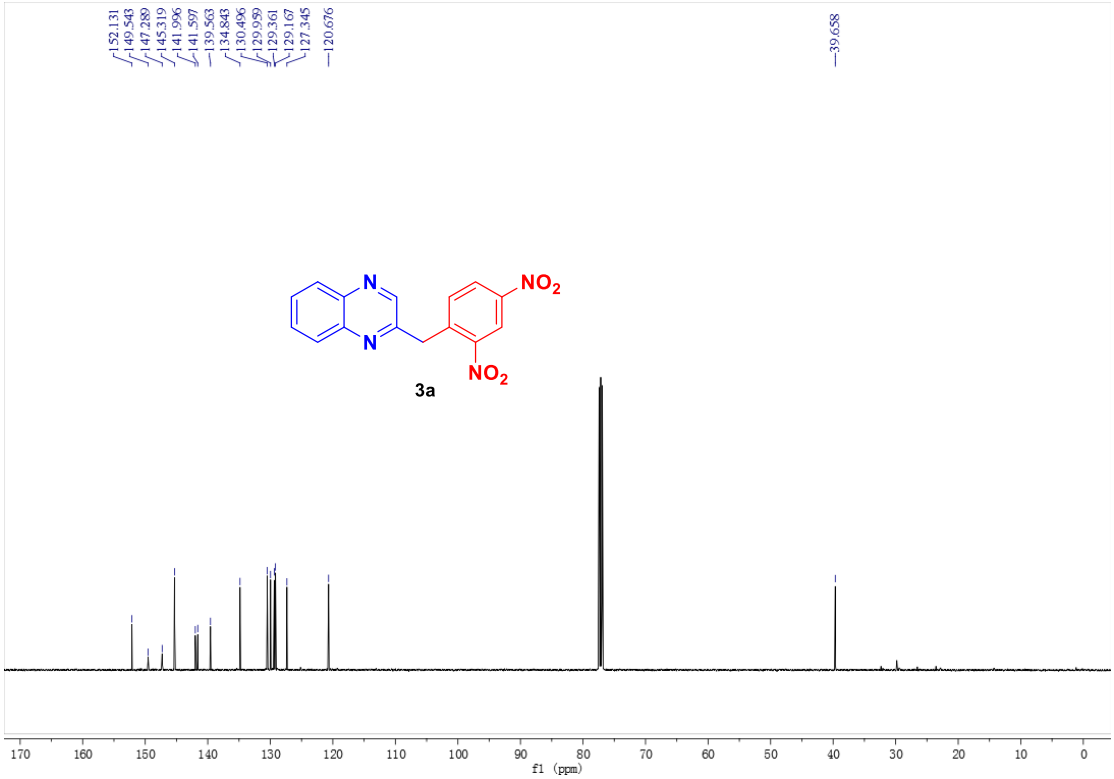


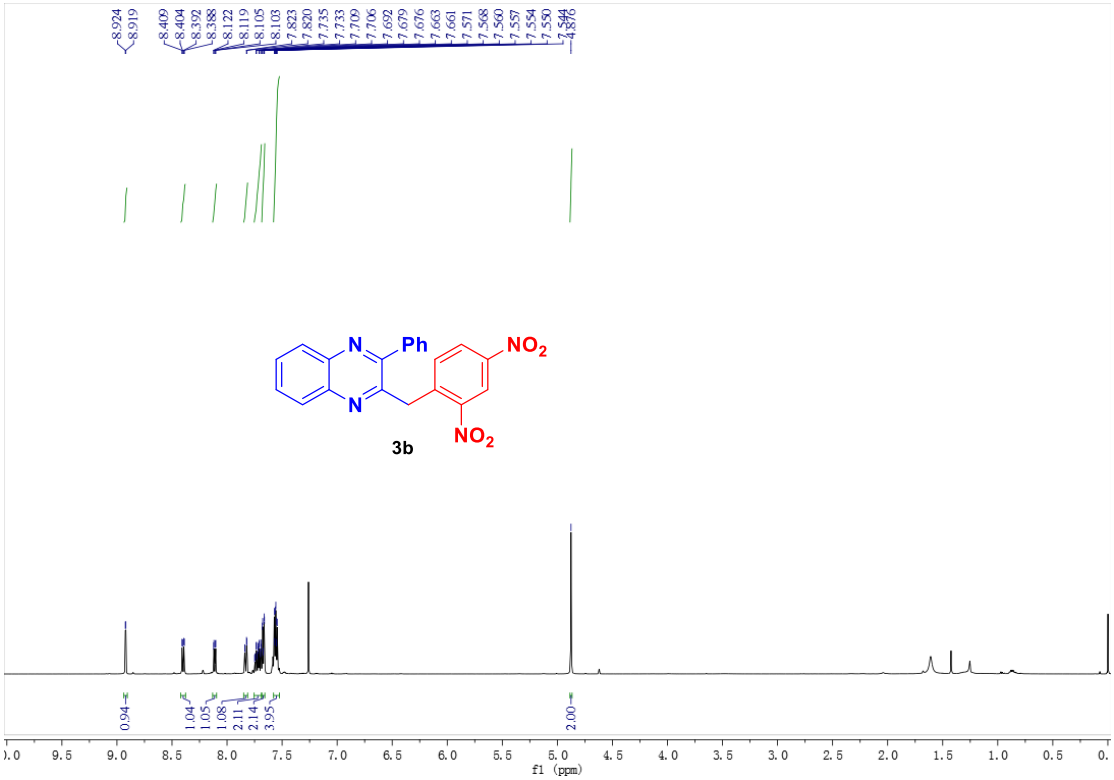
^{1}H NMR of the crude reaction mixture (peak at 2.12 ppm belongs to dimethyl sulfide)



4. ^{1}H NMR, ^{13}C NMR Spectra



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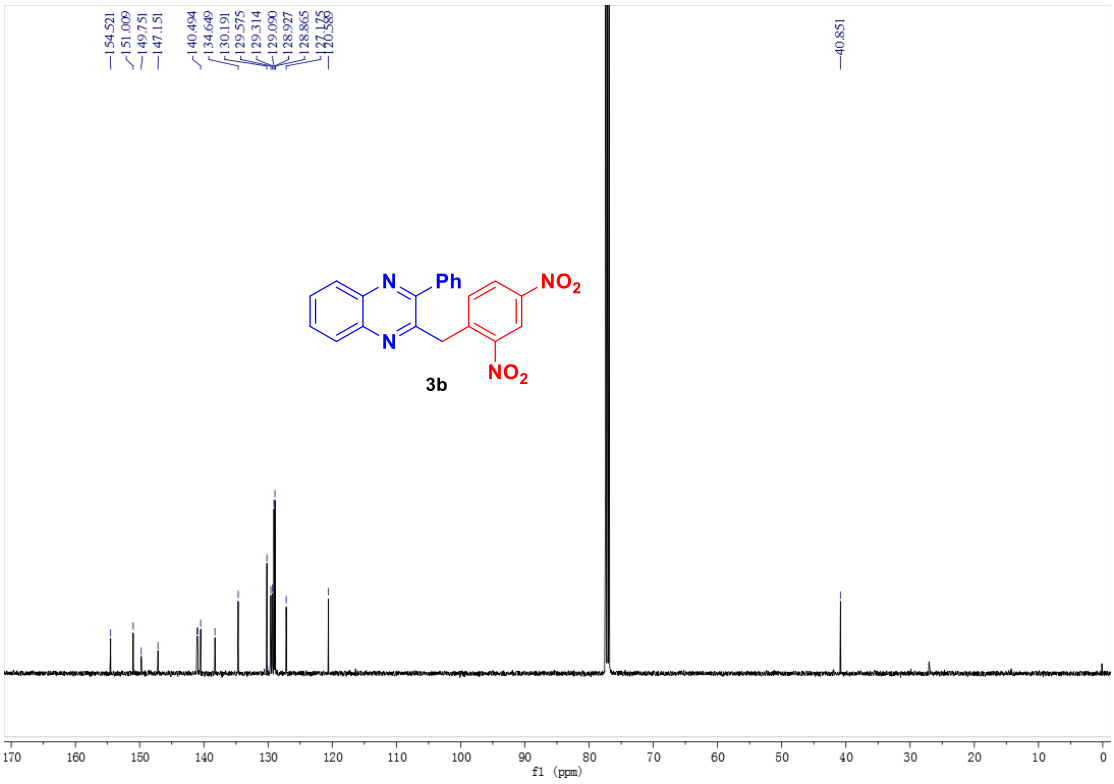
8.919
8.409
8.404
8.392
8.388
8.122
8.119
8.105
8.103
7.823
7.820
7.735
7.733
7.709
7.706
7.692
7.679
7.676
7.663
7.661
7.571
7.568
7.560
7.557
7.554
7.550
7.544
4.876
N
Ph
NO2
N
NO2
3b
0.94
1.04
1.05
1.08
2.11
2.14
3.95
2.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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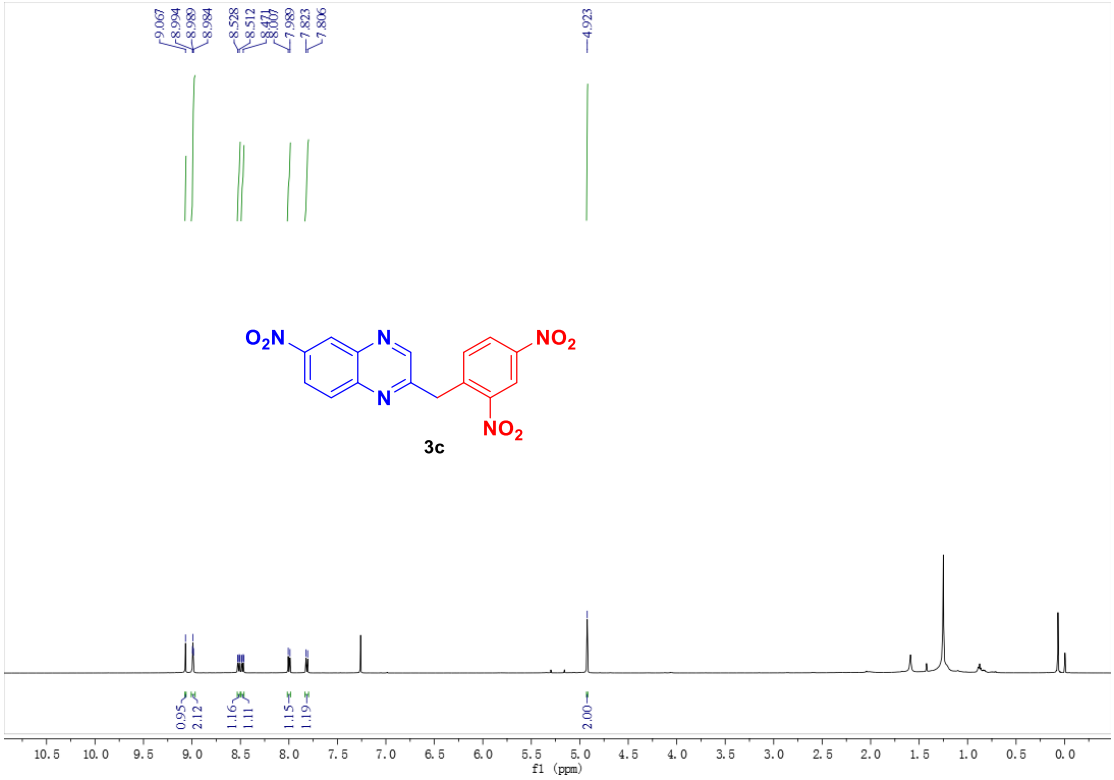
151.009
149.751
147.151
140.494
134.649
130.191
129.575
129.314
129.090
128.927
128.865
121.175
120.589
40.851
N
Ph
NO2
N
NO2
3b
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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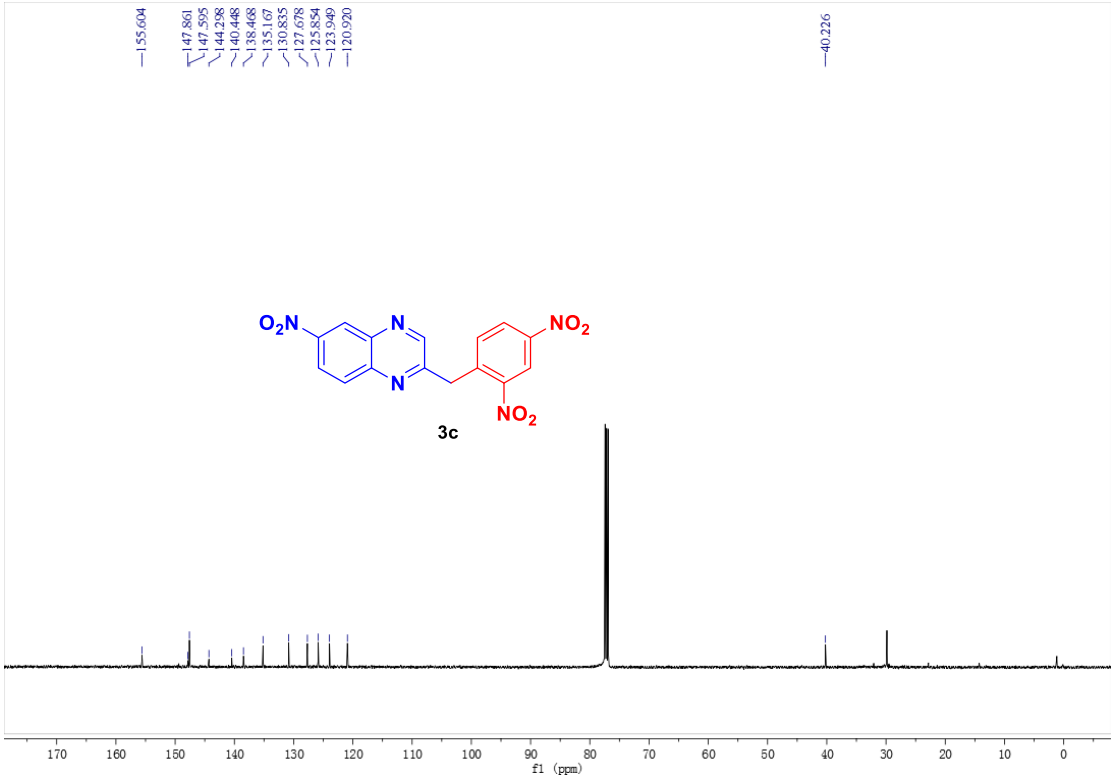
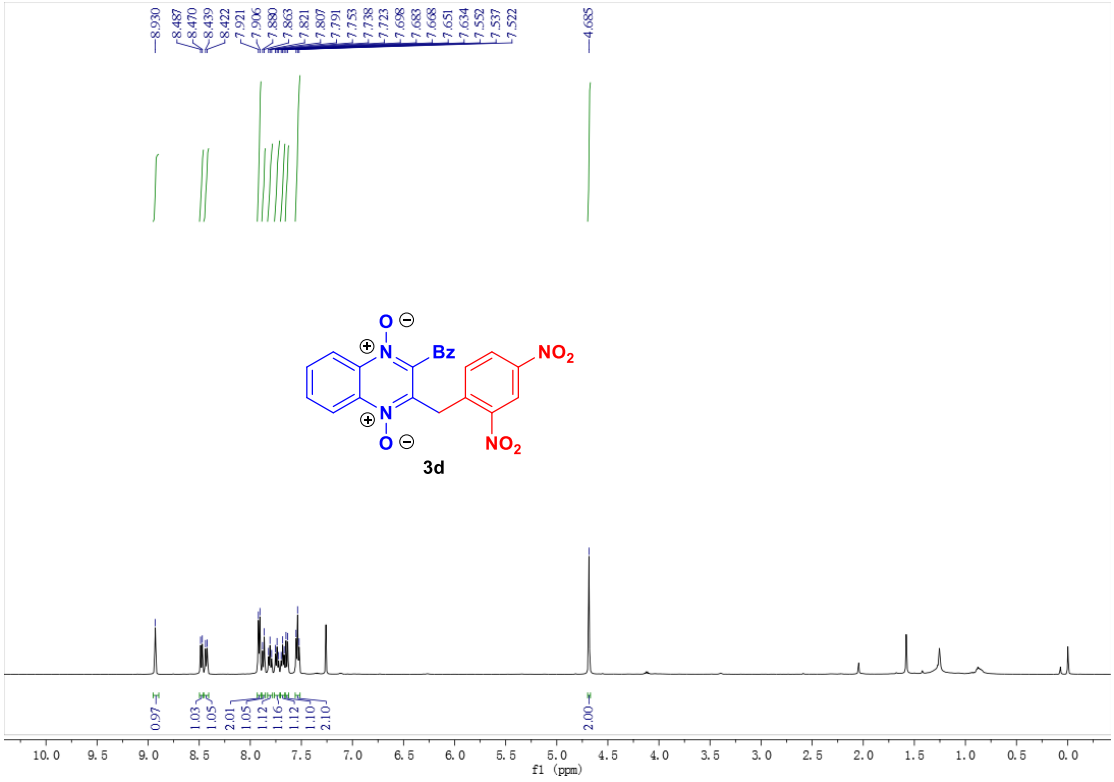
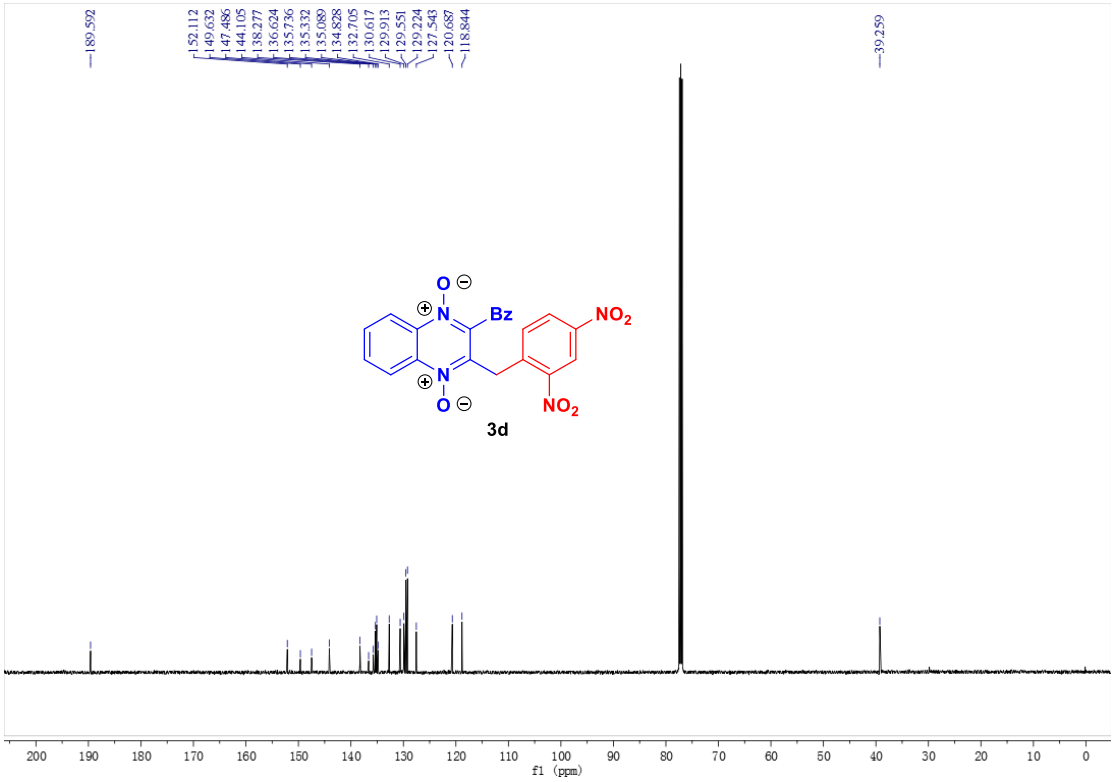
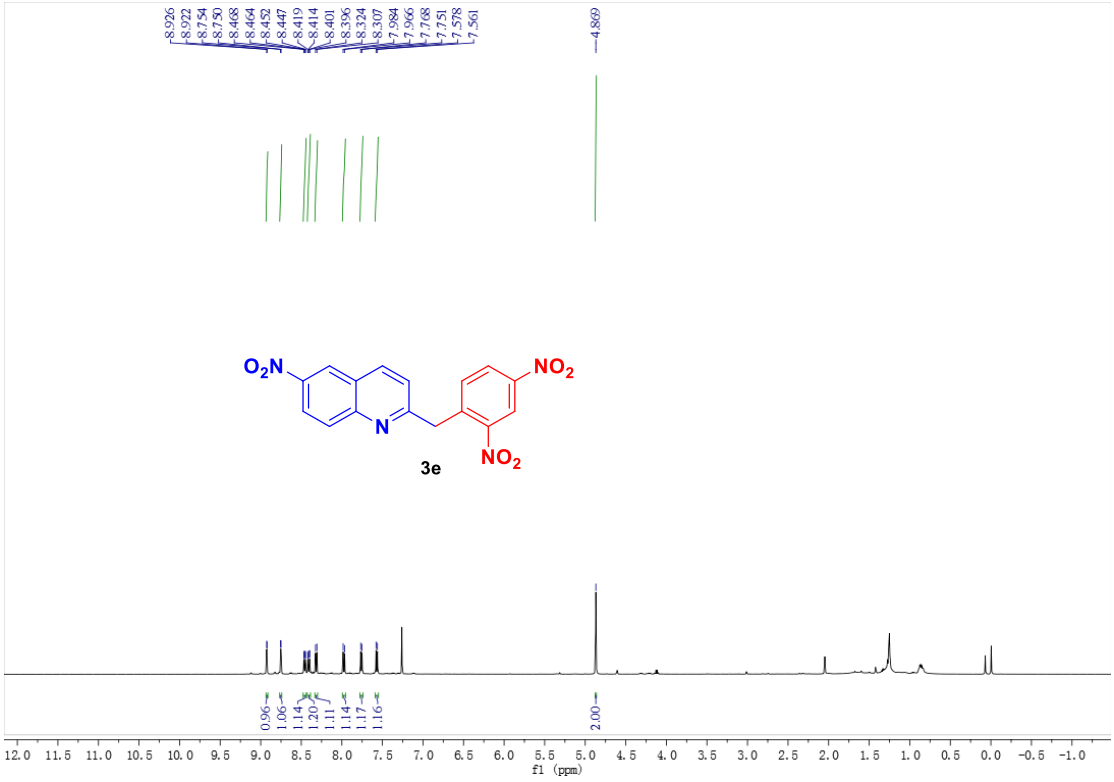
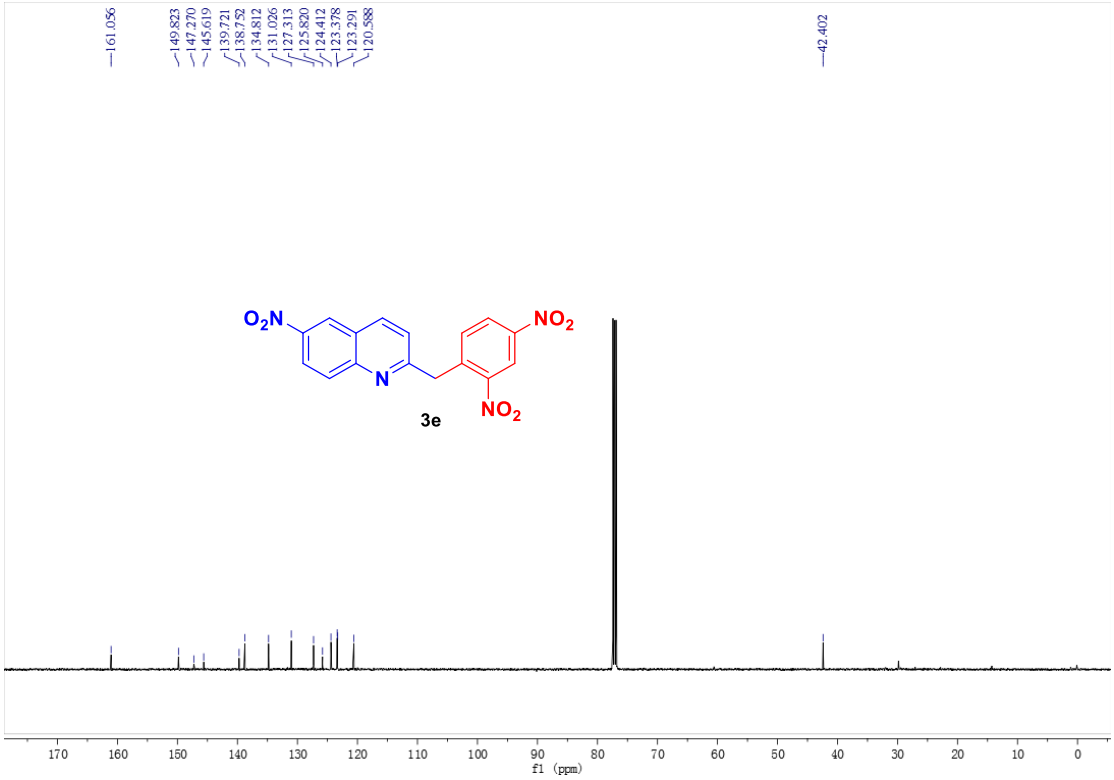
8.989
8.984
8.528
8.512
8.471
8.007
7.989
7.823
7.806
4.923
O2N
N
N
NO2
NO2
3c
0.95
2.12
1.16
1.11
1.15
1.19
2.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


155.604
147.861
147.595
144.258
140.448
138.468
135.167
130.835
127.678
125.854
123.949
120.920
40.226
O2N
N
N
NO2
NO2
3c
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.930
8.487
8.470
8.439
8.422
7.921
7.906
7.880
7.863
7.821
7.807
7.791
7.753
7.738
7.723
7.698
7.683
7.668
7.651
7.634
7.552
7.537
7.522
4.685
Bz
NO2
NO2
3d
0.97
1.03
1.05
2.01
1.05
1.12
1.16
1.12
1.10
2.10
2.00
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)


189.592
152.112
149.632
147.486
144.105
138.277
136.624
135.736
135.332
135.089
134.828
132.705
130.617
129.913
129.551
129.224
127.543
120.687
118.844
39.259
Bz
NO2
NO2
3d
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.926
8.922
8.754
8.750
8.468
8.464
8.452
8.447
8.419
8.414
8.401
8.396
8.324
8.307
7.984
7.966
7.768
7.751
7.578
7.561
4.869
O2N
NO2
NO2
N
3e
0.96
1.06
1.14
1.20
1.11
1.14
1.17
1.16
2.00
12.0 11.5 11.0 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 -0.5 -1.0
f1 (ppm)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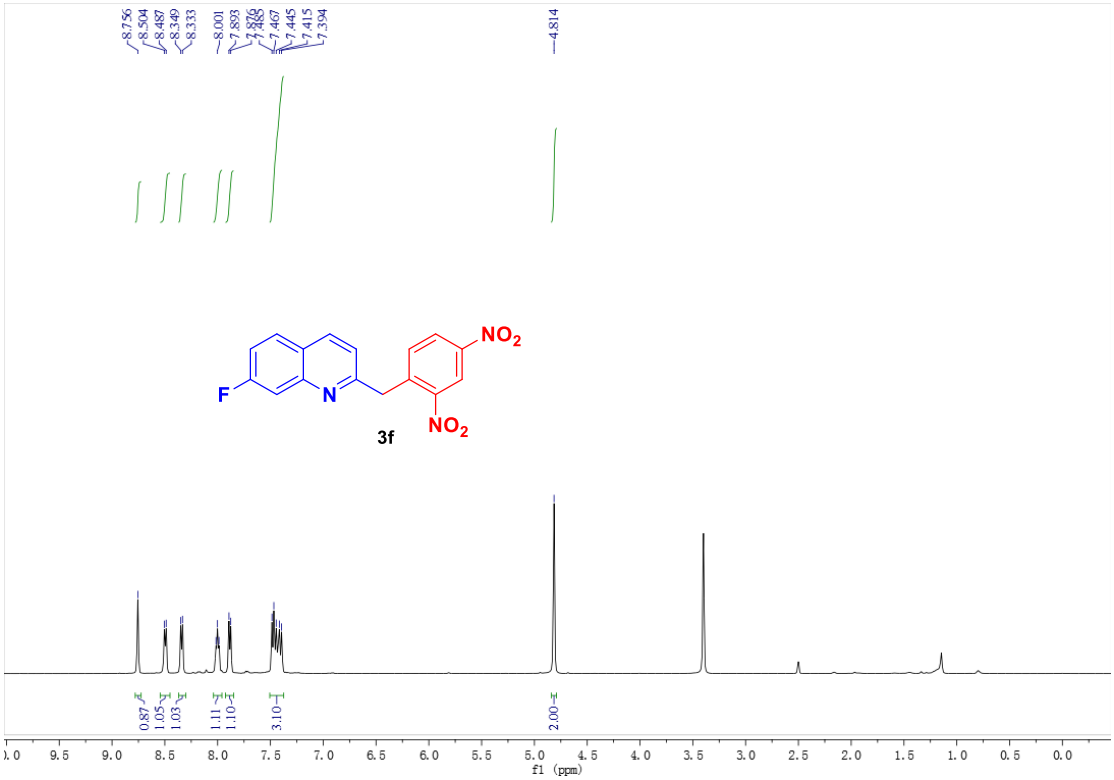
145.619
139.721
138.752
134.812
131.026
127.313
125.820
124.412
123.378
123.291
120.588
42.402
O2N
NO2
NO2
N
3e
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.487
8.349
8.333
8.001
7.893
7.876
7.865
7.467
7.445
7.415
7.394
4.814
NO2
F
N
NO2
3f
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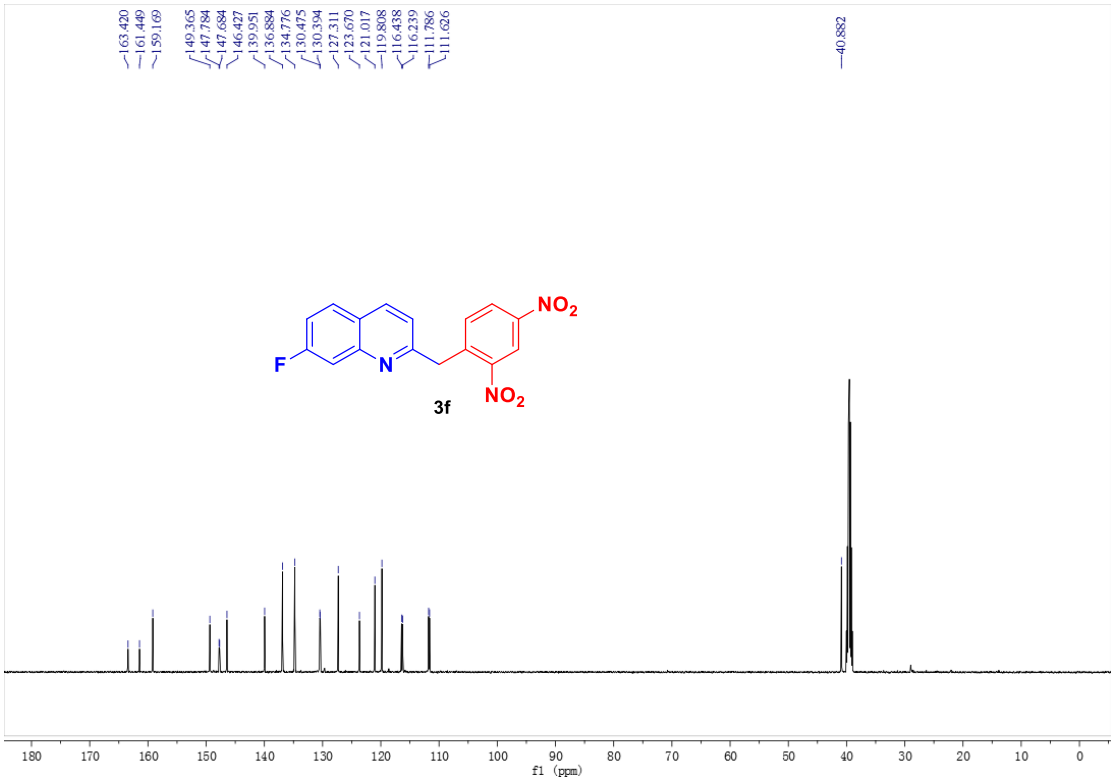
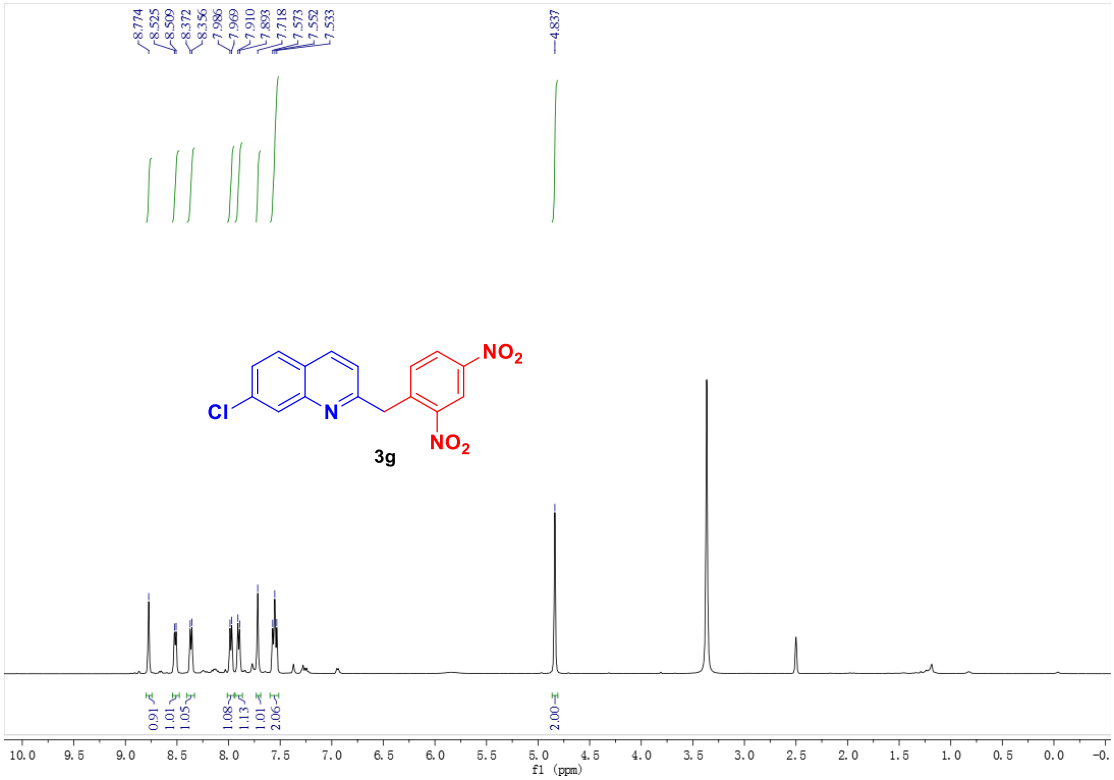
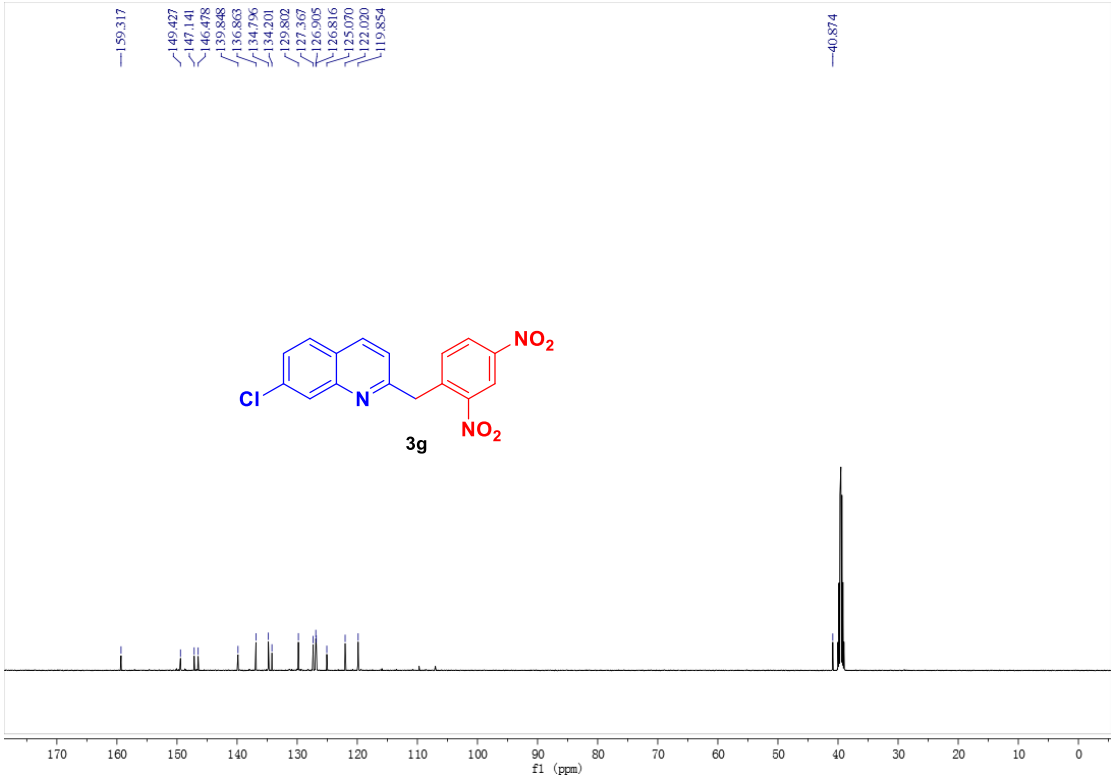
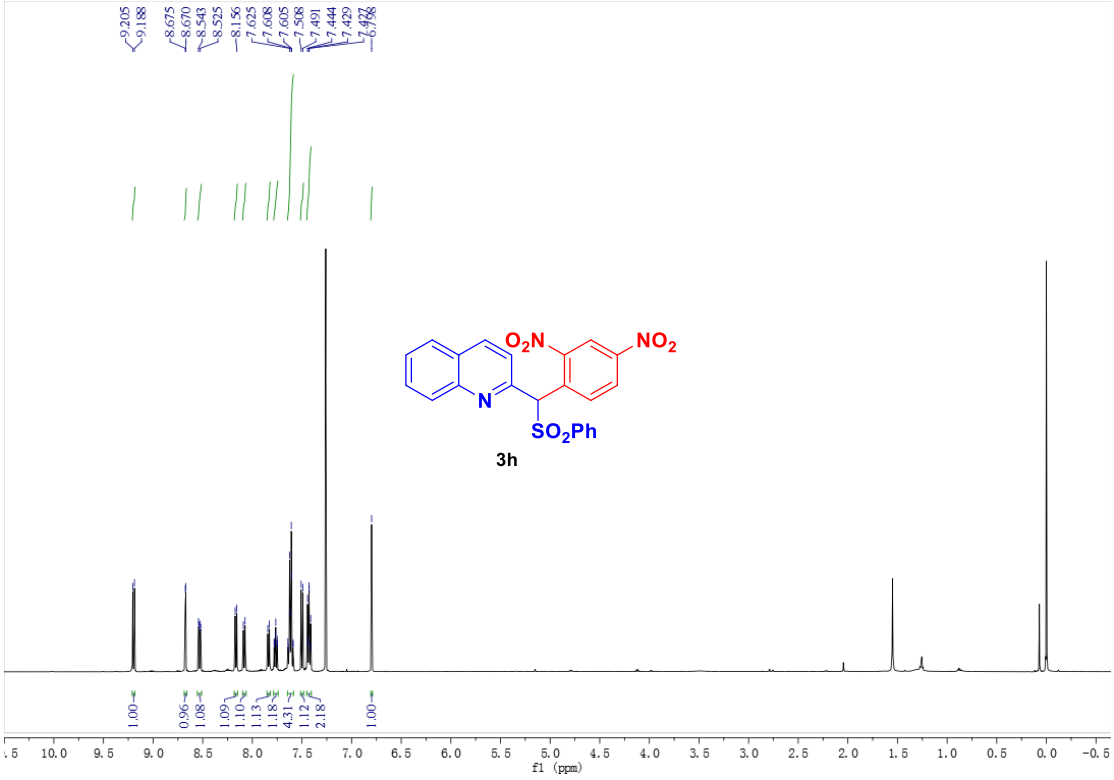
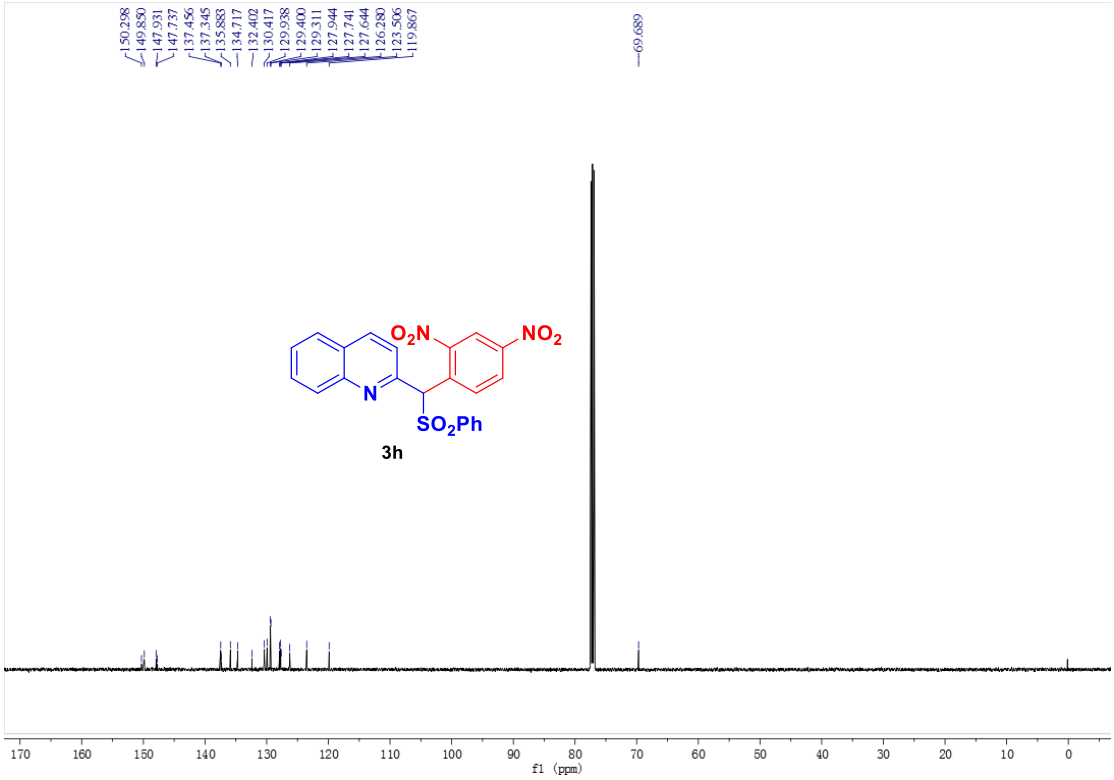
1.03
1.11
1.10
3.10
2.00
f1 (ppm)


163.420
161.449
159.169
149.365
147.784
147.684
146.427
139.951
136.884
134.776
130.475
130.394
127.311
123.670
121.017
119.808
116.438
116.239
111.786
111.626
40.882
NO2
F
N
NO2
3f
f1 (ppm)


8.774
8.525
8.509
8.372
8.356
7.986
7.969
7.910
7.893
7.718
7.573
7.552
7.533
4.837
Cl
N
NO2
NO2
3g
0.91
1.01
1.05
1.08
1.13
1.01
2.06
2.00
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 -0.
f1 (ppm)


159.317
149.427
147.141
146.478
139.848
136.863
134.796
134.201
129.802
127.367
126.905
126.816
125.070
122.020
119.854
40.874
Cl
N
NO2
NO2
3g
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


9.205
9.188
8.675
8.670
8.543
8.525
8.156
7.625
7.608
7.605
7.508
7.491
7.444
7.429
7.427
6.798
O2N
NO2
N
SO2Ph
3h
1.00
0.96
1.08
1.09
1.10
1.13
1.18
4.31
1.12
2.18
1.00
f1 (ppm)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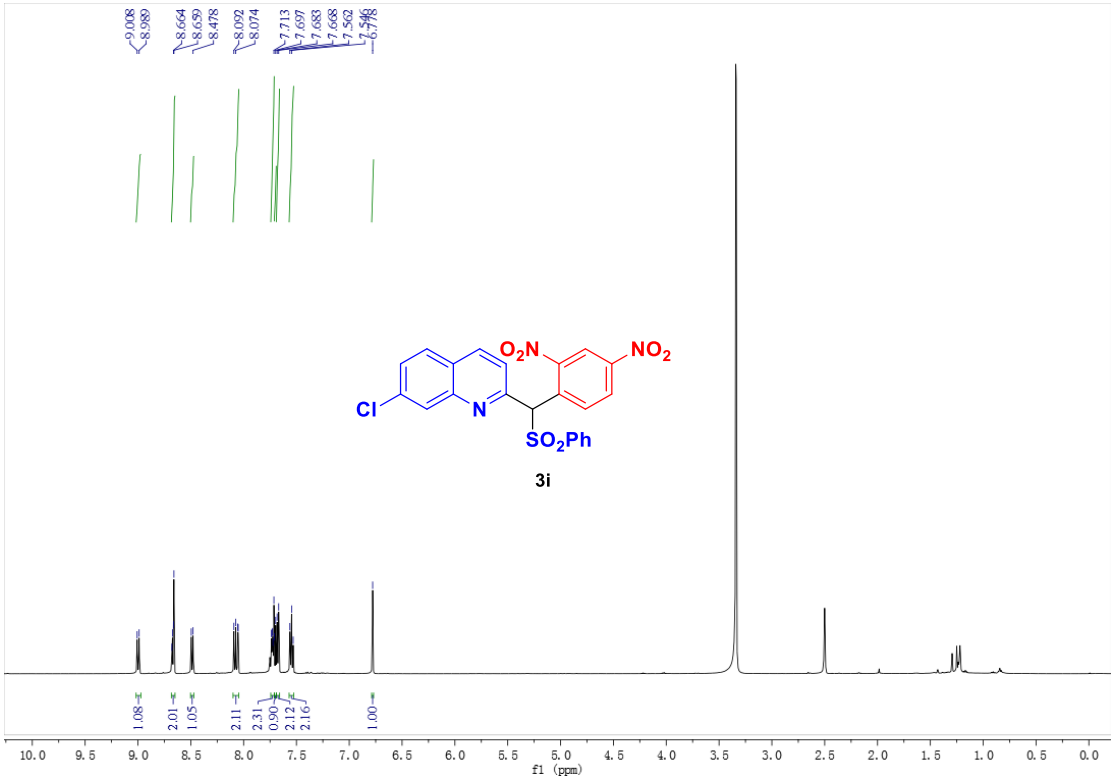
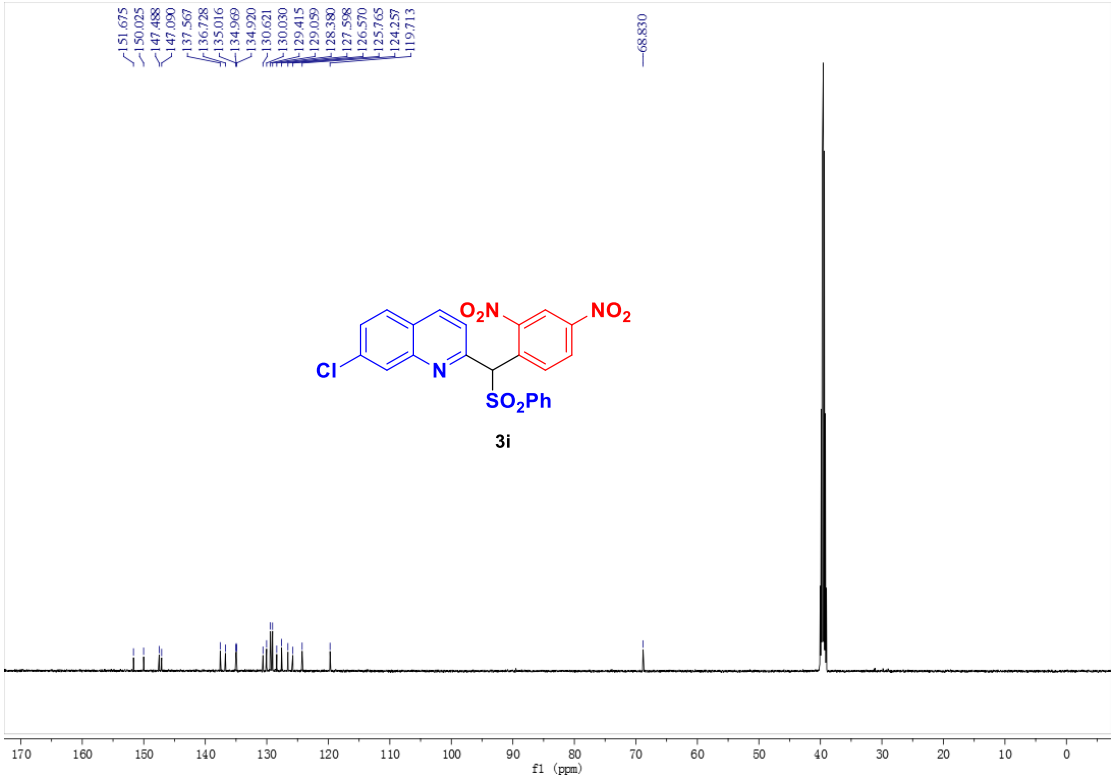
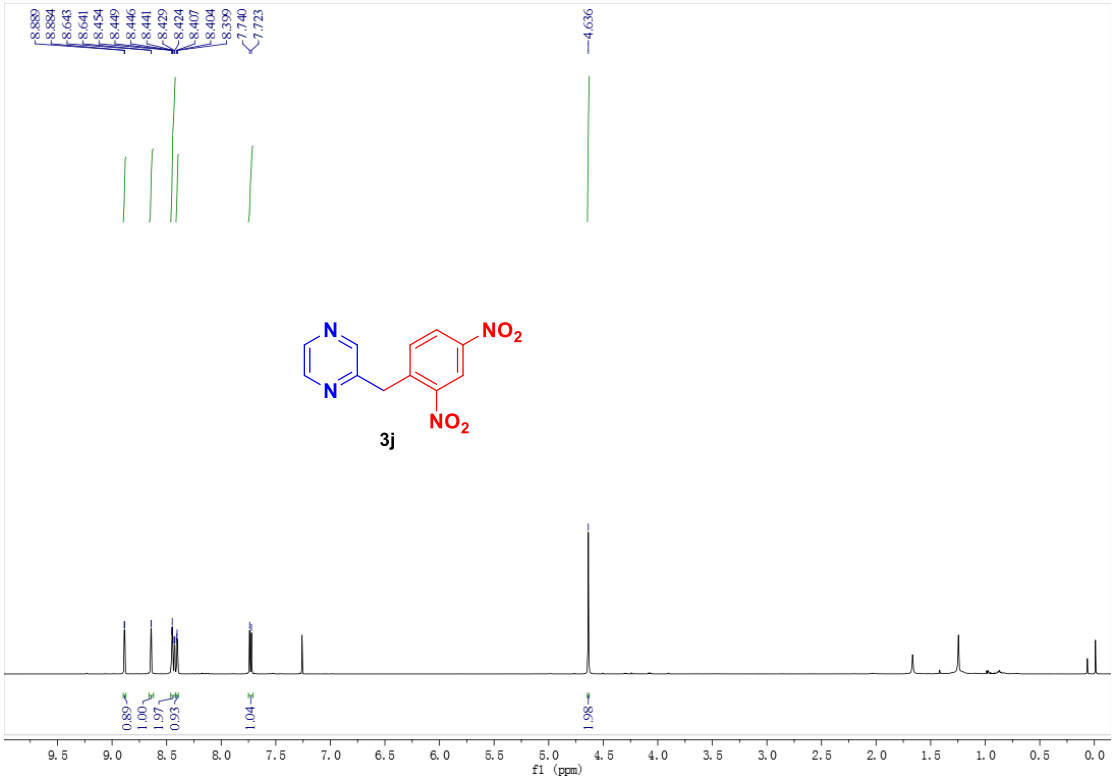
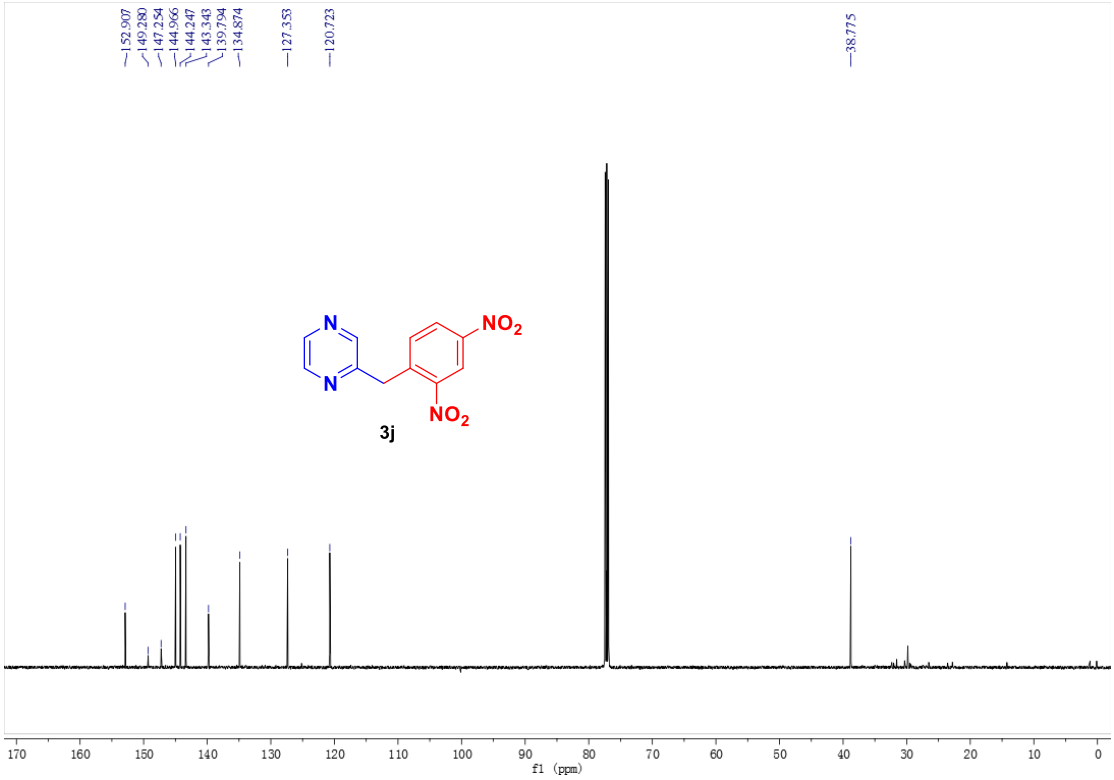
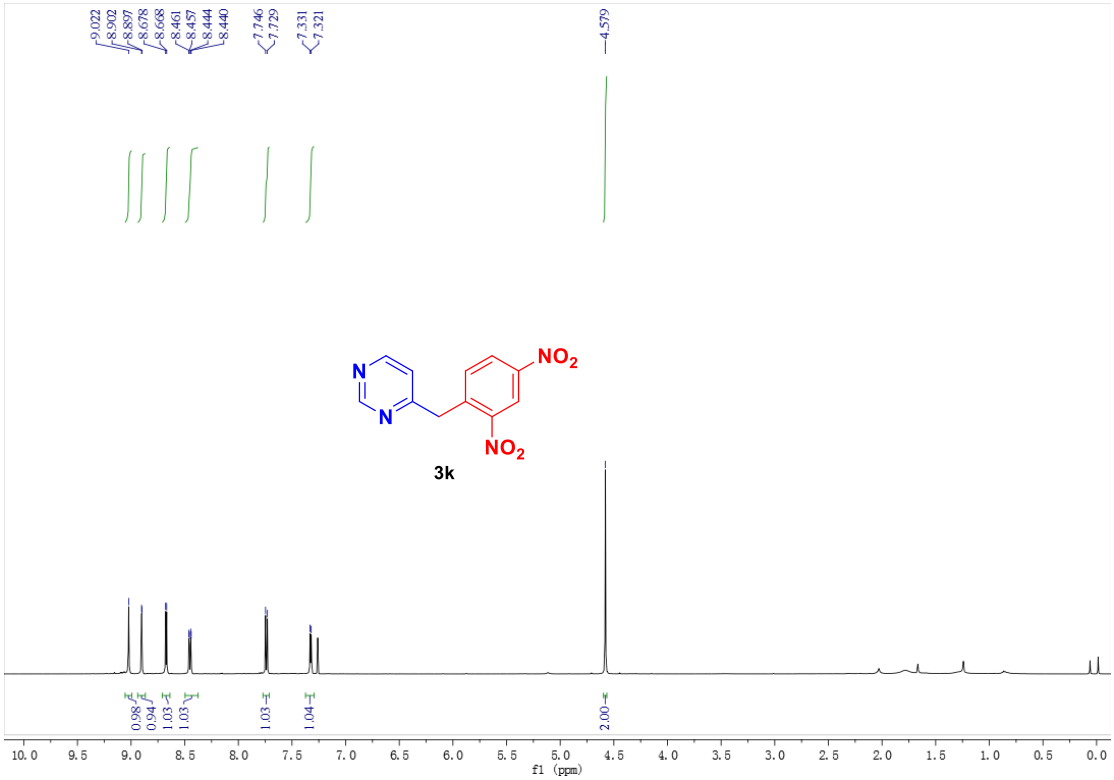
147.931
147.737
137.456
137.345
135.883
134.717
132.402
130.417
129.938
129.400
129.311
127.944
127.741
127.644
126.280
123.506
119.867
69.689
O2N
NO2
N
SO2Ph
3h
f1 (ppm)

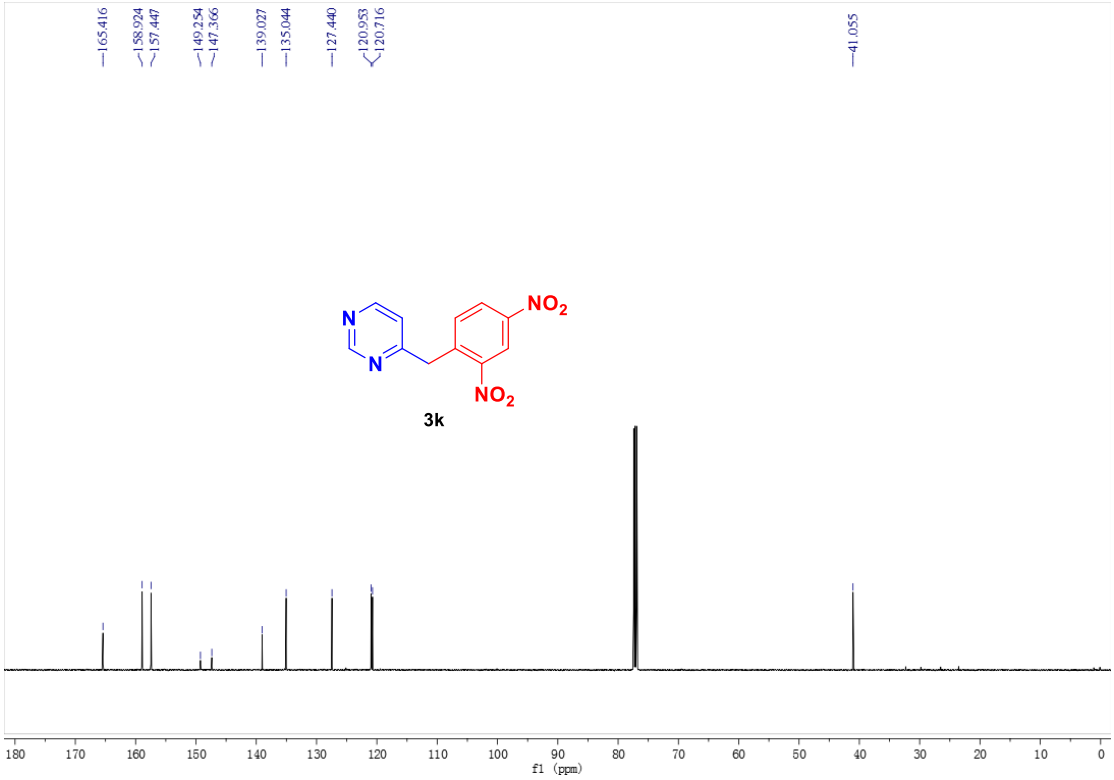

9.008
8.989
8.664
8.659
8.478
8.092
8.074
7.713
7.697
7.683
7.668
7.502
7.486
6.778
O2N
NO2
Cl
N
SO2Ph
3i
1.08
2.01
1.05
2.11
2.31
0.90
2.12
2.16
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

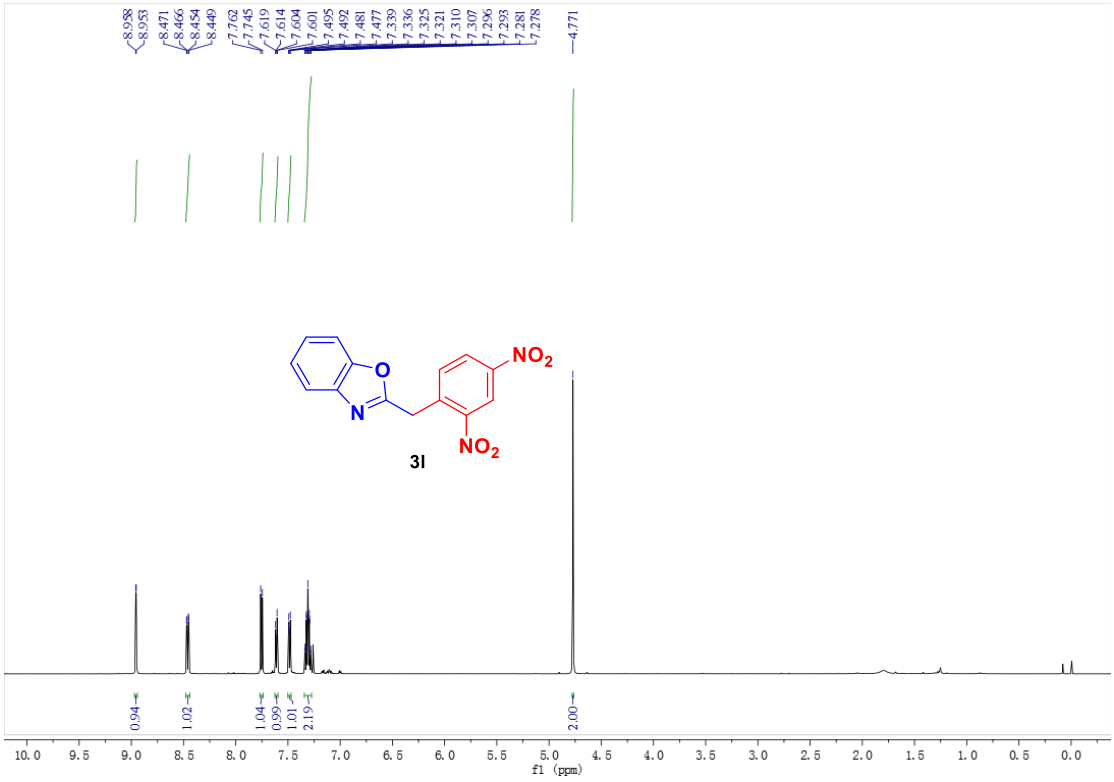

151.675
150.025
147.488
147.090
137.567
136.728
135.016
134.969
134.920
130.621
130.030
129.415
129.059
128.380
127.598
126.570
125.765
124.257
119.713
68.830
O2N
NO2
Cl
N
SO2Ph
3i
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

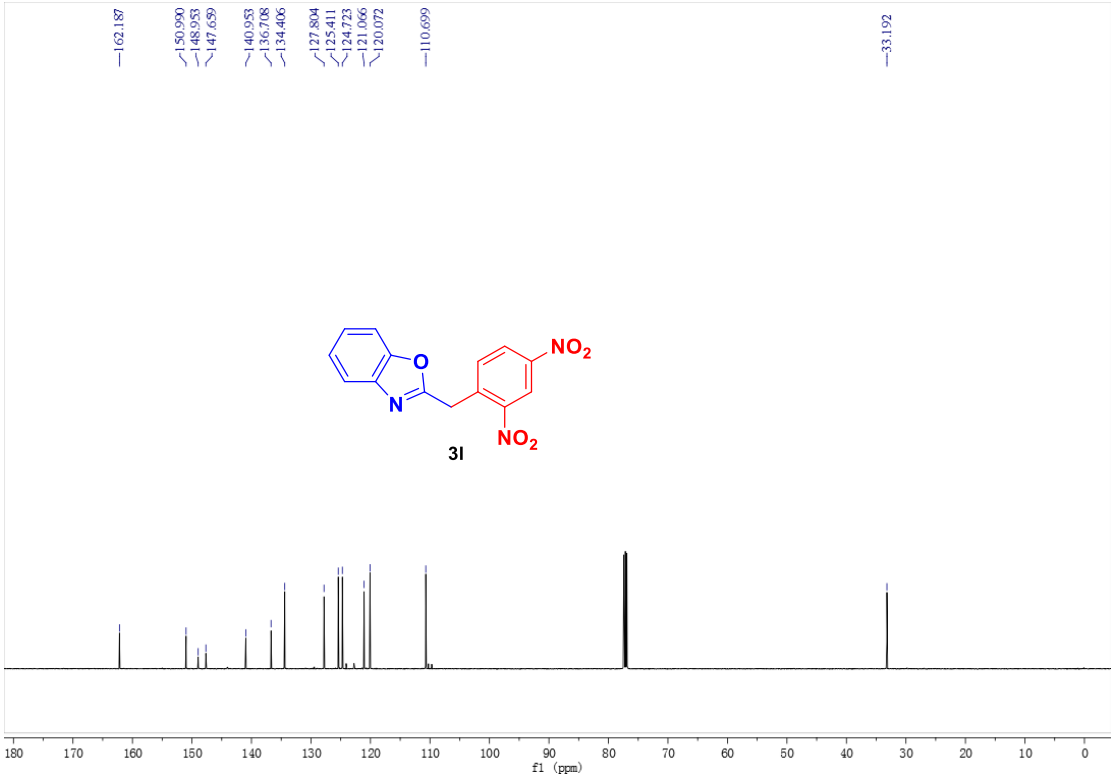

8.889
8.884
8.643
8.641
8.454
8.449
8.446
8.441
8.429
8.424
8.407
8.404
8.399
7.740
7.723
4.636
N
N
NO2
NO2
3j
0.89
1.00
1.97
0.93
1.04
1.98
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

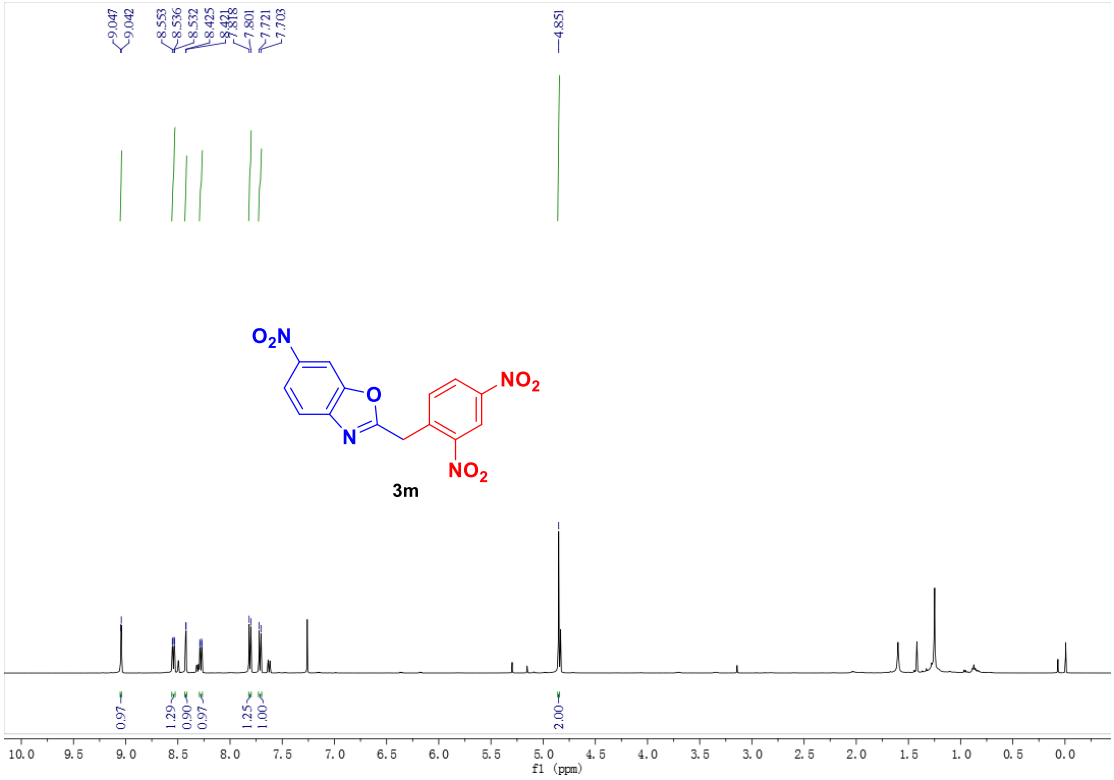

152.907
149.280
147.254
144.966
144.247
143.343
139.794
134.874
127.353
120.723
38.775
N
N
NO2
NO2
3j
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

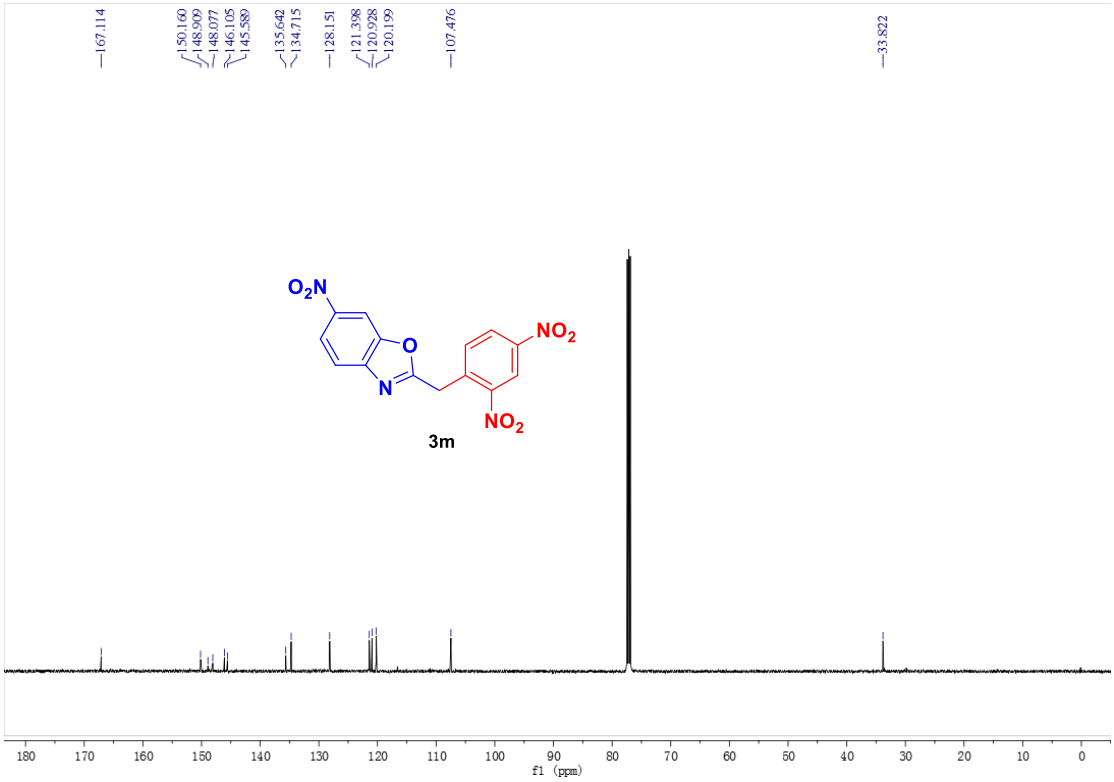

9.022
8.902
8.897
8.678
8.668
8.461
8.457
8.444
8.440
7.746
7.729
7.331
7.321
4.579
N
N
NO2
NO2
3k
0.98
0.94
1.03
1.03
1.03
1.04
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

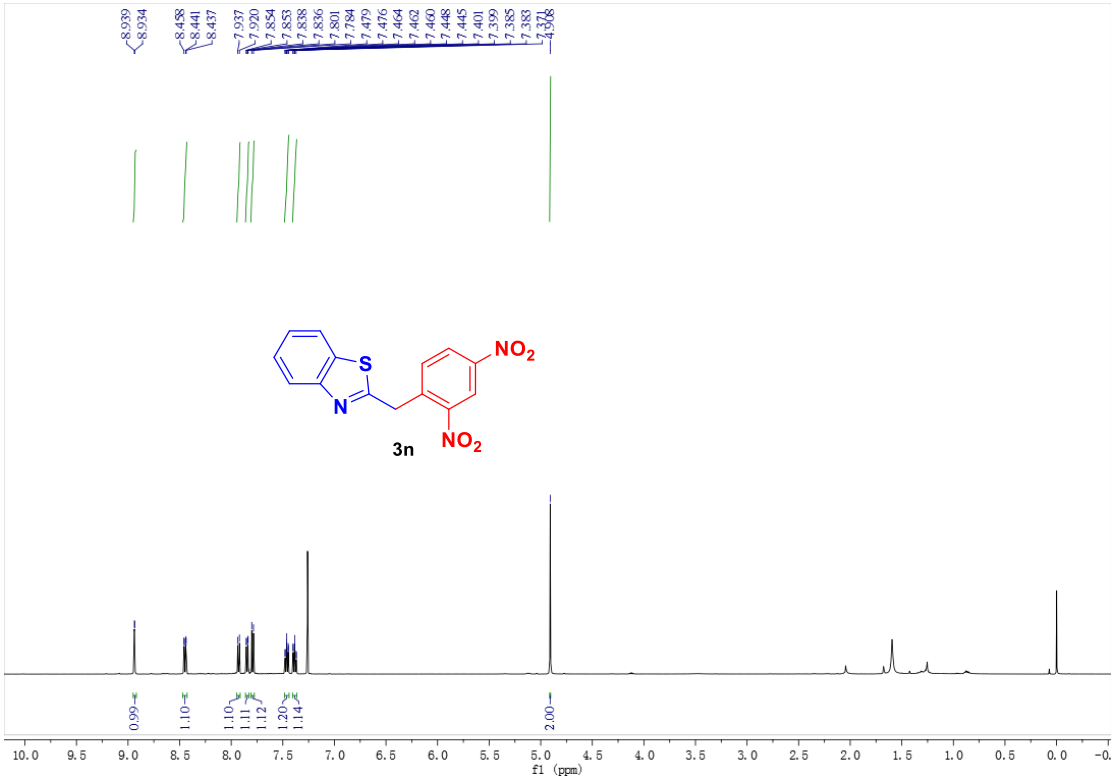

165.416
158.924
157.447
149.254
147.366
139.027
135.044
127.440
120.953
120.716
41.055
N
N
NO2
NO2
3k
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

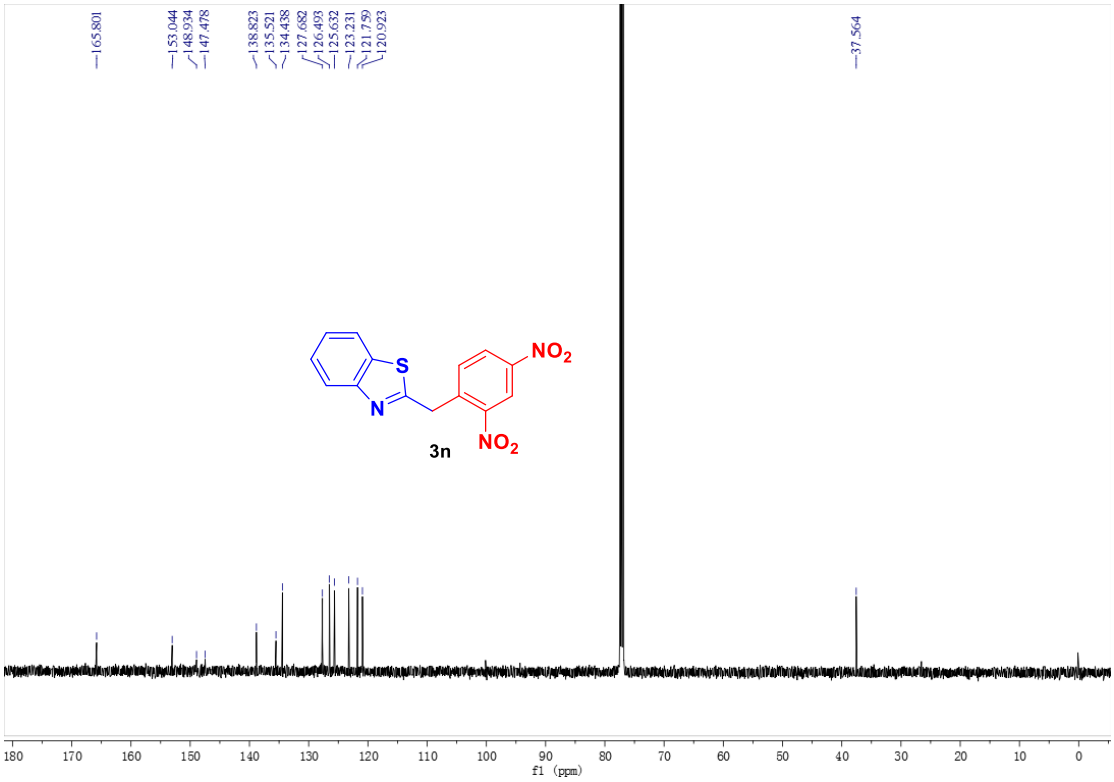

8.958
8.953
8.471
8.466
8.454
8.449
7.762
7.745
7.619
7.614
7.604
7.601
7.495
7.492
7.481
7.477
7.339
7.336
7.325
7.321
7.310
7.307
7.296
7.293
7.281
7.278
4.771
NO2
NO2
O
N
3l
0.94
1.02
1.04
0.99
1.01
2.19
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

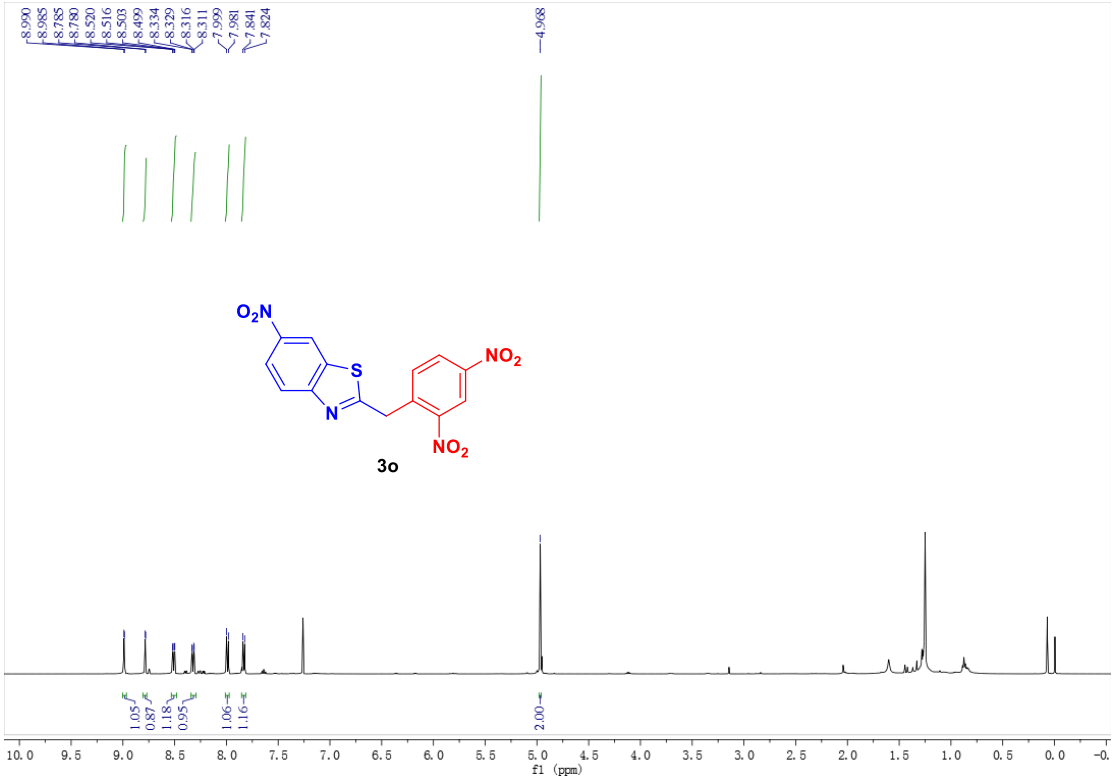

162.187
150.990
148.953
147.659
140.953
136.708
134.406
127.804
125.411
124.723
121.066
120.072
110.699
33.192
NO2
NO2
O
N
3l
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

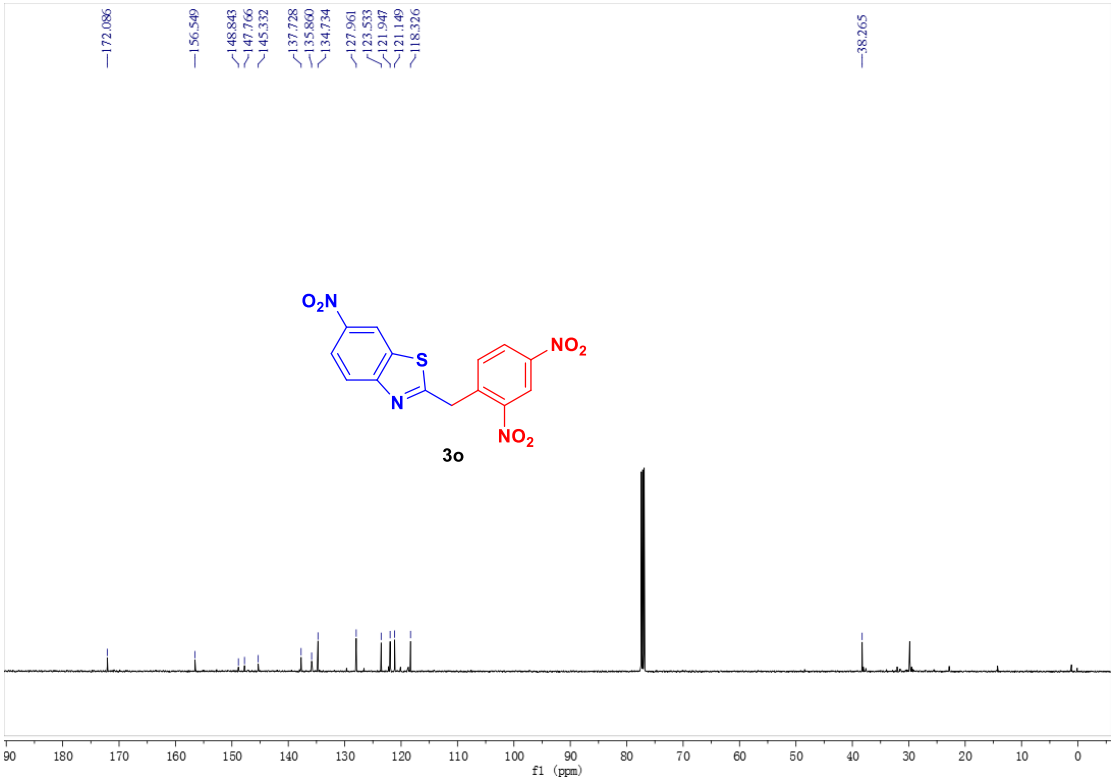

9.047
9.042
8.553
8.536
8.532
8.425
8.421
8.418
7.801
7.721
7.703
4.851
O2N
O
N
NO2
NO2
3m
0.97
1.29
0.90
0.97
1.25
1.00
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

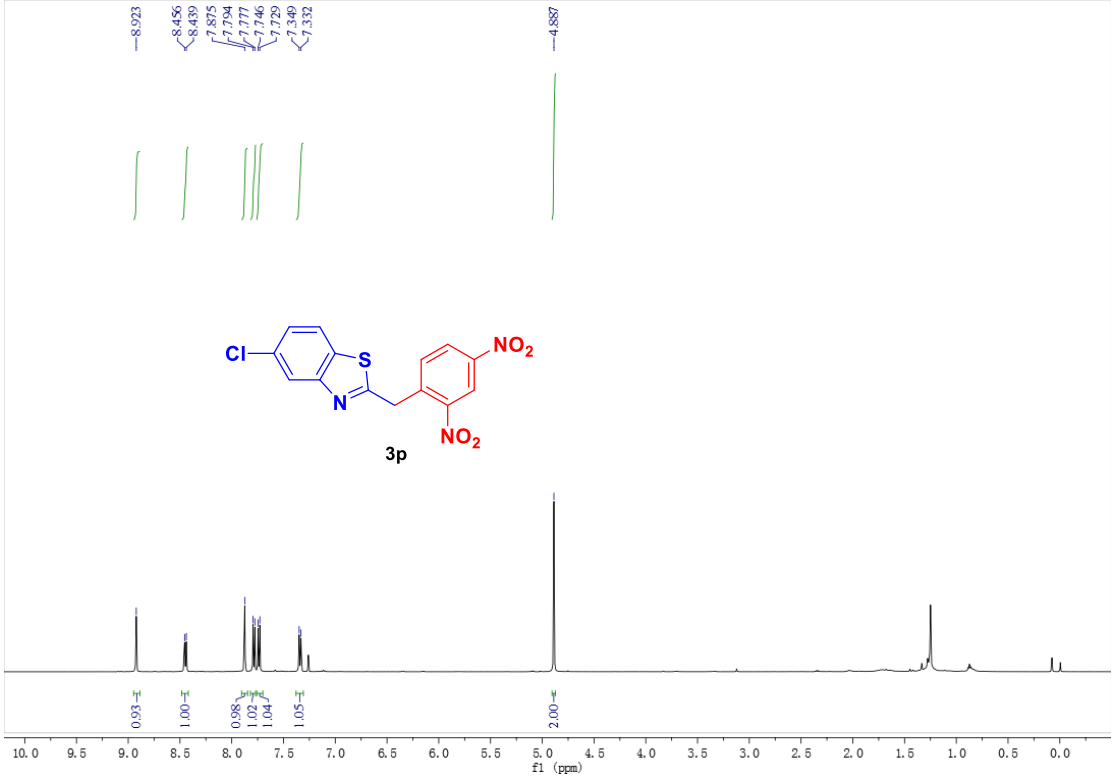

167.114
150.160
148.909
148.077
146.105
145.589
135.642
134.715
128.151
121.398
120.928
120.199
107.476
33.822
O2N
O
N
NO2
NO2
3m
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

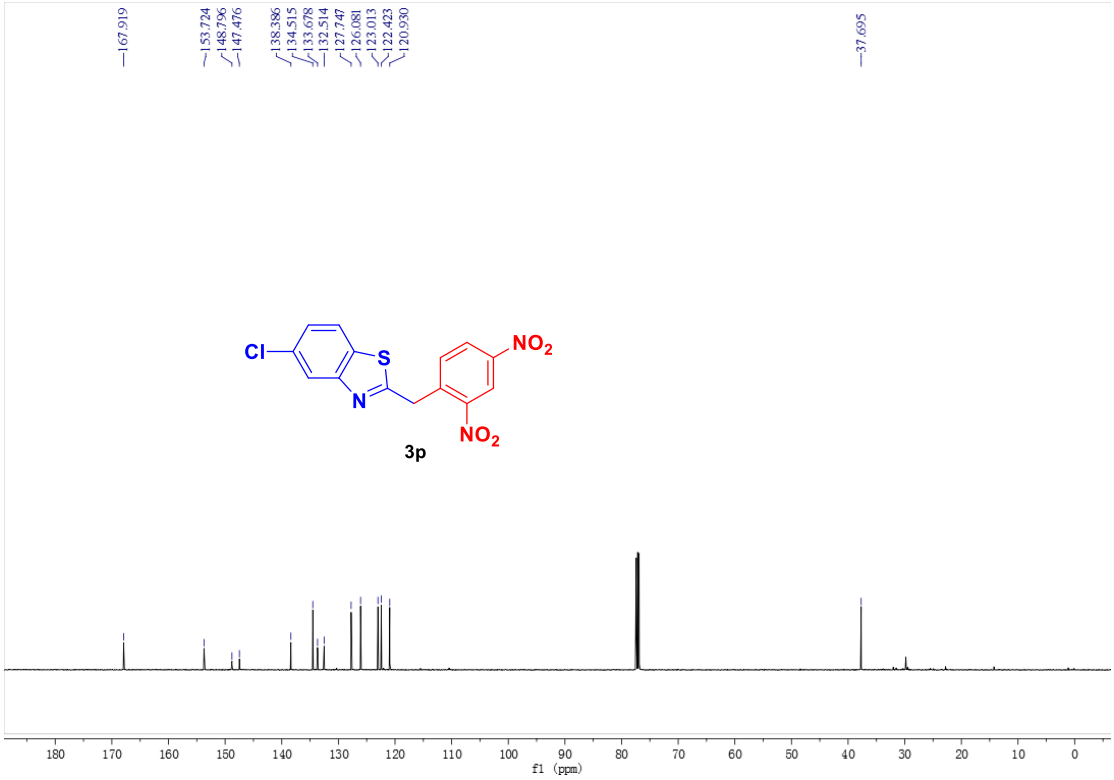

8.939
8.934
8.458
8.441
8.437
7.937
7.920
7.854
7.853
7.838
7.836
7.801
7.794
7.479
7.476
7.464
7.462
7.460
7.448
7.445
7.401
7.399
7.385
7.383
7.371
4.908
S
N
NO2
NO2
3n
0.99
1.10
1.10
1.11
1.12
1.20
1.14
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

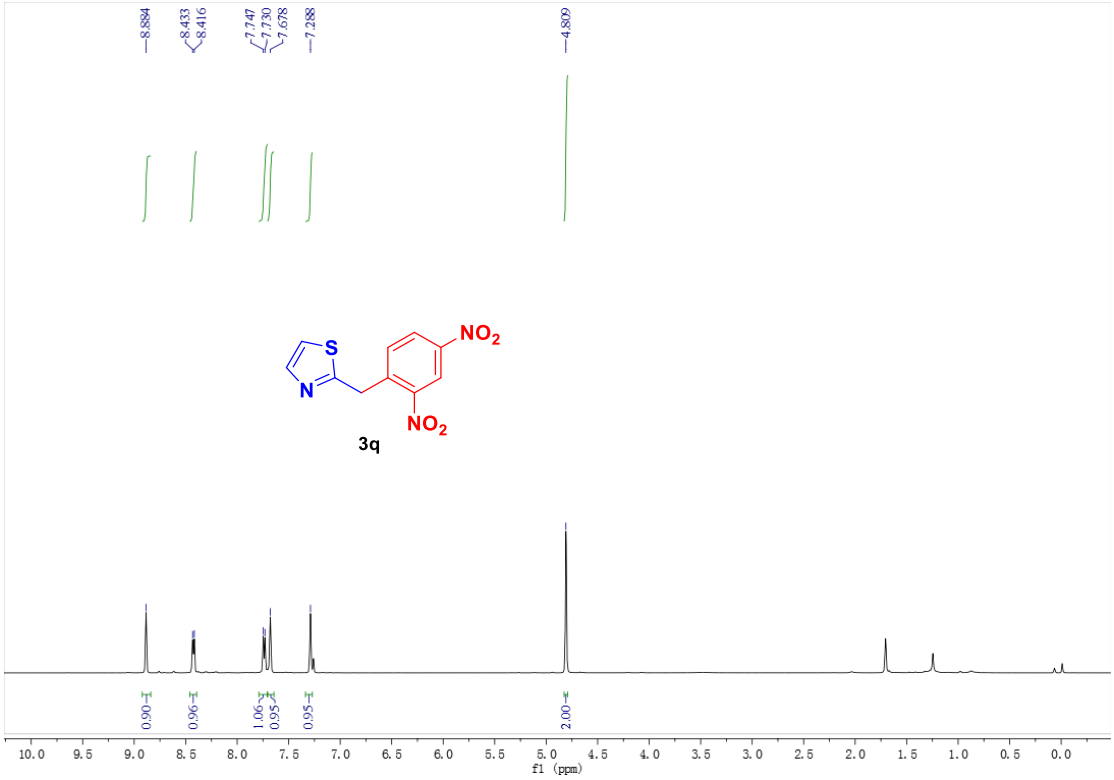

165.801
153.044
148.934
147.478
138.823
135.521
134.438
127.682
126.493
125.632
123.231
121.759
120.923
37.564
S
N
NO2
NO2
3n
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

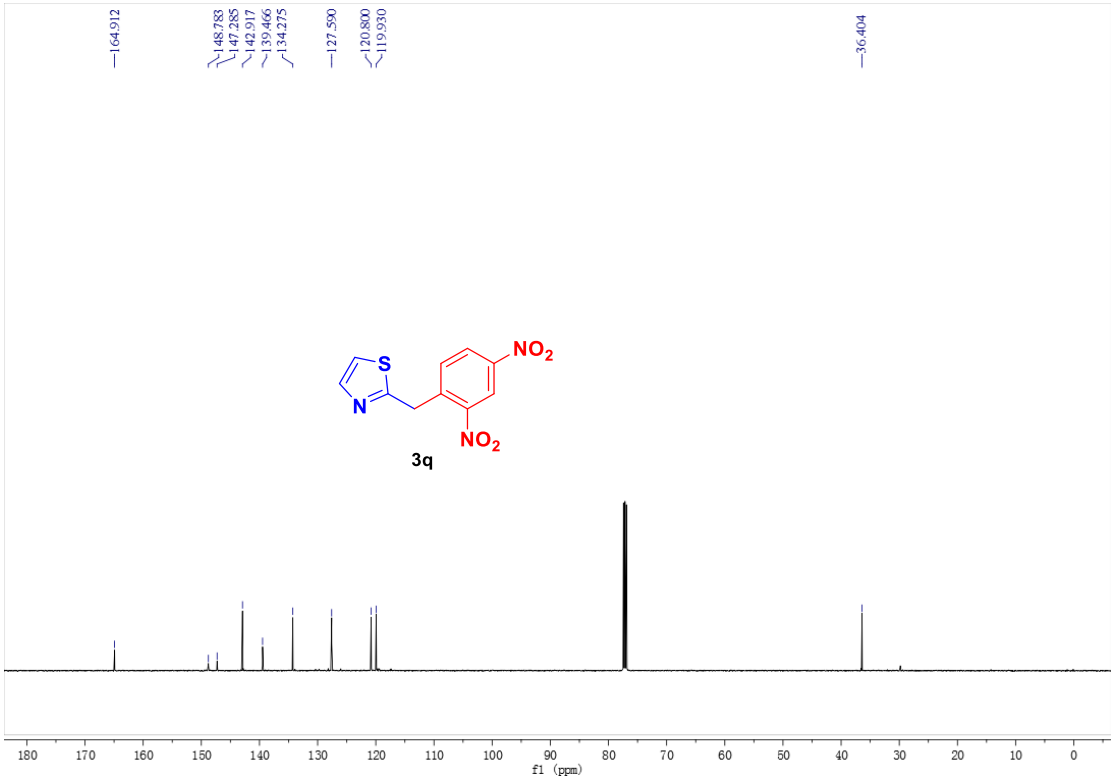

8.990
8.985
8.785
8.780
8.520
8.516
8.503
8.499
8.334
8.329
8.316
8.311
7.999
7.981
7.841
7.824
4.968
O2N
S
N
NO2
NO2
3o
1.05
0.87
1.18
0.95
1.06
1.16
2.00
f1 (ppm)

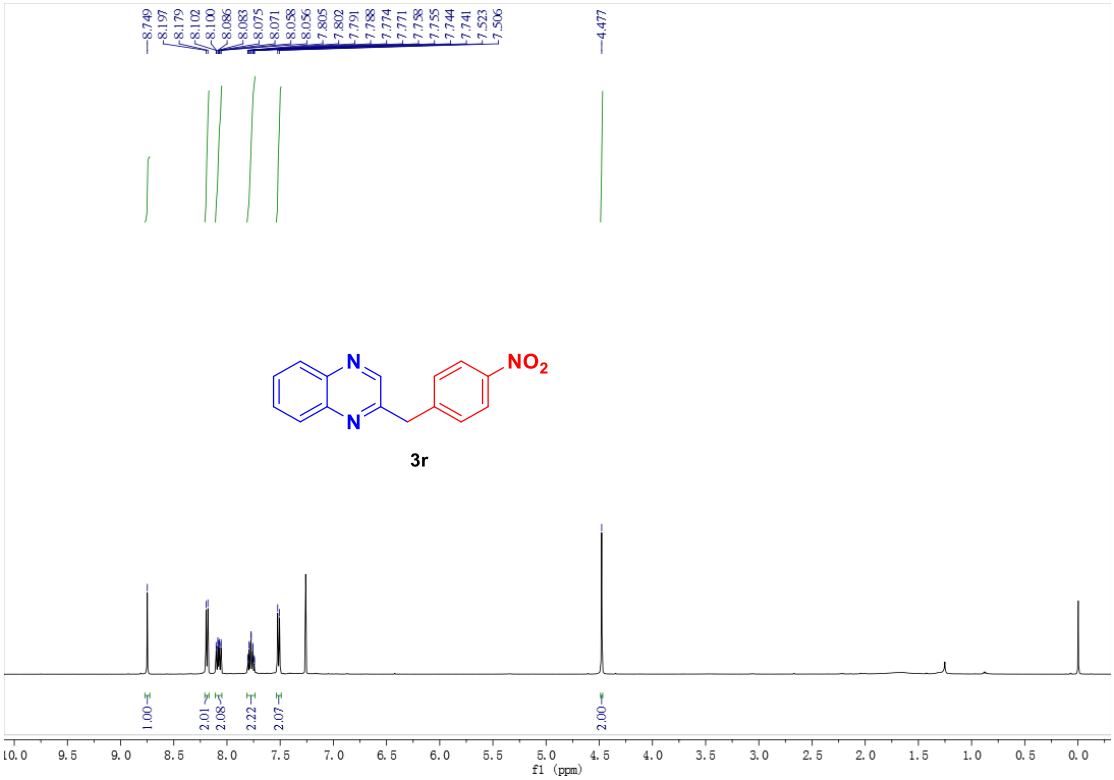

172.086
156.549
148.843
147.766
145.332
137.728
135.860
134.734
127.961
123.533
121.947
121.149
118.326
38.265
O2N
S
N
NO2
NO2
3o
f1 (ppm)

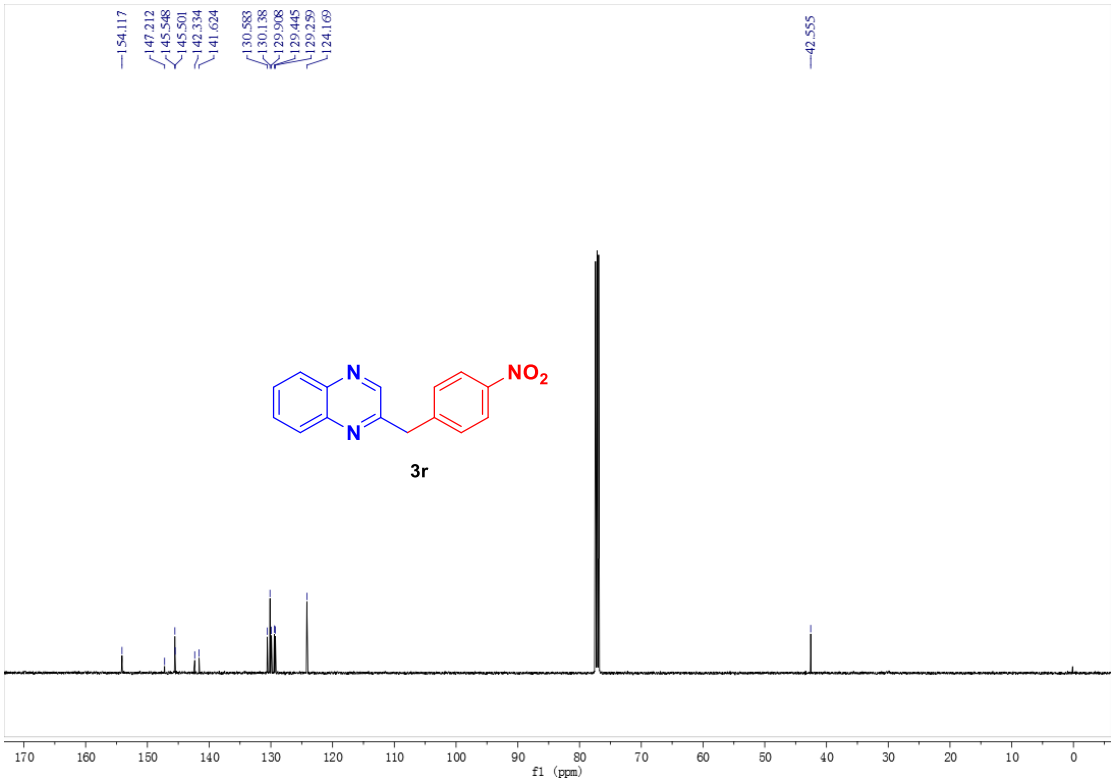

8.923
8.456
8.439
7.875
7.794
7.777
7.746
7.729
7.349
7.332
4.887
Cl
S
N
NO2
NO2
3p
0.93
1.00
0.98
1.02
1.04
1.05
2.00
f1 (ppm)

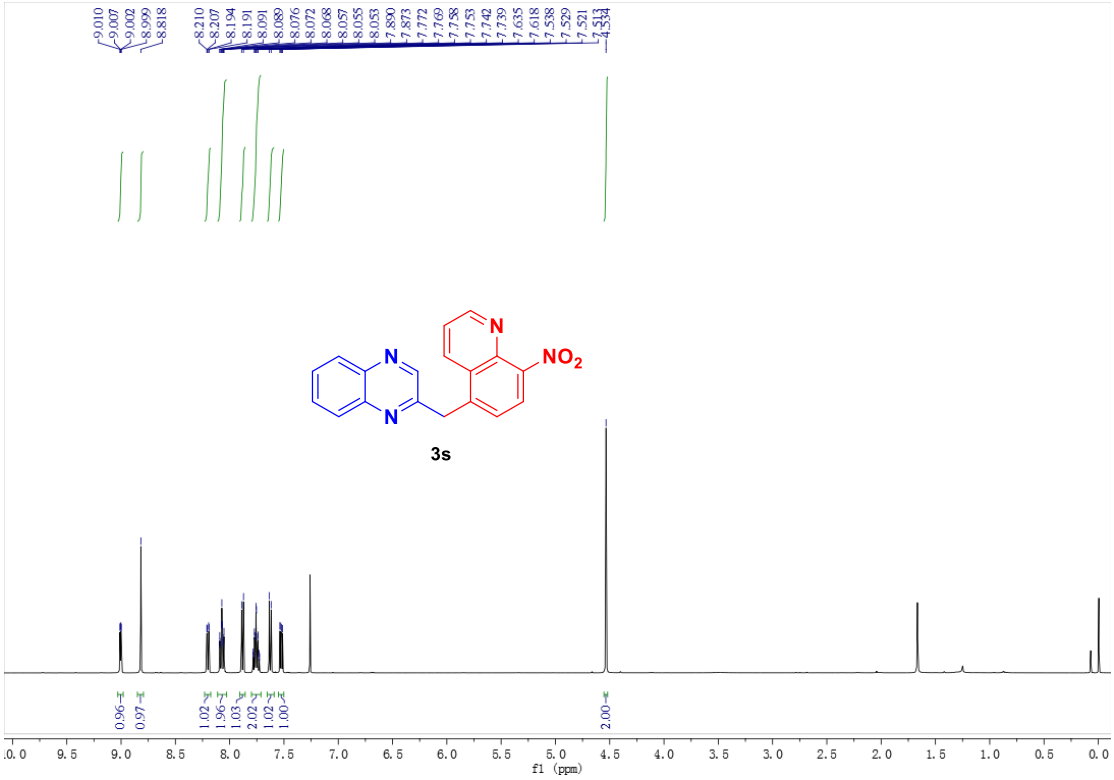

167.919
153.724
148.796
147.476
138.386
134.515
133.678
132.514
127.747
126.081
123.013
122.423
120.930
37.695
Cl
S
N
NO2
NO2
3p
f1 (ppm)

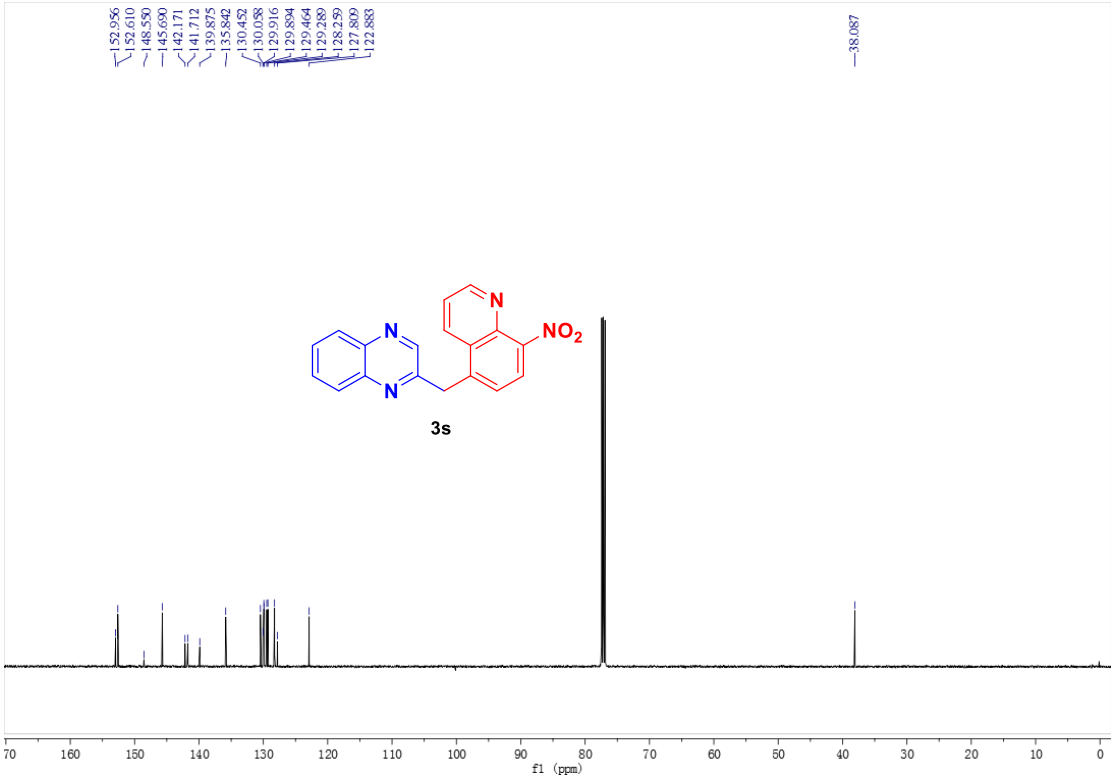

8.884
8.433
8.416
7.747
7.730
7.678
7.288
4.809
S
N
NO2
NO2
3q
0.90
0.96
1.06
0.95
0.95
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

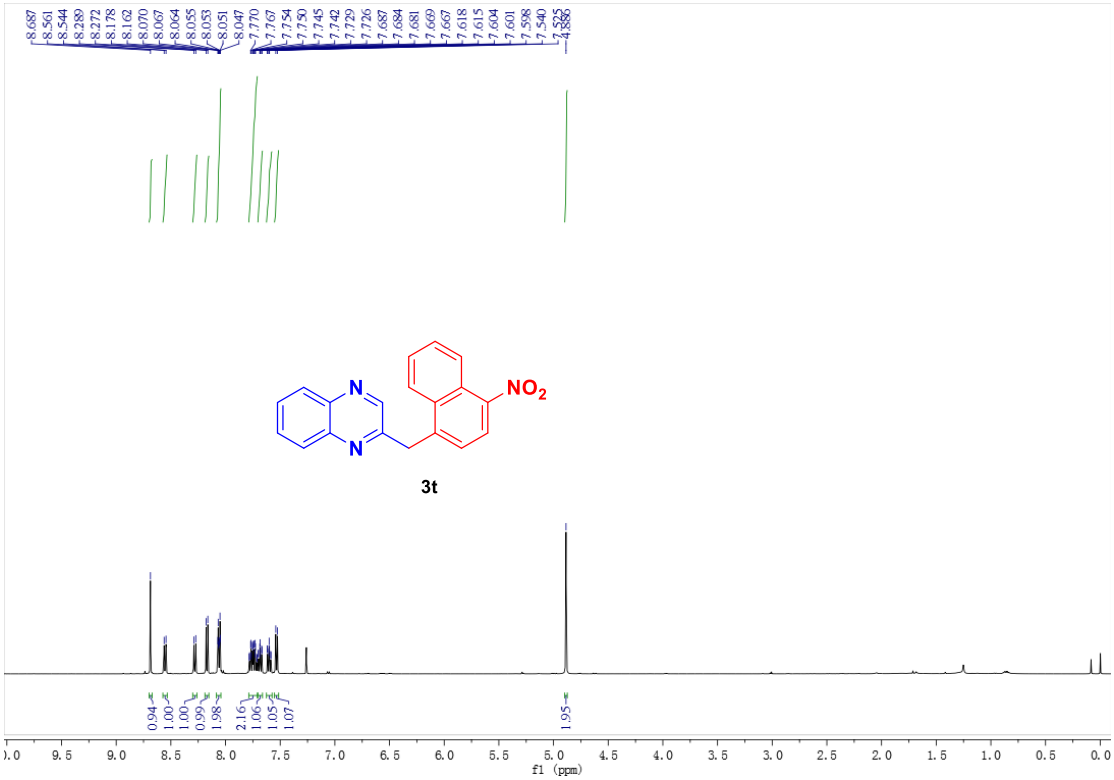

164.912
148.783
147.285
142.917
139.466
134.275
127.590
120.800
119.930
36.404
S
N
NO2
NO2
3q
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

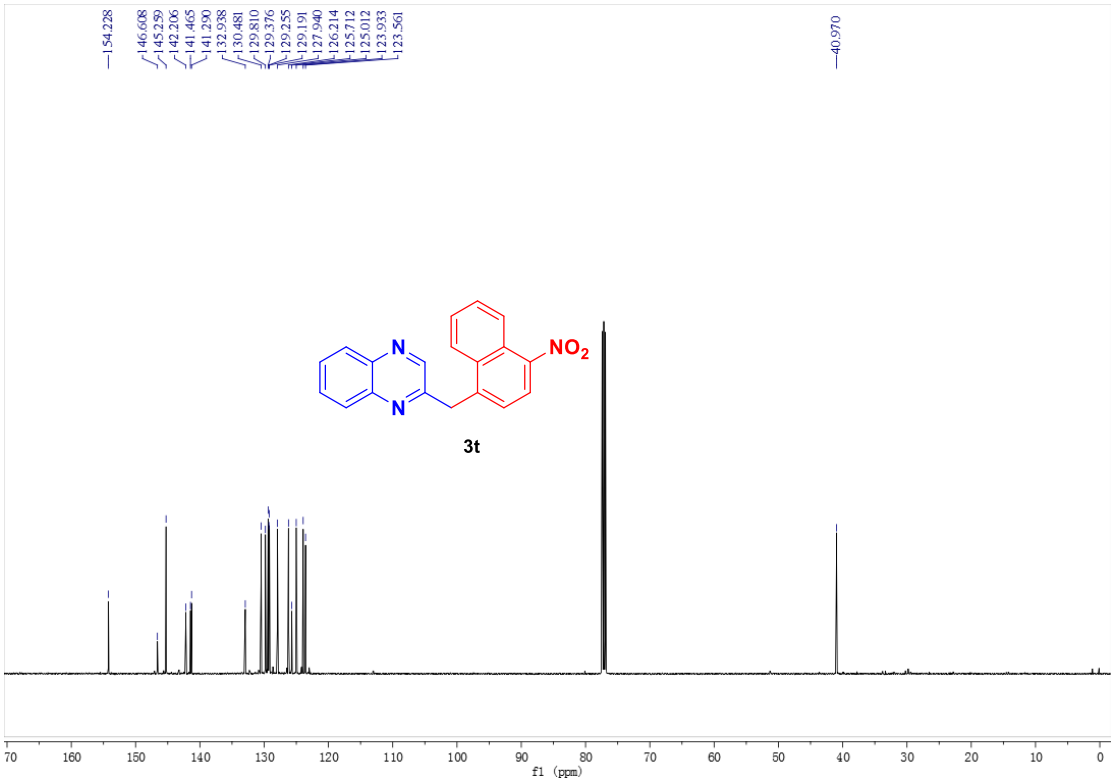

8.749
8.197
8.179
8.102
8.100
8.086
8.083
8.075
8.071
8.058
8.056
7.805
7.802
7.791
7.788
7.774
7.771
7.758
7.755
7.744
7.741
7.523
7.506
4.477
N
N
NO2
3r
1.00
2.01
2.08
2.22
2.07
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

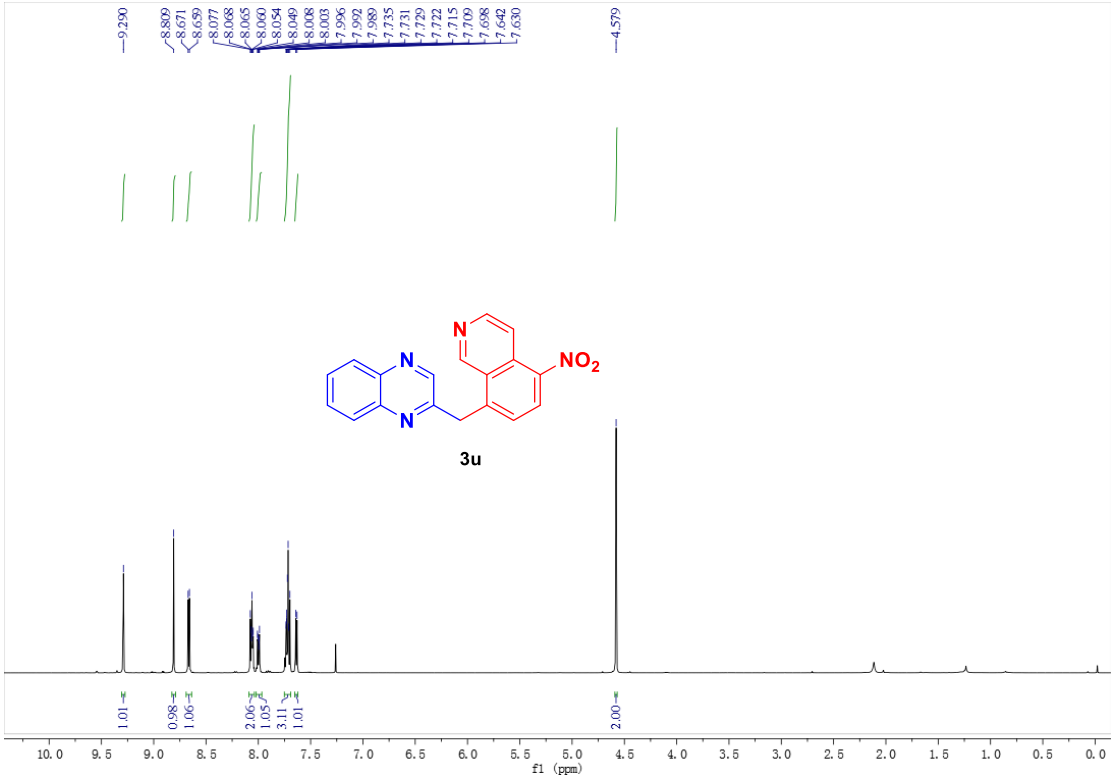

154.117
147.212
145.548
145.501
142.334
141.624
130.583
130.138
129.908
129.445
129.259
124.169
42.555
N
N
NO2
3r
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

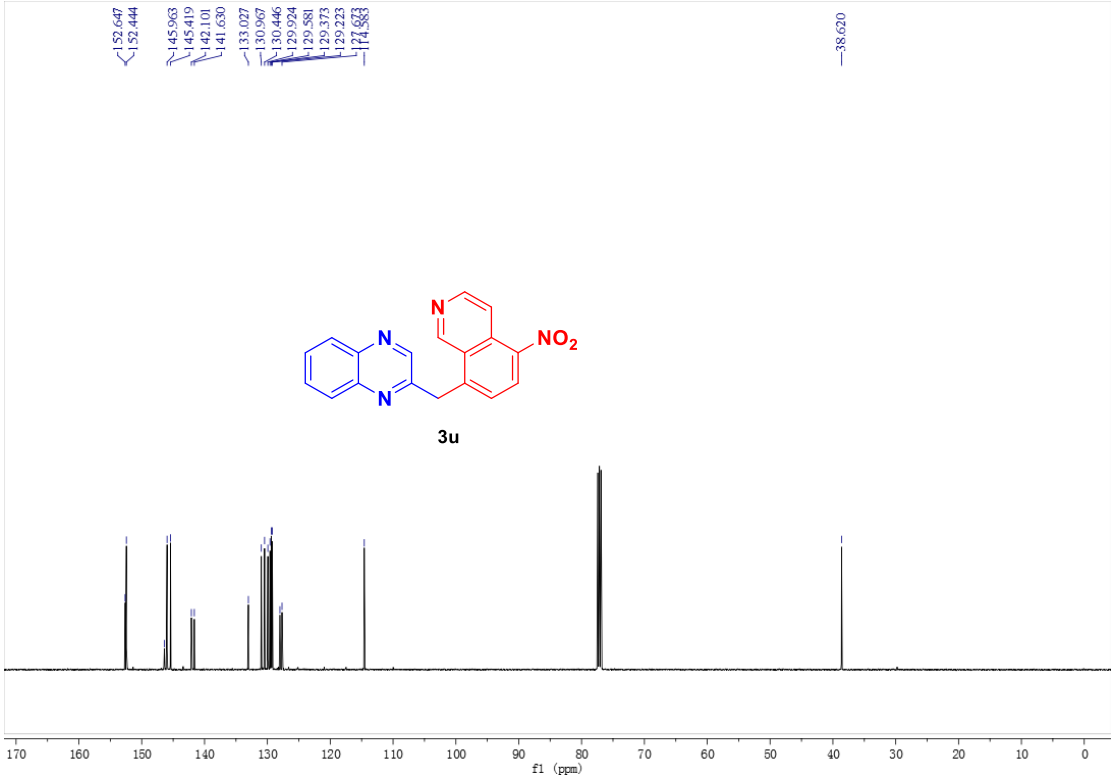

9.010
9.007
9.002
8.999
8.818
8.210
8.207
8.194
8.191
8.091
8.089
8.076
8.072
8.068
8.057
8.055
8.053
7.890
7.873
7.772
7.769
7.758
7.753
7.742
7.739
7.635
7.618
7.538
7.529
7.521
7.313
4.334
N
NO2
N
N
3s
0.96
0.97
1.02
1.96
1.03
2.02
1.02
1.00
2.00
f1 (ppm)

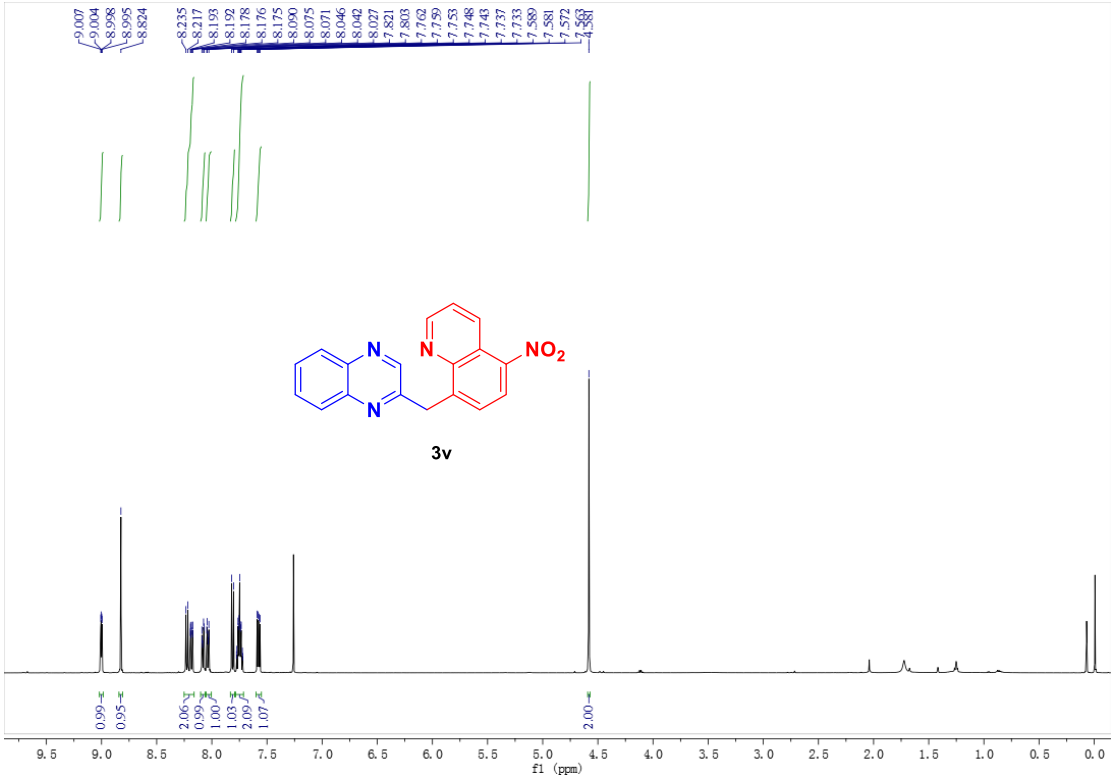

152.956
152.610
148.550
145.690
142.171
141.712
139.875
135.842
130.452
130.058
129.916
129.804
129.464
129.289
128.259
127.809
122.883
38.087
N
NO2
N
N
3s
f1 (ppm)

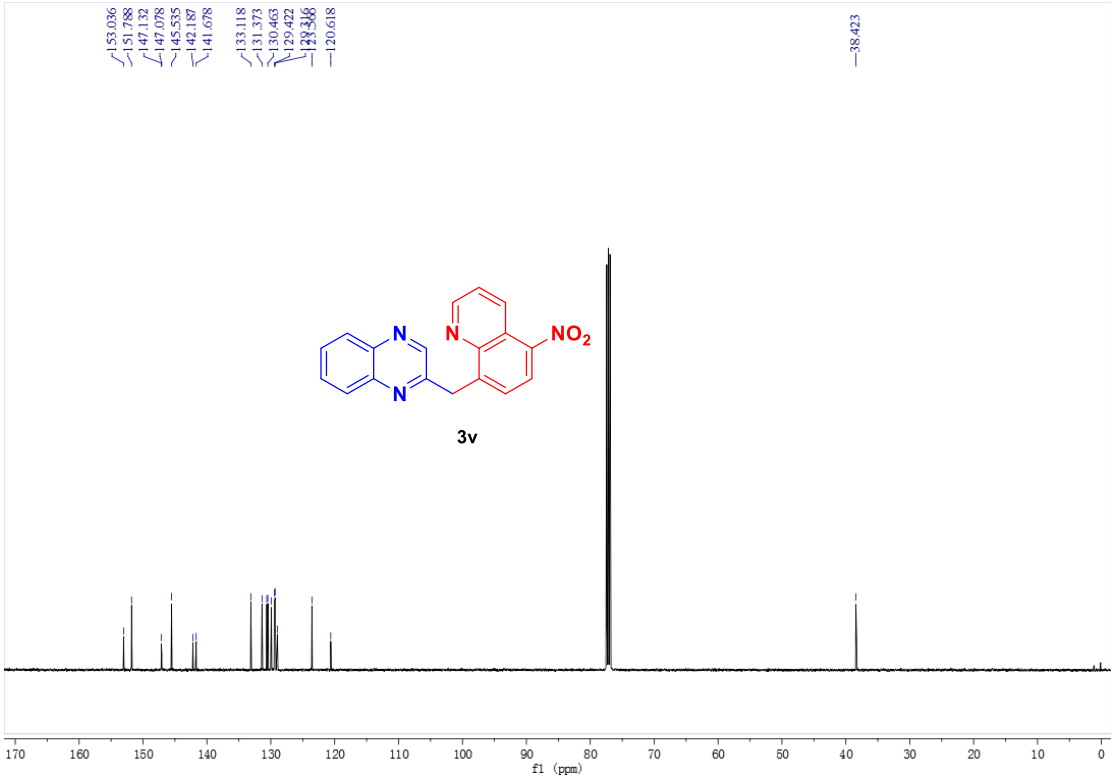

8.687
8.561
8.544
8.289
8.272
8.178
8.162
8.070
8.067
8.064
8.055
8.053
8.051
8.047
7.770
7.767
7.754
7.750
7.745
7.742
7.729
7.726
7.687
7.684
7.681
7.669
7.667
7.618
7.615
7.604
7.601
7.598
7.540
7.525
4.886
N
N
NO2
3t
0.94
1.00
1.00
0.99
1.98
2.16
1.06
1.05
1.07
1.95
f1 (ppm)


154.228
146.608
145.259
142.206
141.465
141.290
132.938
130.481
129.810
129.376
129.255
129.191
127.940
126.214
125.712
125.012
123.933
123.561
40.970
N
N
NO2
3t
f1 (ppm)


9.290
8.809
8.671
8.659
8.077
8.068
8.065
8.060
8.054
8.049
8.008
8.003
7.996
7.992
7.989
7.735
7.731
7.729
7.722
7.715
7.709
7.698
7.642
7.630
4.579
N
N
N
NO2
3u
1.01
0.98
1.06
2.06
1.05
3.11
1.01
2.00
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)


152.647
152.444
145.963
145.419
142.101
141.630
133.027
130.967
130.446
129.924
129.581
129.373
129.223
38.620
N
N
N
NO2
3u
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


9.007
9.004
8.998
8.995
8.824
8.235
8.217
8.193
8.192
8.178
8.176
8.175
8.090
8.075
8.071
8.046
8.042
8.027
7.821
7.803
7.762
7.759
7.753
7.748
7.743
7.737
7.733
7.589
7.581
7.572
4.581
N
N
N
NO2
3v
0.99
0.95
2.06
0.99
1.00
1.03
2.09
1.07
2.00
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)


153.036
151.788
147.132
147.078
145.535
142.187
141.678
133.118
131.373
130.463
129.422
120.618
38.423
N
N
N
NO2
3v
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)