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Visible-Light mediated directed perfluoroalkylation of hydrazones

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Supporting Information

1. General information

All reagents were commercially available and used without further purification. All solvents were dried according to standard procedures. Melting points were measured on a Taike X-4 microscopic melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were measured on a Bruker ACF-400 spectrometer and recorded at 400 and 100 MHz, respectively, using $CDCl_3$ or DMSO as solvent. IR spectra were taken with a Nicolet FT-IR 5DX spectrometer. HRMS were taken with a AB Triple TOF 5600 plus System (AB SCIEX, Framingham,USA). The exact mass calibration was performed automatically before each analysis employing the Automated Calibration Delivery System. EPR spectra were measured on a Bruker A300 spectrometer.

2. Photoreaction setup

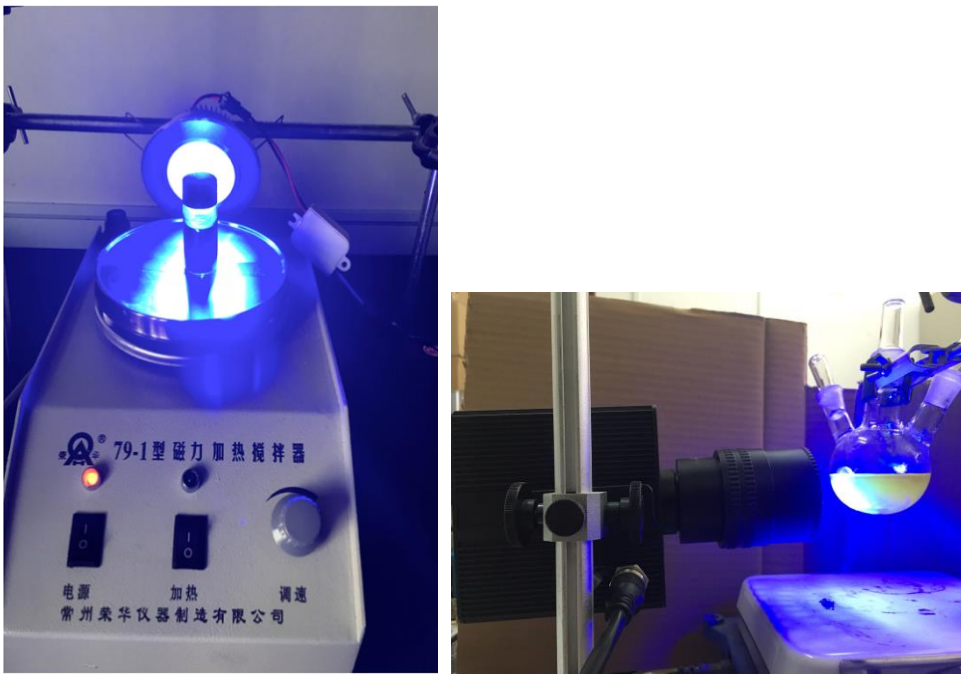
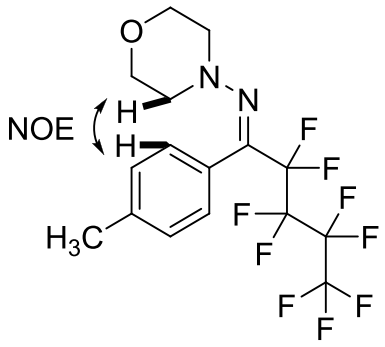
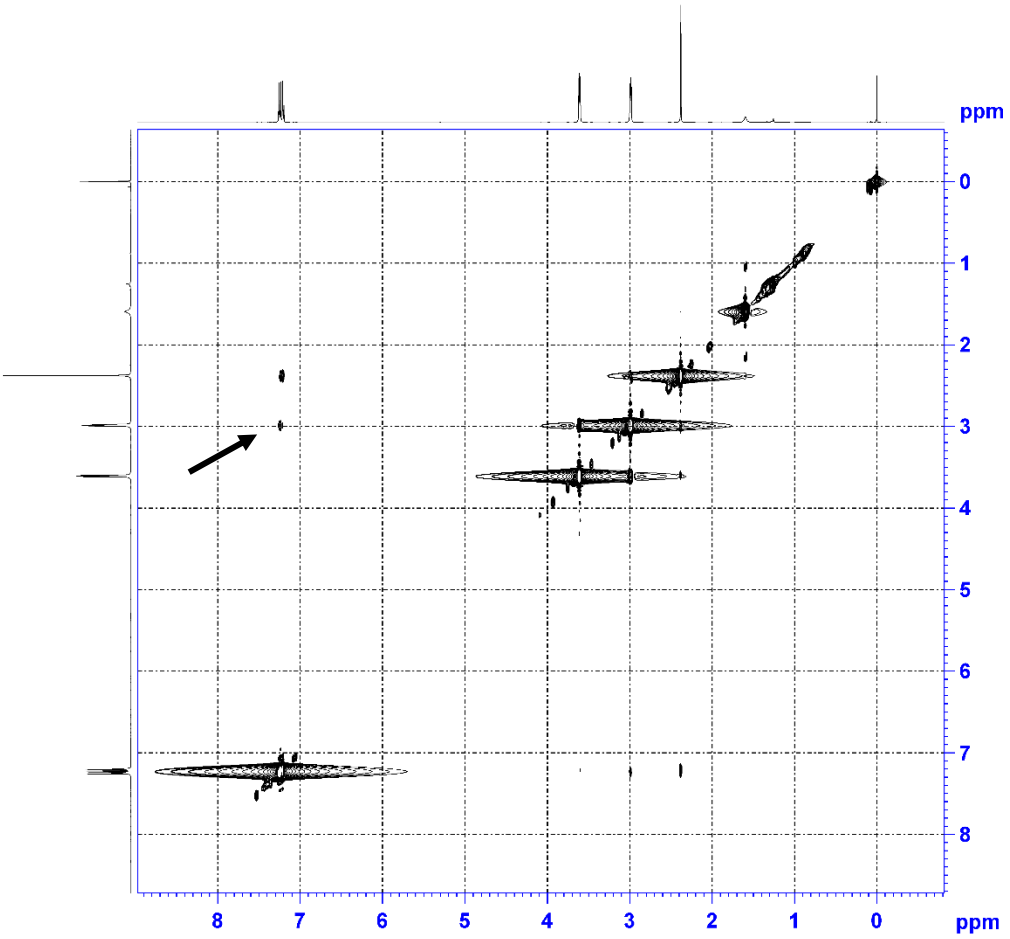


Fig. 1s Reaction apparatus for the small test reactions (left) and gram-scale reaction (right).

3. Determination of the geometry of the C=N double bond

NOESY experiment

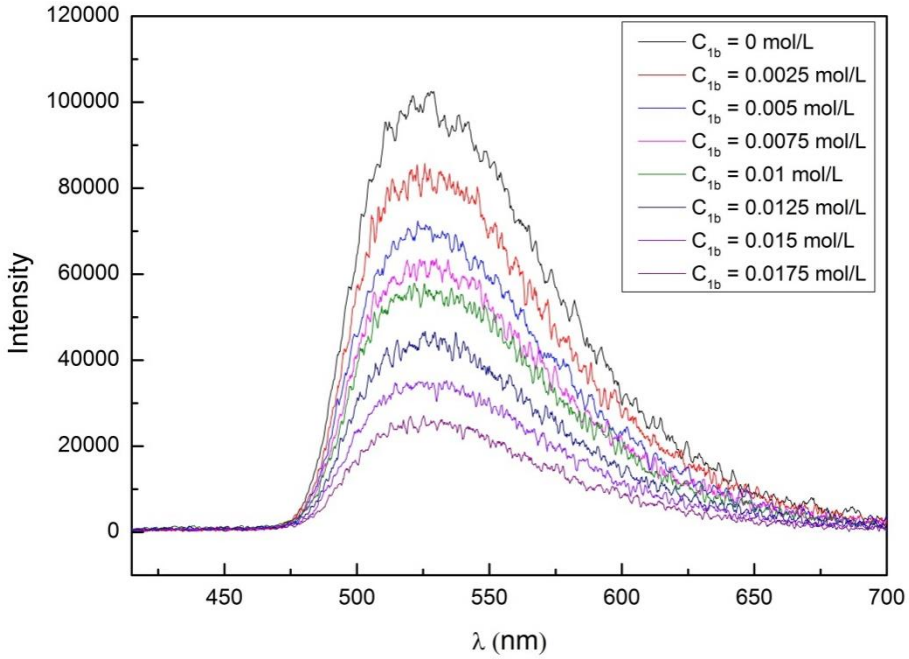




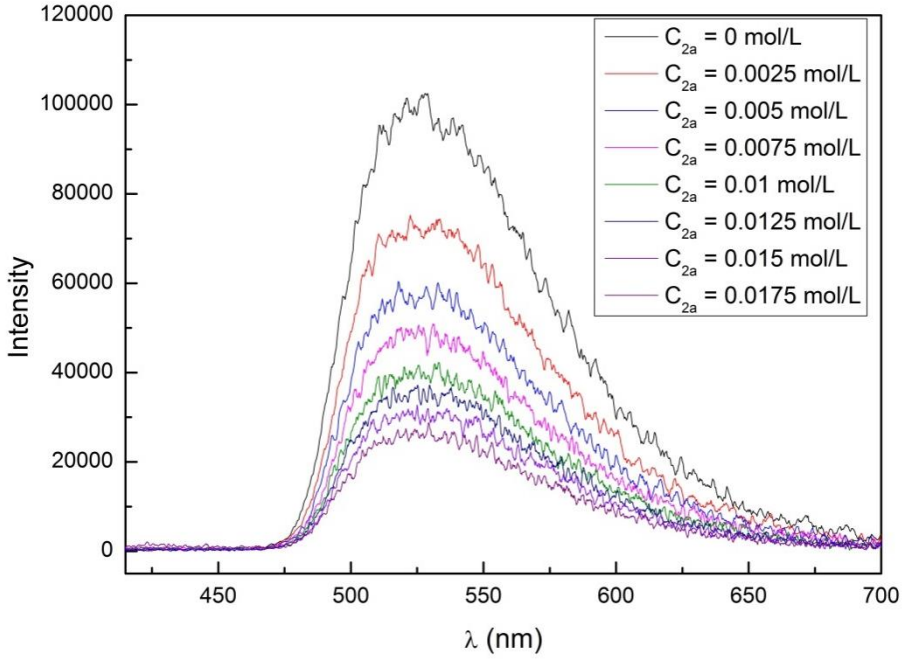
4. Stern-Volmer Fluorescence Quenching Studies

Fluorescence quenching experiments were performed on a JASCO FP-6500Spectrofluorometer. In a typical experiment, a 0.15mM solution of $Ir(ppy)_3$ in CH_3CN was added to the appropriate amount of quencher in a screw-top 1.0 cm quartz cuvette. All solutions were excited at $\lambda = 367$ nm (absorption maximum of the photocatalyst) and the emission intensity at 526 nm was recorded (emission maximum)

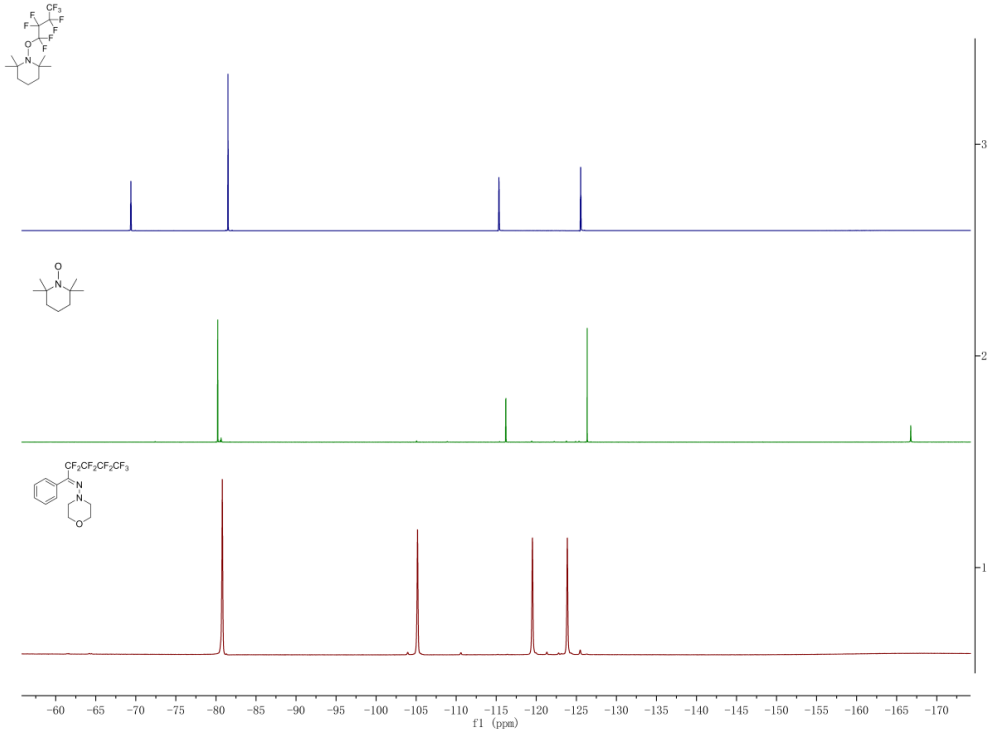
$Ir(ppy)_3$Emission Quenched by 1b



$Ir(ppy)_3$Emission Quenched by 2a



5. The Radical Trapping Experiment:



6. EPR spin trapping experiment with DMPO

Typical spectrometer parameters are shown as follows: Center-Field: 3508 G; Width: 100 G; Receiver Gain: 5.02×10^3; Scans: 1; Modulation Amplitude: 1 G; Modulation Frequency: 9.845957 GHz; Microwave Power: 2.41mW; Time constant: 0.08192 s.
Simulated EPR spectrum (b and c) based on hyperfine coupling constants of a_N = 13.52 Gs and a_F = 1.96Gs (g=2.00948).

7. Synthetic Utility of Methodology

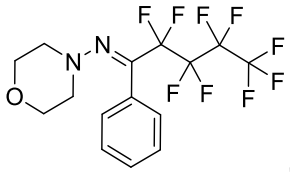
(1) Hydrolysis reaction of hydrazone

3b (0.1085 g, 0.2569 mmol) was added to a 7.5mL 1/1 mixture of HCl (0.3N)/THF. The resulting solution was stirred at room temperature and monitored by TLC. After 24h, the solution was extracted by DCM and washed with aq $NaHCO_3$. The organic layer was dried over $MgSO_4$ and concentrated. The residue was purified by flash chromatography to afford **9** (41 mg, 47 %).

(2) Photoredox three-component couping reaction

In a vial $Ir(ppy)_3$ (2.6 mg, 0.004 mmol, 1 mol%), p-tolualdehyde(0.4 mmol), morpholin-4-amine (0.44 mmol), Na_2HPO_4 (113.6mg, 0.8 mmol) and perfluoroalkyliodide 2 (0.8 mmol) were dissolved in 8mL DMF. The reaction mixture was stirred under irradiation with a 3 W blue LED lamp for 24 hours. After the reaction was completed, the reaction mixture was poured into 60mL water and extracted with EtOAc (8 mL×3). The combined organic layers were dried with anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the crude mixture was directly charged on silica gel and purified by column chromatography with petroleum ether/ethyl acetate as eluents.

8. Spectral data of products 3-9



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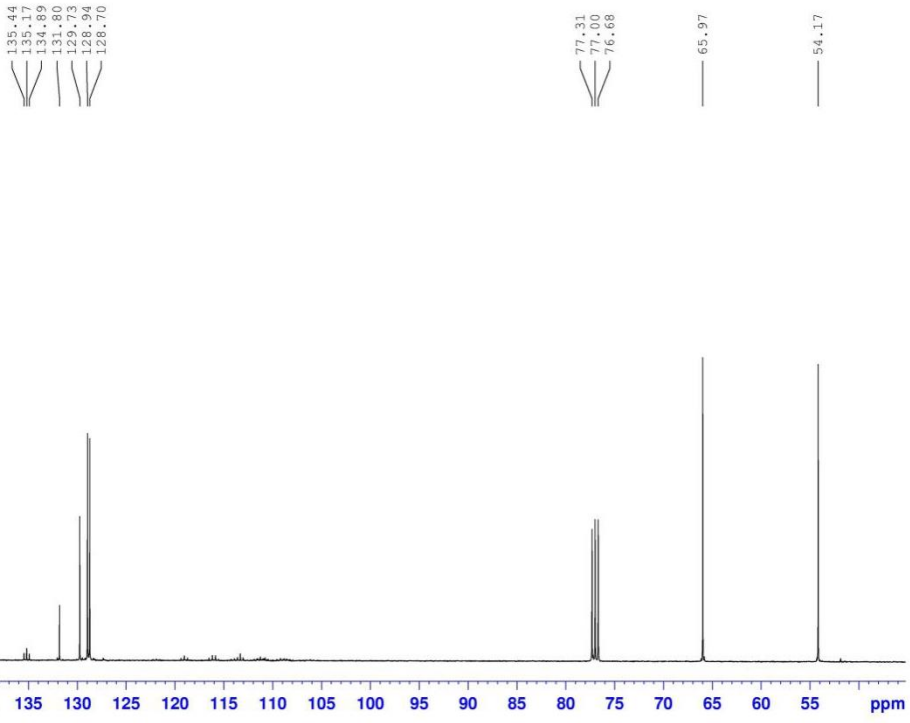

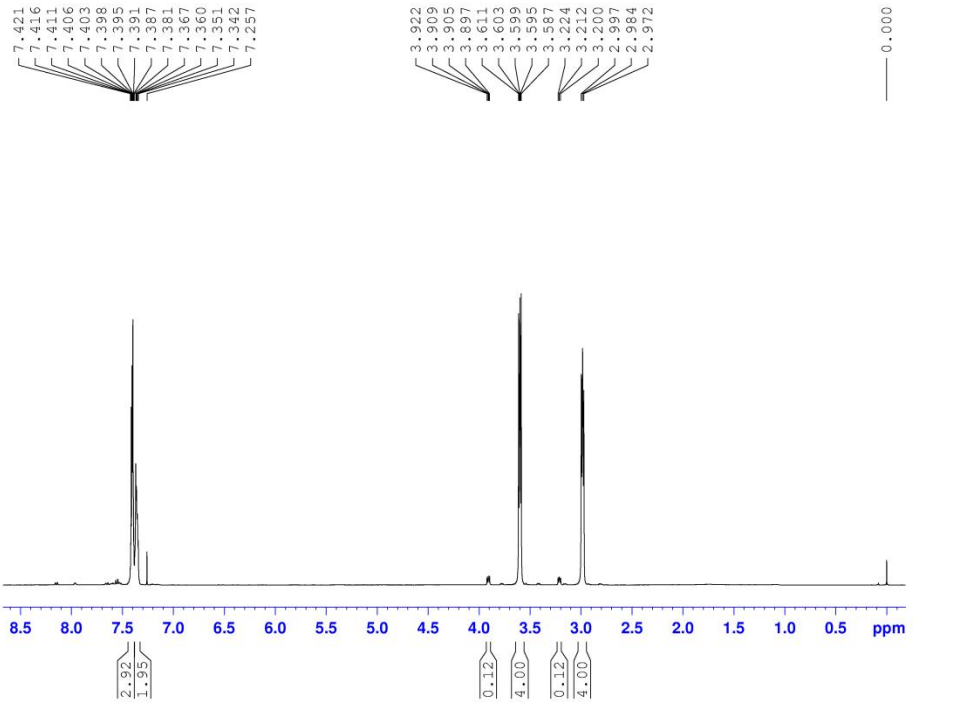

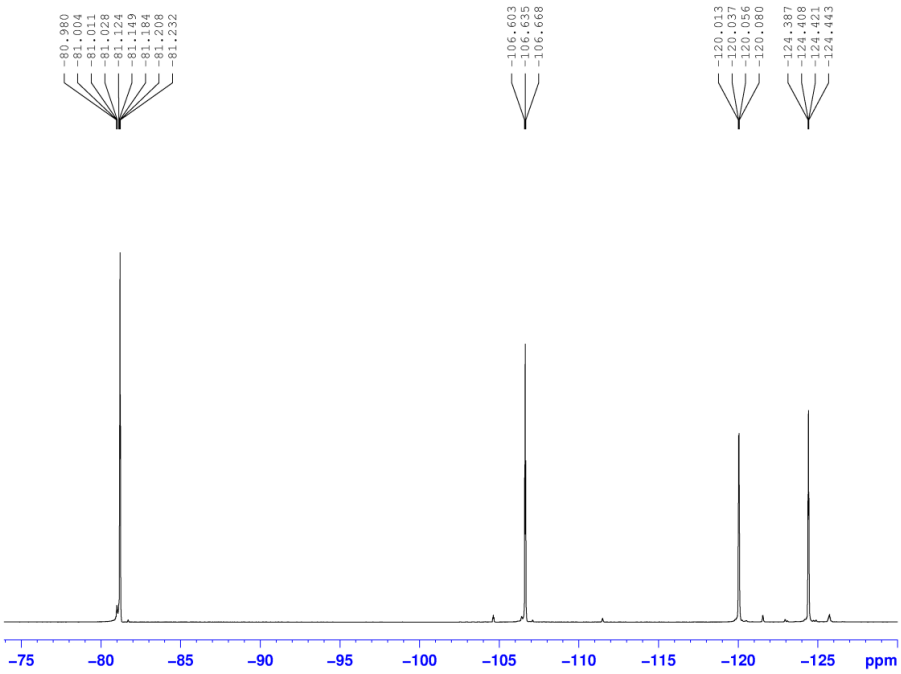
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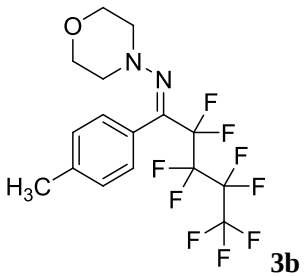
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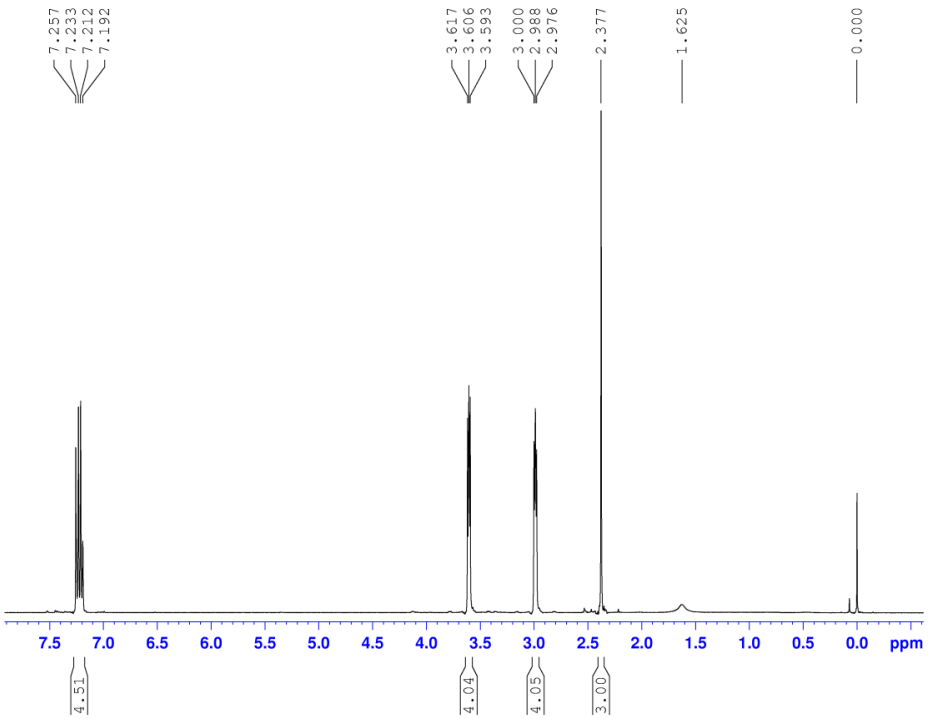
H3C

3b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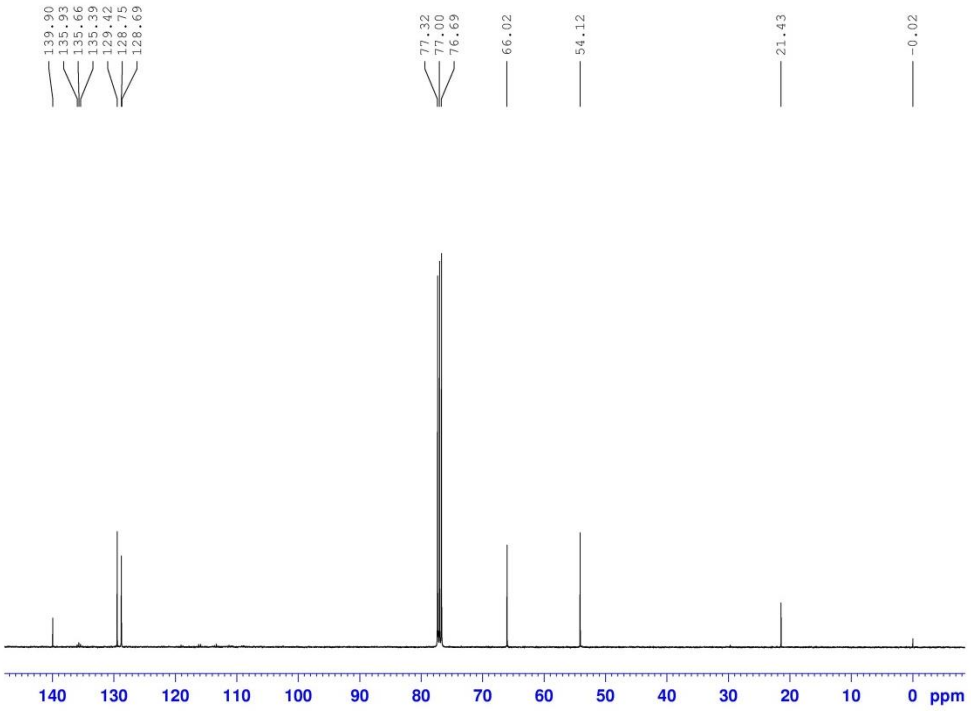
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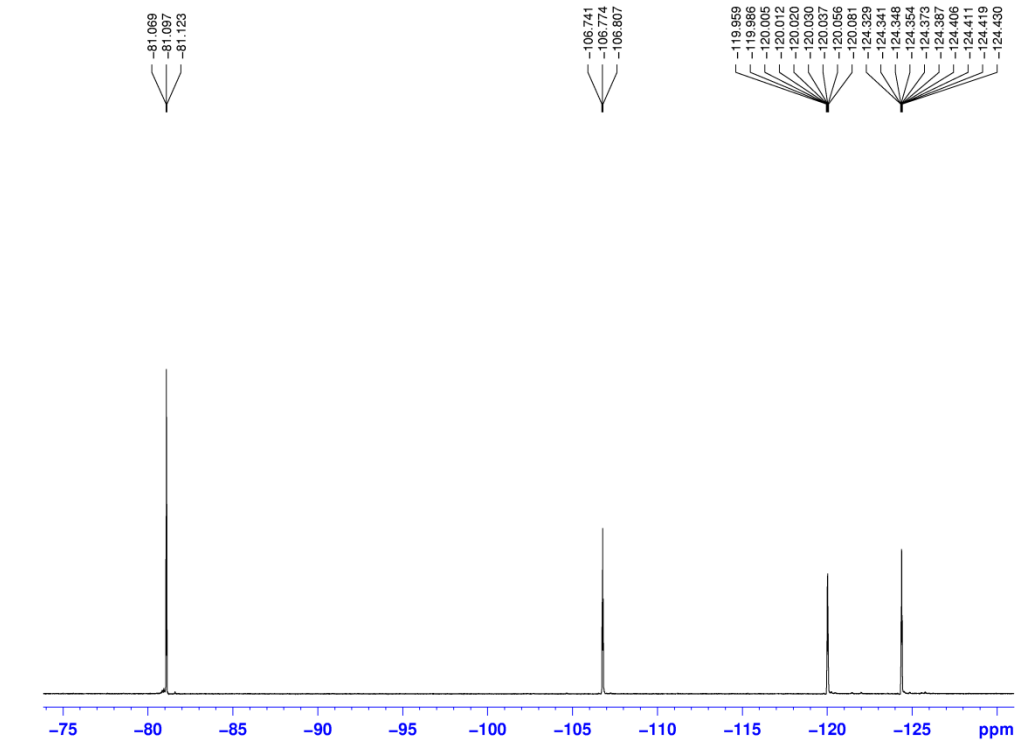
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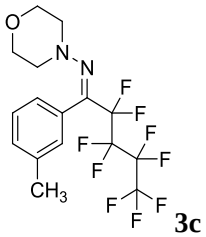

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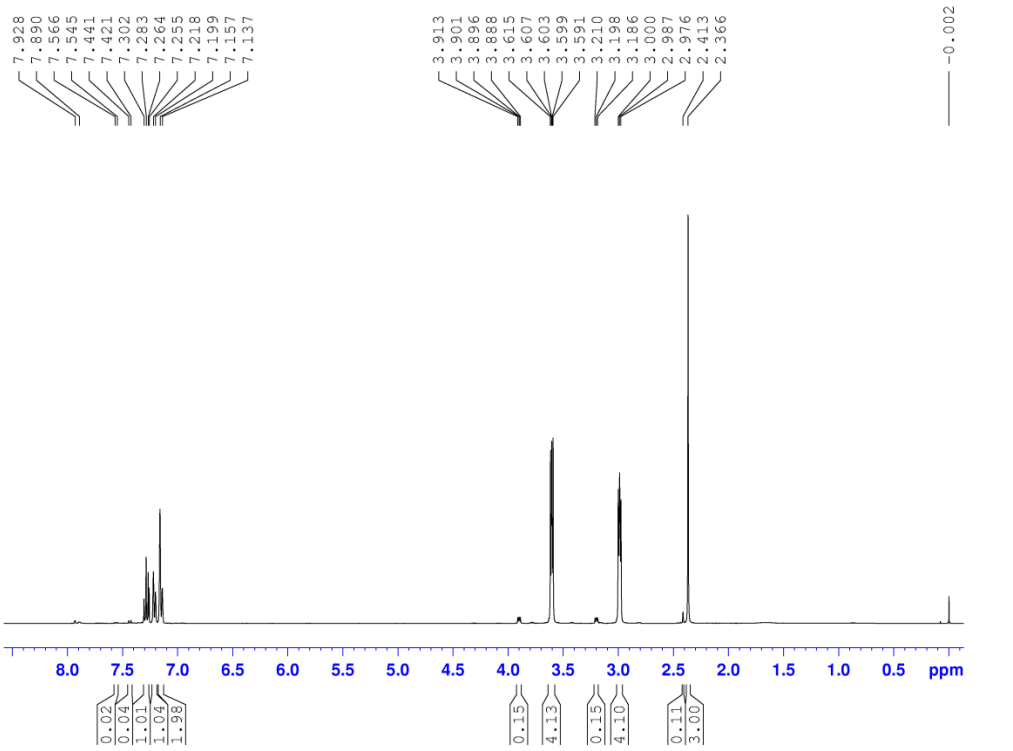
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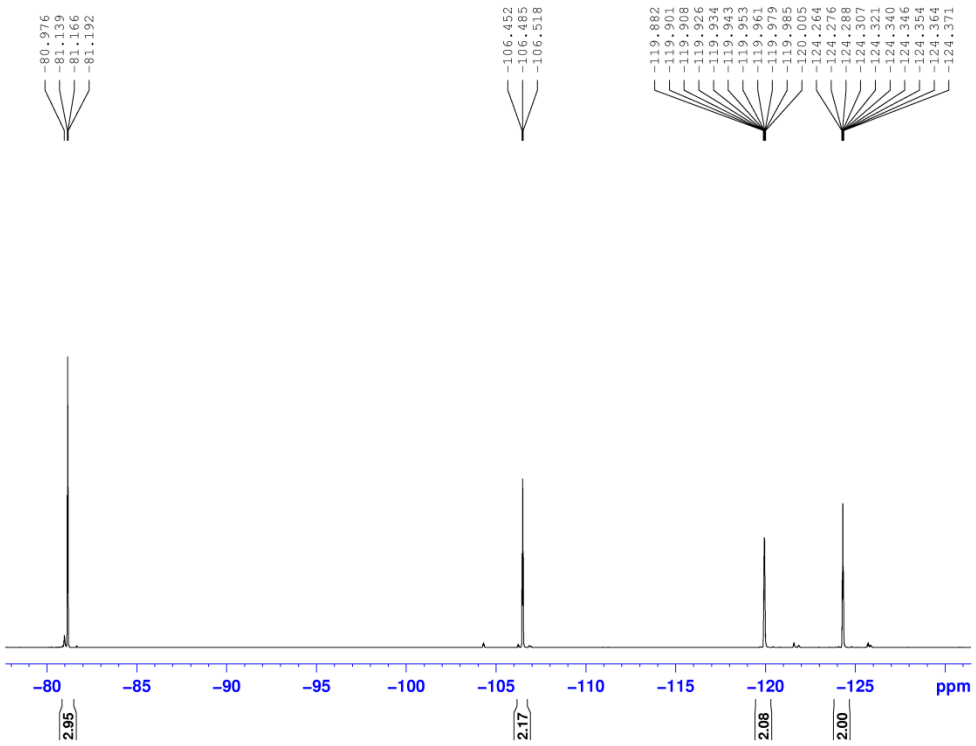
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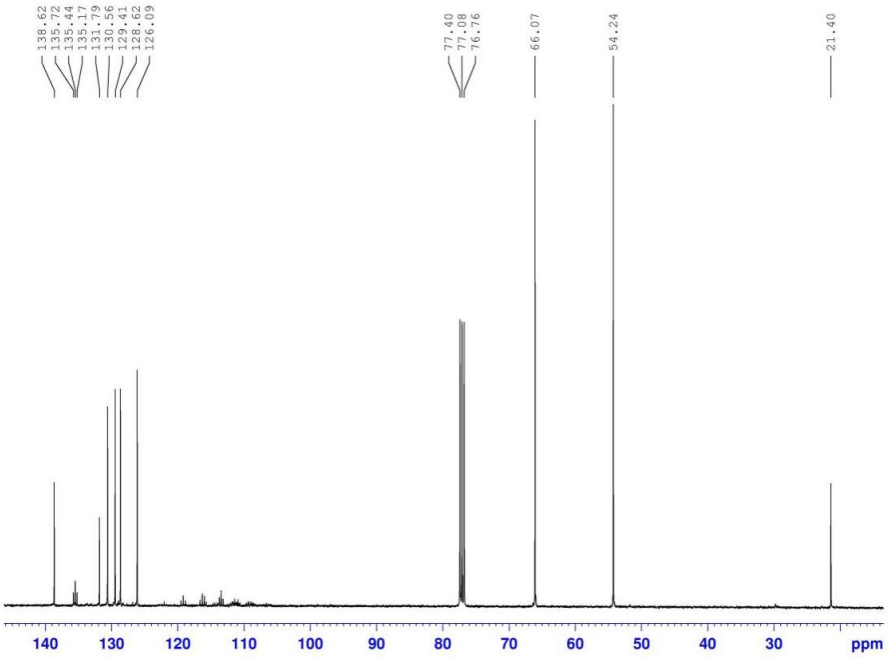
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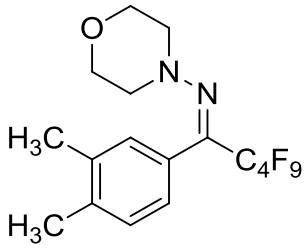
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H3C
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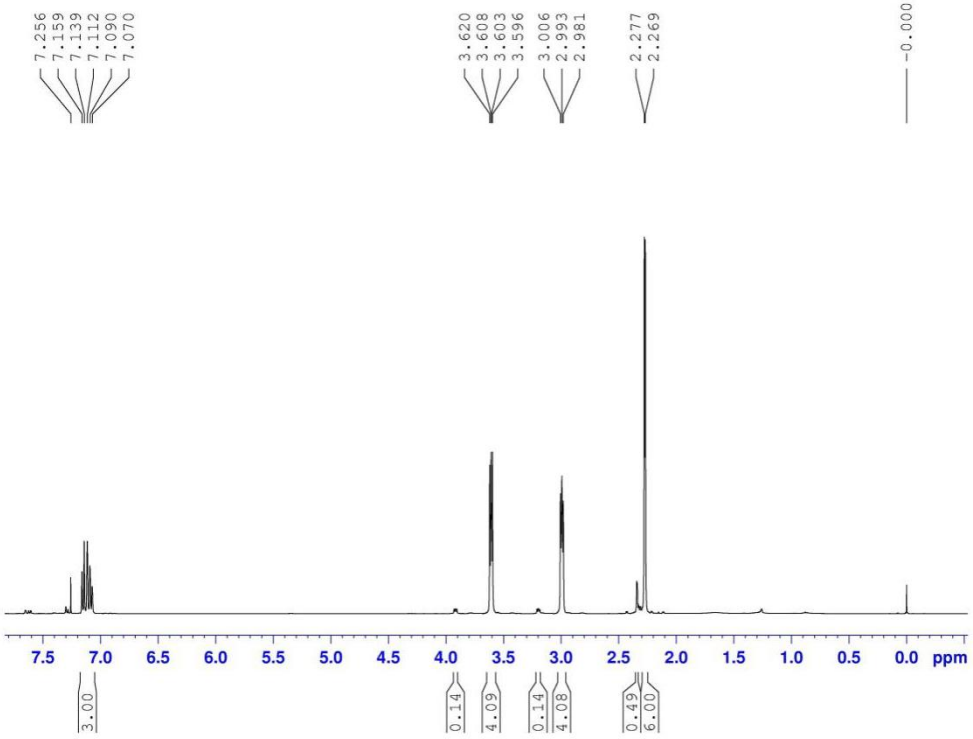
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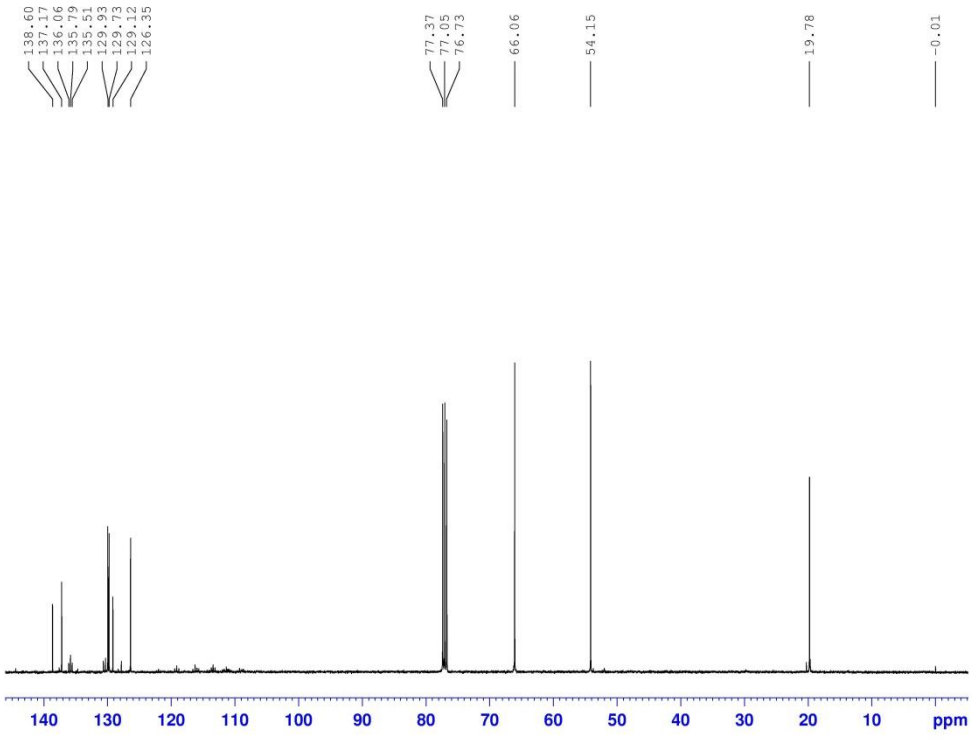
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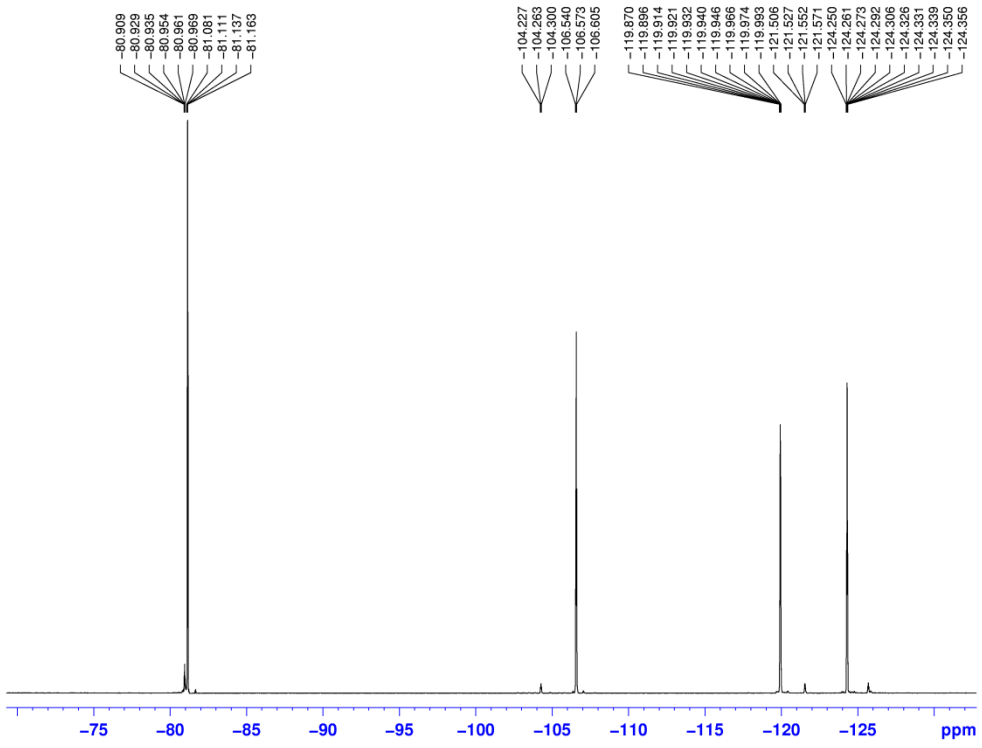
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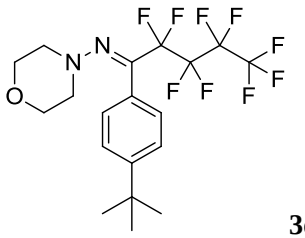

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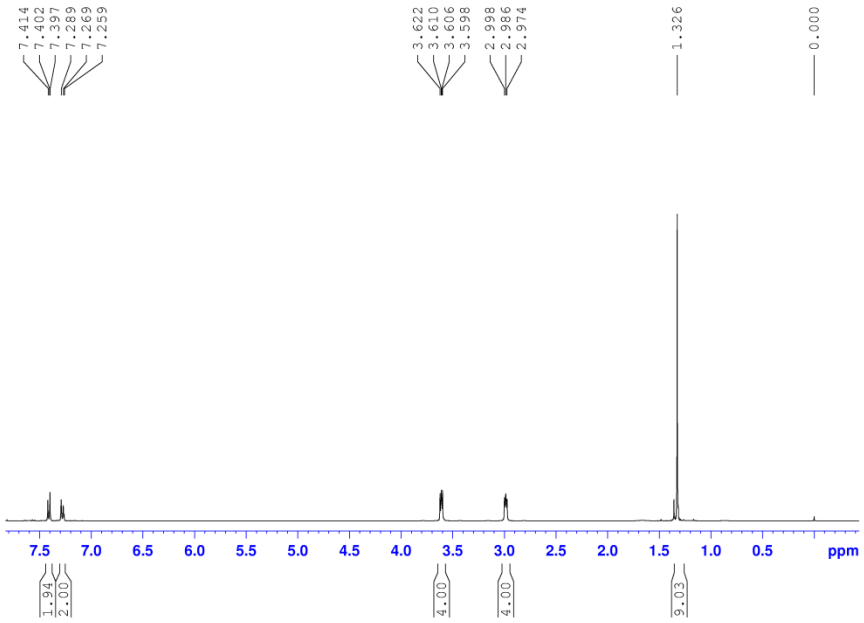
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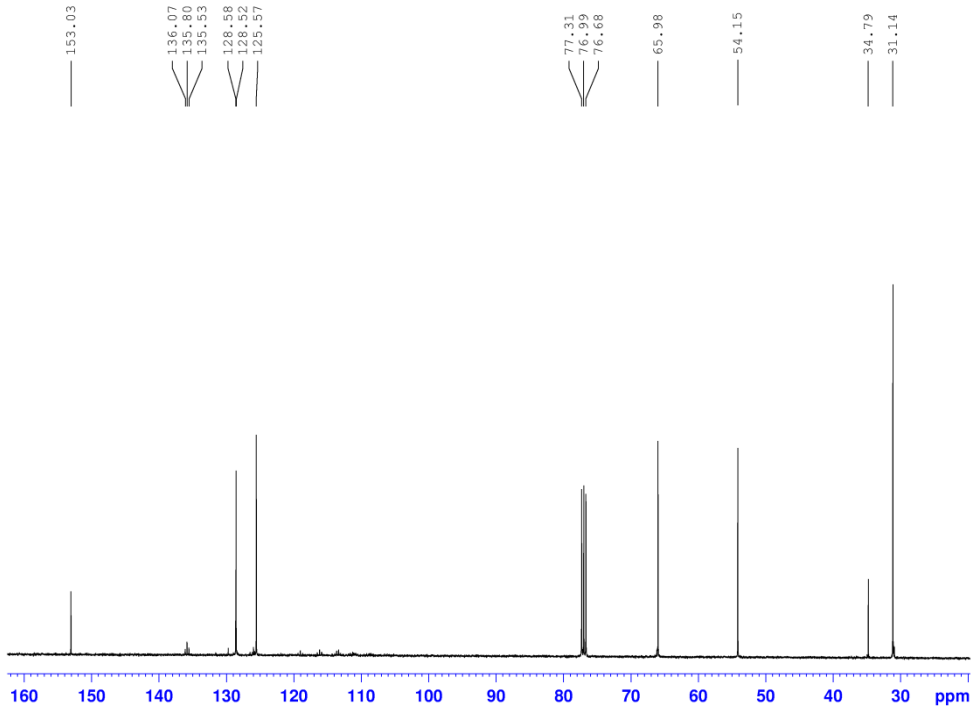
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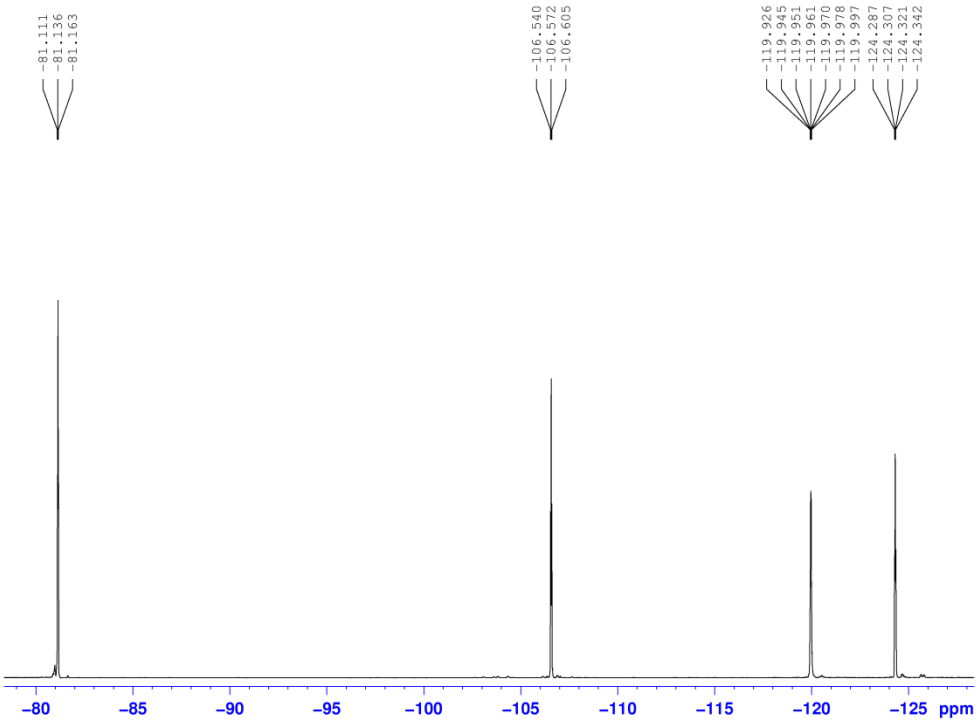
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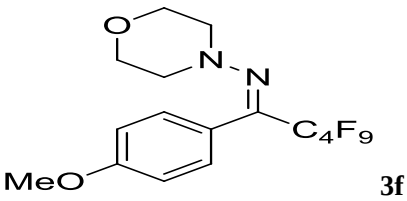
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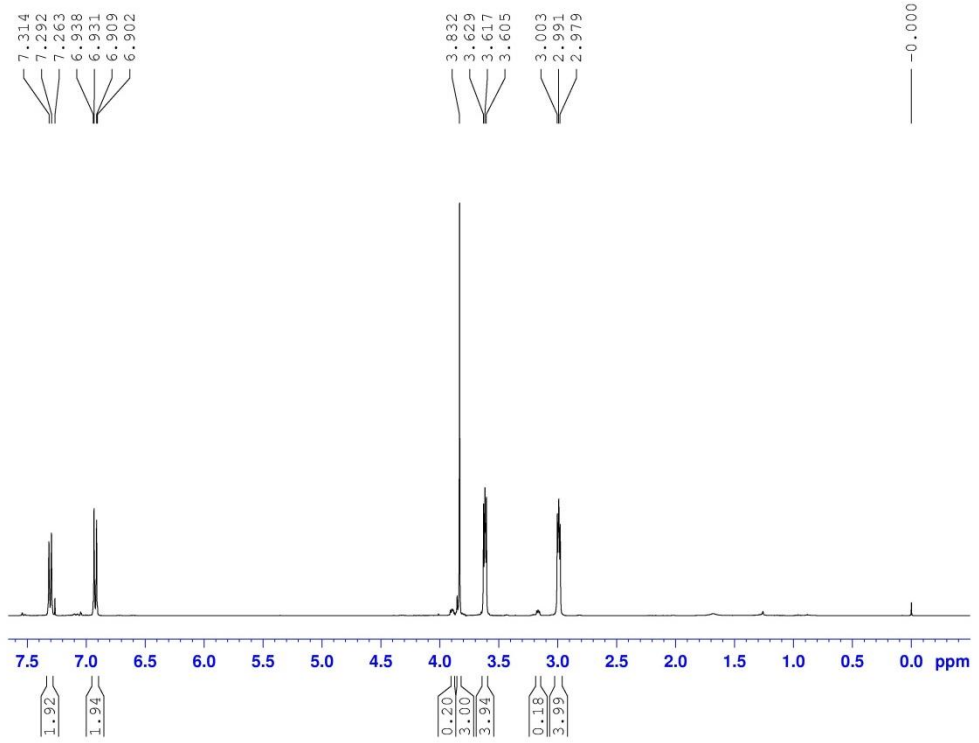
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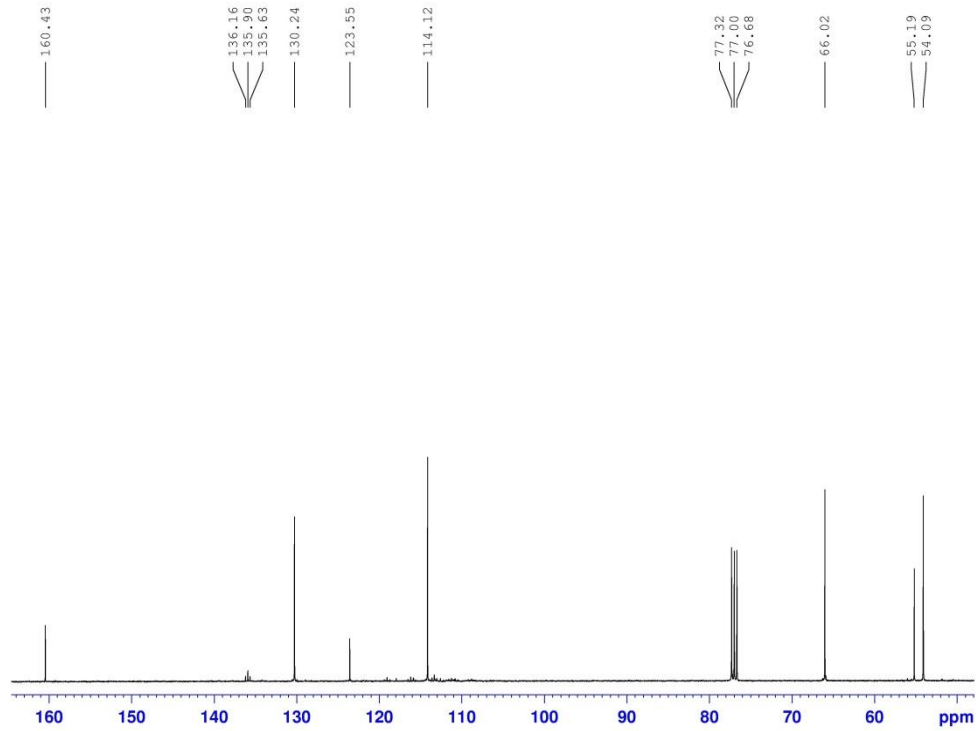
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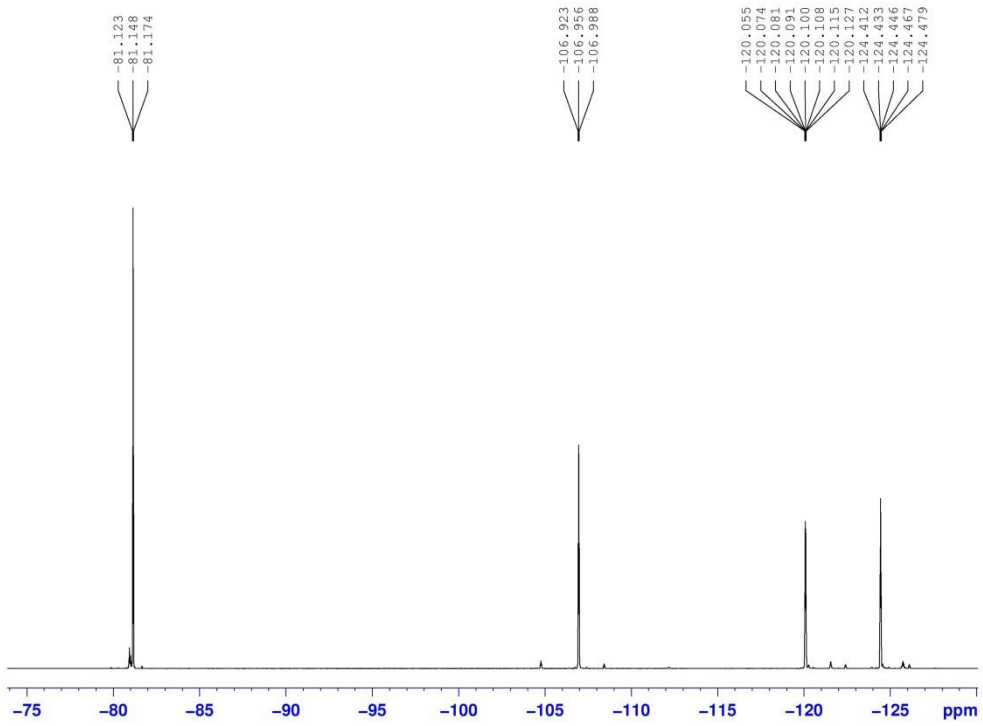
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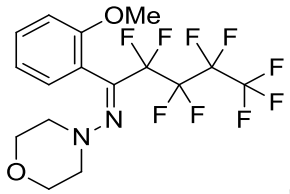
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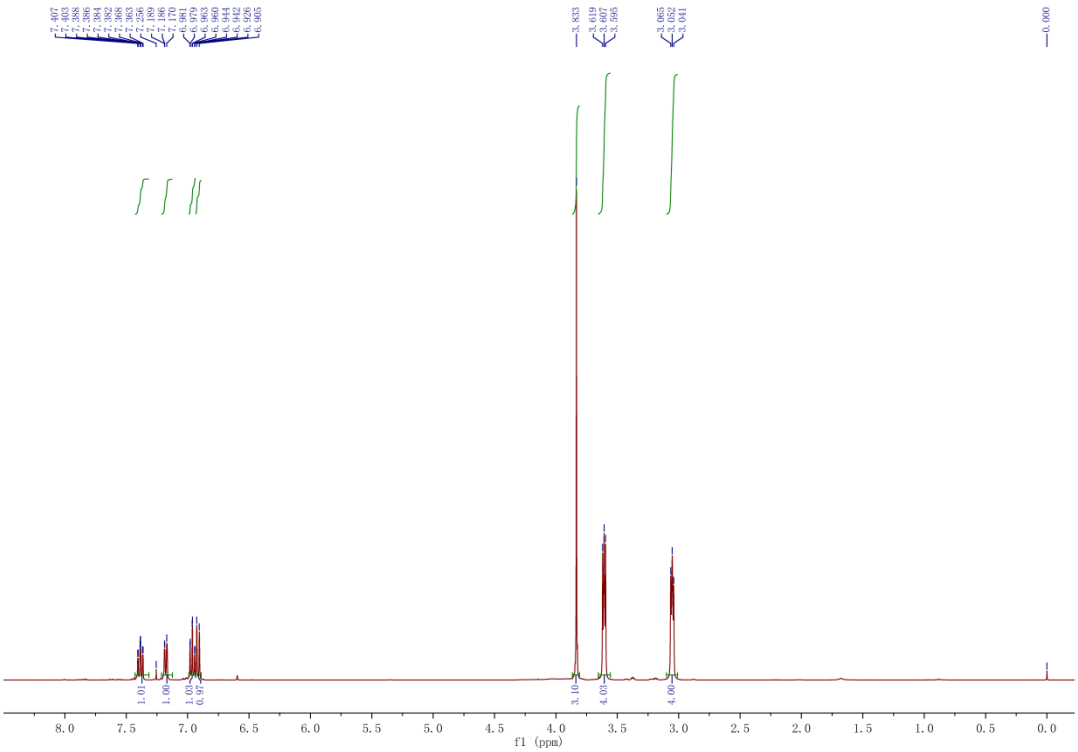
O

3g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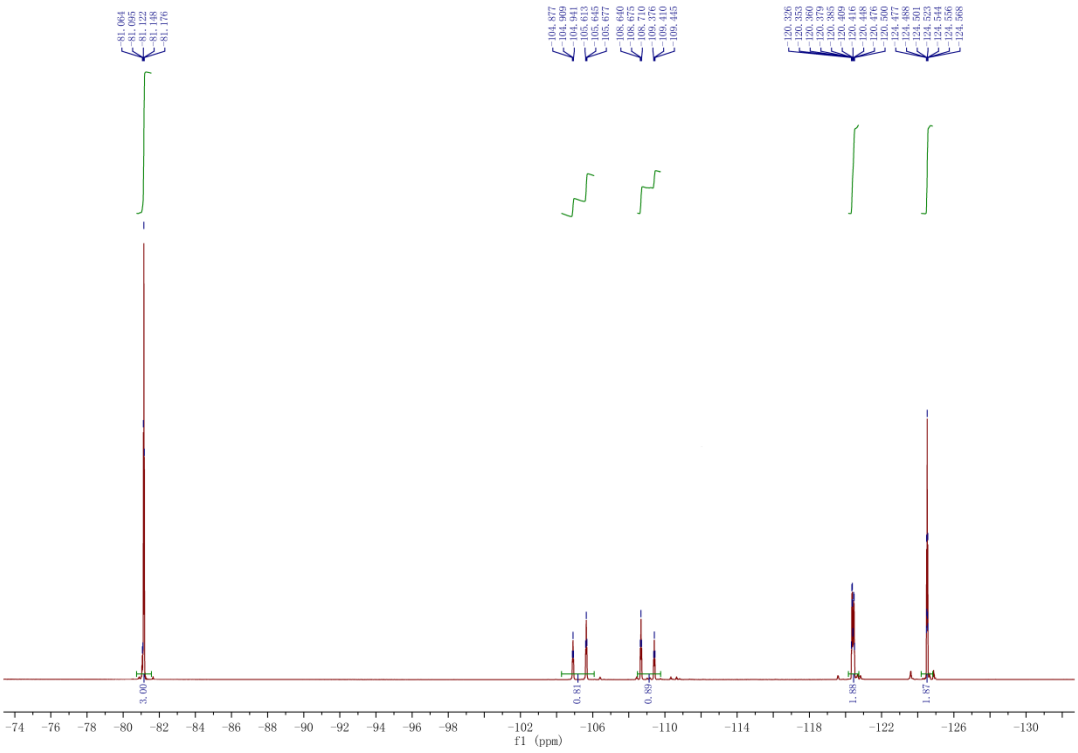
7.405
7.388
7.386
7.384
7.382
7.368
7.363
7.256
7.194
7.186
7.170
6.981
6.979
6.965
6.960
6.944
6.942
6.926
6.905
3.833
3.619
3.607
3.595
3.065
3.052
3.041
0.000
1.01
1.00
1.03
0.97
3.10
4.03
4.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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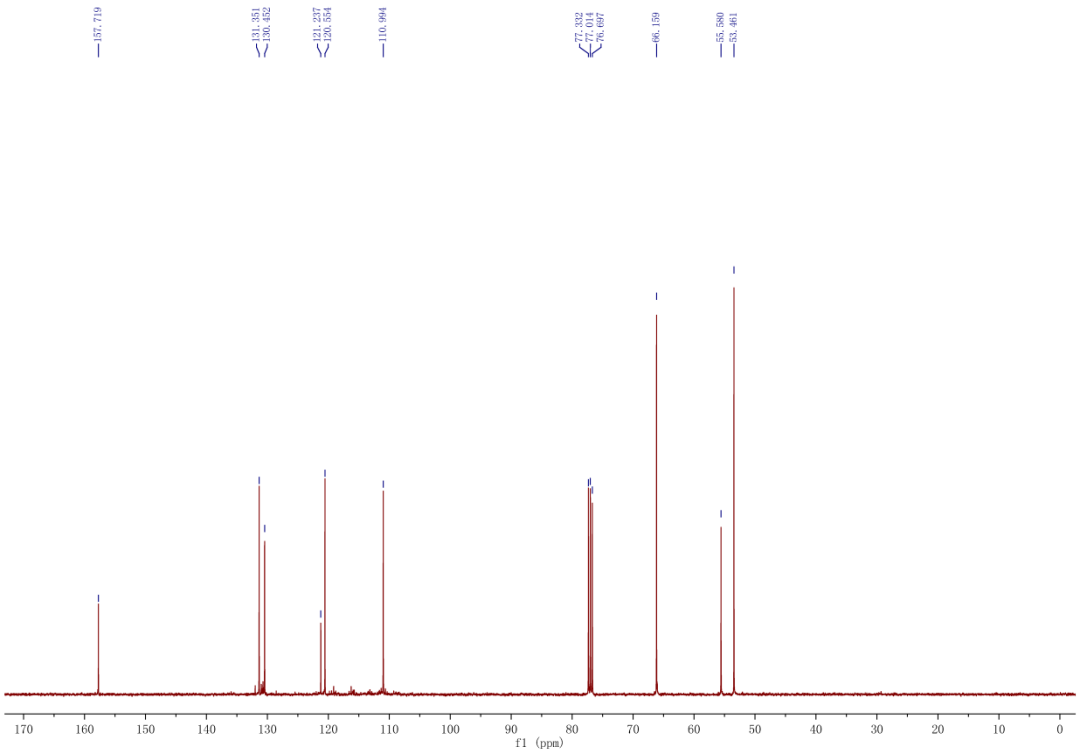
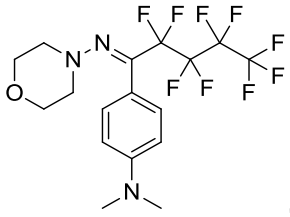
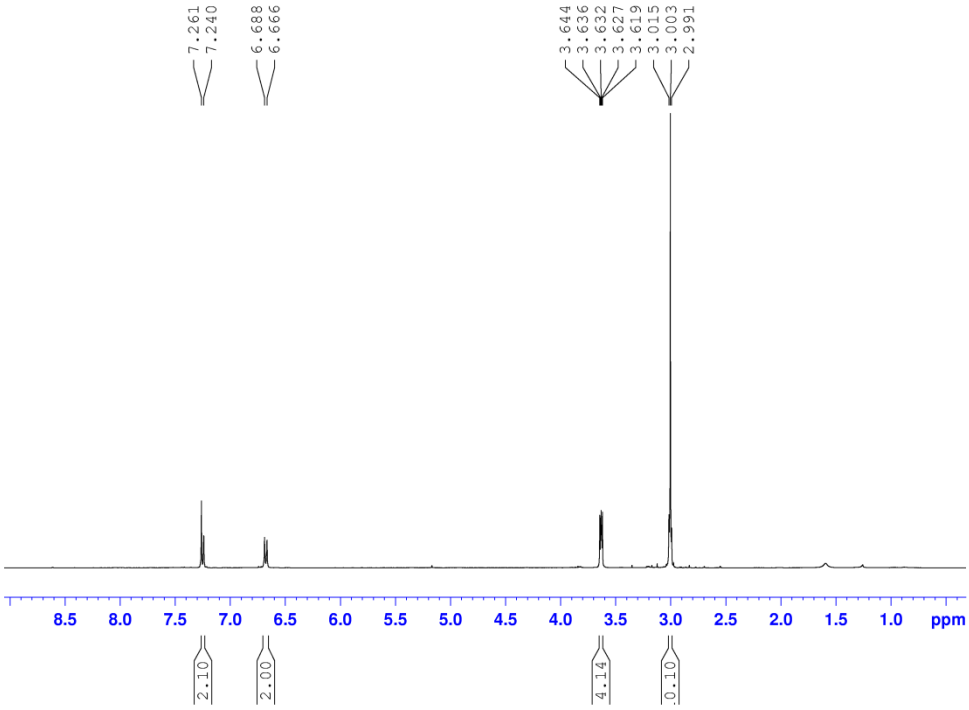
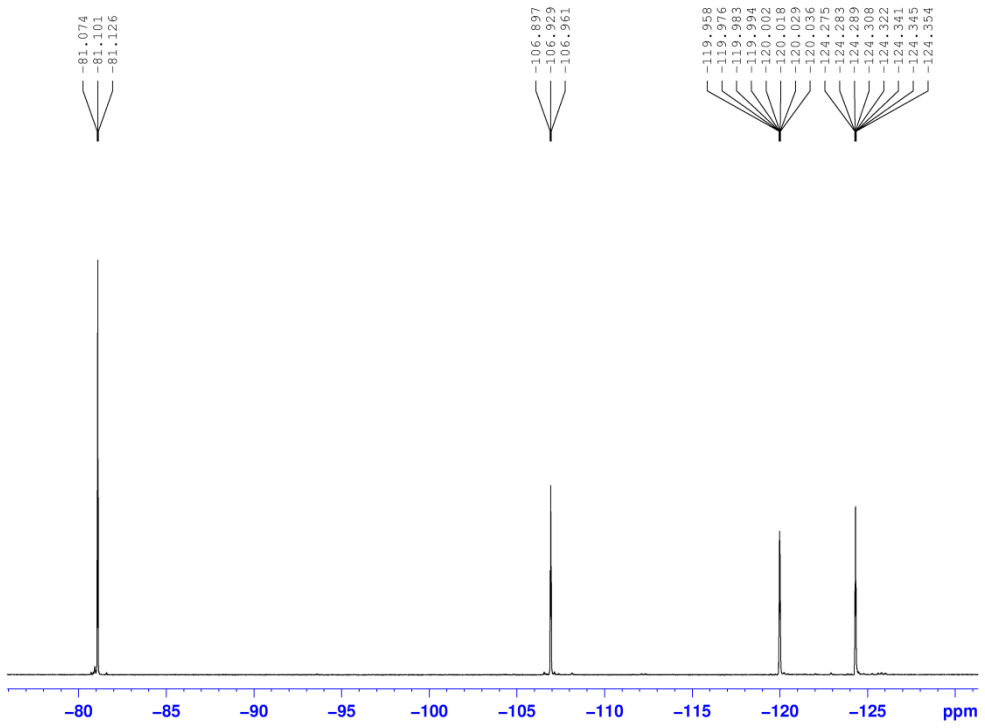
-81.095
-81.122
-81.148
-81.176
-104.877
-104.909
-104.941
-105.613
-105.645
-105.677
-108.640
-108.675
-108.710
-109.376
-109.410
-109.445
-120.326
-120.353
-120.390
-120.379
-120.385
-120.409
-120.446
-120.446
-120.476
-120.500
-124.477
-124.488
-124.501
-124.523
-124.544
-124.556
-124.568
3.00
0.81
0.89
1.88
1.87
-74
-76
-78
-80
-82
-84
-86
-88
-90
-92
-94
-96
-98
-102
-106
-110
-114
-118
-122
-126
-130
f1 (ppm)


157.719
131.351
130.452
121.237
120.554
110.994
77.332
77.014
76.697
66.159
55.580
53.461
f1 (ppm)



3h


7.261
7.240
6.688
6.666
3.644
3.636
3.632
3.627
3.619
3.015
3.003
2.991
ppm
2.10
2.00
4.14
0.10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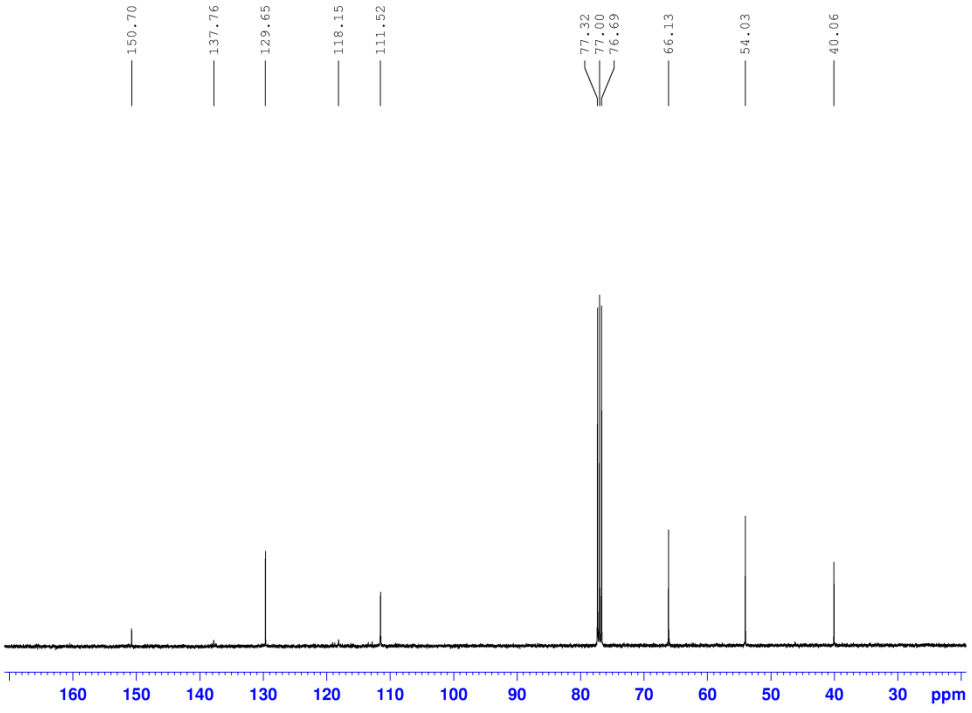
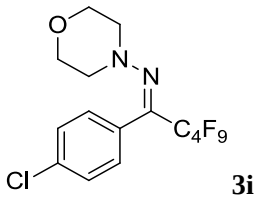
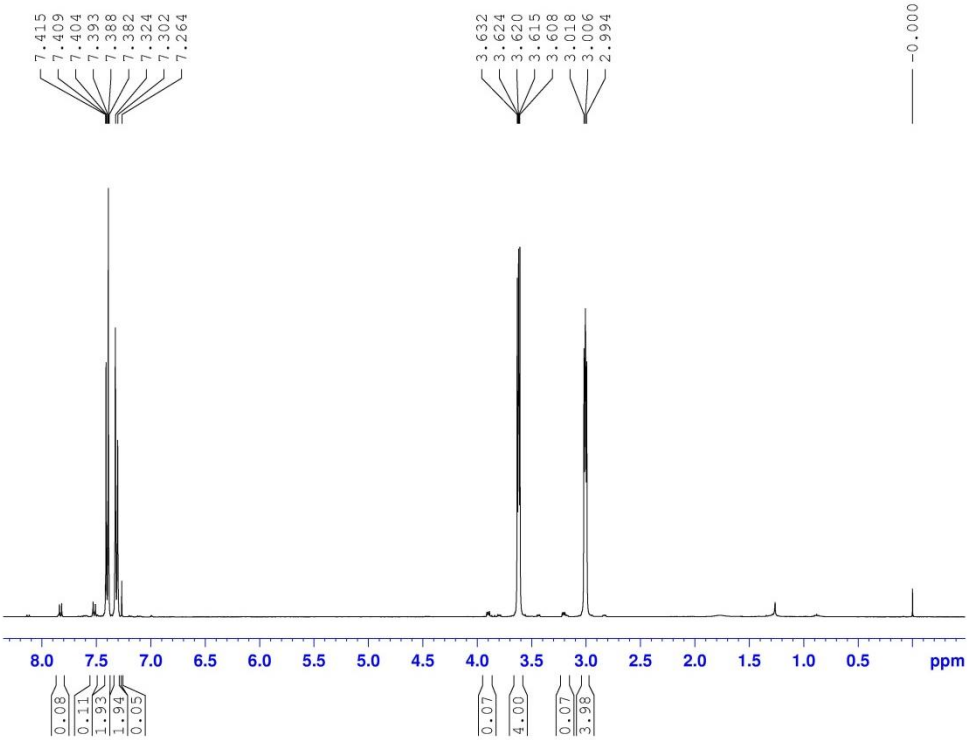
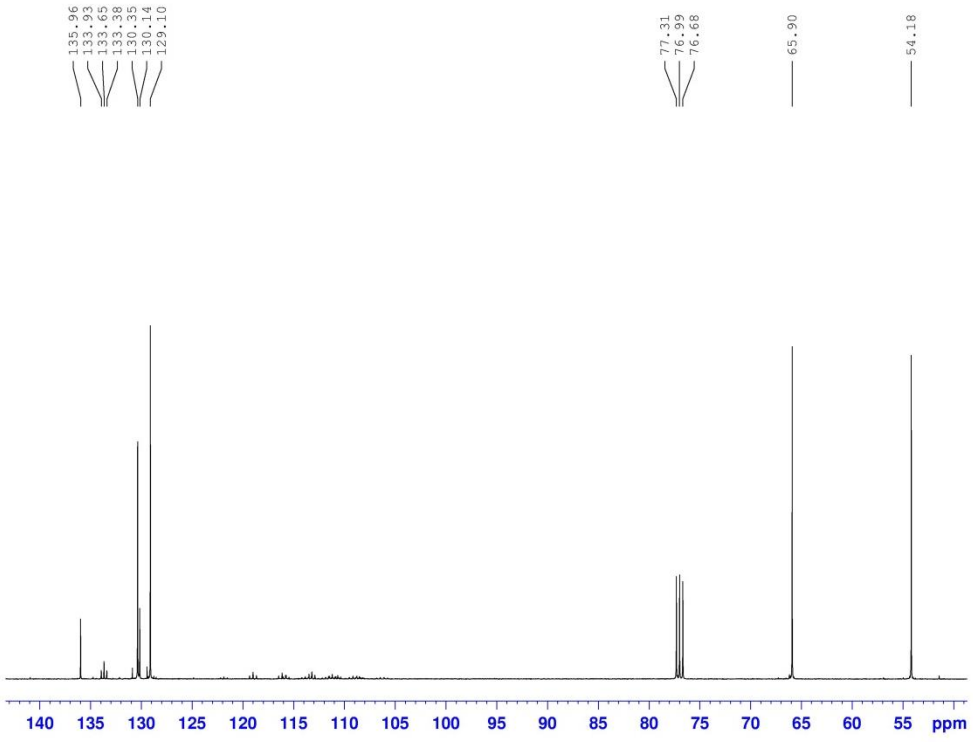
-81.101
-81.126
-106.897
-106.929
-106.961
-119.958
-119.976
-119.983
-119.994
-120.002
-120.018
-120.029
-120.036
-124.275
-124.283
-124.289
-124.308
-124.322
-124.341
-124.345
-124.354
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
ppm

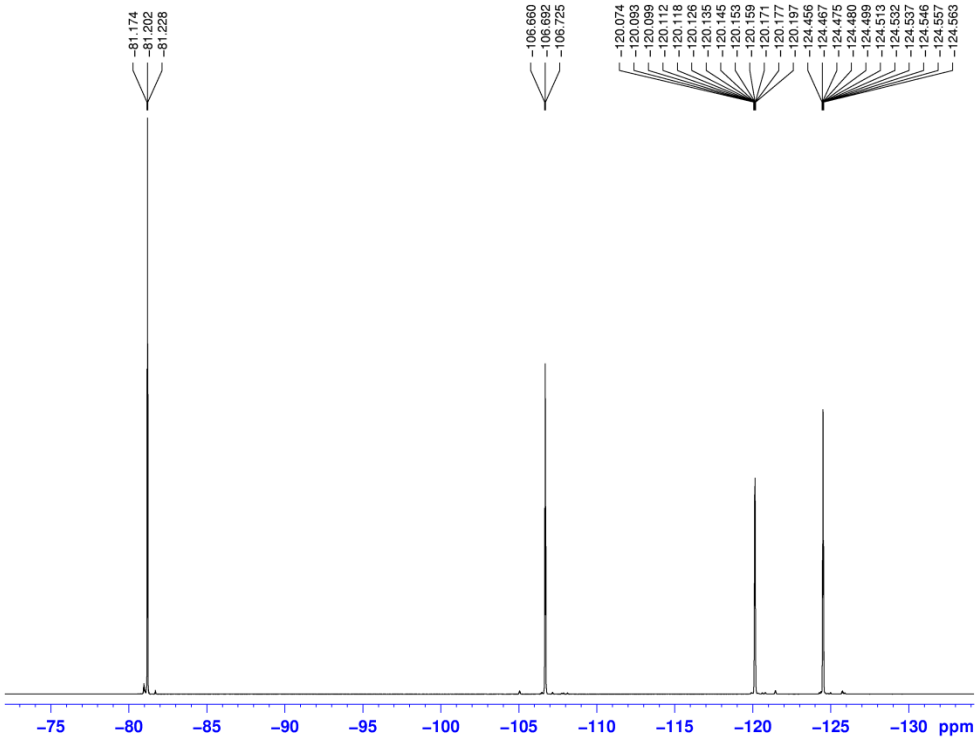

150.70
137.76
129.65
118.15
111.52
77.32
77.00
76.69
66.13
54.03
40.06
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

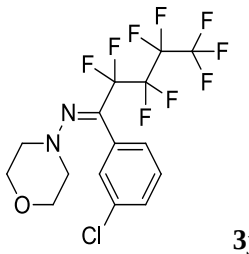


3i

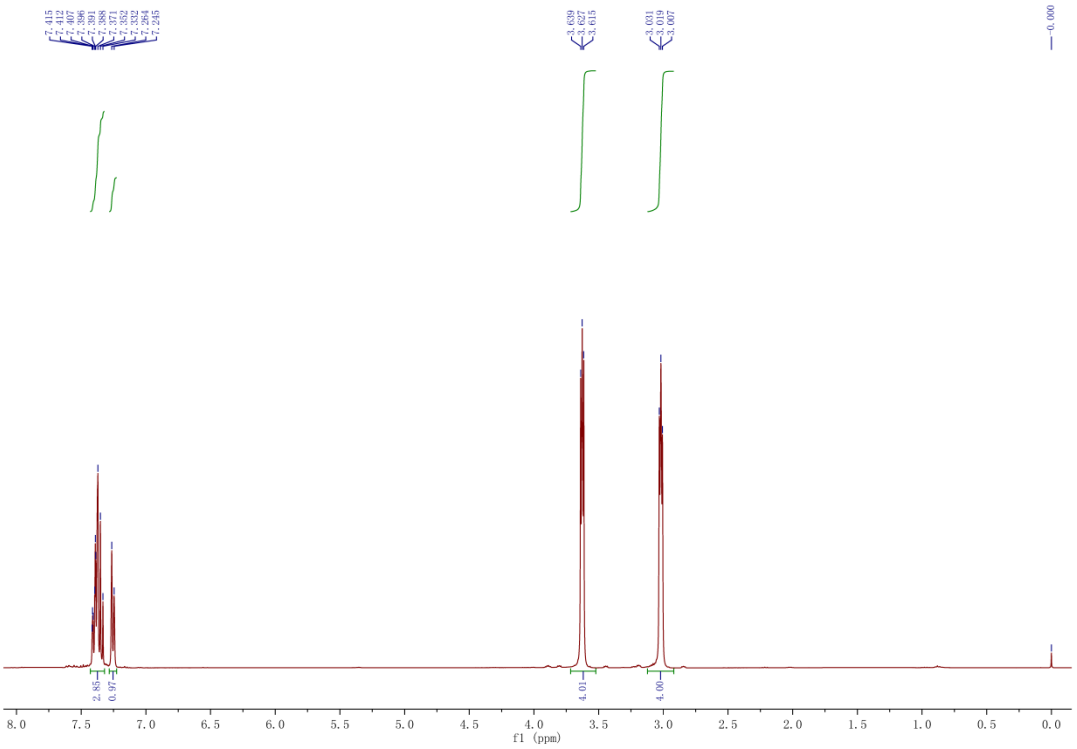

7.415
7.409
7.404
7.393
7.388
7.382
7.324
7.302
7.264
3.632
3.624
3.620
3.615
3.608
3.018
3.006
2.994
-0.000
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.08
0.11
1.93
1.94
0.05
0.07
4.00
0.07
3.98

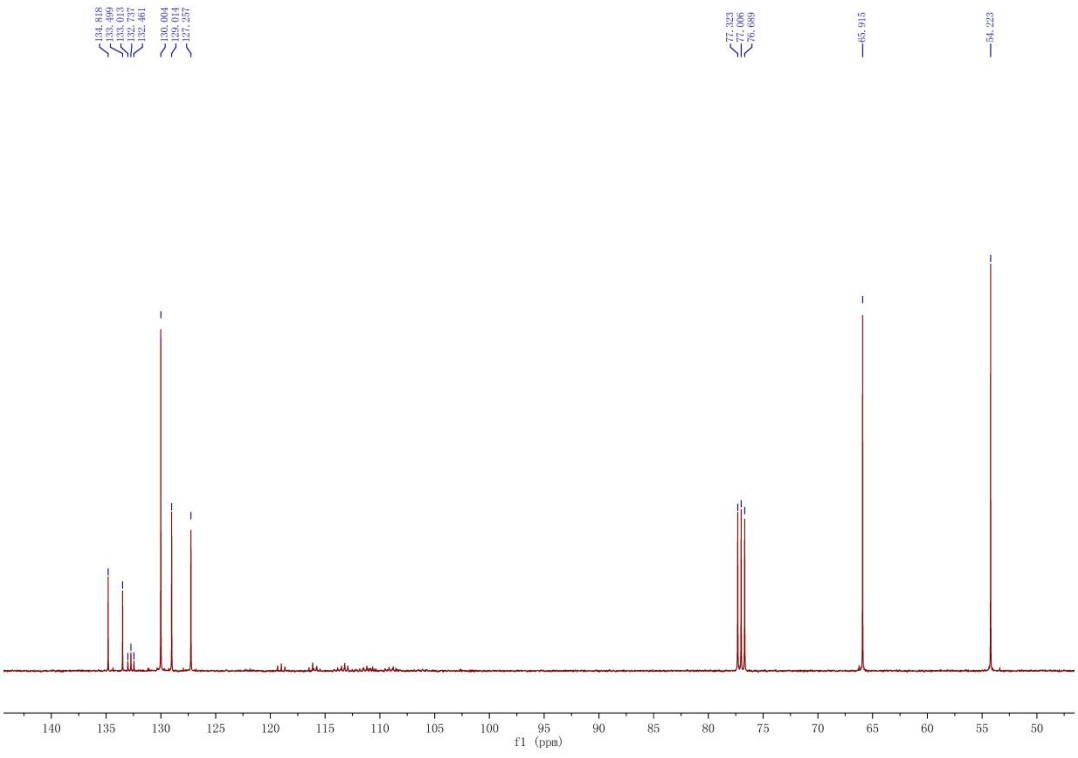

135.96
133.93
133.65
133.38
130.35
130.14
129.10
77.31
76.99
76.68
65.90
54.18
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
ppm

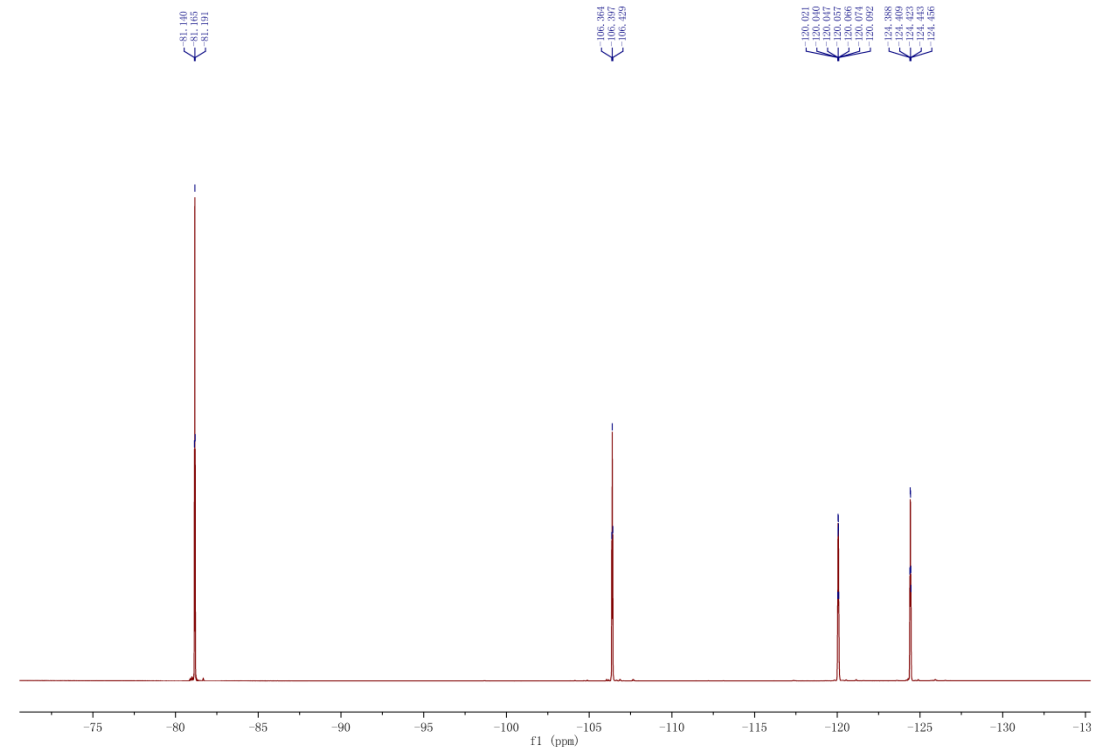

-81.174
-81.202
-81.228
-106.660
-106.692
-106.725
-120.074
-120.093
-120.099
-120.112
-120.118
-120.126
-120.135
-120.145
-120.153
-120.159
-120.171
-120.177
-120.197
-124.456
-124.467
-124.475
-124.480
-124.499
-124.513
-124.532
-124.537
-124.546
-124.557
-124.563
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
ppm

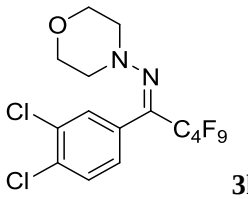

F
F
F
F
F
F
F
F
F
N
N
O
Cl

3j

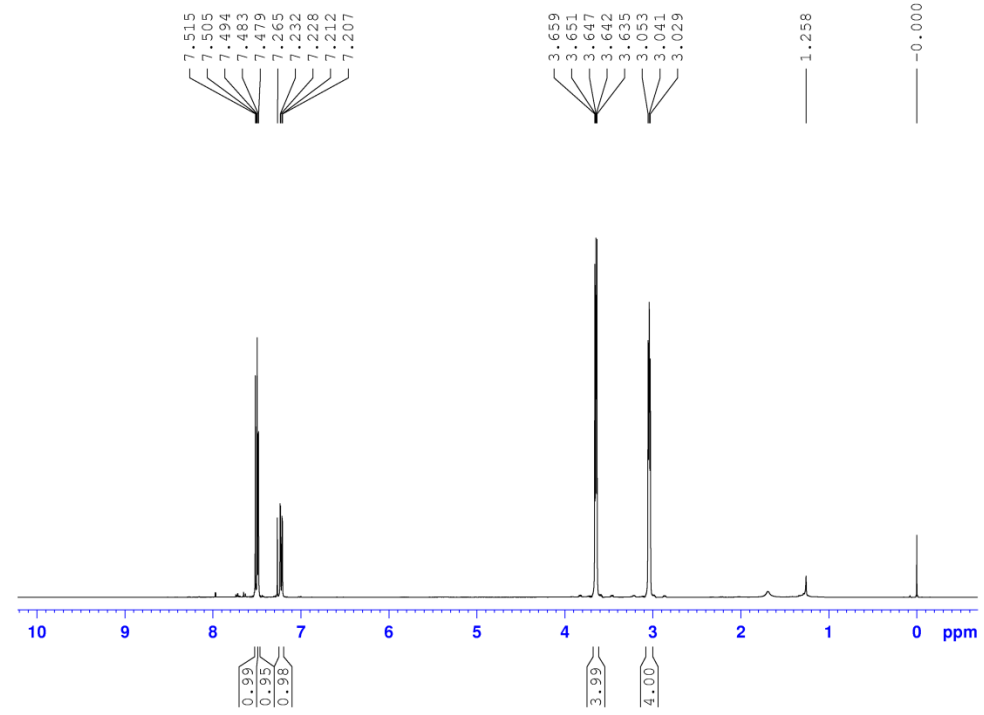

7.415
7.412
7.407
7.396
7.391
7.388
7.371
7.352
7.332
7.264
7.245
3.639
3.627
3.615
3.031
3.019
3.007
0.000
2.85
0.97
4.01
4.00
f1 (ppm)

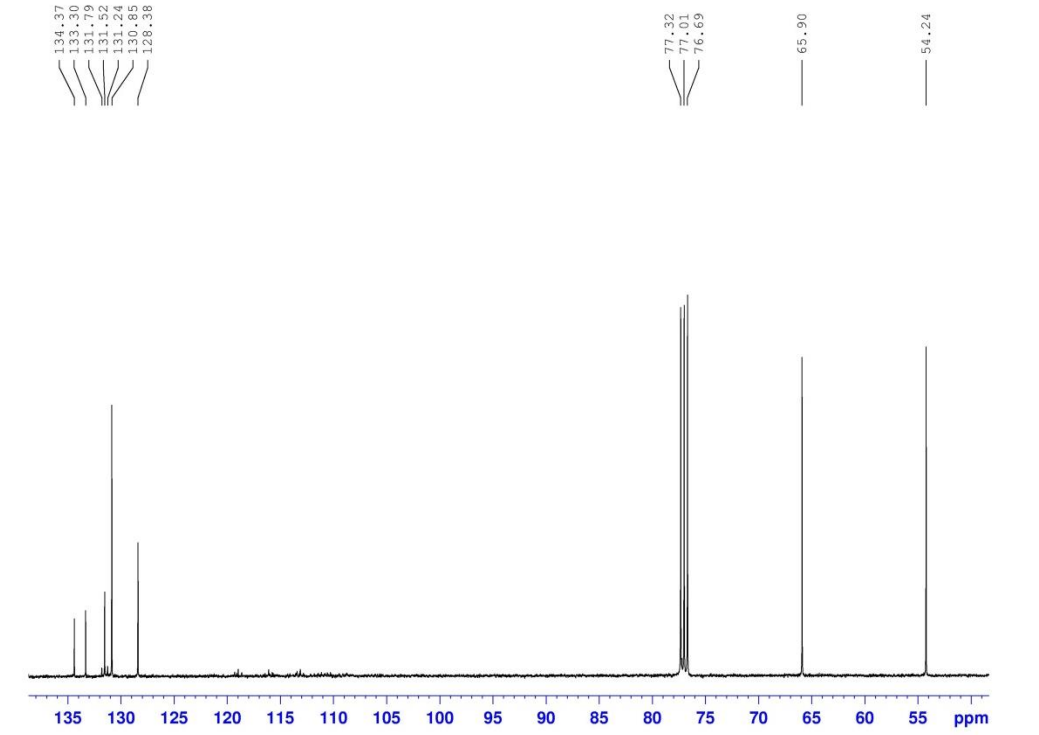

134.818
133.866
133.039
132.737
132.461
130.004
129.014
127.257
77.323
77.006
76.688
65.915
54.223
f1 (ppm)

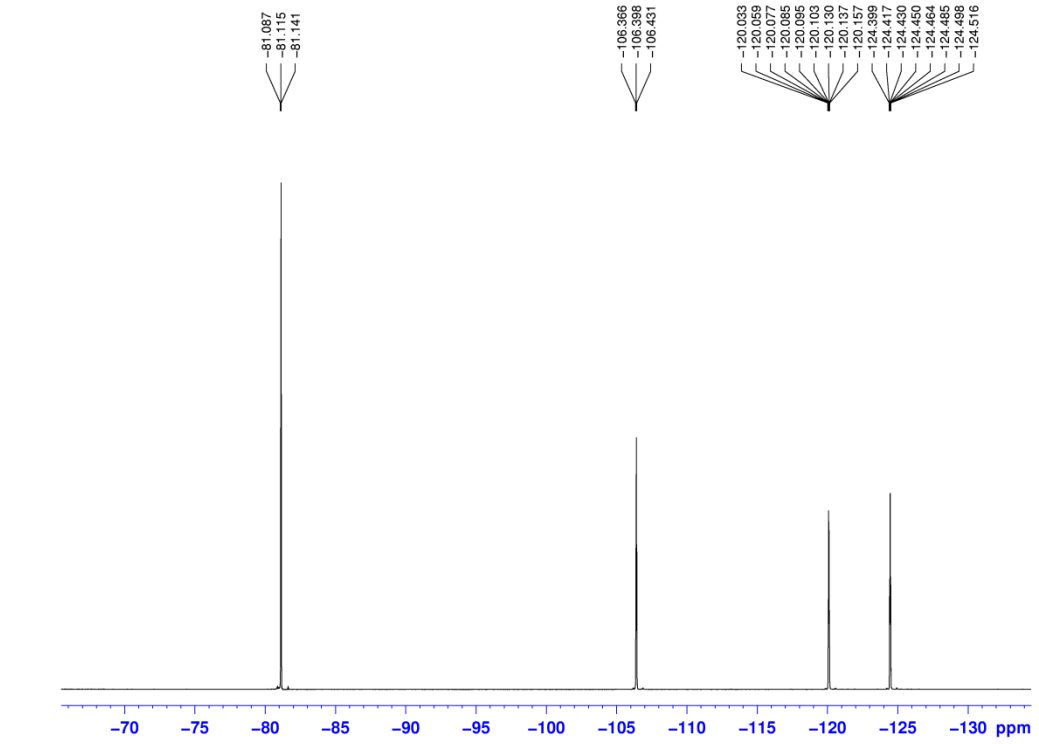

-81.140
-81.165
-81.191
-106.364
-106.397
-106.429
-120.021
-120.040
-120.047
-120.057
-120.066
-120.074
-120.092
-124.388
-124.409
-124.423
-124.443
-124.456
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
f1 (ppm)

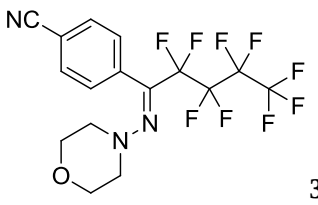

O
N
N
Cl
Cl
C_4F_9

3k

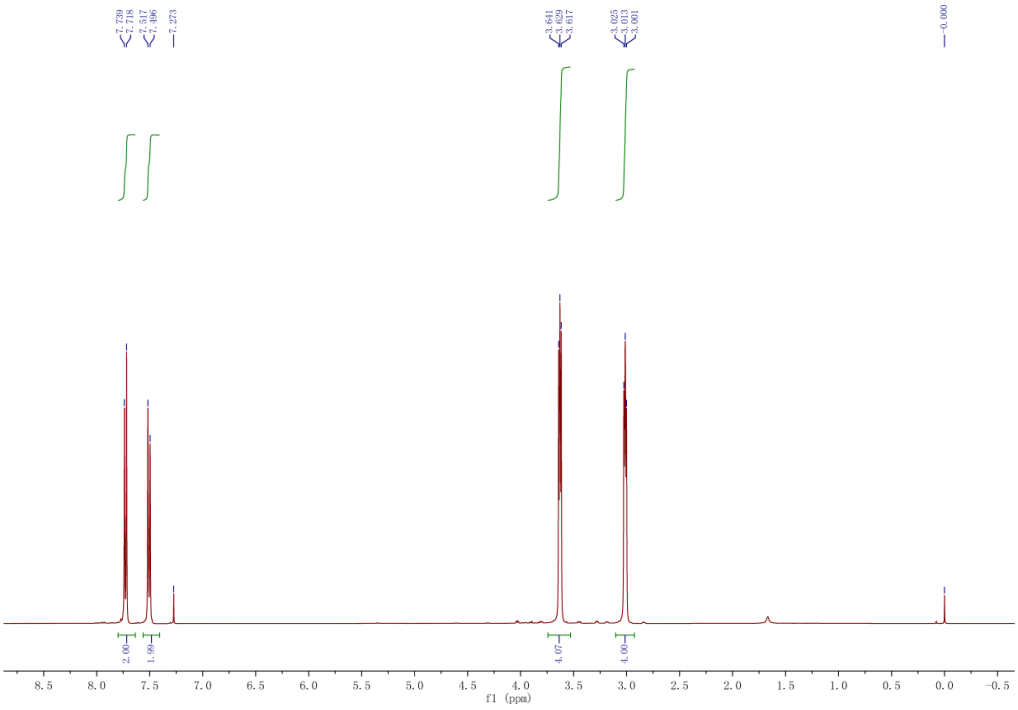

7.515
7.505
7.494
7.483
7.479
7.265
7.232
7.228
7.212
7.207
3.659
3.651
3.647
3.642
3.635
3.053
3.041
3.029
1.258
-0.000
10
9
8
7
6
5
4
3
2
1
0
ppm
0.99
0.95
0.98
3.99
4.00

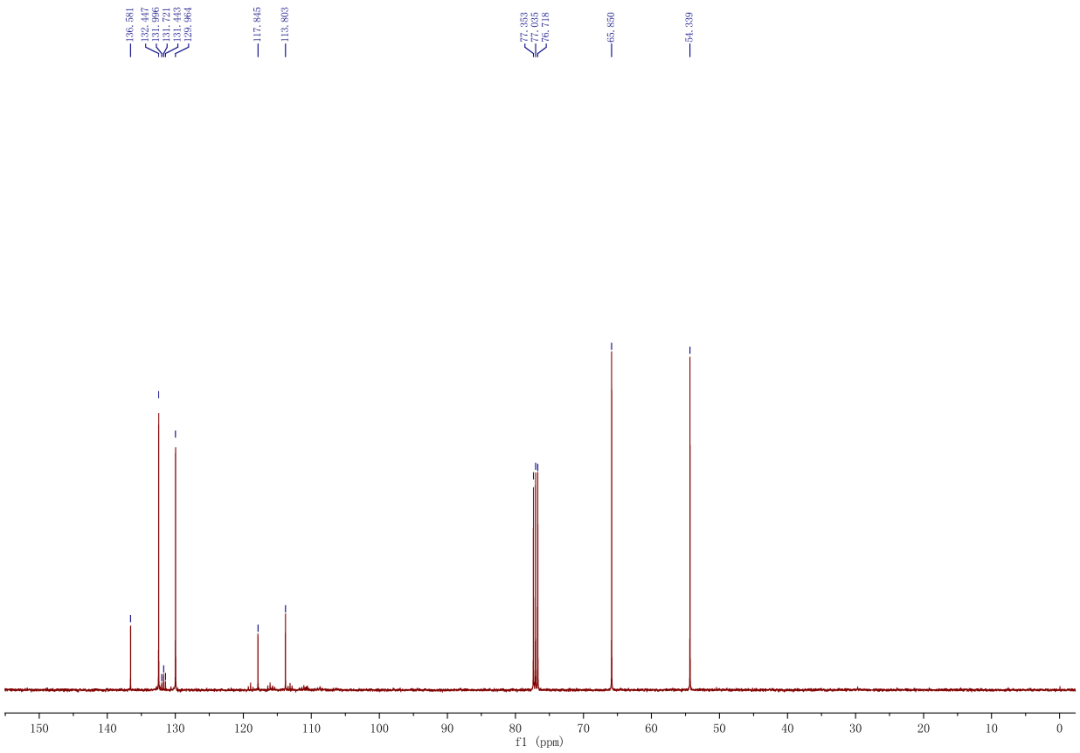

134.37
133.30
131.79
131.52
131.24
130.85
128.38
77.32
77.01
76.69
65.90
54.24
135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 ppm


-81.087
-81.115
-81.141
-106.366
-106.398
-106.431
-120.033
-120.059
-120.077
-120.085
-120.095
-120.103
-120.130
-120.137
-120.157
-124.399
-124.417
-124.430
-124.450
-124.464
-124.485
-124.498
-124.516
-70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 ppm


NC
F
F
F
F
F
F
F
F
F
N
N
O

3l


7.739
7.718
7.517
7.496
7.273
3.641
3.629
3.617
3.025
3.013
3.001
0.000
2.00
1.99
4.07
4.00
f1 (ppm)


136.581
132.447
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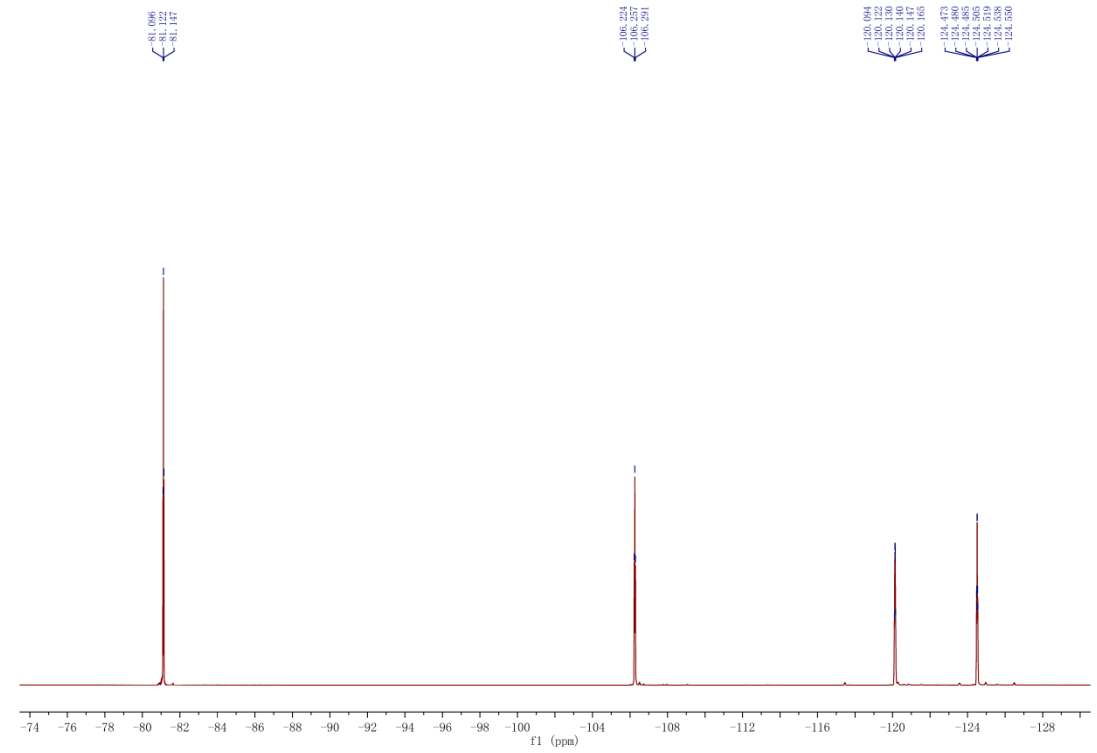
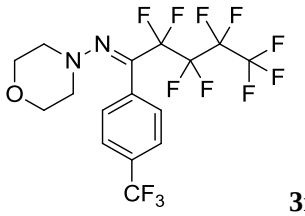
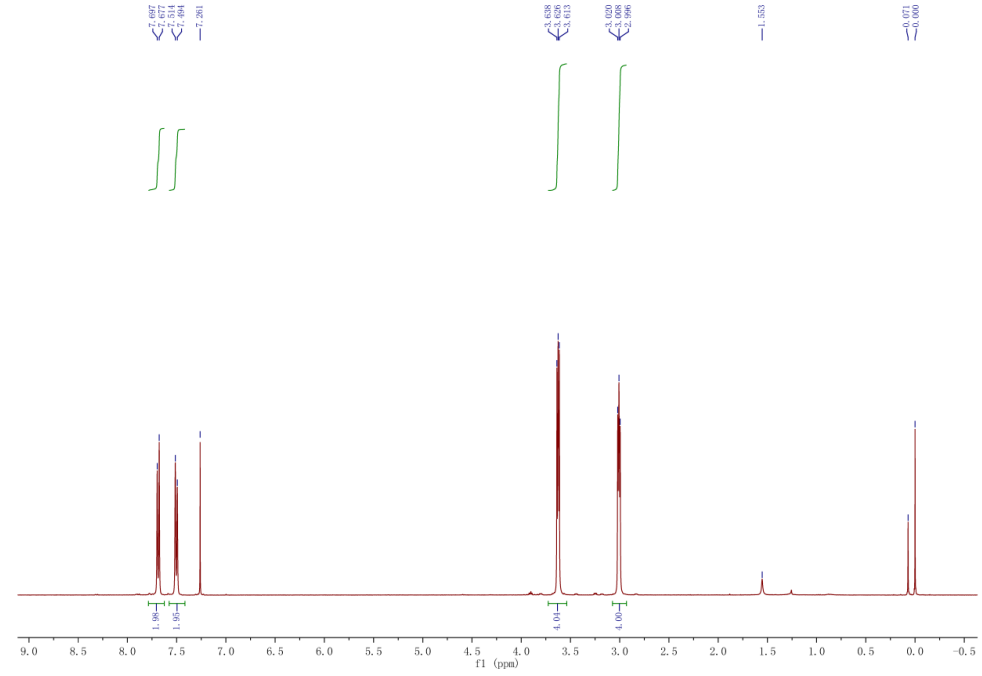
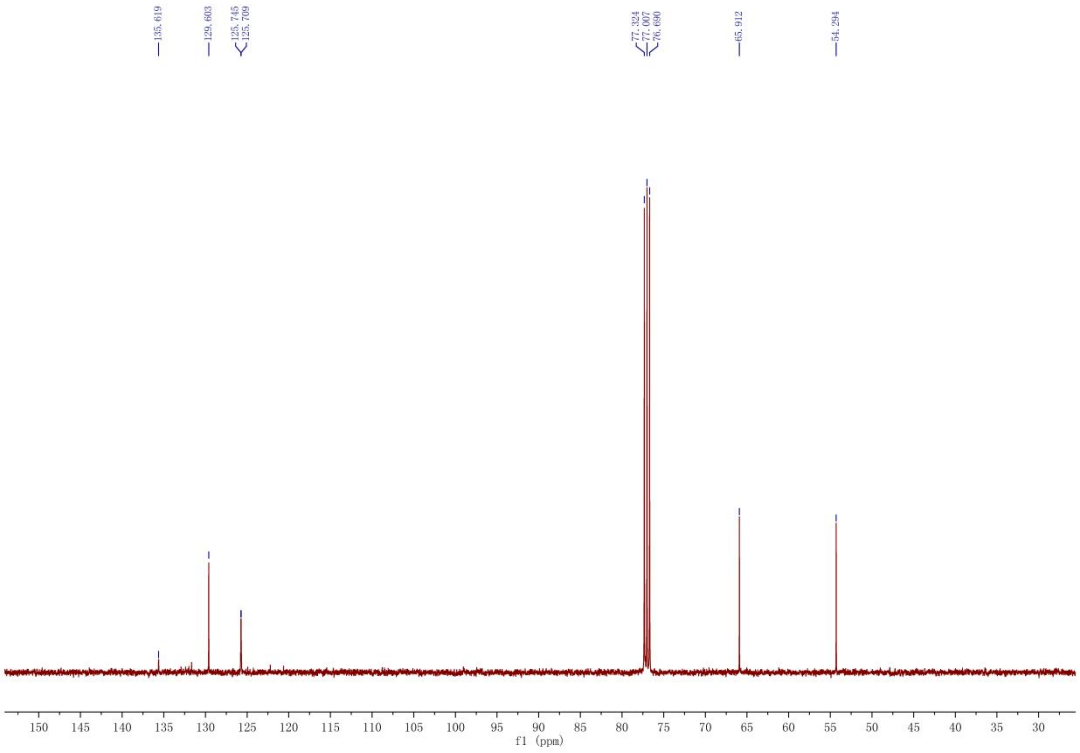
129.864
117.845
113.803
77.353
77.035
76.718
65.850
54.339
f1 (ppm)

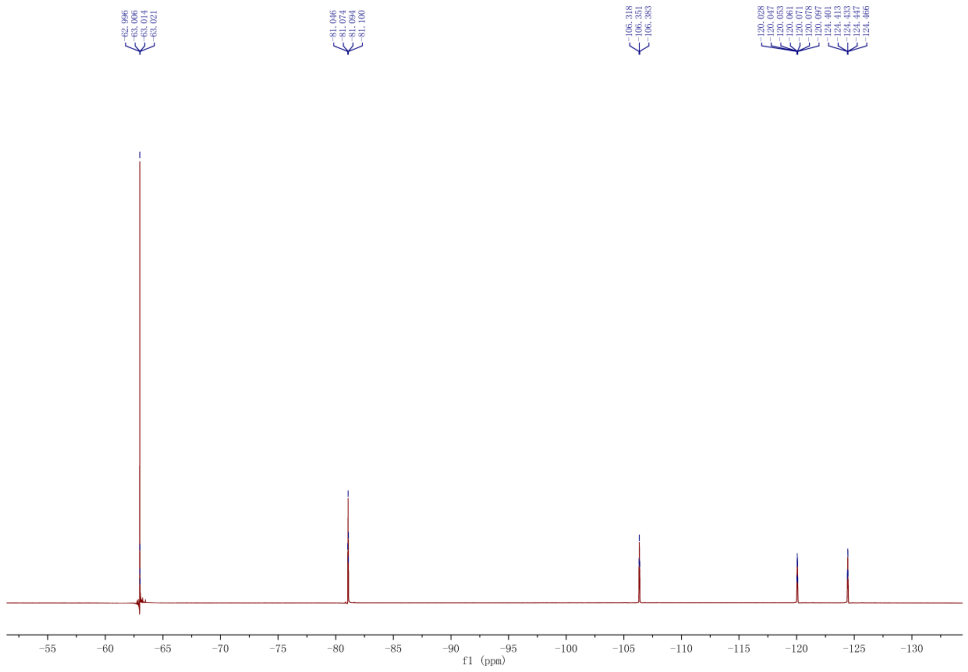

-81.096
-81.122
-81.147
-106.224
-106.257
-106.291
-120.094
-120.122
-120.130
-120.140
-120.147
-120.165
-124.473
-124.480
-124.485
-124.505
-124.519
-124.538
-124.550
f1 (ppm)

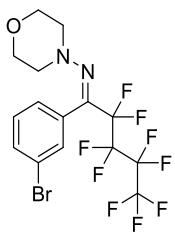


3m

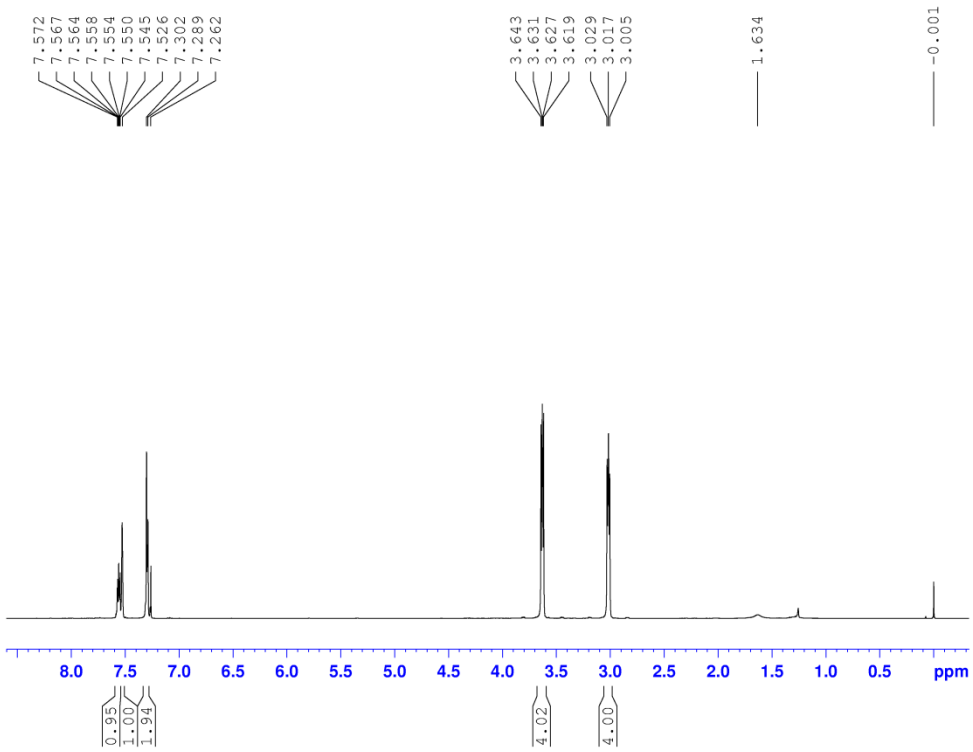

7.697
7.677
7.514
7.494
7.261
8.638
8.626
8.613
3.020
3.008
2.996
1.553
0.071
0.000
1.98
1.95
4.04
4.00
f1 (ppm)

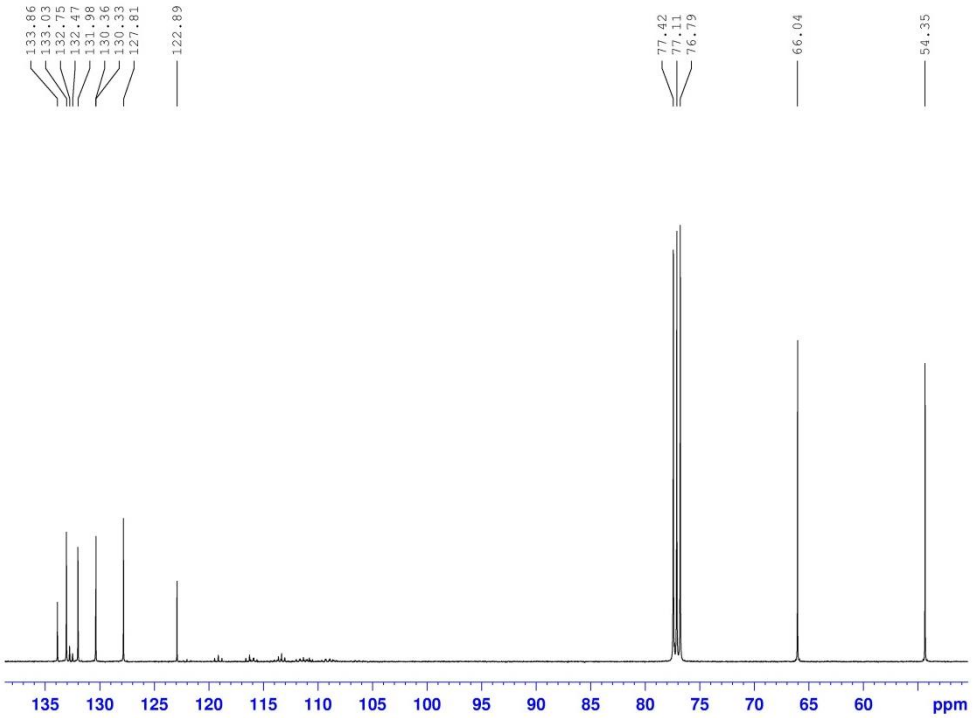

135.619
129.603
125.745
125.709
77.324
77.007
76.690
65.912
54.294
f1 (ppm)

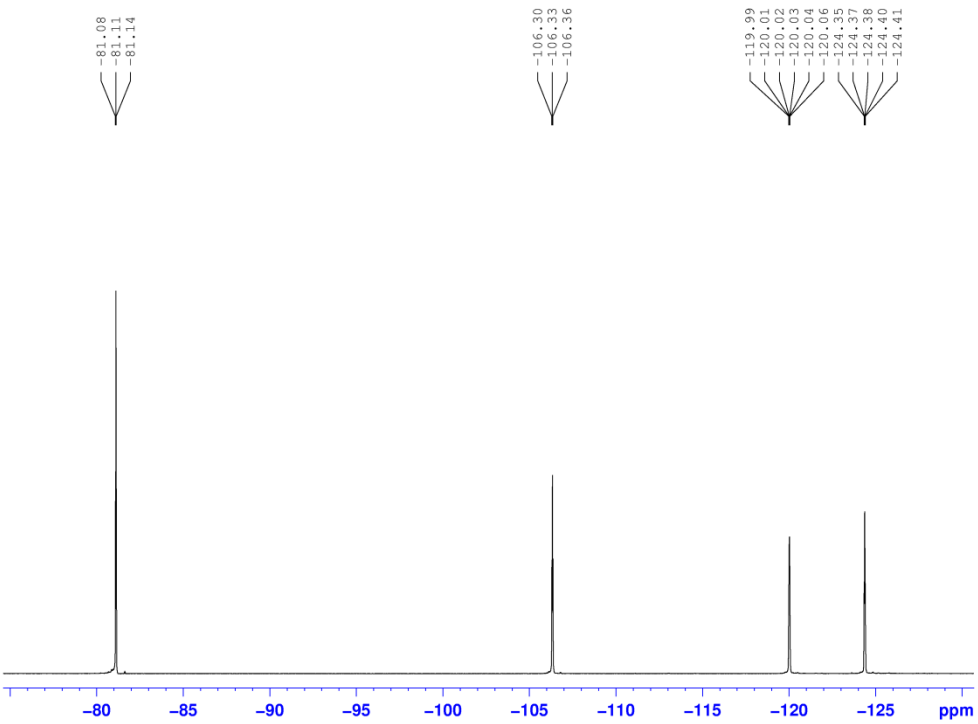

f1 (ppm)

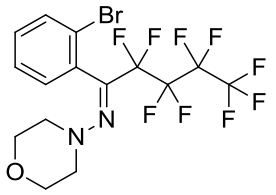


3n

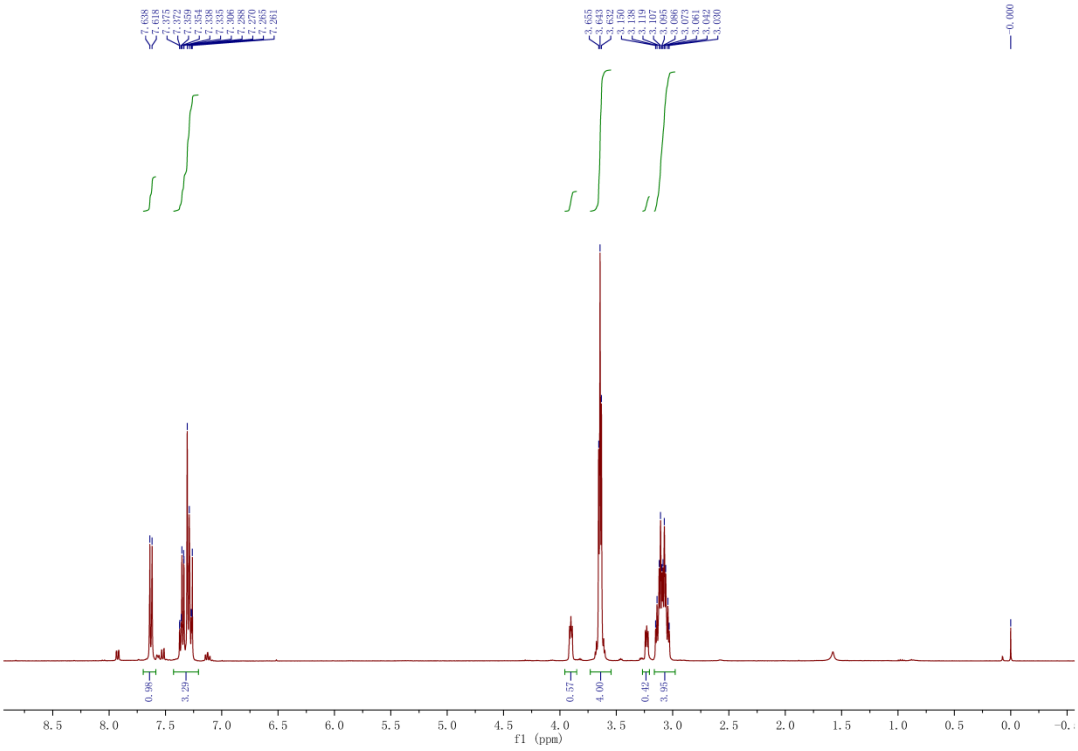

7.572
7.567
7.564
7.558
7.554
7.550
7.545
7.526
7.302
7.289
7.262
3.643
3.631
3.627
3.619
3.029
3.017
3.005
1.634
-0.001
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.95
1.00
1.94
4.02
4.00

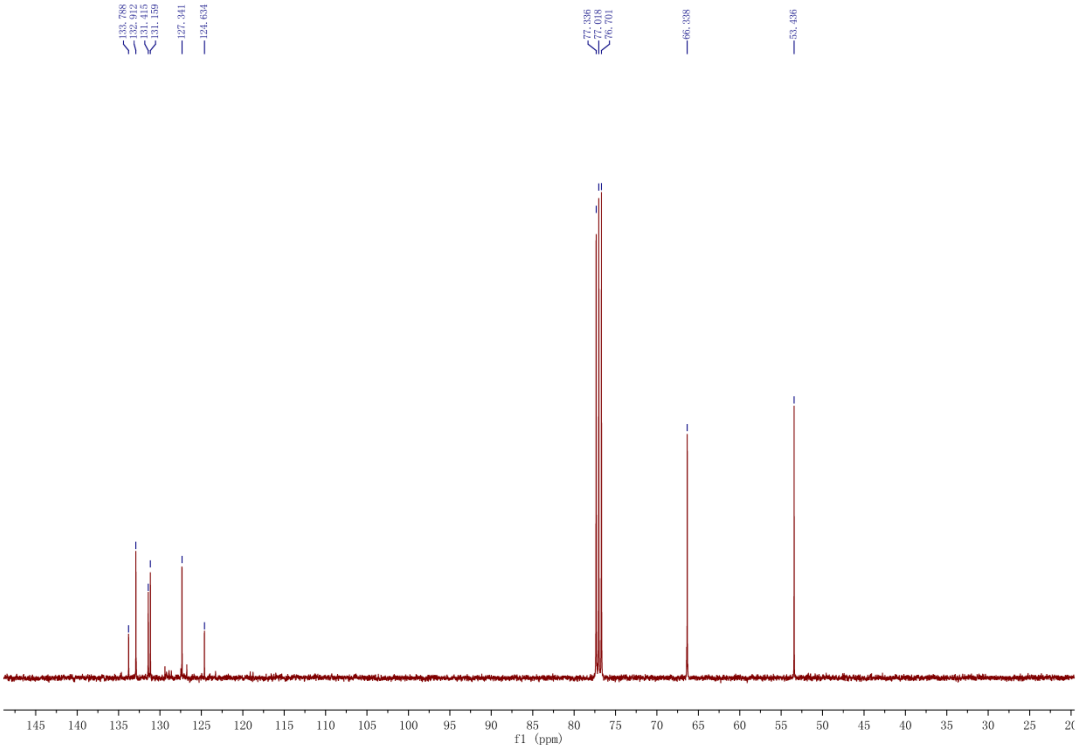

133.86
133.03
132.75
132.47
131.98
130.36
130.33
127.81
122.89
77.42
77.11
76.79
66.04
54.35
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
ppm

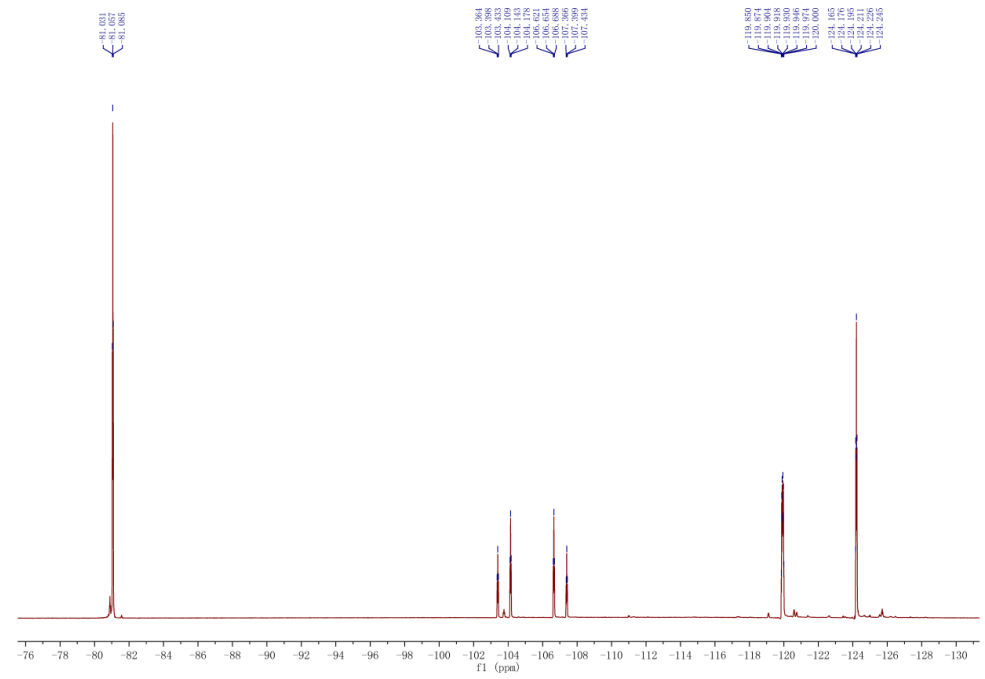

-81.08
-81.11
-81.14
-106.30
-106.33
-106.36
-119.99
-120.01
-120.02
-120.03
-120.04
-120.06
-124.35
-124.37
-124.38
-124.40
-124.41
−80
−85
−90
−95
−100
−105
−110
−115
−120
−125
ppm

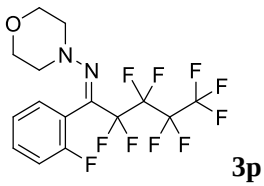

Br
F
F
F
F
F
F
F
F
F
N
N
O

3o

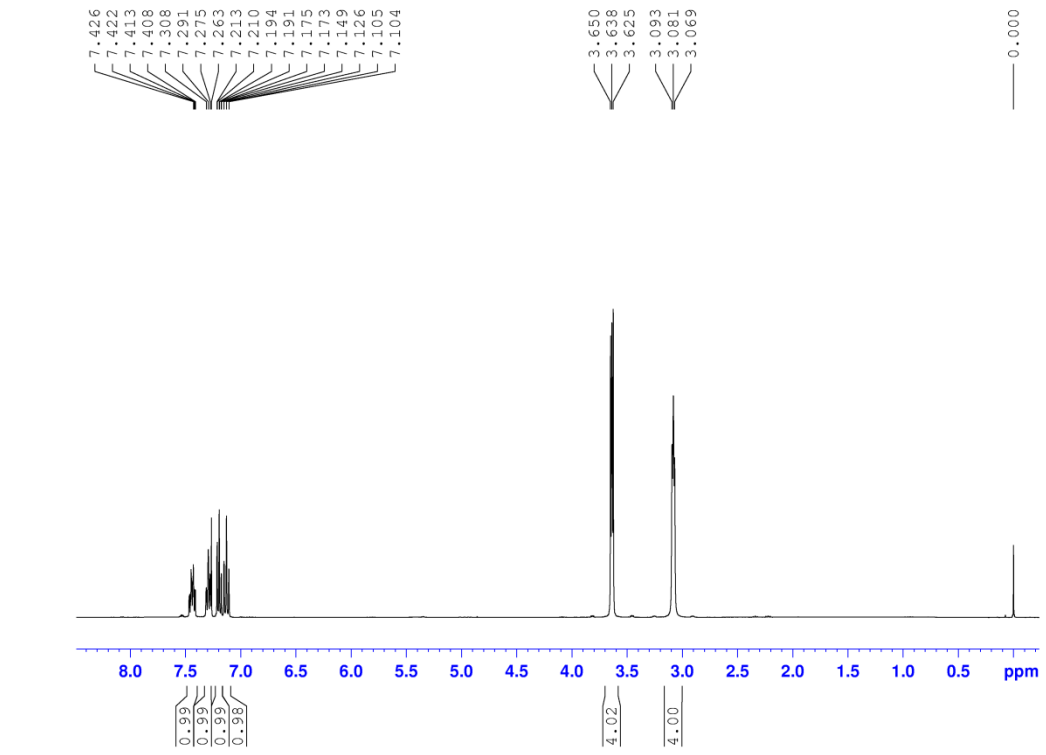

7.638
7.618
7.375
7.372
7.359
7.354
7.338
7.335
7.306
7.288
7.270
7.265
7.261
3.655
3.643
3.632
3.150
3.138
3.119
3.107
3.095
3.086
3.073
3.061
3.042
3.030
0.000
0.98
3.29
0.57
4.00
0.42
3.95
f1 (ppm)

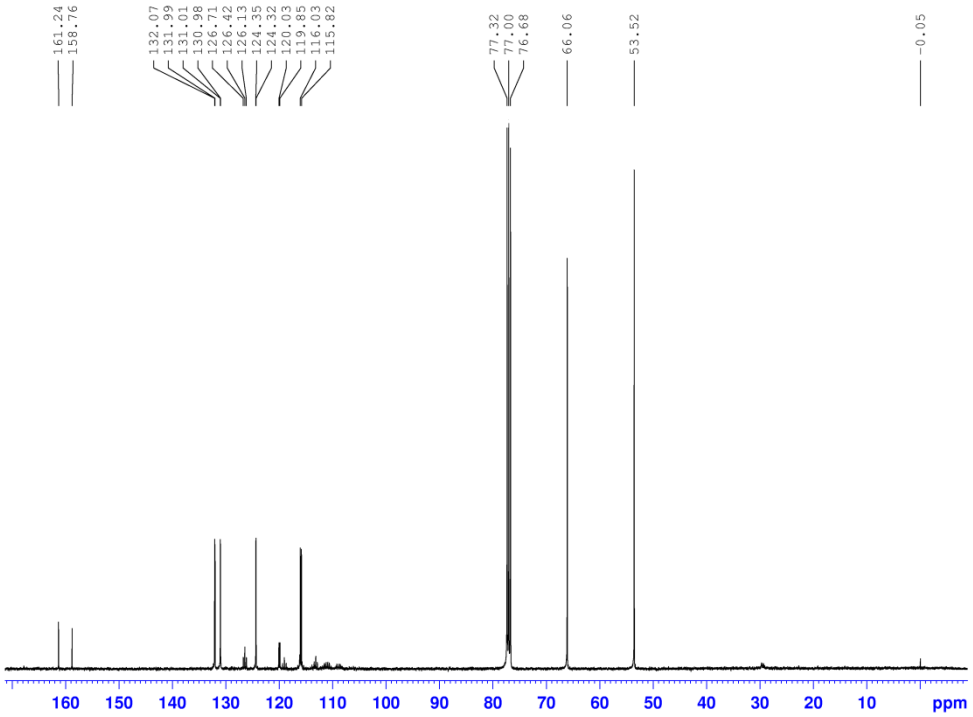

133.788
132.912
131.415
131.159
127.341
124.634
77.336
77.018
76.701
66.338
53.436
f1 (ppm)

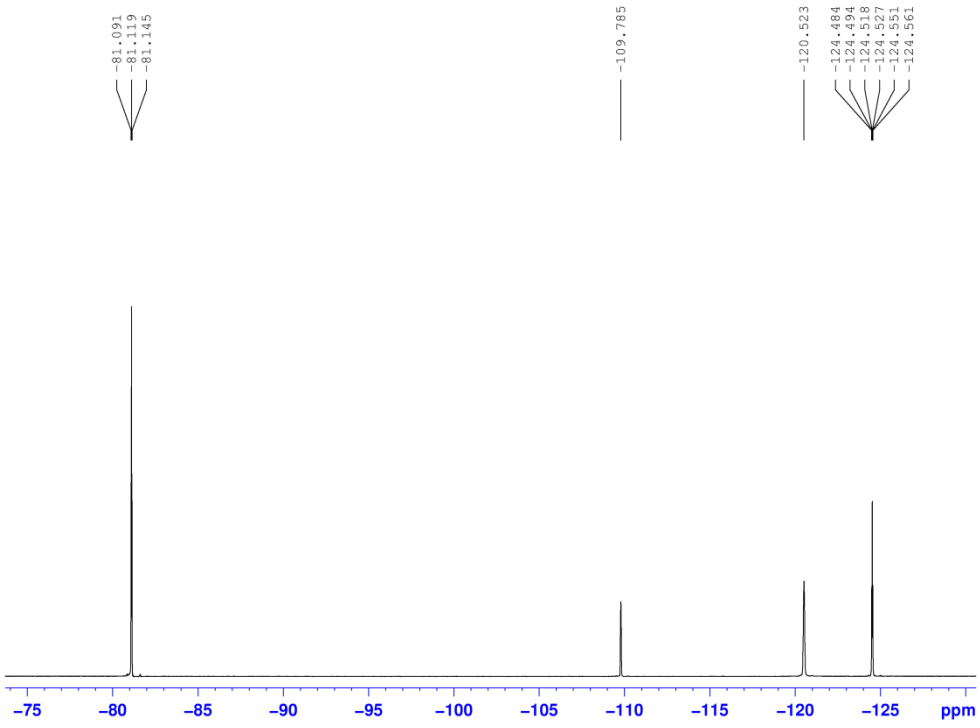


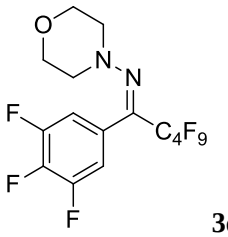


3p

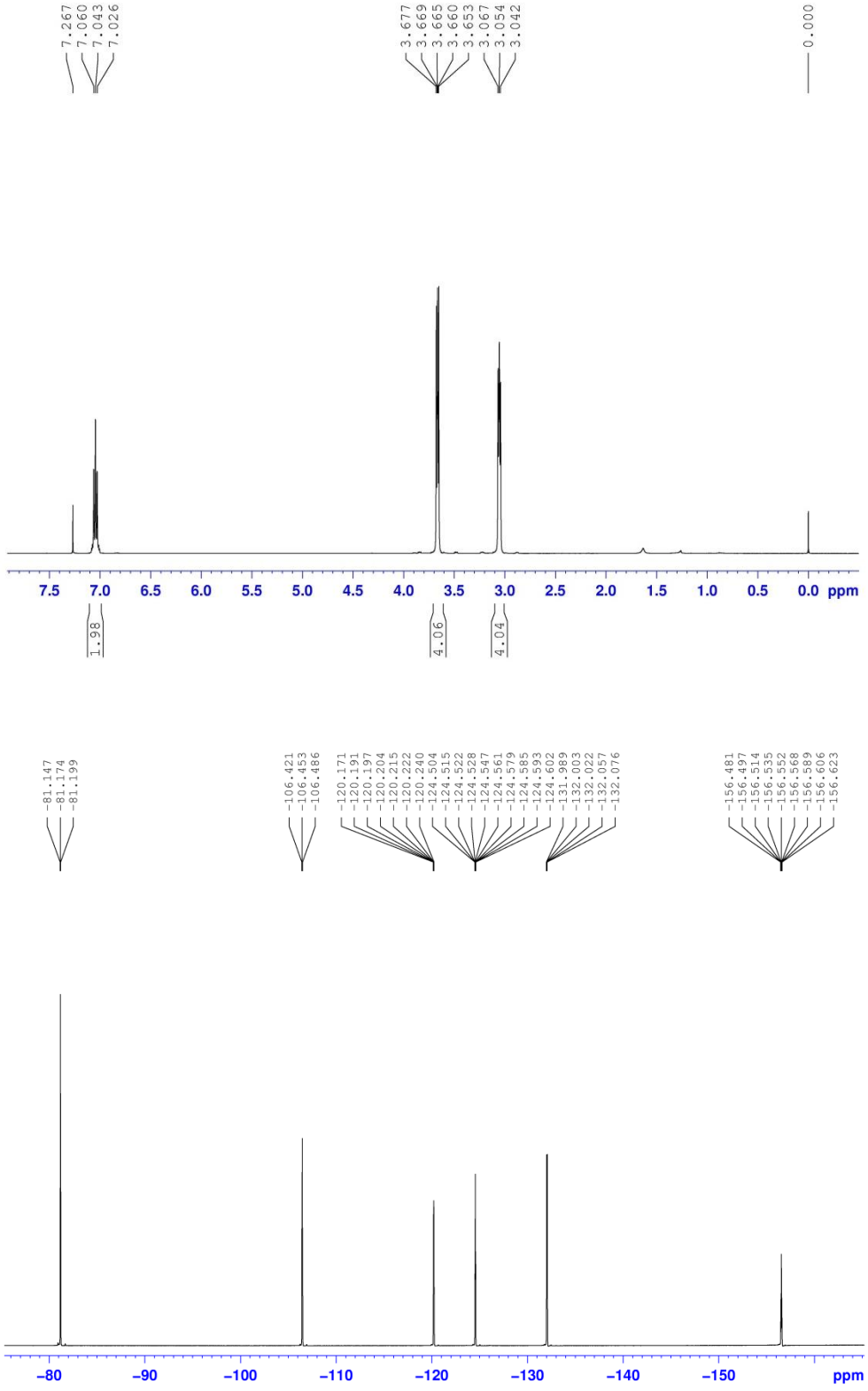


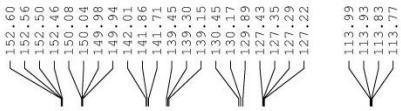

161.24
158.76
132.07
131.99
131.01
130.98
126.71
126.42
126.13
124.35
124.32
120.03
119.85
116.03
115.82
77.32
77.00
76.68
66.06
53.52
-0.05
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

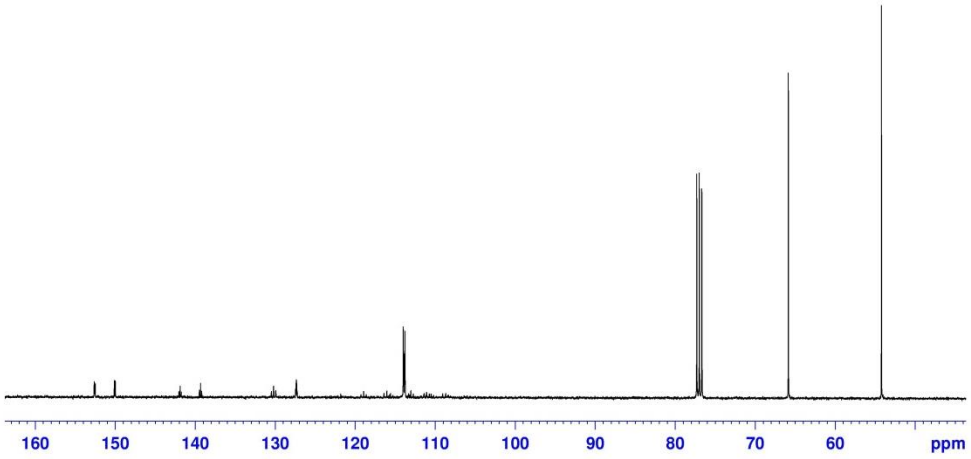

-81.091
-81.119
-81.145
-109.785
-120.523
-124.484
-124.494
-124.518
-124.527
-124.551
-124.561
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
ppm

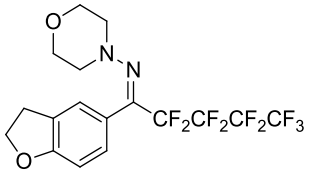

O
N
N
F
F
F
C_4F_9

3q

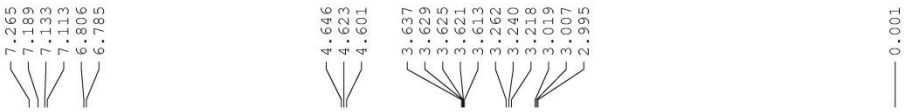

7.267
7.060
7.043
7.026
3.677
3.669
3.665
3.660
3.653
3.067
3.054
3.042
0.000
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm
1.98
4.06
4.04
-81.147
-81.174
-81.199
-106.421
-106.453
-106.486
-120.171
-120.191
-120.197
-120.204
-120.215
-120.222
-120.240
-124.504
-124.515
-124.522
-124.528
-124.547
-124.561
-124.579
-124.585
-124.593
-124.602
-131.989
-132.003
-132.022
-132.057
-132.076
-156.481
-156.497
-156.514
-156.535
-156.552
-156.568
-156.589
-156.606
-156.623
-80
-90
-100
-110
-120
-130
-140
-150
ppm

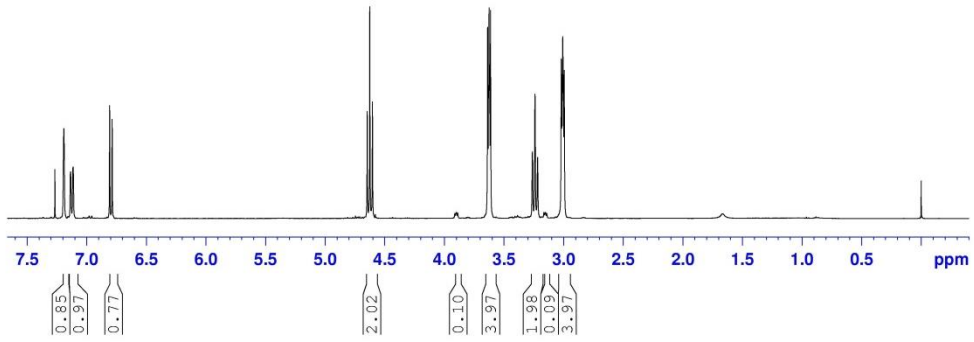

152.60
152.56
152.50
152.46
150.08
150.04
149.98
149.94
142.01
141.86
141.71
139.45
139.30
139.15
130.45
130.17
129.89
127.43
127.35
127.29
127.22
113.99
113.93
113.83
113.77
77.29
76.98
76.66
65.85
54.21

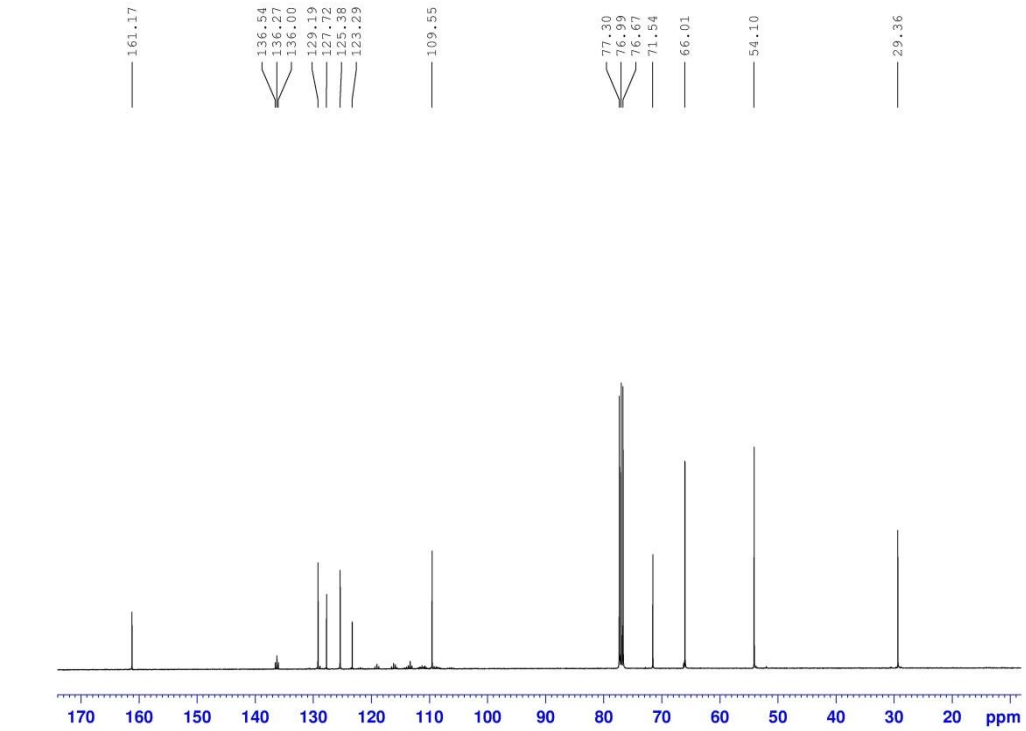

160
150
140
130
120
110
100
90
80
70
60
ppm

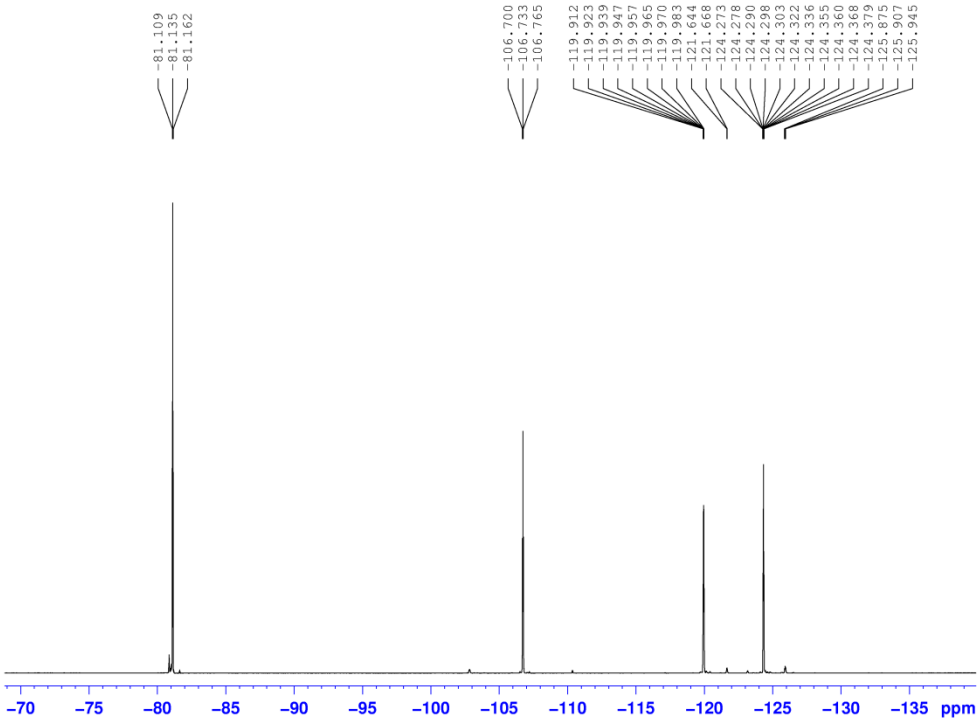

O
N
N
CF2CF2CF2CF3
O

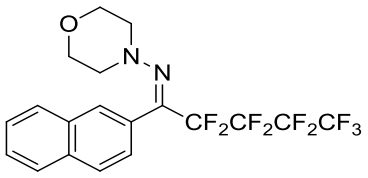
3r


7.265
7.189
7.133
7.113
6.806
6.785
4.646
4.623
4.601
3.637
3.629
3.625
3.621
3.613
3.262
3.240
3.218
3.019
3.007
2.995
0.001

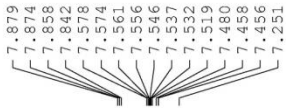

7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.85
0.97
0.77
2.02
0.10
3.97
1.98
0.09
3.97

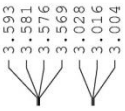

161.17
136.54
136.27
136.00
129.19
127.72
125.38
123.29
109.55
77.30
76.99
76.67
71.54
66.01
54.10
29.36
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


-81.109
-81.135
-81.162
-106.700
-106.733
-106.765
-119.912
-119.923
-119.939
-119.947
-119.957
-119.965
-119.970
-119.983
-121.644
-121.668
-124.273
-124.278
-124.290
-124.298
-124.303
-124.322
-124.336
-124.355
-124.360
-124.368
-124.379
-125.875
-125.907
-125.945
−70 −75 −80 −85 −90 −95 −100 −105 −110 −115 −120 −125 −130 −135 ppm

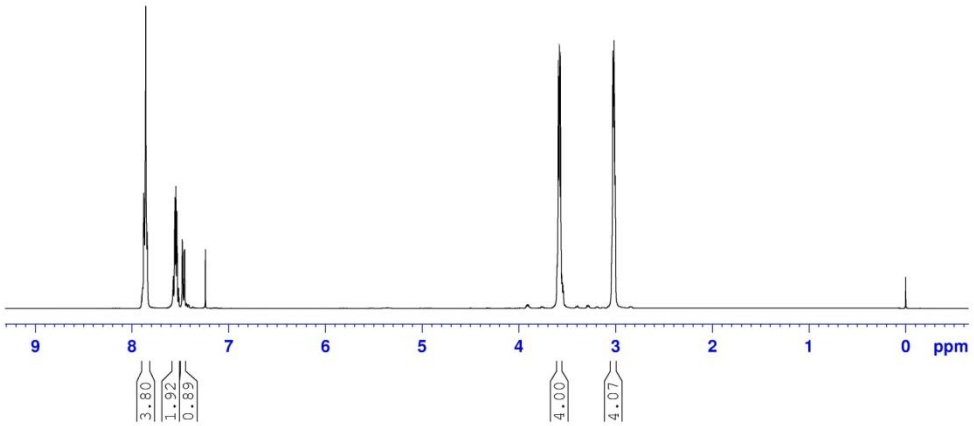


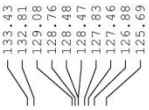
3s-(*E*)


7.879
7.874
7.858
7.842
7.578
7.574
7.561
7.556
7.546
7.537
7.532
7.519
7.480
7.458
7.456
7.251


3.593
3.581
3.576
3.569
3.028
3.016
3.004

0.000

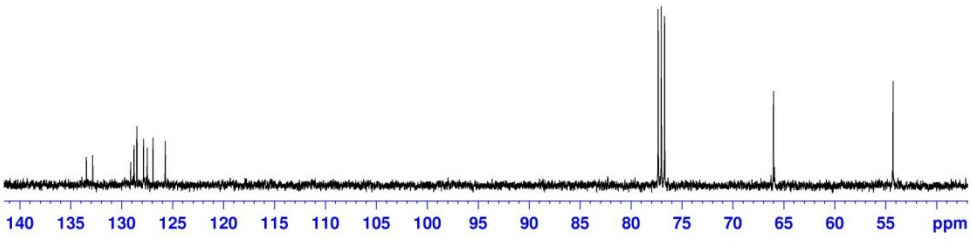

9
8
7
6
5
4
3
2
1
0
ppm
3.80
1.92
0.89
4.00
4.07

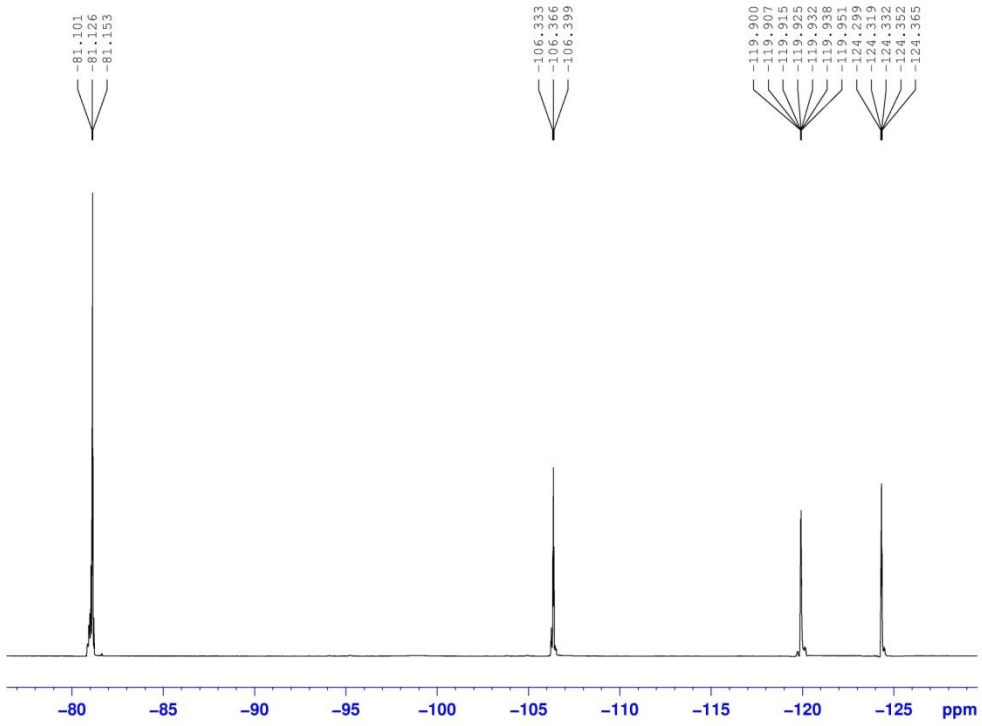

133.43
132.81
129.08
128.76
128.48
128.47
127.83
127.46
126.88
125.69


77.33
77.01
76.69

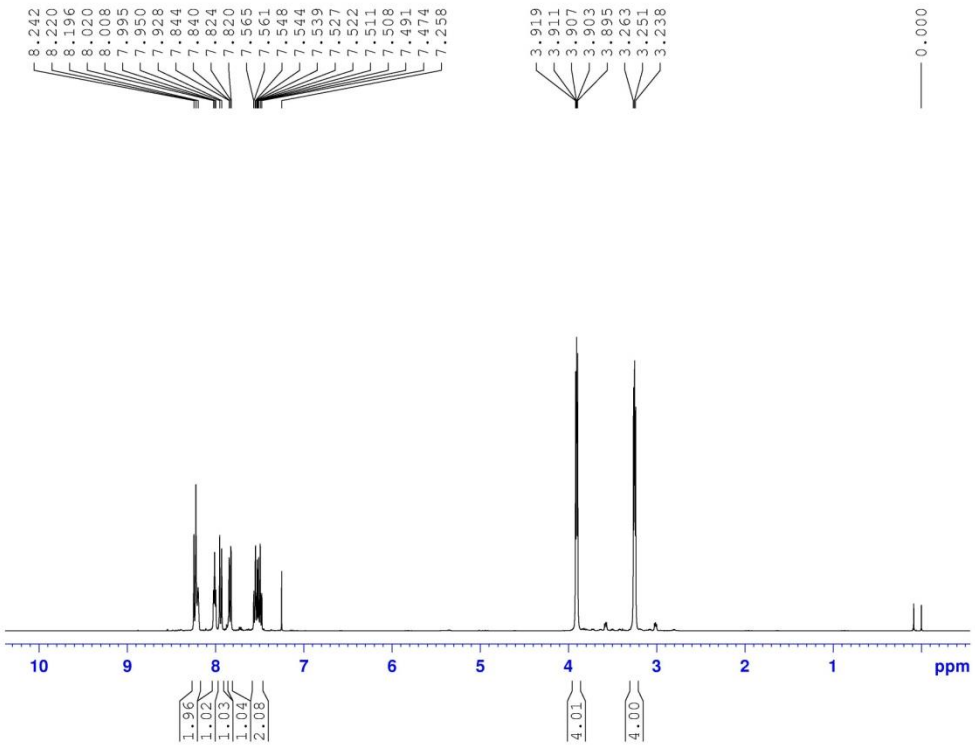
66.00

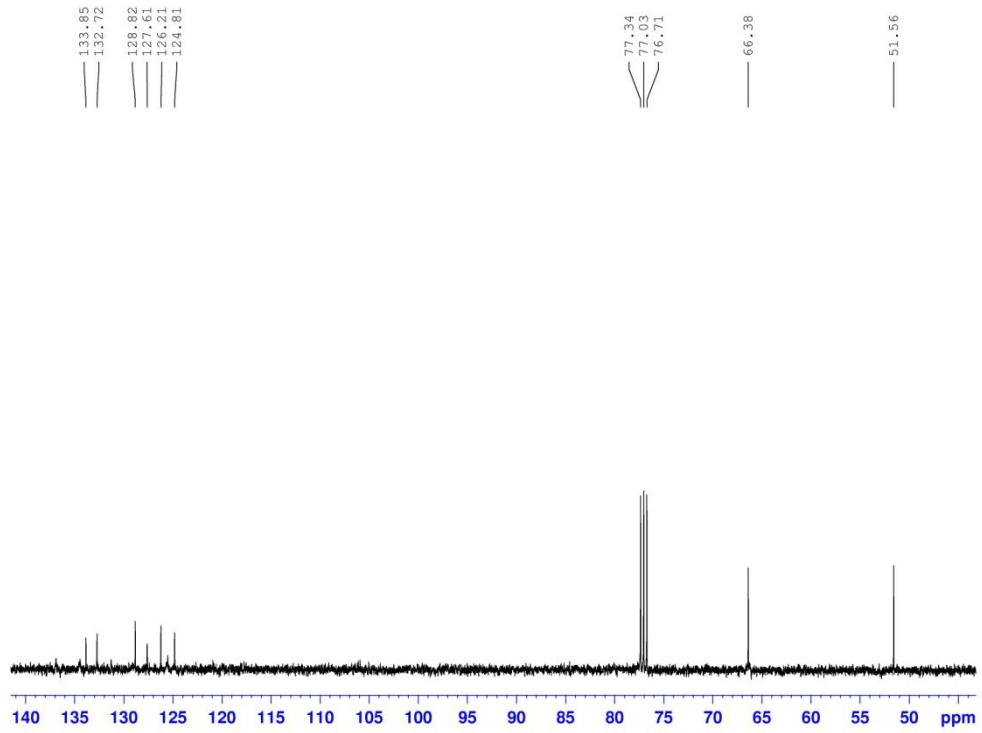

54.27

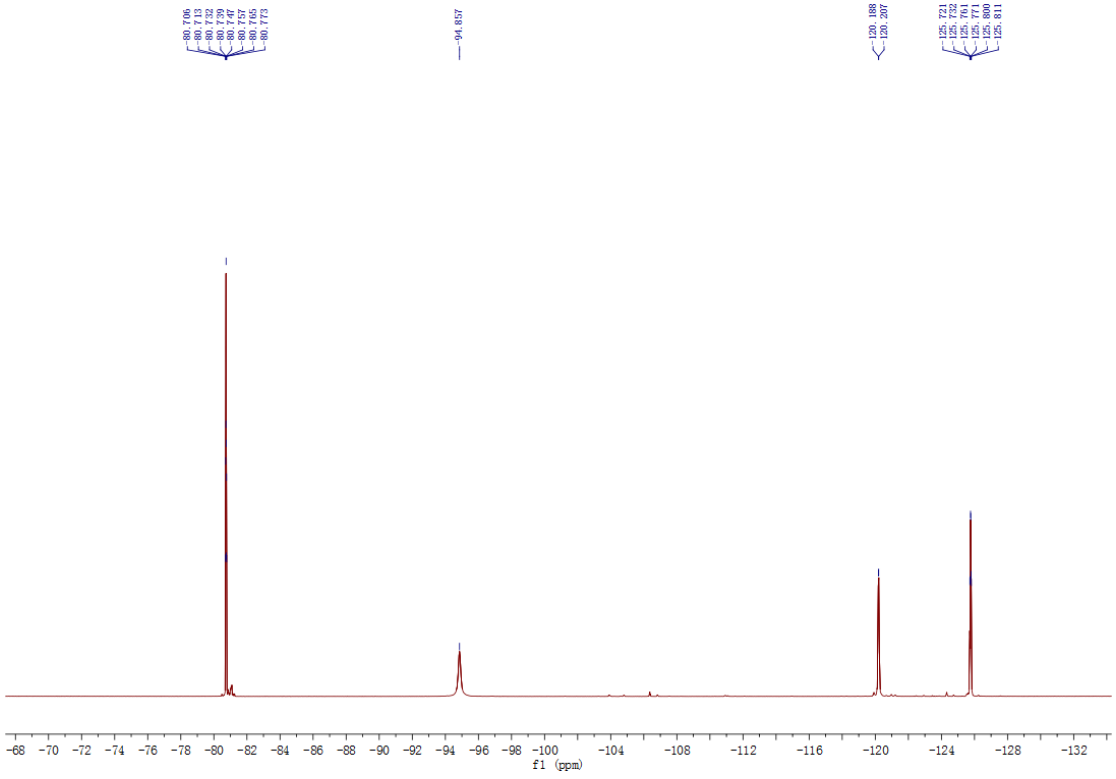

140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
ppm

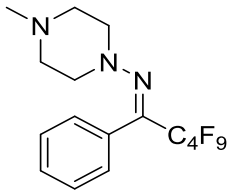

-81.101
-81.126
-81.153
-106.333
-106.366
-106.399
-119.900
-119.907
-119.915
-119.925
-119.932
-119.938
-119.951
-124.299
-124.319
-124.332
-124.352
-124.365
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
ppm

3s-(Z)

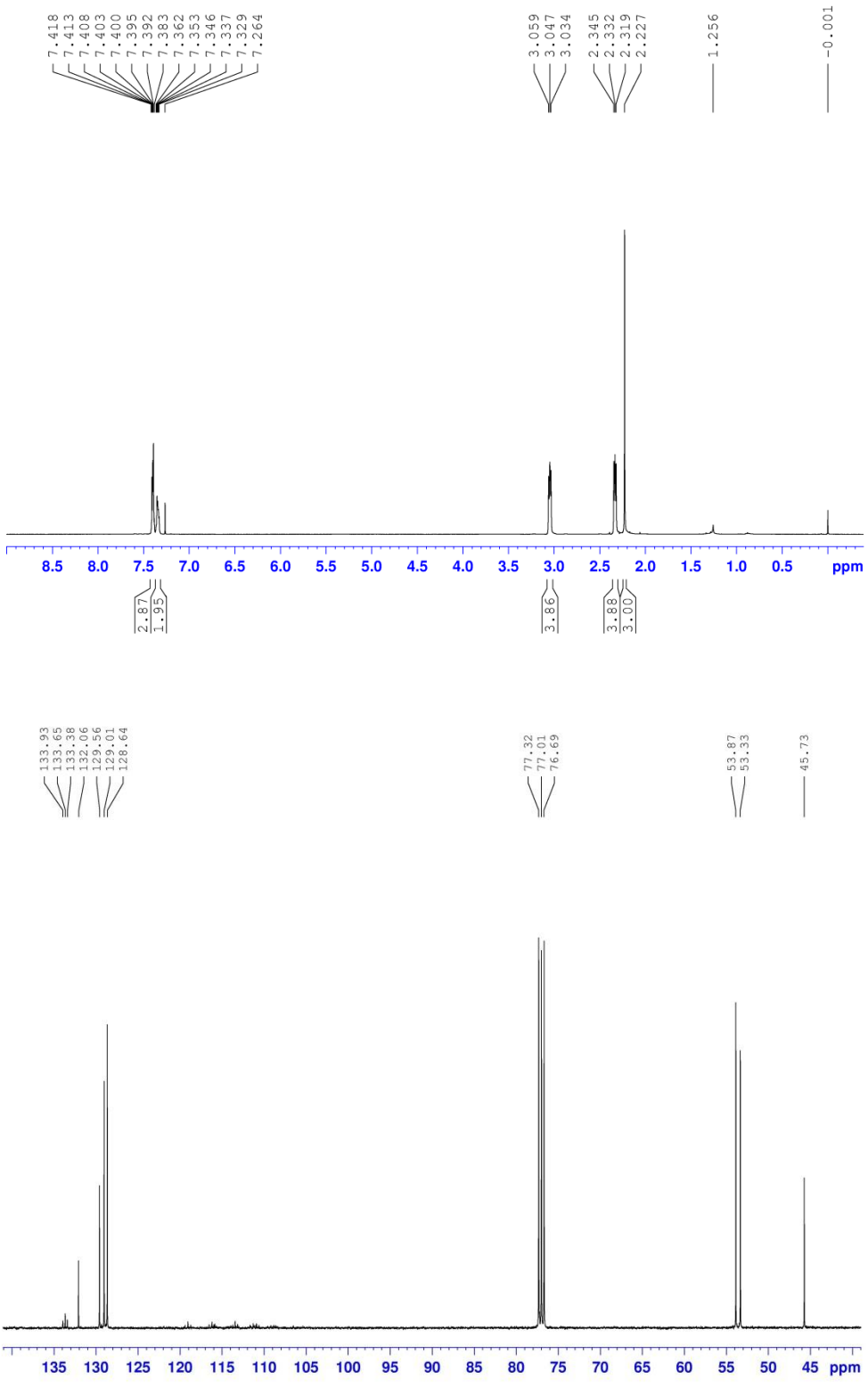

8.242
8.220
8.196
8.020
8.008
7.995
7.950
7.928
7.844
7.840
7.824
7.820
7.565
7.561
7.548
7.544
7.539
7.527
7.522
7.511
7.508
7.491
7.474
7.258
3.919
3.911
3.907
3.903
3.895
3.263
3.251
3.238
0.000
10
9
8
7
6
5
4
3
2
1
ppm
1.96
1.02
1.03
1.04
2.08
4.01
4.00

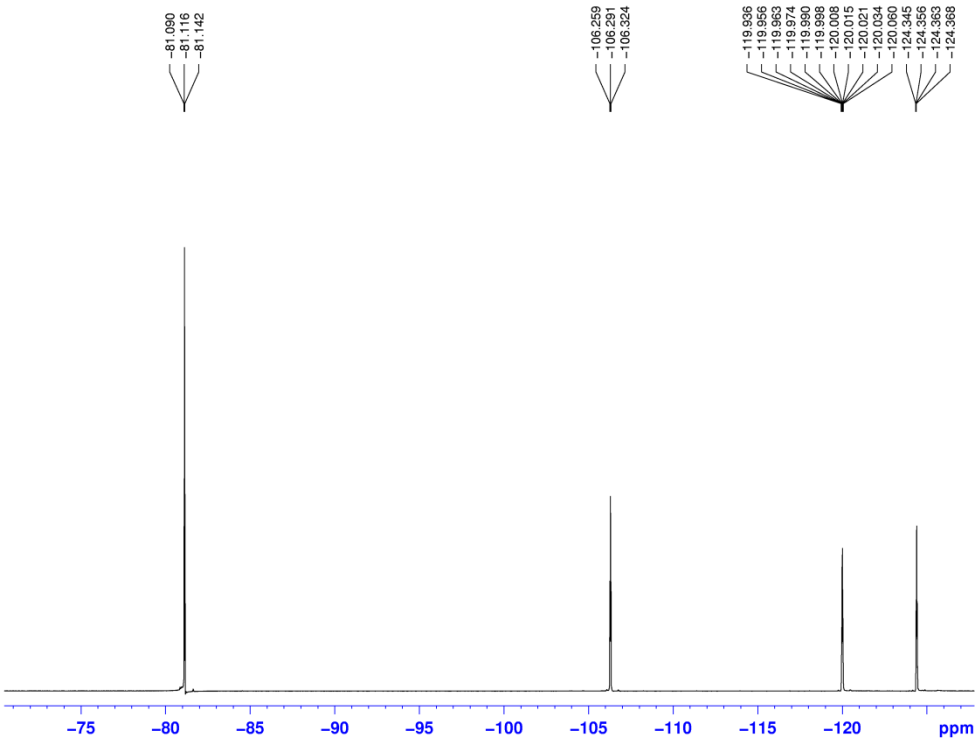

133.85
132.72
128.82
127.61
126.21
124.81
77.34
77.03
76.71
66.38
51.56
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 ppm

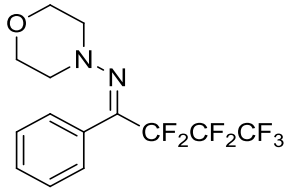

-80.706
-80.713
-80.732
-80.739
-80.747
-80.757
-80.765
-80.773
-94.857
120.188
120.207
125.721
125.732
125.764
125.771
125.800
125.811
-68 -70 -72 -74 -76 -78 -80 -82 -84 -86 -88 -90 -92 -94 -96 -98 -100 -104 -108 -112 -116 -120 -124 -128 -132
f1 (ppm)


N
N
N
C_4F_9

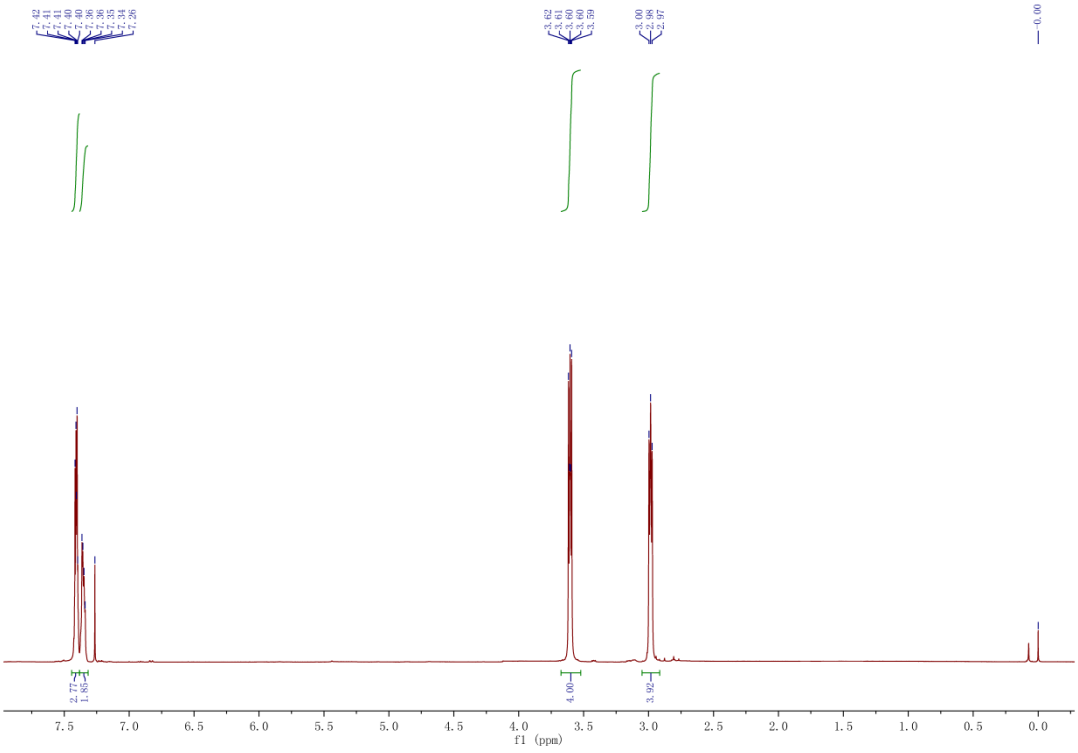
3t

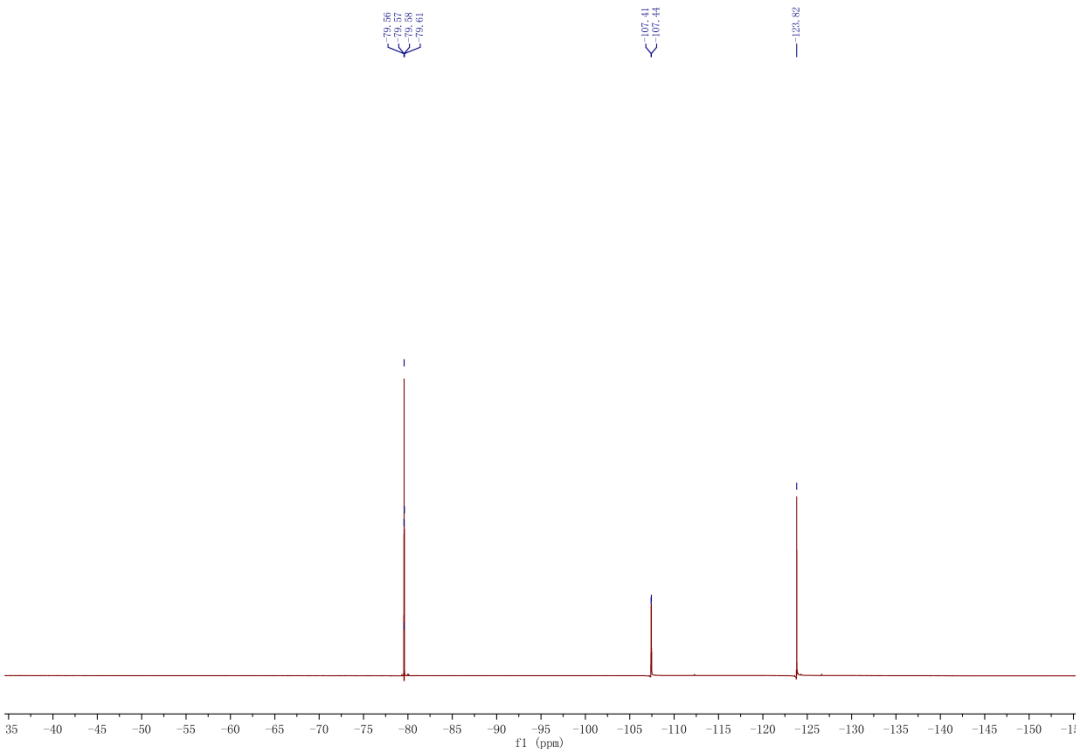

7.418
7.413
7.408
7.403
7.400
7.395
7.392
7.383
7.362
7.353
7.346
7.337
7.329
7.264
3.059
3.047
3.034
2.345
2.332
2.319
2.227
1.256
-0.001
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.87
1.95
3.86
3.88
3.00
133.93
133.65
133.38
132.06
129.56
129.01
128.64
77.32
77.01
76.69
53.87
53.33
45.73
135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 ppm

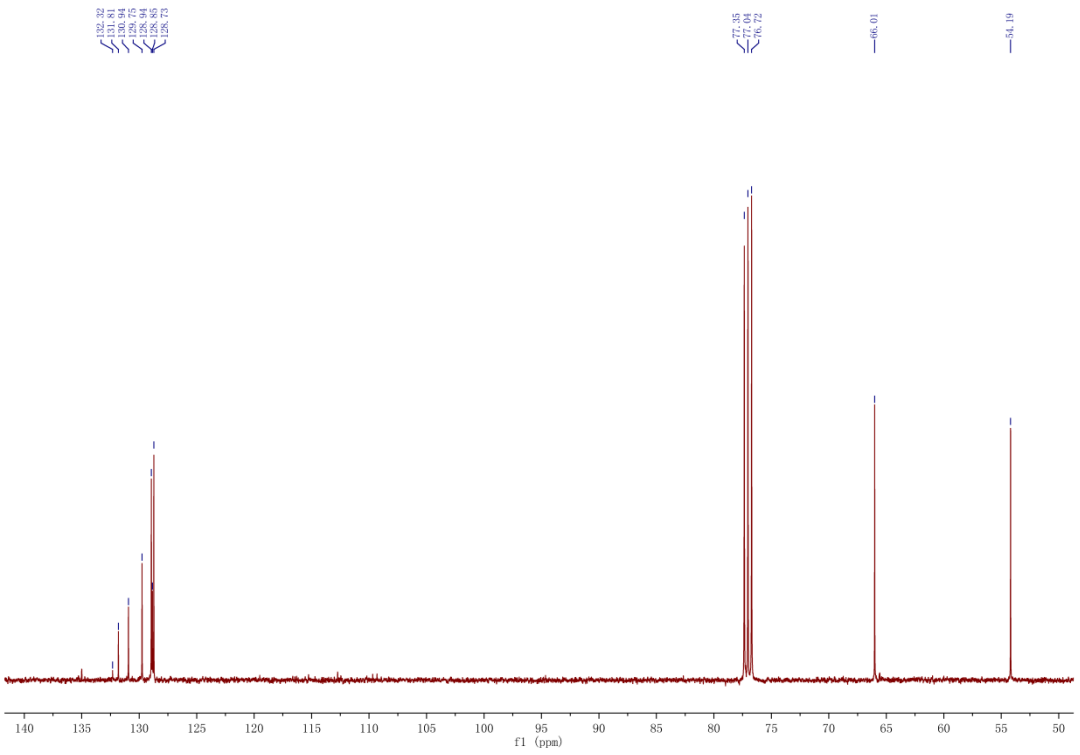

-81.090
-81.116
-81.142
-106.259
-106.291
-106.324
-119.936
-119.956
-119.963
-119.974
-119.990
-119.998
-120.008
-120.015
-120.021
-120.034
-120.060
-124.345
-124.356
-124.363
-124.368
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
ppm

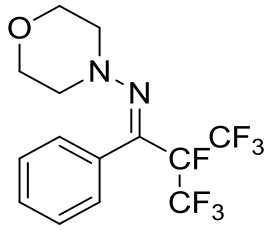

O
N
N
CF2CF2CF3

3u

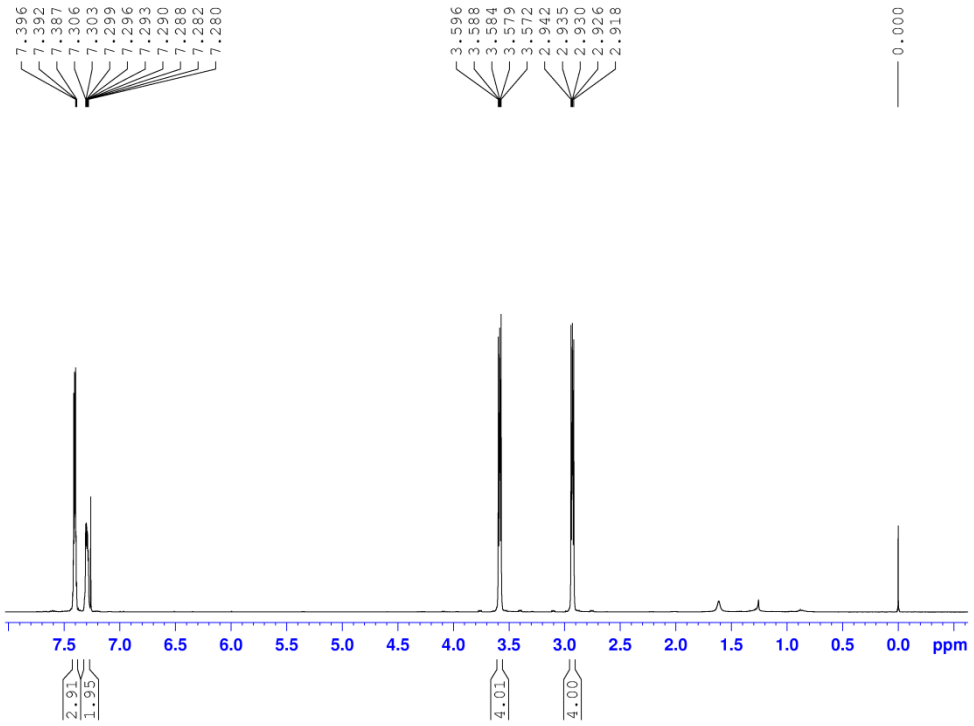

7.42
7.41
7.40
7.40
7.36
7.35
7.34
7.26
3.62
3.61
3.60
3.59
3.00
2.98
2.97
0.00
2.77
1.85
4.00
3.92
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

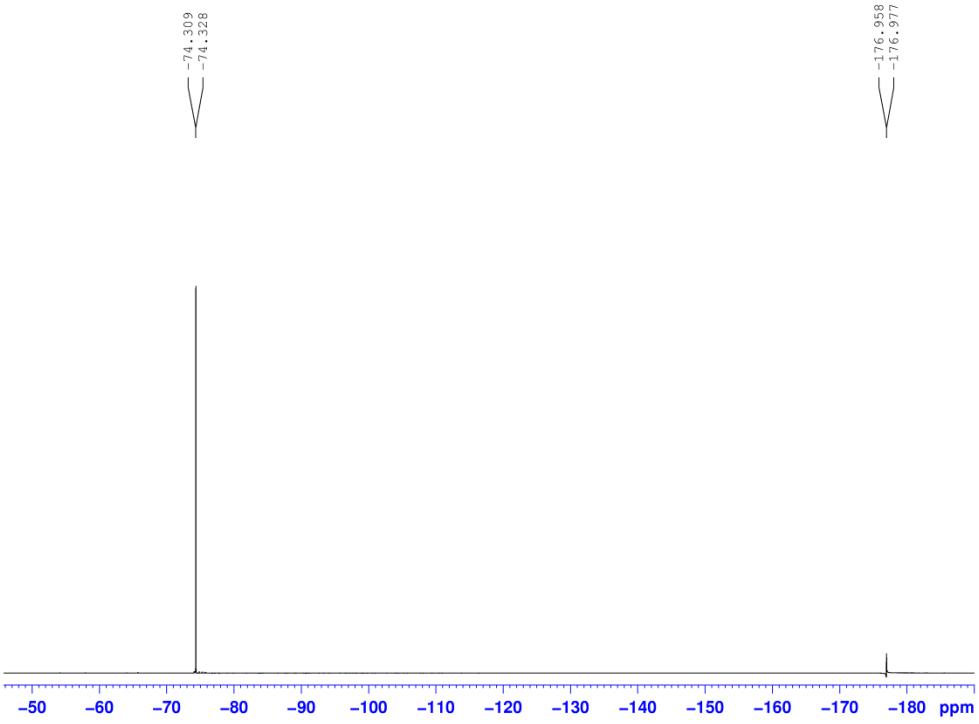

79.56
79.57
79.68
79.61
107.41
107.44
123.82
f1 (ppm)

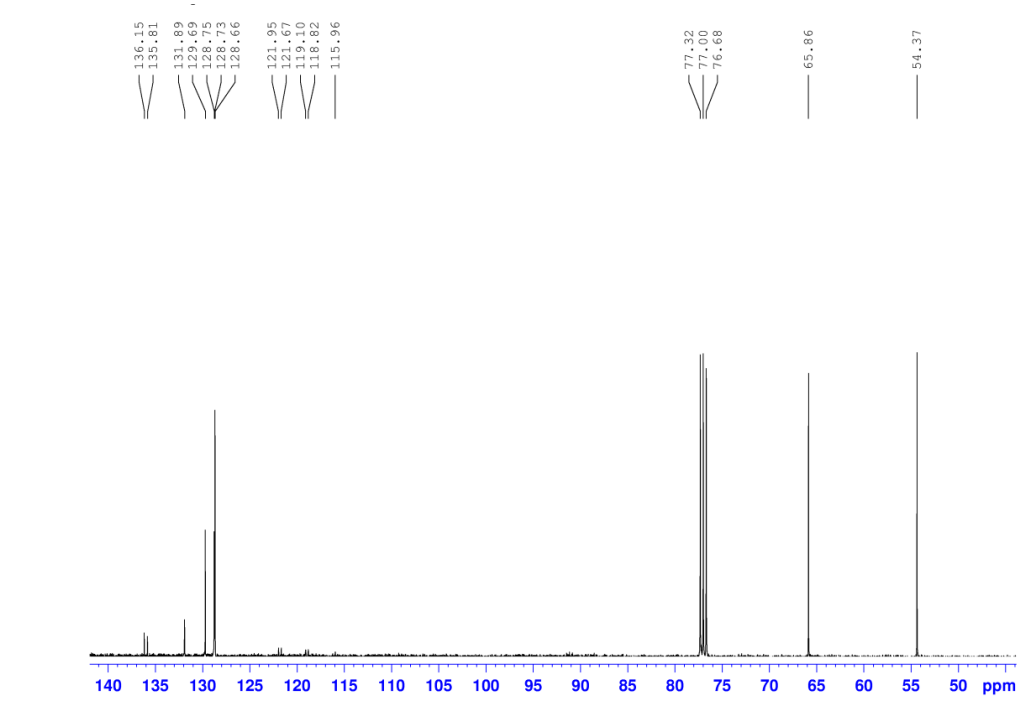

132.32
131.84
130.94
129.75
128.94
128.85
128.73
77.35
77.04
76.72
66.01
54.19
f1 (ppm)

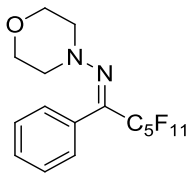


3v

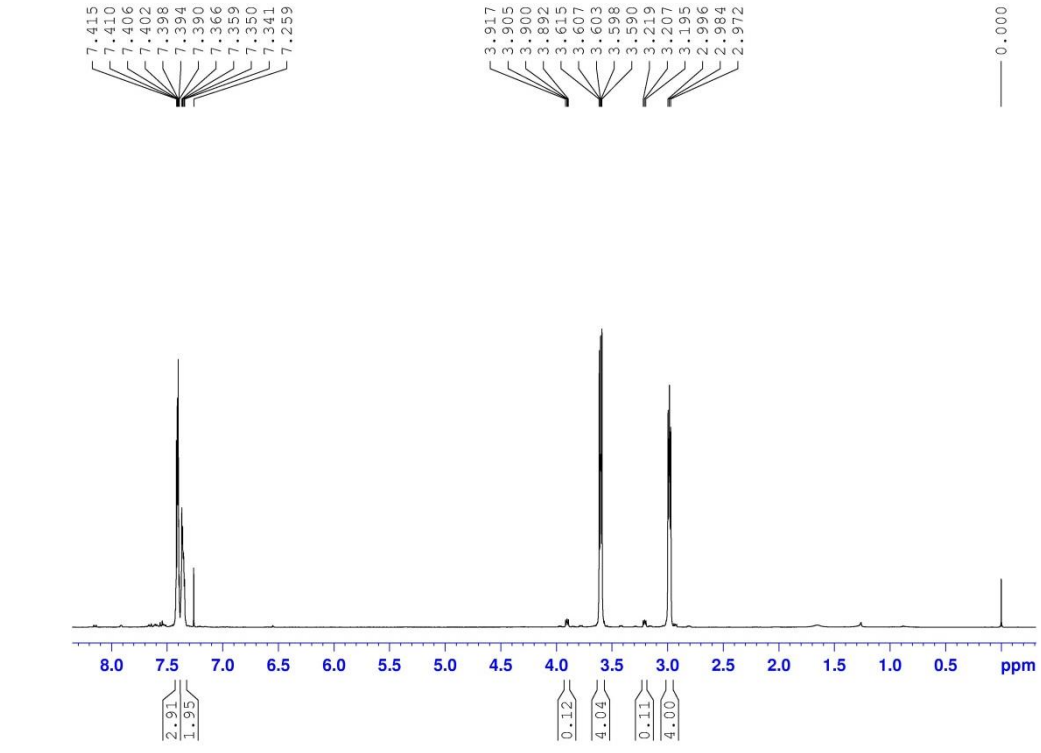

7.396
7.392
7.387
7.306
7.303
7.299
7.296
7.293
7.290
7.288
7.282
7.280
3.596
3.588
3.584
3.579
3.572
2.942
2.935
2.930
2.926
2.918
0.000
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.91
1.95
4.01
4.00

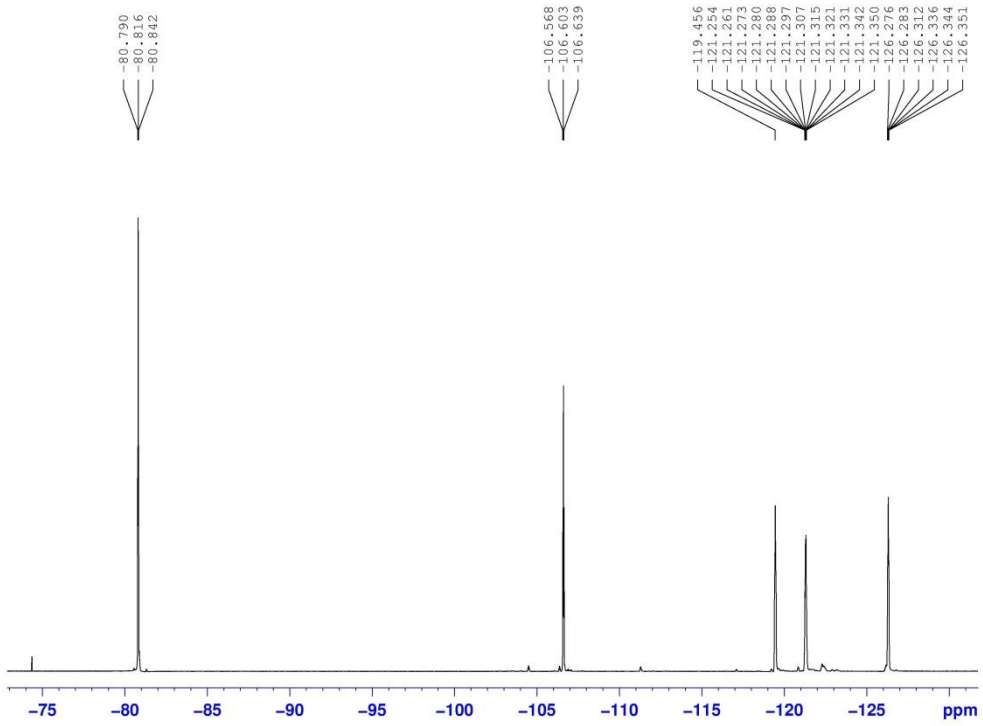

-74.309
-74.328
-176.958
-176.977
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

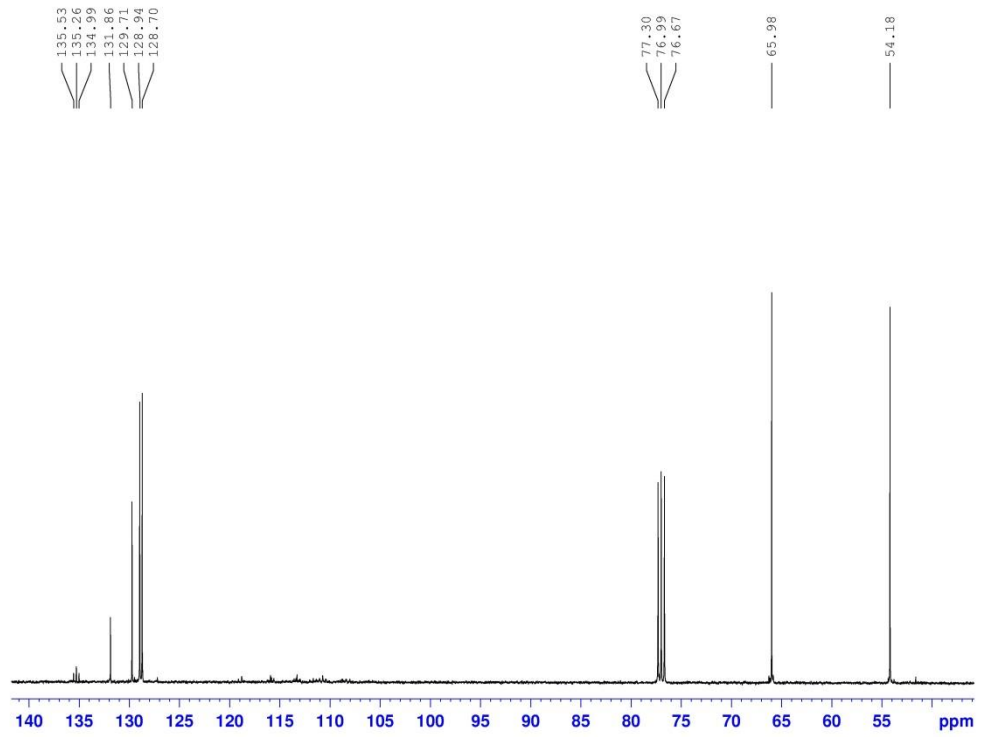

136.15
135.81
131.89
129.69
128.75
128.73
128.66
121.95
121.67
119.10
118.82
115.96
77.32
77.00
76.68
65.86
54.37
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 ppm

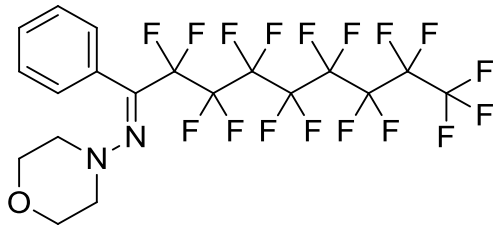

O
N
N
C5F11

3w


7.415
7.410
7.406
7.402
7.398
7.394
7.390
7.366
7.359
7.350
7.341
7.259
3.917
3.905
3.900
3.892
3.615
3.607
3.603
3.598
3.590
3.219
3.207
3.195
2.996
2.984
2.972
0.000
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 ppm
2.91
1.95
0.12
4.04
0.11
4.00


-80.790
-80.816
-80.842
-106.568
-106.603
-106.639
-119.456
-121.254
-121.261
-121.273
-121.280
-121.288
-121.297
-121.307
-121.315
-121.321
-121.331
-121.342
-121.350
-126.276
-126.283
-126.312
-126.336
-126.344
-126.351
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
ppm


135.53
135.26
134.99
131.86
129.71
128.94
128.70
77.30
76.99
76.67
65.98
54.18
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
ppm



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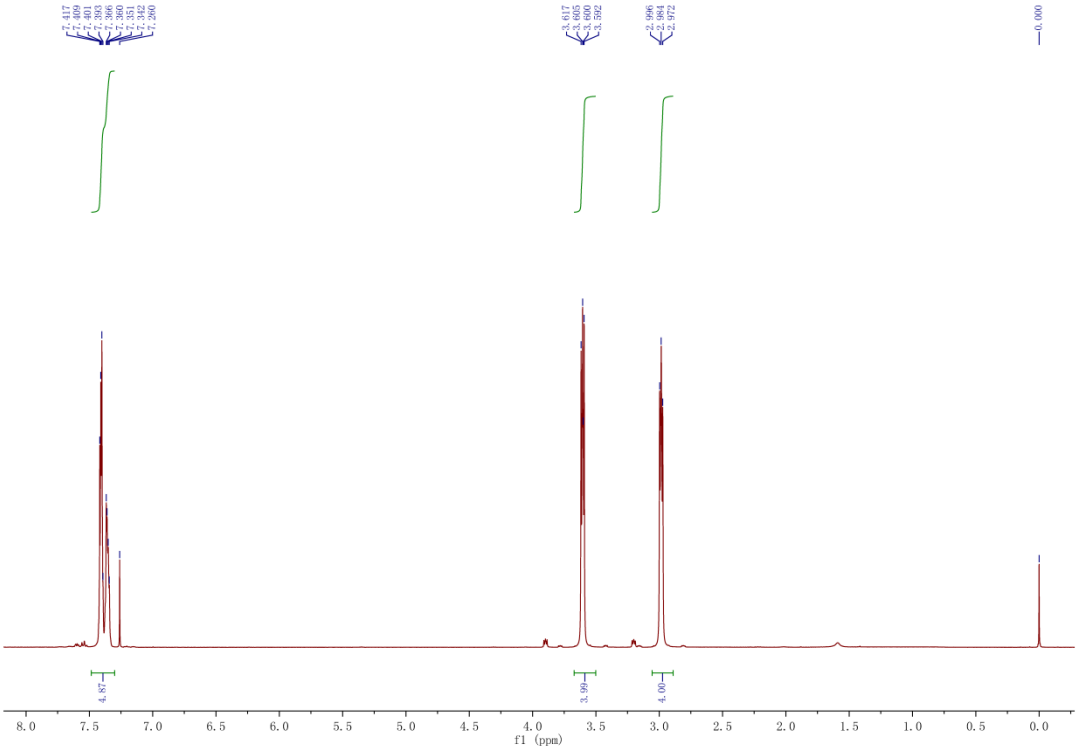
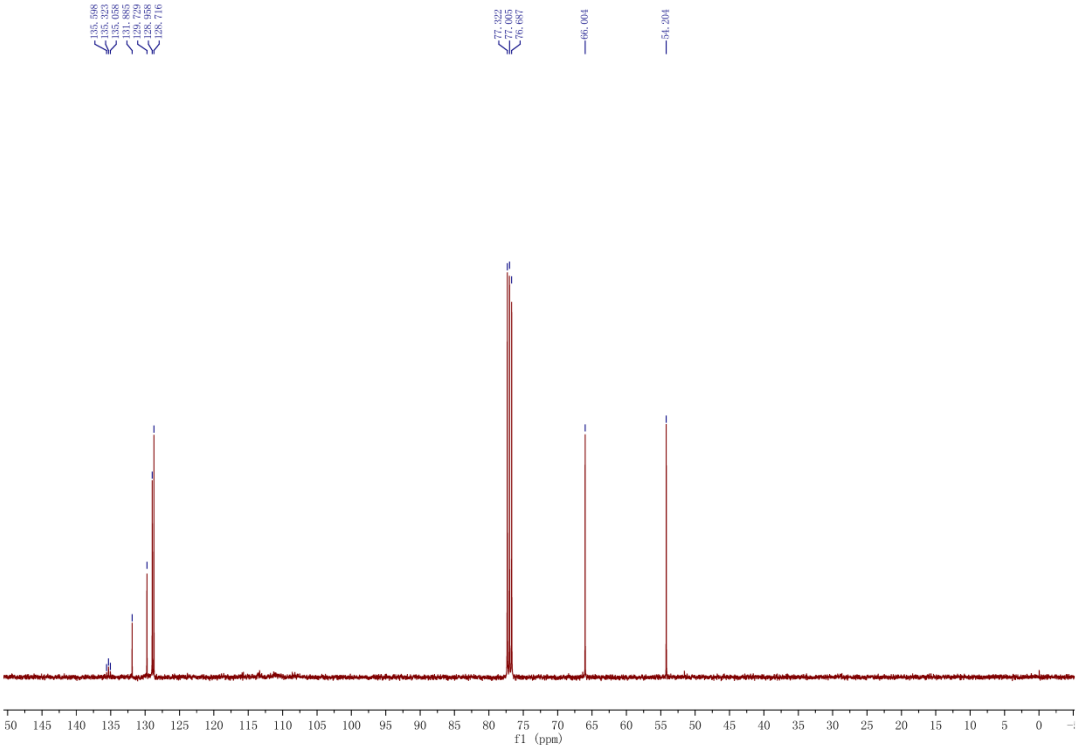
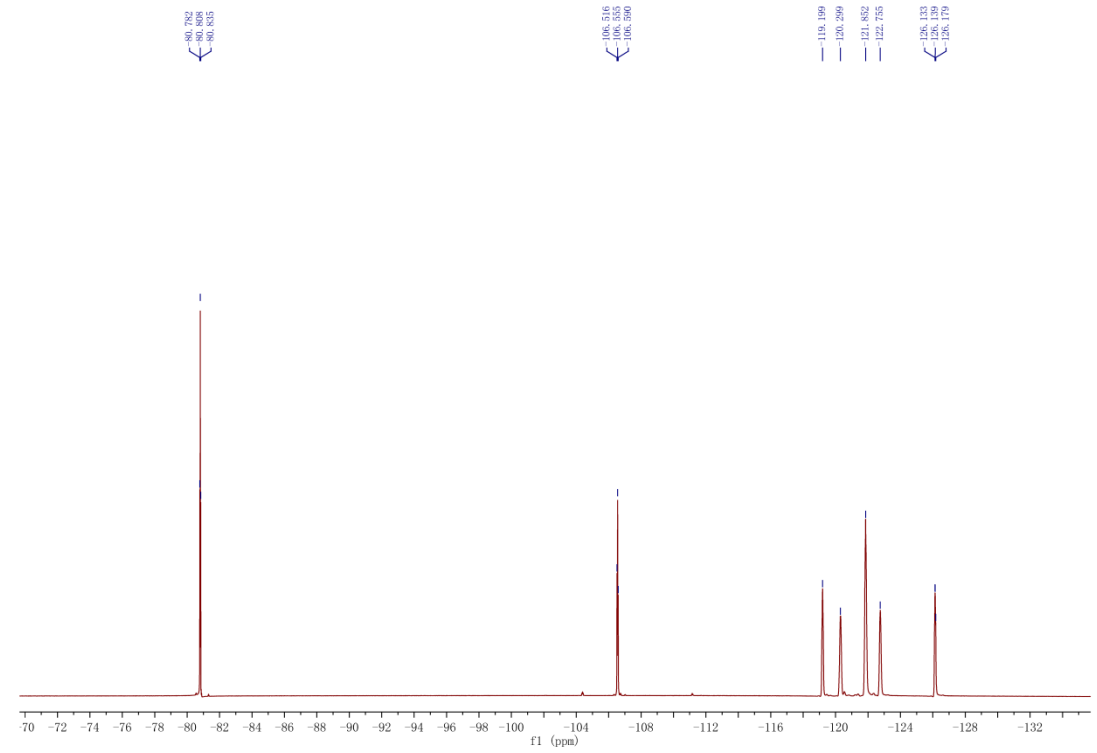
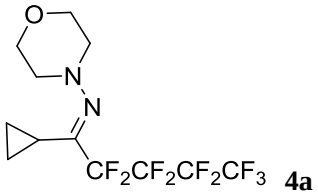
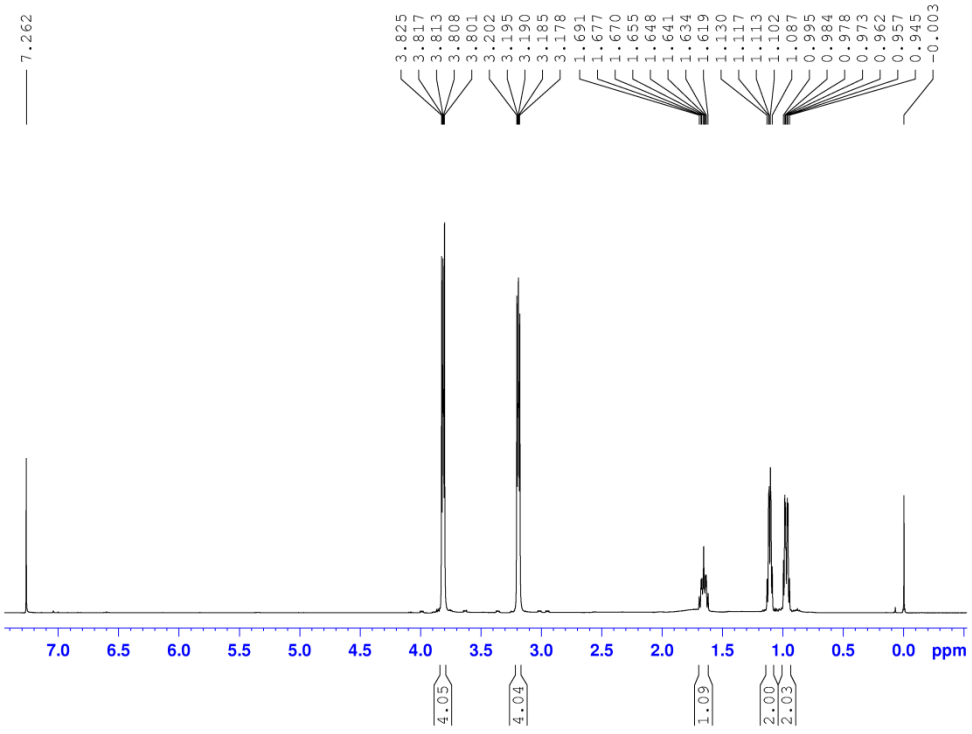

7.417
7.409
7.401
7.393
7.366
7.360
7.351
7.342
7.260
3.617
3.605
3.600
3.592
2.996
2.984
2.972
0.000
4.87
3.99
4.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

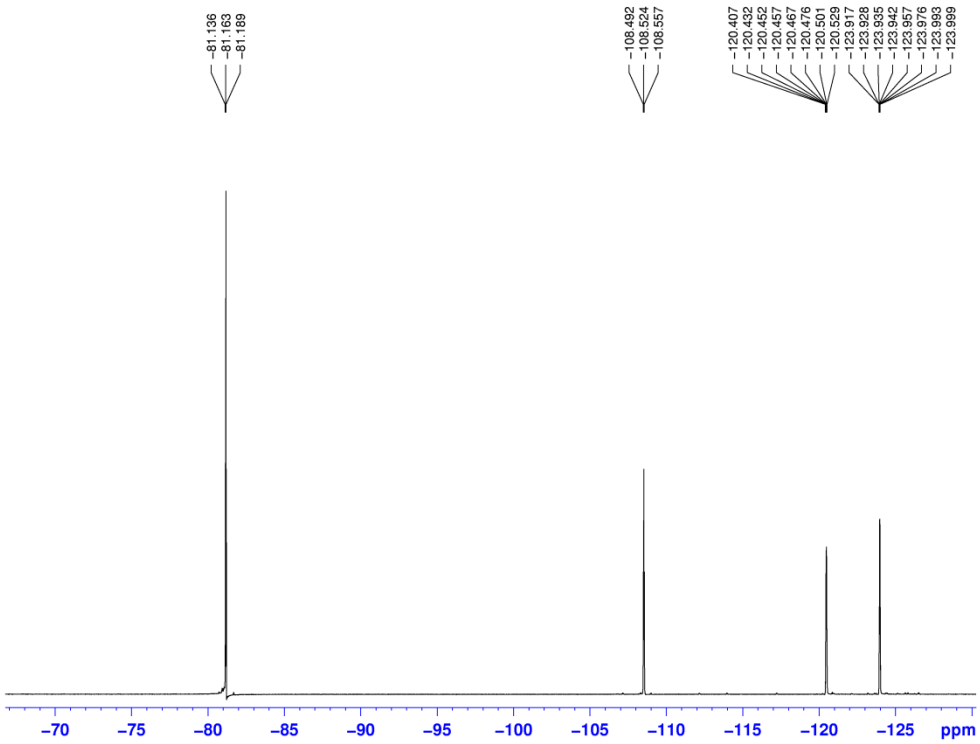

135.598
135.323
135.058
131.885
131.729
128.458
128.716
77.322
77.005
76.687
66.004
54.204
50
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)

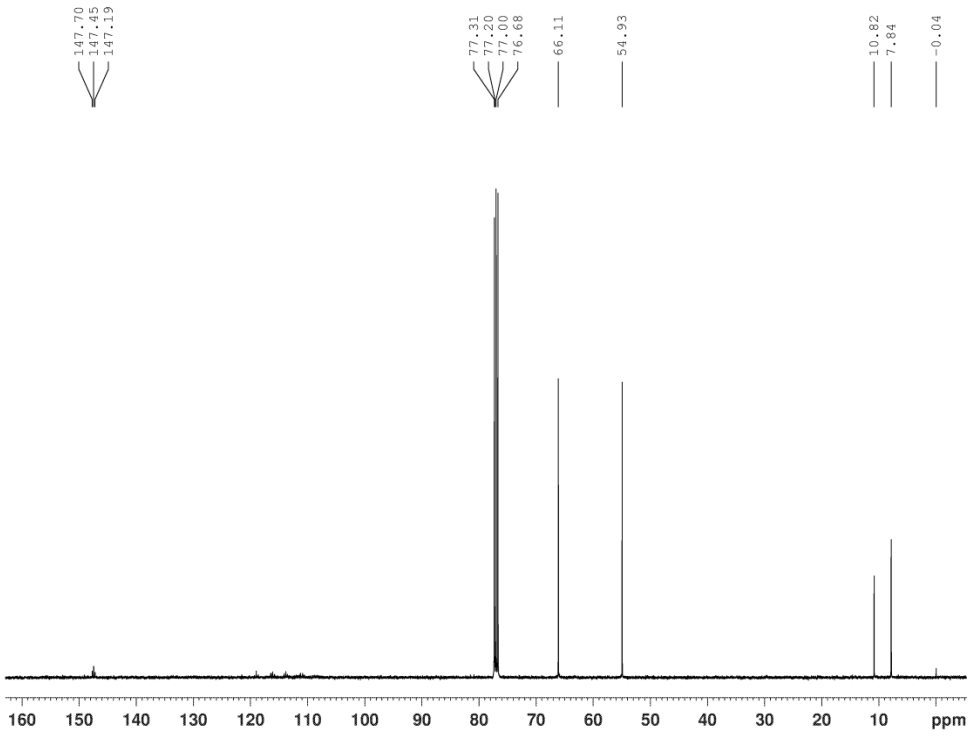

-80.782
-80.808
-80.835
-106.516
-106.555
-106.590
-119.199
-120.299
-121.852
-122.755
-126.133
-126.139
-126.179
f1 (ppm)

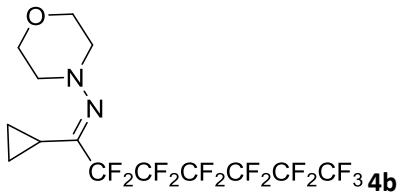


4a

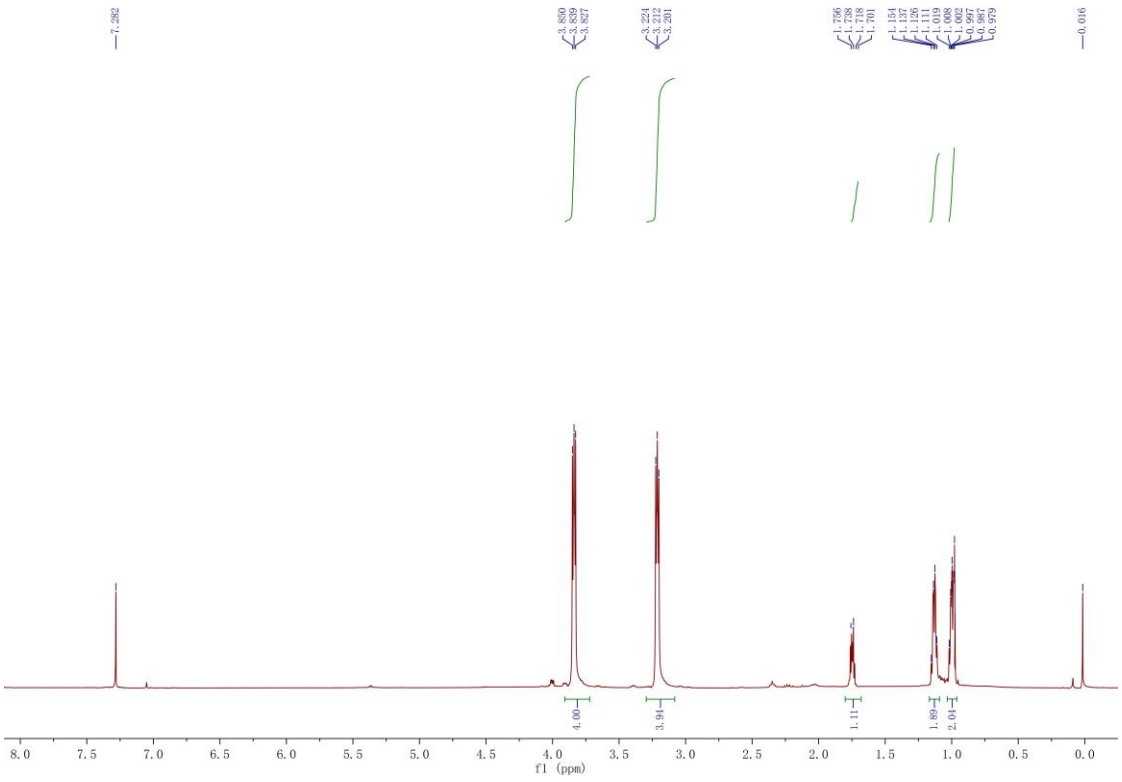

7.262
3.825
3.817
3.813
3.808
3.801
3.202
3.195
3.190
3.185
3.178
1.691
1.677
1.670
1.655
1.648
1.641
1.634
1.619
1.130
1.117
1.113
1.102
1.087
0.995
0.984
0.978
0.973
0.962
0.957
0.945
-0.003
ppm
4.05
4.04
1.09
2.00
2.03

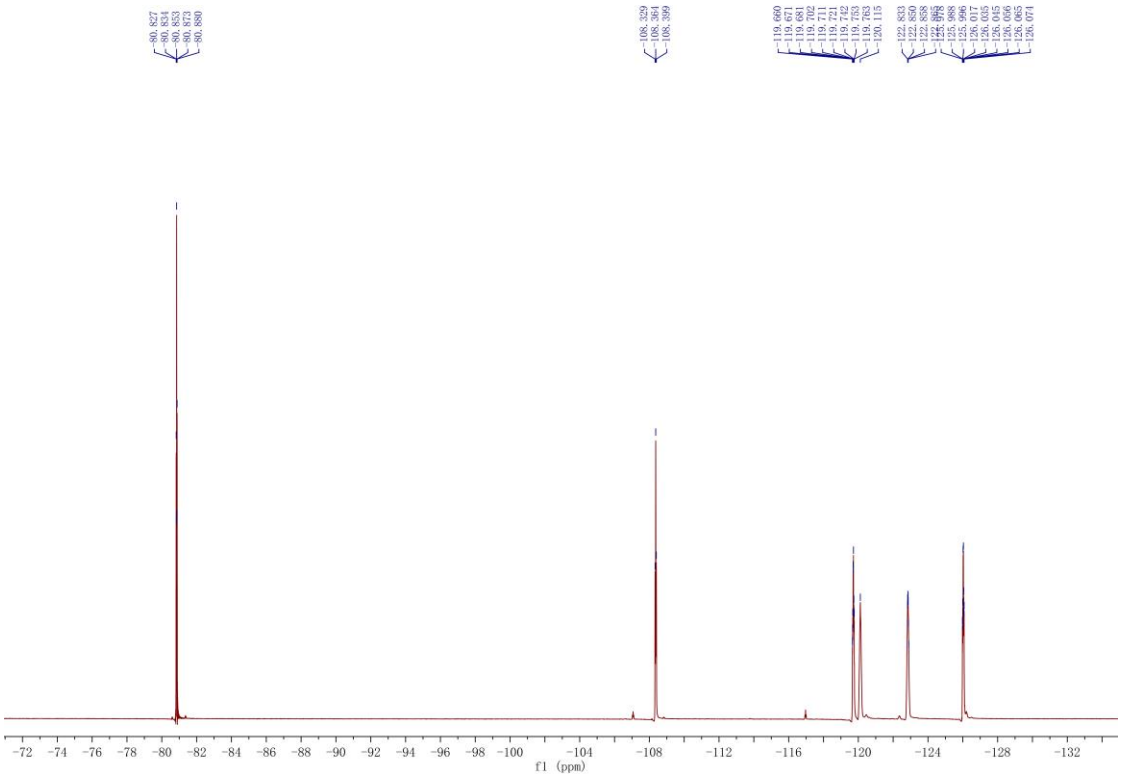

-81.136
-81.163
-81.189
-108.492
-108.524
-108.557
-120.407
-120.432
-120.452
-120.457
-120.467
-120.476
-120.501
-120.529
-123.917
-123.928
-123.935
-123.942
-123.957
-123.976
-123.993
-123.999
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
ppm

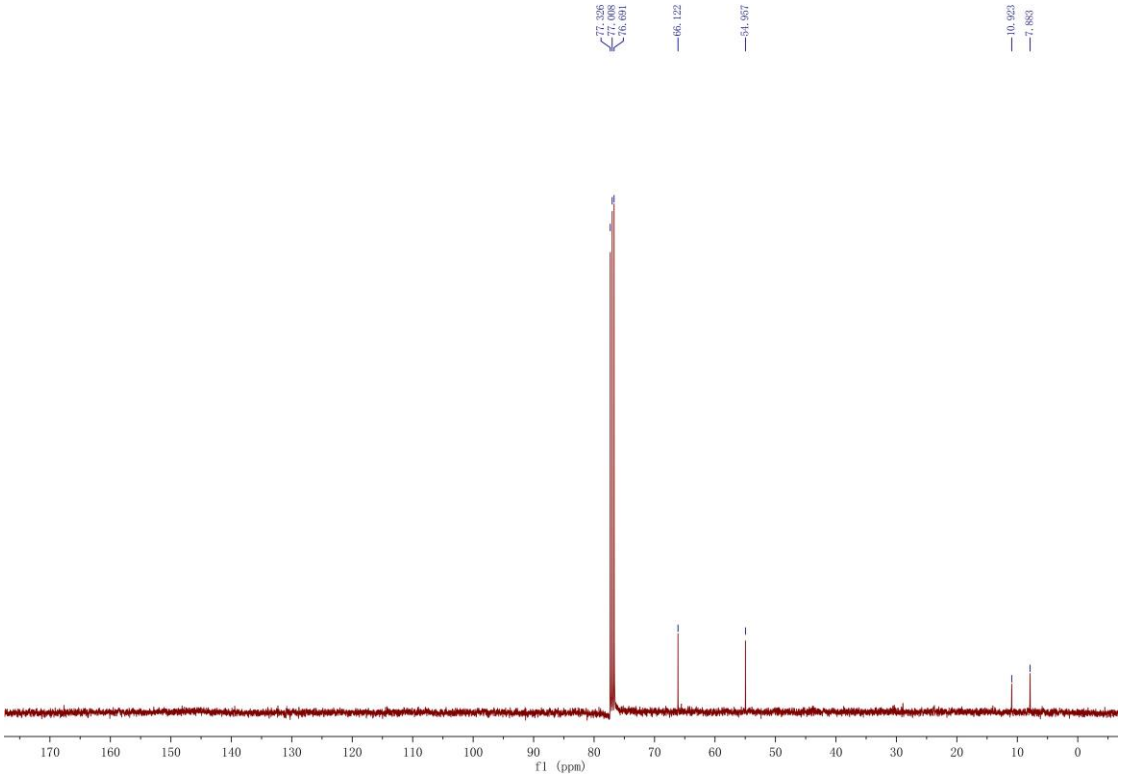

147.70
147.45
147.19
77.31
77.20
77.00
76.68
66.11
54.93
10.82
7.84
-0.04
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

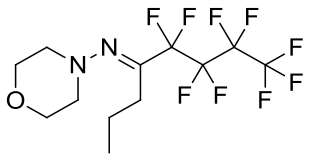

O
N
N
CF2CF2CF2CF2CF2CF3

4b

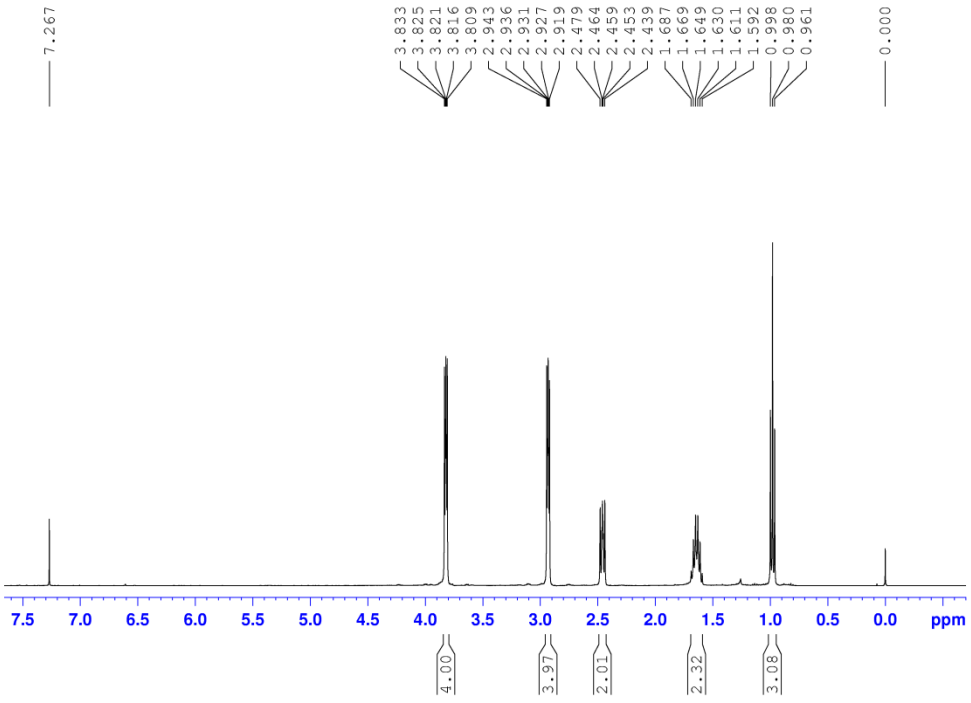

7.262
3.850
3.839
3.827
3.224
3.212
3.201
1.766
1.738
1.718
1.701
1.154
1.137
1.126
1.111
1.019
1.008
1.002
0.997
0.987
0.979
0.016
4.00
3.94
1.11
1.89
2.01
f1 (ppm)

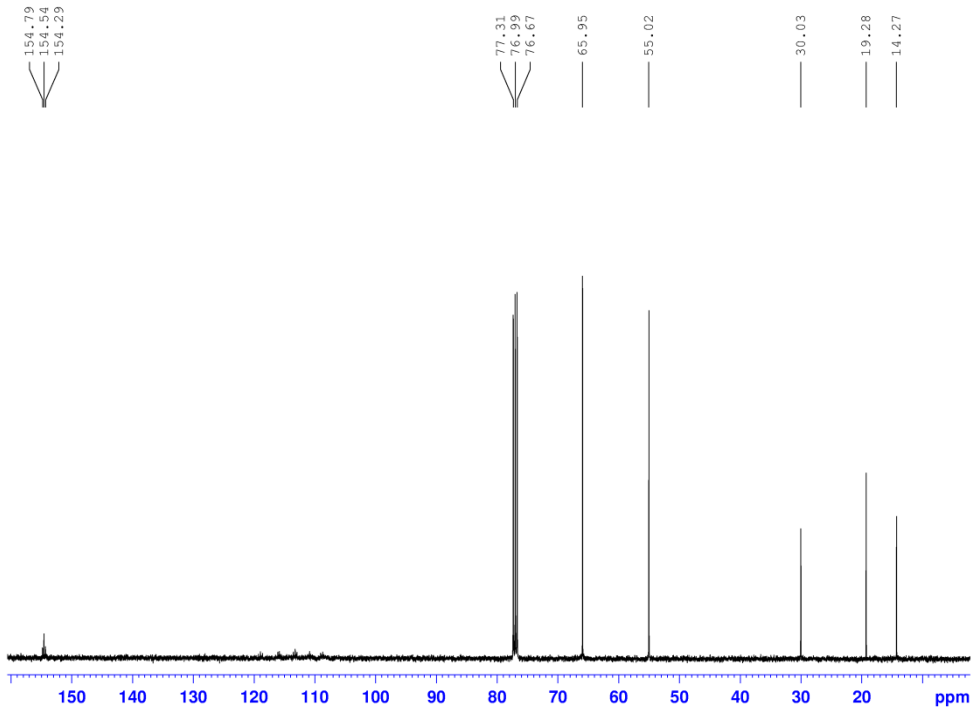

-80.827
-80.834
-80.853
-80.873
-80.880
-108.329
-108.364
-108.399
119.660
119.671
119.681
119.702
119.711
119.721
119.742
119.753
119.763
120.115
122.833
122.859
122.885
125.988
125.996
126.017
126.035
126.045
126.056
126.065
126.074
f1 (ppm)

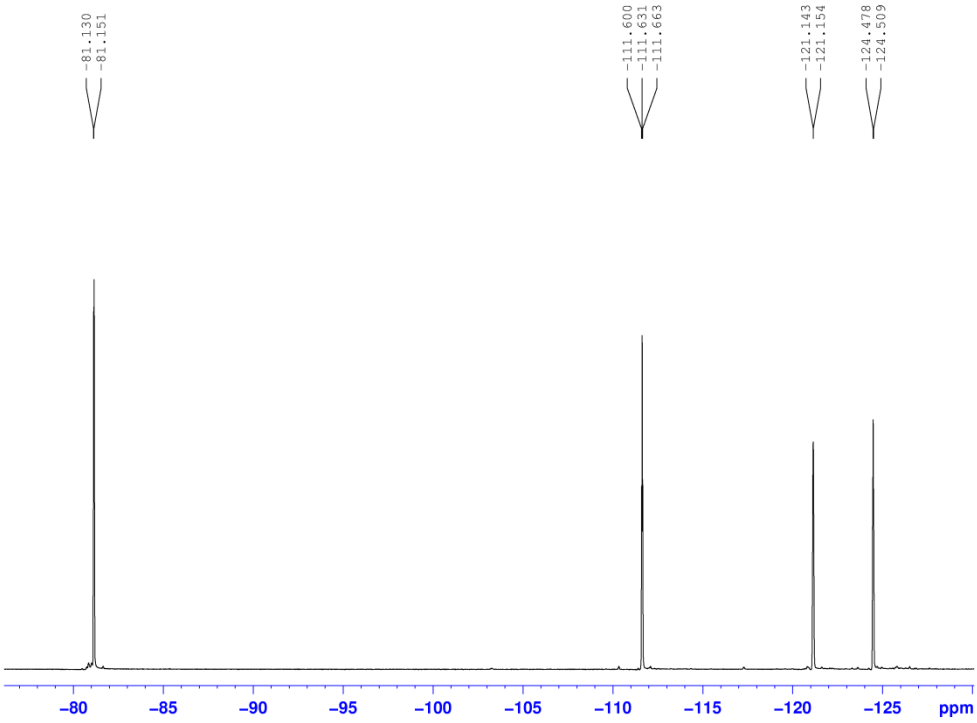

77.326
77.008
76.691
66.122
54.967
10.923
7.883
f1 (ppm)

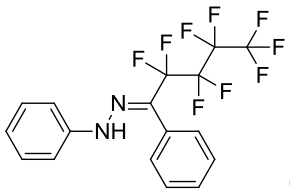


5

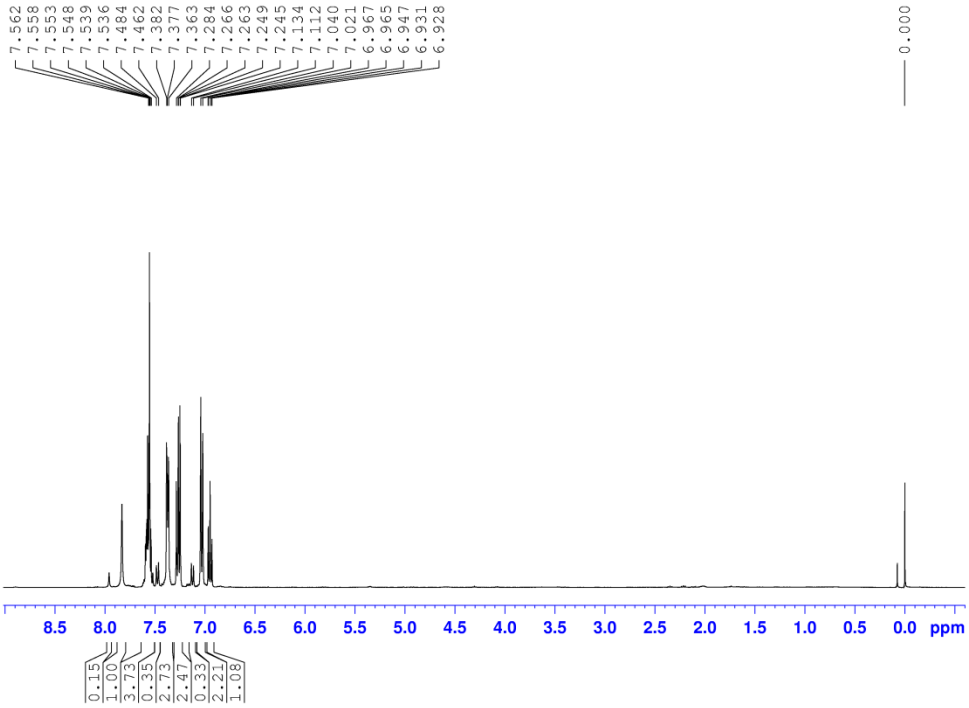

7.267
3.833
3.825
3.821
3.816
3.809
2.943
2.936
2.931
2.927
2.919
2.479
2.464
2.459
2.453
2.439
1.687
1.669
1.649
1.630
1.611
1.592
0.998
0.980
0.961
0.000
ppm
4.00
3.97
2.01
2.32
3.08

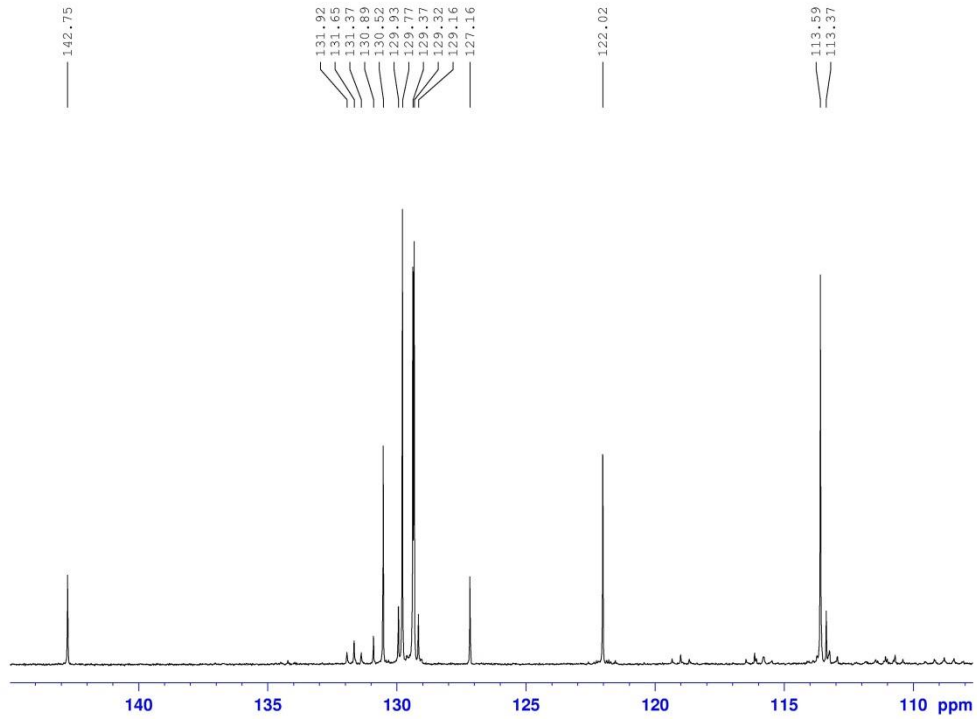

154.79
154.54
154.29
77.31
76.99
76.67
65.95
55.02
30.03
19.28
14.27
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

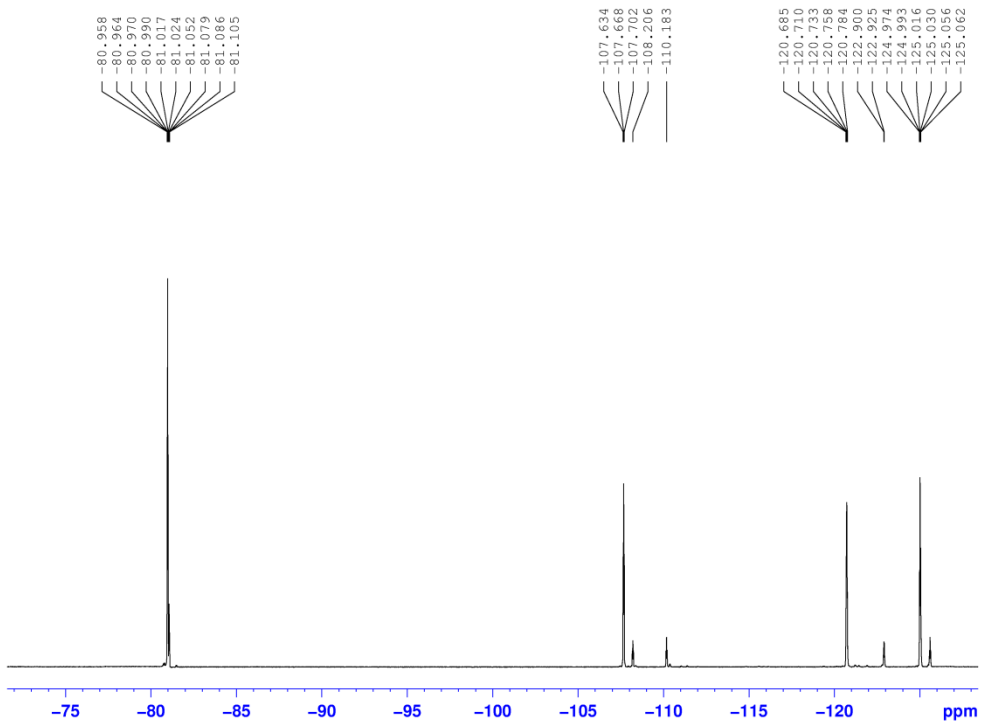

-81.130
-81.151
-111.600
-111.631
-111.663
-121.143
-121.154
-124.478
-124.509
−80
−85
−90
−95
−100
−105
−110
−115
−120
−125
ppm

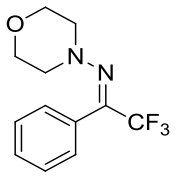

F
F
F
F
F
F
F
F
F
N
NH

6

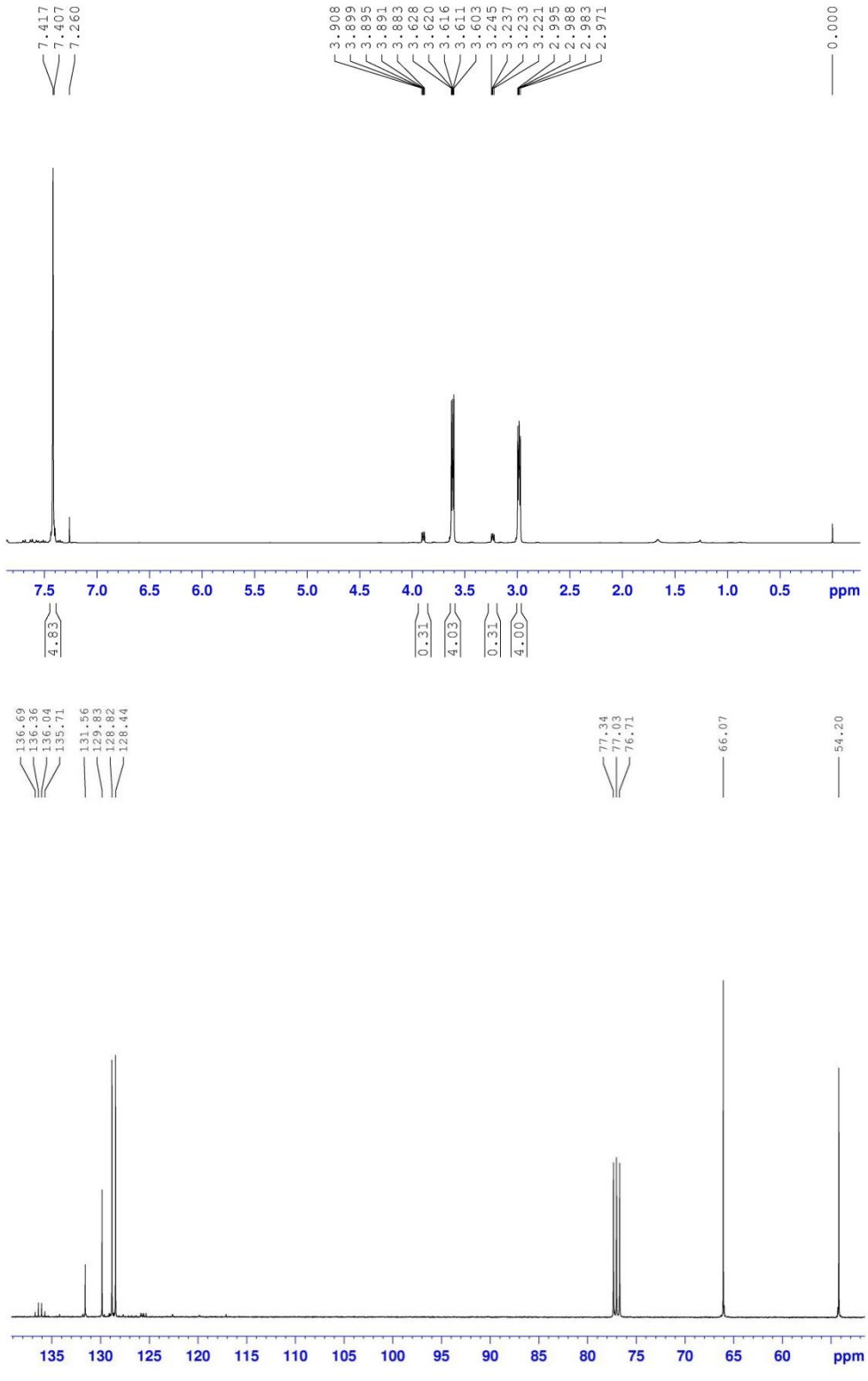

7.562
7.558
7.553
7.548
7.539
7.536
7.484
7.462
7.382
7.377
7.363
7.284
7.266
7.263
7.249
7.245
7.134
7.112
7.040
7.021
6.967
6.965
6.947
6.931
6.928
0.000
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.15
1.00
3.73
0.35
2.73
2.47
0.33
2.21
1.08

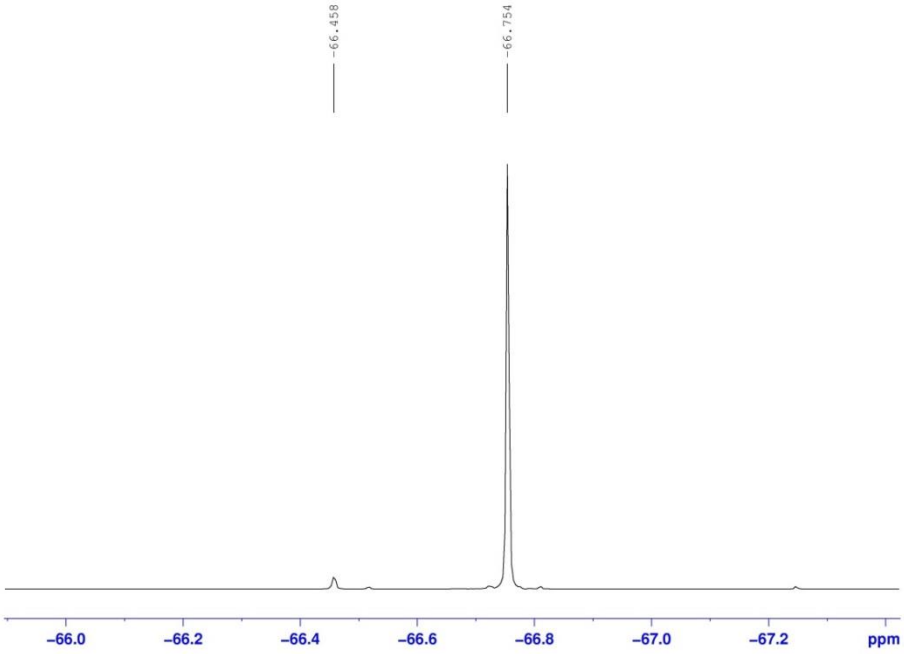

142.75
131.92
131.65
131.37
130.89
130.52
129.93
129.77
129.37
129.32
129.16
127.16
122.02
113.59
113.37
140
135
130
125
120
115
110
ppm


-80.958
-80.964
-80.970
-80.990
-81.017
-81.024
-81.052
-81.079
-81.086
-81.105
-107.634
-107.668
-107.702
-108.206
-110.183
-120.685
-120.710
-120.733
-120.758
-120.784
-122.900
-122.925
-124.974
-124.993
-125.016
-125.030
-125.056
-125.062
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
ppm



7a


7.417
7.407
7.260
3.908
3.899
3.895
3.891
3.883
3.628
3.620
3.616
3.611
3.603
3.245
3.237
3.233
3.221
2.995
2.988
2.983
2.971
0.000
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
ppm
4.83
0.31
4.03
0.31
4.00
136.69
136.36
136.04
135.71
131.56
129.83
128.82
128.44
77.34
77.03
76.71
66.07
54.20
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
ppm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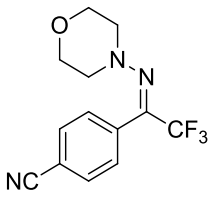
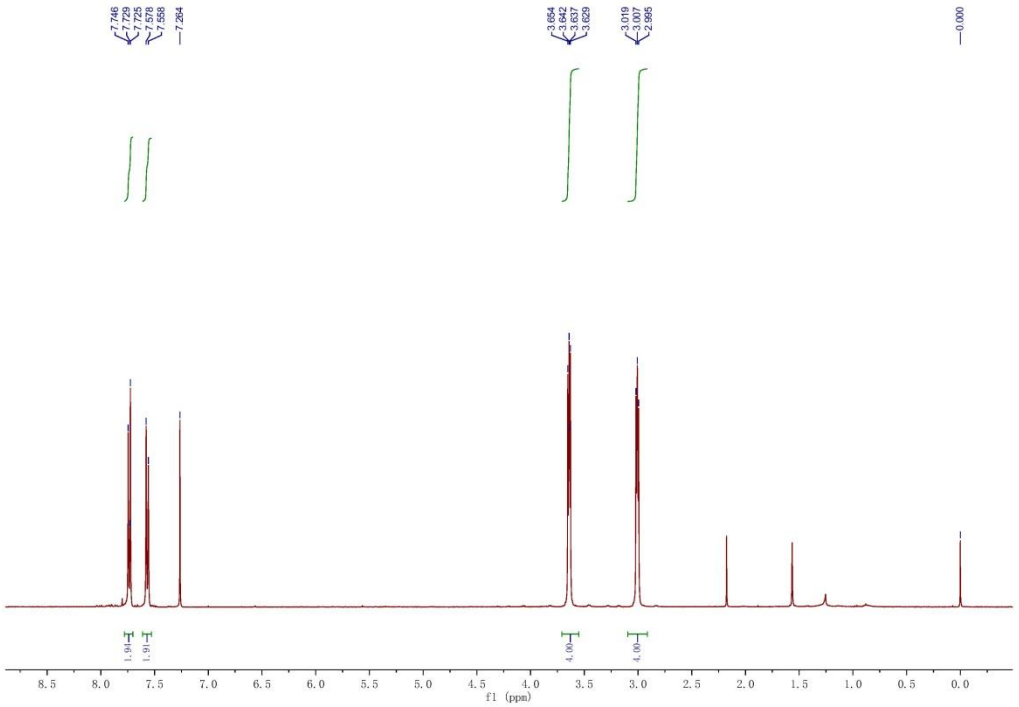
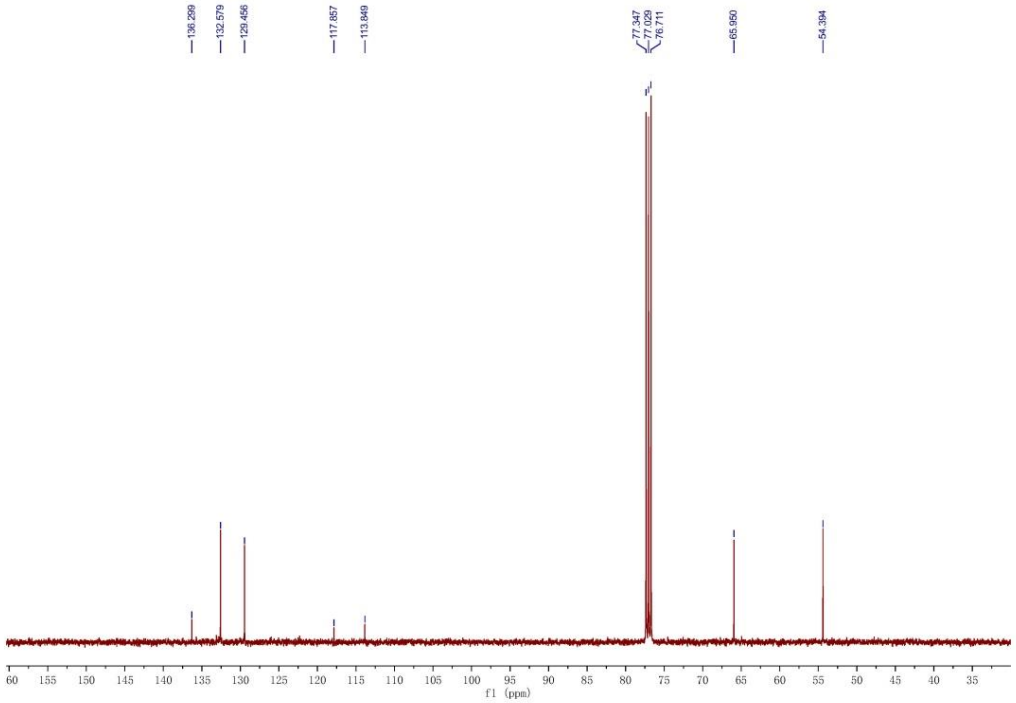
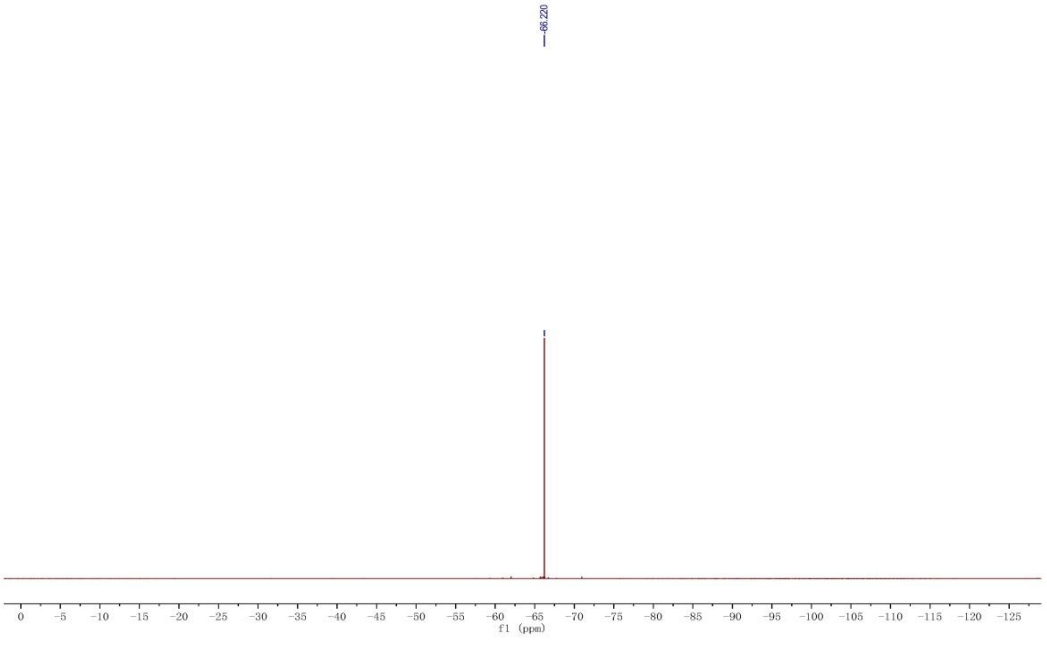
-66.754
-66.0
-66.2
-66.4
-66.6
-66.8
-67.0
-67.2
ppm

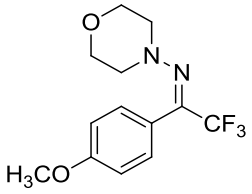

O
N
N
CF3
NC

7b

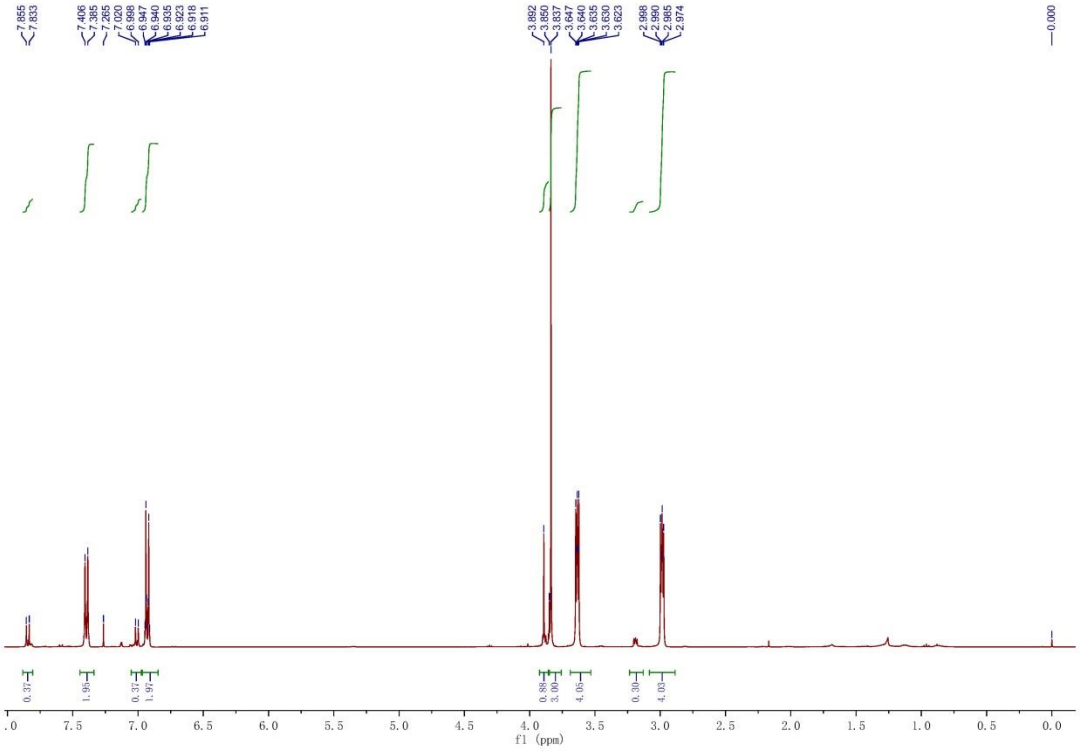

7.746
7.729
7.725
7.573
7.558
7.264
3.654
3.642
3.637
3.629
3.019
3.007
2.985
0.000
1.91
1.91
4.00
4.00
f1 (ppm)

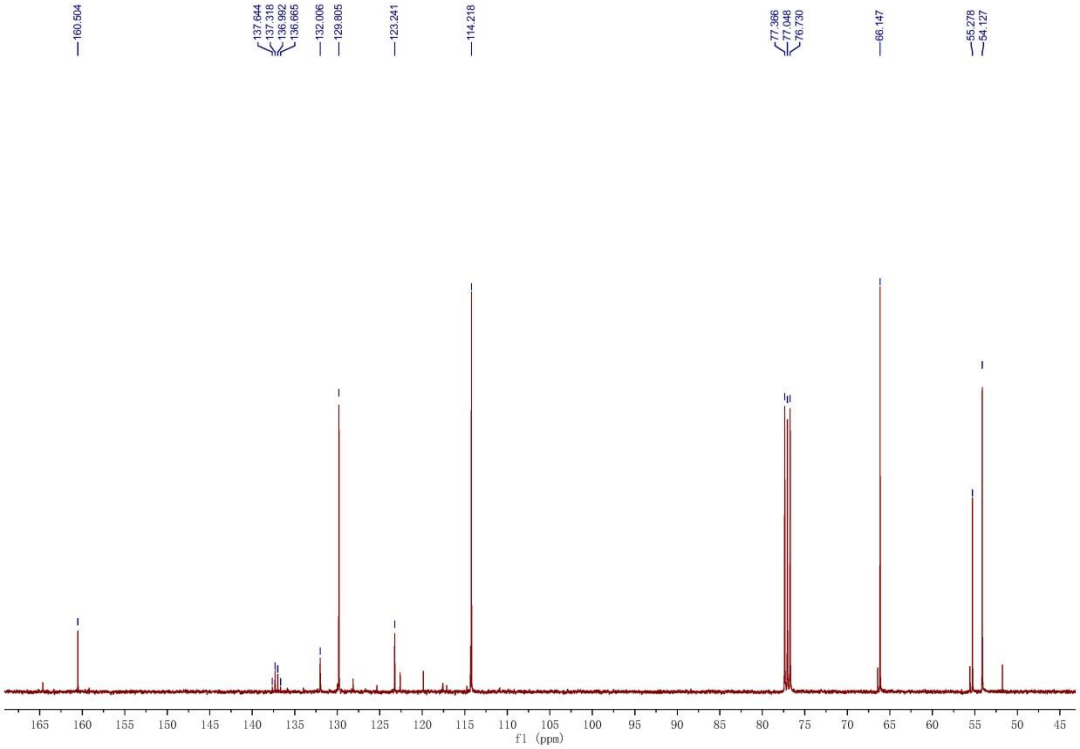

136.299
132.579
129.456
117.657
113.849
77.347
77.029
76.711
65.950
54.394
f1 (ppm)

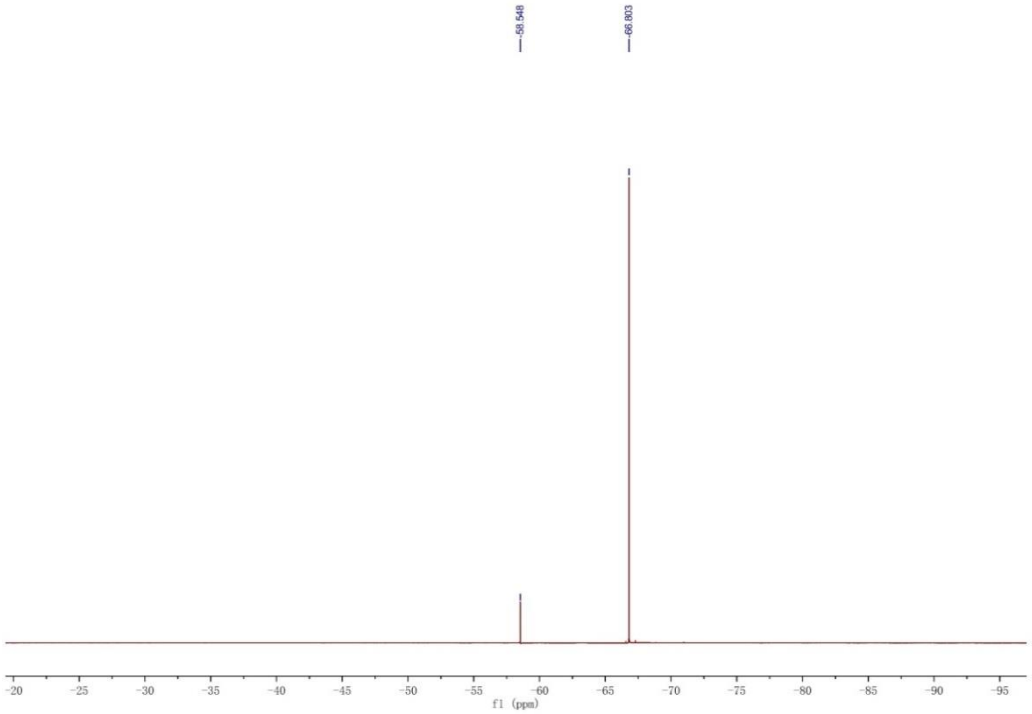

66.220
f1 (ppm)

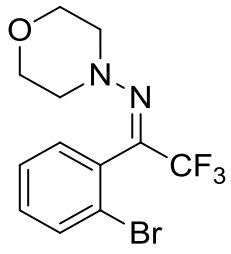


7c

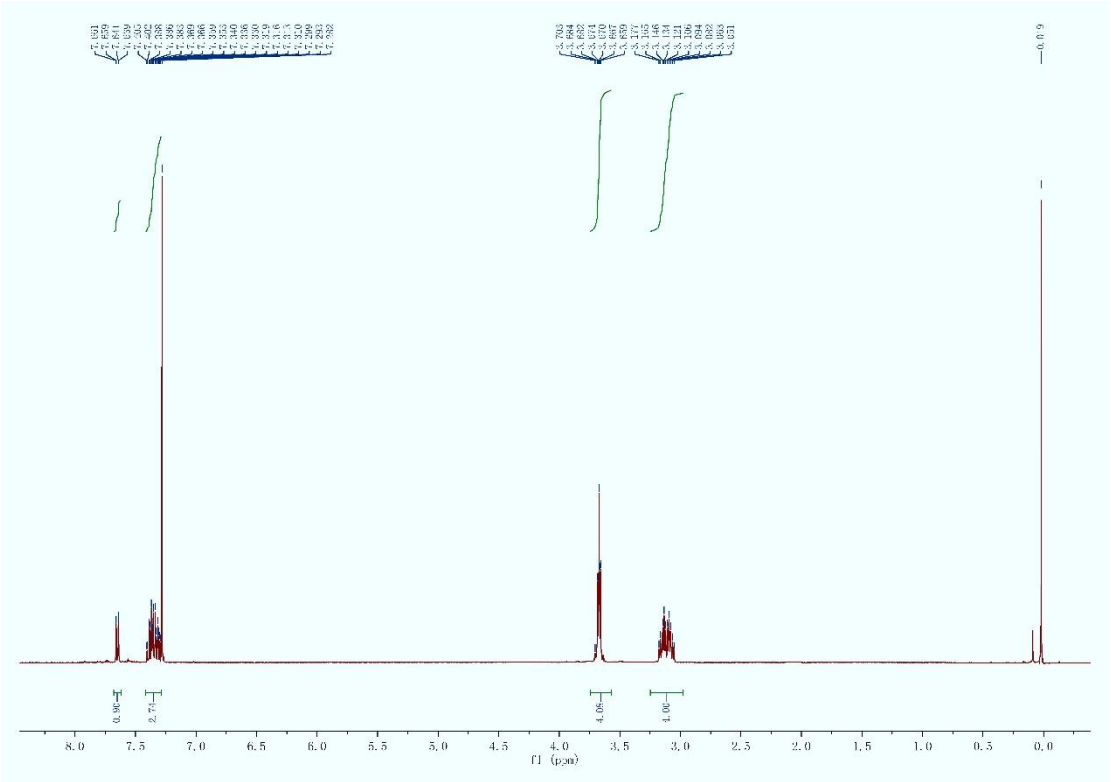

7.855
7.833
7.406
7.385
7.265
7.020
6.998
6.947
6.940
6.935
6.923
6.918
6.911
3.892
3.850
3.837
3.647
3.640
3.635
3.630
3.623
2.998
2.986
2.985
2.974
0.000
0.37
1.99
0.37
1.97
0.88
3.00
4.05
0.30
4.03
f1 (ppm)

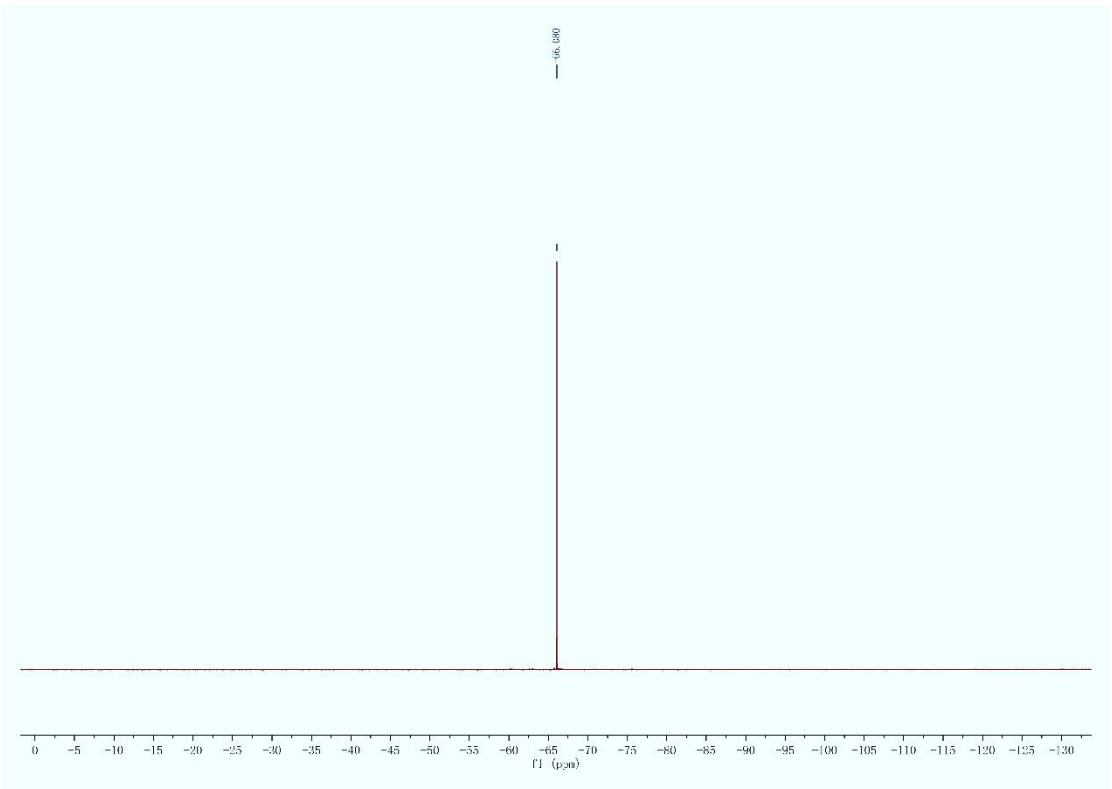

160.504
137.644
137.318
136.992
136.665
132.006
129.805
123.241
114.218
77.366
77.048
76.730
66.147
55.278
54.127
f1 (ppm)

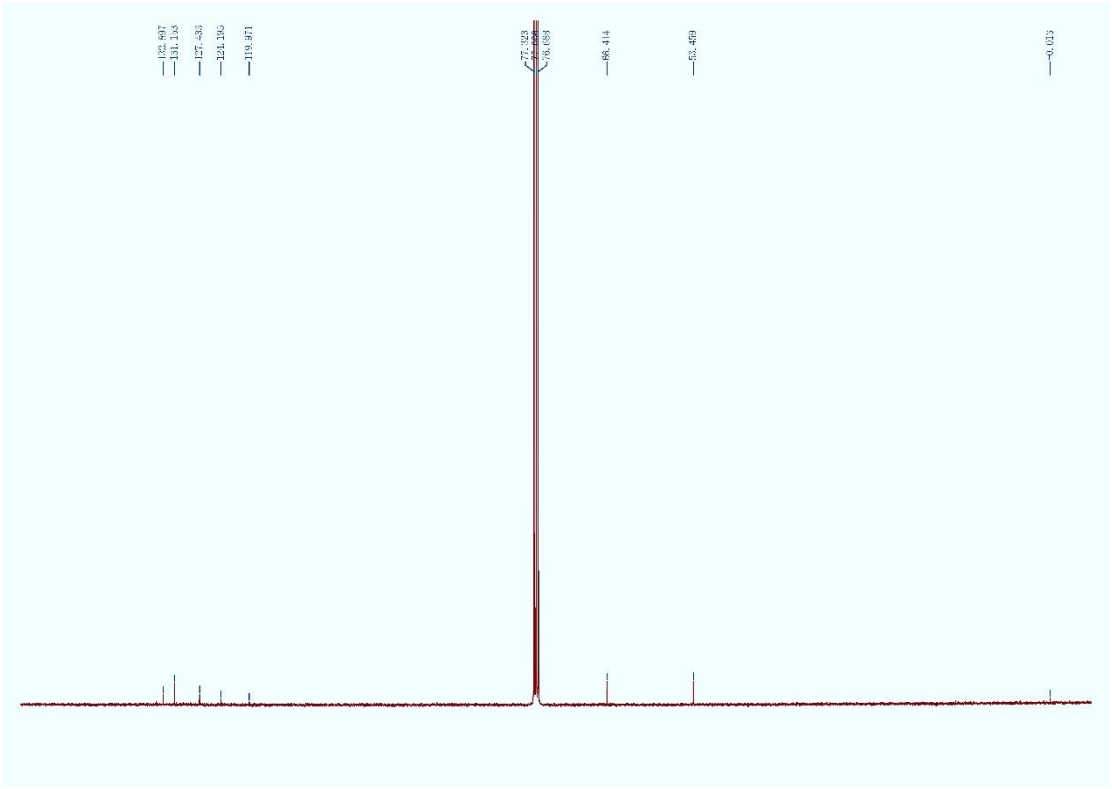

-58.548
-66.803
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
f1 (ppm)

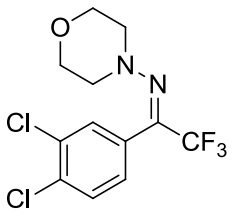

O
N
N
CF3
Br

7d

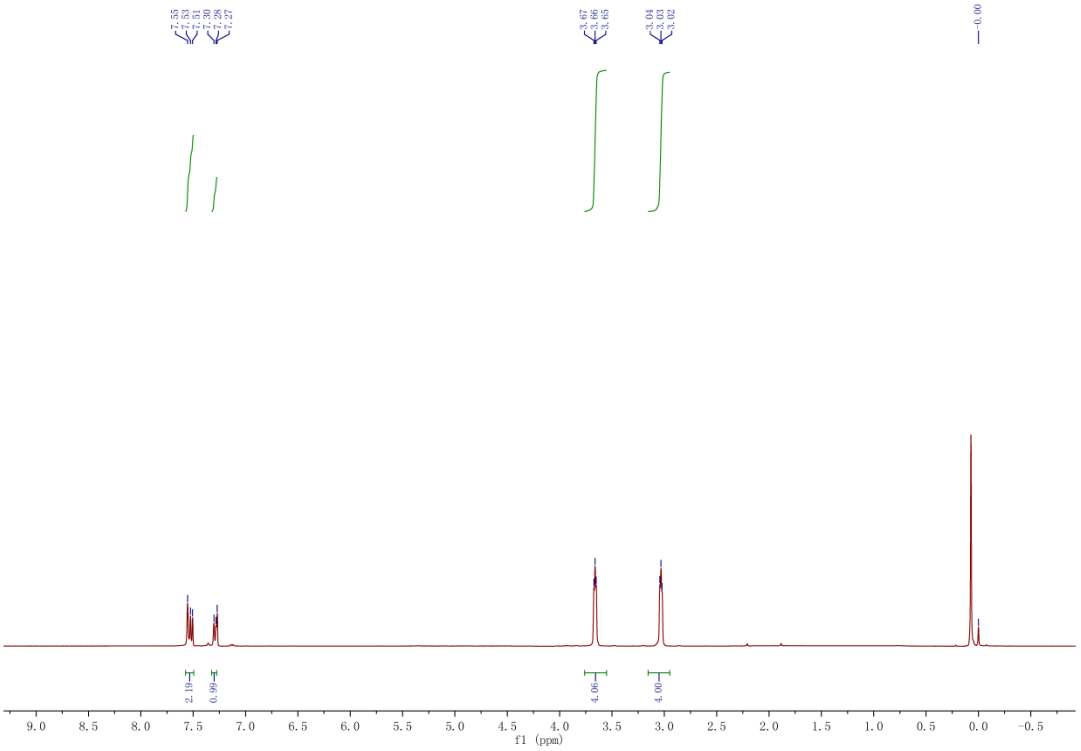

0.96
2.71
4.06
4.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

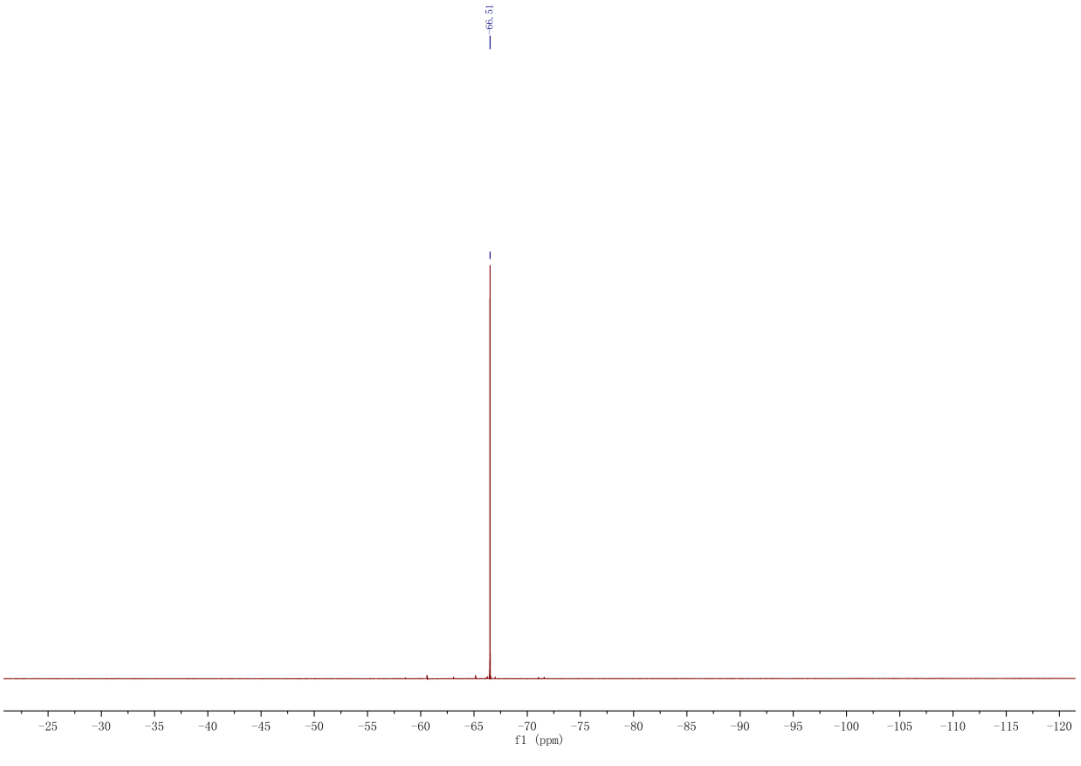

-66.690
0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130
f1 (ppm)

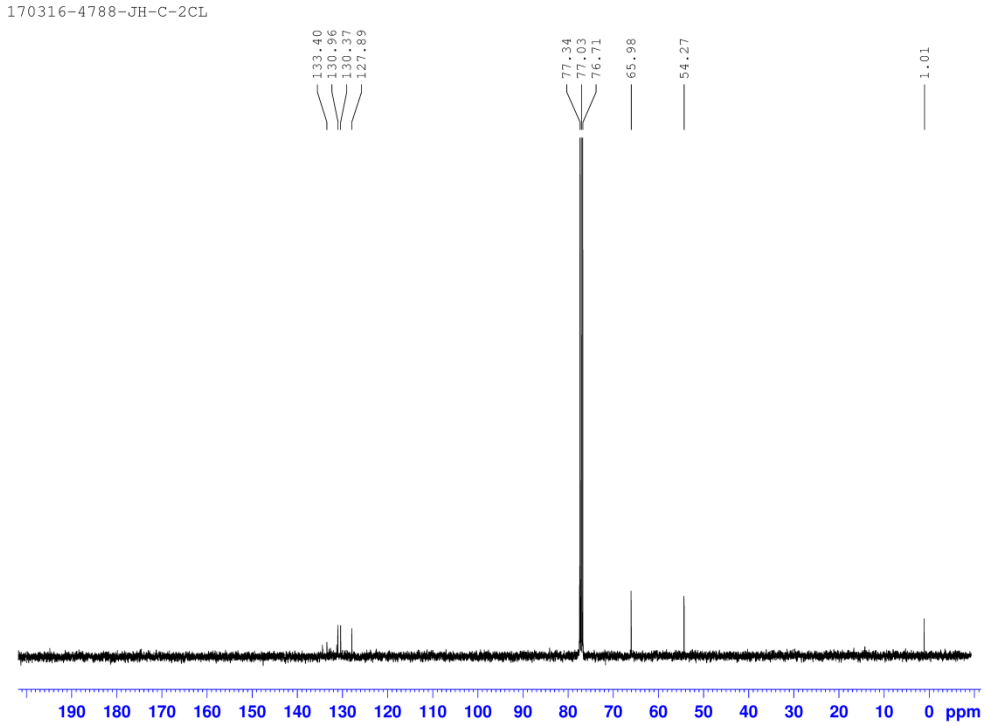

132.897
131.158
127.483
124.295
119.971
77.323
76.689
68.414
53.469
0.033

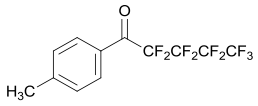

O
N
N
Cl
Cl
CF3

8

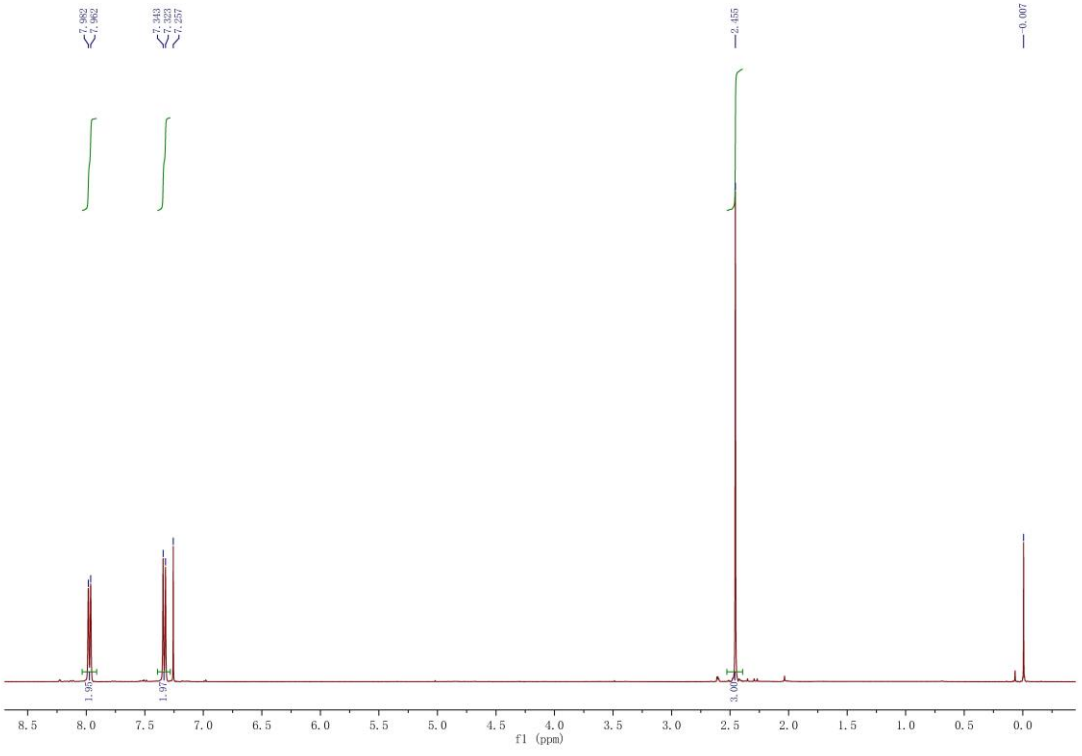

7.55
7.53
7.51
7.30
7.29
7.27
3.67
3.66
3.65
3.04
3.03
3.02
0.00
2.19
0.99
4.06
4.00
f1 (ppm)

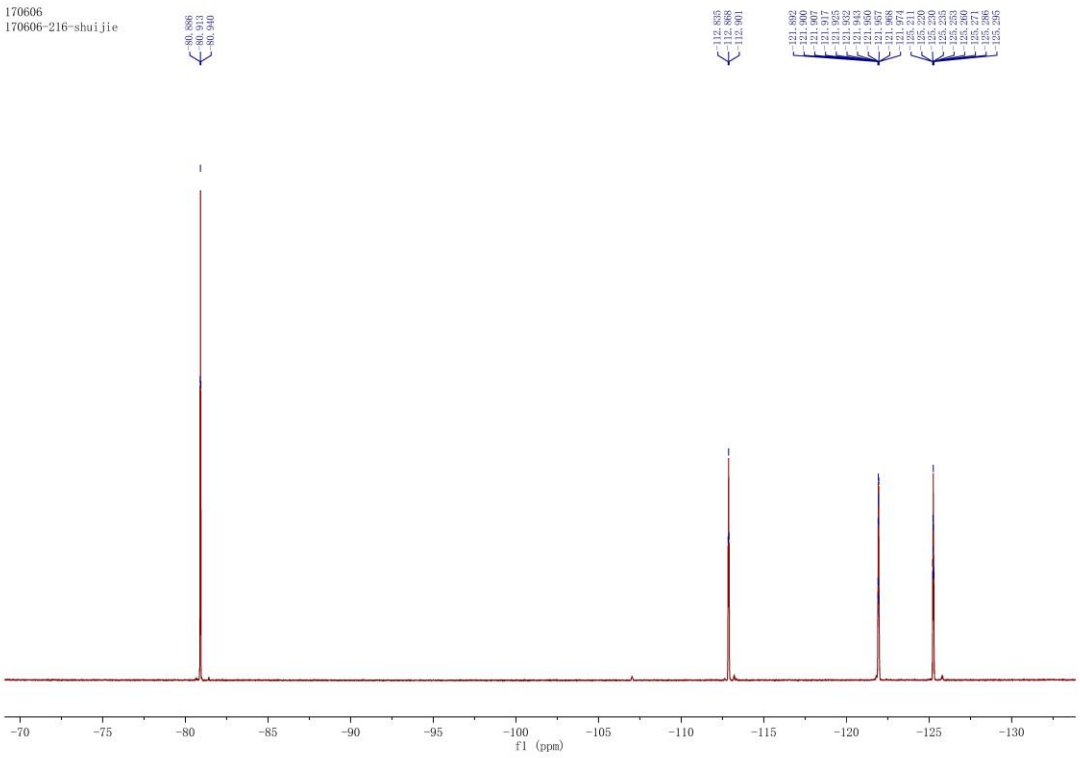

-66.51
f1 (ppm)

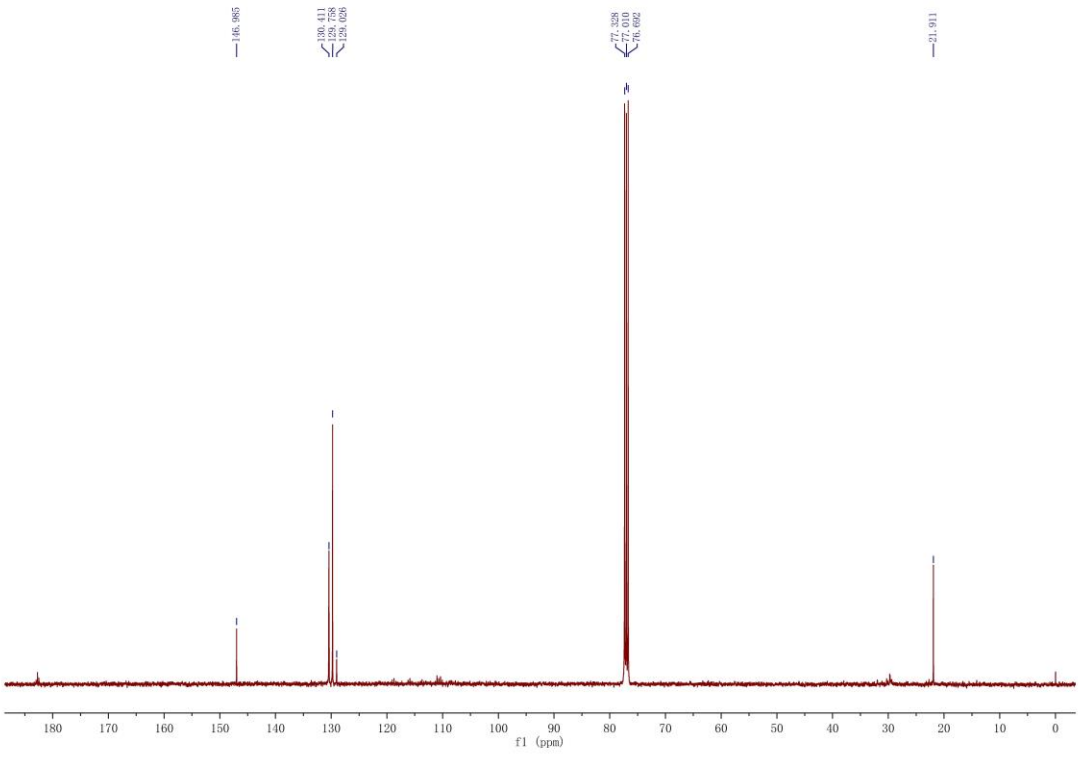

170316-4788-JH-C-2CL
133.40
130.96
130.37
127.89
77.34
77.03
76.71
65.98
54.27
1.01
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


O
CF2CF2CF2CF3
H3C

9


7.982
7.982
7.343
7.323
7.257
2.455
-0.007
1.97
1.97
3.00
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)


170606
170606-216-shuijie
80.886
80.913
80.940
112.835
112.888
112.901
121.892
121.900
121.907
121.917
121.925
121.932
121.943
121.950
121.957
121.968
121.974
125.211
125.220
125.230
125.235
125.253
125.260
125.271
125.286
125.295
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
f1 (ppm)


146.985
130.411
129.738
129.029
77.328
77.010
76.692
21.911
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)