Electronic Supplementary Material (ESI) for RSC Advances.

DIPEA-induced activation of OH^- for the synthesis of amide via photocatalysis

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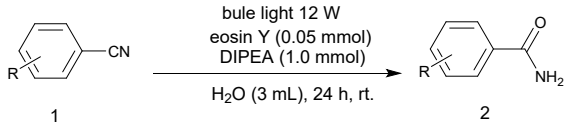
1. General information

All reagents were purchased from commercial sources and used without further purification. All solvents were dried in a standard manner. The nitrile wastewater used in the study was attained from a chemical plant in China (Fujian Province). Reactions were monitored by TLC on silica gel plates. Column chromatography was performed over silica gel (200-300 mesh) and petroleum ether/ethyl acetate. All products were characterized by NMR. ^{1}H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra were recorded at 101 MHz (Bruker DPX) with DMSO-d_6 as solvent. Chemical shifts are reported in ppm using TMS as internal standard. NMR by the services provided at the Shandong Liaocheng University. HPLC were recorded on an SHIMDZU LC-20A instrument with a HP5-MS 30 m x 0.25 mm capillary apolar columns.

2. General procedure for the catalytic reactions



1 2

In a round bottom flask equipped with a stir bar was added nitrile (0.5 mmol), DIPEA (1.0 mmol, 2.0 equiv.), and esion Y (0.05 mmol, 0.1 equiv). The mixture was stirred at room temperature for 24 h blue light LED (12W) in 3 mL H_2O solvent. The reaction mixture was extracted with ethyl acetate (3×15 mL). The combined organic layer was washed with brine (10 mL), dried over $MgSO_4$. The concentrated residue was purified by column chromatography on a silica gel to afford the pure product 2a.

3. General procedure for the gram scale experiment

In 50 ml round bottom flask equipped with a stir bar was added nitrile (10.0 mmol), DIPEA (15.0 mmol, 1.5 equiv), and esion Y (1.0 mmol, 0.1 equiv). The mixture was stirred at room temperature for 36 h blue light LED (12W) in 25 mL H_2O solvent. The reaction mixture was extracted with ethyl acetate (3×15 mL). After the reaction was completed the solution of the crude product was concentrated in vacuo, and the residue was purified by column chromatography on a silica gel (petroleum ether/ethyl acetate=3/1) to afford the target product as a white solid.

4. Characterization data

benzamide (2a)[1]

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.01 (s, 1H), 7.93–7.86 (m, 2H), 7.55–7.48 (m, 1H), 7.48–7.42 (m, 2H), 7.39 (s, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.42, 134.71, 131.69, 128.67, 127.93.

4-chlorobenzamide (2b) [1]

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.05 (s, 1H), 7.92–7.87 (m, 2H), 7.55–7.50 (m, 2H), 7.47 (s, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.30, 136.56, 133.49, 129.87, 128.76.

2-chlorobenzamide (2c) [1]

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.89 (s, 1H), 7.60 (s, 1H), 7.52–7.34 (m, 4H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.67, 137.60, 131.03, 130.11, 130.07, 129.13, 127.49.

2-iodobenzamide (2d) [1]

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.88 (dd, J = 7.9, 0.8 Hz, 1H), 7.83 (s, 1H), 7.52 (s, 1H), 7.43 (td, J = 7.5, 1.1 Hz, 1H), 7.35 (dd, J = 7.6, 1.7 Hz, 1H), 7.15 (td, J = 7.7, 1.8 Hz, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 171.20, 143.57, 139.64, 131.08, 128.41, 128.26, 93.59.

2-nitrobenzamide (2e)[2]

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.18 (s, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.81-7.60 (m, 4H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.74, 147.68, 133.81, 133.05, 131.08, 129.31, 124.42.

3-nitrobenzamide (2f) [1]

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.72–8.66 (m, 1H), 8.40–8.28 (m, 3H), 7.76 (t, J = 8.0 Hz, 1H), 7.72 (s, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.20, 148.24, 136.22, 134.26, 130.48, 126.31, 122.69.

4-nitrobenzamide (2g)[3]

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.34–8.26 (m, 3H), 8.12–8.07 (m, 2H), 7.73 (s, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.71, 149.51, 140.43, 129.37, 123.89.

4-acetylbenzamide (2h)[4]

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.15 (s, 1H), 8.05–7.96 (m, 4H), 7.57 (s, 1H), 2.62 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 198.22, 167.60, 139.12, 138.56, 128.56, 128.23, 27.42.

2-bromobenzamide (2i) [1]

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.89 (s, 1H), 7.65 (d, J = 7.9 Hz, 1H), 7.59 (s, 1H), 7.42 (d, J = 4.2 Hz, 2H), 7.38–7.31 (m, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 169.62, 139.77, 133.20, 131.15, 129.04, 127.97, 119.10.

2-methoxybenzamide (2j) [1]

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.86 (dd, J = 7.7, 1.9 Hz, 1H), 7.70 (s, 1H), 7.58 (s, 1H), 7.47 (ddd, J

= 8.4, 7.3, 1.9 Hz, 1H), 7.11 (d, *J* = 7.9 Hz, 1H), 7.03 (td, *J* = 7.6, 0.9 Hz, 1H), 3.88 (s, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.87, 157.74, 132.97, 131.27, 123.05, 120.87, 112.39, 56.22.

3-methoxybenzamide (2k)[2]

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.01 (s, 1H), 7.52–7.44 (m, 2H), 7.41 (s, 1H), 7.36 (t, *J* = 7.9 Hz, 1H), 7.08 (ddd, *J* = 8.2, 2.6, 0.9 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.22, 159.61, 136.17, 129.80, 120.17, 117.53, 113.12, 55.65.

4-methoxybenzamide (2l) [1]

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.95–7.75 (m, 3H), 7.20 (s, 1H), 7.02–6.94 (m, 2H), 3.80 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.96, 162.05, 129.82, 126.94, 113.85, 55.76.

4-methylbenzamide (2m) [3]

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.92 (s, 1H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.29 (s, 1H), 7.24 (d, *J* = 7.9 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.35, 141.55, 131.92, 129.20, 127.98, 21.39.

3-methylbenzamide (2n) [1]

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.94 (s, 1H), 7.71 (s, 1H), 7.70–7.65 (m, 1H), 7.40–7.28 (m, 3H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.53, 137.89, 134.72, 132.23, 128.54, 125.06, 21.41.

3-fluorobenzamide (2o) [3]

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.08 (s, 1H), 7.77–7.71 (m, 1H), 7.67 (ddd, *J* = 10.1, 2.5, 1.6 Hz, 1H), 7.60–7.47 (m, 2H), 7.41–7.33 (m, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.05, 167.03, 163.65, 161.22, 137.18, 137.11, 130.89, 130.81, 124.08, 124.06, 118.70, 118.49, 114.79, 114.57.

4-fluorobenzamide (2p) [3]

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.03 (s, 1H), 7.99–7.92 (m, 2H), 7.43 (s, 1H), 7.31–7.22 (m, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.35, 165.63, 163.16, 131.20, 131.18, 130.63, 130.54, 115.65, 115.43.

2-aminobenzamide (2q)[5]

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.73 (s, 1H), 7.54 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.13 (ddd, *J* = 8.4, 7.1, 1.5 Hz, 1H), 7.07 (s, 1H), 6.69 (dd, *J* = 8.3, 1.1 Hz, 1H), 6.56 (s, 2H), 6.48 (ddd, *J* = 8.1, 7.1, 1.2 Hz, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 171.41, 150.23, 131.98, 128.81, 116.48, 114.48, 113.75.

3-aminobenzamide (2r) [3]

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.73 (s, 1H), 7.14 (s, 1H), 7.09–7.02 (m, 2H), 7.01–6.96 (m, 1H), 6.72–6.66 (m, 1H), 5.19 (s, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 169.22, 149.04, 135.67, 129.01, 116.96, 115.15, 113.58.

4-aminobenzamide (2s) [3]

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.62–7.56 (m, 2H), 7.52 (s, 1H), 6.85 (s, 1H), 6.57–6.49 (m, 2H), 5.60 (s, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.53, 152.13, 129.59, 121.41, 112.93.

thiophene-3-carboxamide (2t)[6]

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.14 (dd, *J* = 3.0, 1.3 Hz, 1H), 7.81 (s, 1H), 7.55 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.50 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.26 (s, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 164.23, 138.44, 129.52, 127.64, 127.02.

isonicotinamide (2u) [1]

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.72 (dd, *J* = 4.6, 1.4 Hz, 2H), 8.26 (s, 1H), 7.78 (dd, *J* = 4.5, 1.5 Hz, 2H), 7.74 (s, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.83, 150.68, 141.74, 121.87.

2-phenylacetamide (2v)[7]

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.50 (s, 1H), 7.34–7.26 (m, 4H), 7.25–7.20 (m, 1H), 6.93 (s, 1H),

3.40 (s, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.81, 136.97, 129.54, 128.62, 126.74, 42.75.

2-(p-tolyl)acetamide (2w) [1]

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.42 (s, 1H), 7.15 (d, J = 8.1 Hz, 2H), 7.10 (d, J = 7.9 Hz, 2H), 6.86 (s, 1H), 3.32 (s, 2H), 2.27 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.91, 135.68, 133.90, 129.38, 129.17, 42.34, 21.11.

1-naphthamide (2x)[8]

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.36–8.30 (m, 1H), 8.09-7.94 (m, 3H), 7.66 (dd, J = 7.0, 1.2 Hz, 1H), 7.64–7.59 (m, 1H), 7.59–7.51 (m, 3H); ^{13}C NMR (101 MHz,DMSO-d_6) δ 171.08, 135.12, 133.67, 130.25, 130.19, 128.64, 127.08, 126.60, 126.06, 125.61, 125.41.

isobutyramide (2y) [3]

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.22 (s, 1H), 6.72 (s, 1H), 2.33 (hept, J = 6.9 Hz, 1H), 0.99 (d, J = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 179.04, 34.19, 19.88.

propionamide (2z)[9]

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.26 (s, 1H), 6.76 (s, 1H), 2.05 (q, J = 7.6 Hz, 2H), 0.97 (t, J = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, DMSO) δ 175.95, 28.64, 10.11.

4-nitrophthalamide(2aa)[11] ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.37 – 8.26 (m, 2H), 8.07 (s, 1H), 8.01 (s, 1H), 7.71 (d, J = 8.3 Hz, 1H), 7.63 (s, 2H). ^{13}C NMR (101 MHz, DMSO-*d6*) δ 169.21, 168.21, 147.56, 143.11, 137.68, 129.62, 124.87, 122.88.

1*H*-indole-3-carboxamide (2ab) [11] ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.65 – 11.52 (m, 1H), 8.21 (d, J = 7.2 Hz, 1H), 8.09 (d, J = 2.7 Hz, 1H), 7.45 (d, J = 7.8 Hz, 2H), 7.18 – 7.10 (m, 2H), 7.02 – 6.72 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.23, 136.70, 129.00, 126.72, 122.29, 121.56, 120.85, 112.27, 110.93.

pyrazinamide (2ac) [11] ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.19 (d, J = 1.5 Hz, 1H), 8.85 (d, J = 2.5 Hz, 1H), 8.71 (dd, J = 2.5, 1.5 Hz, 1H), 8.28 (s, 1H), 7.88 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 165.59, 147.85, 145.50, 144.07, 143.84.

5. References

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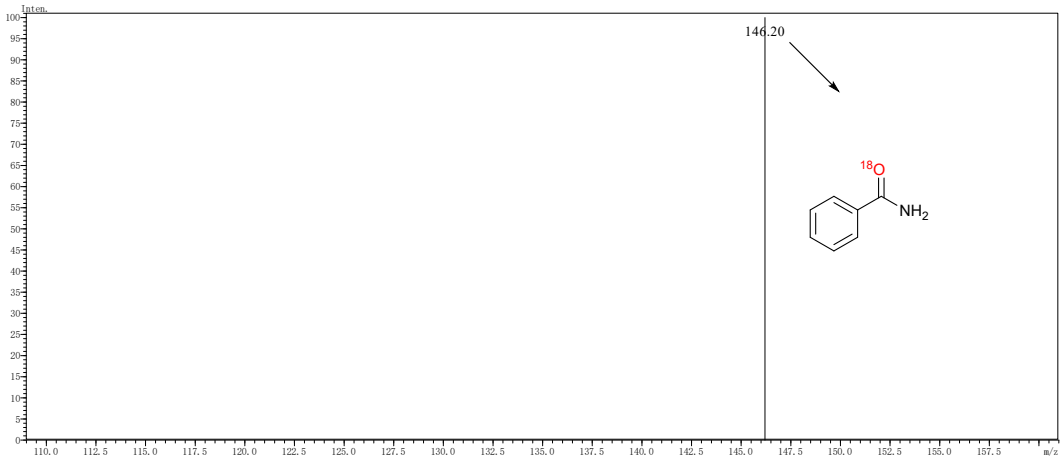
11. (a) Ghosh, K.; Iqubal, M. A.; Molla, R. A. ; Mishra, A.; Kamaluddin ; Islam, S. M. *Catal. Sci. Technol.*, **2015**, *5*, 1606-1622; (b) Guo,B.; de Vries, J. G.; Otten, E. *Chem. Sci.*, **2019**,*10*, 10647-10652; (c) Nedra, T., Abdullah, S. A.; and Naceur H. *Asian J Chem.,* 2019, 31, 1398-1404.

6. MS data of $H_2{}^{18}O$ Labeling Experiments

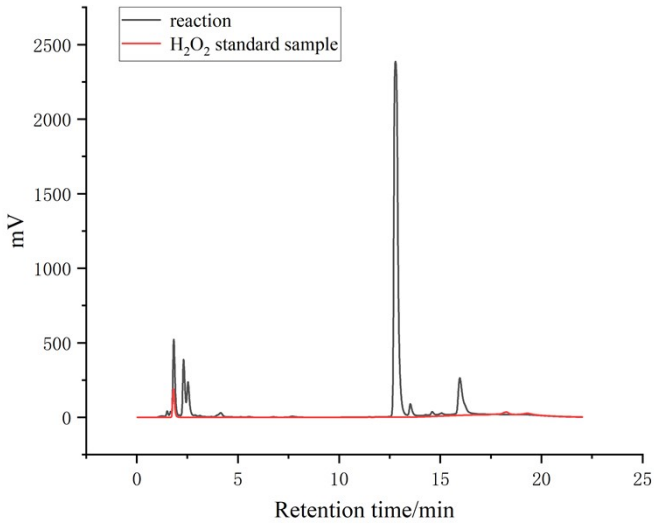


7. HPLC validation experiment of hydrogen peroxide

The chromatographic conditions: HPLC were recorded on an SHIMDZU LC-20A instrument with a HP5-MS 30 m x 0.25 mm Capillary Apolar Columns. Mobile phase: A phase is water, B phase is methanol; The detection wavelength was 240 nm; Injection volume: 10 μL; The gradient elution procedure is shown in Table. HPLC results showed that H_2O_2 was detected at the retention time of 1.81

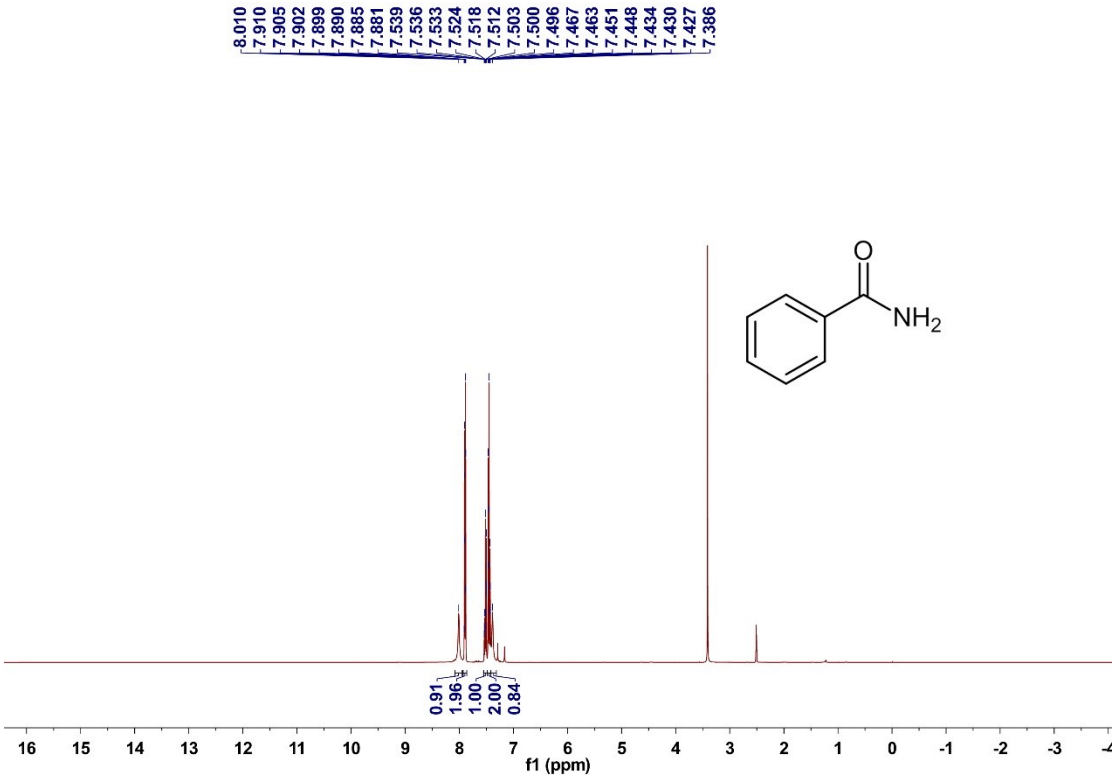
Table 1 HPLC gradient elution procedure

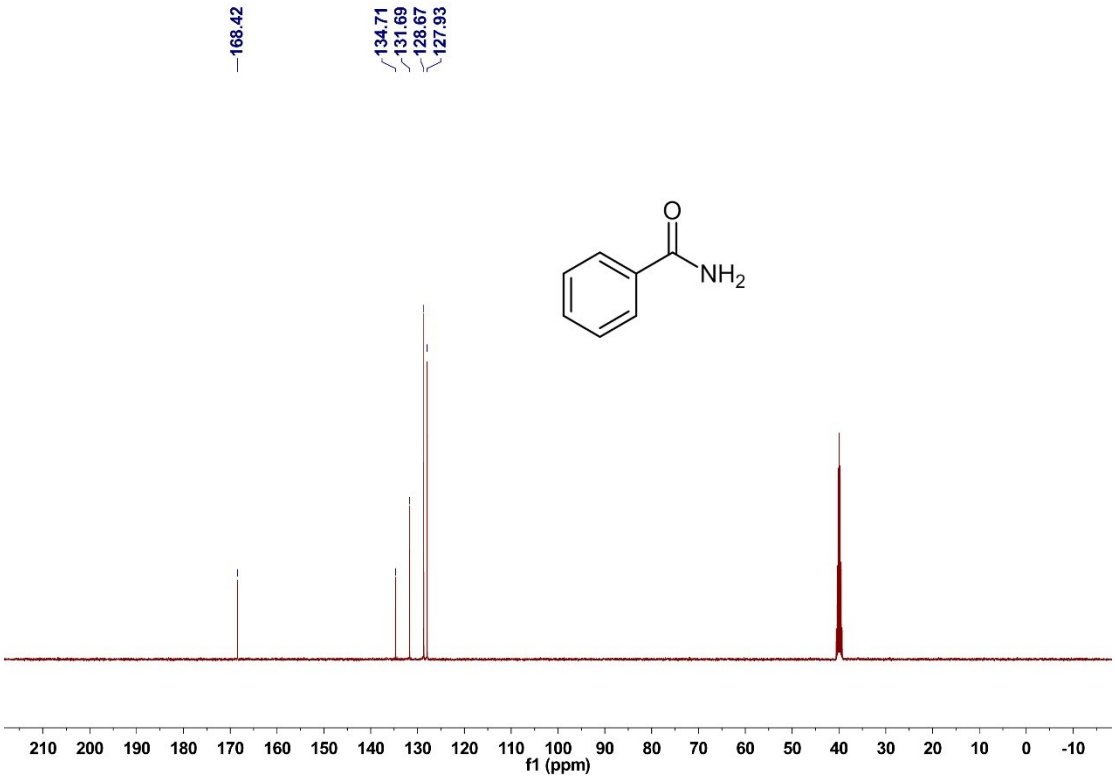
Time/min	flow rate/(mL/min)	A phase (water) volume fraction (%)	B phase (methanol) volume fraction (%)
0.0	1.0	92	8
5.0	1.0	92	8
10.0	1.0	40	60
15.0	1.0	40	60
18.0	1.0	92	8
22.0	1.0	92	8



1H NMR and 13C NMR spectra for the products

2a

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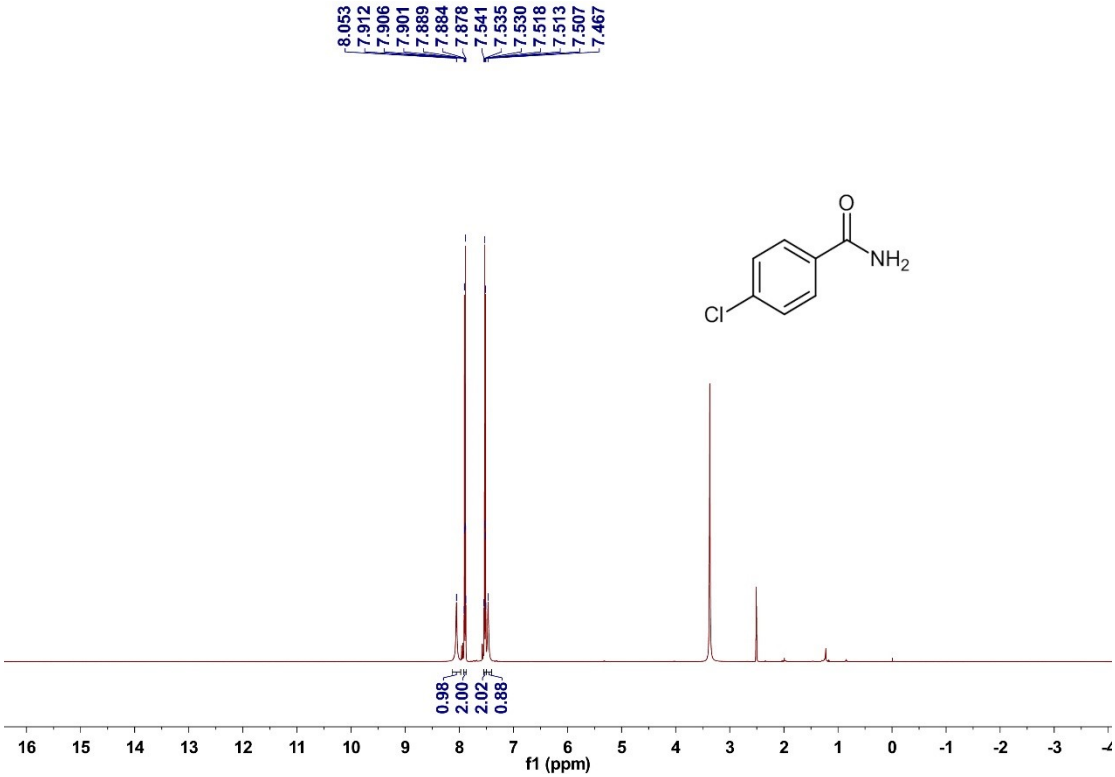
f1 (ppm)

2b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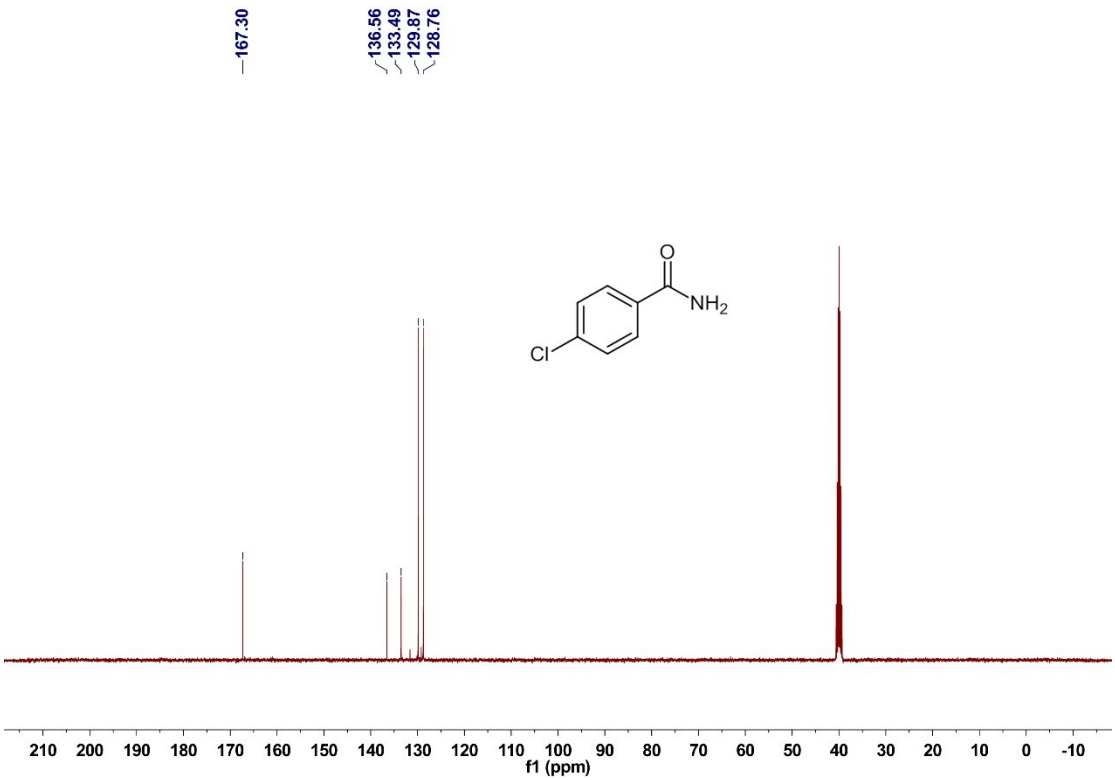
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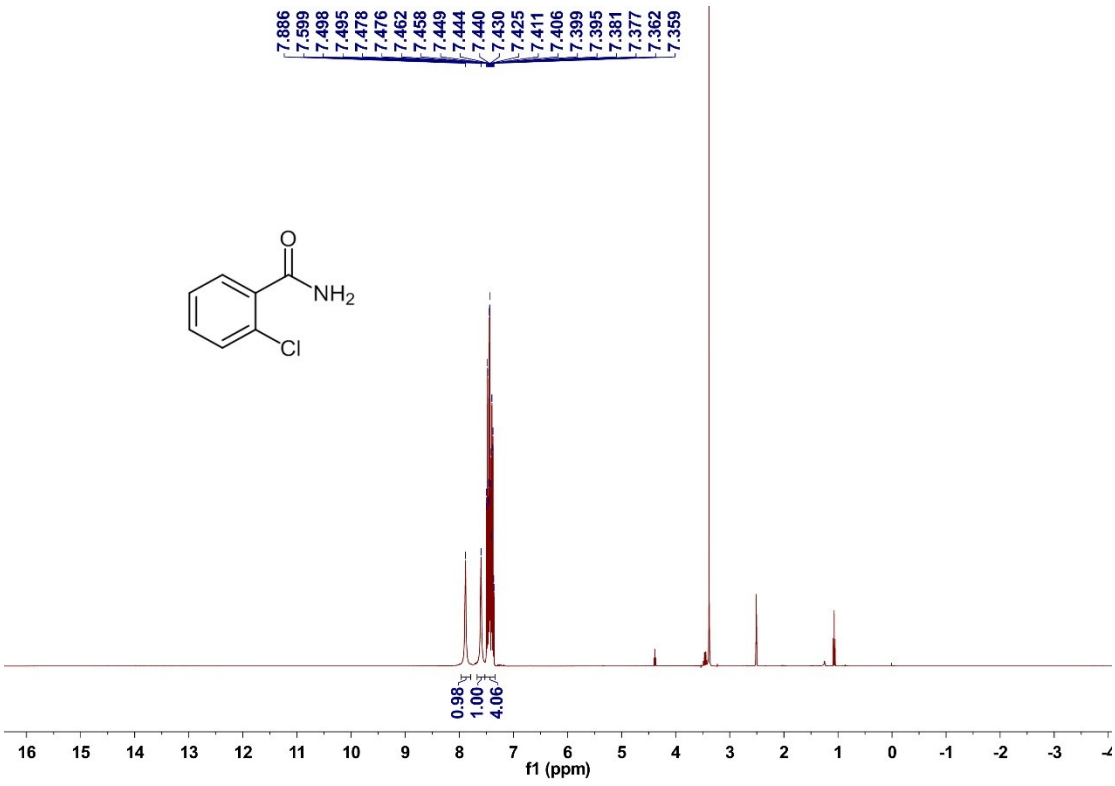
2c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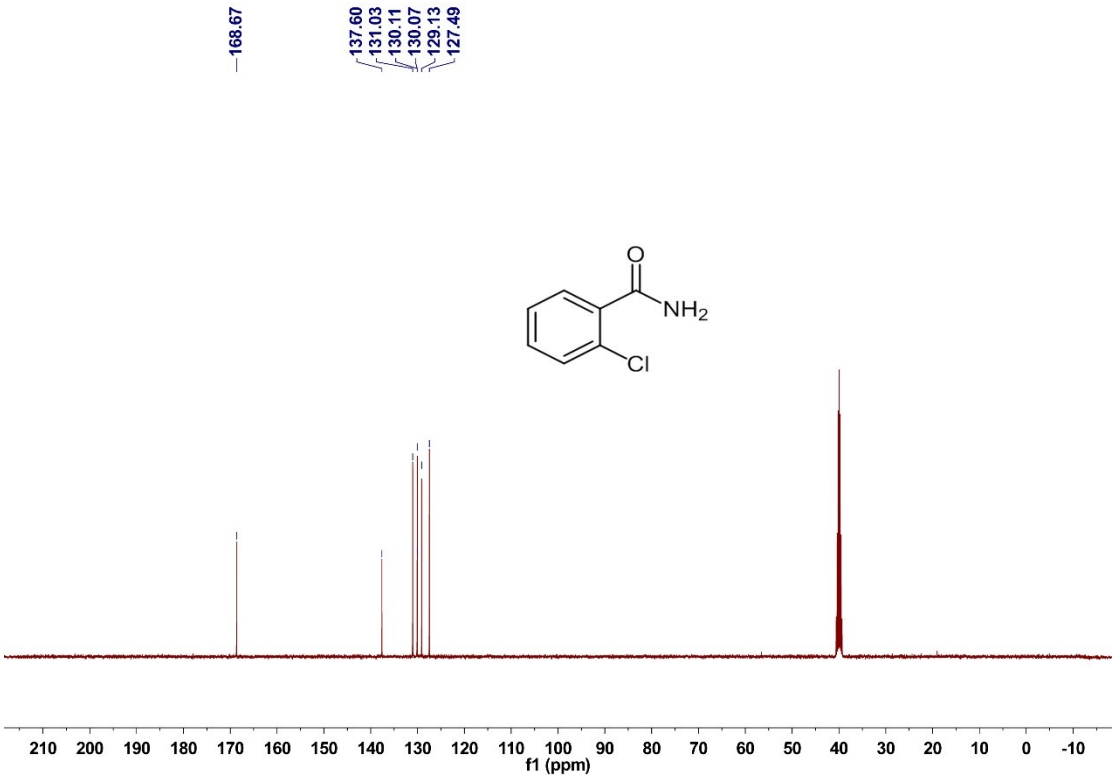
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Cl
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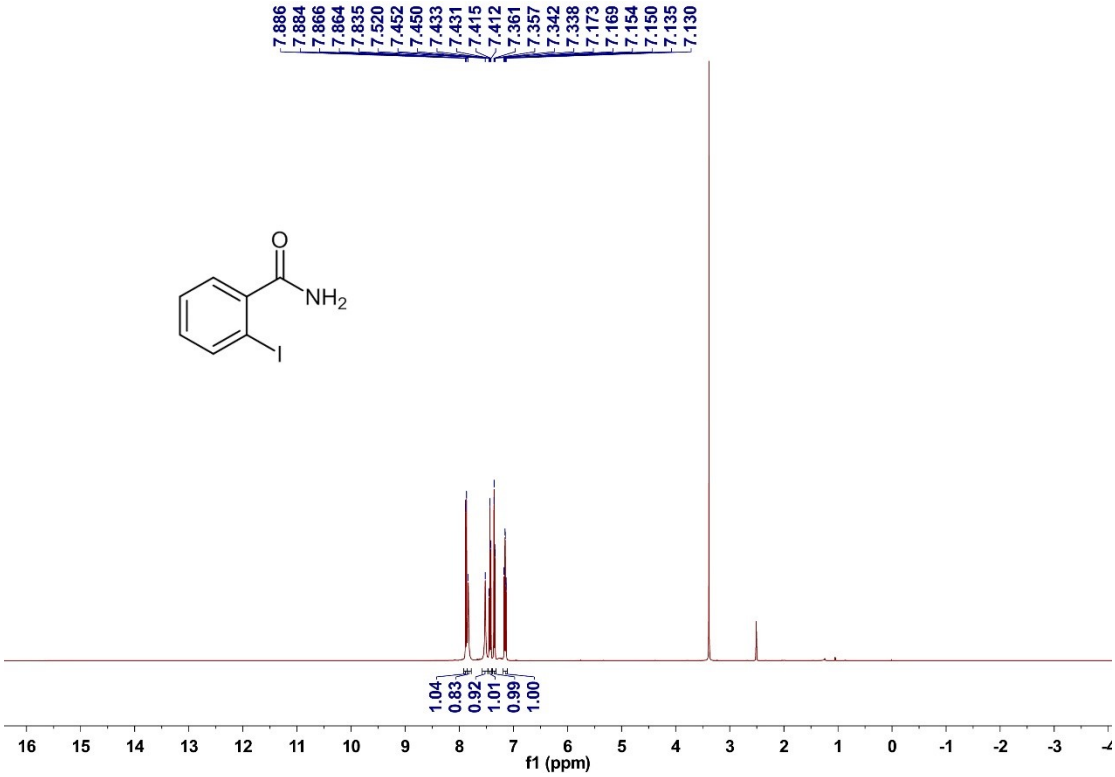
f1 (ppm)

2d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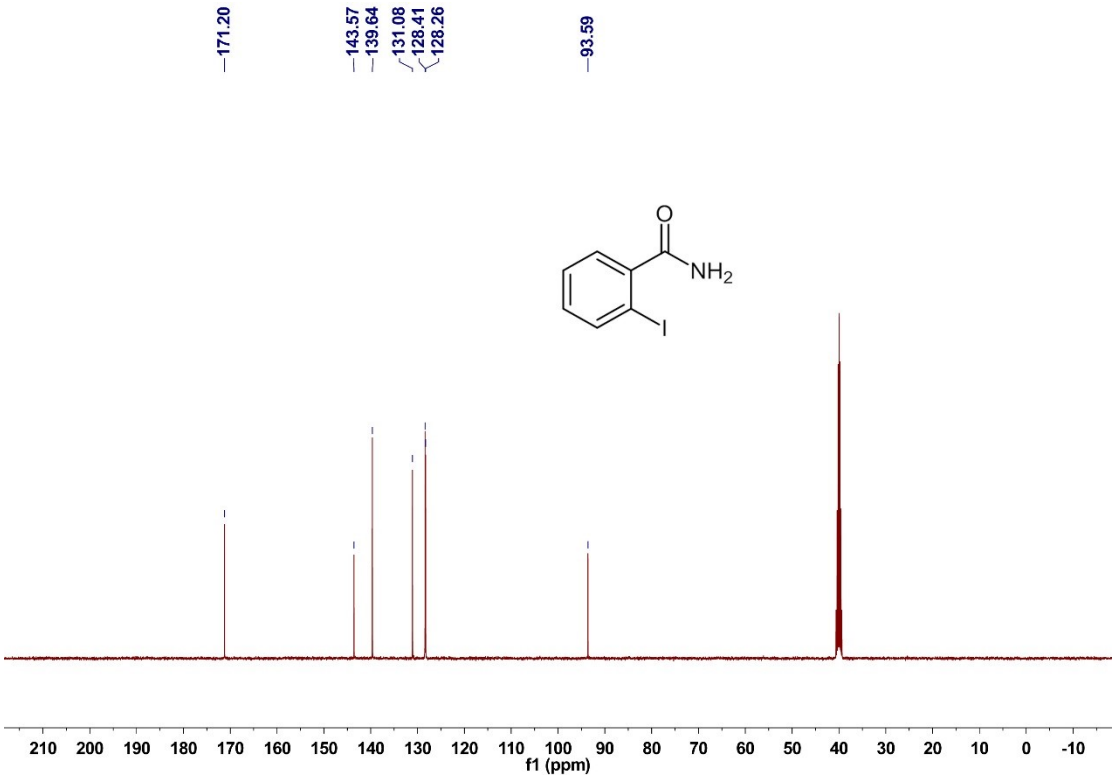
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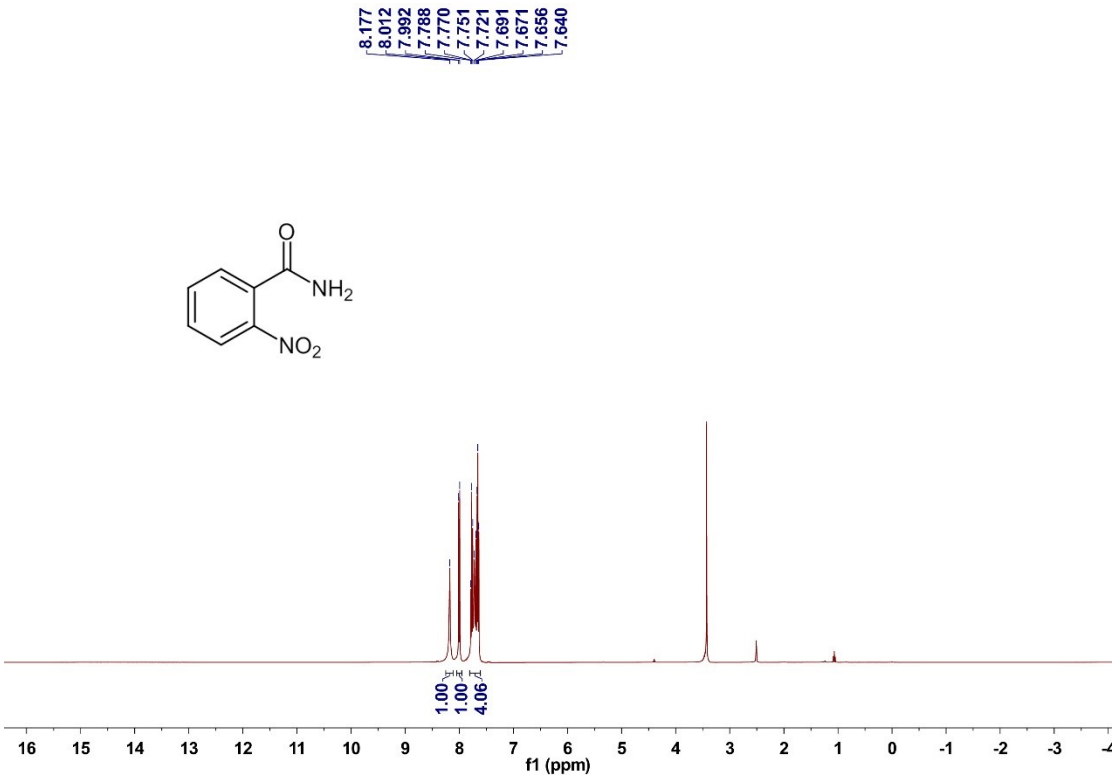
f1 (ppm)

2e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7.640
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NO2
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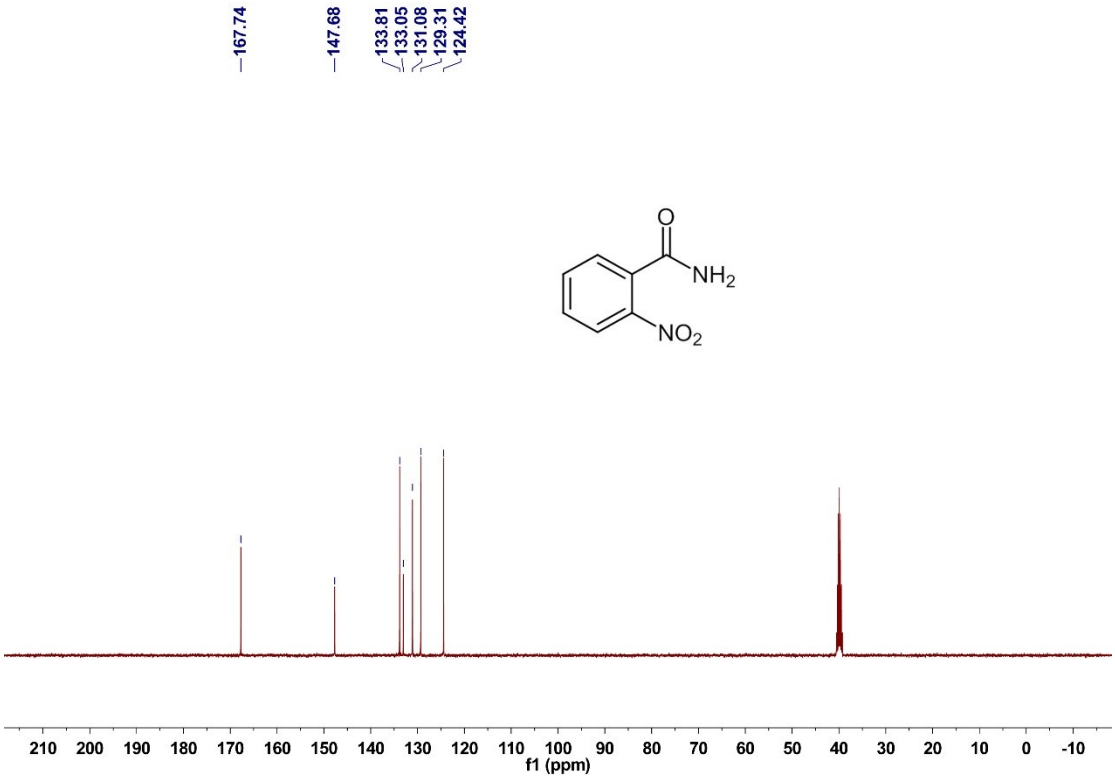
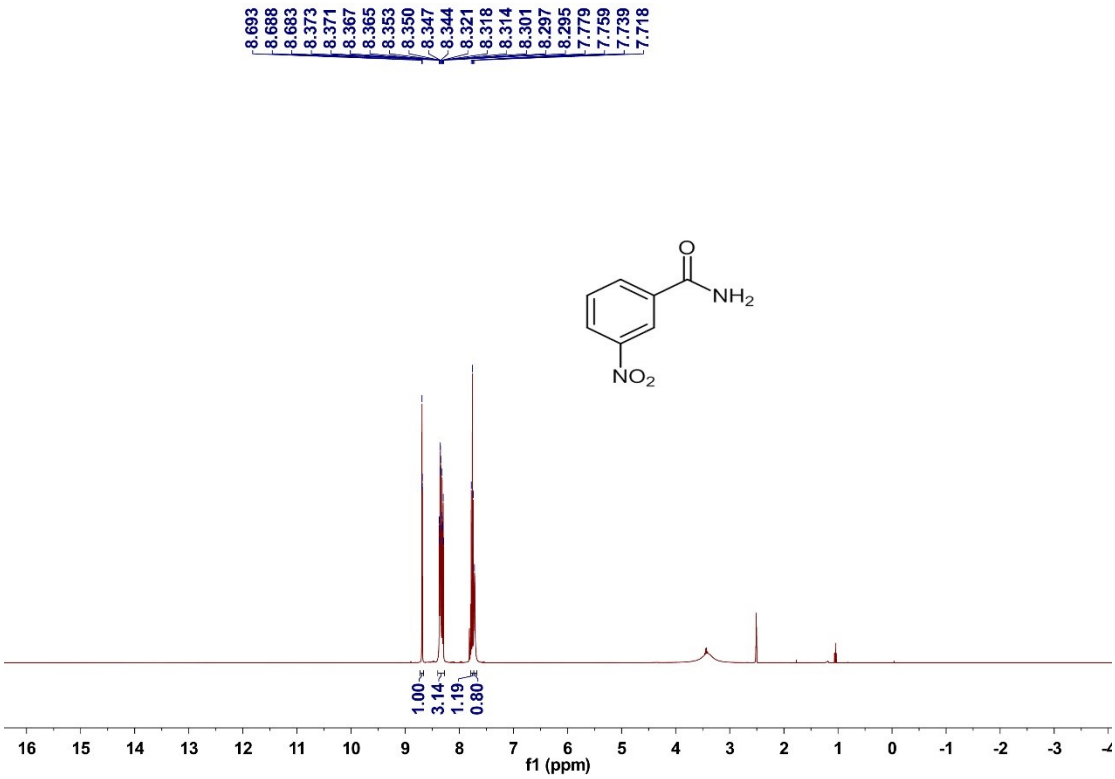
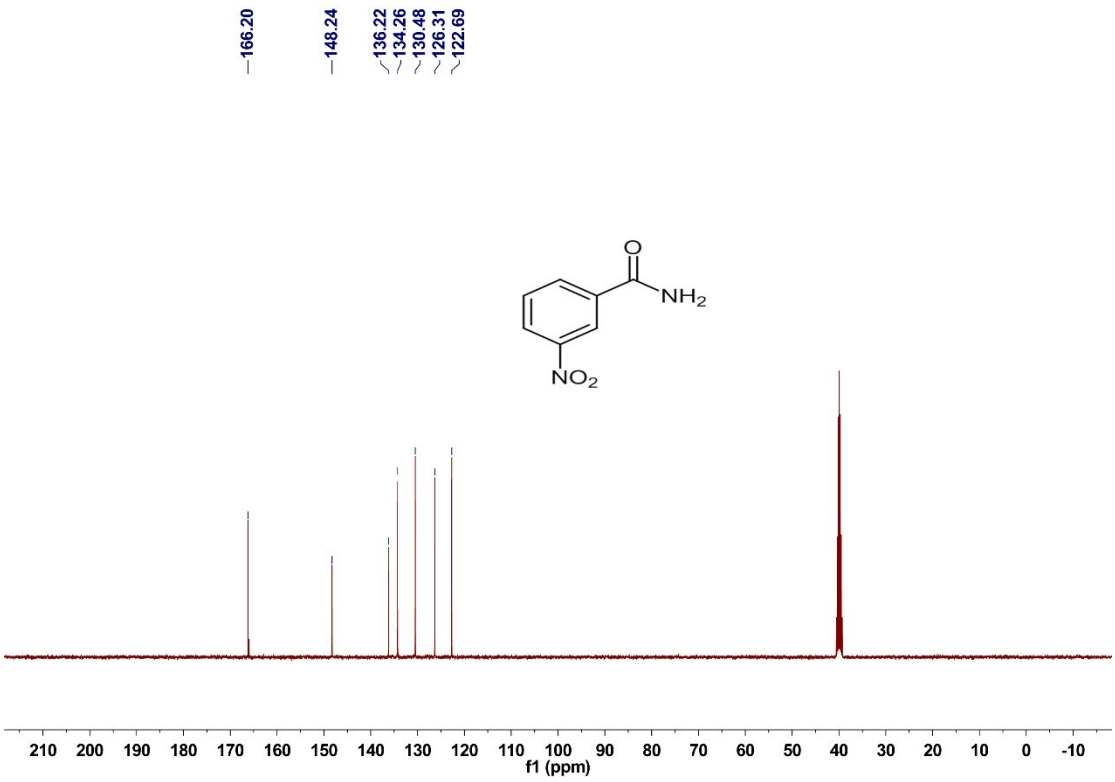
1.00
4.06
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

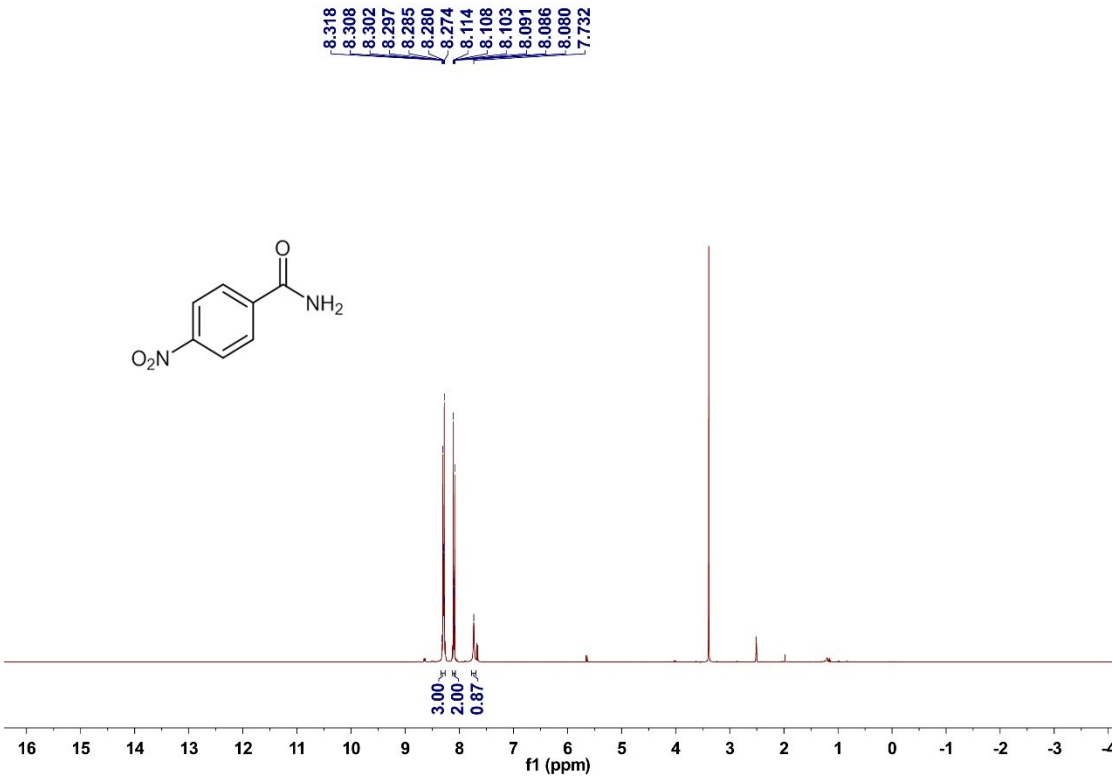

167.74
147.68
133.81
133.05
131.08
129.31
124.42
O
NH2
NO2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

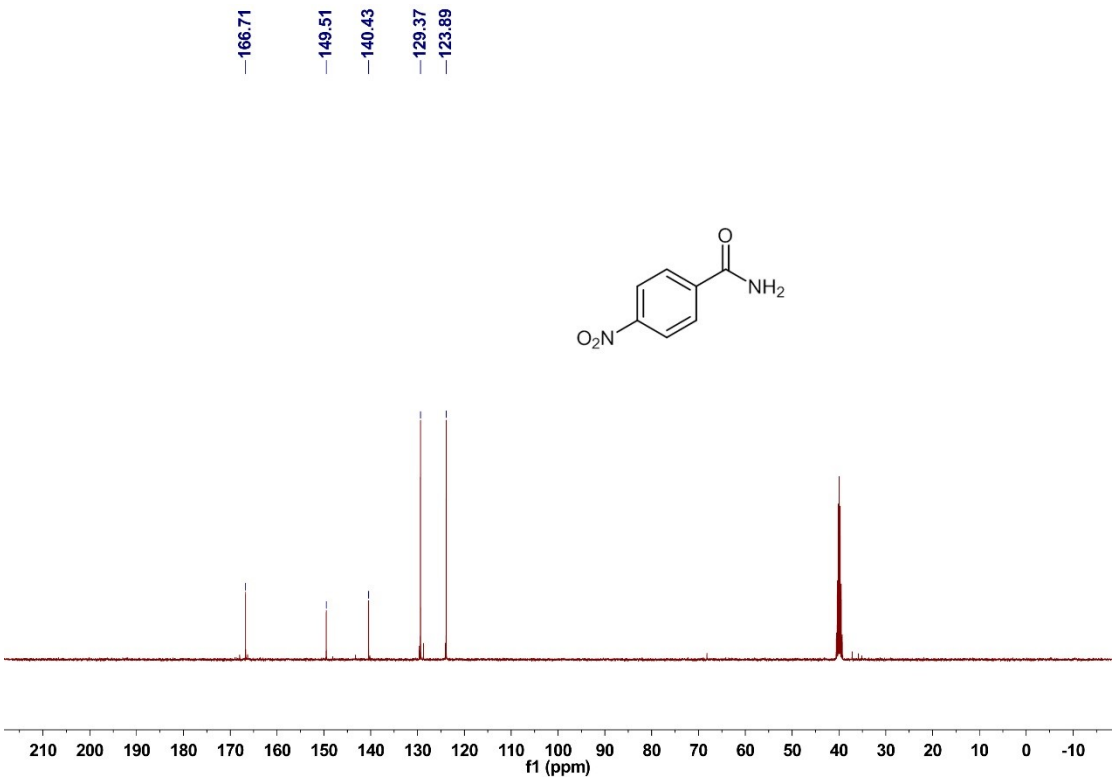
2f


8.693
8.688
8.683
8.373
8.371
8.367
8.365
8.353
8.350
8.347
8.344
8.321
8.318
8.314
8.301
8.297
8.295
7.779
7.759
7.739
7.718
O
NH2
NO2
1.00
3.14
1.19
0.80
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

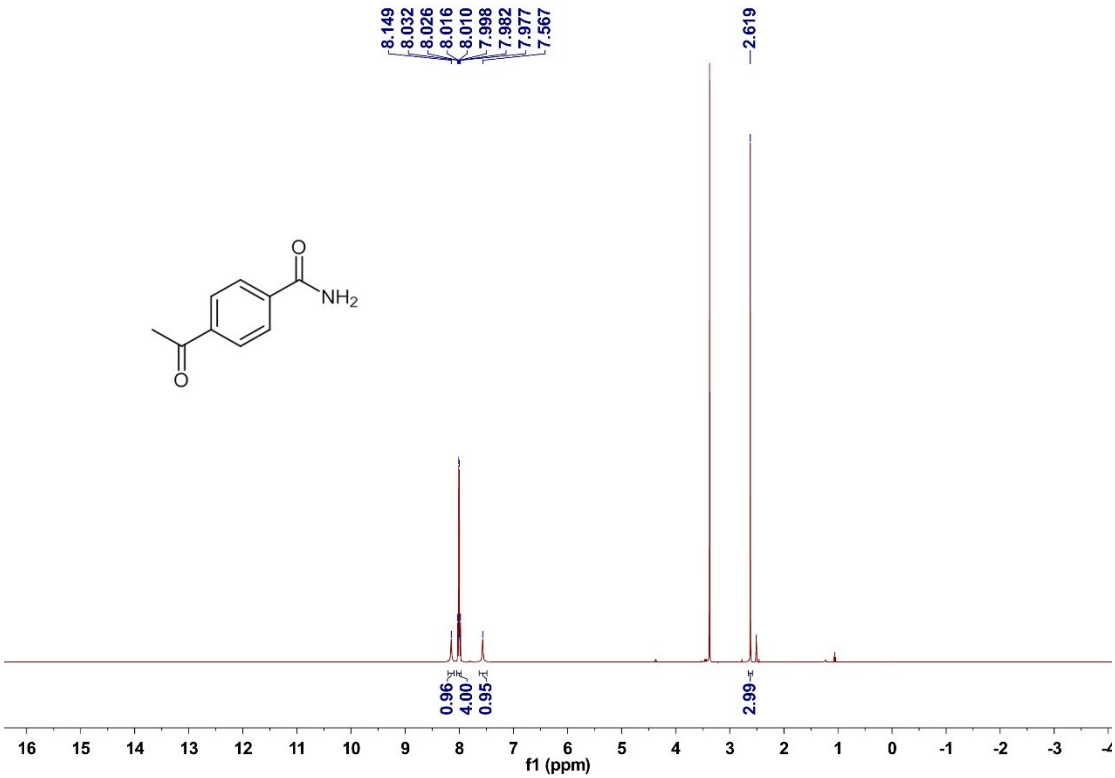

166.20
148.24
136.22
134.26
130.48
126.31
122.69
O
NH2
NO2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

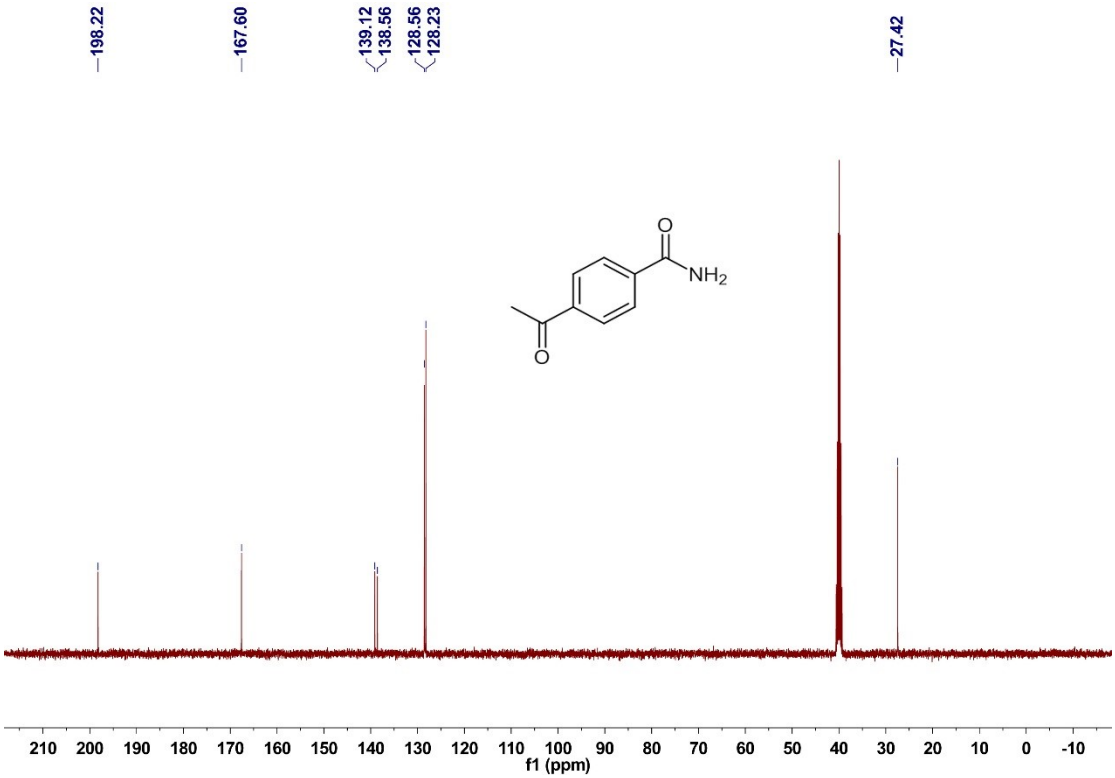
2g


8.318
8.308
8.302
8.297
8.285
8.280
8.274
8.114
8.108
8.103
8.091
8.086
8.080
7.732
O
NH2
O2N
3.00
2.00
0.87
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

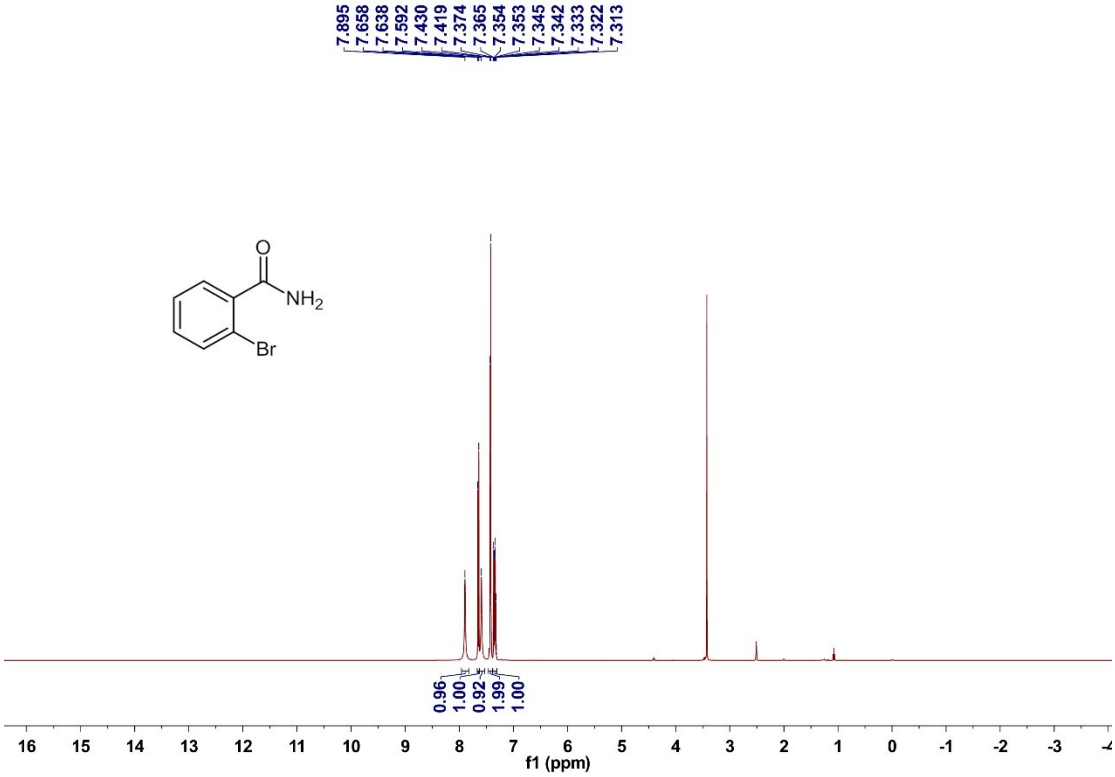

166.71
149.51
140.43
129.37
123.89
O
NH2
O2N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

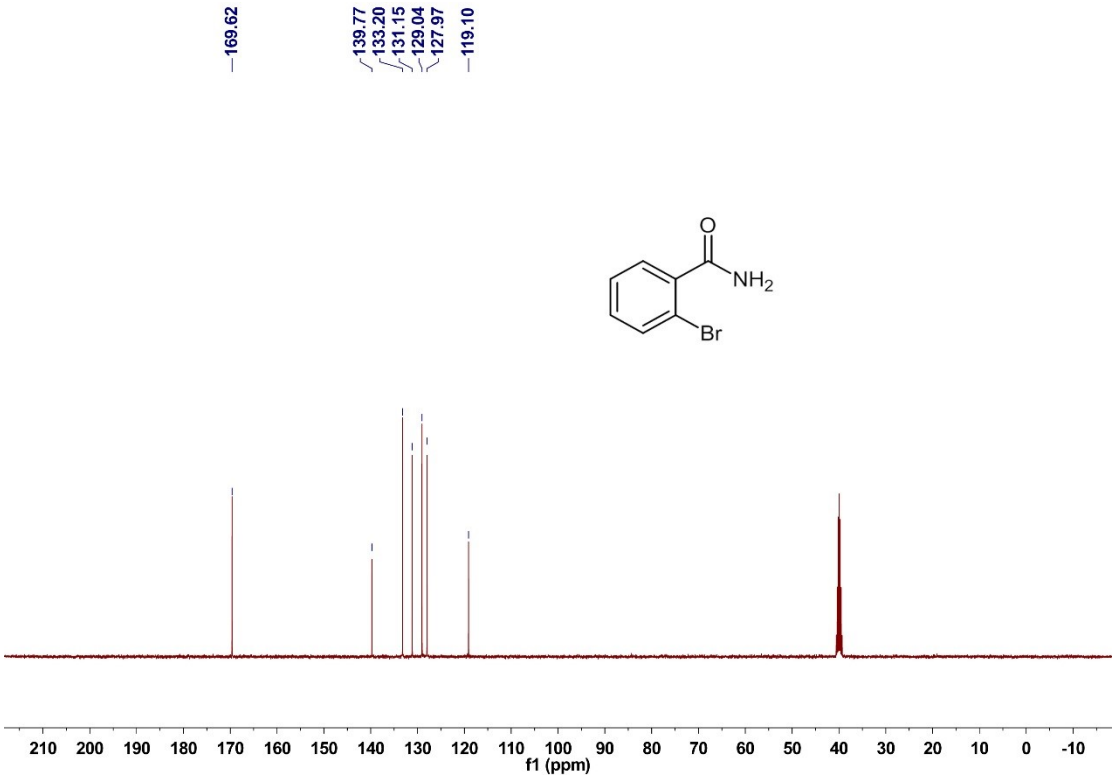
2h


8.149
8.032
8.026
8.016
8.010
7.998
7.982
7.977
7.567
2.619
O
NH2
O
0.96
4.00
0.95
2.99
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

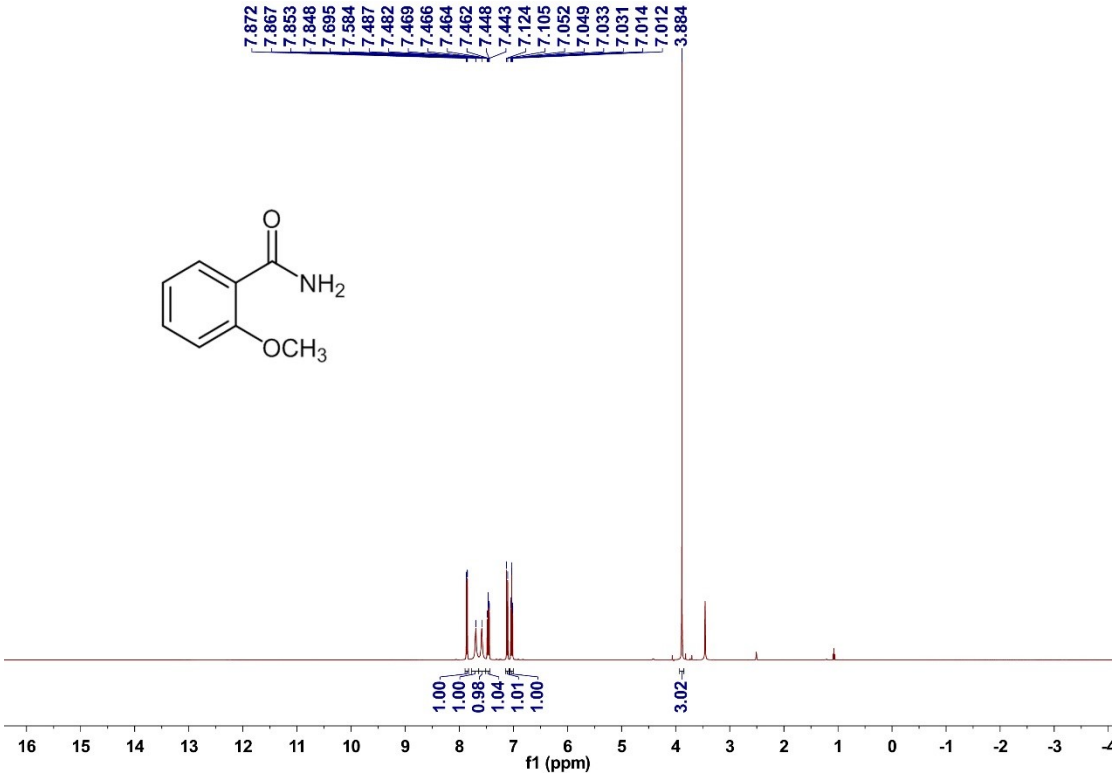

198.22
167.60
139.12
138.56
128.56
128.23
27.42
O
NH2
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

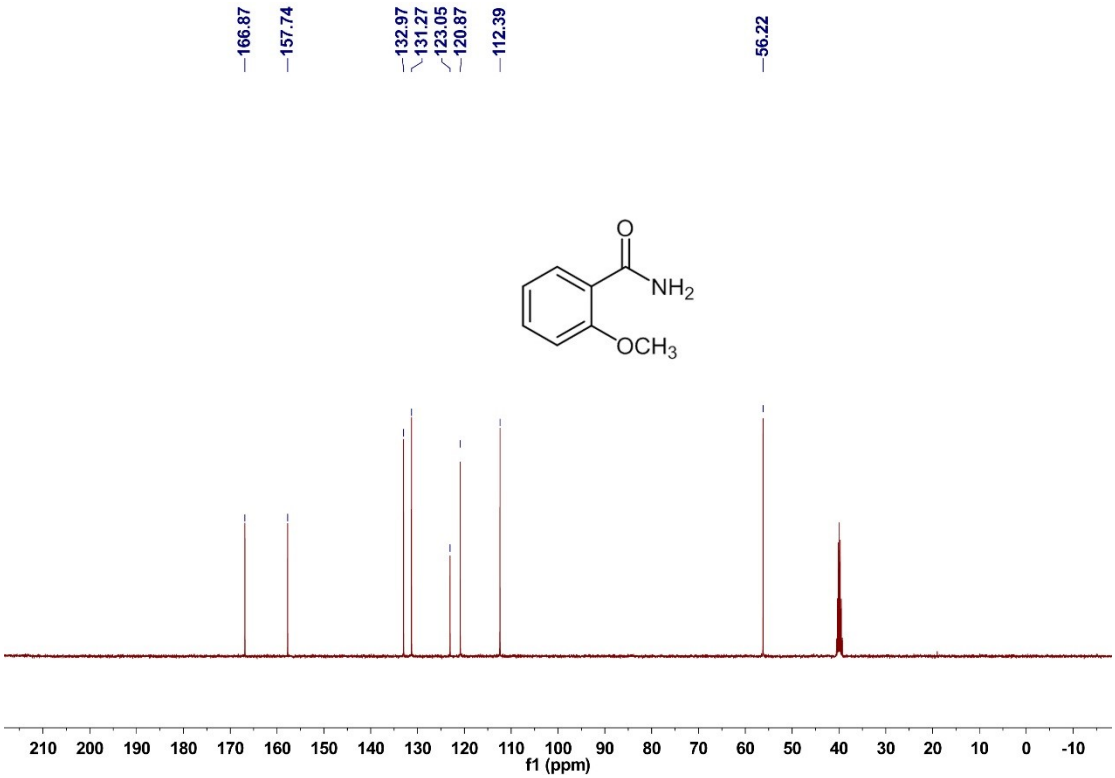
2i


7.895
7.658
7.638
7.592
7.430
7.419
7.374
7.365
7.354
7.353
7.345
7.342
7.333
7.322
7.313
O
NH2
Br
0.96
1.00
0.92
1.99
1.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

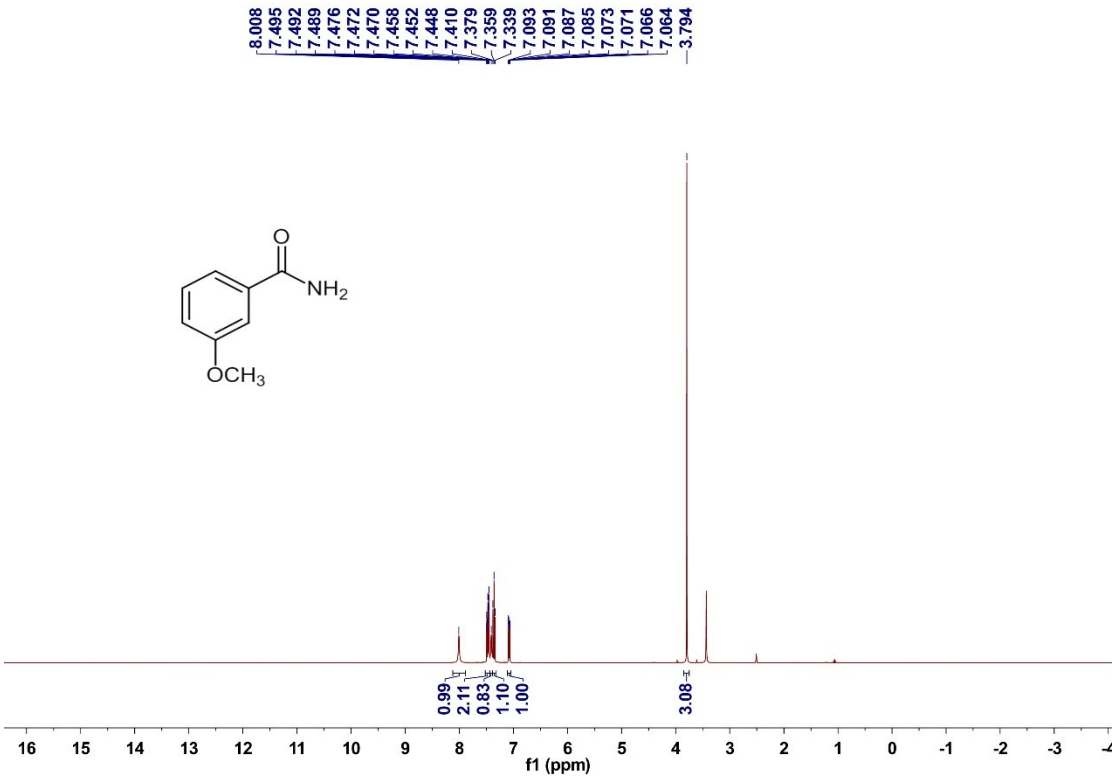

169.62
139.77
133.20
131.15
129.04
127.97
119.10
O
NH2
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

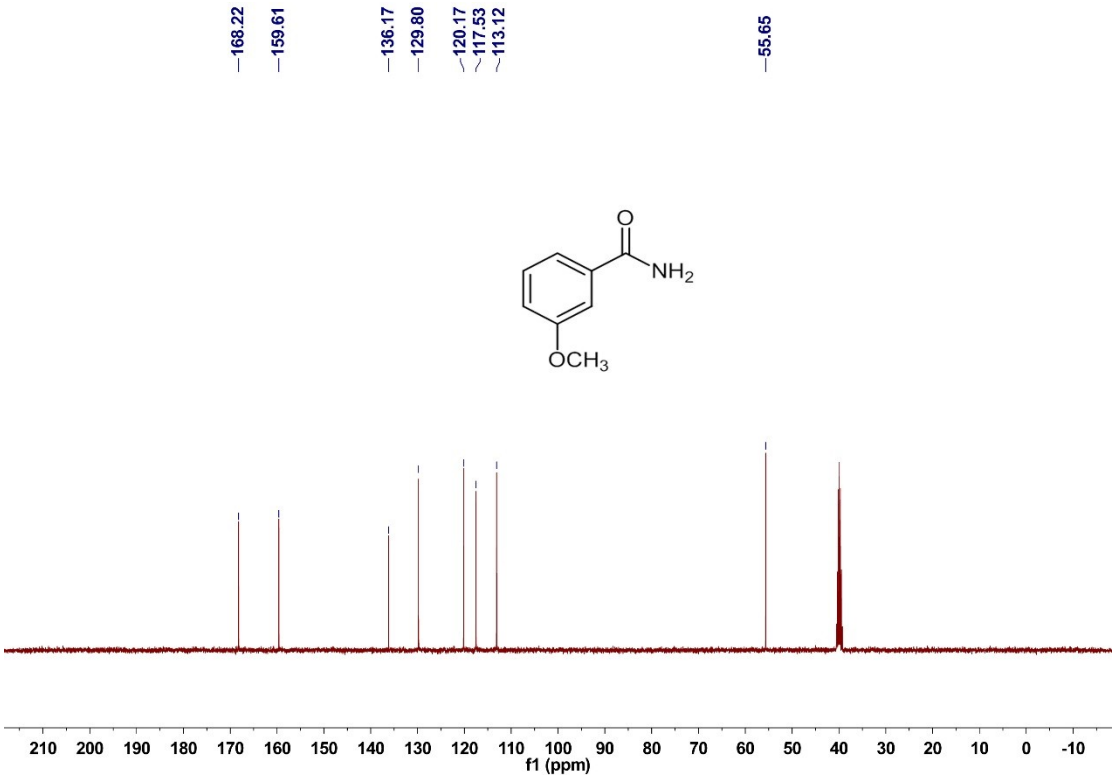
2j


7.872
7.867
7.853
7.848
7.695
7.584
7.487
7.482
7.469
7.466
7.464
7.462
7.448
7.443
7.124
7.105
7.052
7.049
7.033
7.031
7.014
7.012
3.884
O
NH2
OCH3
1.00
1.00
0.98
1.04
1.01
1.00
3.02
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

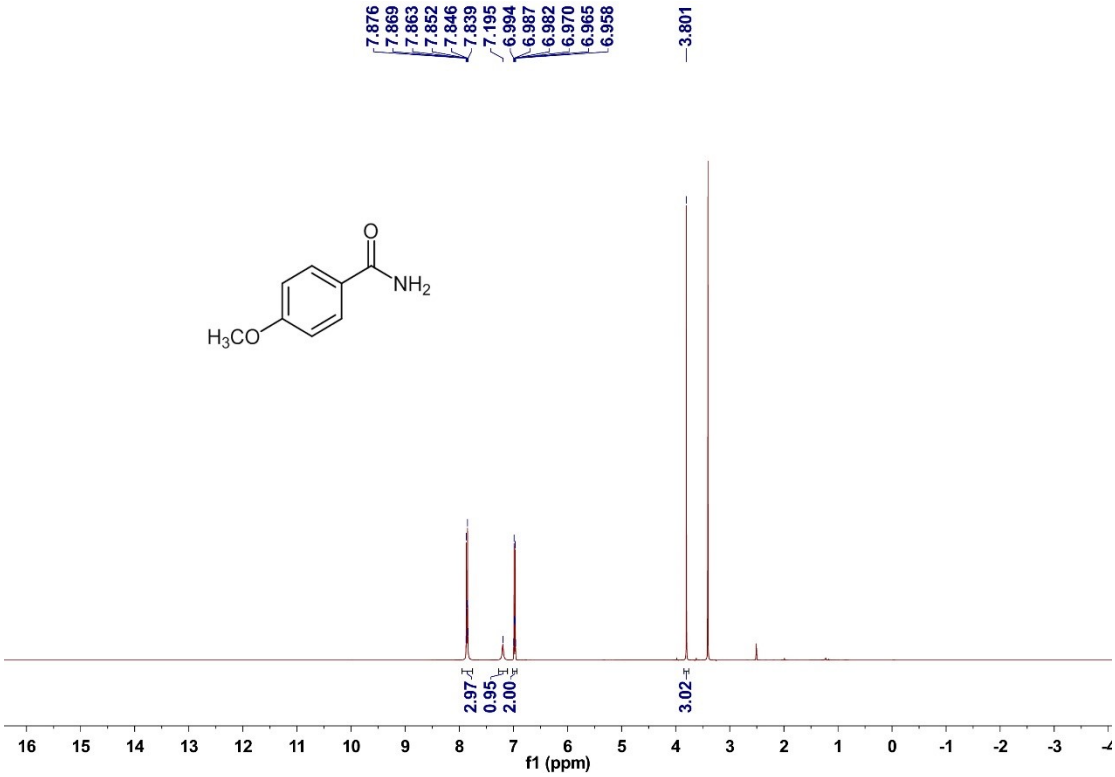

166.87
157.74
132.97
131.27
123.05
120.87
112.39
56.22
O
NH2
OCH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

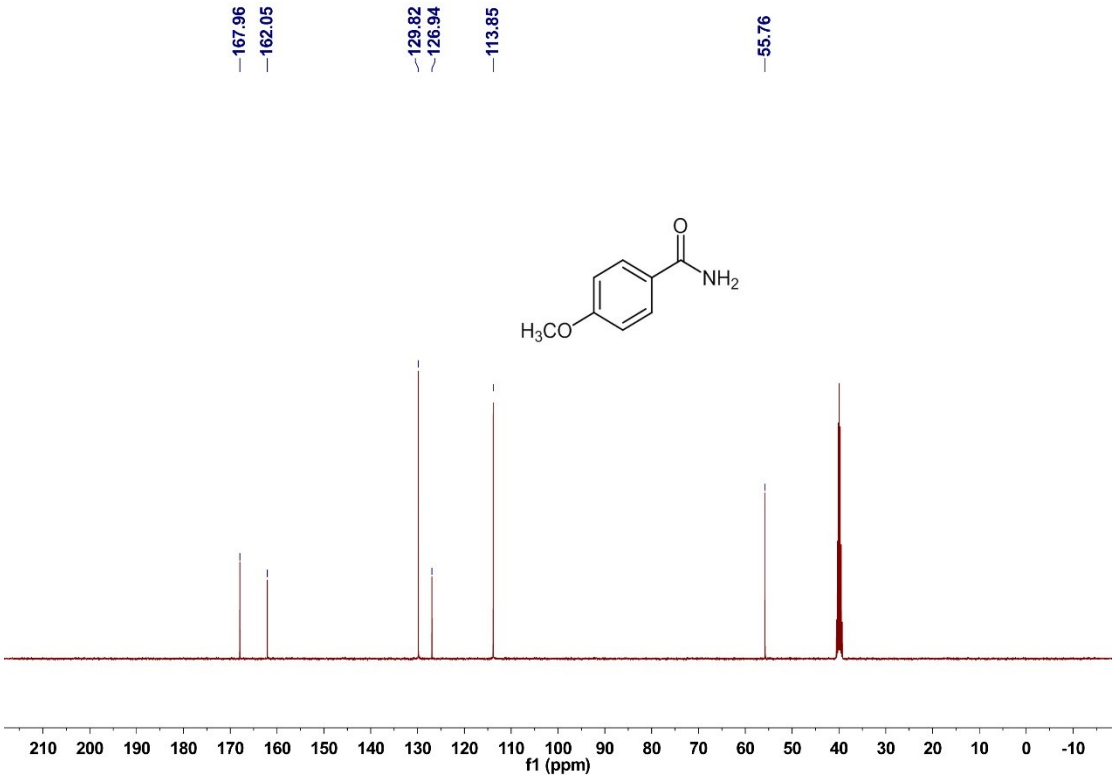
2k


8.008
7.495
7.492
7.489
7.476
7.472
7.470
7.458
7.452
7.448
7.410
7.379
7.359
7.339
7.093
7.091
7.087
7.085
7.073
7.071
7.066
7.064
3.794
O
NH2
OCH3
0.99
2.11
0.83
1.10
1.00
3.08
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

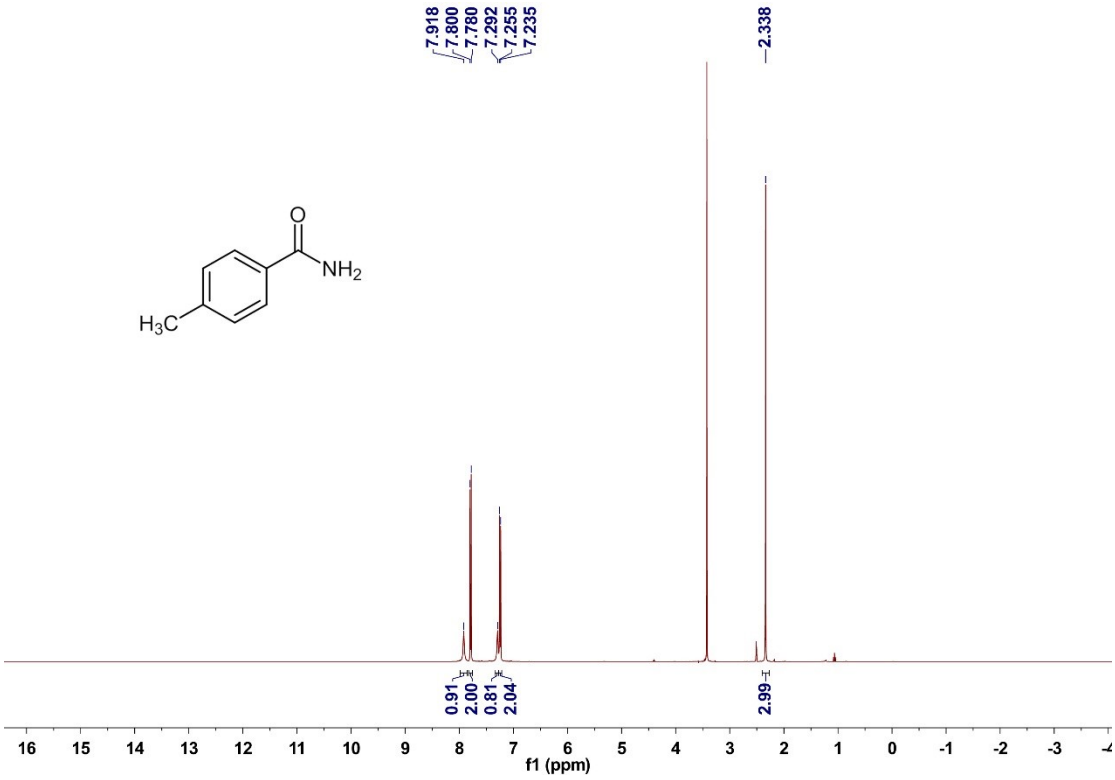

168.22
159.61
136.17
129.80
120.17
117.53
113.12
55.65
O
NH2
OCH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

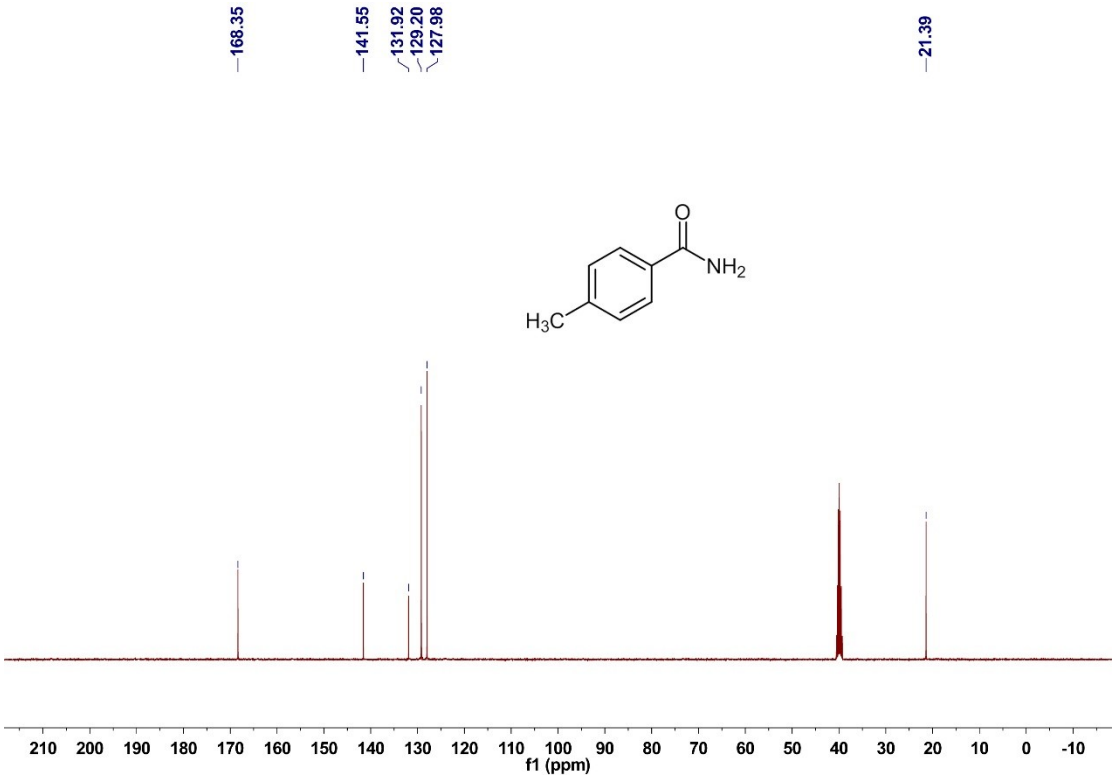
2l


7.876
7.869
7.863
7.852
7.846
7.839
7.195
6.994
6.987
6.982
6.970
6.965
6.958
3.801
O
NH2
H3CO
2.97
0.95
2.00
3.02
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

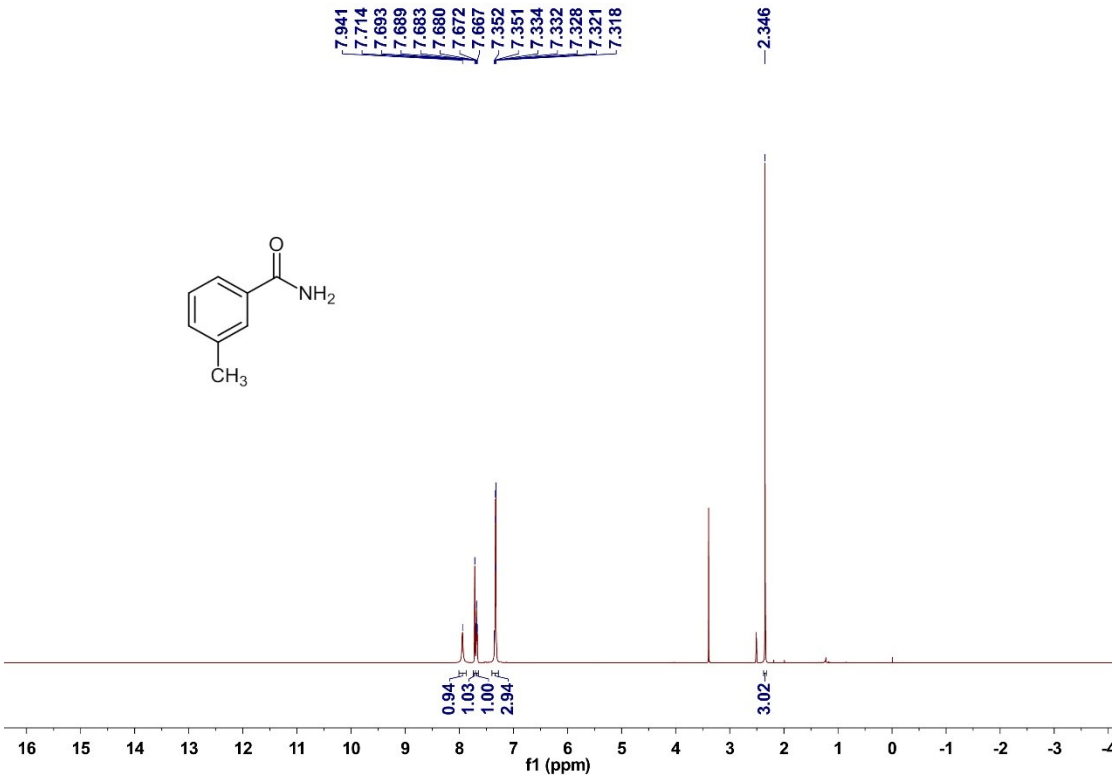

167.96
162.05
129.82
126.94
113.85
55.76
O
NH2
H3CO
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

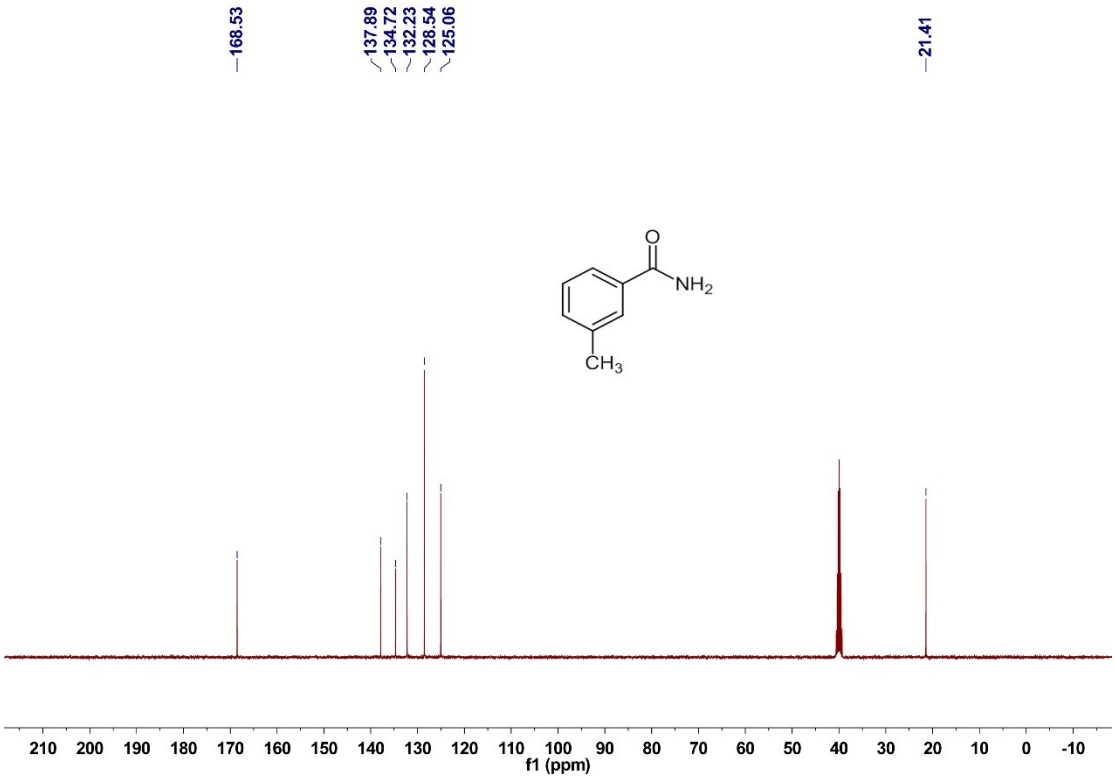
2m


7.918
7.800
7.780
7.292
7.255
7.235
2.338
O
NH2
H3C
0.91
2.00
0.81
2.04
2.99
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

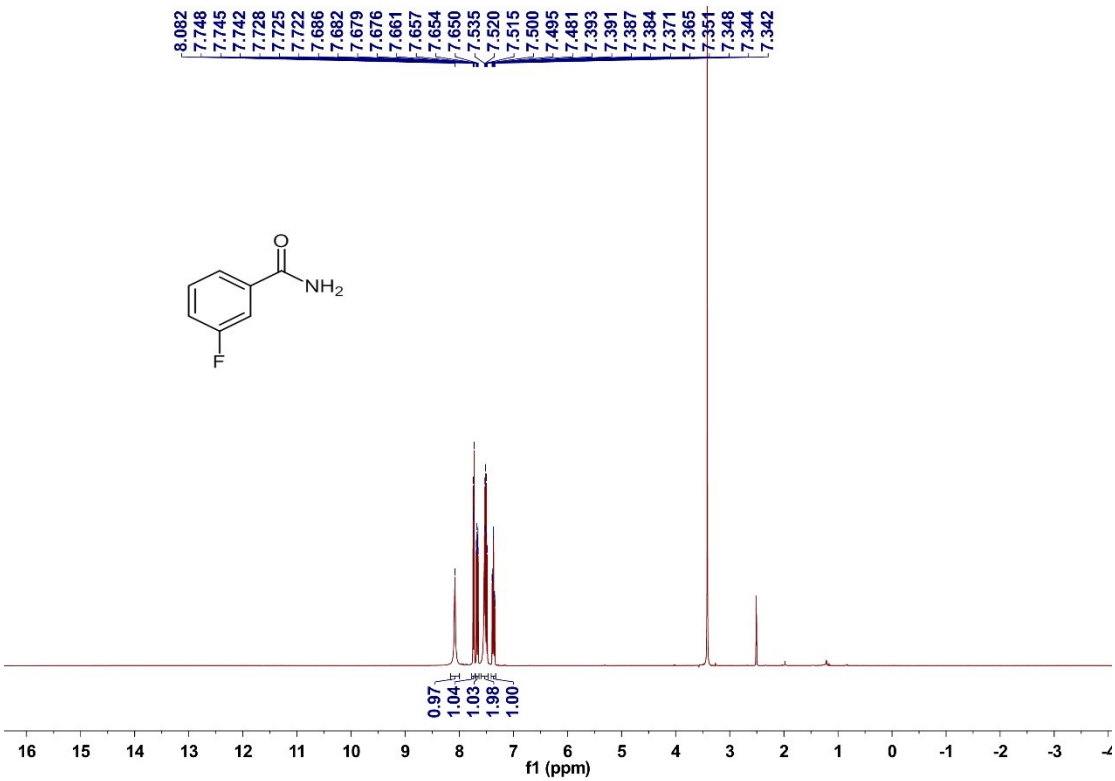

168.35
141.55
131.92
129.20
127.98
21.39
O
NH2
H3C
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

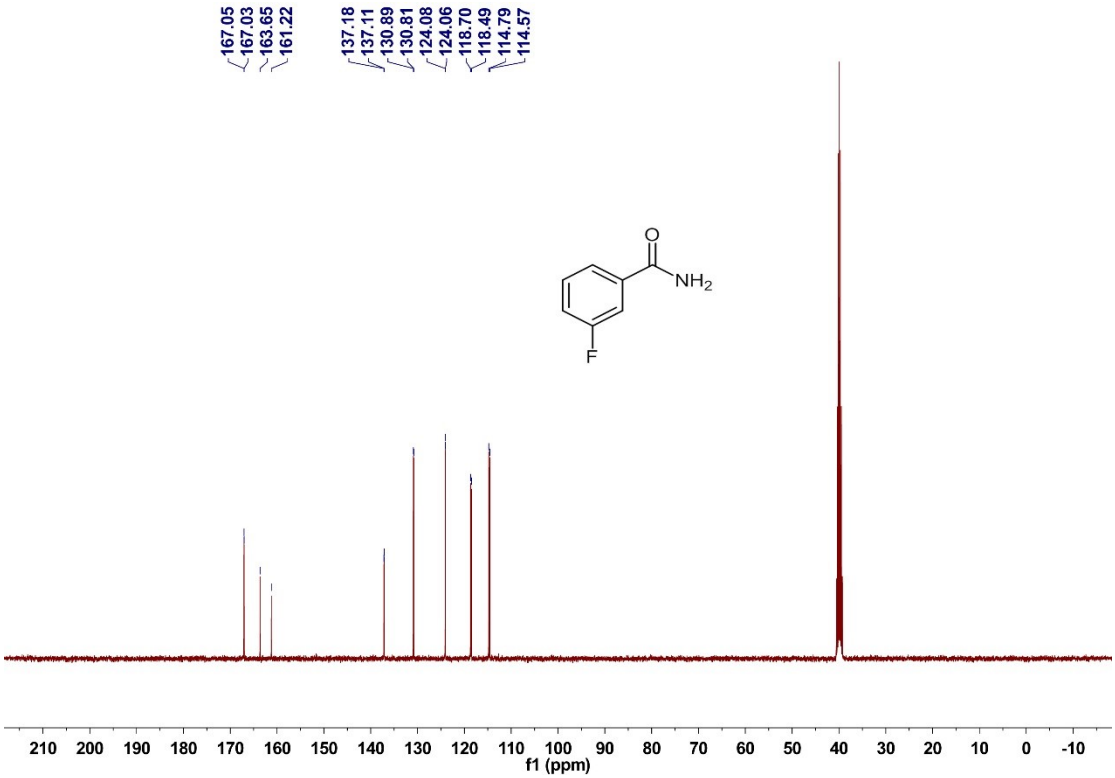
2n


7.941
7.714
7.693
7.689
7.683
7.680
7.672
7.667
7.352
7.351
7.334
7.332
7.328
7.321
7.318
2.346
O
NH2
CH3
0.94
1.03
1.00
2.94
3.02
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

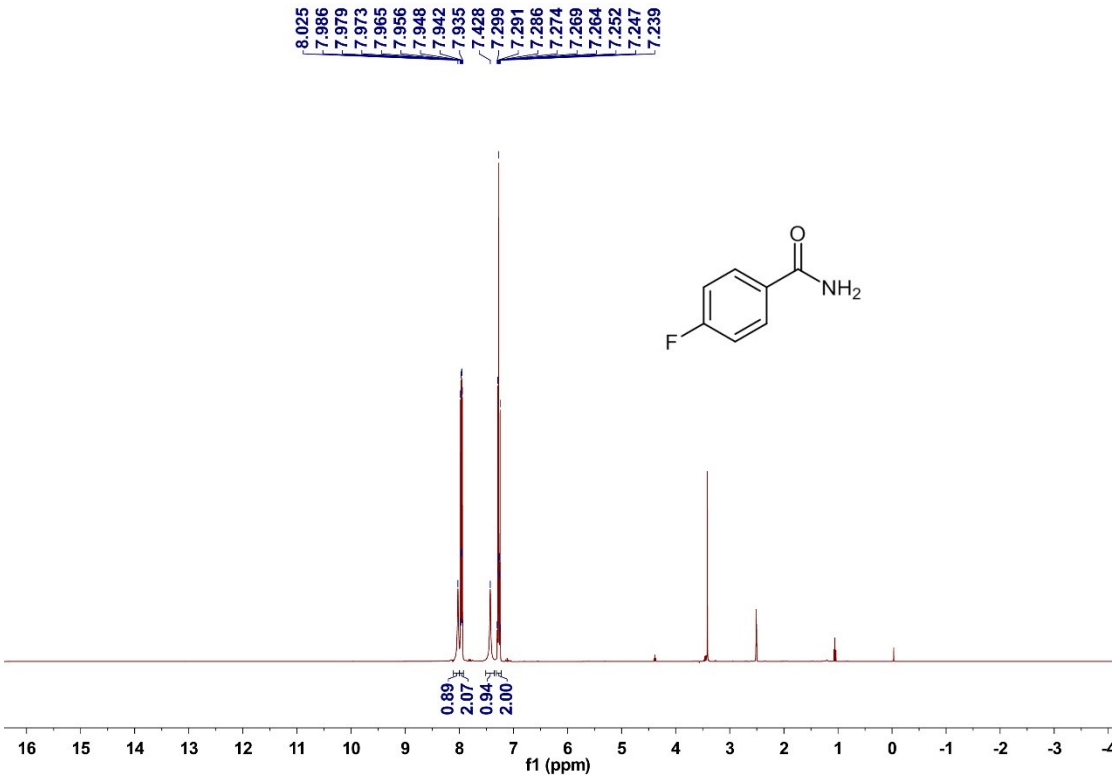

168.53
137.89
134.72
132.23
128.54
125.06
21.41
O
NH2
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

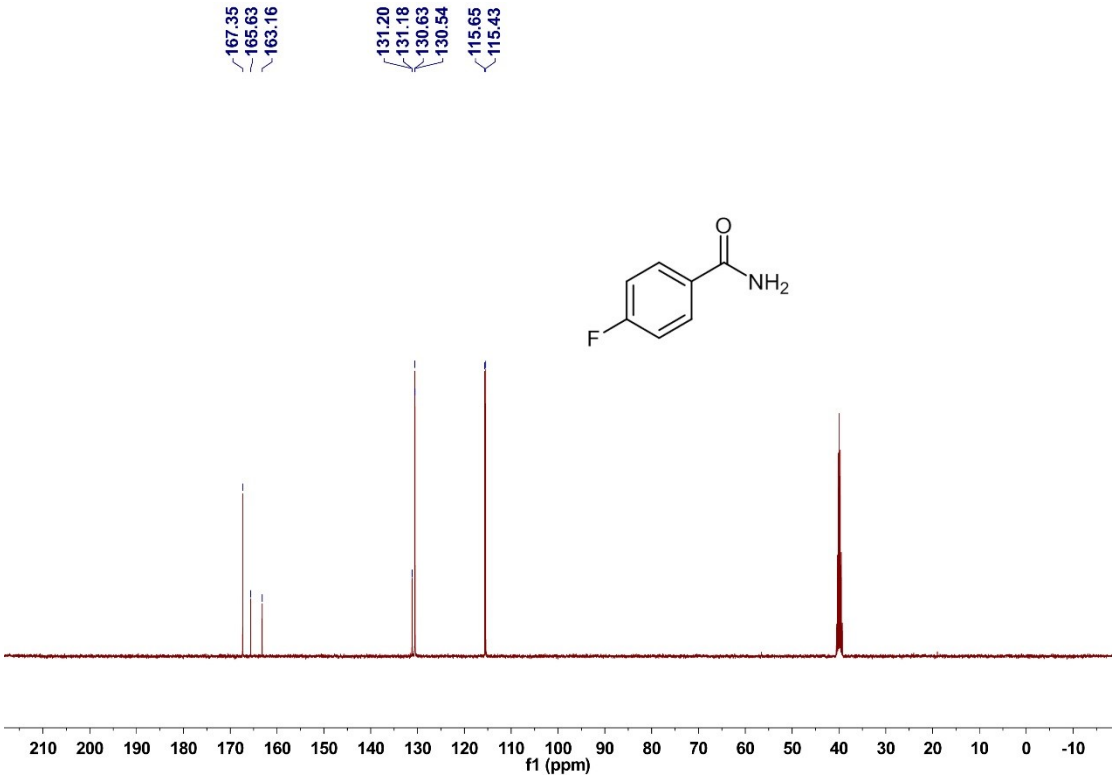
2o


8.082
7.748
7.745
7.742
7.728
7.725
7.722
7.686
7.682
7.679
7.676
7.661
7.657
7.654
7.650
7.535
7.520
7.515
7.500
7.495
7.481
7.393
7.391
7.387
7.384
7.371
7.365
7.351
7.348
7.344
7.342
O
NH2
F
0.97
1.04
1.03
1.98
1.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

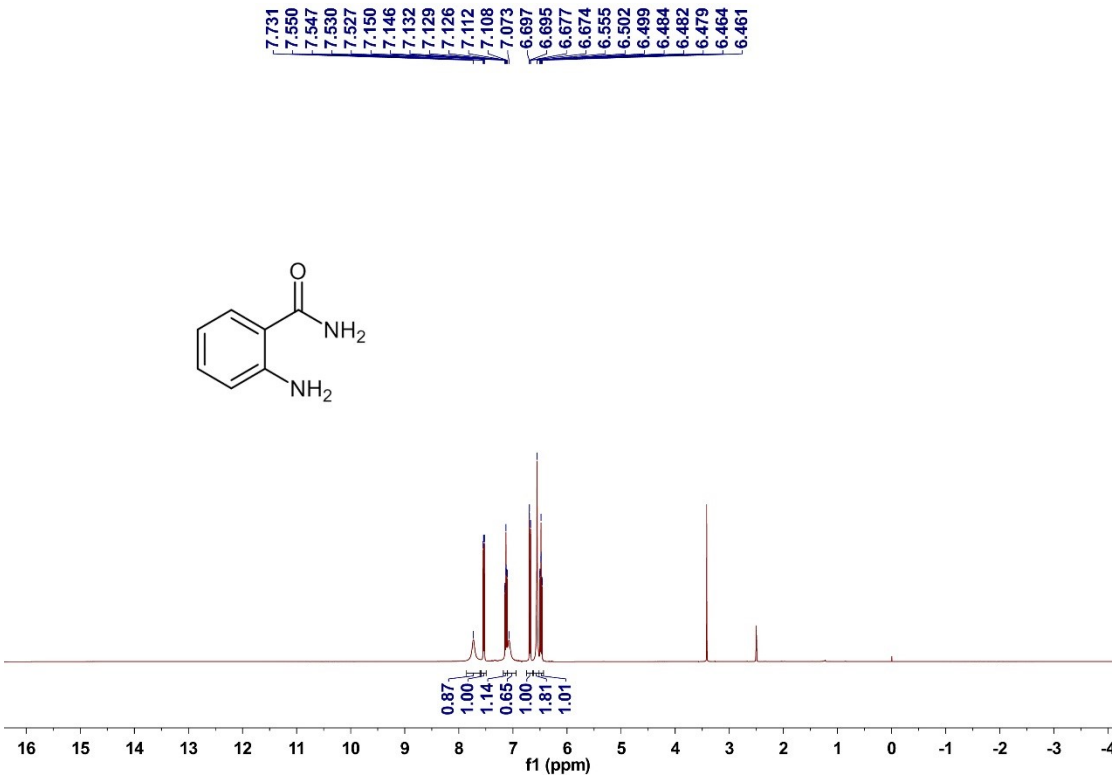

167.05
167.03
163.65
161.22
137.18
137.11
130.89
130.81
124.08
124.06
118.70
118.49
114.79
114.57
O
NH2
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

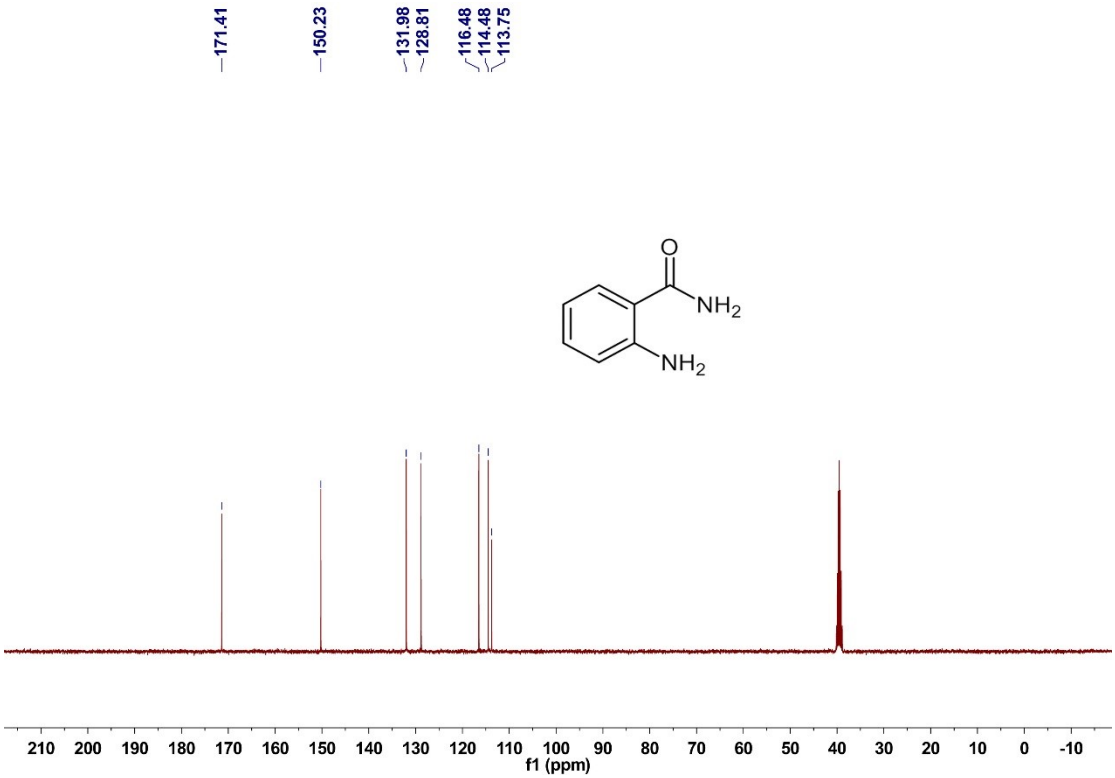
2p


8.025
7.986
7.979
7.973
7.965
7.956
7.948
7.942
7.935
7.428
7.299
7.291
7.286
7.274
7.269
7.264
7.252
7.247
7.239
O
NH2
F
0.89
2.07
0.94
2.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

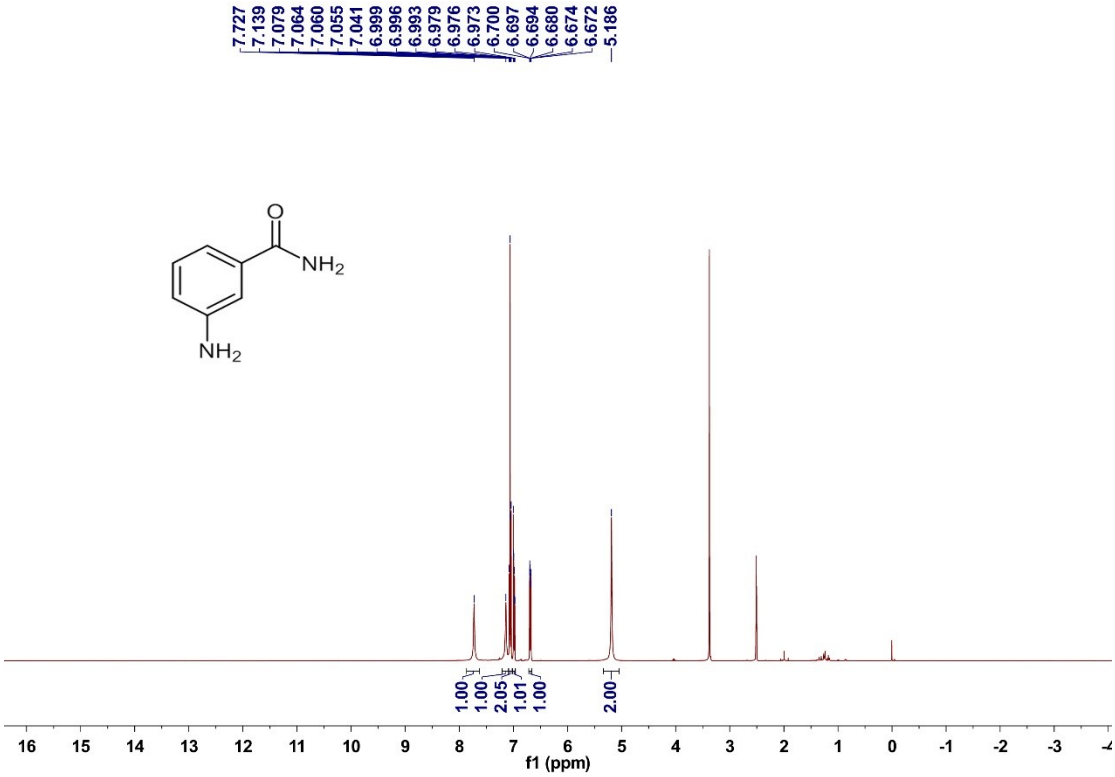

167.35
165.63
163.16
131.20
131.18
130.63
130.54
115.65
115.43
O
NH2
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

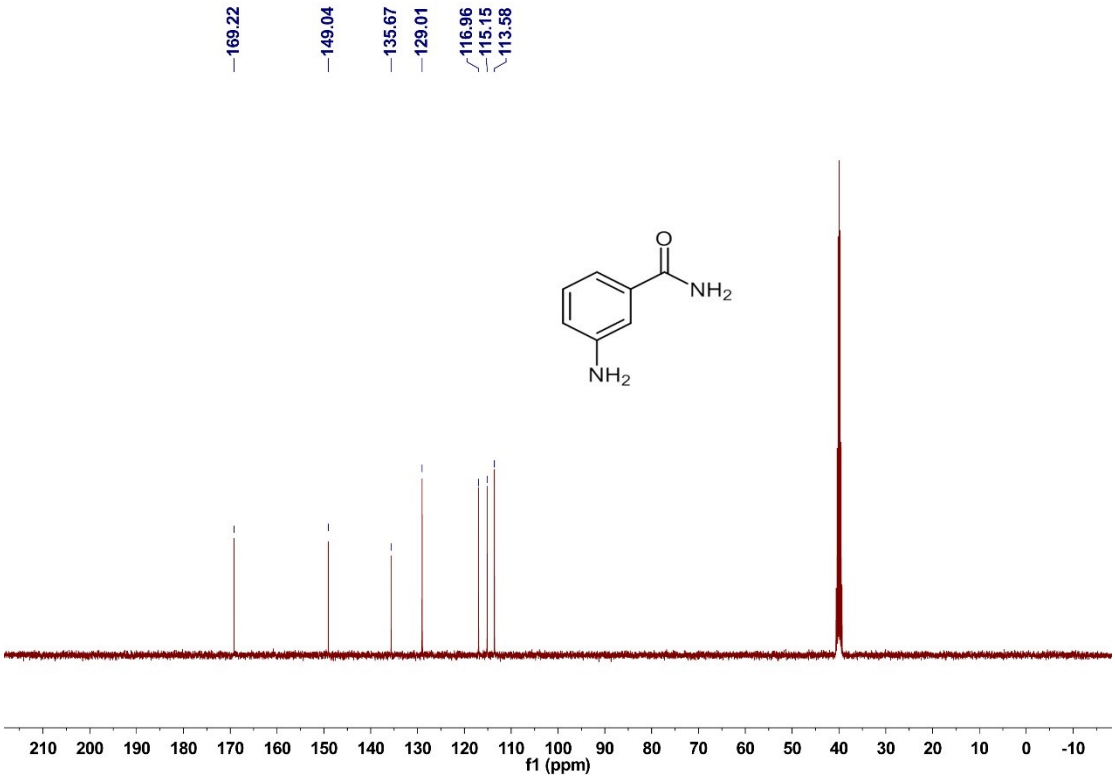
2q


7.731
7.550
7.547
7.530
7.527
7.150
7.146
7.132
7.129
7.126
7.112
7.108
7.073
6.697
6.695
6.677
6.674
6.555
6.502
6.499
6.484
6.482
6.479
6.464
6.461
O
NH2
NH2
0.87
1.00
1.14
0.65
1.00
1.81
1.01
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

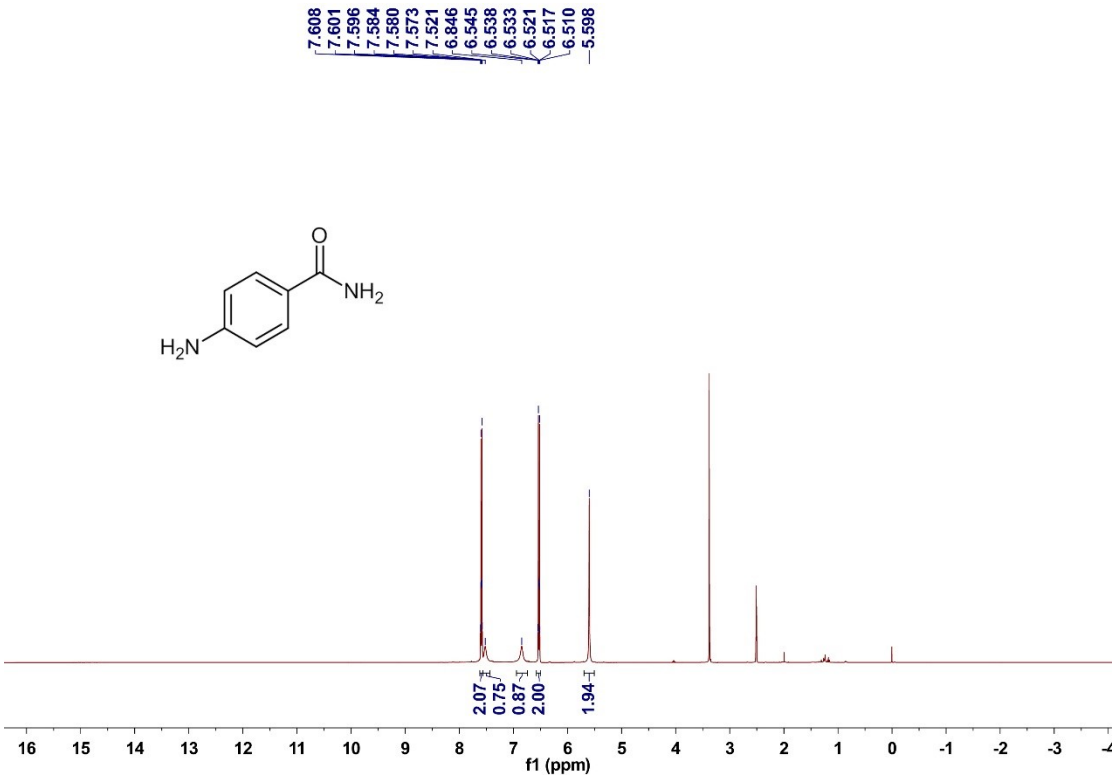

171.41
150.23
131.98
128.81
116.48
114.48
113.75
O
NH2
NH2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

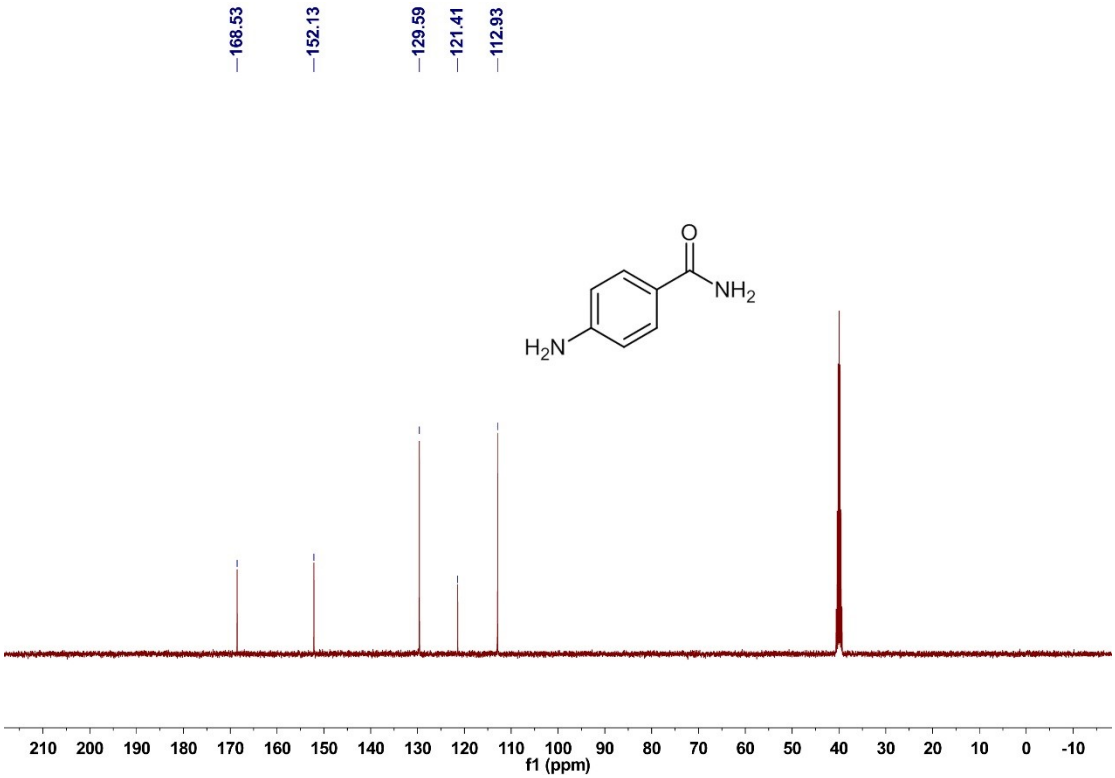
2r


7.727
7.139
7.079
7.064
7.060
7.055
7.041
6.999
6.996
6.993
6.979
6.976
6.973
6.700
6.697
6.694
6.680
6.674
6.672
5.186
O
NH2
NH2
1.00
1.00
2.05
1.01
1.00
2.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

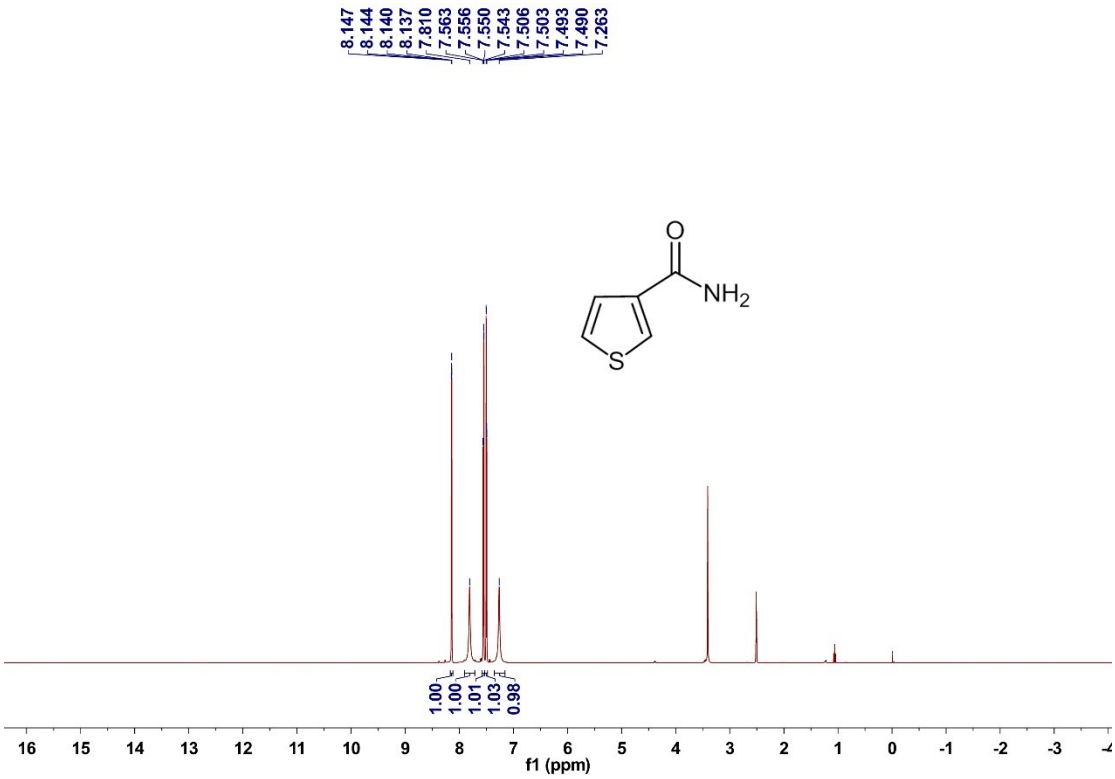

169.22
149.04
135.67
129.01
116.96
115.15
113.58
O
NH2
NH2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

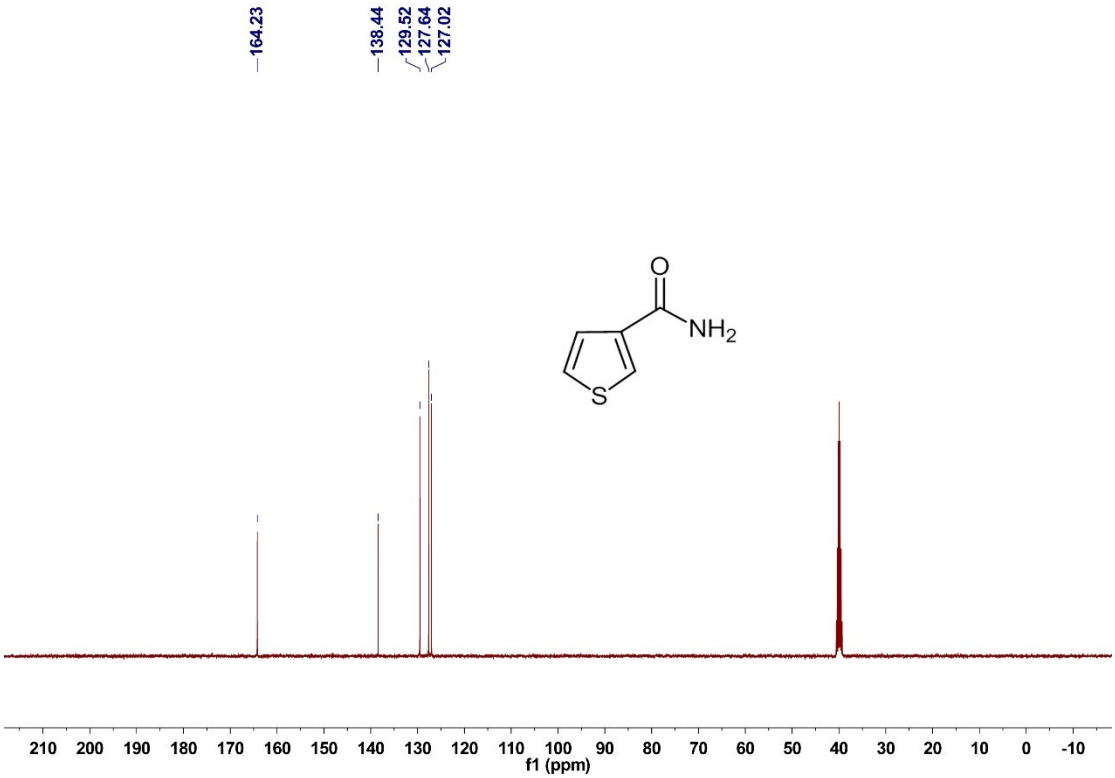
2s


7.608
7.601
7.596
7.584
7.580
7.573
7.521
6.846
6.545
6.538
6.533
6.521
6.517
6.510
5.598
O
NH2
H2N
2.07
0.75
0.87
2.00
1.94
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

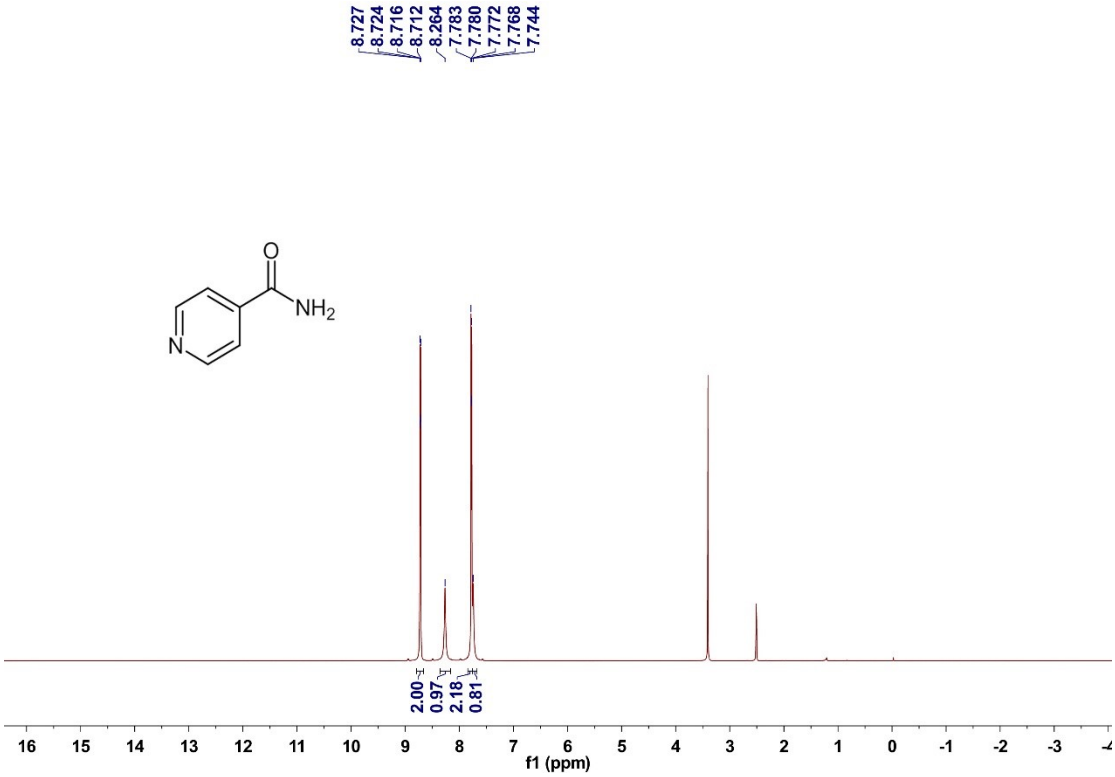

168.53
152.13
129.59
121.41
112.93
O
NH2
H2N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

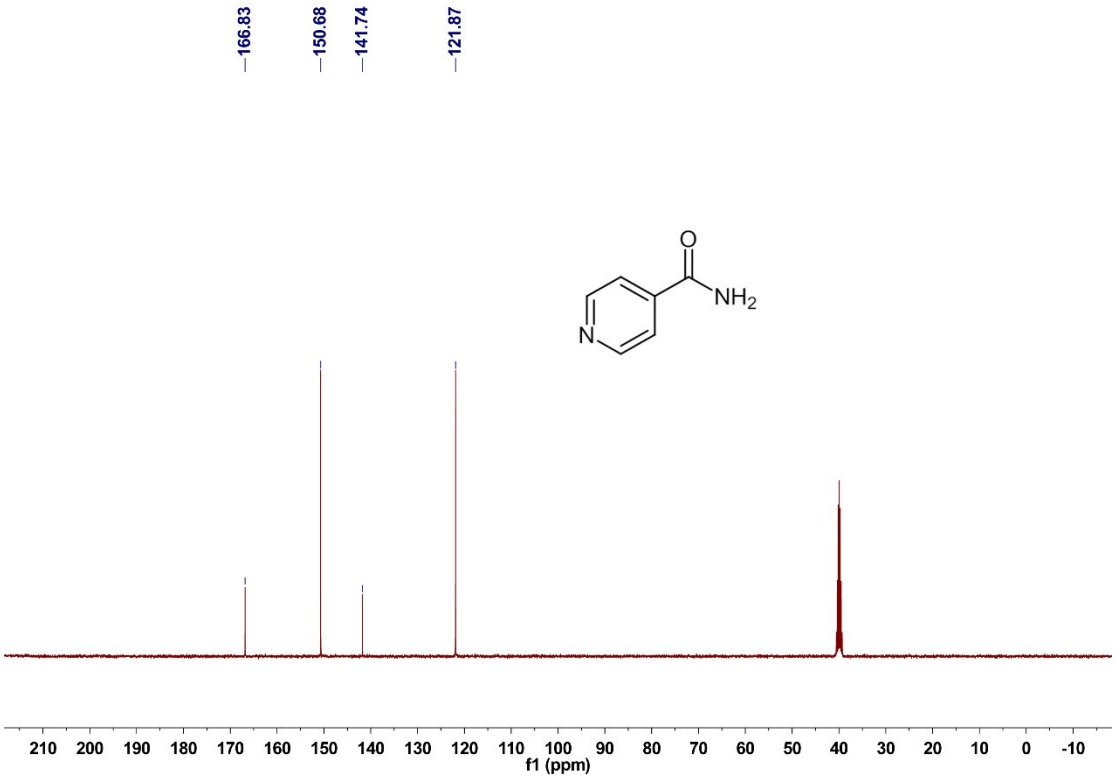
2t


8.147
8.144
8.140
8.137
7.810
7.563
7.556
7.550
7.543
7.506
7.503
7.493
7.490
7.263
O
NH2
S
1.00
1.00
1.01
1.03
0.98
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

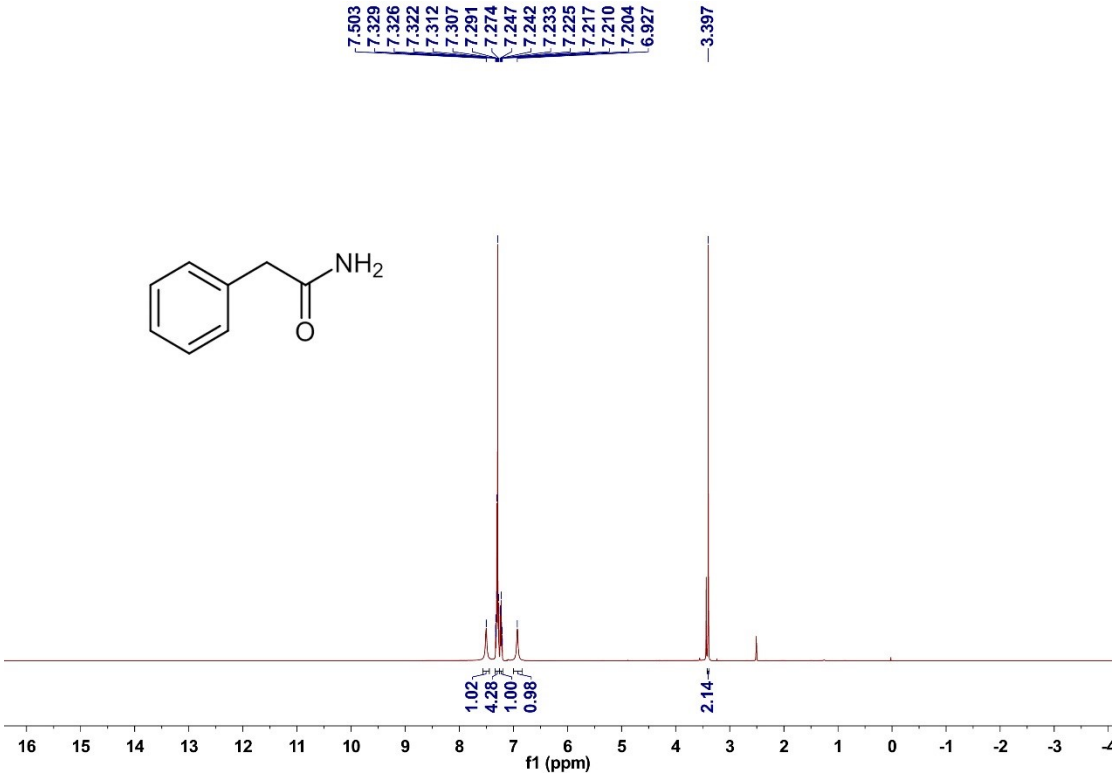

164.23
138.44
129.52
127.64
127.02
O
NH2
S
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

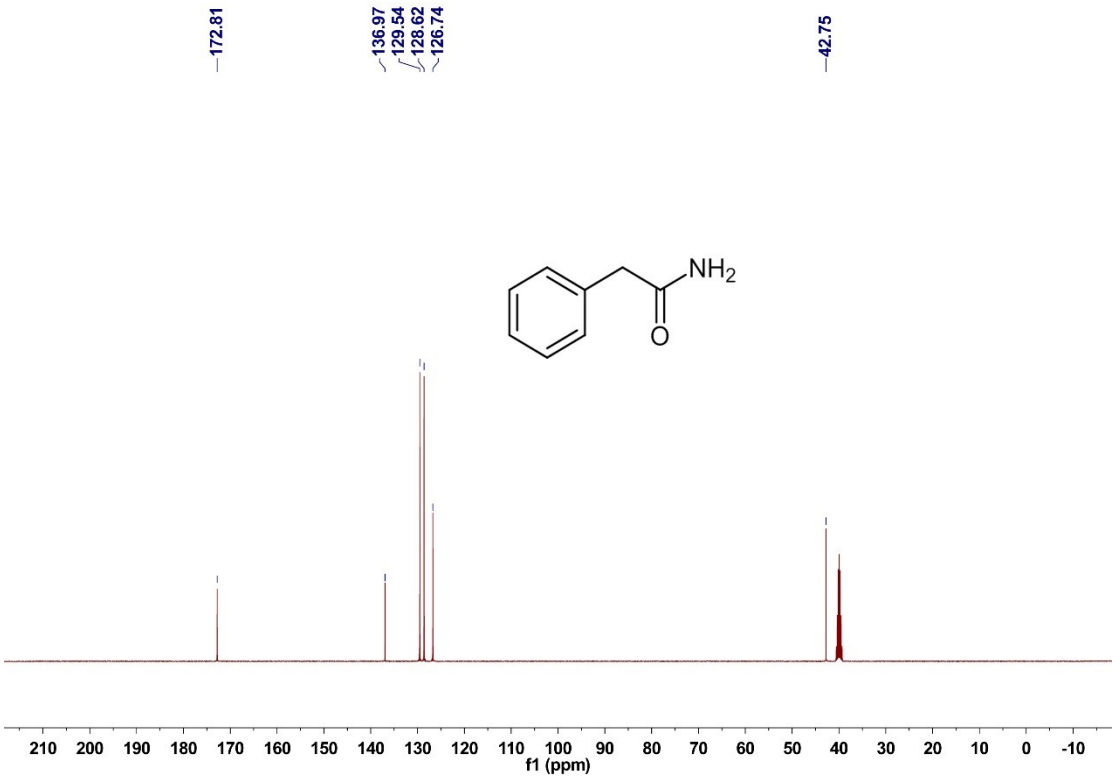
2u


8.727
8.724
8.716
8.712
8.264
7.783
7.780
7.772
7.768
7.744
O
NH2
N
2.00
0.97
2.18
0.81
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

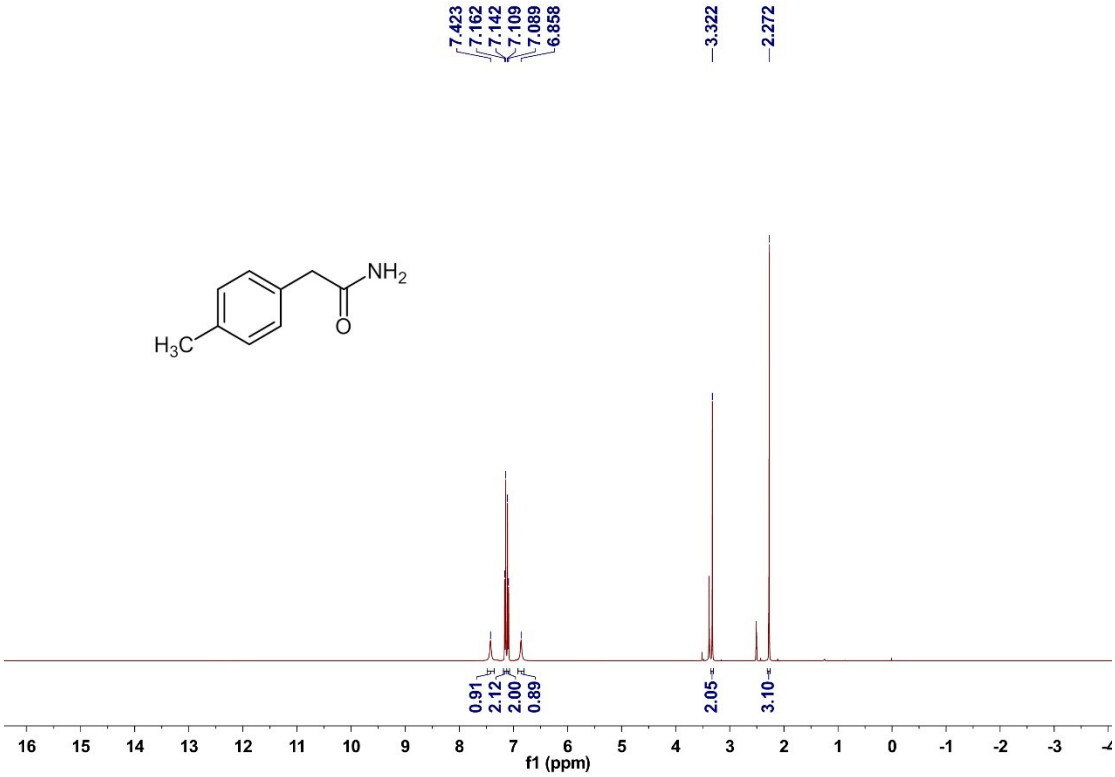

166.83
150.68
141.74
121.87
O
NH2
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

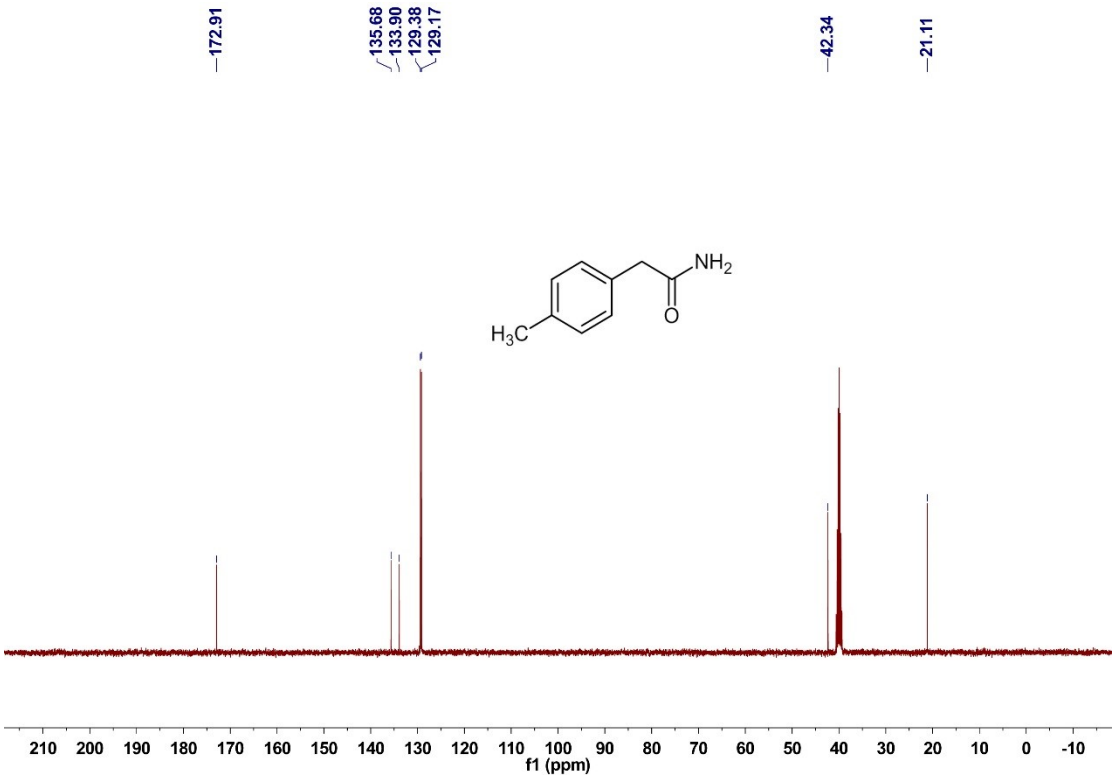
2v


7.503
7.329
7.326
7.322
7.312
7.307
7.291
7.274
7.247
7.242
7.233
7.225
7.217
7.210
7.204
6.927
3.397
NH2
O
1.02
4.28
1.00
0.98
2.14
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

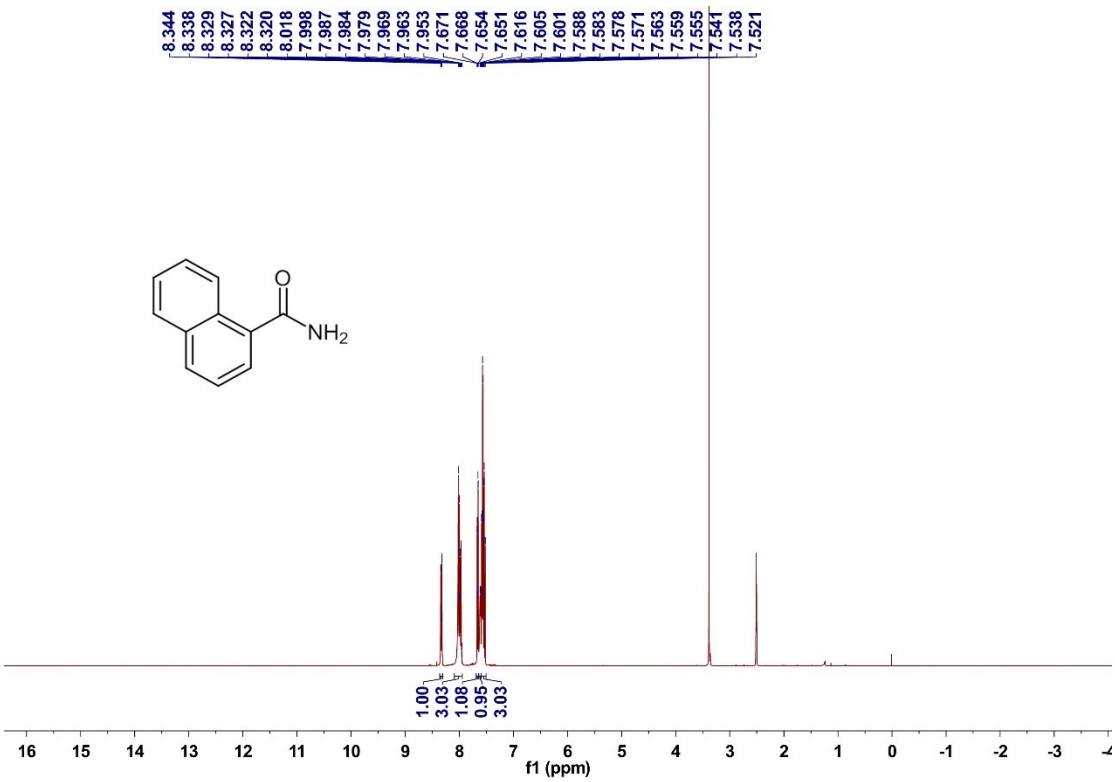

172.81
136.97
129.54
128.62
126.74
42.75
NH2
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

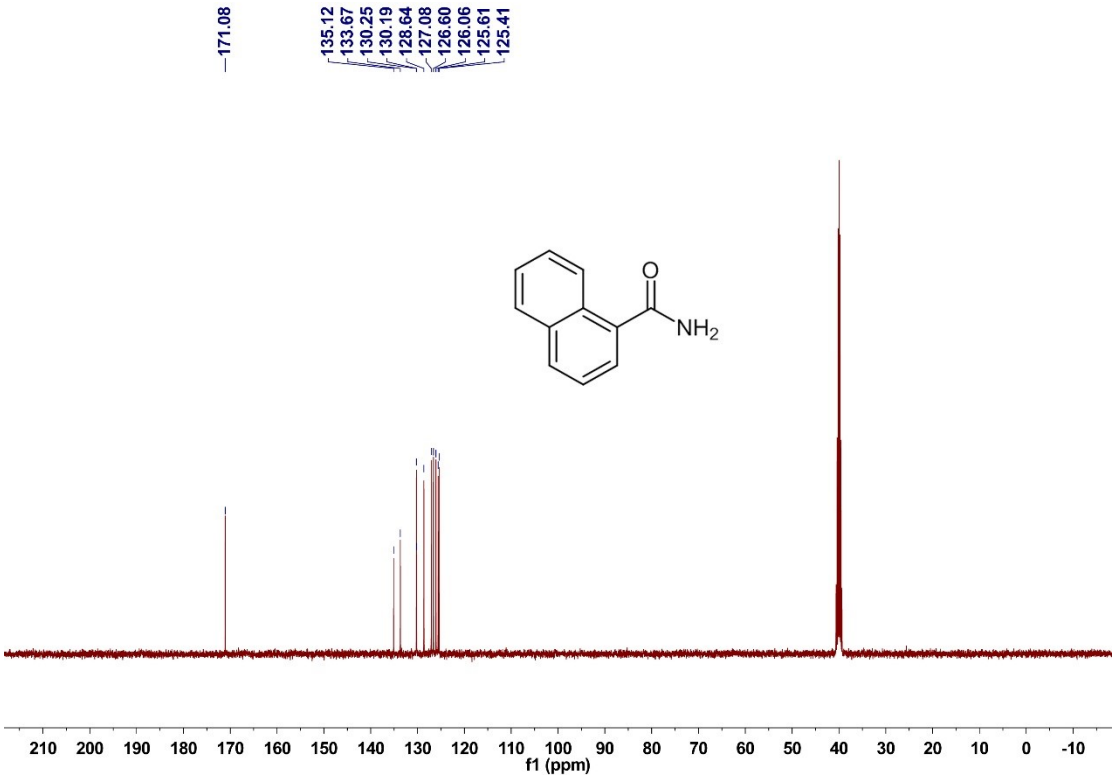
2w


7.423
7.162
7.142
7.109
7.089
6.858
3.322
2.272
NH2
O
H3C
0.91
2.12
2.00
0.89
2.05
3.10
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

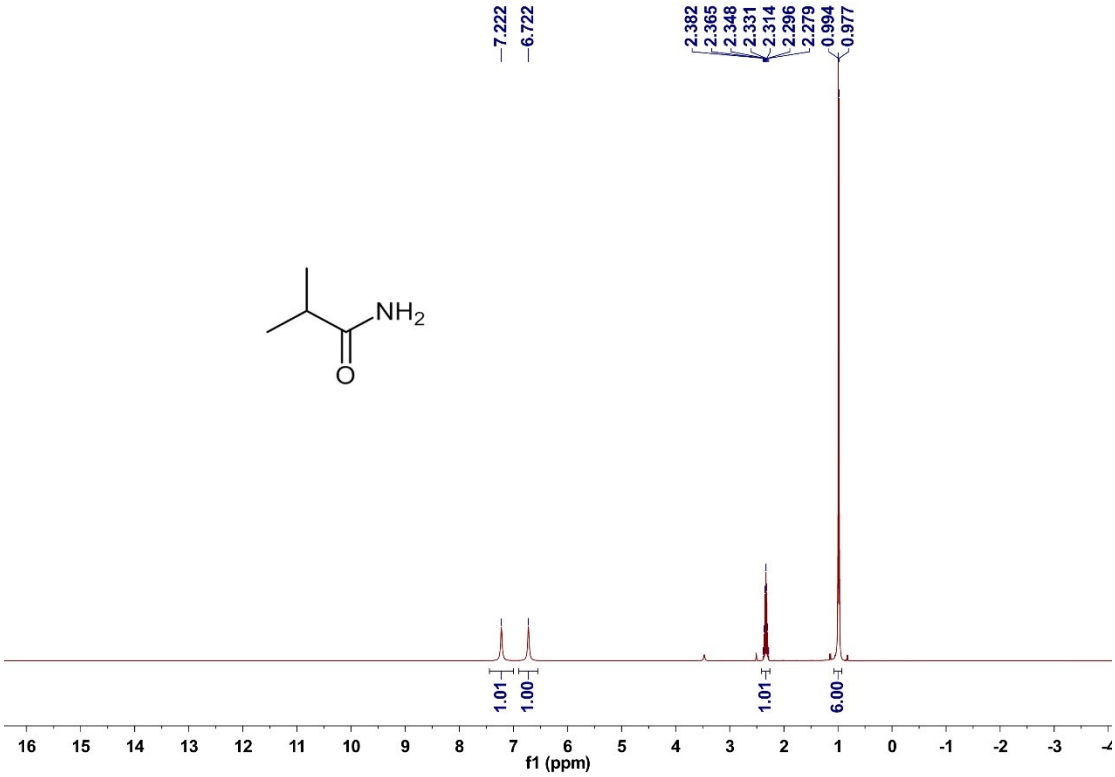

172.91
135.68
133.90
129.38
129.17
42.34
21.11
NH2
O
H3C
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

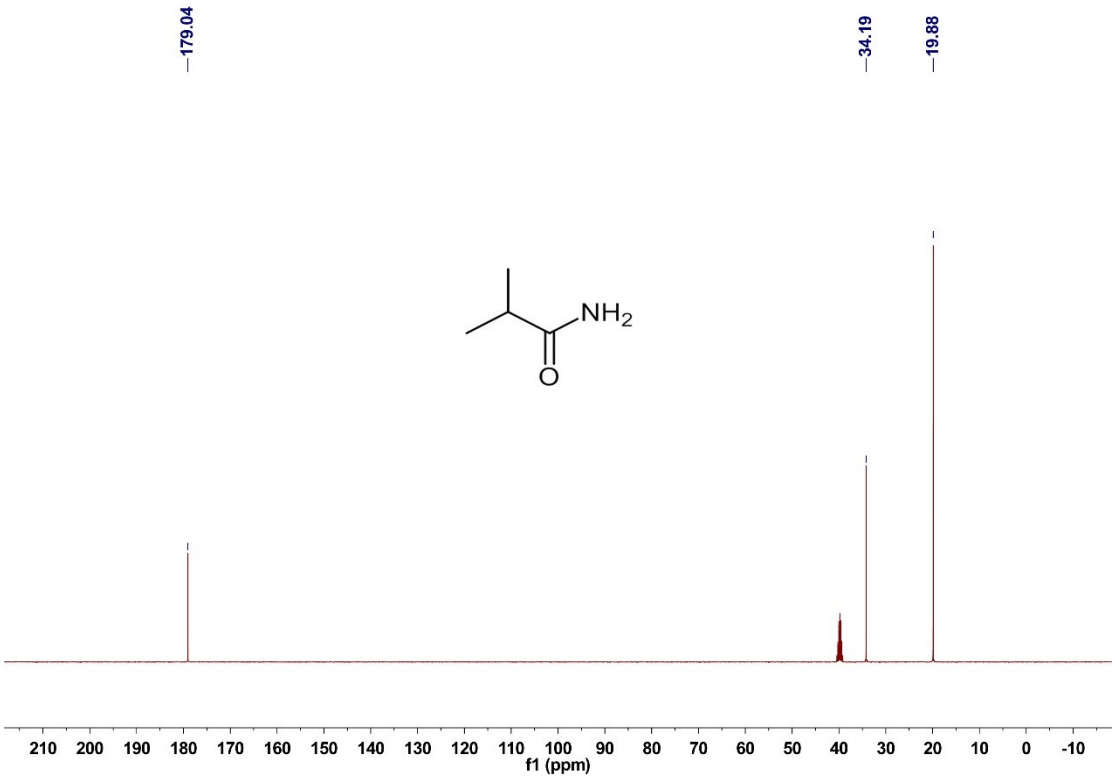
2x


8.344
8.338
8.329
8.327
8.322
8.320
8.018
7.998
7.987
7.984
7.979
7.969
7.963
7.953
7.671
7.668
7.654
7.651
7.616
7.605
7.601
7.588
7.583
7.578
7.571
7.563
7.559
7.555
7.541
7.538
7.521
O
NH2
1.00
3.03
1.08
0.95
3.03
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

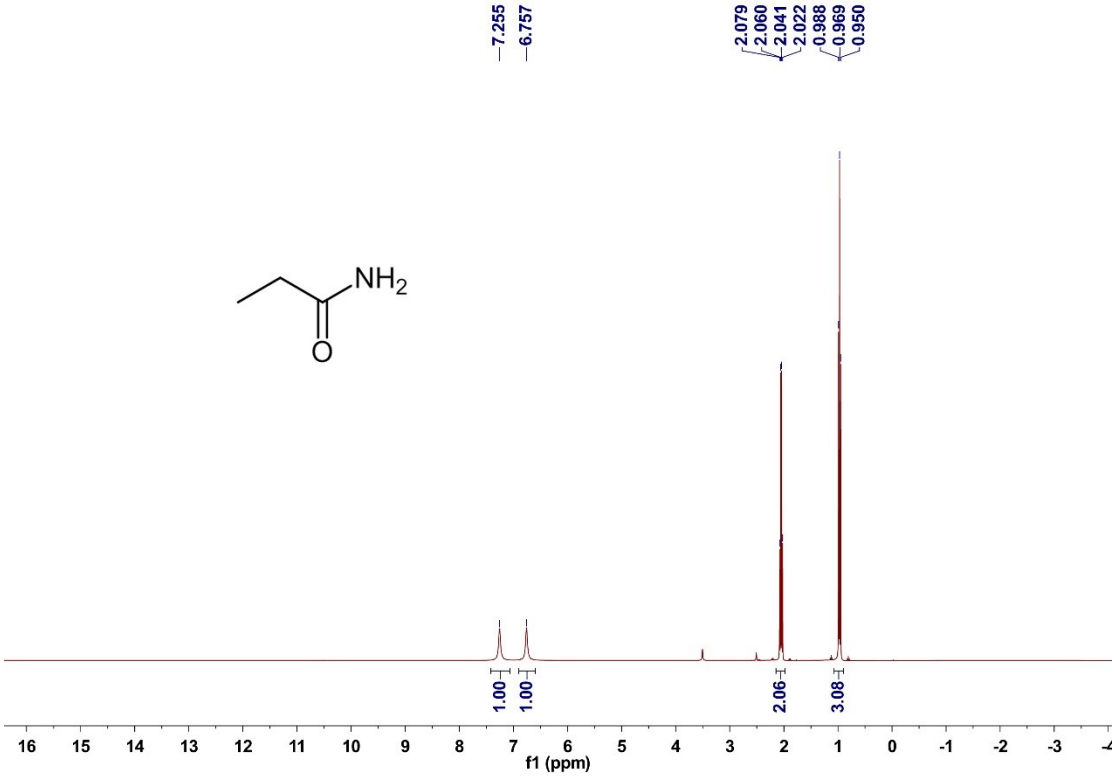

171.08
135.12
133.67
130.25
130.19
128.64
127.08
126.60
126.06
125.61
125.41
O
NH2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

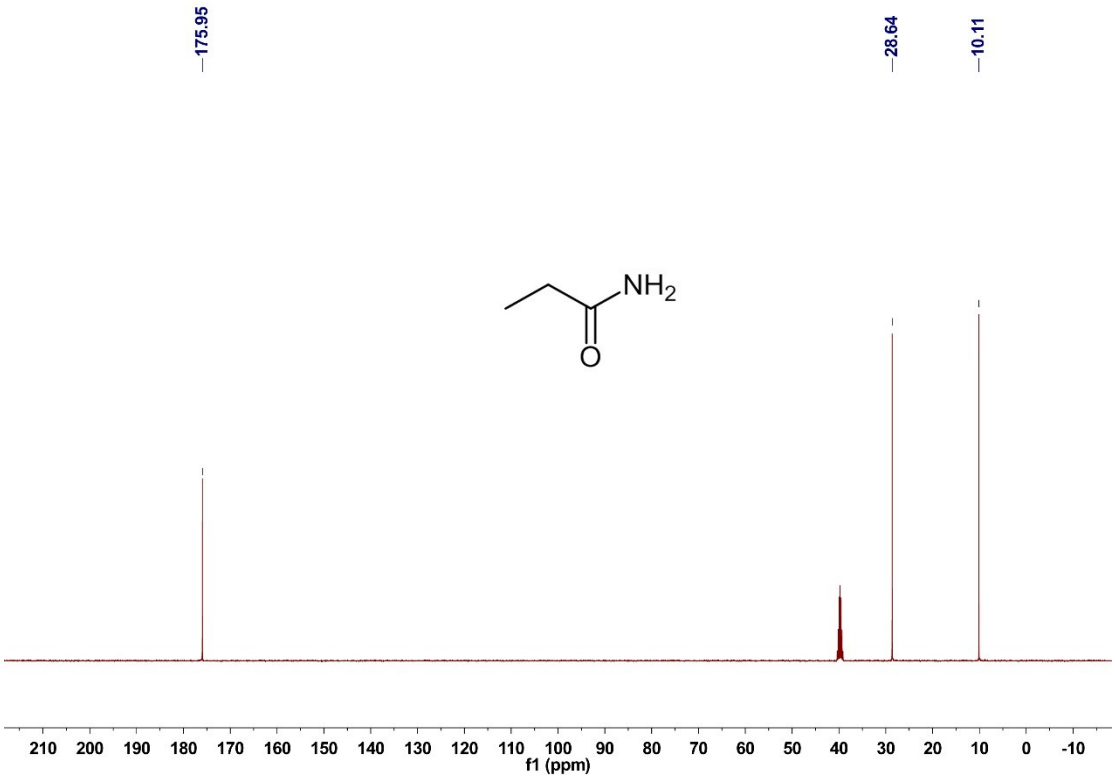
2y


7.222
6.722
2.382
2.365
2.348
2.331
2.314
2.296
2.279
0.994
0.977
NH2
O
1.01
1.00
1.01
6.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

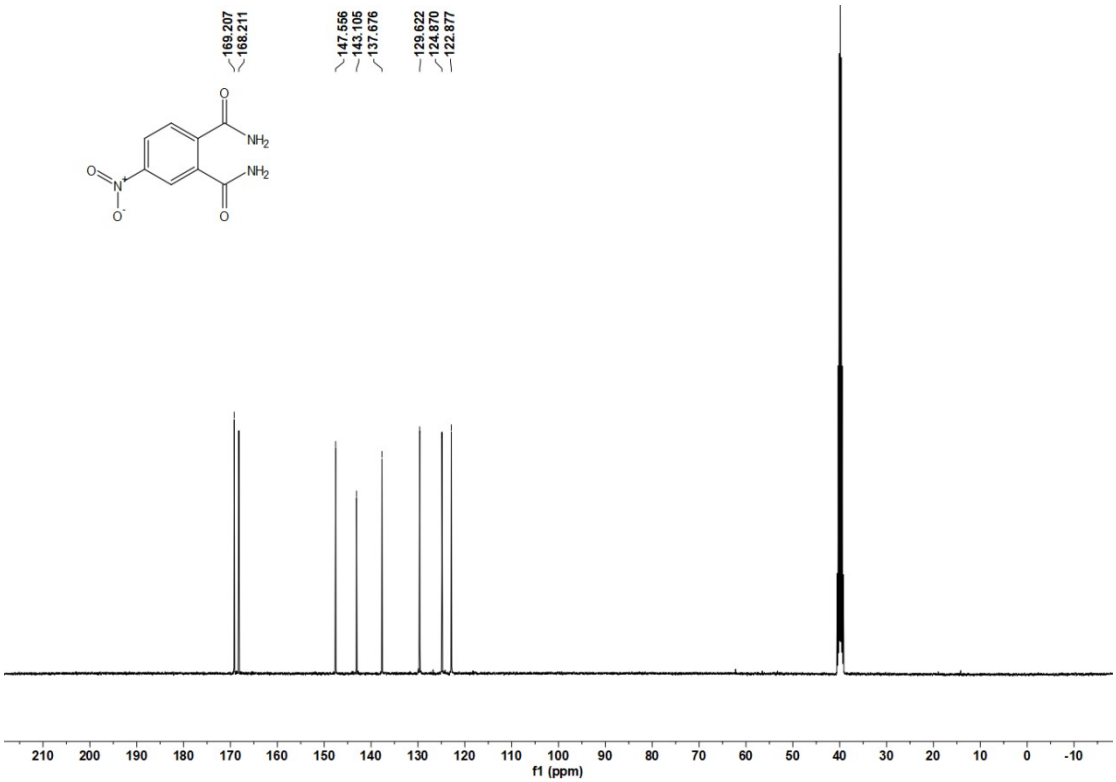

179.04
34.19
19.88
NH2
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

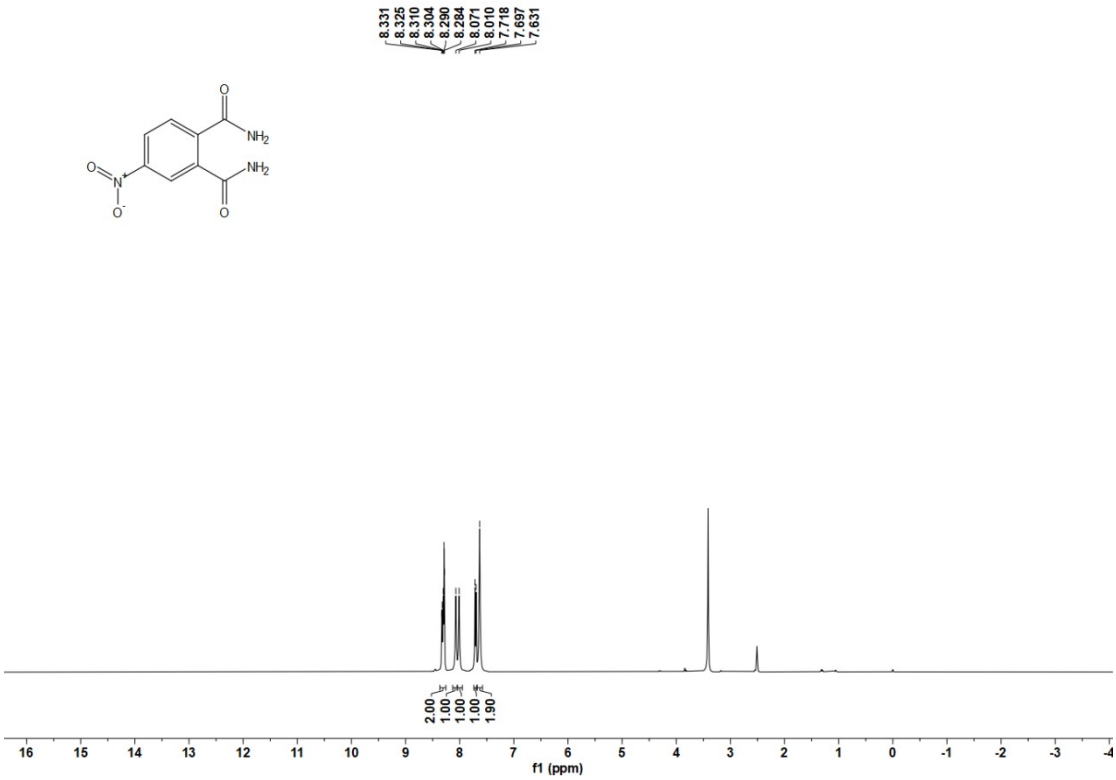
2z


7.255
6.757
2.079
2.060
2.041
2.022
0.988
0.969
0.950
NH2
O
1.00
1.00
2.06
3.08
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

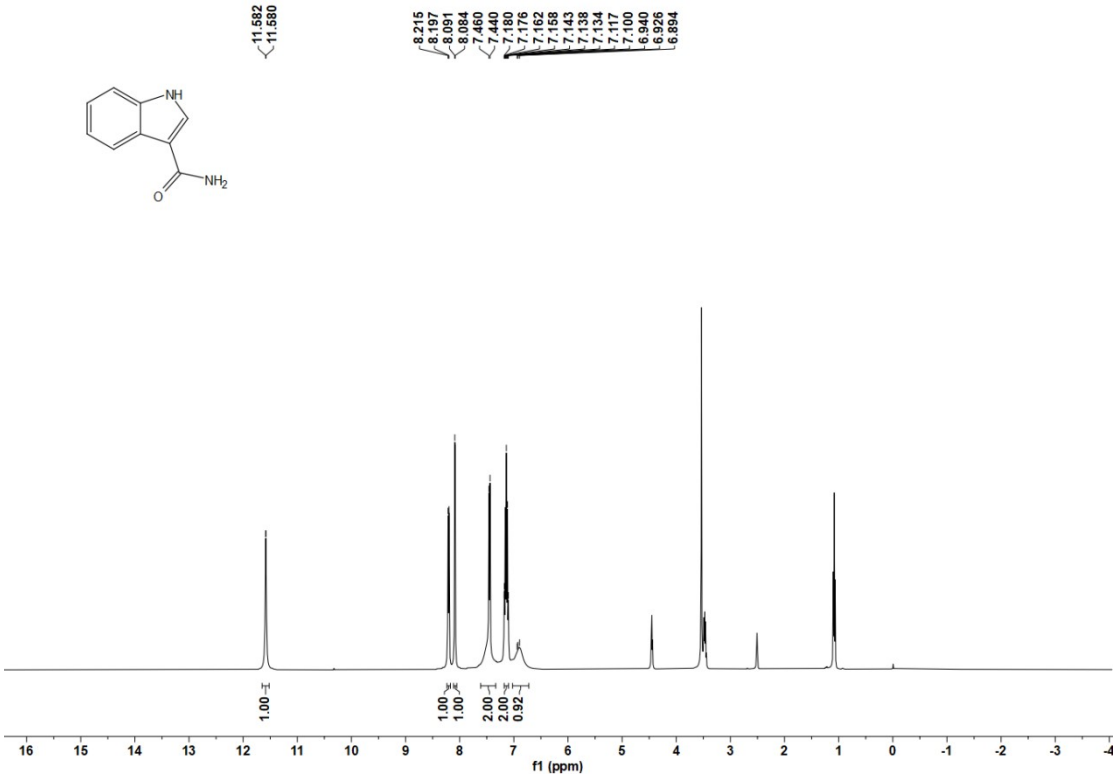

175.95
28.64
10.11
NH2
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

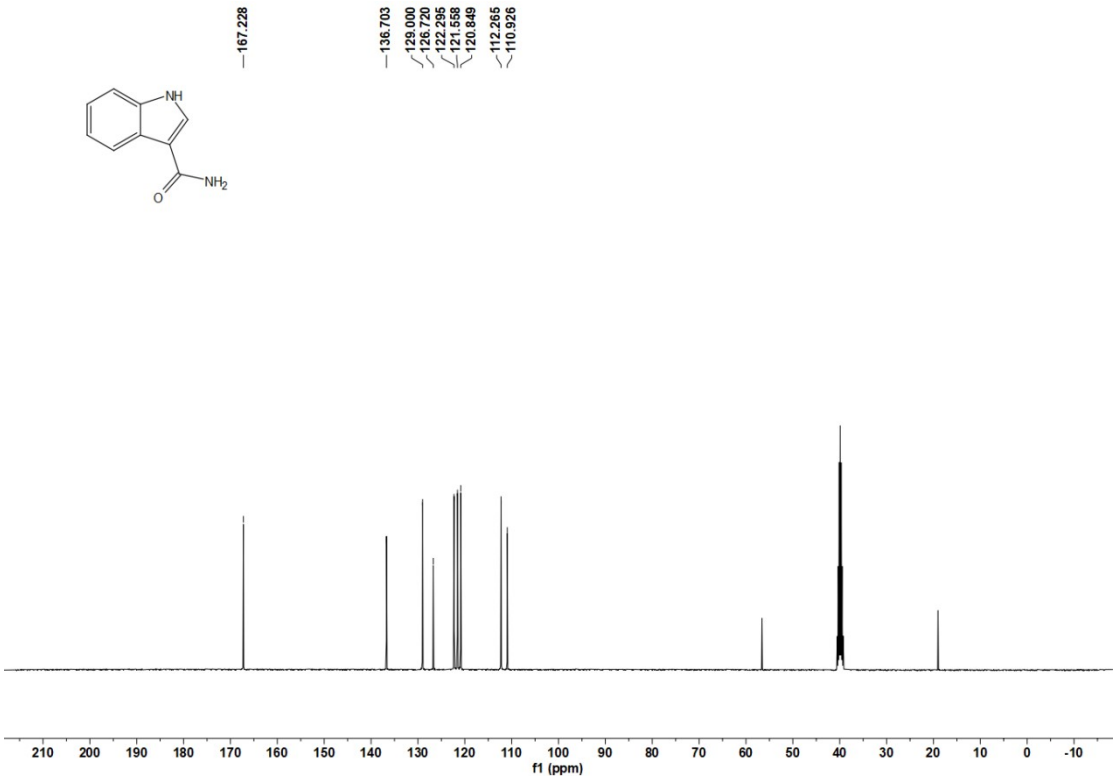
2aa


169.207
168.211
147.556
143.105
137.676
129.622
124.870
122.877
O
NH2
NH2
O
O
N+
O-
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)

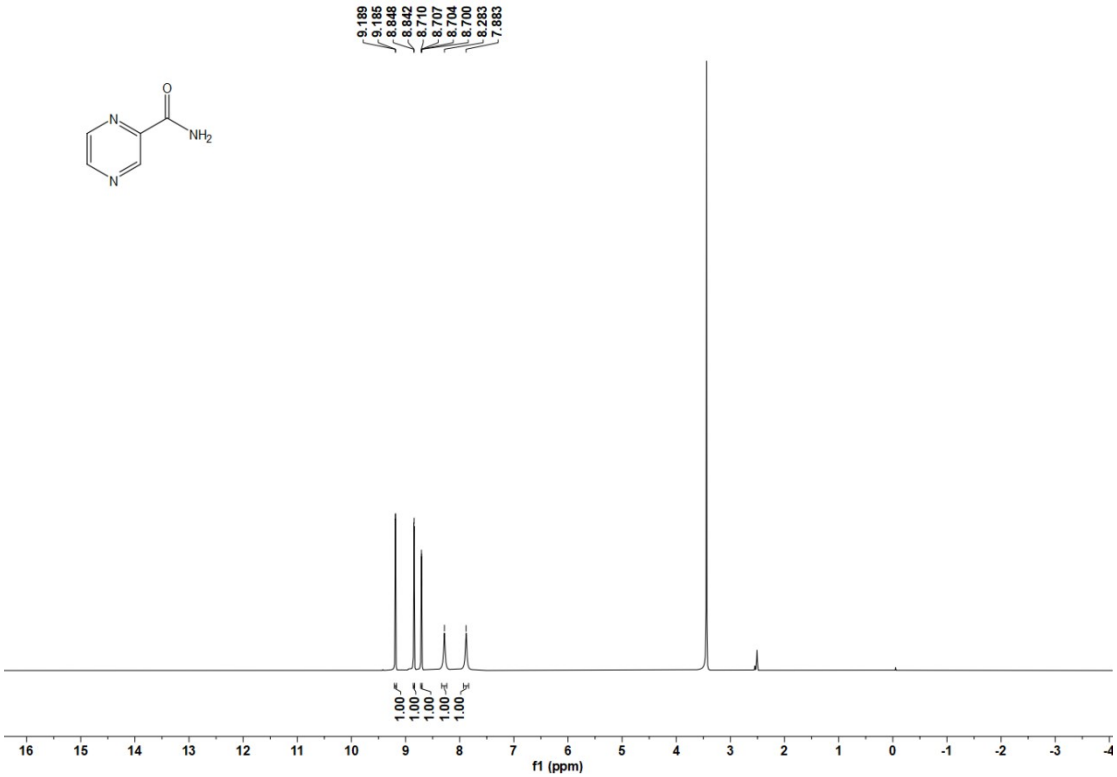

8.331
8.325
8.310
8.304
8.290
8.284
8.071
8.010
7.718
7.697
7.651
O
NH2
NH2
O
O
N+
O-
2.00
1.00
1.00
1.00
1.90
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

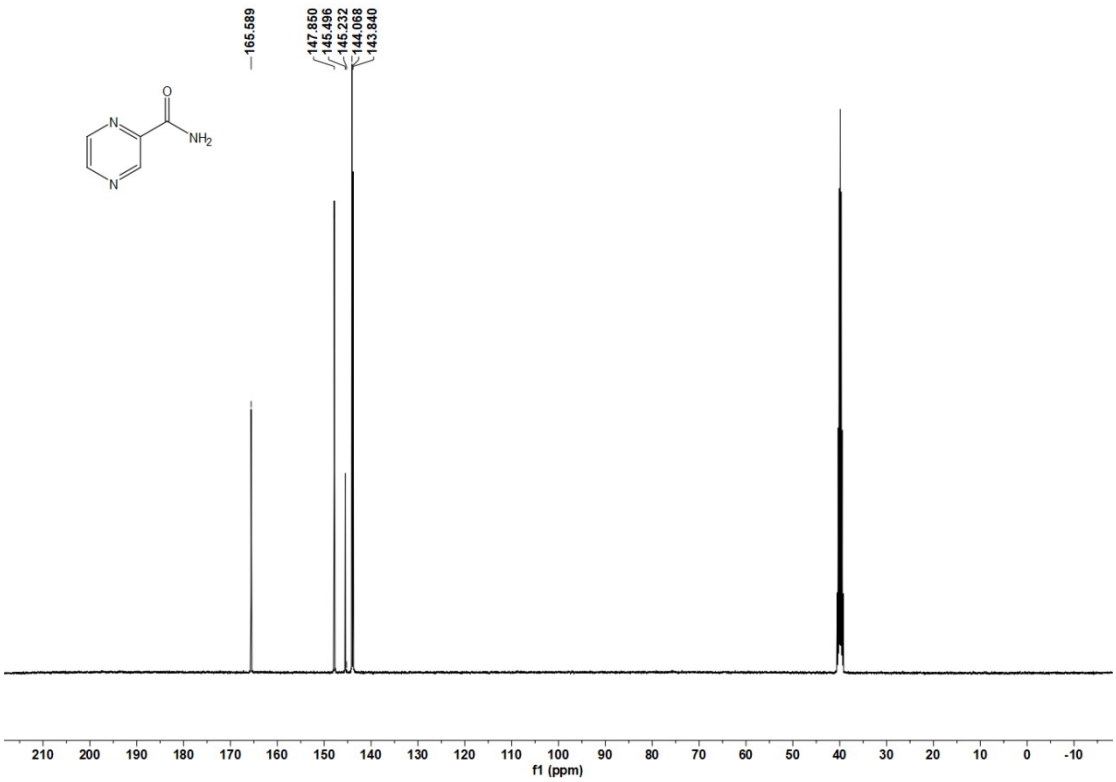
2ab


11.582
11.580
8.215
8.197
8.091
8.084
7.460
7.440
7.180
7.176
7.162
7.158
7.143
7.138
7.134
7.117
7.100
6.940
6.926
6.894
NH
NH2
O
1.00
1.00
1.00
2.00
2.00
0.92
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

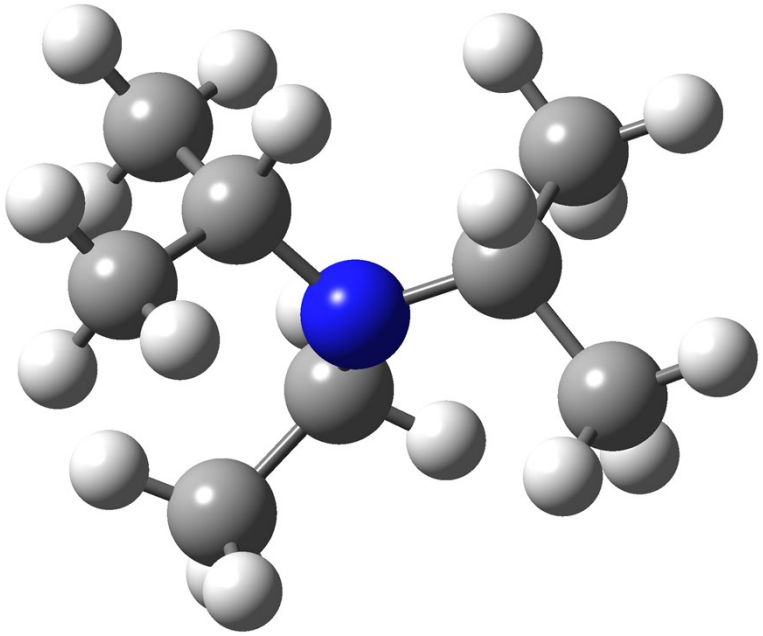

167.228
136.703
129.000
126.720
122.295
121.558
120.849
112.265
110.926
NH
NH2
O
f1 (ppm)

2ac


9.189
9.185
8.848
8.842
8.710
8.707
8.704
8.700
8.283
7.883
O
NH2
N
N
1.00
1.00
1.00
1.00
1.00
f1 (ppm)


165.589
147.850
145.496
145.232
144.068
143.840
O
NH2
N
N
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)

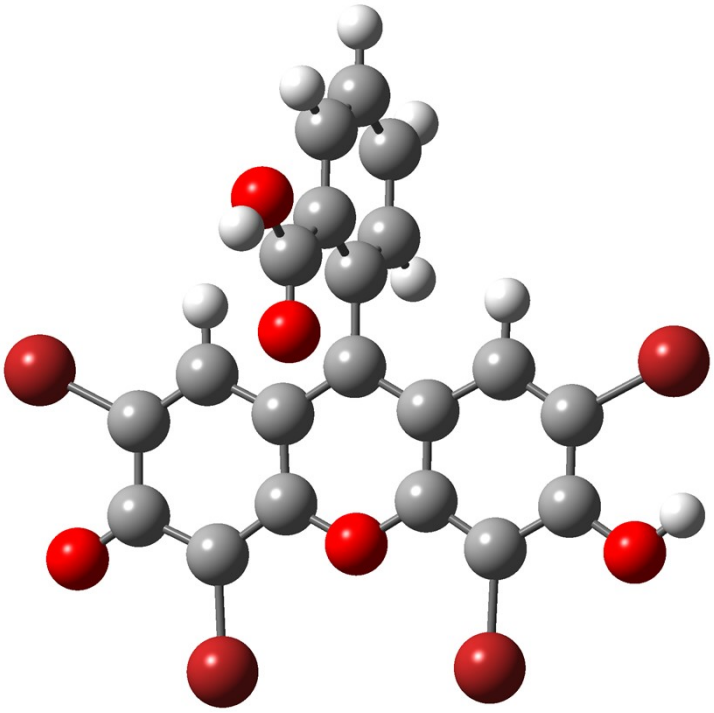
7 Optimized Structures and Cartesian Coordinates



A

Energies= -371.141599 a.u

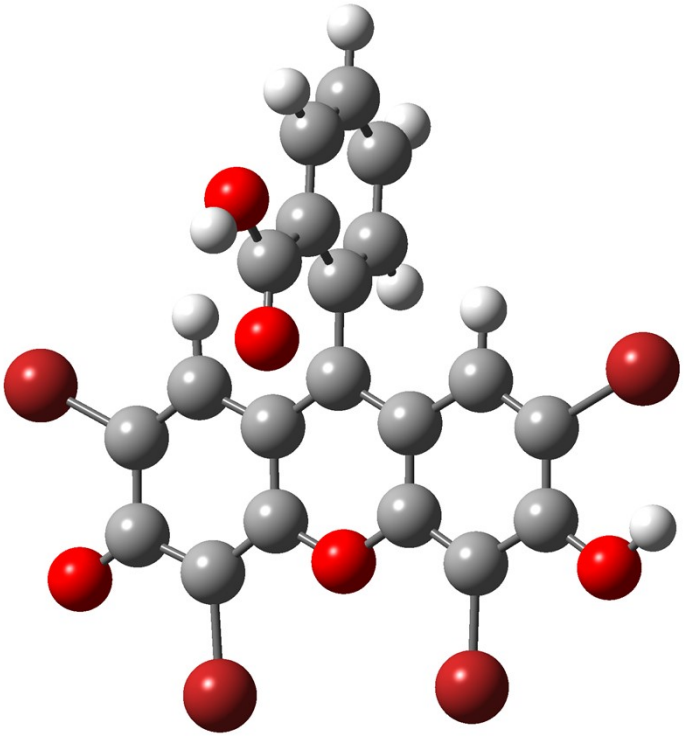
N	-0.08551700	-0.10559000	-0.22262200
C	-1.44164100	0.46145100	-0.35971700
H	-1.34408100	1.25603800	-1.11031100
C	1.00824600	0.89217900	-0.30155600
H	0.53271100	1.83365800	-0.60428900
C	2.00855700	0.53675200	-1.41742800
H	1.47708000	0.36054400	-2.35799700
H	2.72650600	1.35282200	-1.57133200
H	2.57766100	-0.36809800	-1.18041400
C	1.74123900	1.18981500	1.02062000
H	2.44556000	2.01630900	0.87190800
H	1.04533900	1.48179100	1.81454500
H	2.32029500	0.33058400	1.37728600
C	-2.42695900	-0.55914900	-0.95060200
H	-2.00223100	-1.01962700	-1.84814100
H	-2.67931800	-1.35785700	-0.24351100
H	-3.36566500	-0.06217500	-1.22218600
C	-2.00934500	1.10584200	0.92210700
H	-1.34408300	1.88999200	1.30088800
H	-2.98820700	1.56205300	0.72995000
H	-2.14164900	0.36211400	1.71699100
C	0.04841200	-1.17687200	0.76517200
H	-0.92657600	-1.66516100	0.85127300
H	0.28222000	-0.80160600	1.77650800
C	1.07125200	-2.25475700	0.38511900
H	0.86217600	-2.64265600	-0.61740700
H	2.09788400	-1.87507300	0.39281700
H	1.02444100	-3.08609200	1.09947400



Eosin Y$^{\bullet+}$

Energies=-11439.750934 a.u

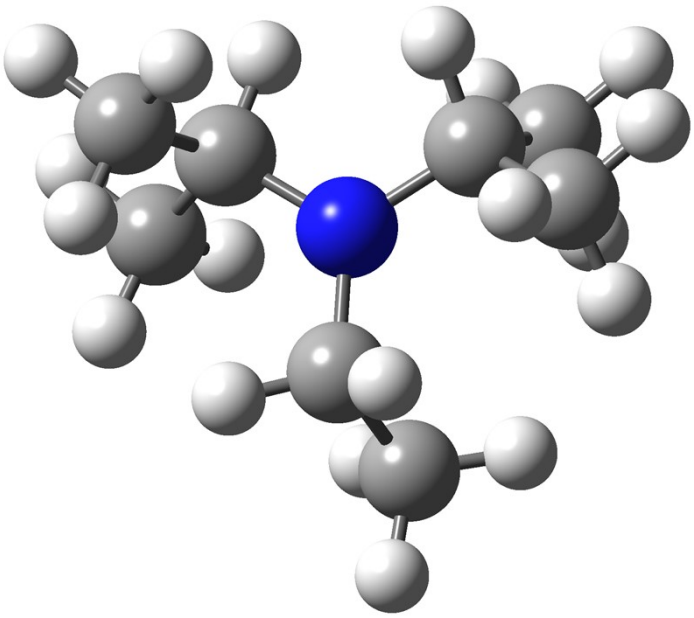
C	3.62873800	-0.98598600	-0.09124300
C	2.40903800	-1.67598900	-0.03367800
C	1.22157000	-0.94894900	-0.09104800
C	1.20031400	0.47395600	-0.21039100
C	2.44936300	1.15079000	-0.26515300
C	3.61964800	0.44341000	-0.20828500
C	-0.04546500	1.14223900	-0.24148600
C	-1.23771600	0.37198800	-0.21524900
C	-1.13271100	-1.04084600	-0.09588500
C	-2.25610200	-1.85819800	-0.04385200
C	-3.61160800	-1.27249100	-0.11538700
C	-3.66860300	0.20603500	-0.24661500
C	-2.54165600	0.96549000	-0.29155600
H	2.46769800	2.22968500	-0.35121500
H	-2.61486200	2.04138500	-0.38798800
Br	2.38277900	-3.54929000	0.11786800
Br	5.29652100	1.32733900	-0.27945500
Br	-5.37092600	0.97779700	-0.34823000
Br	-2.10347600	-3.69862300	0.11442900
O	-4.61689300	-1.97343400	-0.07107800
C	-0.10471500	2.62314700	-0.43502400
C	-0.23963200	3.52068700	0.64720400
C	-0.03726100	3.12673800	-1.73909900
C	-0.30844100	4.89763600	0.40312900
C	-0.10941500	4.50309600	-1.96960700
H	0.06348000	2.44290400	-2.57699000
C	-0.24591200	5.38808600	-0.90028800
H	-0.40946000	5.57649100	1.24231700
H	-0.05942700	4.87762000	-2.98746800
H	-0.30204700	6.45715300	-1.07887000
C	-0.29461800	2.96831600	2.02791500
O	-0.22153400	1.77649700	2.27775900
O	-0.43070400	3.90895900	2.97425300
H	-0.45891600	3.45527800	3.83846200
O	0.07546400	-1.64693000	-0.03020600
O	4.74957000	-1.68825900	-0.03598000
H	5.52596400	-1.09289000	-0.08409300



Eosin Y

Energies= -11439.968326 a.u

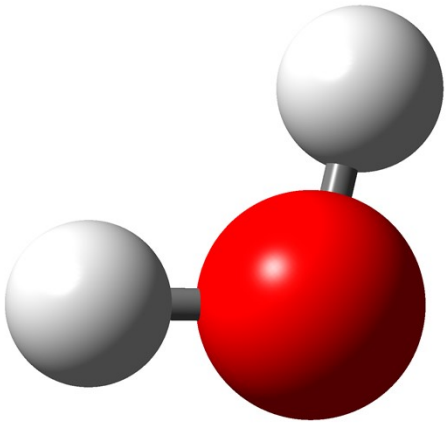
C	-0.07007500	1.13160800	-0.25205800
C	-1.21905700	-1.01964300	-0.08169200
C	-1.25266100	0.42429000	-0.20409300
C	-2.55307800	1.04578100	-0.25220100
H	-2.60842800	2.12413800	-0.33652200
C	-3.68467500	0.30813900	-0.19395400
C	-3.69275900	-1.17517400	-0.07513900
C	-2.35309400	-1.77412200	-0.02341000
C	-0.06463200	2.61581000	-0.44619800
C	0.05212500	3.54568000	0.61225700
C	-0.18238600	3.09860100	-1.75606300
C	0.04470600	4.92056800	0.33242100
C	-0.18433400	4.46805300	-2.02283600
H	-0.27693700	2.38760200	-2.57154300
C	-0.06997000	5.38221100	-0.97590000
H	0.12757200	5.62217700	1.15409000
H	-0.27871300	4.81584800	-3.04754800
H	-0.07360700	6.44960500	-1.17531700
C	0.17507400	3.06876700	2.01958900
O	0.26028200	1.90682500	2.36171600
O	0.18813500	4.08406600	2.91776200
H	0.26994600	3.66251700	3.79354000
Br	-5.38325800	1.14513600	-0.26306100
O	-4.72851900	-1.82679000	-0.02695500
O	-0.01554200	-1.66291600	-0.02598600
Br	-2.25508400	-3.65501800	0.12778400
C	3.57199100	-1.11428700	-0.11546900
C	3.59835000	0.29240200	-0.23770400
C	2.44231700	1.04358400	-0.28613900
C	1.18489100	0.41727100	-0.21290000
C	1.15372400	-0.98840300	-0.09360000
C	2.32487000	-1.74886900	-0.04553000
H	2.50328400	2.12057200	-0.37960500
Br	5.30715300	1.14917200	-0.33858600
Br	2.22981200	-3.62842500	0.11043800
O	4.68268600	-1.86806800	-0.06750900
H	5.46078300	-1.28128200	-0.12573800



B

Energies= -370.968345a.u

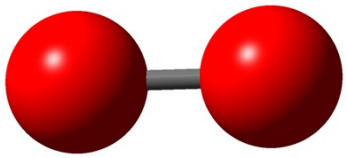
N	**0.04586900**	**0.07594500**	**-0.18355600**
C	**-1.14338000**	**0.91231200**	**0.07664500**
H	**-0.77713900**	**1.94229100**	**-0.02295400**
C	**1.35697700**	**0.60410200**	**0.24344600**
H	**1.12951100**	**1.44825000**	**0.90063500**
C	**-1.58698600**	**0.72237700**	**1.55230800**
H	**-0.76827200**	**0.90310900**	**2.25430100**
H	**-2.37771300**	**1.44929600**	**1.75899900**
H	**-1.98541100**	**-0.28107900**	**1.72018500**
C	**-2.28965800**	**0.69366200**	**-0.91097100**
H	**-3.06589800**	**1.43293500**	**-0.69365200**
H	**-1.97247300**	**0.84635800**	**-1.94725900**
H	**-2.74644800**	**-0.29561100**	**-0.81571500**
C	**2.18859600**	**-0.42406300**	**1.02327000**
H	**1.65271200**	**-0.79274000**	**1.90242900**
H	**2.49519900**	**-1.27399700**	**0.40693200**
H	**3.09872600**	**0.07497600**	**1.36904200**
C	**2.09961900**	**1.14837400**	**-1.00121300**
H	**1.50150300**	**1.89177800**	**-1.53616700**
H	**3.01924000**	**1.63177900**	**-0.65815300**
H	**2.37323800**	**0.34555000**	**-1.69220700**
C	**-0.03868900**	**-1.20649900**	**-0.87684100**
H	**-0.68789000**	**-1.07166700**	**-1.74633800**
H	**0.96167200**	**-1.45951300**	**-1.23051900**
C	**-0.58864100**	**-2.34868300**	**0.00852000**
H	**0.02838300**	**-2.49874400**	**0.89719200**
H	**-1.62135100**	**-2.16836100**	**0.31467900**
H	**-0.56569600**	**-3.26571500**	**-0.58752400**



H_20

Energies= -76.471995 a.u

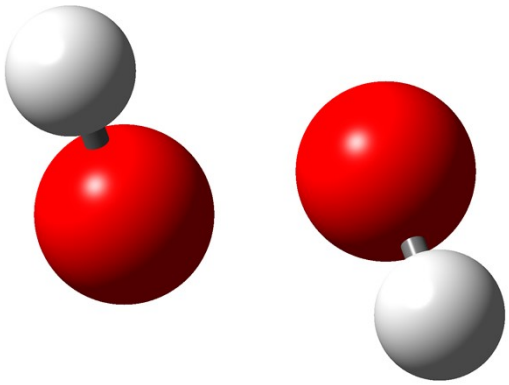
O	**0.00000000**	**0.00000000**	**0.11972000**
H	**0.00000000**	**0.76156000**	**-0.47887900**
H	**0.00000000**	**-0.76156000**	**-0.47887900**



$O2^{\bullet-}$

Energies= -150.519076 a.u

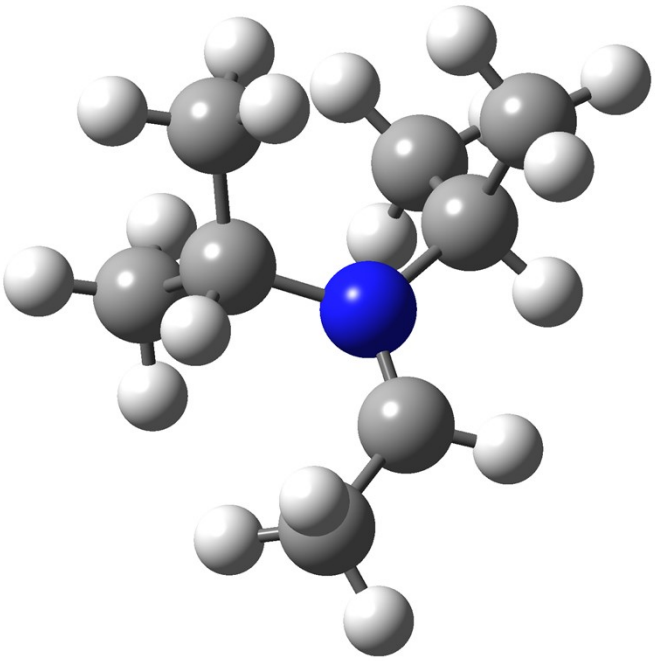
O	**0.00000000**	**0.00000000**	**0.67654300**
O	**0.00000000**	**0.00000000**	**-0.67654300**



H_2O_2

Energies= -151.617242 a.u

O	**-0.71823600**	**-0.11814100**	**-0.05445400**
H	**-1.01376800**	**0.66962200**	**0.43555200**
O	**0.71823800**	**0.11813000**	**-0.05445400**
H	**1.01375400**	**-0.66953900**	**0.43571200**

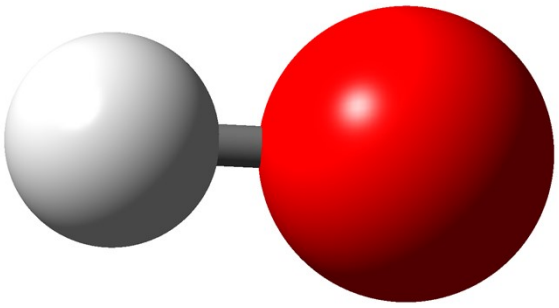


C

Energies= -370.395517 a.u

N	**-0.24763000**	**-0.42606000**	**-0.05107100**
C	**-0.64528000**	**0.98790000**	**0.33851100**
H	**-1.60808400**	**0.86019900**	**0.83515400**
C	**1.19309000**	**-0.84352200**	**-0.33746000**
H	**1.07320000**	**-1.80789300**	**-0.83902000**

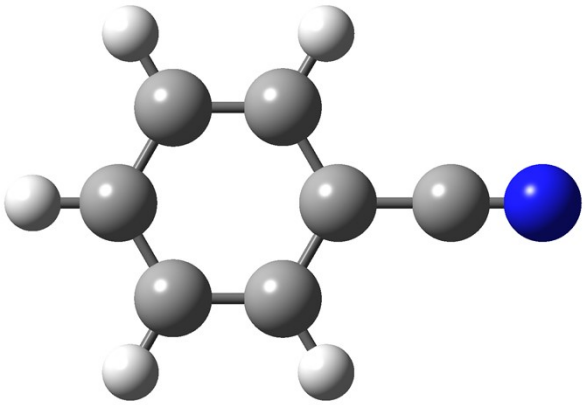
C	-0.86353200	1.85194100	-0.91256400
H	-1.52662400	1.36565400	-1.63509100
H	-1.33573700	2.78897700	-0.60170500
H	0.07342900	2.10124800	-1.41351600
C	0.29148800	1.63405600	1.36160000
H	-0.16657400	2.58096500	1.66393600
H	0.40472100	1.02229500	2.26019900
H	1.27791200	1.86670600	0.95559200
C	1.90417800	0.08908800	-1.31910100
H	1.33773300	0.21682400	-2.24555400
H	2.12601900	1.07013000	-0.89351600
H	2.86053300	-0.37604900	-1.57800300
C	1.97668300	-1.09095500	0.95735600
H	1.41785900	-1.72592700	1.65204800
H	2.89930400	-1.61795100	0.69418300
H	2.25741000	-0.16896600	1.46785800
C	-1.15768200	-1.33760900	-0.15867800
H	-0.80087900	-2.32565500	-0.44396400
C	-2.62286200	-1.18769600	0.07558600
H	-3.14460400	-2.06134400	-0.31976600
H	-2.83075200	-1.13798500	1.15404200
H	-3.03795700	-0.28802500	-0.38688500



OH^-

Energies= -75.978159 a.u

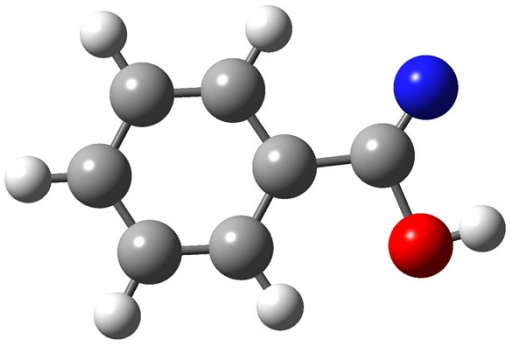
O	0.00000000	0.00000000	0.10970700
H	0.00000000	0.00000000	-0.87765300



1a

Energies= -324.583672 a.u

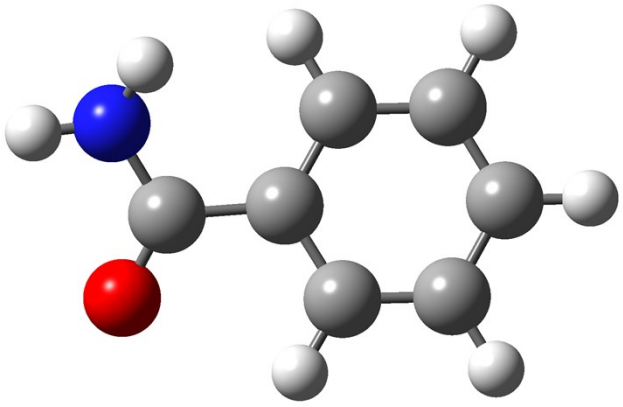
C	**-1.48403400**	**-1.21086500**	**-0.00000100**
C	**-0.09146600**	**-1.21746700**	**0.00001600**
C	**0.61027900**	**-0.00004600**	**-0.00000200**
C	**-0.09142400**	**1.21744800**	**0.00000700**
C	**-1.48395900**	**1.21091100**	**0.00000700**
C	**-2.18066100**	**0.00002400**	**-0.00001300**
H	**-2.02616600**	**-2.15194500**	**-0.00001200**
H	**0.45872800**	**-2.15284100**	**0.00001200**
H	**0.45886700**	**2.15276500**	**0.00000300**
H	**-2.02609200**	**2.15199000**	**0.00000200**
H	**-3.26703600**	**0.00007600**	**-0.00001500**
C	**2.04504100**	**-0.00002600**	**-0.00000800**
N	**3.20843600**	**0.00001200**	**-0.00000400**



D

Energies= -400.543876 a.u

C	-1.90954000	1.16605900	0.00000600
C	-2.56010800	-0.07539500	-0.00013600
C	-1.79227000	-1.24159600	-0.00010000
C	-0.39524500	-1.17338300	0.00013800
C	0.26951400	0.06617800	0.00028800
C	-0.51961700	1.23037400	0.00016300
H	-2.49635000	2.08494600	0.00009400
H	-3.64813000	-0.12989000	-0.00039700
H	-2.28530500	-2.21432000	-0.00035700
H	0.20197500	-2.07859900	0.00028900
H	0.02658500	2.17133100	0.00011900
C	1.76357500	0.23499500	0.00004400
N	2.42676100	1.27562900	-0.00026100
O	2.34869500	-1.14074500	-0.00003800
H	3.28647900	-0.88030200	-0.00004000



2a

Energies= -401.085404 a.u

C	-0.22024800	-0.02240200	-0.01853400
C	0.51521500	-1.20800400	0.10919500
C	1.90718200	-1.17382800	0.13726800
C	2.57989700	0.04573800	0.02399100
C	1.85483900	1.22978100	-0.12273500
C	0.46044700	1.19702900	-0.14331100
H	-0.02826700	-2.14414100	0.18391700
H	2.46926200	-2.09760500	0.24437800
H	3.66619500	0.07251000	0.04218400
H	2.37443900	2.17813000	-0.22971300
H	-0.09205500	2.12060800	-0.29338200
C	-1.71841200	-0.13669100	-0.03399900
O	-2.28789100	-1.19439000	-0.27170800
N	-2.42077600	1.02379800	0.20674200
H	-3.41776600	0.90053300	0.32715100
H	-1.99676300	1.76876800	0.74069300

8 Computational methods

Density functional theory (DFT) calculations were carried out by using Gaussian 16 program[1]. All the structures were optimized by using the combination of Becke's hybrid 3-parameter exchange functional[2] and Lee-Yang-Parr's correlation functional[3] known as B3LYP method in conjunction with the 6-31G(d) basis set to ensure these structure without imaginary frequencies. Then, the energy of the reaction mechanism is calculated at the B3LYP/6-311++G** level based on the optimized structures, and the solvation model based on electron density (SMD)[4] with H_2O solvent attached was used throughout. Dimensional plots of molecular configurations were generated with the GaussView program[5].

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