Supporting Information

Efficient and selective aerobic oxidation of alcohols catalysed by MOF-derived Co catalysts

Cuihua Bai, Aiqin Li, Xianfang Yao, Hongli Liu, Yingwei Li*

State Key Laboratory of Pulp and Paper Engineering, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China.

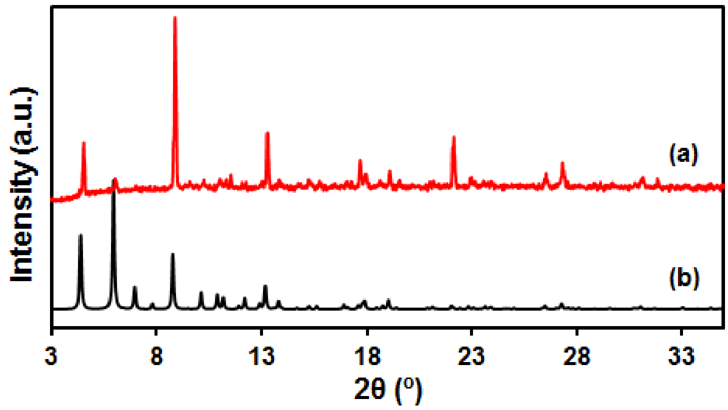


Figure S1. Powder XRD patterns of MOF **1**: (a) as-synthesized, (b) simulated.

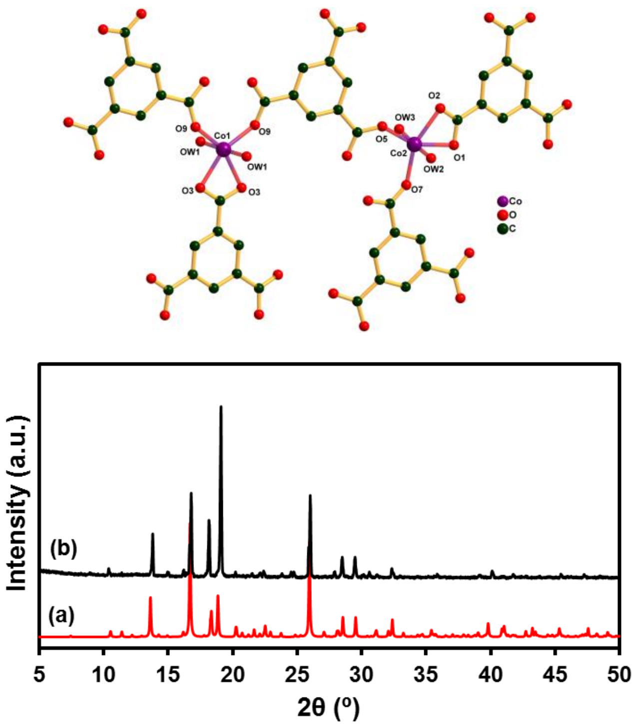


Figure S2. Structure diagram of MOF **2**(*Chem. Mater.*,2001, **13**, 4387-4392), and powder XRD patterns of MOF**2**: (a) simulated, (b) as-synthesized.

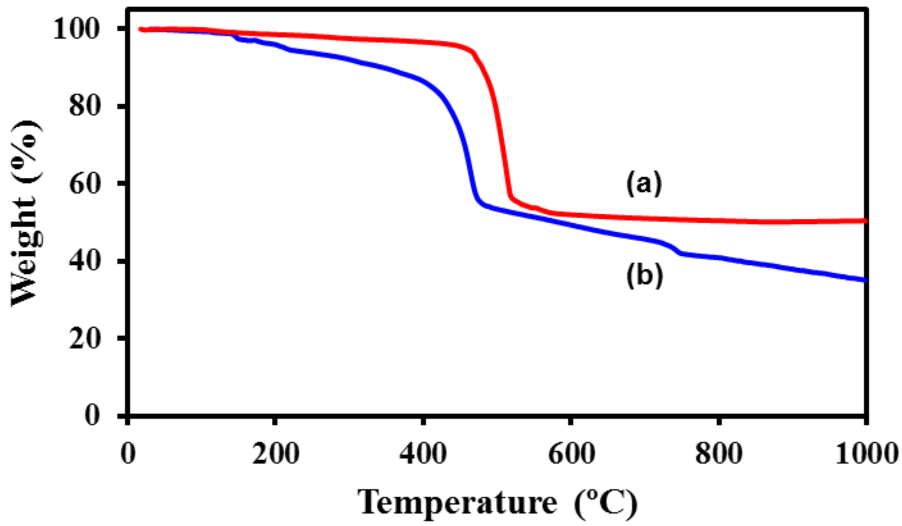


Figure S3.TGA curves of the as-synthesized MOFs: (a) MOF **2**, (b) MOF **1**.

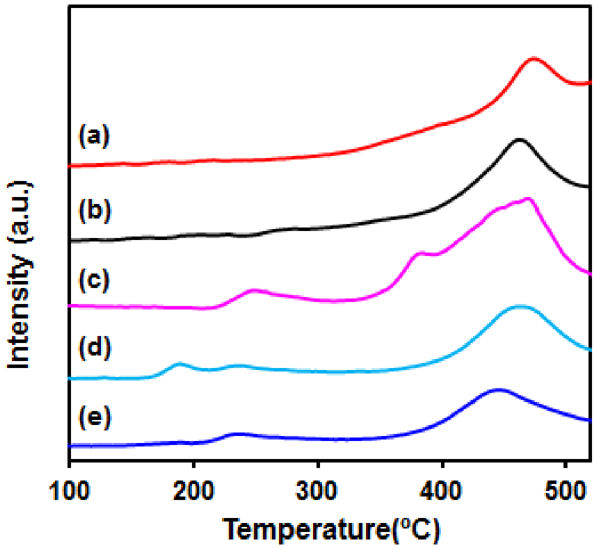
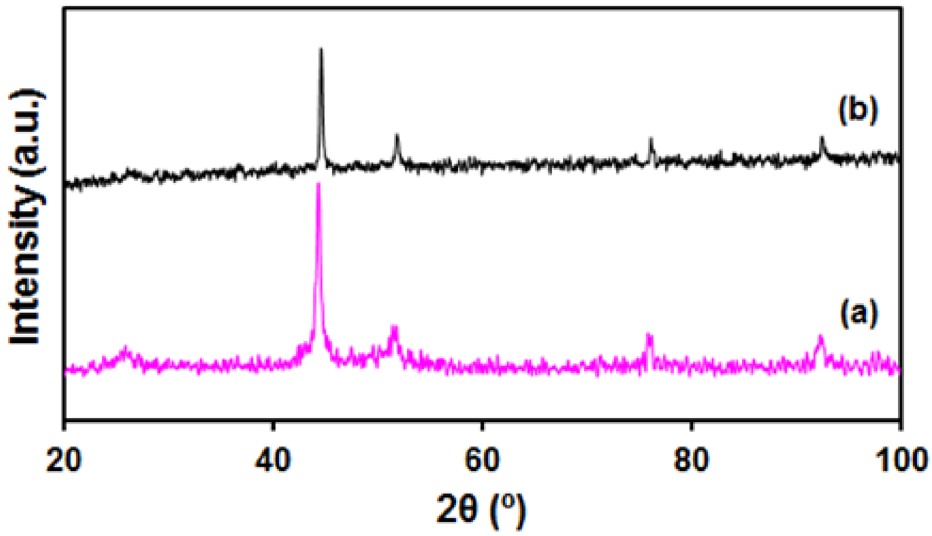


Figure S4. CO_2-TPD profiles of Co/C-Nx materials:(a) Co/C-N500, (b) Co/C-N600, (c) Co/C-N700, (d) Co/C-N800, and (e) Co/C-N900.



FigureS5. Powder XRD patterns of (a) Co/C-N700, and (b) Co/C700.

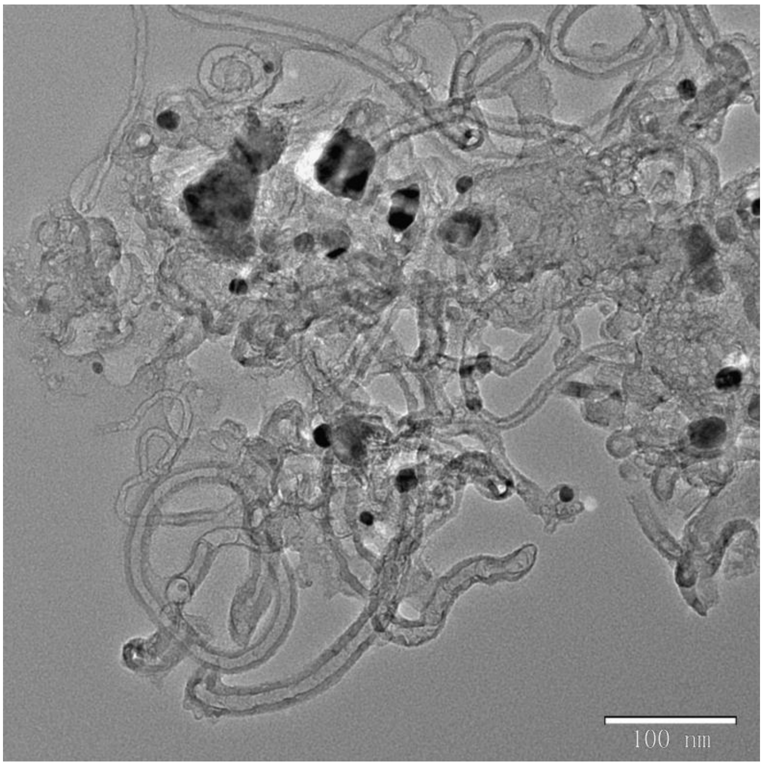


Figure S6.TEM image of Co/C-N900.

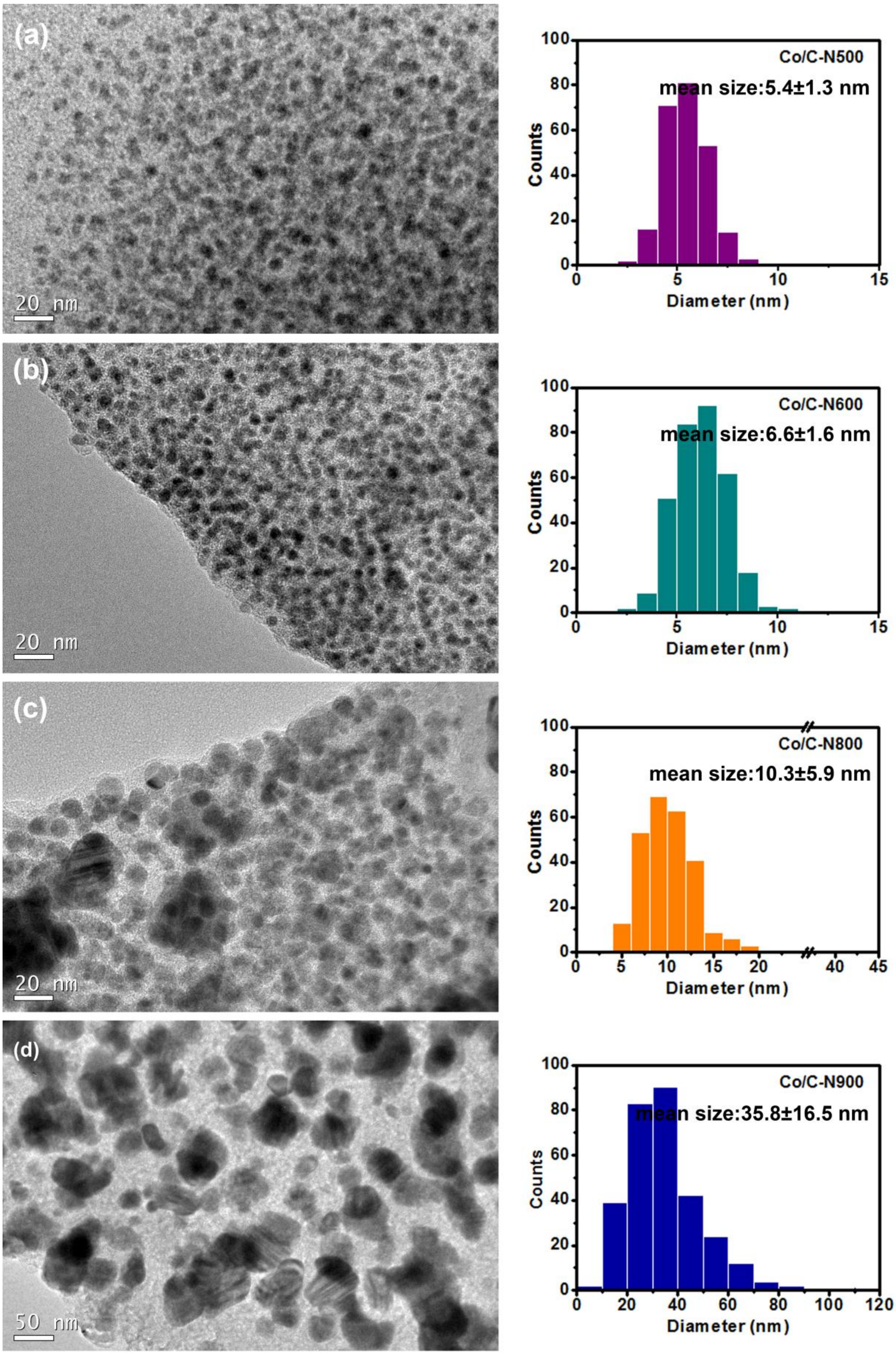


Figure S7.TEM images and size distribution of Co/C-N500 (a), Co/C-N600 (b), Co/C-N800 (c), and Co/C-N900 (d).

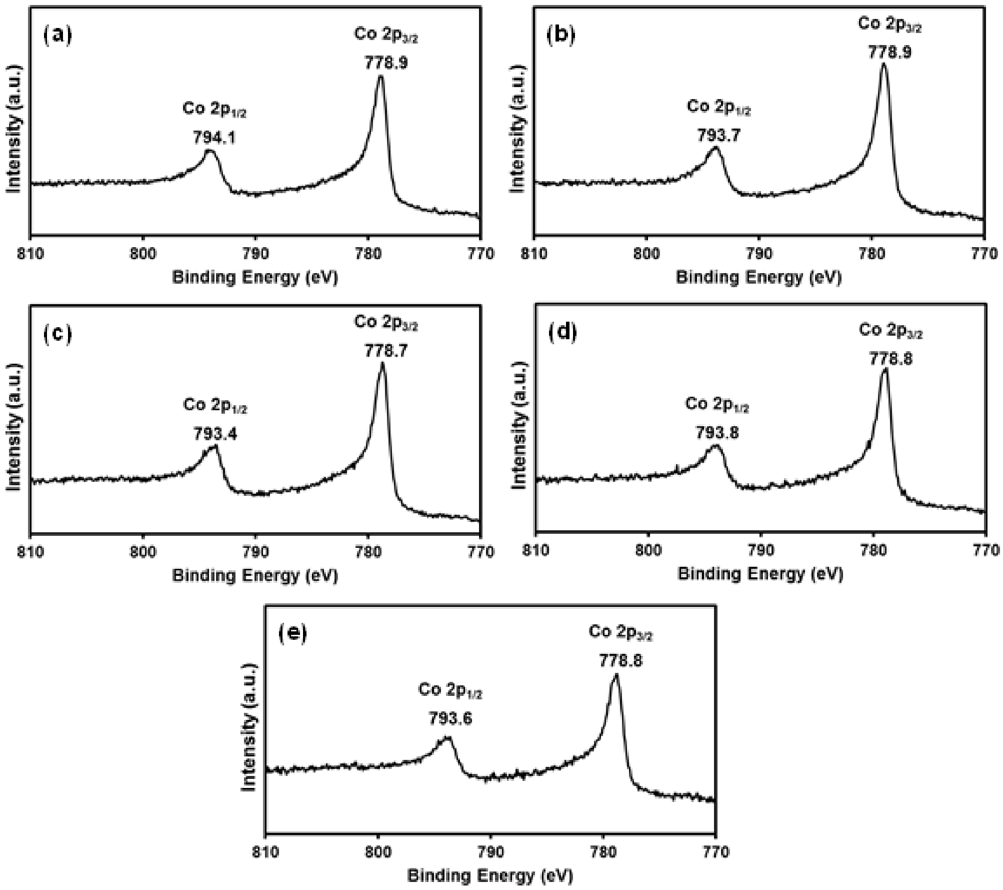


Figure S8. Co2p spectra of Co/C-N500 (a), Co/C-N600 (b), Co/C-N700 (c), Co/C-N800 (d), and Co/C-N900 (e).

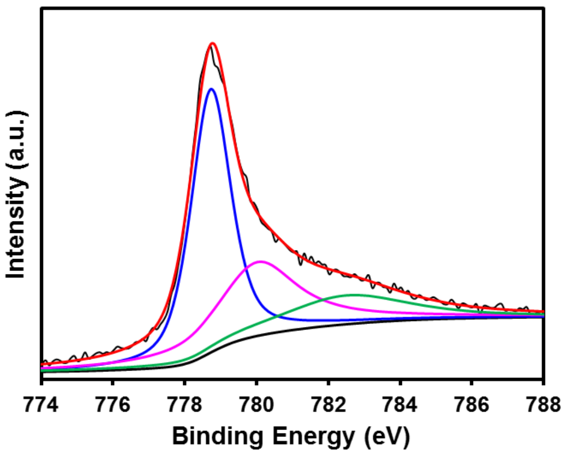


Figure S9. Co2p$_{3/2}$ spectra of Co/C-N700.

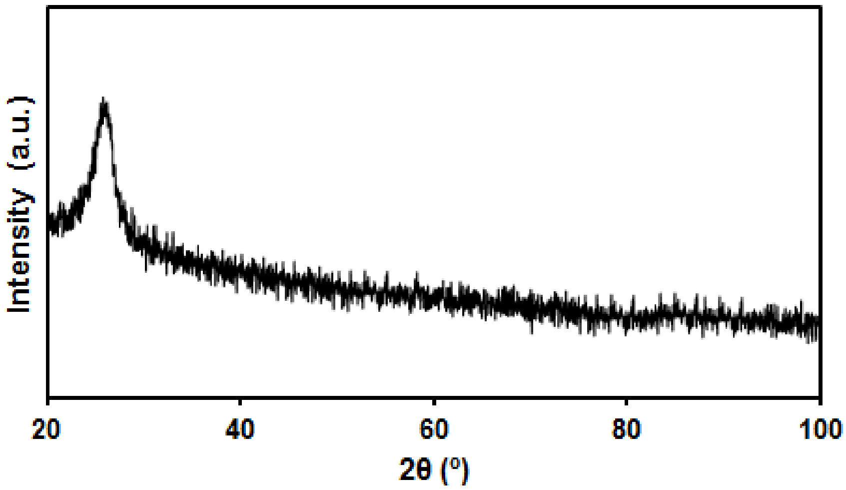


Figure S10. Powder XRD of C-N700.

.

Figure S11. Magnetic separation of the Co/C-N700 catalyst after reaction.

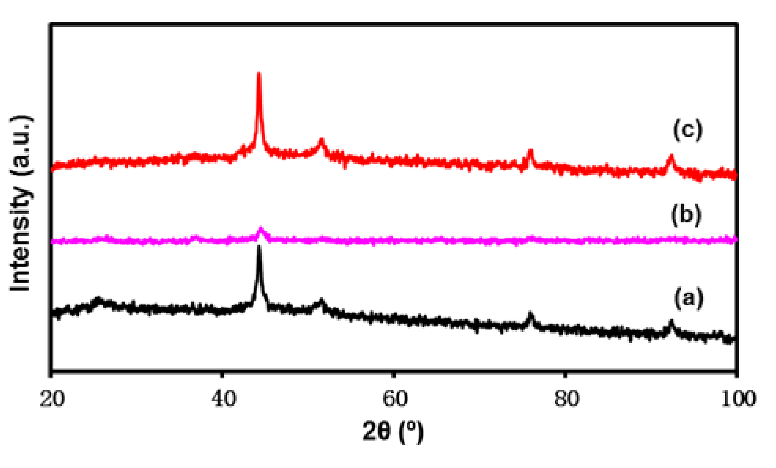


Figure S12. Powder XRD patterns of (a) Co/C-N700, (b) recycled Co/C-N700 before the H_2reduction treatment, and (c) recycled Co/C-N700 after the H_2reduction treatment, respectively.

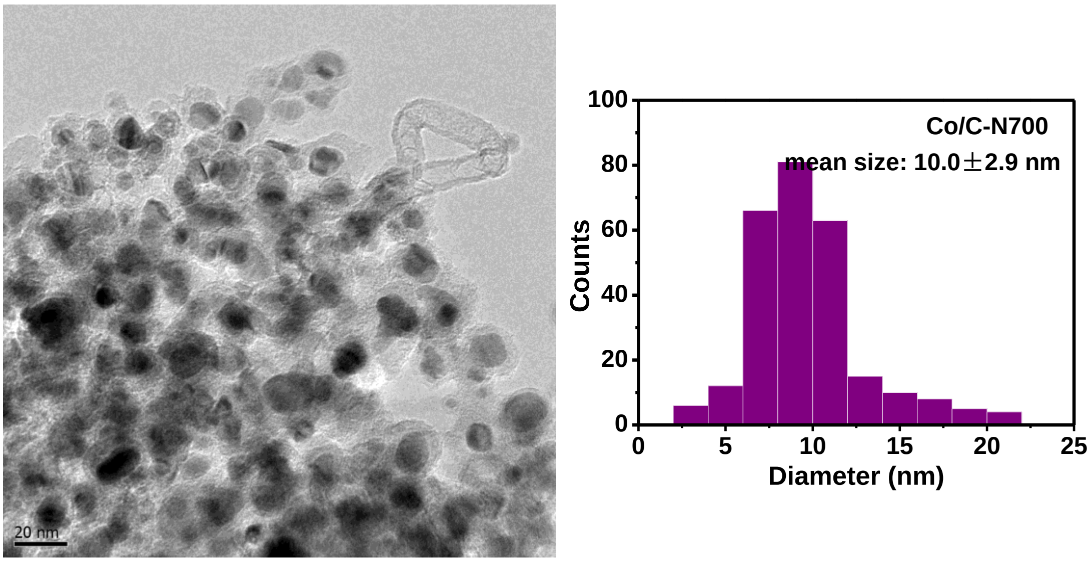


Figure S13. TEM images and size distribution of recycled Co/C-N700 after H_2 reduction treatment.

Table S1. Reusability of the Co/C-N700 catalyst without H_2 reduction.

Use	1st	2nd	3rd	4th	5th
Yield(%)	98	80	67	65	64

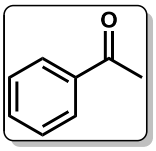
Reaction conditions: **1a**(0.5 mmol), Co/C-N700 (10 mol% Co), H_2O (2 mL), air (1 bar), 110 ℃, 48 h.

Table S2. Recovery and reuse of the Co/C-N700 catalyst after H_2 reduction.

Use	1st	2nd	3rd	4th	5th
Yield(%)	98	99	97	98	98

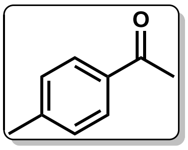
Reaction conditions: **1a** (0.5 mmol), Co/C-N700 (10 mol% Co), H_2O (2 mL), air (1 bar), 110 ℃, 48 h.

Spectra data for the products



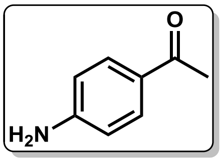
acetophenone (2a)

^{1}H NMR (400 MHz, $CDCl_3$) δ=7.95 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 2.60 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=198.07, 137.05, 133.01, 128.48, 128.21, 26.49. GC-MS (EI): found: 120(M^+), calcd for C_8H_8O (M^+): 120.2.



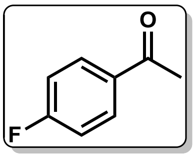
1-(p-tolyl)ethanone (2b)

^{1}H NMR (400 MHz, $CDCl_3$) δ=7.83 (d, *J* = 6.6 Hz, 2H), 7.22 (d, *J* = 7.2 Hz, 2H), 2.53 (d, *J* = 2.8 Hz, 3H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=197.45, 143.55, 134.45, 128.96, 128.16, 26.17, 21.30. GC-MS (EI): found: 134(M^+), calcd for $C_9H_{10}O$ (M^+): 134.2.



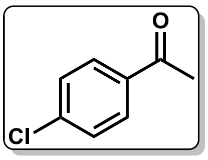
1-(4-aminophenyl)ethanone (2c)

^{1}H NMR (400 MHz, $CDCl_3$) δ=7.80 (d, *J* = 8.0 Hz, 2H), 6.64 (d, *J* = 8.2 Hz, 2H), 4.17 (s, 2H), 2.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=196.49, 151.16, 130.76, 127.79, 113.68, 26.02. GC-MS (EI): found: 135(M^+), calcd for C_8H_9NO (M^+): 135.2.



1-(4-fluorophenyl)ethanone (2d)

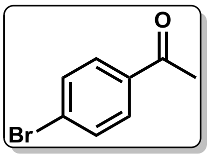
^{1}H NMR (400 MHz, $CDCl_3$) δ=7.94-7.90 (m, 2H), 7.24-7.19 (m, 2H), 2.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=196.88, 167.71, 165.15, 132.93, 132.91, 132.18, 132.08, 116.36, 116.13, 27.81. GC-MS (EI): found: 138(M^+), calcd for C_8H_7FO (M^+): 138.1.



1-(4-chlorophenyl)ethanone (2e)

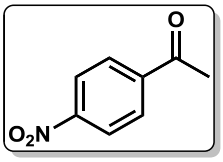
^{1}H NMR (400 MHz, $CDCl_3$) δ=7.89 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 2H), 2.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=196.70, 139.44, 135.34, 129.62, 128.78, 26.43. GC-MS (EI): found: 154(M^+), calcd for

C_8H_7ClO (M^+): 154.6.



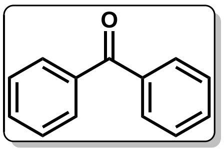
1-(4-bromophenyl)ethanone (2f)

^{1}H NMR (400 MHz, $CDCl_3$) δ=7.82 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 2.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=197.00, 135.83, 131.88, 129.82, 128.29, 26.50. GC-MS (EI): found: 199(M^+), calcd for C_8H_7BrO (M^+): 199.0.



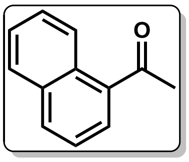
1-(4-nitrophenyl)ethanone (2g)

^{1}H NMR (400 MHz, $CDCl_3$) δ=8.32 (d, *J* = 7.6 Hz, 2H), 8.12 (d, *J* = 8.6 Hz, 2H), 2.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=196.27, 150.39, 141.43, 129.29, 123.85, 26.95. GC-MS (EI): found: 165(M^+), calcd for $C_8H_7NO_3$ (M^+): 165.2.



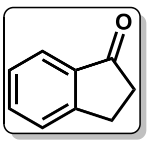
benzophenone (2h)

^{1}H NMR (400 MHz, $CDCl_3$) δ=7.80 (d, *J* = 7.4 Hz, 4H), 7.59 (t, *J* = 7.4 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=196.74, 137.59, 132.38, 130.03, 128.25. GC-MS (EI): found: 182(M^+), calcd for $C_{13}H_{10}O$ (M^+): 182.2.



1-(naphthalen-1-yl)ethanone (2i)

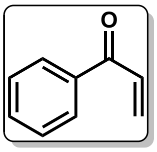
^{1}H NMR (400 MHz, $CDCl_3$) δ=8.74 (d, *J* = 8.6 Hz, 1H), 7.97 – 7.80 (m, 3H), 7.61 – 7.53 (m, 1H), 7.51 -7.42 (m, 2H), 2.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=201.67, 135.30, 133.86, 132.90, 130.03, 128.57, 128.29, 127.92, 126.31, 125.90, 124.21, 29.82. GC-MS (EI): found: 170(M^+), calcd for $C_{12}H_{10}O$ (M^+): 170.2.



2,3-dihydro-1H-inden-1-one (2j)

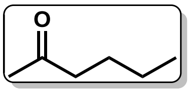
^{1}H NMR (400 MHz, $CDCl_3$) δ=7.76 (d, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 7.8

Hz, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 3.19 – 3.07 (m, 2H), 2.74 – 2.62 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=207.04, 155.13, 137.08, 134.56, 127.26, 126.67, 123.70, 36.19, 25.78. GC-MS (EI): found: 132(M^+), calcd for C_9H_8O (M^+): 132.2.



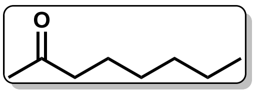
1-phenylprop-2-en-1-one (2k)

^{1}H NMR (400 MHz, $CDCl_3$) δ=7.94 (d, *J* = 7.6 Hz, 2H), 7.55 -7.51 (m, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.18 -7.13 (m, 1H), 6.44 (d, *J* = 17.6 Hz, 1H), 5.92 (d, *J* = 10.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=190.64, 136.87, 132.27, 131.55, 129.97, 128.48, 128.44. GC-MS (EI): found: 132(M^+), calcd for C_9H_8O (M^+): 132.2.



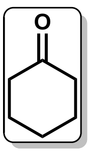
hexan-2-one (2m)

^{1}H NMR (400 MHz, $CDCl_3$) δ=2.42 (t, *J* = 7.4 Hz, 2H), 2.13 (s, 3H), 1.60 – 1.52 (m, 2H), 1.35 – 1.29 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=209.20, 43.41, 29.71, 25.88, 22.20, 13.72. GC-MS (EI): found: 100(M^+), calcd for $C_6H_{12}O$ (M^+): 100.2.



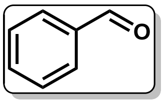
octan-2-one (2n)

^{1}H NMR (400 MHz, $CDCl_3$) δ=2.42 (t, *J* = 7.4 Hz, 2H), 2.13 (s, 3H), 1.60-1.53 (m, 2H), 1.33 – 1.28 (m, 6H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=209.21, 43.72, 31.51, 29.71, 28.77, 23.76, 22.40, 13.91. GC-MS (EI): found: 128(M^+), calcd for $C_8H_{16}O$ (M^+): 128.2.



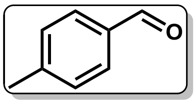
cyclohexanone (2o)

^{1}H NMR (400 MHz, $CDCl_3$) δ=2.34 (t, *J* = 6.6 Hz, 4H), 1.90 – 1.84 (m, 4H), 1.75 – 1.70 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=211.98, 41.85, 26.90, 24.88. GC-MS (EI): found: 98(M^+), calcd for $C_6H_{10}O$ (M^+): 98.1.



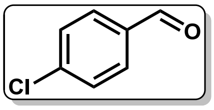
benzaldehyde (2p)

^{1}H NMR (400 MHz, $CDCl_3$) δ=10.02 (s, 1H), 7.88 (d, *J* = 7.4 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.53(t, *J* = 7.4 Hz, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ=192.43, 136.32, 134.42, 129.69, 128.93. GC-MS (EI): found: 106(M^+), calcd for C_7H_6O (M^+): 106.1.



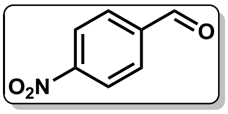
4-methylbenzaldehyde (2q)

^{1}H NMR (400 MHz, $CDCl_3$) δ=9.95 (s, 1H), 7.77 (d, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 2.43 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ=191.98, 145.50, 134.13, 129.79, 129.64, 21.79. GC-MS (EI): found: 120(M^+), calcd for C_8H_8O (M^+): 120.2.



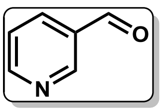
4-chlorobenzaldehyde (2r)

^{1}H NMR (400 MHz, $CDCl_3$) δ=9.99 (s, 1H), 7.83 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ=190.87, 140.98, 134.73, 130.91, 129.47. GC-MS (EI): found: 140(M^+), calcd for C_7H_5ClO (M^+): 140.6.



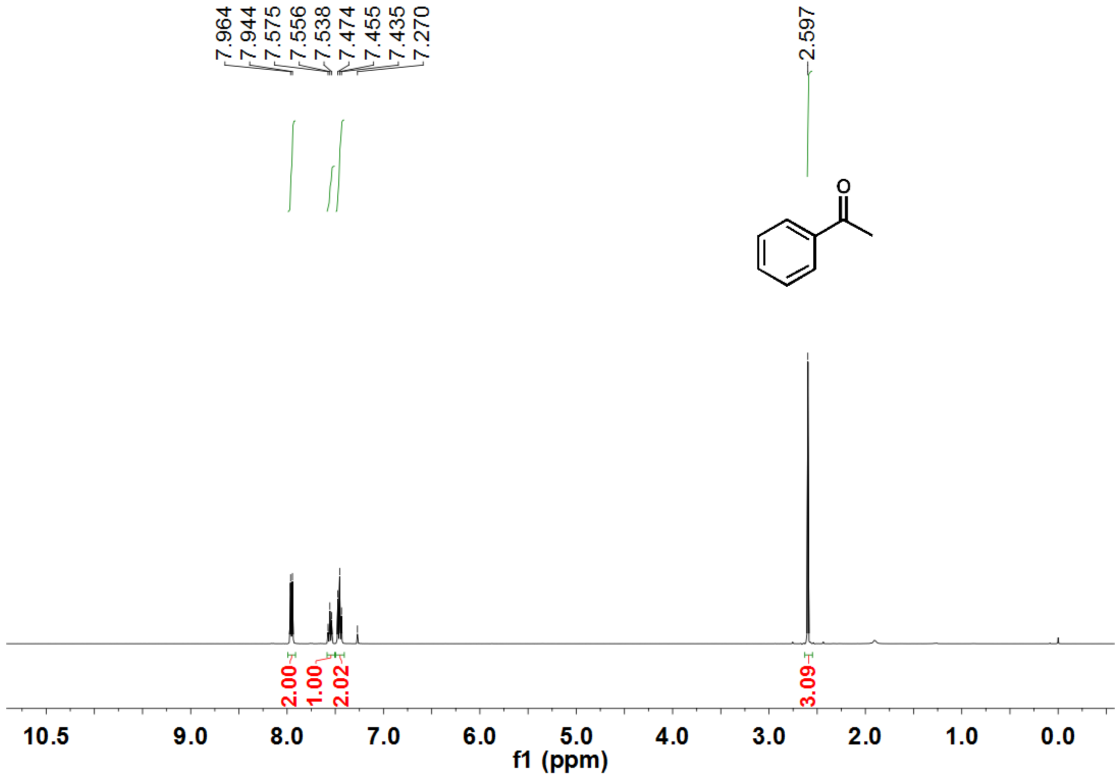
4-nitrobenzaldehyde (2s)

^{1}H NMR (400 MHz, $CDCl_3$) δ=10.17 (s, 1H), 8.40 (d, *J* = 8.6 Hz, 2H), 8.08 (d, *J* = 8.6 Hz, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ=190.24, 146.87, 140.05, 130.47, 124.31. GC-MS (EI): found: 151(M^+), calcd for $C_7H_5NO_3$ (M^+): 151.1.

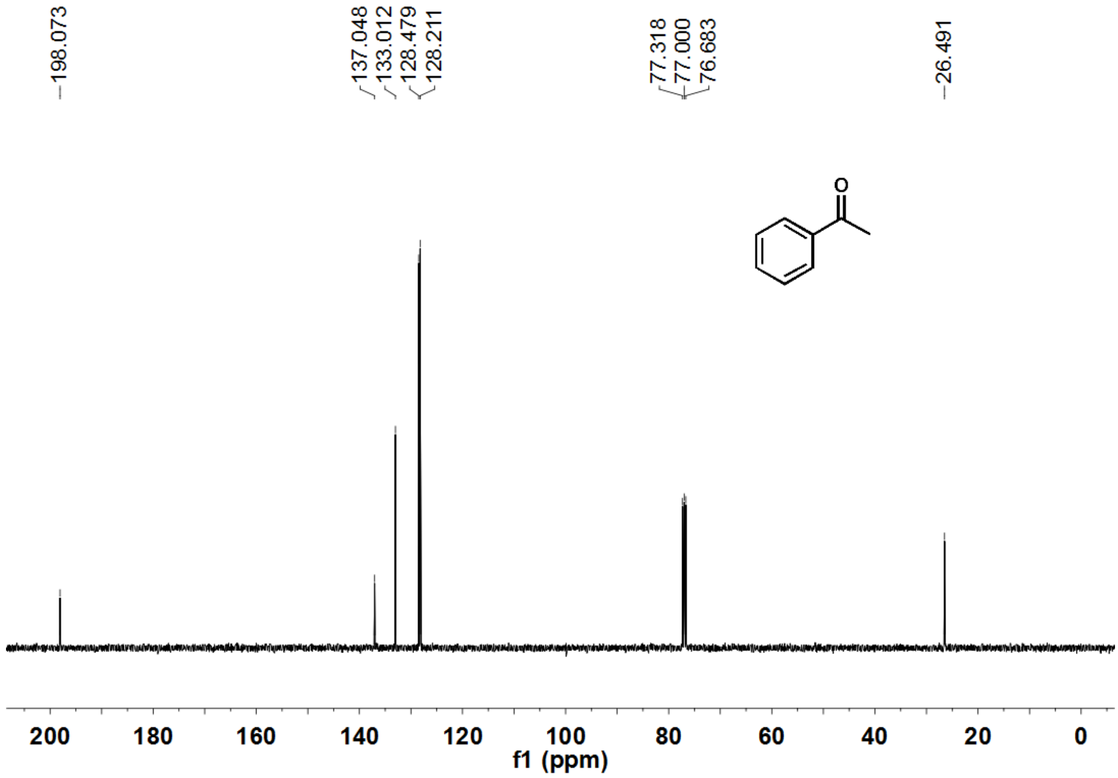


nicotinaldehyde (2t)

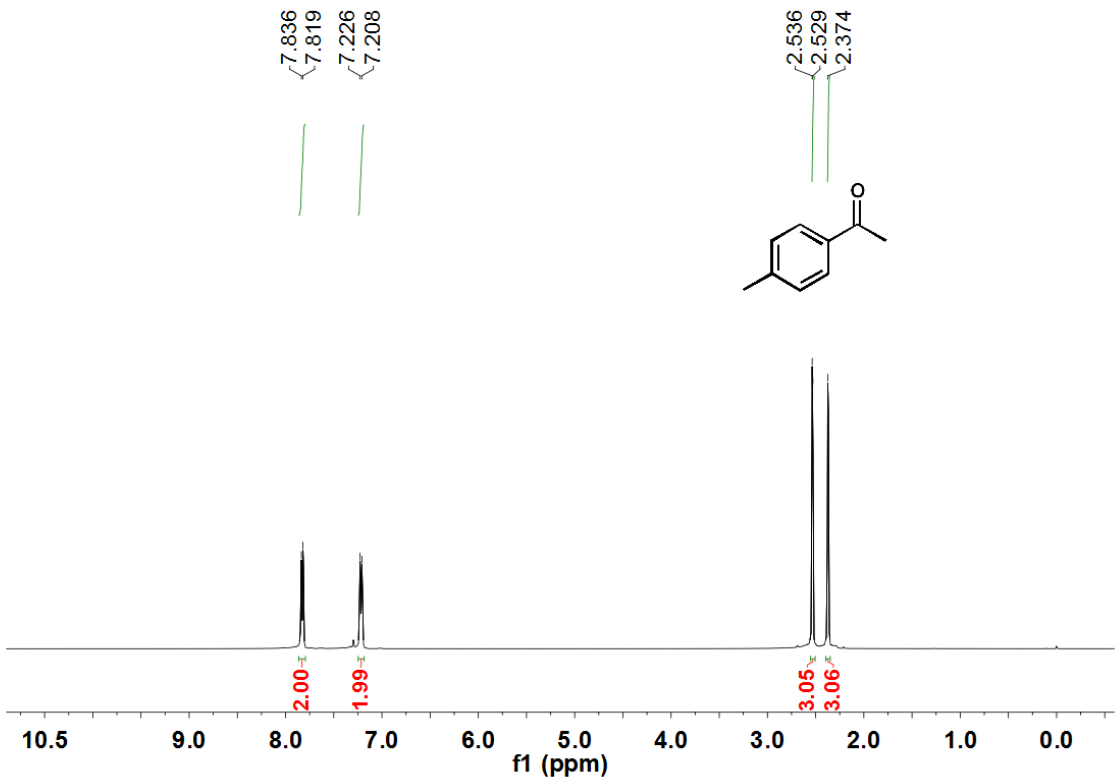
^{1}H NMR (400 MHz, $CDCl_3$) δ=10.02 (s, 1H), 8.99 (s, 1H), 8.74 (d, *J* = 7.8 Hz, 1H), 8.01 (d, *J* = 5.0 Hz, 1H), 7.44-7.40 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=192.16, 156.38, 150.25, 137.81, 134.99, 123.15. GC-MS (EI): found: 107(M^+), calcd for C_6H_5NO (M^+): 107.1.

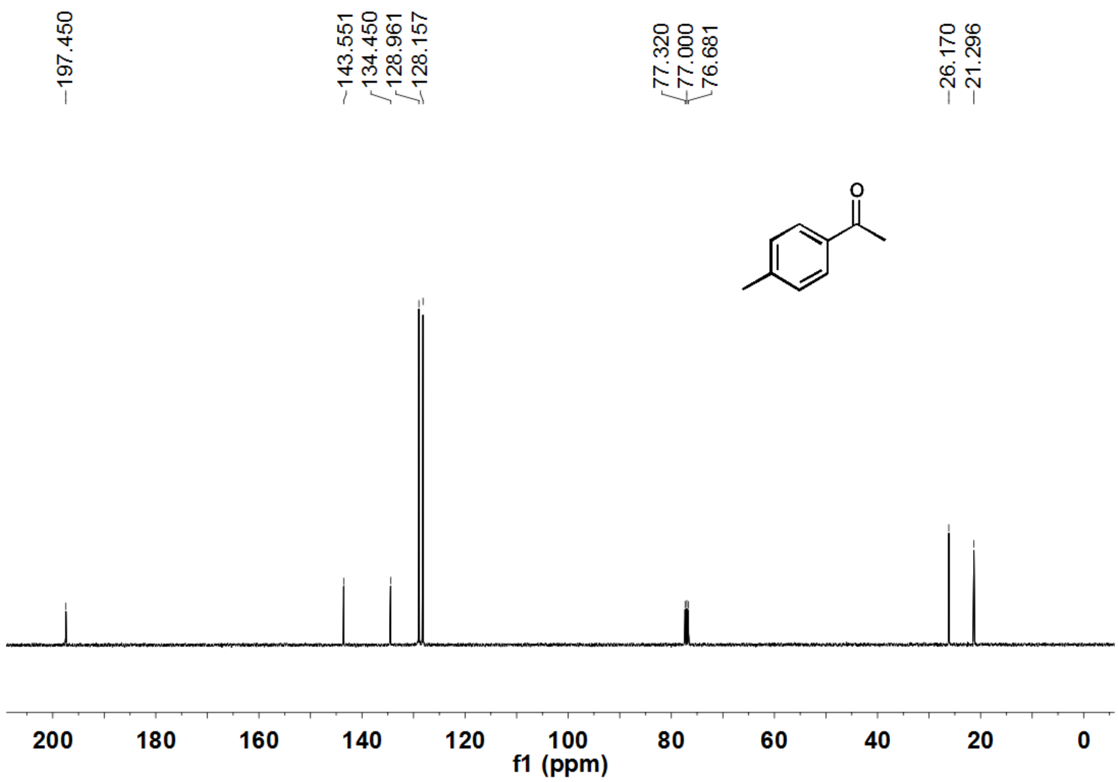


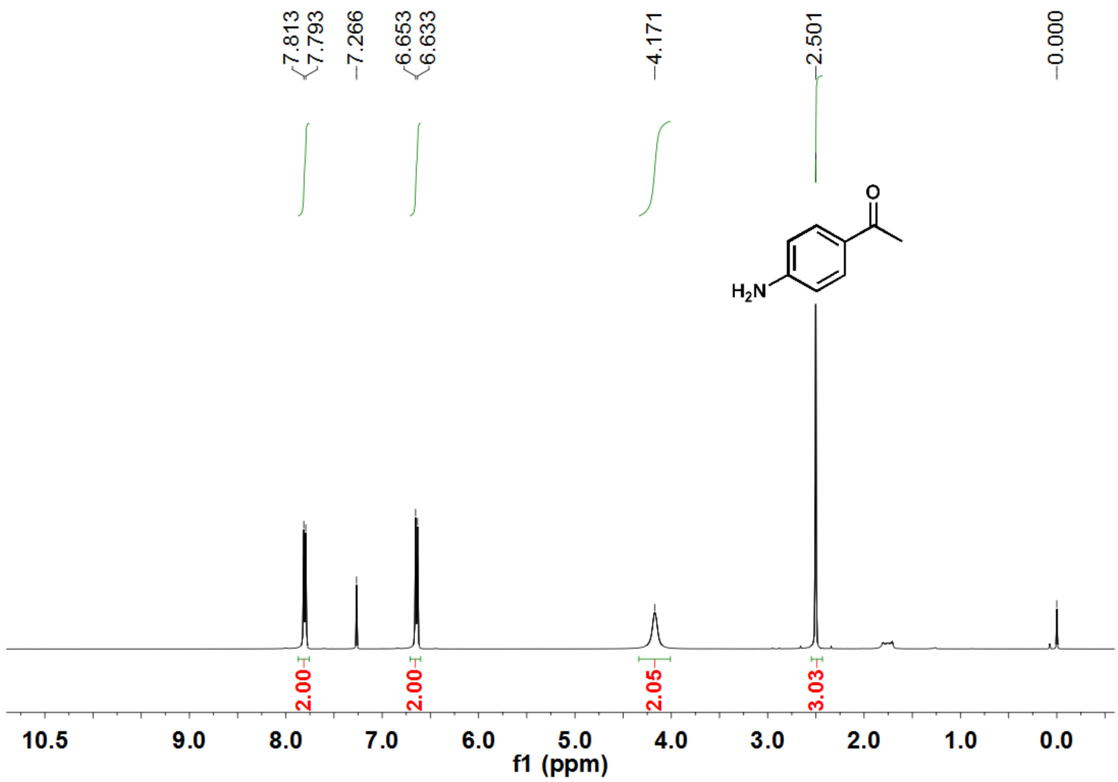
7.964
7.944
7.575
7.556
7.538
7.474
7.455
7.435
7.270
2.597
O
2.00
1.00
2.02
3.09
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)



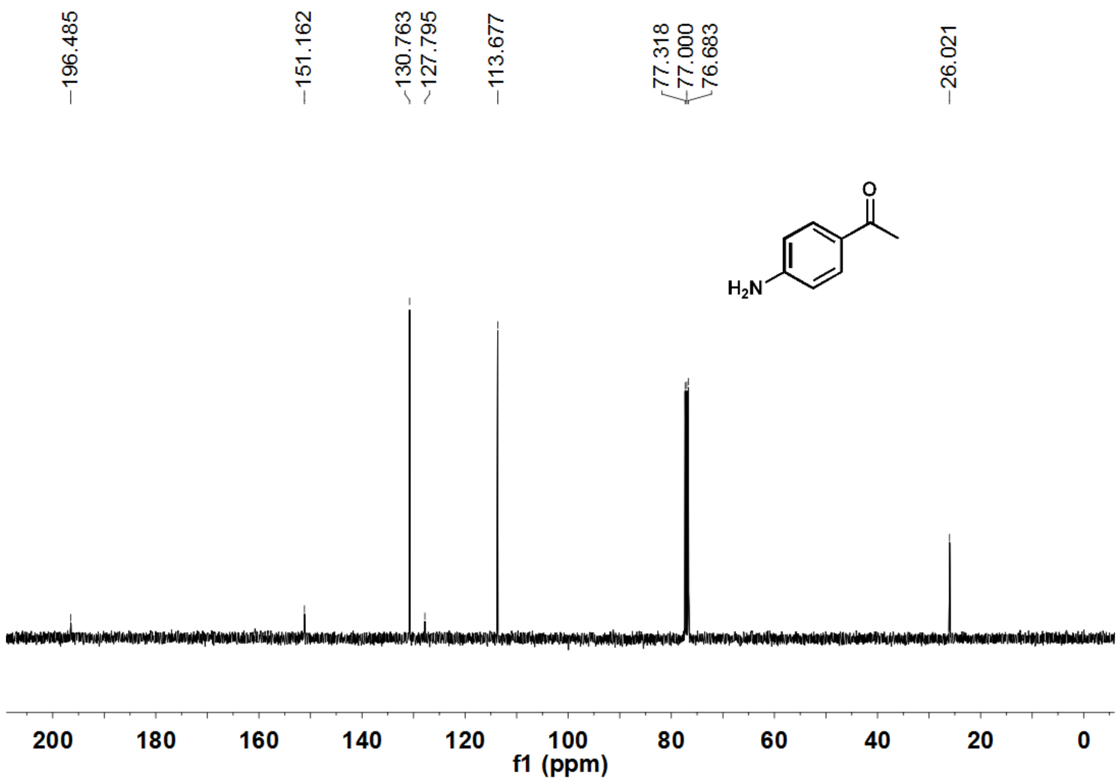
198.073
137.048
133.012
128.479
128.211
77.318
77.000
76.683
26.491
O
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.836
7.819
7.226
7.208
2.536
2.529
2.374
O
2.00
1.99
3.05
3.06
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

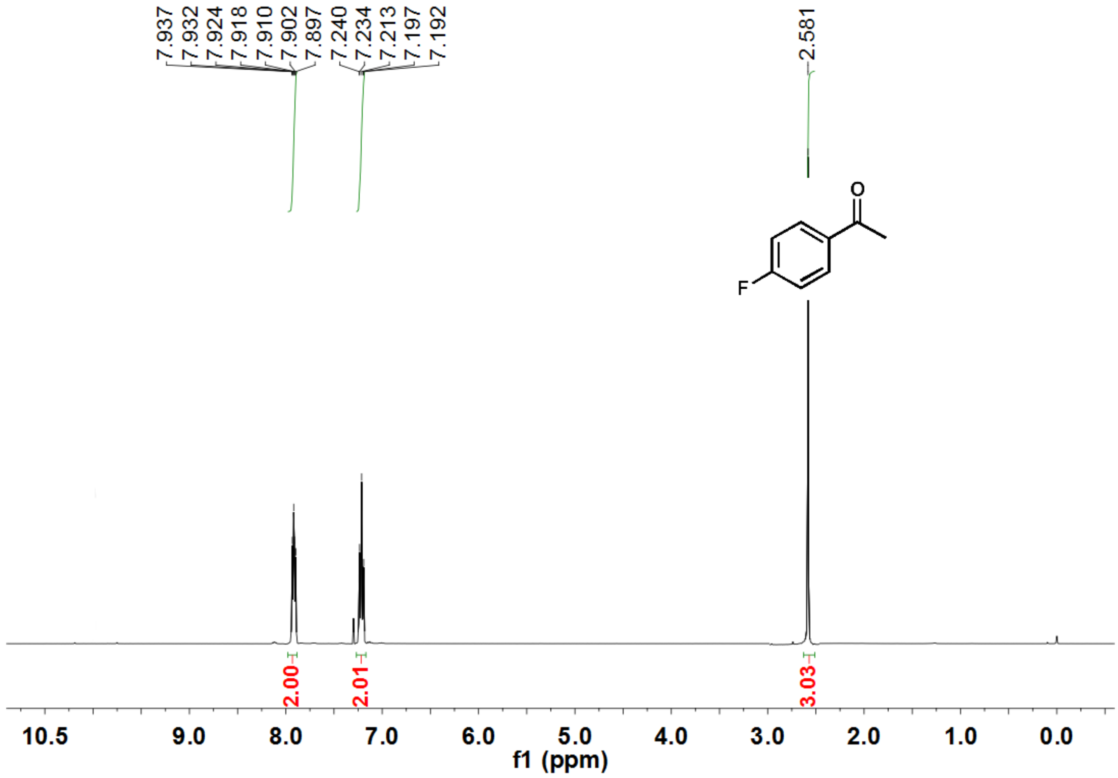

197.450
143.551
134.450
128.961
128.157
77.320
77.000
76.681
26.170
21.296
O
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

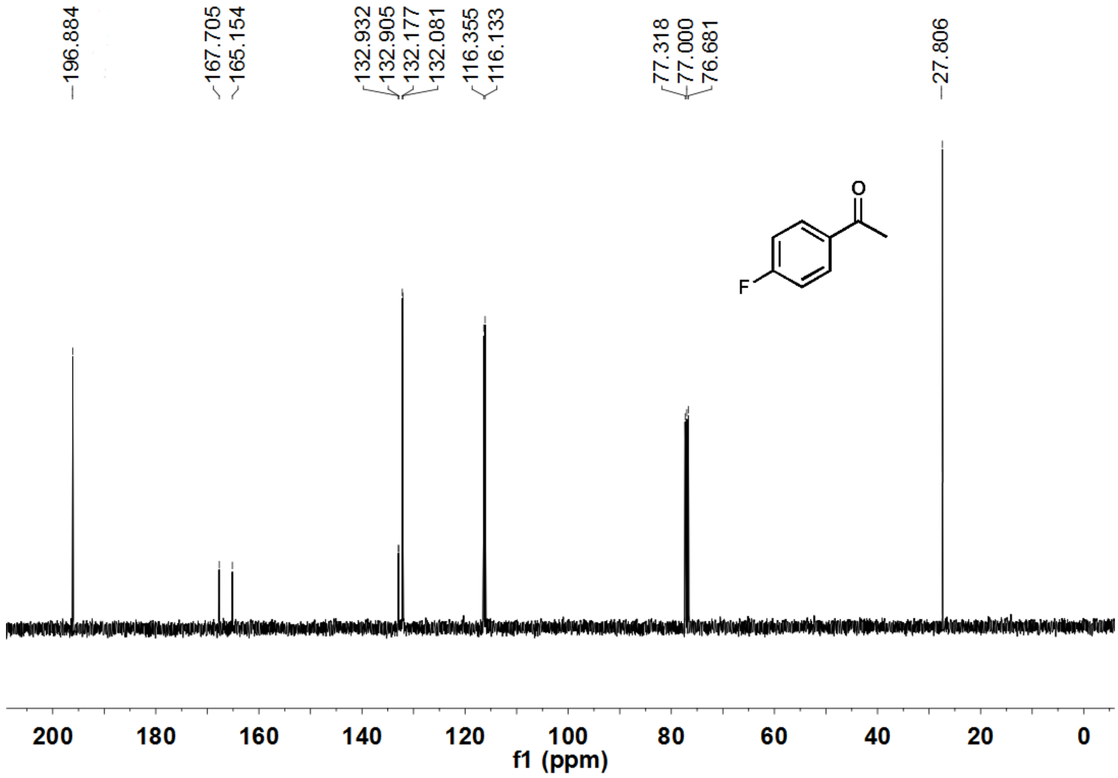


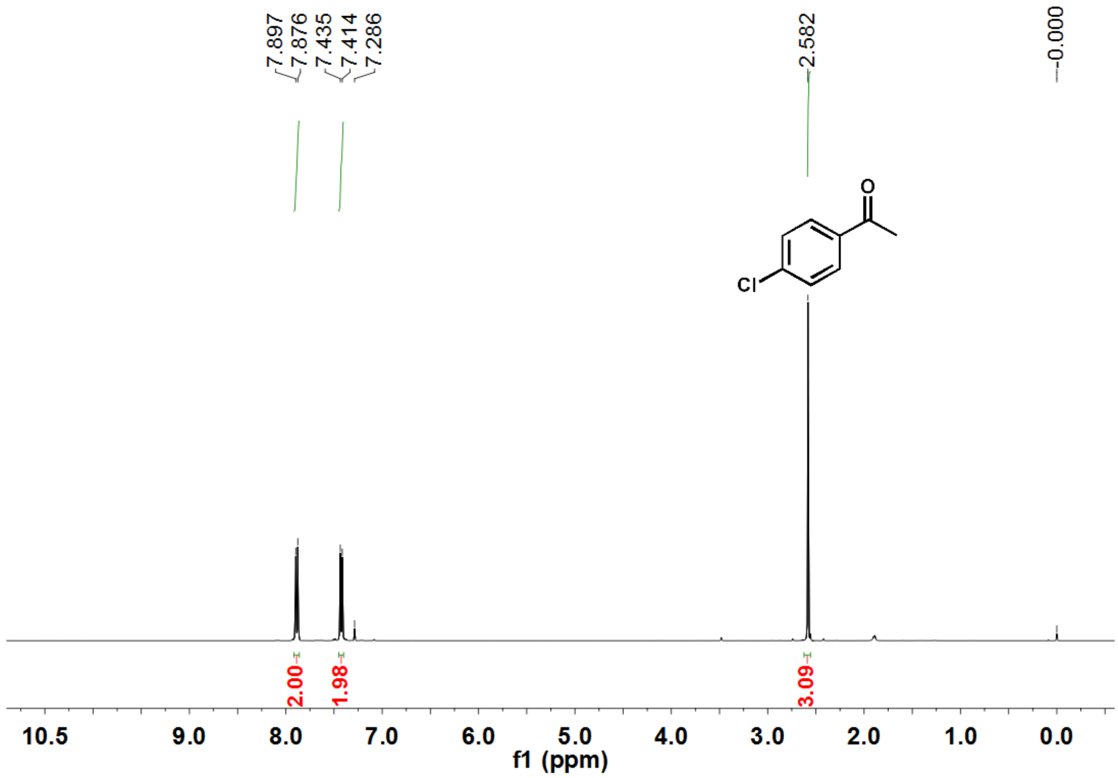
7.813
7.793
7.266
6.653
6.633
4.171
2.501
0.000
O
H2N
2.00
2.00
2.05
3.03
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

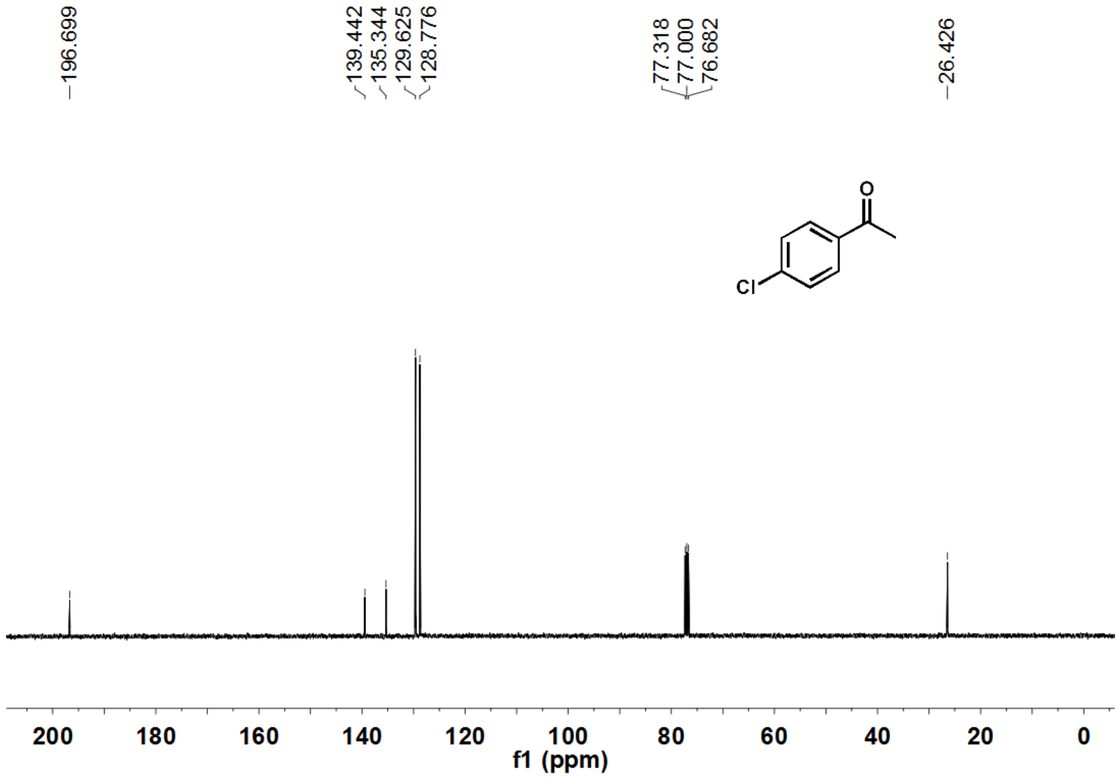


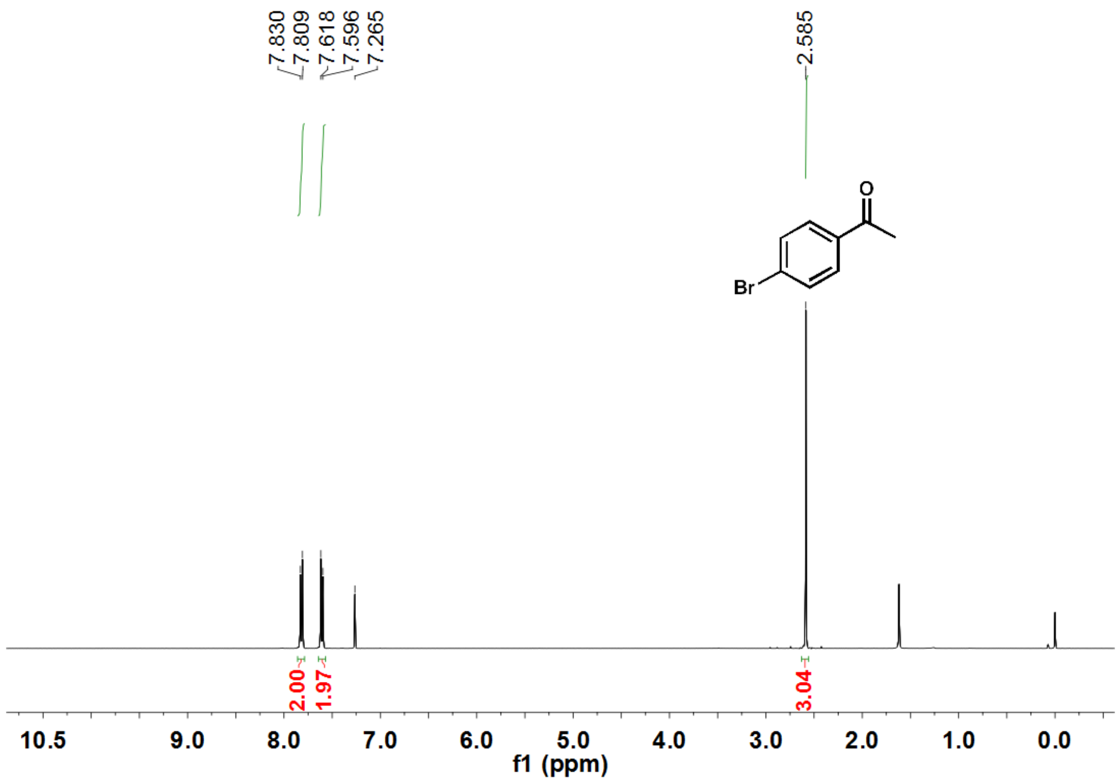
196.485
151.162
130.763
127.795
113.677
77.318
77.000
76.683
26.021
O
H2N
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

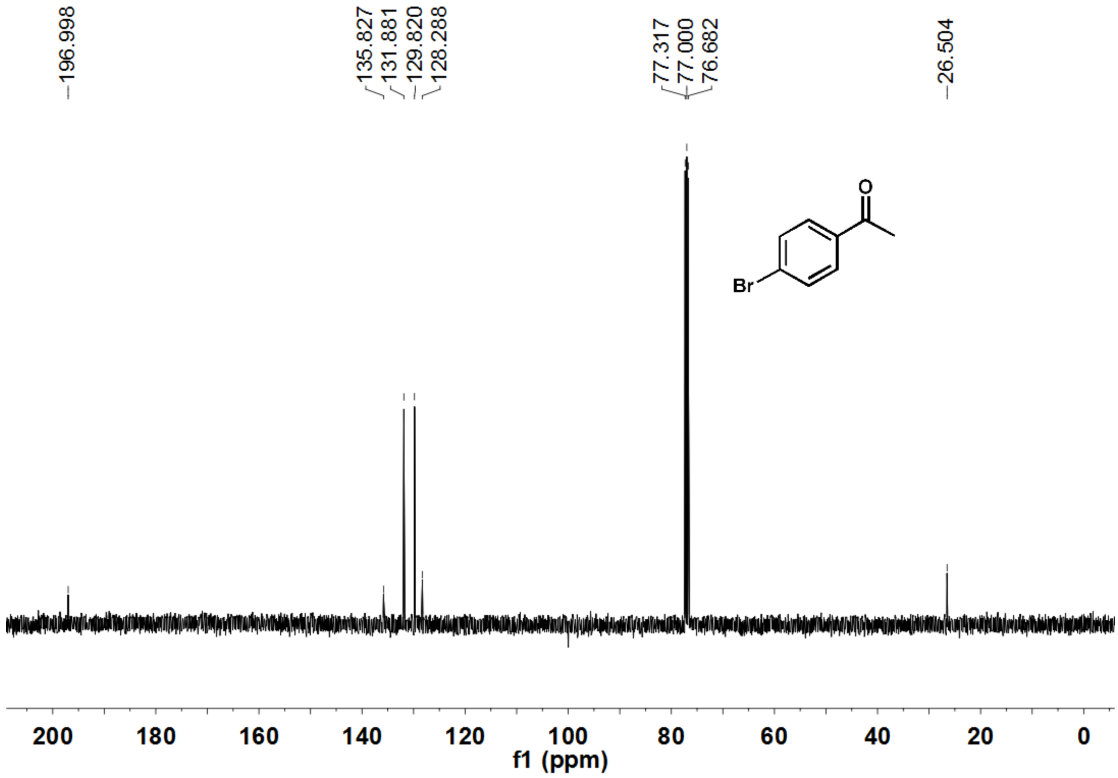

7.937
7.932
7.924
7.918
7.910
7.902
7.897
7.240
7.234
7.213
7.197
7.192
2.581
O
F
2.00
2.01
3.03
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

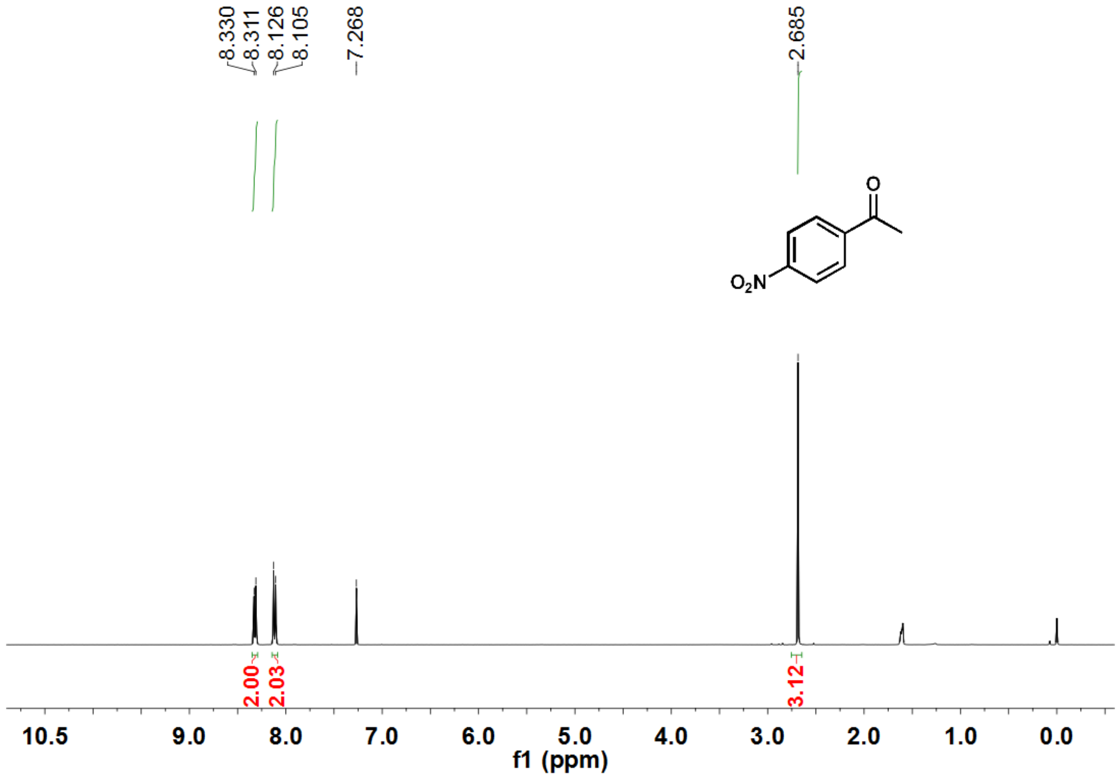

196.884
167.705
165.154
132.932
132.905
132.177
132.081
116.355
116.133
77.318
77.000
76.681
27.806
O
F
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

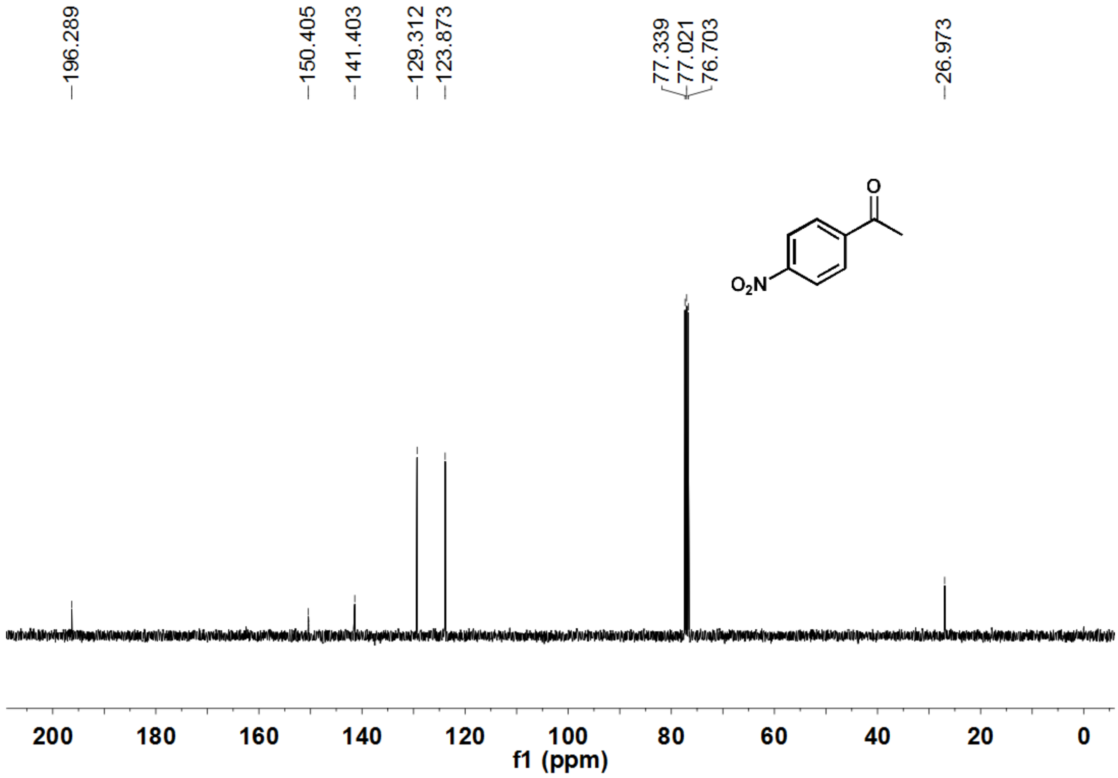

7.897
7.876
7.435
7.414
7.286
2.582
-0.000
O
Cl
2.00
1.98
3.09
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

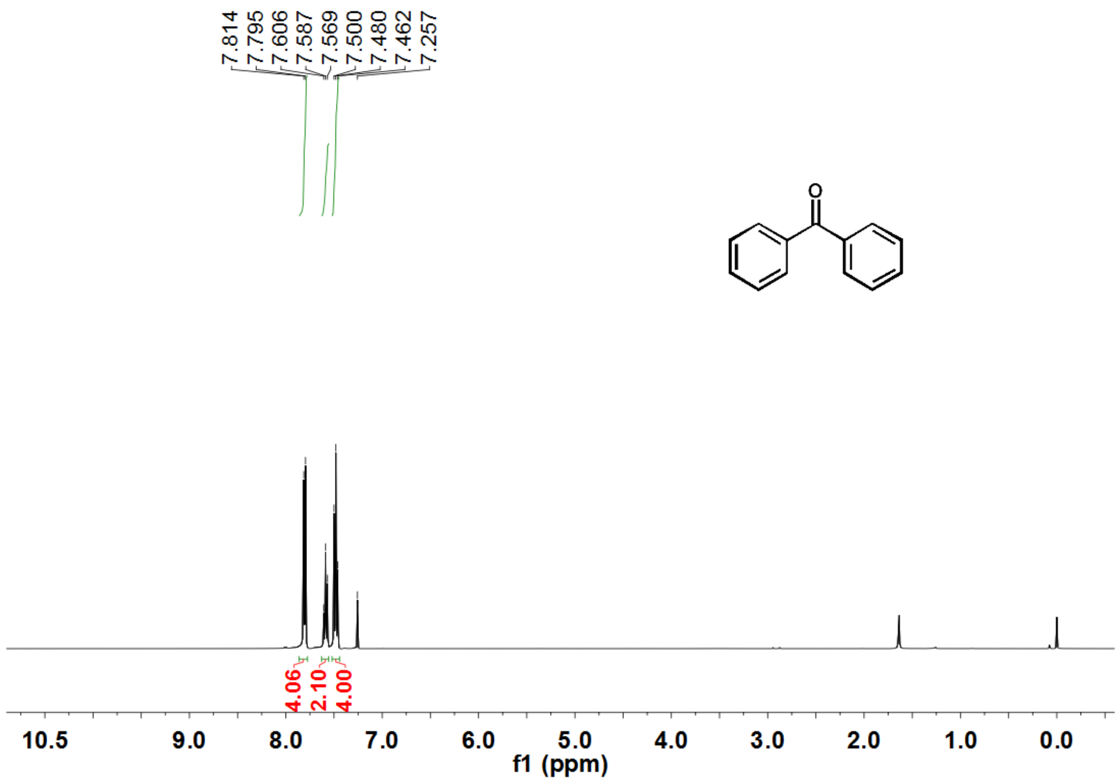

196.699
139.442
135.344
129.625
128.776
77.318
77.000
76.682
26.426
O
Cl
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

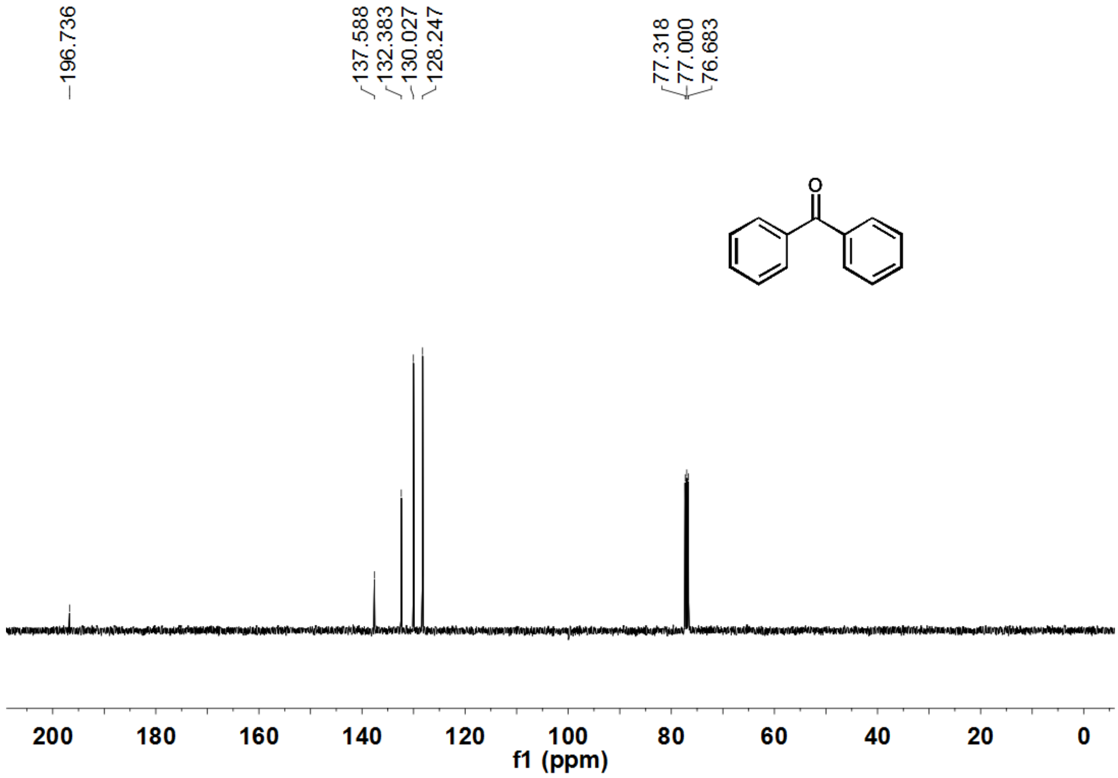

7.830
7.809
7.618
7.596
7.265
2.585
O
Br
2.00
1.97
3.04
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

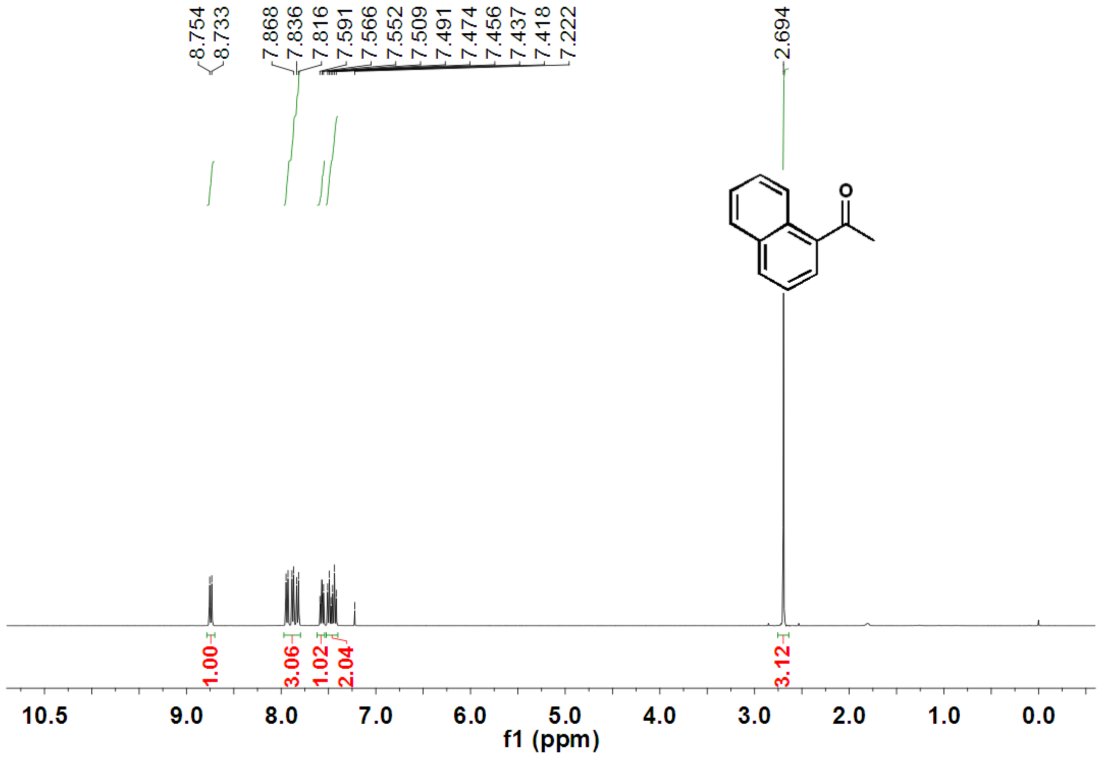

196.998
135.827
131.881
129.820
128.288
77.317
77.000
76.682
26.504
O
Br
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


8.330
8.311
8.126
8.105
7.268
2.685
O
O2N
2.00
2.03
3.12
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

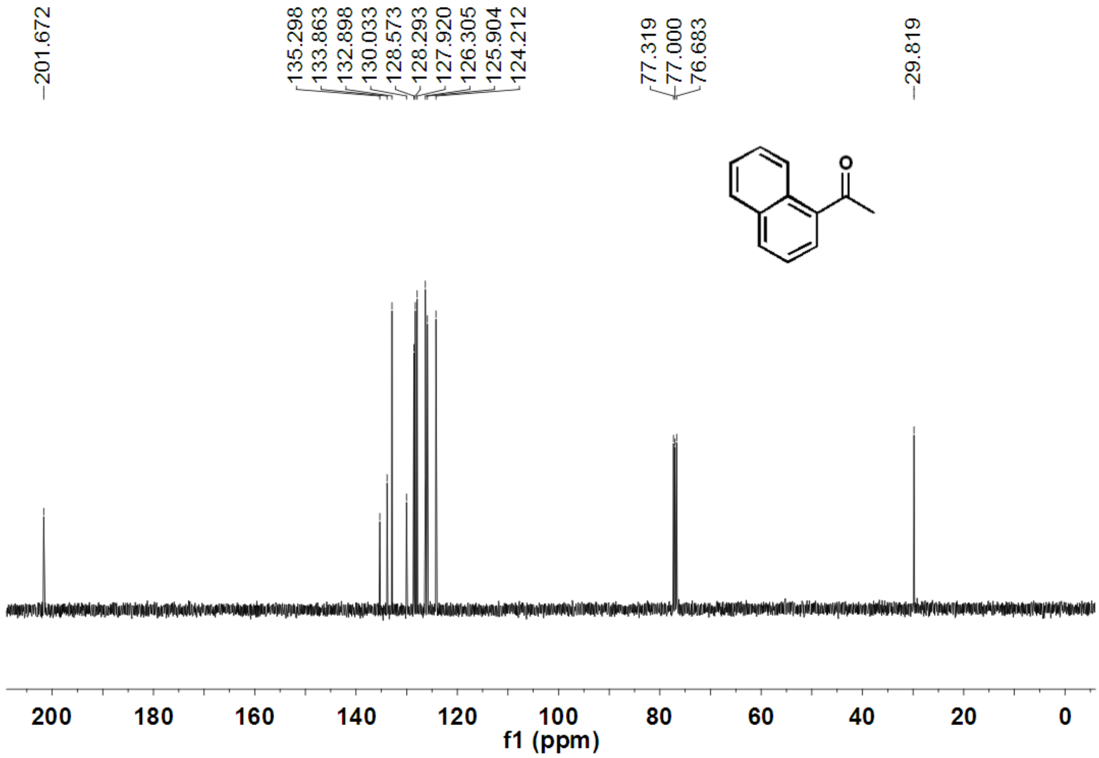

196.289
150.405
141.403
129.312
123.873
77.339
77.021
76.703
26.973
O
O2N
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.814
7.795
7.606
7.587
7.569
7.500
7.480
7.462
7.257
O
4.06
2.10
4.00
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

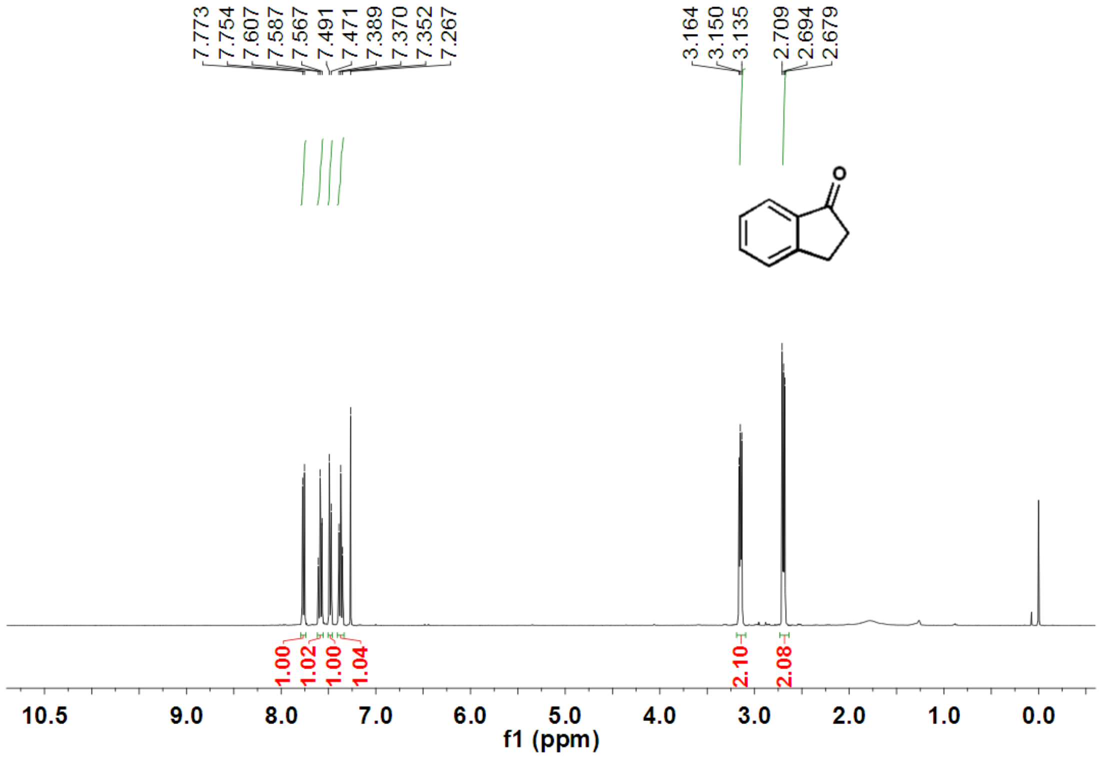

196.736
137.588
132.383
130.027
128.247
77.318
77.000
76.683
O
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

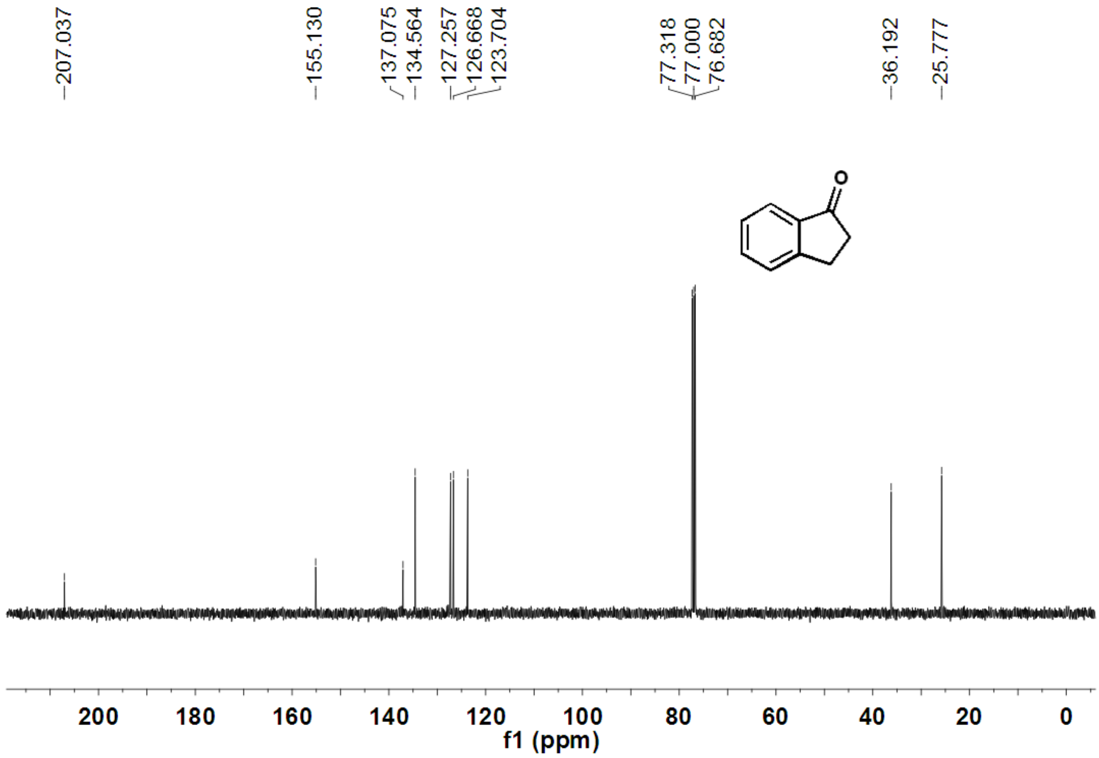


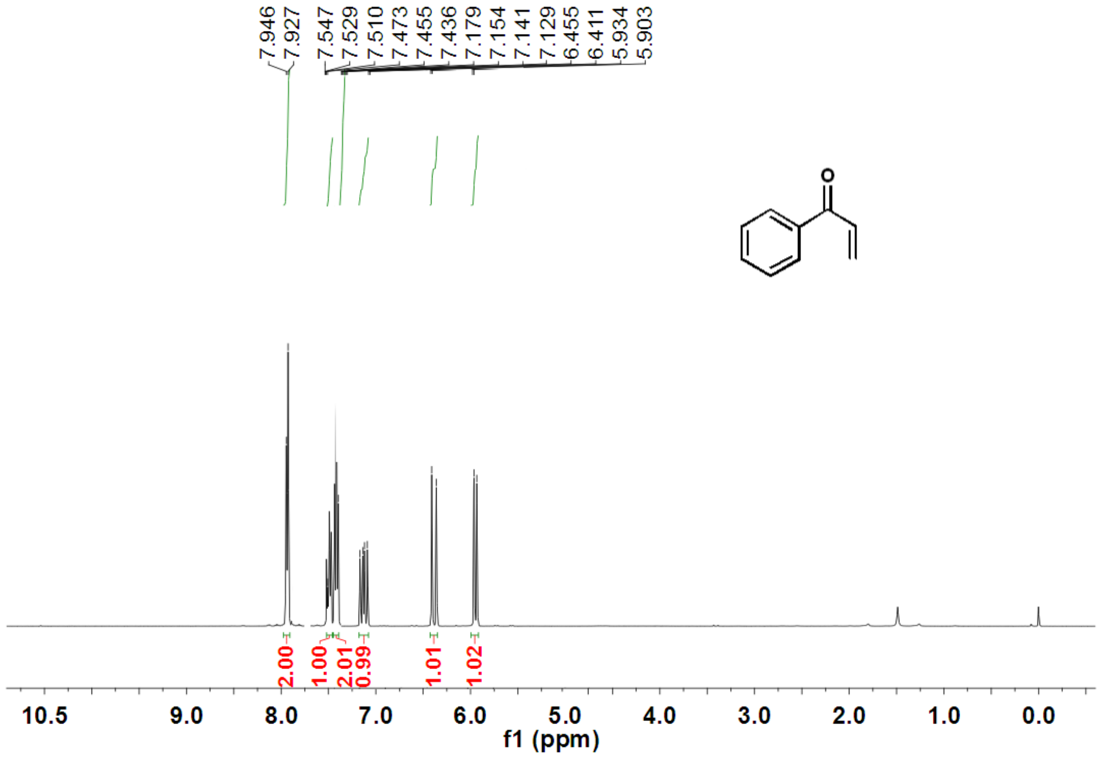
8.754
8.733
7.868
7.836
7.816
7.591
7.566
7.552
7.509
7.491
7.474
7.456
7.437
7.418
7.222
2.694
O
1.00
3.06
1.02
2.04
3.12
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

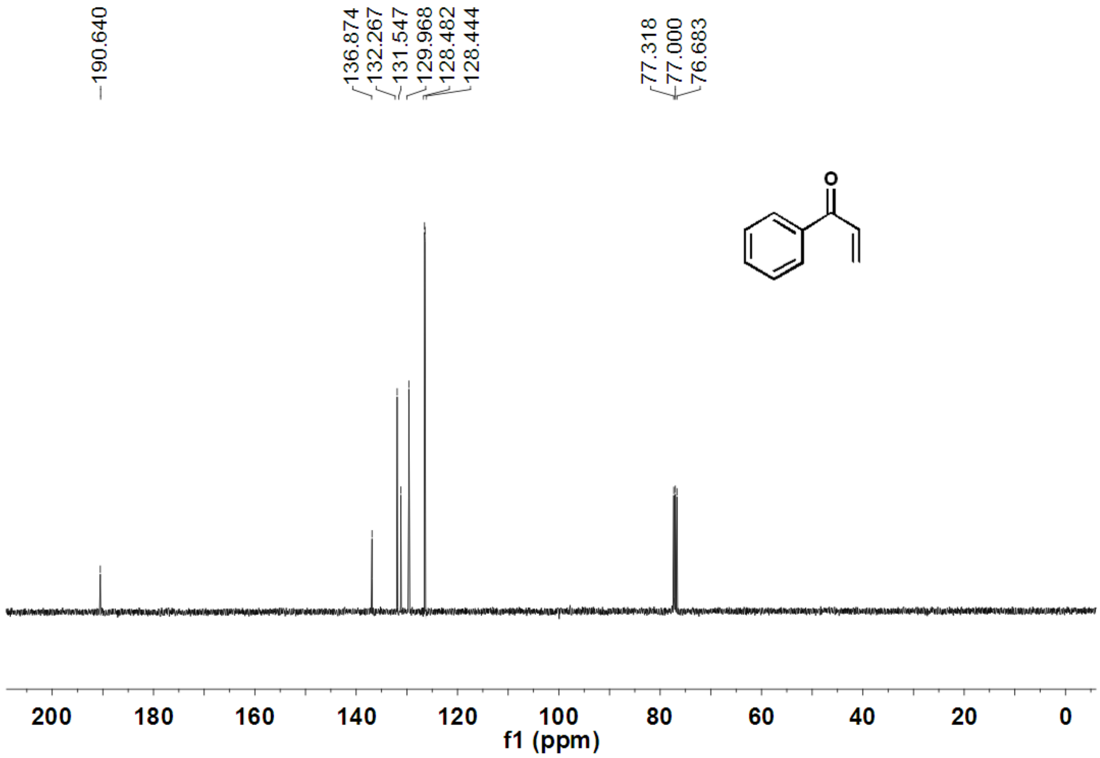


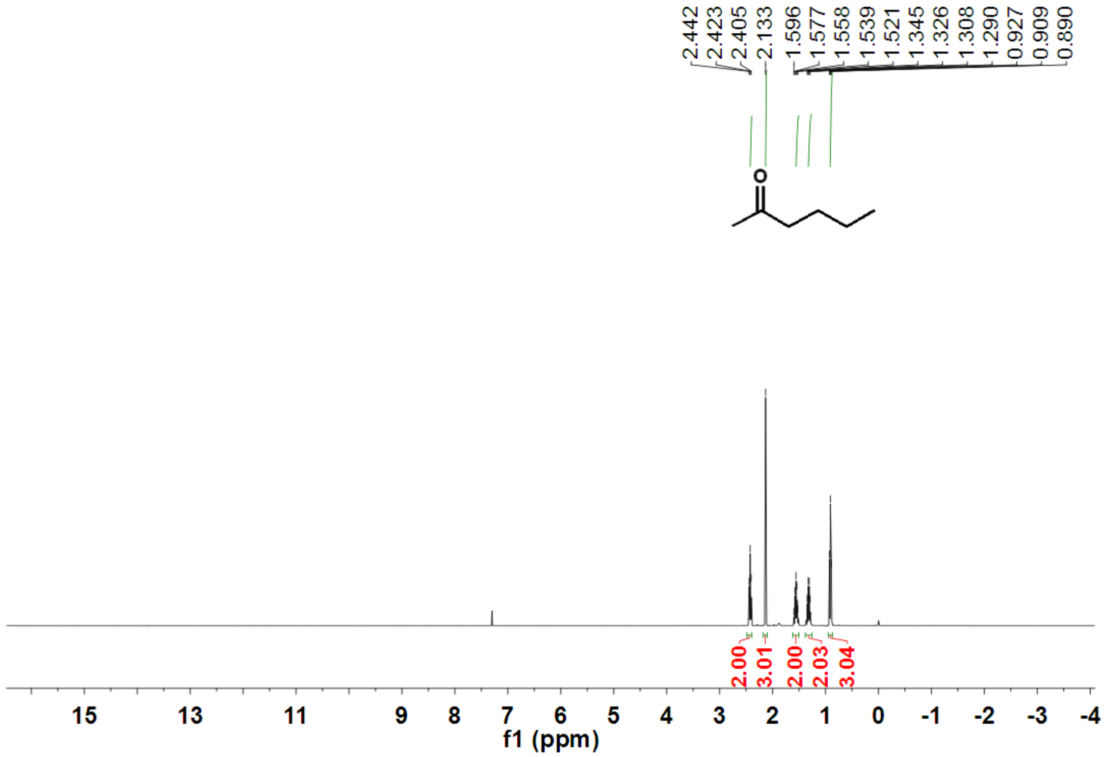
201.672
135.298
133.863
132.898
130.033
128.573
128.293
127.920
126.305
125.904
124.212
77.319
77.000
76.683
29.819
O
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

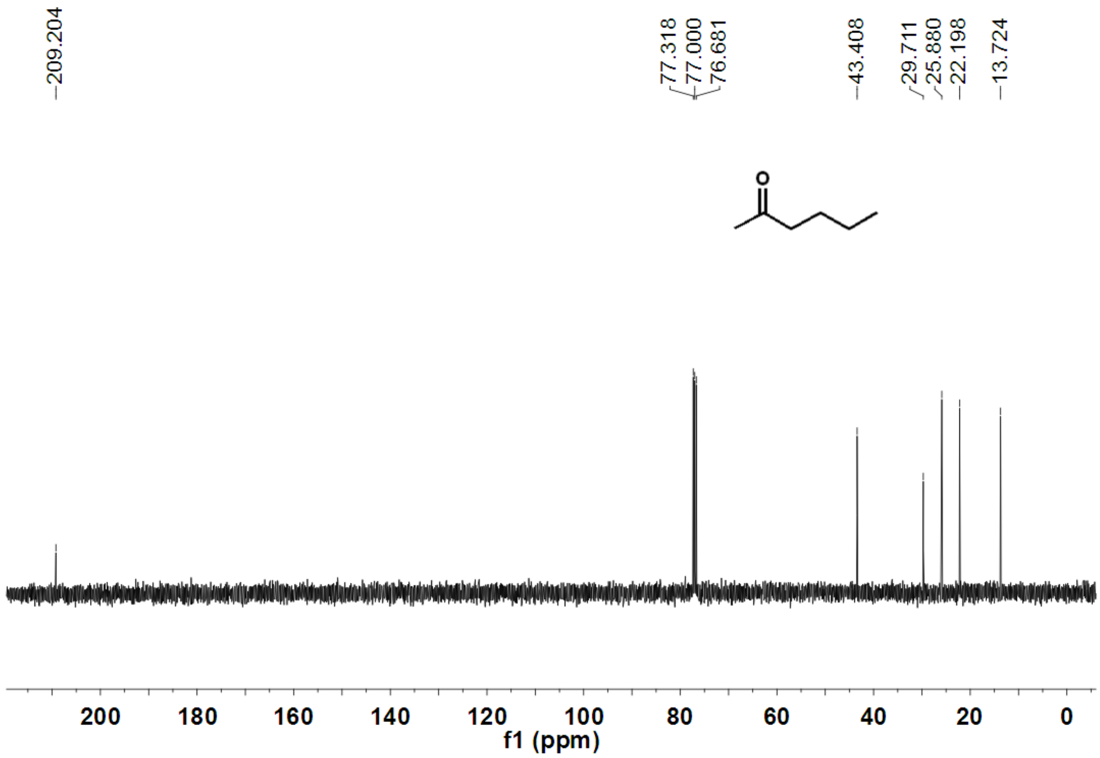

7.773
7.754
7.607
7.587
7.567
7.491
7.471
7.389
7.370
7.352
7.267
3.164
3.150
3.135
2.709
2.694
2.679
O
1.00
1.02
1.00
1.04
2.10
2.08
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

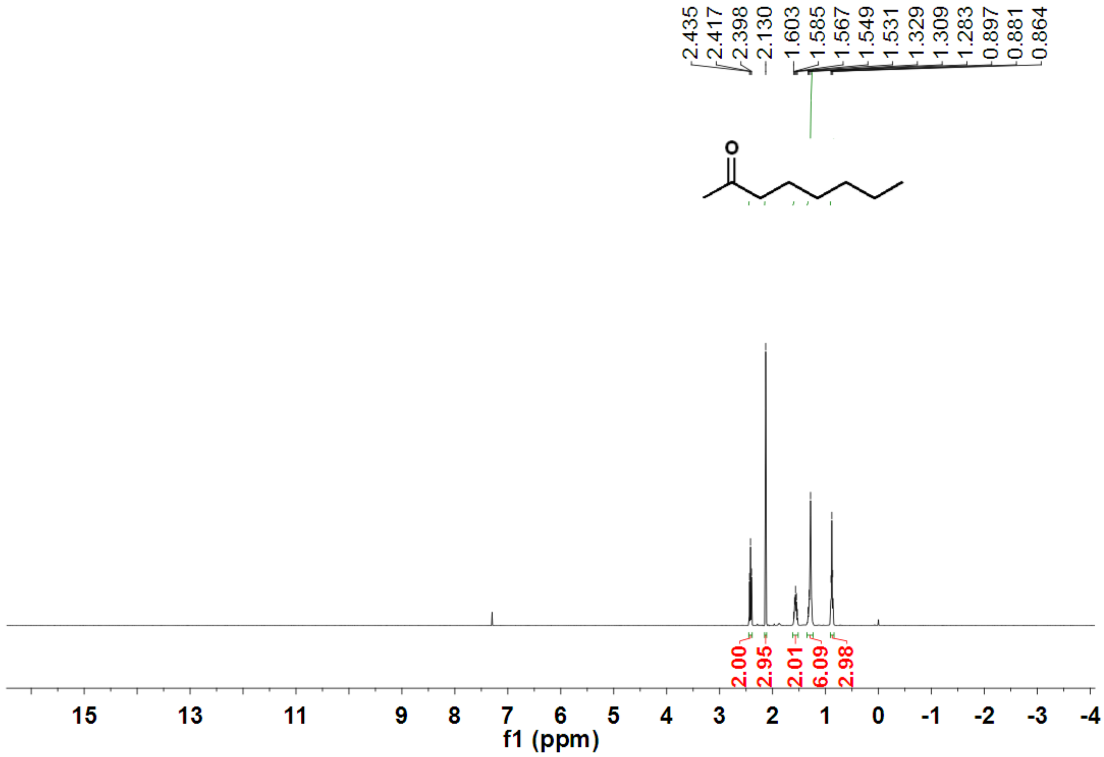

207.037
155.130
137.075
134.564
127.257
126.668
123.704
77.318
77.000
76.682
36.192
25.777
O
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

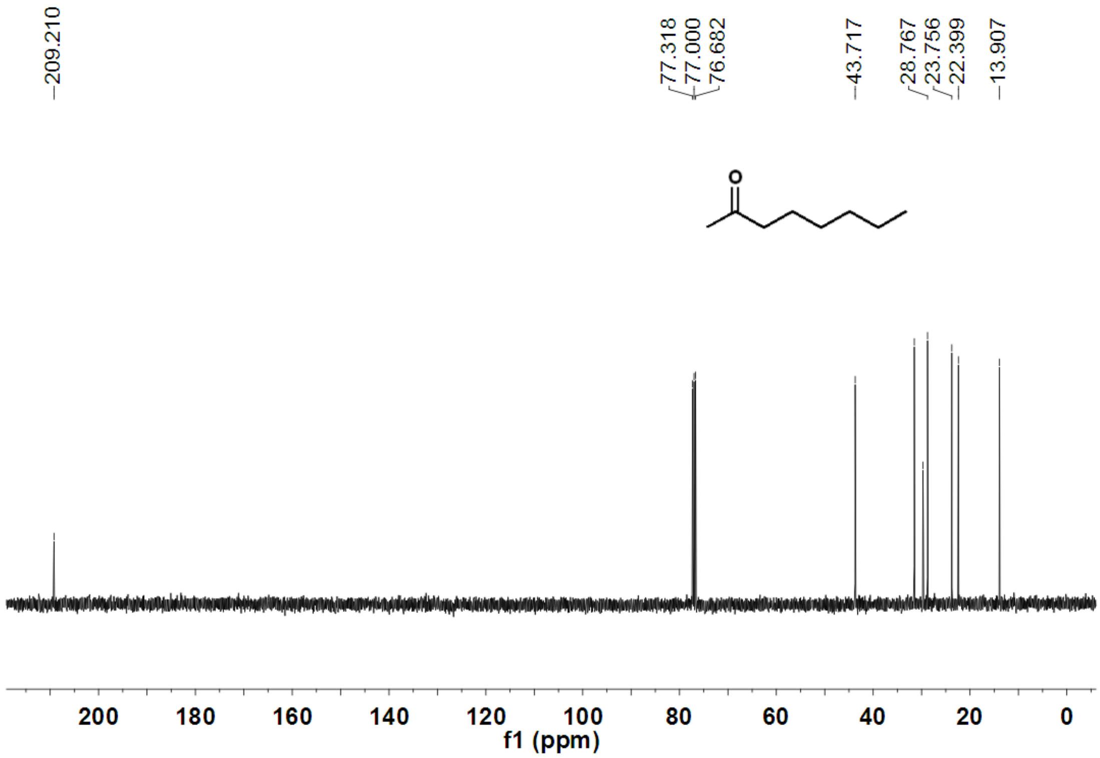

7.946
7.927
7.547
7.529
7.510
7.473
7.455
7.436
7.179
7.154
7.141
7.129
6.455
6.411
5.934
5.903
O
2.00
1.00
2.01
0.99
1.01
1.02
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

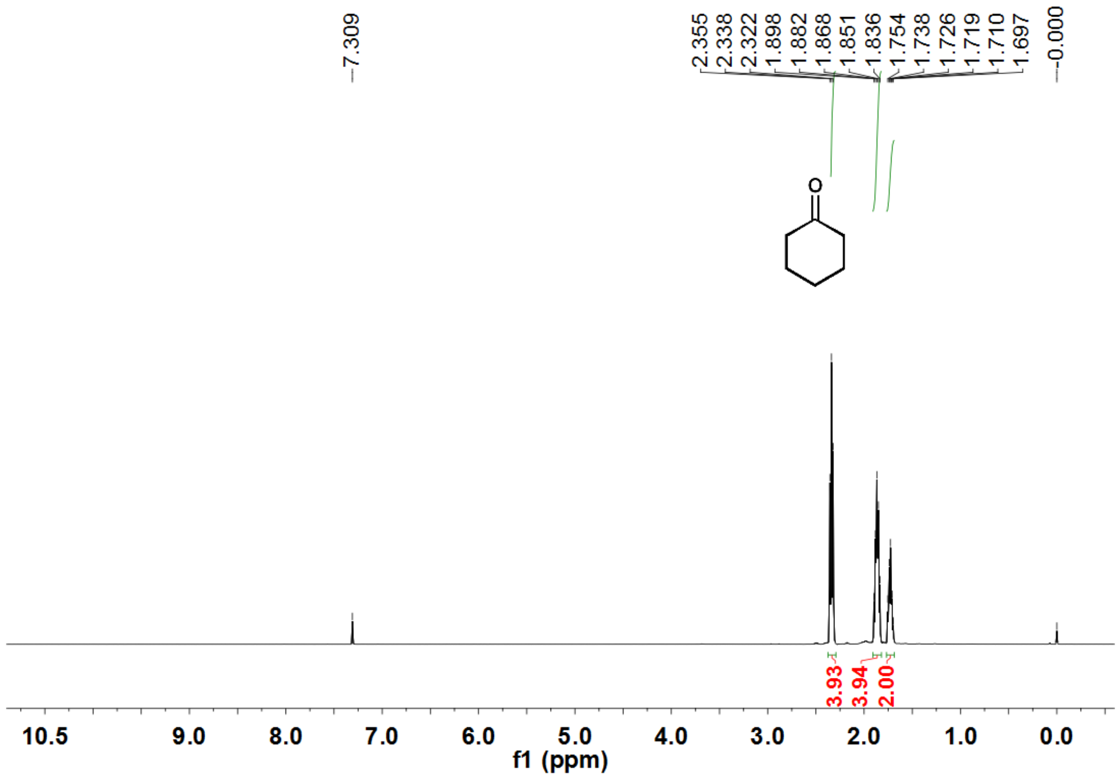

190.640
136.874
132.267
131.547
129.968
128.482
128.444
77.318
77.000
76.683
O
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


2.442
2.423
2.405
2.133
1.596
1.577
1.558
1.539
1.521
1.345
1.326
1.308
1.290
0.927
0.909
0.890
2.00
3.01
2.00
2.03
3.04
f1 (ppm)

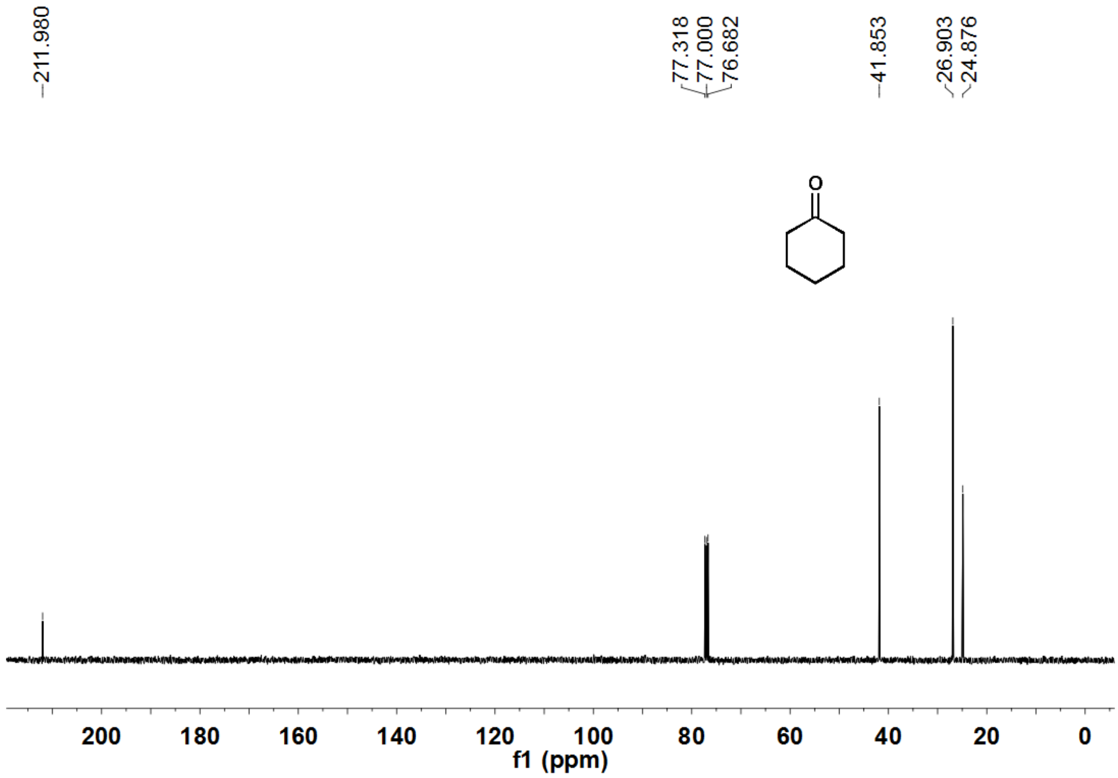

209.204
77.318
77.000
76.681
43.408
29.711
25.880
22.198
13.724
f1 (ppm)


2.435
2.417
2.398
2.130
1.603
1.585
1.567
1.549
1.531
1.329
1.309
1.283
0.897
0.881
0.864
O
2.00
2.95
2.01
6.09
2.98
15 13 11 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

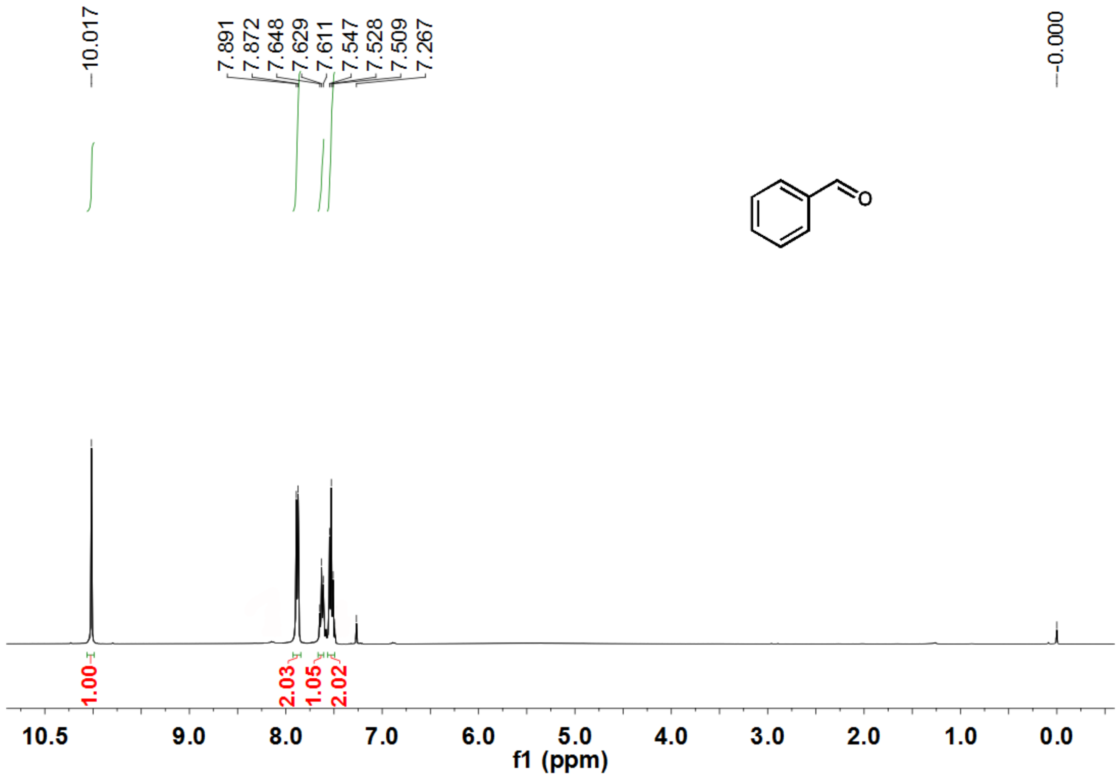

209.210
77.318
77.000
76.682
43.717
28.767
23.756
22.399
13.907
O
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)

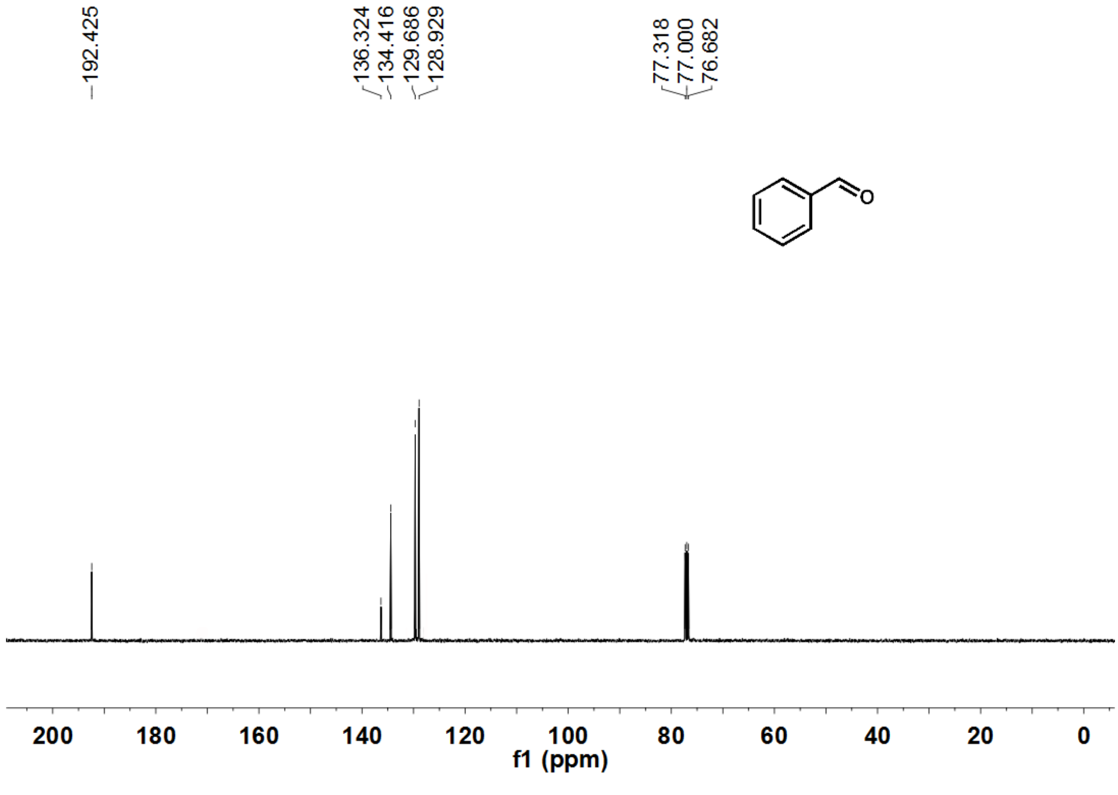


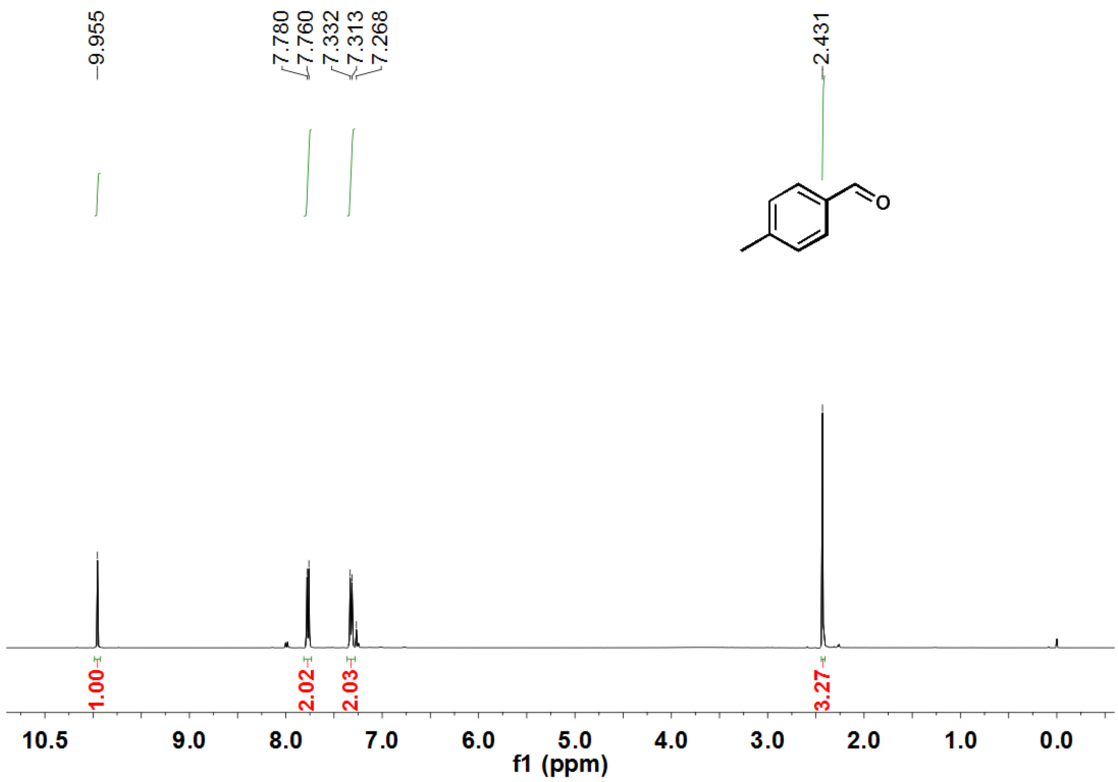
7.309
2.355
2.338
2.322
1.898
1.882
1.868
1.851
1.836
1.754
1.738
1.726
1.719
1.710
1.697
0.000
O
3.93
3.94
2.00
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

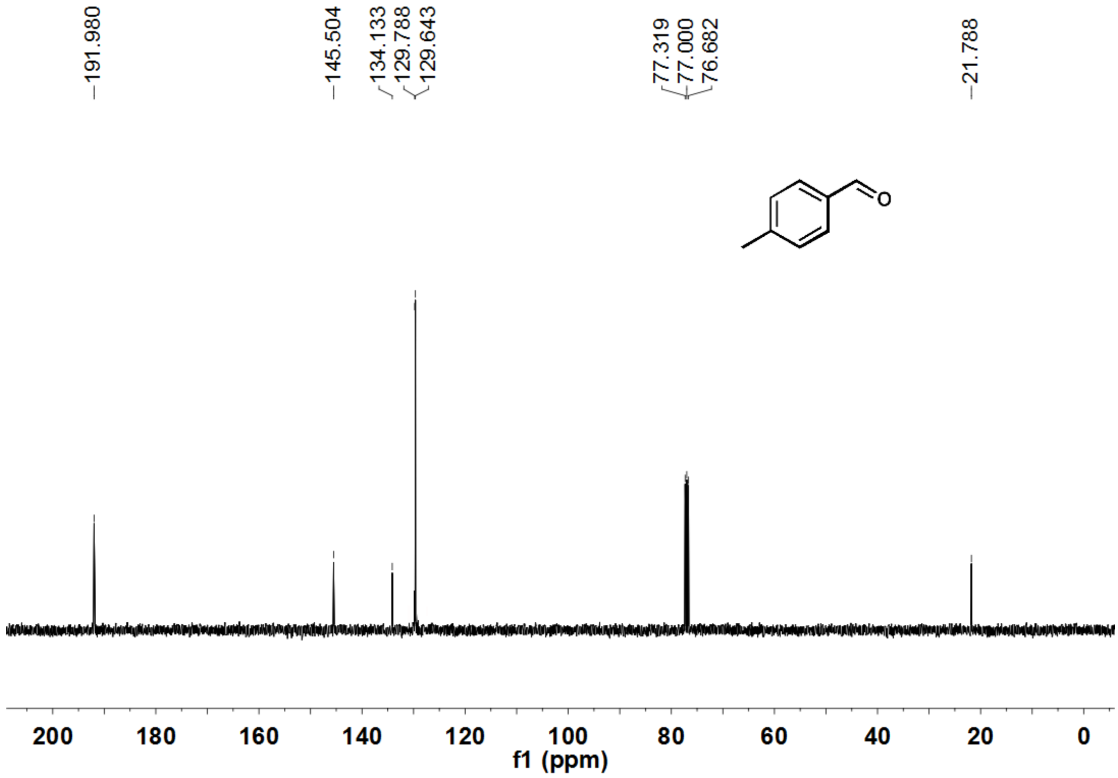


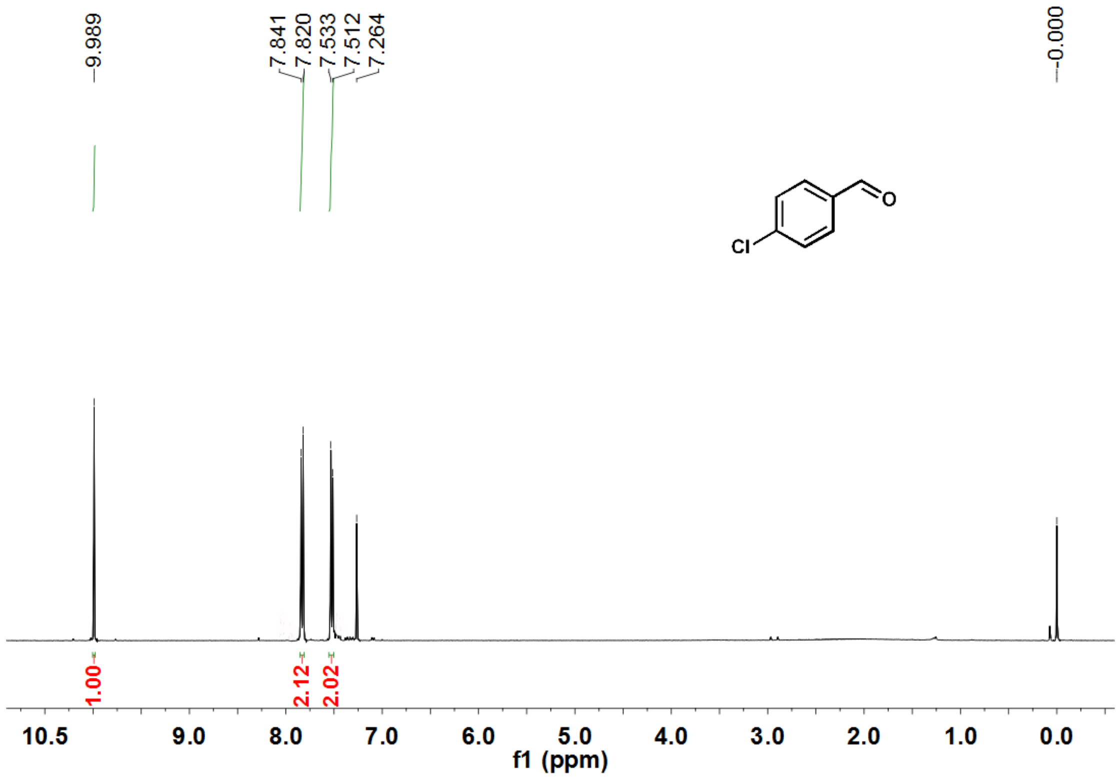
211.980
77.318
77.000
76.682
41.853
26.903
24.876
O
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

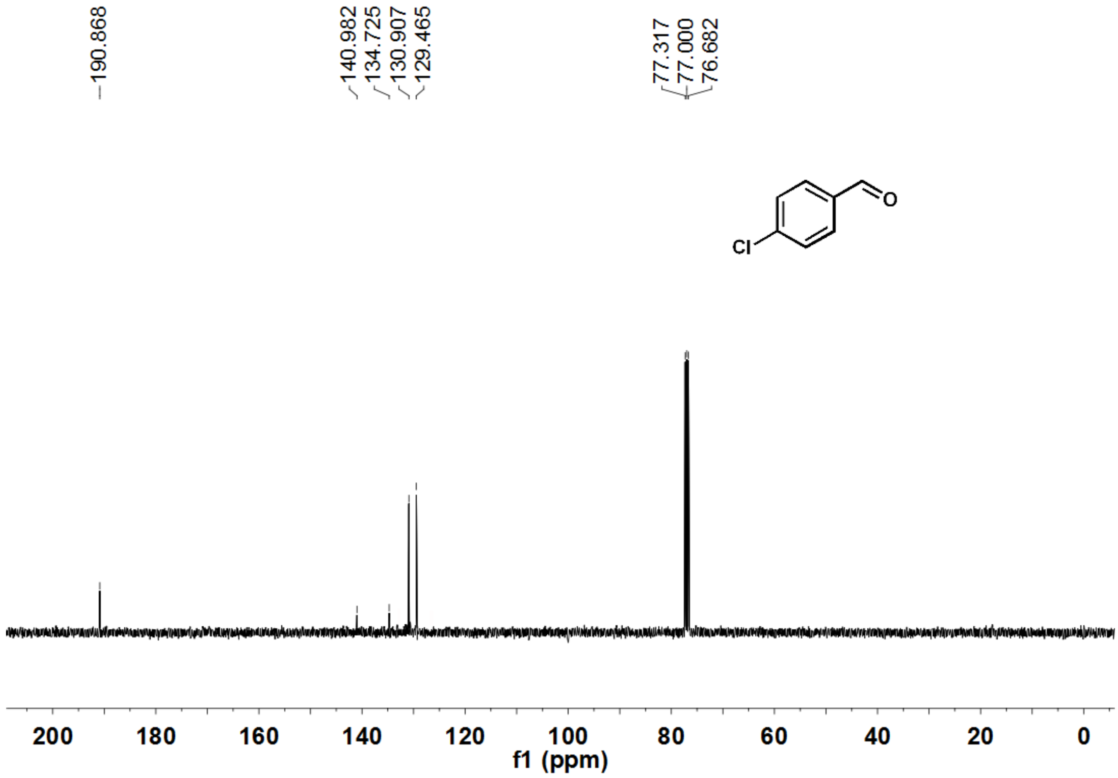

10.017
7.891
7.872
7.648
7.629
7.611
7.547
7.528
7.509
7.267
0.000
O
1.00
2.03
1.05
2.02
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

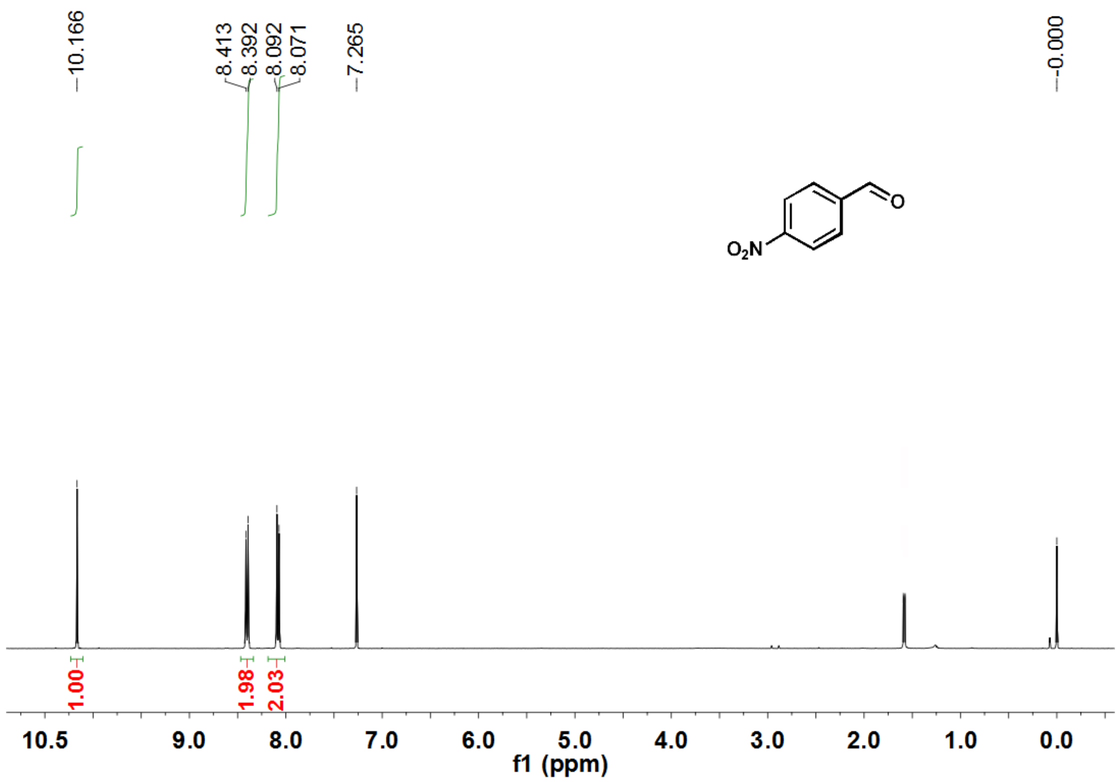

192.425
136.324
134.416
129.686
128.929
77.318
77.000
76.682
O
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

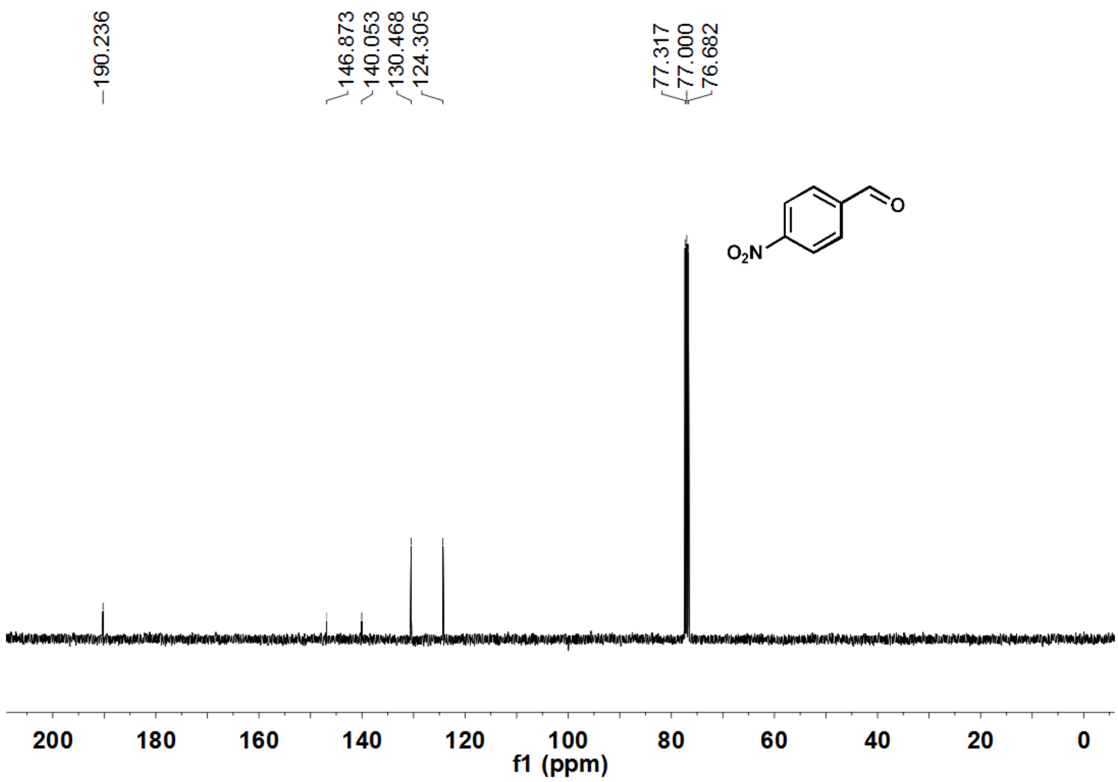

9.955
7.780
7.760
7.332
7.313
7.268
2.431
O
1.00
2.02
2.03
3.27
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

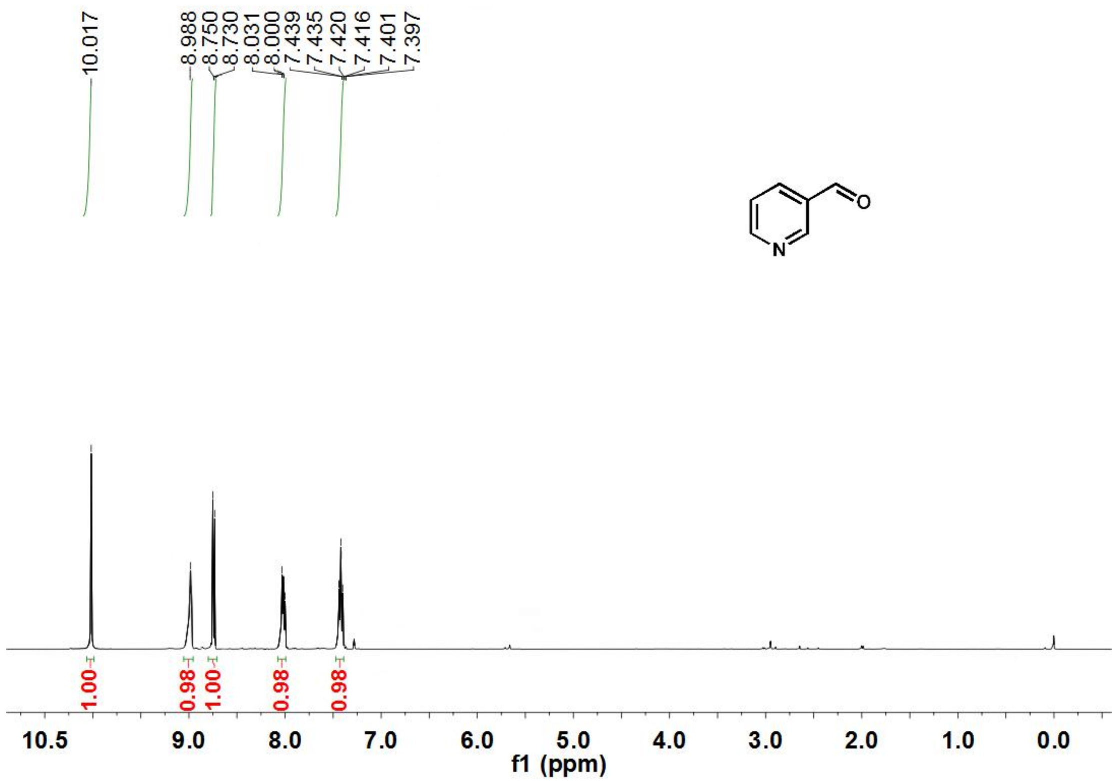

191.980
145.504
134.133
129.788
129.643
77.319
77.000
76.682
21.788
O
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

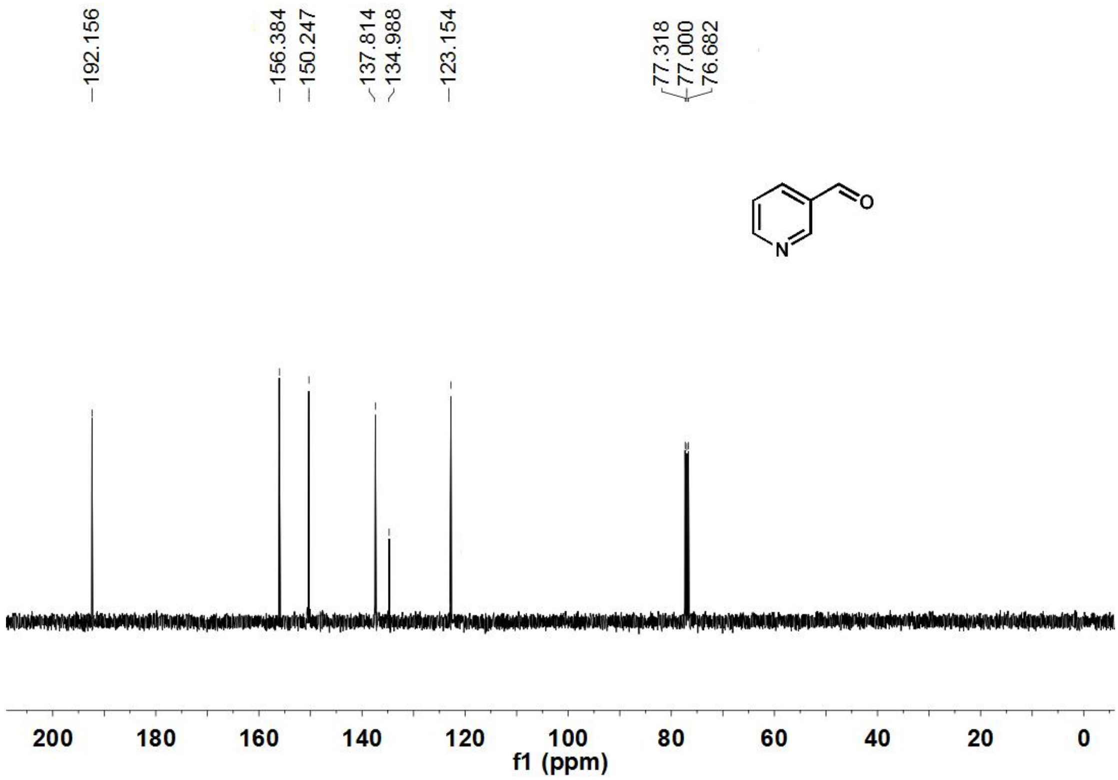

9.989
7.841
7.820
7.533
7.512
7.264
0.000
Cl
O
1.00
2.12
2.02
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


190.868
140.982
134.725
130.907
129.465
77.317
77.000
76.682
Cl
O
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


10.166
8.413
8.392
8.092
8.071
7.265
0.000
O_2N
O
1.00
1.98
2.03
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


190.236
146.873
140.053
130.468
124.305
77.317
77.000
76.682
O_2N
O
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


10.017
8.988
8.750
8.730
8.031
8.000
7.439
7.435
7.420
7.416
7.401
7.397
N
O
1.00
0.98
1.00
0.98
0.98
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


192.156
156.384
150.247
137.814
134.988
123.154
77.318
77.000
76.682
N
O
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)