Development of a Brønsted acid Al-MIL-53 Metal–Organic Framework catalyst and its Application in [4+2] Cycloadditions

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Supporting Information

General Information. The phase composition of the samples were investigated by X-ray powder diffraction (XRD, M21X, Cu Kα radiation, λ=0.154178 nm). Their morphology and structure of the as-obtained product was characterized by scanning electron microscopy (SEM, ZEISS SUPRA55). Further information of the structure were revealed by transmission electron microscopy (TEM, TEI Tecnai F20) and high-resolution TEM (HRTEM, TEI Tecnai F20) using TEI Tecnai F20. The samples for the SEM, TEM and HRTEM measurements were first dispersed in ethanol and sonicated for a few minutes, and then supported onto the silicon slice and the holey carbon film on a Cu grid, respectively. The chemical compositions were analyzed using X-ray photoelectron spectrometer (XPS, ESCALAB 250Xi) and inductively coupled plasma-atomic emission spectrometry (ICP-AES, Vavian 715-ES). Thermogravimetric analysis (TG) were conducted by a TGA instrument (Netzsch STA449F) at a heating rate of 10^{o}C/min under an N_2 flow. The specific surface areas were calculated by nitrogen sorption–desorption isotherms using a Micromeritics ASAP 2420 adsorption analyzer. The pore size distributions were derived from the adsorption branches of isotherms by using the Barrett–Joyner–Halenda (BJH) model. Fourier transform Infrared spectra (FTIR) were acquired on a Nicolet 6700 using the KBr pellet technique. The catalytic results were analyzed by a gas chromatography-mass spectrum (GC-MS, Agilent7890/5975C-GC/MSD).

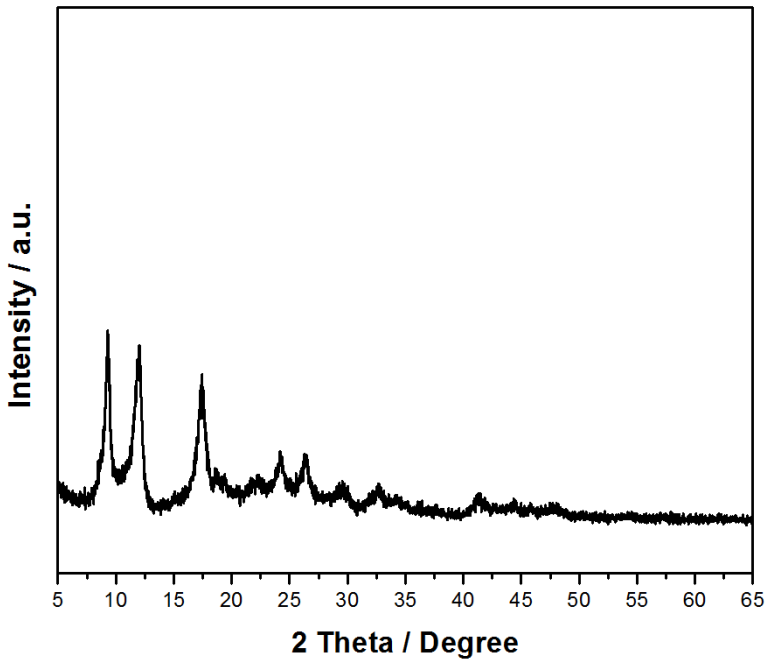
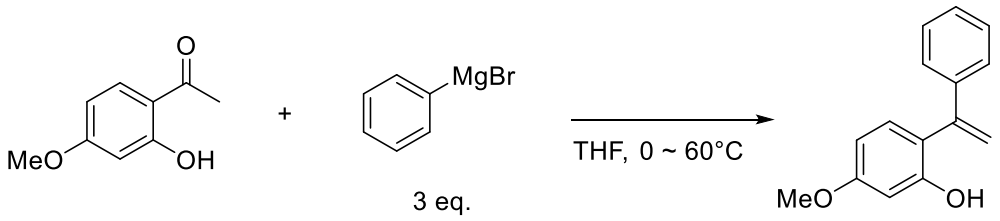


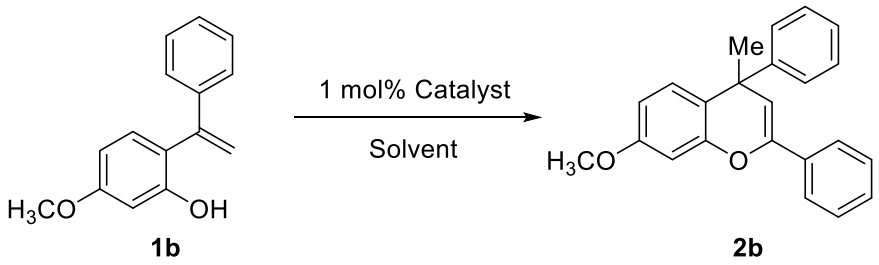
Fig S1. Powder XRD of recycled Al-MIL-53-ArSO_3H.

Synthesis of 5-methoxy-2-(1-phenylvinyl)phenol



Bromobenzene (24.6 mmol) was added dropwise to magnesium turning (590 mg, 24.6 mmol) in THF (20 ml) and a gentle reflux was kept. The solution was further stirred for 30 min. Then 2-hydroxyacetophenone (12 mmol) was added to the resulting solution at 0 ºC. The reaction mixture was warmed to room temperature and stirred overnight. At the end of the reaction, 15 ml acetic acid was added and the reaction mixture was extracted with ethyl acetate three times. The combined organic layer was washed with sat. NaCl aq. and dried over Na_2SO_4. The organic solvent was removed under reduced pressure to afford a crude product, which was washed with hexanes to afford 5-methoxy-2-(1-phenylvinyl)phenol in 89% yield.

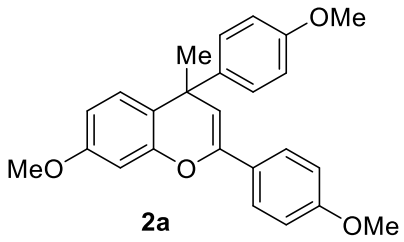
[4+2] Catalytic reaction conditions



1b **2b**

For a general catalytic reaction, 1 mol% of the Al-MIL-53-ArSO_3H was added to 1.00 mL solvent, which was in an oven dried round bottom reaction vessel. To the reaction vessel was added 1.0 mmol of 5-methoxy-2-(1-phenylvinyl)phenol. The solution was stirred at 40 ºC for 3 h. The reaction mixture was passed through a silica gel plug and eluted with 5 mL of dichloromethane. Then, the filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography over silica gel to afford the dimeric product **2b**. The yield was calculated based on the isolated product.

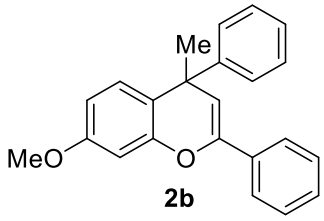
7-methoxy-2,4-bis(4-methoxyphenyl)-4-methyl-4H-chromene



2a

The crude mixture was purified by flash column chromatography with elution by 20:1–15:1, hexanes : EtOAc. Yield: 95%, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (m 2H), 7.31 (m, 2H), 6.93 (m, 2H), 6.89 (d, J = 8.6 Hz, 1H), 6.85 (m, 2H), 6.68 (d, J = 2.6 Hz, 1H), 6.58 (dd, J = 8.6, 2.6 Hz, 1H), 5.34 (s, 1H), 3.84(s, 3H), 3.82(s, 3H), 3.79(s, 3H), 1.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 160.0, 158.9, 157.8, 151.2, 145.8, 142.9, 129.3, 128.5 (2C), 127.1, 126.2 (2C), 121.5, 113.9 (2C), 113.6 (2C), 110.7, 106.2, 101.1, 55.5 (2C), 55.3, 38.8, 30.9; IR (thin film, cm^{-1}): 2970, 2833, 1714, 1670, 1510, 1248, 1164, 1032; HRMS (ESI+): (m/z) ($M+H^+$) calculated for $C_{25}H_{25}O_4$ 389.1753, found 389.1750.

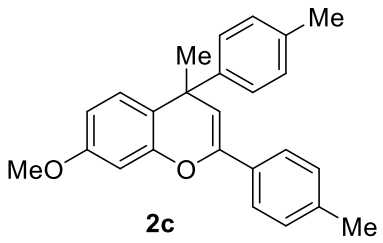
7-methoxy-4-methyl-2,4-diphenyl-4H-chromene



2b

The crude mixture was purified by flash column chromatography with elution by 20:1–15:1, Hexanes : EtOAc. Yield: 91%, 1H NMR (500 MHz, CDCl3): δ 7.77 (m, 2H), 7.46-7.33 (m, 7H), 6.22 (m, 1H), 6.92 (d, J = 8.3 Hz, 1H), 6.73 (d, J = 2.0 Hz ,1H), 6.61 (dd, J = 8.3, 2.0, 1H), 5.51 (s, 1H), 3.84 (s, 3H), 1.91 (s, 3H); 13C NMR (100 MHz, CDCl3): 158.9, 151.1, 150.2, 146.0, 134.3, 129.4, 128.5,128.4 (2C), 128.3 (2C), 127.4 (2C), 126.1, 124.8 (2C), 121.0, 110.8, 107.5, 107.46, 101.0, 55.5, 39.4, 30.6; IR (thin film, cm-1): 2932, 1713, 1668, 1622, 1503, 1443, 1325, 1163, 1027; HRMS (ESI+): (m/z) (M+H+) calculated for $C_{23}H_{21}O_2$ 329.1542, found 329.1550.

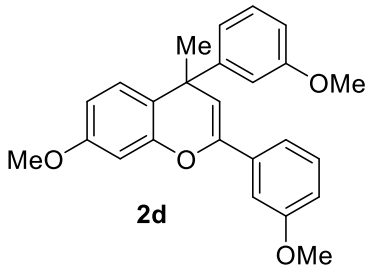
7-methoxy-4-methyl-2,4-di-p-tolyl-4H-chromene



2c

The crude mixture was purified by flash column chromatography with elution by 20:1–15:1, Hexanes : EtOAc. Yield: 82%, 1H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, J = 8.2 Hz 2H), 7.30 (d, J = 8.2 Hz, 2H), 7.20 (d, J = 8.2 Hz 2H), 7.11 (d, J = 8.2 Hz, 1H), 6.89 (d, J = 8.6 Hz, 1H), 6.67 (d, J = 2.6 Hz, 1H), 6.56 (dd, J = 8.6, 2.6 Hz, 1H), 5.40 (s, 1H), 3.81(s, 3H), 2.39(s, 3H), 2.32(s, 3H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 158.9, 151.2, 147.6, 146.2, 138.4, 135.6, 131.7, 129.3, 129.1 (2C), 129.0 (2C), 127.4 (2C), 124.7 (2C), 121.4, 110.7, 107.0, 101.1, 55.5, 39.1, 30.7, 21.4, 21.0. IR (thin film, cm^{-1}): 2974, 2824, 1712, 1524, 1233, 1158, 1018; HRMS (ESI+): (m/z) ($M+H^+$) calculated for $C_{25}H_{25}O_2$ 357.1855, found 357.1859.

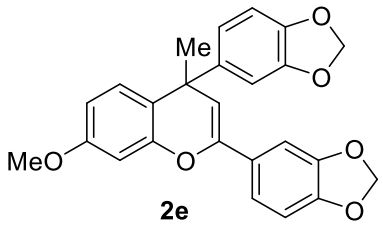
7-methoxy-2,4-bis(3-methoxyphenyl)-4-methyl-4H-chromene



2d

The crude mixture was purified by flash column chromatography with elution by 10:1–8:1, Hexanes : EtOAc. Yield: 86%, 1H NMR (500 MHz, CDCl3): δ 7.31-7.22 (m, 4H), 7.00 (d, J = 7.8 Hz ,1H), 6.91-6.88 (m, 2H), 6.73 (dd, J = 8.2, 1.8 Hz, 1H), 6.67 (d, J = 2.5 Hz ,1H), 6.57 (dd, J = 8.6 ,2.6 Hz ,1H), 5.46 (s, 1H), 3.86 (s, 3H), 3.81 (s, 3H), 3.77 (s, 3H), 1.84 (s, 3H); 13C NMR (100 MHz, CDCl3): 159.8, 159.6, 158.9, 151.9, 151.0, 145.9, 135.7, 129.5, 129.3, 129.2, 120.8, 120.1, 117.3, 114.1, 110.8, 110.7, 110.5, 107.61, 107.58, 101.0, 55.50, 55.48, 55.3, 39.5, 30.6; IR (thin film, cm-1): 2975, 1715, 1670, 1515, 1241, 1163, 1033; HRMS (ESI+): (m/z) (M+H+) calculated for C25H25O4 389.1753, found 389.1752.

2,4-bis(benzo[d][1,3]dioxol-5-yl)-7-methoxy-4-methyl-4H-chromene

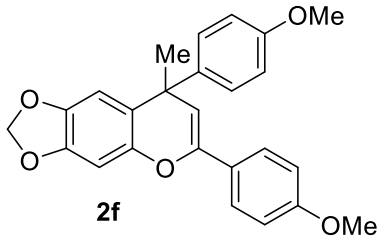


2e

The crude mixture was purified by flash column chromatography with elution by 15:1–10:1, Hexanes : EtOAc. Yield: 77%, 1H NMR (400 MHz, CDCl3): δ 7.23 (dd, J = 8.2, 1.7 Hz, 1H), 7.17 (d, J = 1.7 Hz, 1H), 6.87 (d, J = 8.2 Hz, 1H), 6.85 (dd, J = 8.1, 1.9 Hz, 1H), 6.83 (d, J = 8.1 Hz ,1H), 6.82 (d, J = 8.1, 1H), 6.73 (d, J = 8.0 Hz, 1H), 6.63 (d, J = 2.6 Hz, 1H), 6. 56 (dd, J = 8.0, 2.6 Hz,

1H), 5.98 (s, 2H), 5.91 (d, J = 1.5 Hz, 1H), 5.89 (d, J = 1.5 Hz, 1H), 5.26 (s, 1H), 3.80(s, 3H), 1.78 (s, 3H); 13C NMR (100 MHz, CDCl3): 158.9, 150.9, 147.9, 147.7, 145.8, 144.8, 129.2, 128.6, 121.0, 119.9, 118.8, 110.8, 108.8, 108.2, 107.7, 106.5, 106.4, 105.6, 105.1, 101.4, 101.1, 101.0, 55.5, 39.2, 30.9; IR (thin film, cm-1): 2978, 1714, 1670, 1621, 1503, 1485, 1301, 1166, 1036; HRMS (ESI+): (m/z) (M+H+) calculated for C25H21O6 417.1338 found 417.1340.

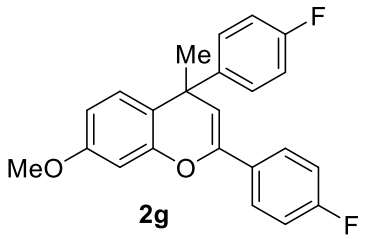
6,8-bis(4-methoxyphenyl)-8-methyl-8H-[1,3]dioxolo[4,5-g]chromene



2f

The crude mixture was purified by flash column chromatography with elution by 20:1–15:1, Hexanes : EtOAc. Yield: 92%, 1H NMR (400 MHz, CDCl3): δ 7.65 (d, J = 8.8 Hz 2H), 7.34 (d, J = 8.7 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 6.66 (s, 1H), 6.40 (s, 1H), 5.89 (s, 1H), 5.87 (s, 1H), 5. 28 (s, 1H), 3.84(s, 3H), 3.80 (s, 3H), 1.82 (s, 3H); 13C NMR (100 MHz, CDCl3): 159.9, 157.8, 146.5, 145.8, 145.0, 143.6, 142.6, 128.4 (2C), 126.9, 126.1 (2C), 121.0, 113.8 (2C), 113.6 (2C), 107.0, 104.9, 101.2, 98.0, 55.4, 55.3, 39.4, 30.8; IR (thin film, cm-1): 2934, 1712, 1609, 1509, 1246, 1170, 1031; HRMS (ESI+): (m/z) (M+H+) calculated for C25H23O5 403.1545, found 403.1544.

2,4-bis(4-fluorophenyl)-7-methoxy-4-methyl-4H-chromene

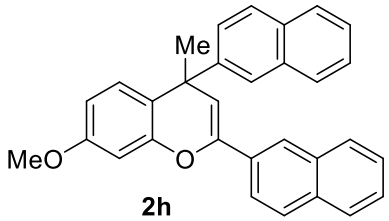


2g

The crude mixture was purified by flash column chromatography with elution by 10:1–8:1, Hexanes : EtOAc. Yield: 71%, 1H NMR (500 MHz, CDCl3): δ 7.68 (m, 2H), 7.33 (m, 2H), 7.07 (m, 2H), 6.98 (m, 2H), 6.84 (d, J = 8.6 Hz ,1H), 6.65 (d, J = 2.5 Hz ,1H), 6.57 (dd, J = 8.6, 2.5, 1H), 5.34 (s, 1H), 3.81 (s, 3H), 1.83 (s, 3H); 13C NMR (125 MHz, CDCl3): 163.1 (d, 1JC-F=226.3 Hz), 161.2 (d, 1JC-F= 223.0 Hz), 159.0, 150.9, 146.0 (d, 4JC-F= 3.3 Hz), 145.4, 130.4 (d, 4JC-F= 3.3 Hz), 129.3, 129.0 (d, 3JC-F= 7.8 Hz, 2C), 126.6 (d, 3JC-F= 7.8 Hz, 2C), 120.7, 115.4 (d, 2JC-F= 25 Hz, 2C), 115.0 (d, 2JC-F= 25 Hz, 2C), 111.0, 107.0, 101.1, 55.6, 39.0, 30.9 ; IR (thin film,

cm-1): 2925, 1716, 1670, 1622, 1505, 1163, 1040; HRMS (ESI+): (m/z) (M+H+) calculated for C23H19O2F2 365.1353, found 365.1333.

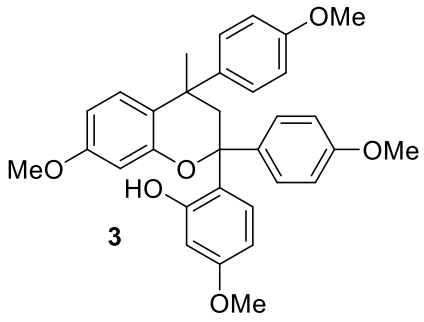
7-methoxy-4-methyl-2,4-di(naphthalen-2-yl)-4H-chromene



2h

The crude mixture was purified by flash column chromatography with elution by 10:1–8:1, Hexanes : EtOAc. Yield: 74%, ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.30 (s, 1H), 7.93-7.75 (m, 8H), 7.53-7.45 (m, 5H), 6.91 (d, J = 8.6 Hz, 1H), 6.81 (d, J = 2.6 Hz, 1H), 6.58 (dd, J = 8.6, 26 Hz, 1H), 5.66 (s, 1H), 3.85(s, 3H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 159.1, 151.2, 147.3, 146.3, 133.40, 133.35, 133.2, 132.0, 131.4, 129.6, 128.6 (2C), 128.3, 128.14, 128.08, 127.7, 127.6 (2C), 126.5, 126.4, 126.2, 125.9, 124.0, 123.9, 122.6, 110.9, 107.9, 101.1, 55.6, 39.8, 30.7; IR (thin film, cm^{-1}): 3056, 2979, 1712, 1503, 1357, 1132, 1040; HRMS (ESI+): (m/z) ($M+H^+$) calculated for $C_{31}H_{25}O_2$ 429.1855, found 429.1853.

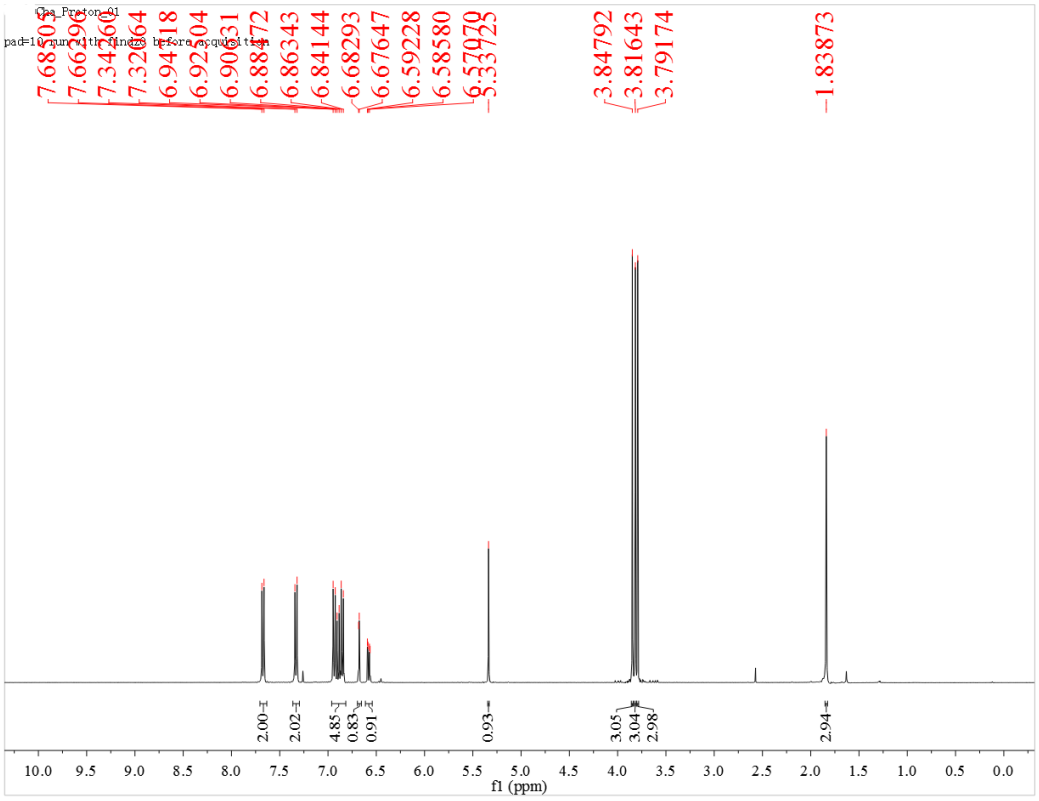
5-methoxy-2-(7-methoxy-2,4-bis(4-methoxyphenyl)-4-methylchroman-2-yl)phenol



3

The crude mixture was purified by flash column chromatography with elution by 8:1–4:1, Hexanes : EtOAc. Yield: 40%, ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 (s, 1H), 7.22 (d, J = 8.9 Hz ,2H), 6.93 (d, J = 8.8 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 6.80 (d, J = 8.8 Hz ,2H), 6.68-6.65 (m,4H), 6.53 (dd, J = 8.8, 2.5 Hz ,1H), 6.21 (d, J = 2.5 Hz ,1H), 6.08(dd, J = 8.8, 2.5 Hz ,1H), 3.83 (s, 3H), 3.75 (s, 3H), 3.74 (s, 3H), 3.67 (s, 3H), 3.09 (d, J = 14.5 Hz ,1H), 2.75 (d, J = 14.5 Hz ,1H), 1.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 160.2, 159.2, 158.7, 157.5, 155.7, 152.7, 142.3, 135.90, 135.85, 130.4, 128.3, 127.9, 127.3, 122.1, 120.5, 113.6, 113.2, 112.9, 109.3, 105.2, 105.0, 102.7, 101.5, 101.4, 83.8, 55.4, 55.22. 55.20, 55.1, 49.4, 39.4, 31.2; IR (thin film, cm^{-1}): 2978, 1650, 1505, 1288, 1230, 987; HRMS (ESI+): (m/z) ($M+H^+$) calculated for $C_{32}H_{33}O_6$ 513.2277, found 513.2271.

Compound 2a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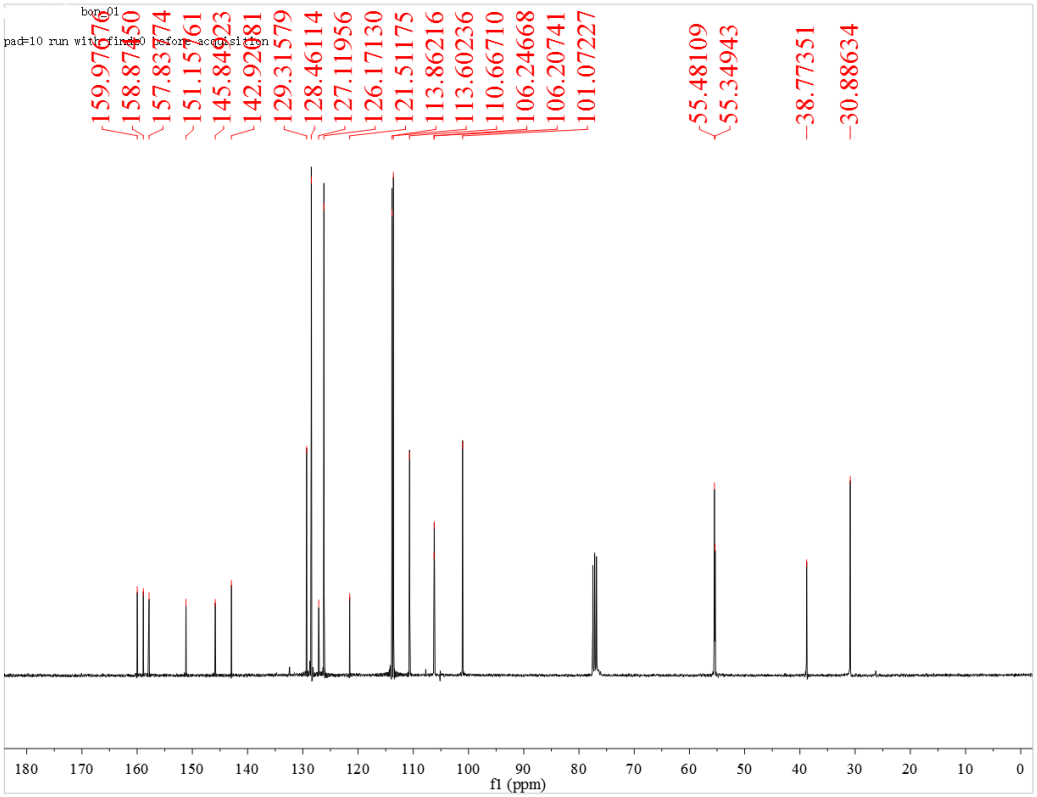
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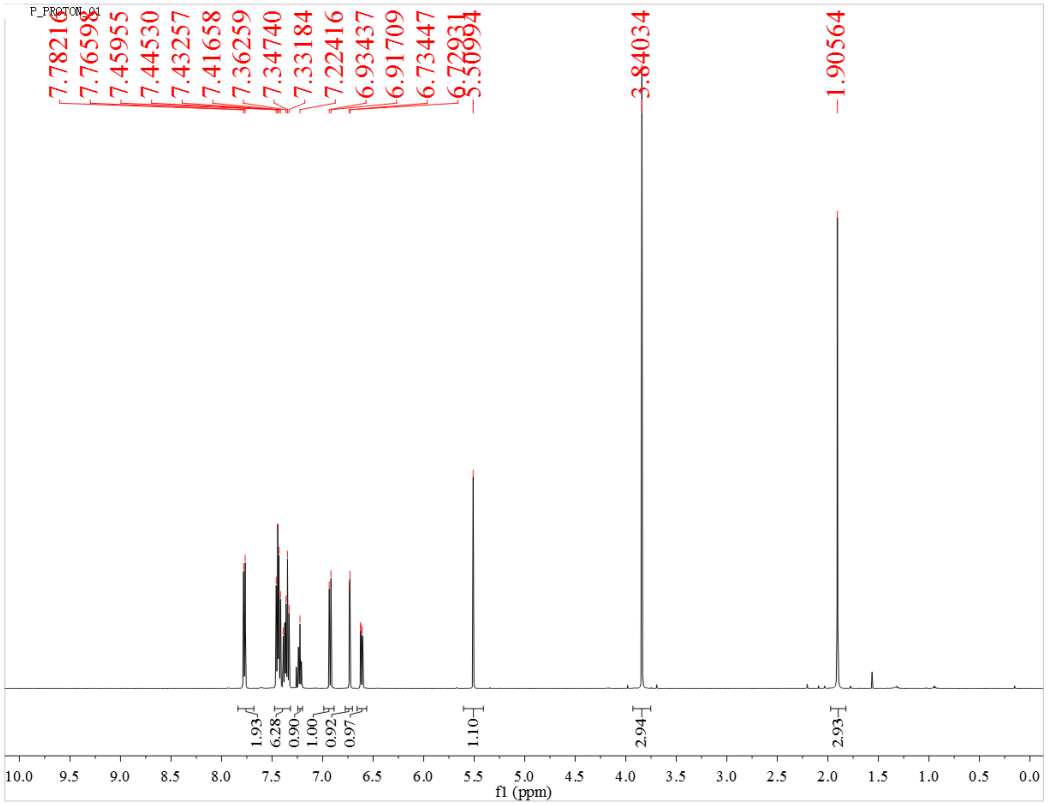
Compound 2b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2.93
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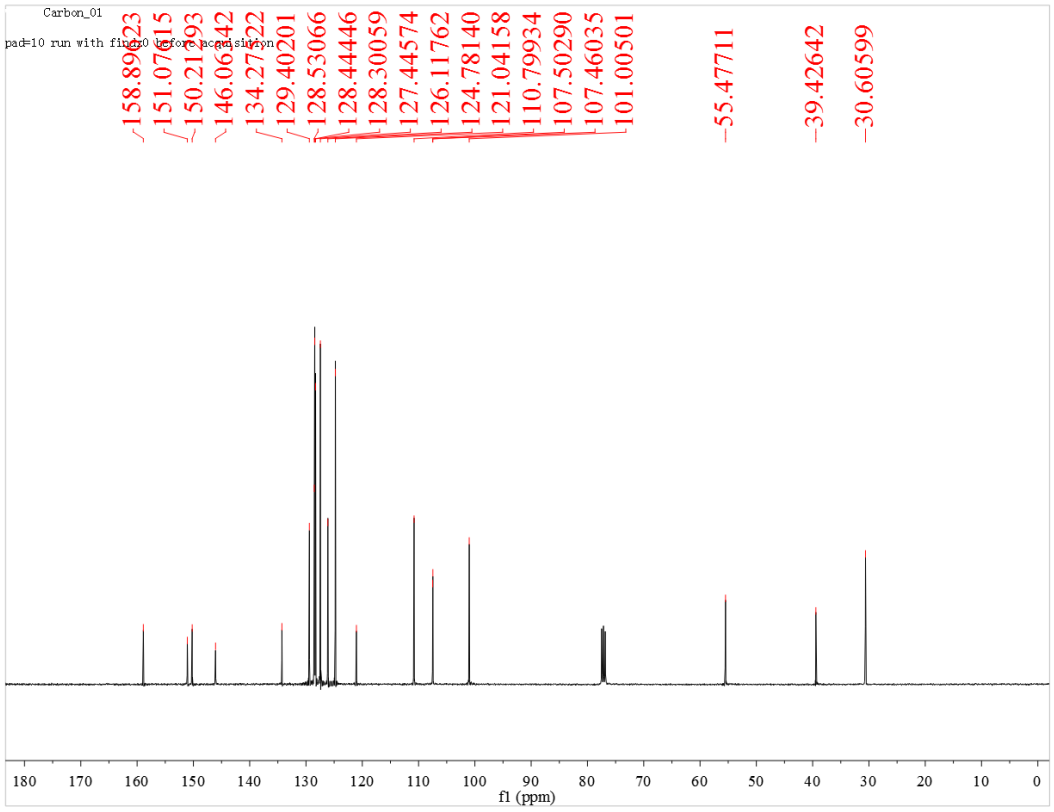
f1 (ppm)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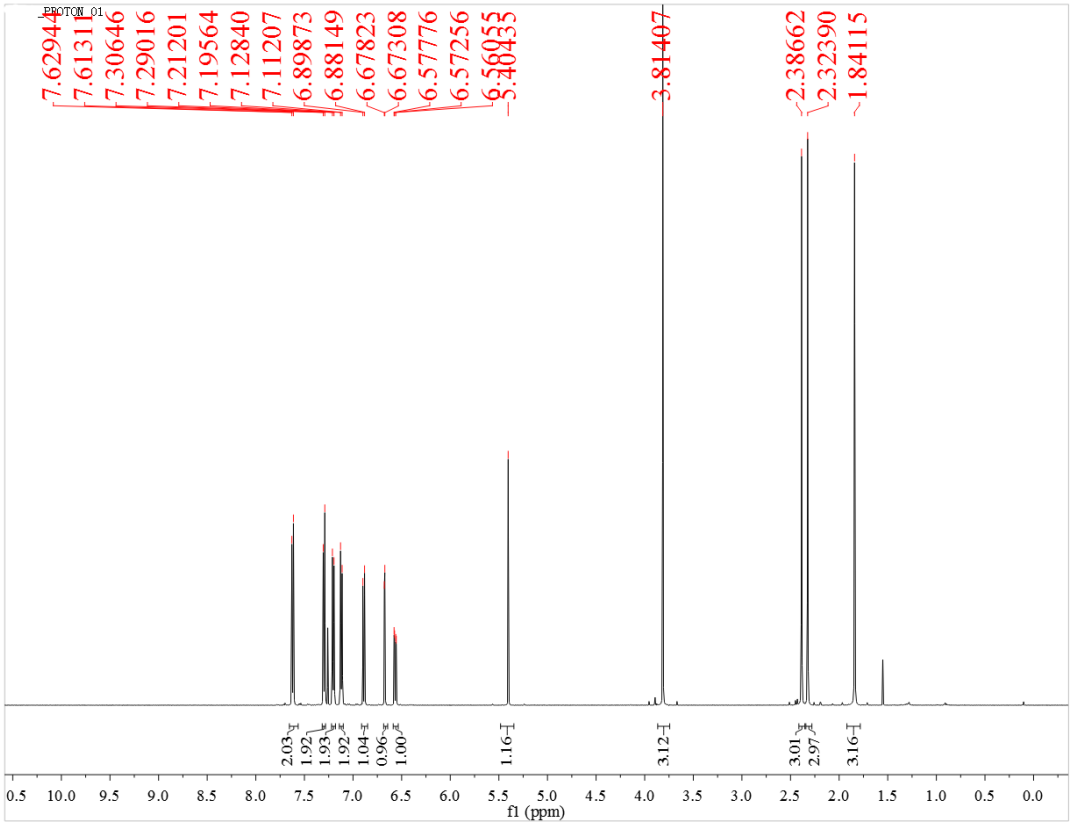
f1 (ppm)

Compound 2c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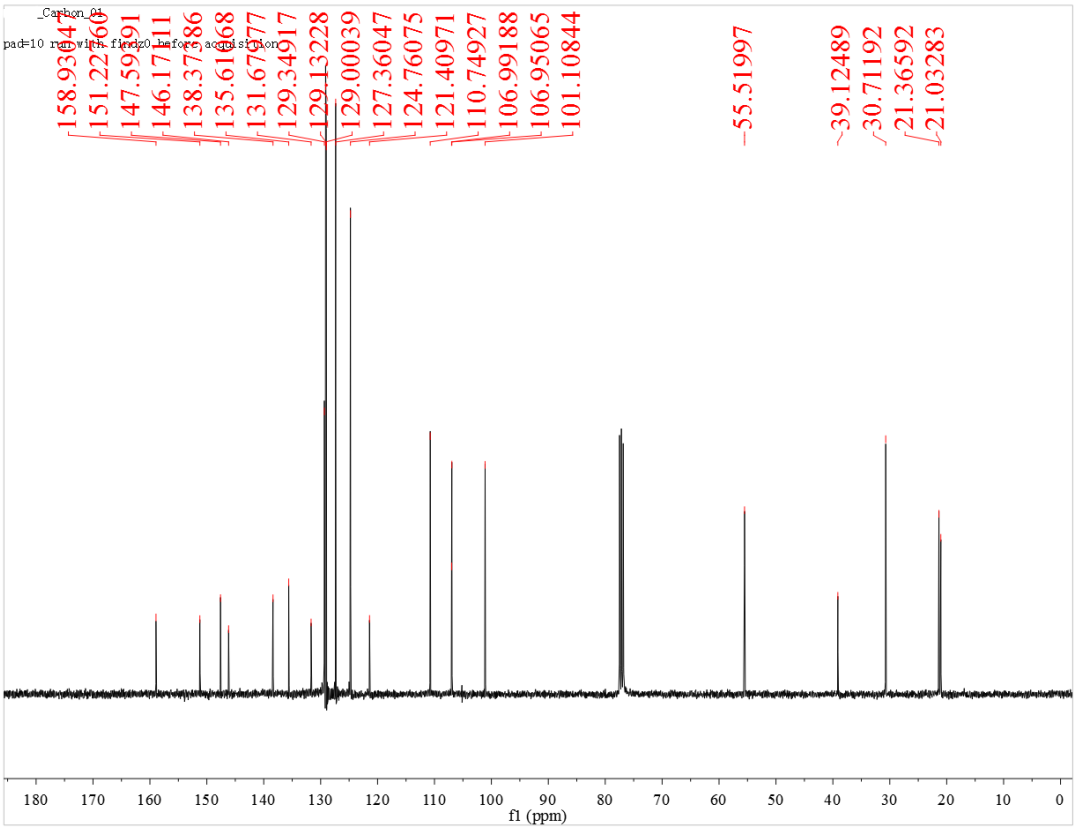
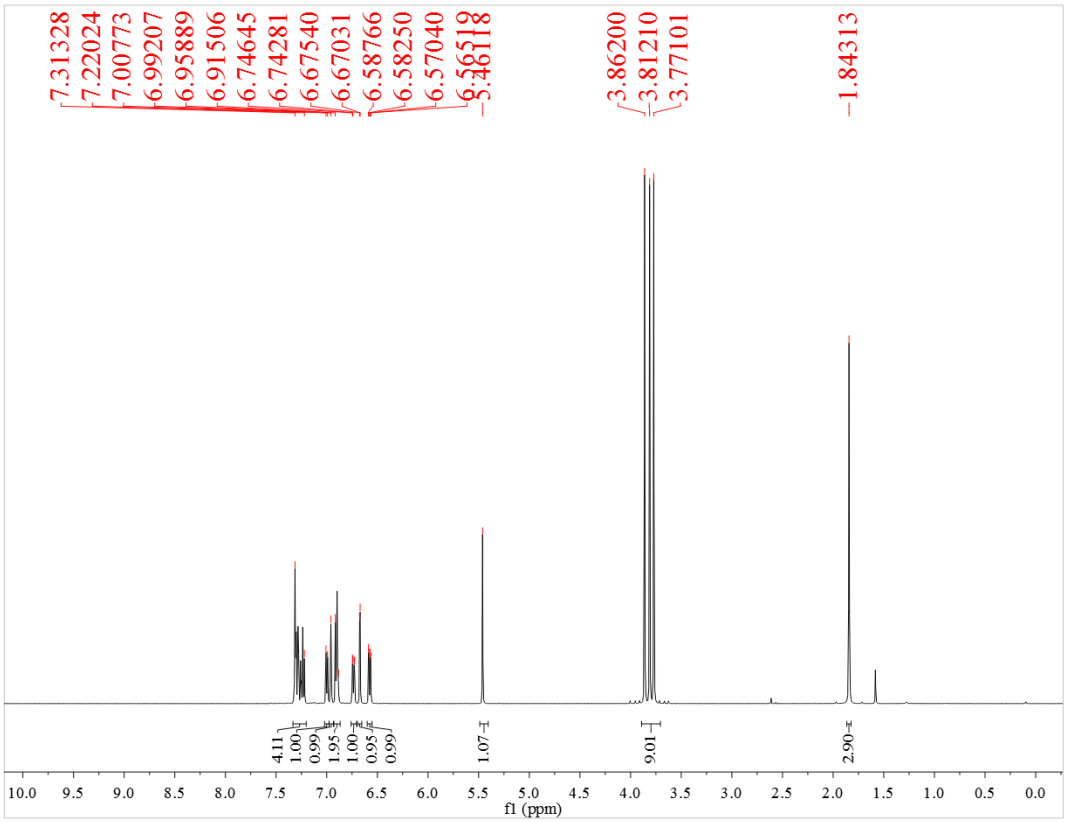
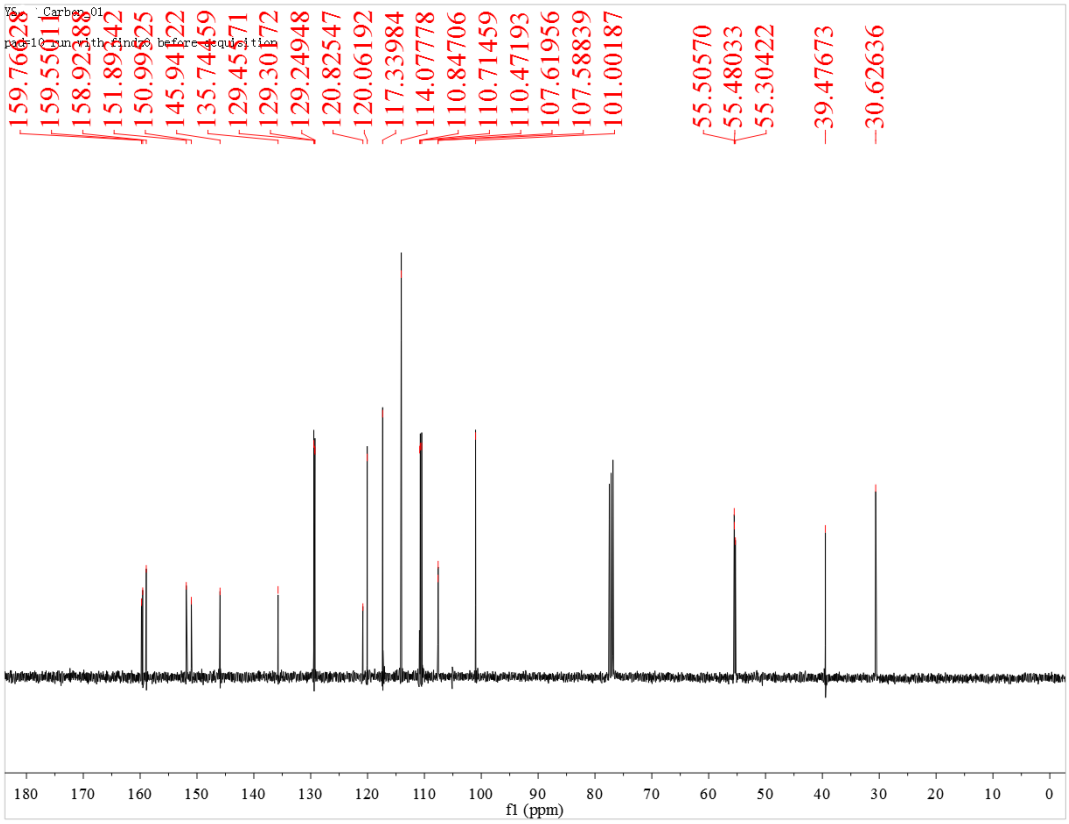
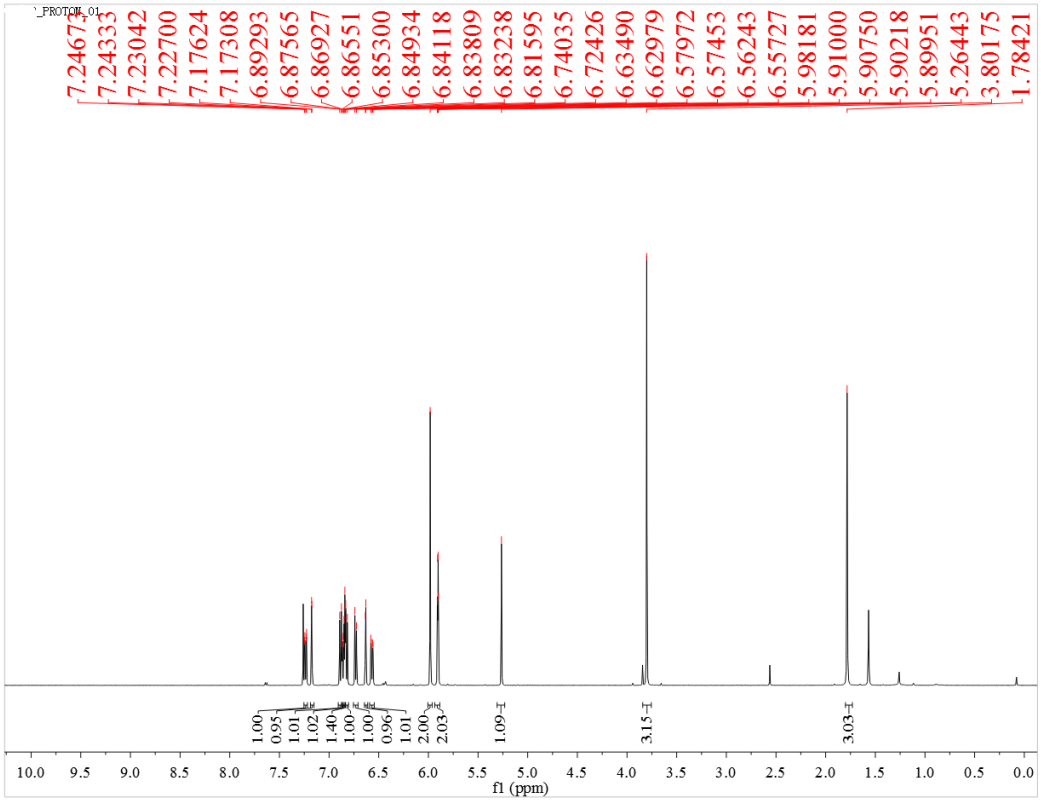

Carbon_01
pad=10 nary=1 fl=dz0 before acquisition
158.93044
151.22260
147.59291
146.17111
138.37386
135.61668
131.67777
129.34917
129.13228
129.00039
127.36047
124.76075
121.40971
110.74927
106.99188
106.95065
101.10844
55.51997
39.12489
30.71192
21.36592
21.03283
f1 (ppm)

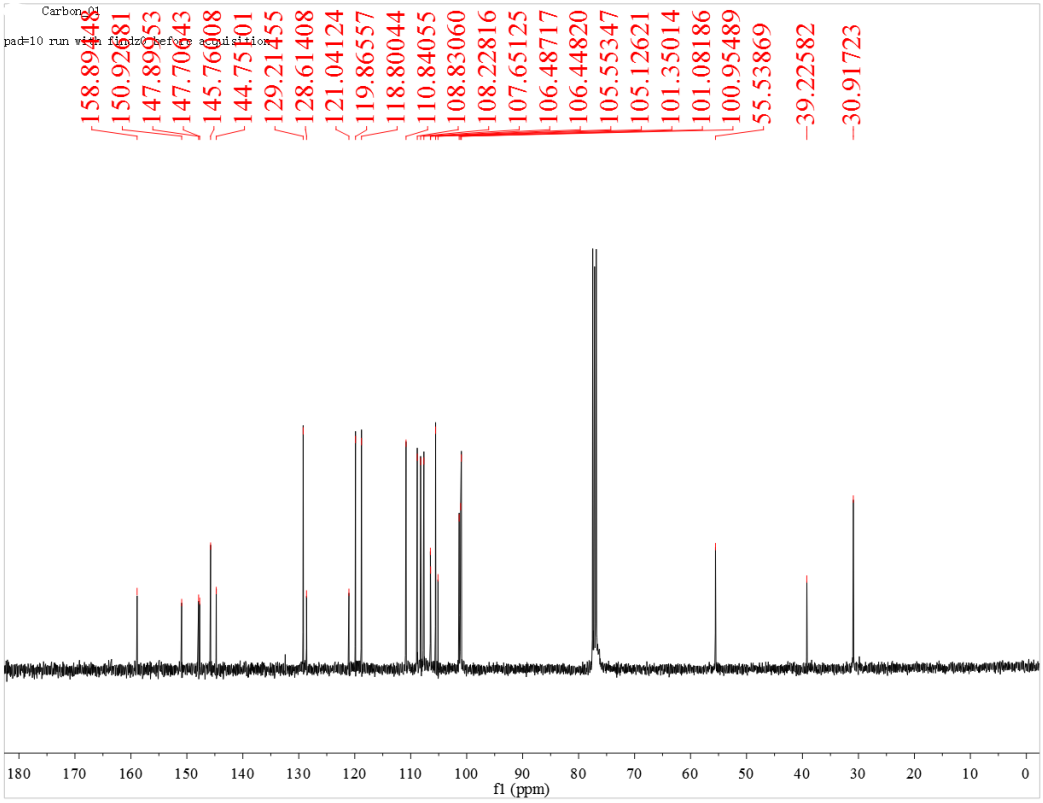
Compound 2d


7.31328
7.22024
7.00773
6.99207
6.95889
6.91506
6.74645
6.74281
6.67540
6.67031
6.58766
6.58250
6.57040
6.56519
5.48118
3.86200
3.81210
3.77101
1.84313
4.11
1.00
0.99
1.95
1.00
0.95
0.99
1.07
9.01
2.90
f1 (ppm)

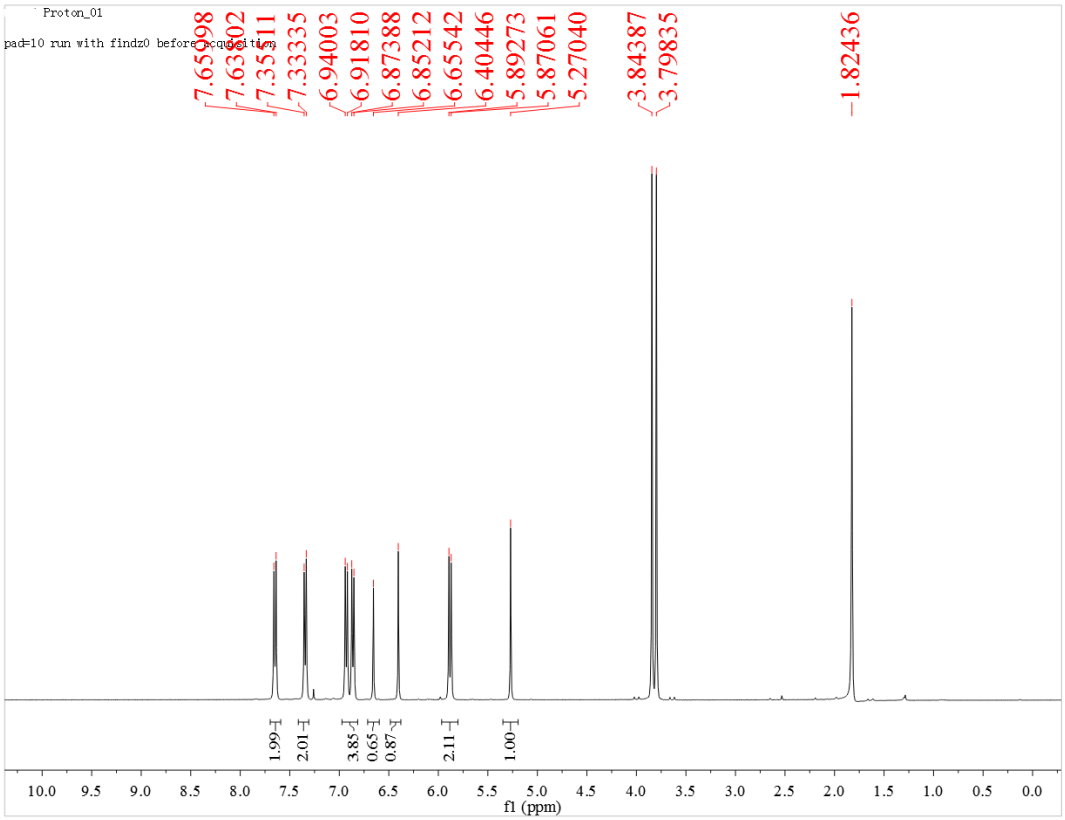

159.76228
159.55111
158.92885
151.89442
150.99225
145.94422
135.74459
129.45771
129.30772
129.24948
120.82547
120.06192
117.33984
114.07778
110.84706
110.71459
110.47193
107.61956
107.58839
101.00187
55.50570
55.48033
55.30422
39.47673
30.62636
f1 (ppm)

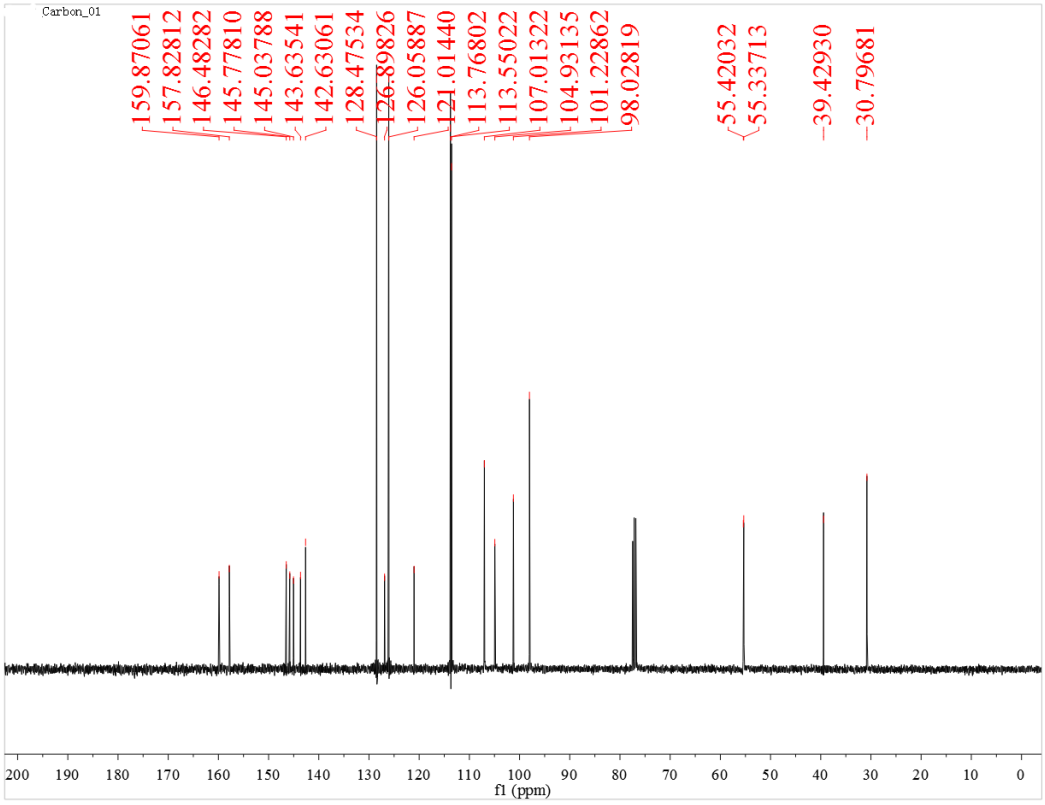
Compound 2e


7.24677
7.24335
7.23042
7.22700
7.17624
7.17308
6.89293
6.87565
6.86927
6.86551
6.85300
6.84934
6.84118
6.83809
6.83238
6.81595
6.74035
6.72426
6.63490
6.62979
6.57972
6.57453
6.56243
6.55727
5.98181
5.91000
5.90750
5.90218
5.89951
5.26443
3.80175
1.78421
1.00
0.95
1.01
1.02
1.40
1.00
1.00
0.96
1.01
2.00
2.03
1.09
3.15
3.03
f1 (ppm)

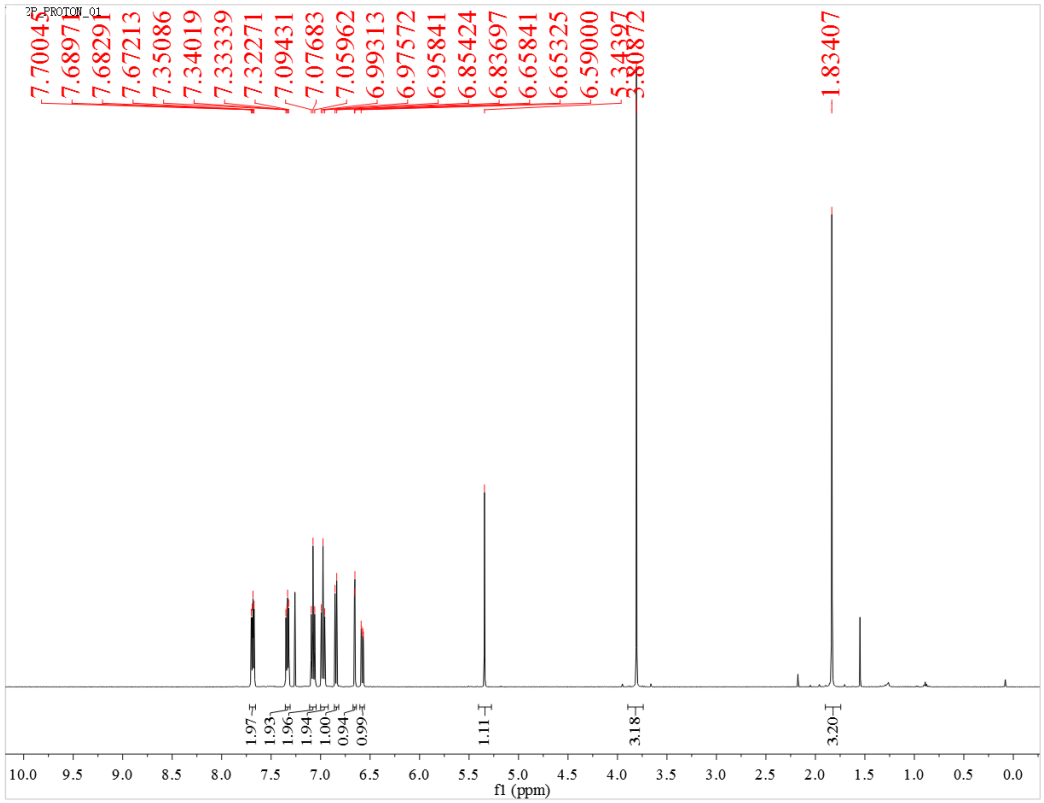

Carbon_01
158.89448
150.92481
147.89553
147.70643
145.76608
144.75101
129.21455
128.61408
121.04124
119.86557
118.80044
110.84055
108.83060
108.22816
107.65125
106.48717
106.44820
105.55347
105.12621
101.35014
101.08186
100.95489
55.53869
39.22582
30.91723
f1 (ppm)

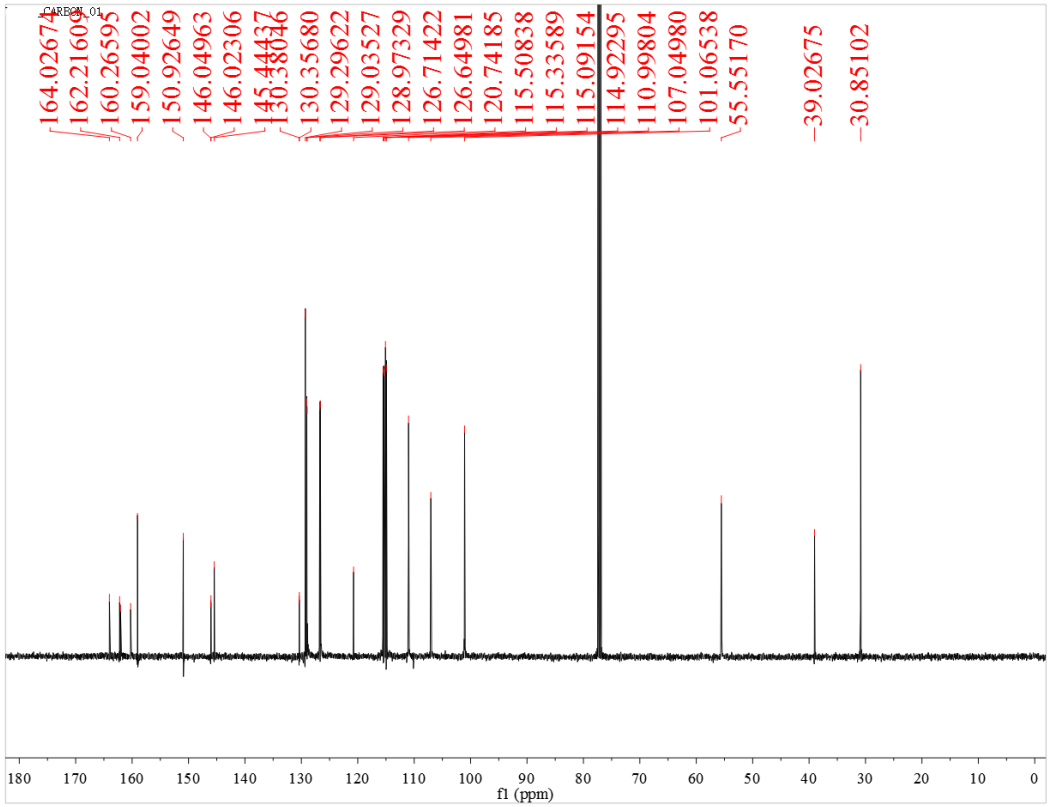
Compound 2f


Proton_01
pad=10 run with findz0 before acquisition
7.65998
7.63502
7.35511
7.33335
6.94003
6.91810
6.87388
6.85212
6.65542
6.40446
5.89273
5.87061
5.27040
3.84387
3.79835
1.82436
1.99
2.01
3.85
0.65
0.87
2.11
1.00
f1 (ppm)

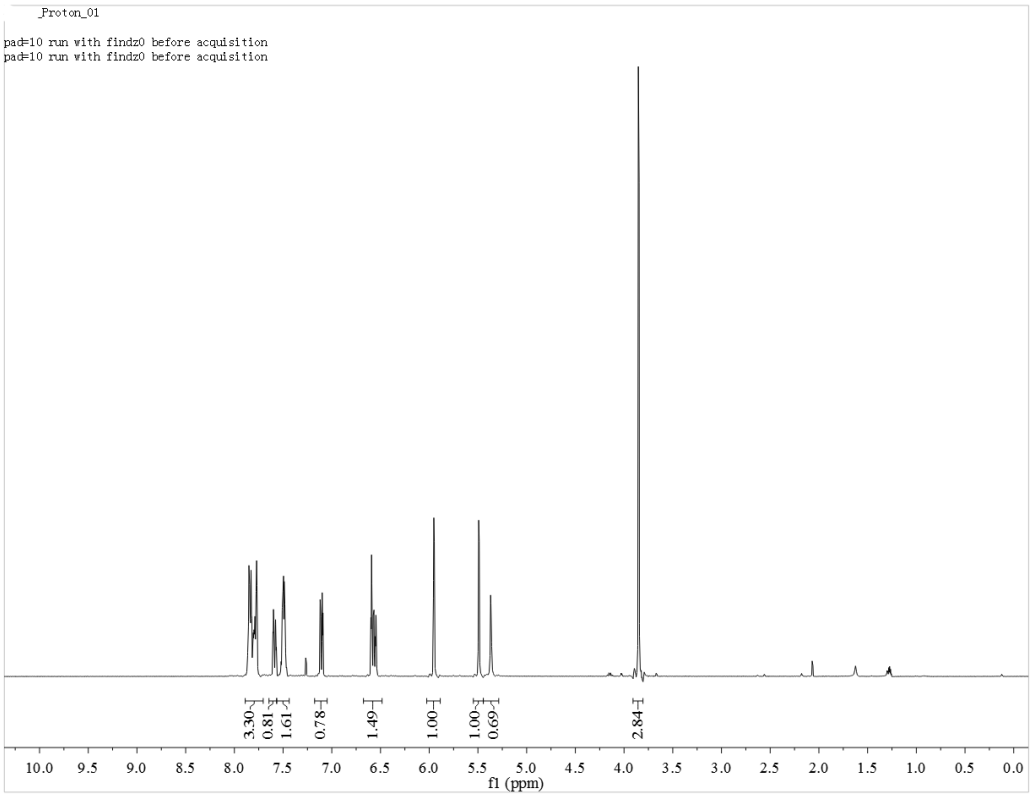

Carbon_01
159.87061
157.82812
146.48282
145.77810
145.03788
143.63541
142.63061
128.47534
126.89826
126.05887
121.01440
113.76802
113.55022
107.01322
104.93135
101.22862
98.02819
55.42032
55.33713
39.42930
30.79681
f1 (ppm)

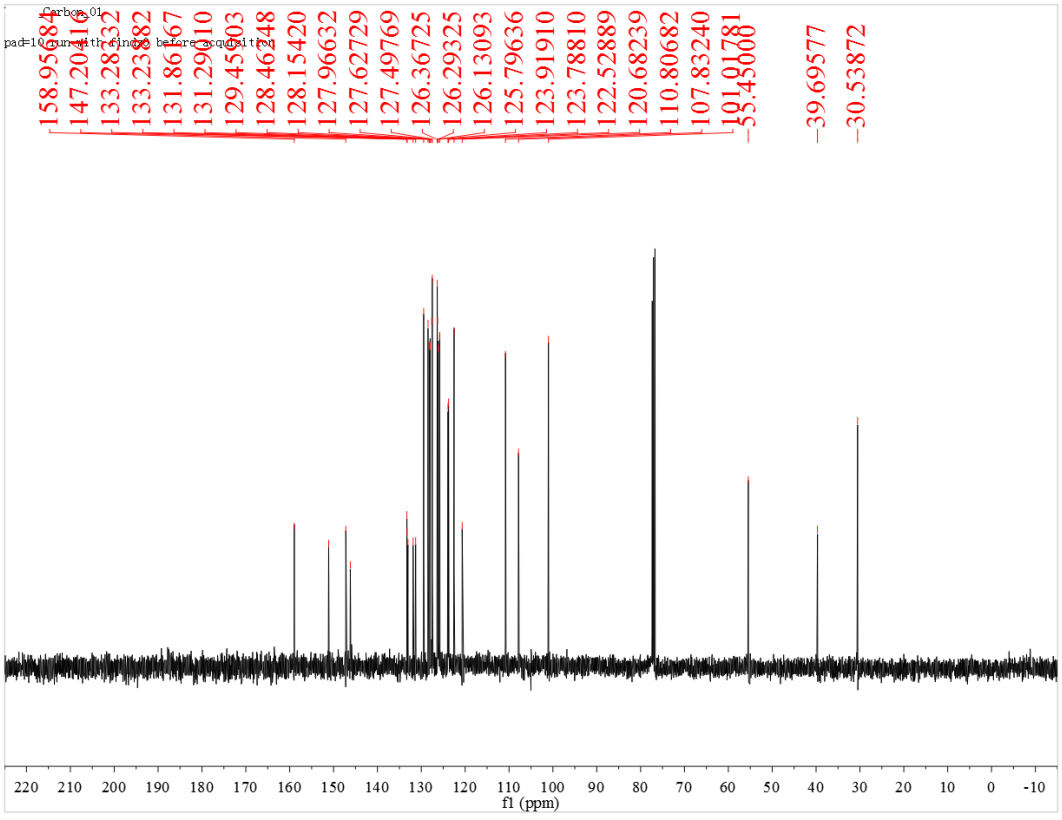
Compound 2g


7.70047
7.68971
7.68291
7.67213
7.35086
7.34019
7.33339
7.32271
7.09431
7.07683
7.05962
6.99313
6.97572
6.95841
6.85424
6.83697
6.65841
6.65325
6.59000
5.34397
3.80872
1.83407
1.97
1.93
1.96
1.94
1.00
0.94
0.99
1.11
3.18
3.20
f1 (ppm)

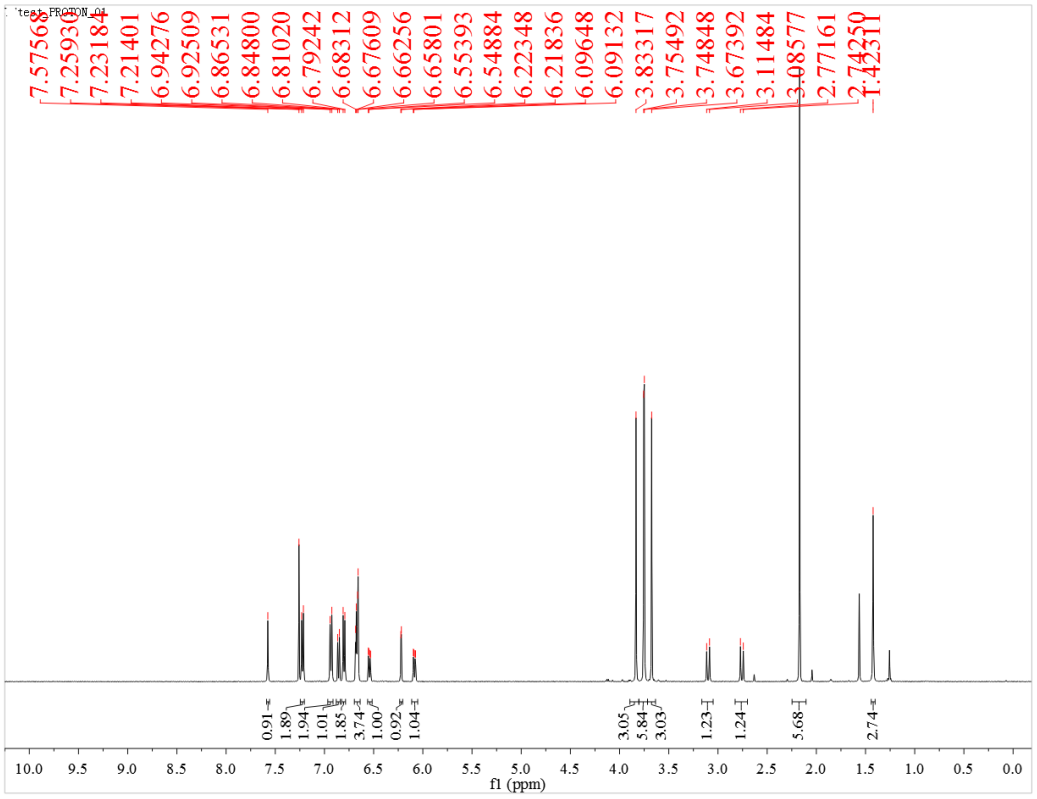

164.02674
162.21609
160.26595
159.04002
150.92649
146.04963
146.02306
130.35680
129.29622
129.03527
128.97329
126.71422
126.64981
120.74185
115.50838
115.33589
115.09154
114.92295
110.99804
107.04980
101.06538
55.55170
39.02675
30.85102
f1 (ppm)

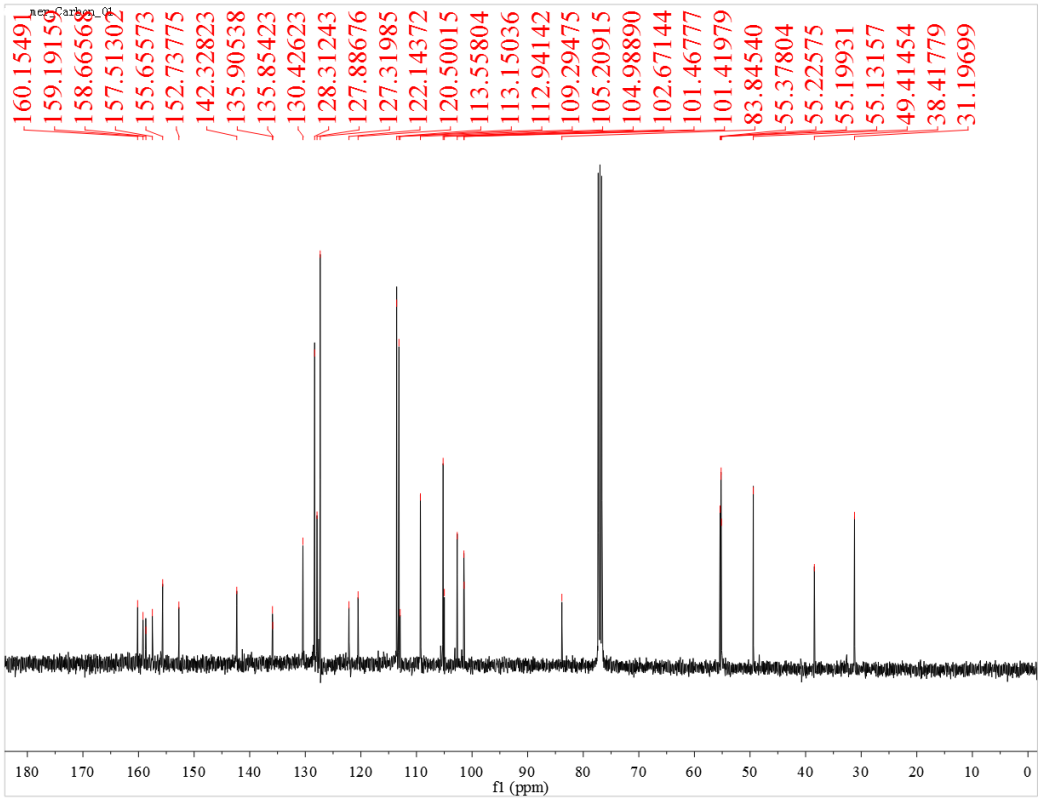
Compound 2h


_Proton_01
pad=10 run with findz0 before acquisition
pad=10 run with findz0 before acquisition
3.30
0.81
1.61
0.78
1.49
1.00
1.00
0.69
2.84
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)


Carbon_01
pad=10 run with findz0 before acquisition
158.95084
147.20176
133.28432
133.23882
131.86667
131.29910
129.45003
128.46748
128.15420
127.96632
127.62729
127.49769
126.36725
126.29325
126.13093
125.79636
123.91910
123.78810
122.52889
120.68239
110.80682
107.83240
101.91781
55.45000
39.69577
30.53872
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Compound 3


7.57568
7.25930
7.23184
7.21401
6.94276
6.92509
6.86531
6.84800
6.81020
6.79242
6.68312
6.67609
6.66256
6.65801
6.55393
6.54884
6.22348
6.21836
6.09648
6.09132
3.83317
3.75492
3.74848
3.67392
3.11484
3.08577
2.77161
2.74250
1.42311
0.91
1.89
1.94
1.01
1.85
3.74
1.00
0.92
1.04
3.05
5.84
3.03
1.23
1.24
5.68
2.74
f1 (ppm)


160.15491
159.19159
158.66569
157.51302
155.65573
152.73775
142.32823
135.90538
135.85423
130.42623
128.31243
127.88676
127.31985
122.14372
120.50015
113.55804
113.15036
112.94142
109.29475
105.20915
104.98890
102.67144
101.46777
101.41979
83.84540
55.37804
55.22575
55.19931
55.13157
49.41454
38.41779
31.19699
f1 (ppm)