Continuous Nitration of Solid Aromatic Compounds with HNO_3 via Mechanochemistry

Arshad Hussain[1, 2†], Vishnu Ganthimeri[1†] and Amol A. Kulkarni[1, 2*]

[1]Chemical Engineering & Process Development Division, CSIR-National Chemical Laboratory, Pashan, Pune 411008, India.

[2]Academy of Scientific and Innovative Research (AcSIR), Ghaziabad 201002, India.

*Correspondence: Dr. Amol A. Kulkarni (aa.kulkarni@ncl.res.in)

†Equal contribution

Supporting Information

S1: GC-Mass method for the analysis of all the organic mass and calculations.

S2: MS identification for the nitrated products.

S3: 1H, 13C NMR of the products.

S4: Images taken during the experiments.

S1: GC-Mass analysis conditions:

GC Model: Agilent 7890 B GC coupled with 5977A MSD (mass selective detector)

Column: HP-5 MS column (0.5 µm X 0.32 mm X 10 m)

Solvent: Ethyl acetate (Density = 0.9 g/cc)

Method:

Inltet Temperature : 250 °C
Spit ratio: 50:50
Inlet Volume: 1 µL
Column: HP-5
Flow-rate: 1. ml/min

Oven Temperature: Ramping

Rate °C /min	Value (°C)	Hold Time (min)	Run time (min)
	50	1	
20	280	5	16

Agilent GC-MS

The retention time of every reaction component under the analysis condition are shown in the table 1.

Method for calculation of %GC Yield and Isolated Yield.

S.No.	Compound Name	Retention Time (mins)	Molecular Weight (g/mol) from GC-Mass
1	Naphthalene	4.53	128.1
2	1-Nitronaphthalene	7.521	173.1
3	2-Nitronaphthalene	7.647	173.1
4	Anthracene	8.372	178.1
5	9-Nitroanthracene	10.186	223.1
6	Anthraquinone	9.401	208
7	Salicylic Acid	4.585	138
8	5-Nitrosalicylic Acid	5.04	183
9	3-Nitrosalicylic Acid	5.055	183
10	3-Hydroxybenzaldehyde	5.497	122.1
11	3-Hydroxy-2-nitrobenzaldehyde	5.84	167
12	3-Hydroxy-4-nitrobenzaldehyde	5.361	167

% Yield (referred in the manuscript as % GC yield):

The internal response factor was used to do the GC analysis of reactants and products. The values of response factor for an internal standard and the calibrated mass of isomers on GC were used for estimating the % yield as the ratio of mass of specific isomer and the overall conversion of the limiting substrate.

%Isolated Yield:

Upon separating the isomers from the product mixture using column chromatography, the actual mass of the individual product isomers was used for estimating the isolated yield as follows.

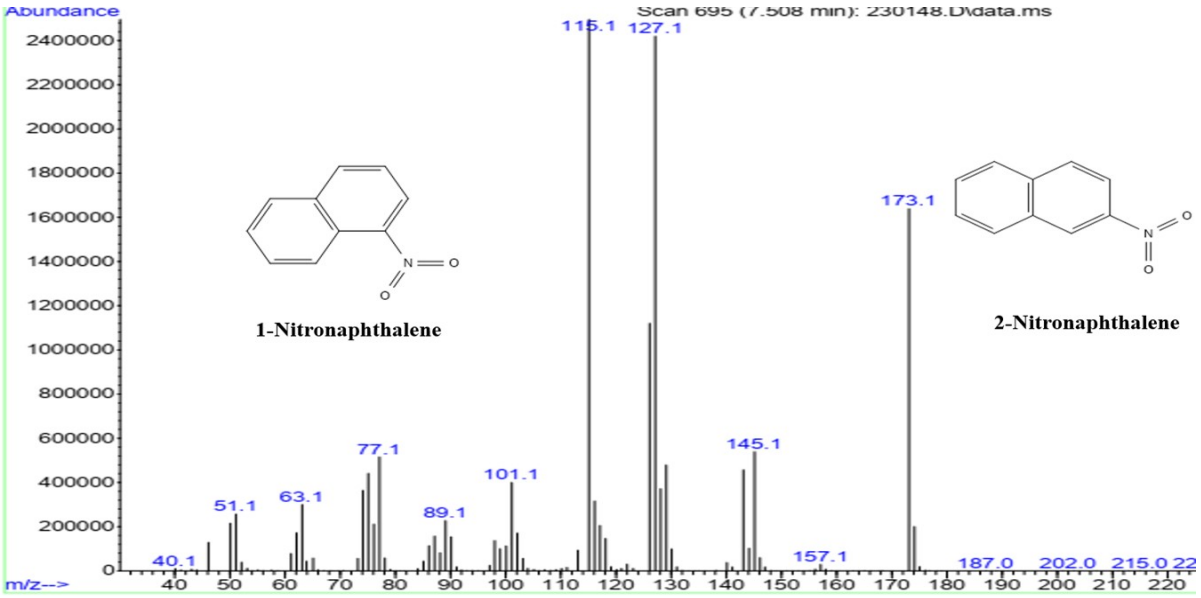
$$\begin{bmatrix} \%\ Isolated\ Yield \\ of\ isomer\ A \end{bmatrix} = \left[\frac{Mass\ of\ Isomer\ A\ in\ hand\ after\ purification}{Mass\ of\ isomer\ A\ based\ on\ GC\ analysis}\right] * 100$$

Table S 1: GC-Mass details of the substrates and products

13	2,6-ditertbutylphenol	6.217	206.2
14	2,6-ditert-4-nitrobutylphenol	8.87	251.2
15	2,5-dimethylphenol	4.189	122.1
16	2,5-dimethyl-4-nitrophenol	7.593	167.1
17	P-methoxyphenol	4.804	124.1
18	2-Nitro-p-methoxyphenol	5.71	169
19	p-Bromophenol	5.26	172
20	p-bromo-2-nitrophenol	5.877	216.8
21	p-Aminophenol	5.25	109.1
22	p-amino-2-nitrophenol	5.85	154

S2: The GC-mass identification are shown below

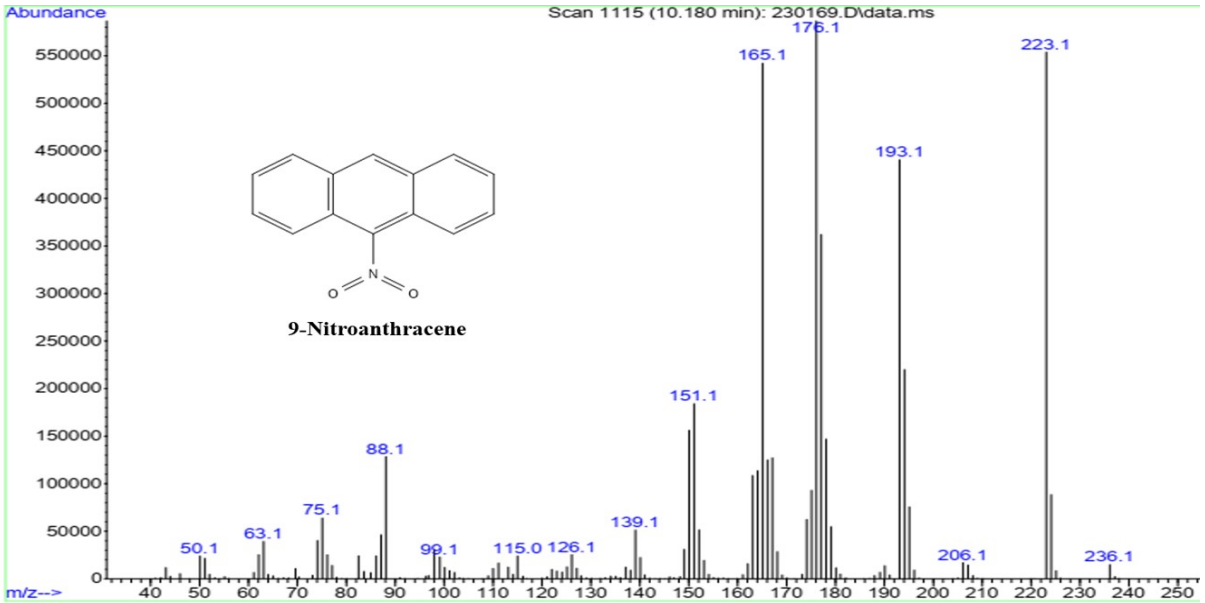
Nitro- Naphthalene



MW= 173.1

Figure S 1: MS spectrum of Nitro naphthalene

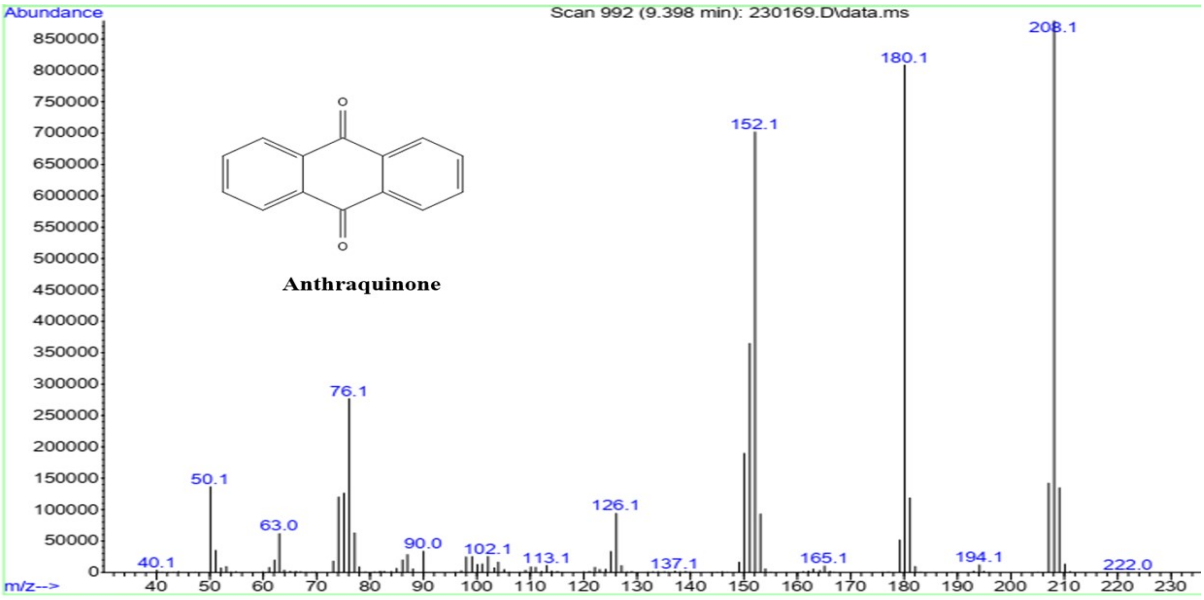
9-Nitroanthracene



MW= 223.1

Figure S 2: MS spectrum of 9-Nitroanthracene

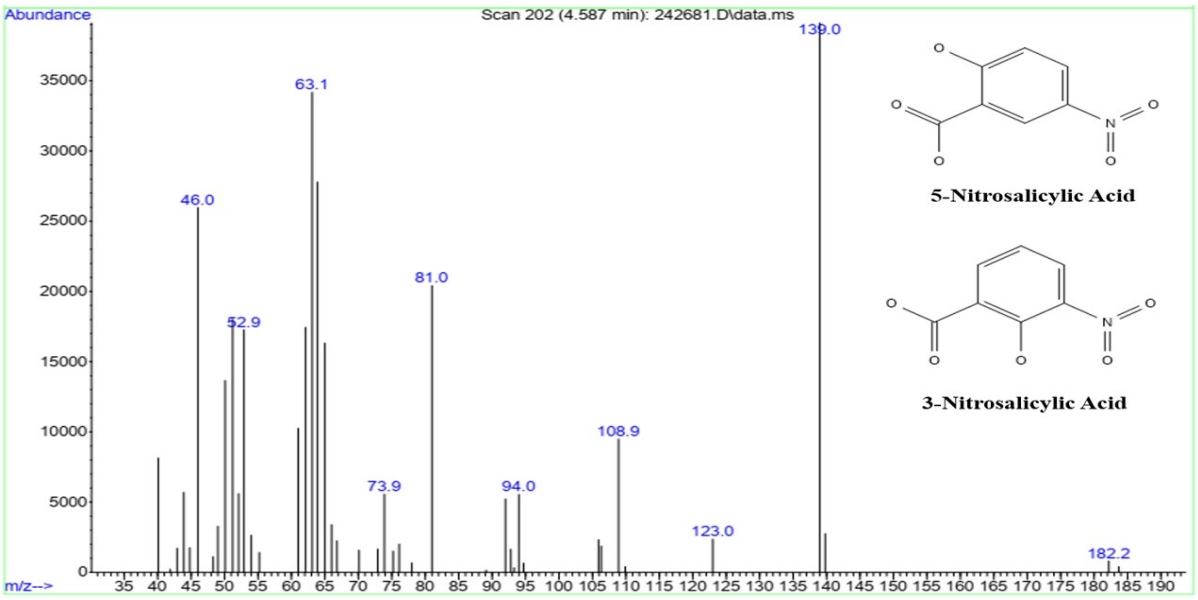
Anthraquinone



MW= 208

Figure S 3: MS spectrum of Anthraquinone

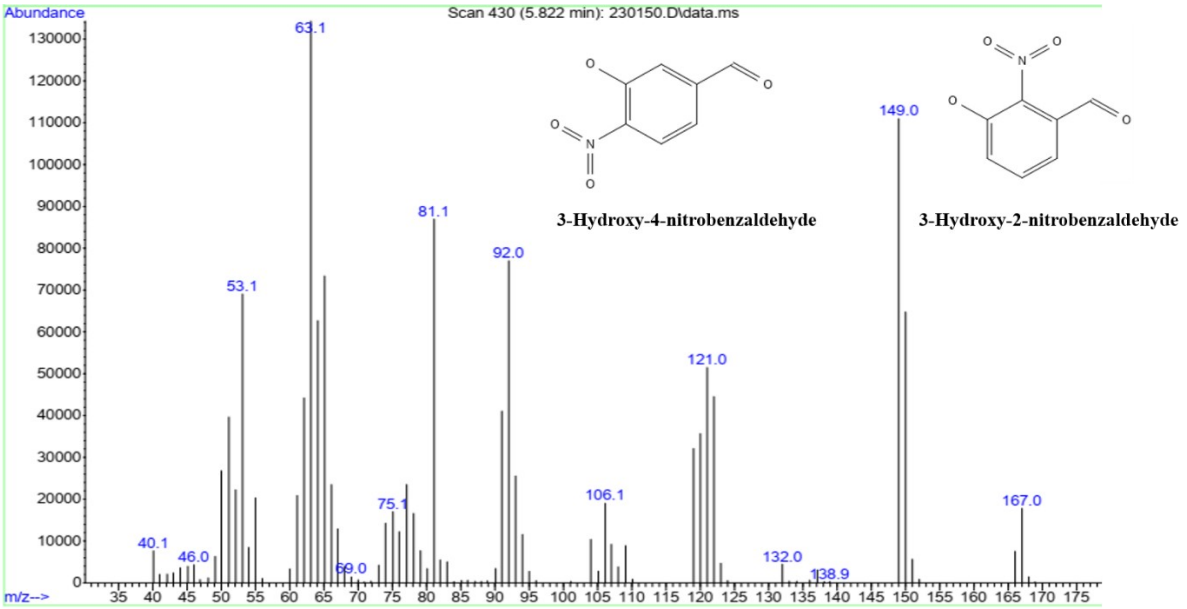
Nitro-salicylic acid



MW= 183

Figure S 4: MS spectrum of Nitro salicylic acid

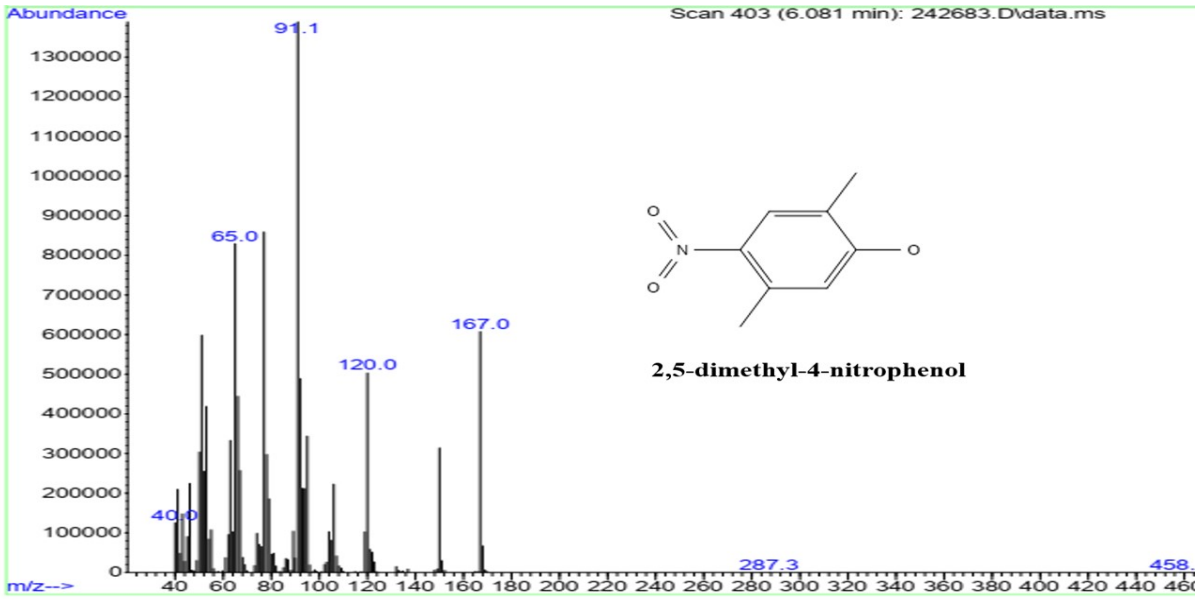
3-Hydroxynitrobenzaldehyde



MW= 167

Figure S 5: MS spectrum of 3-Hydroxynitrobenzaldehyde

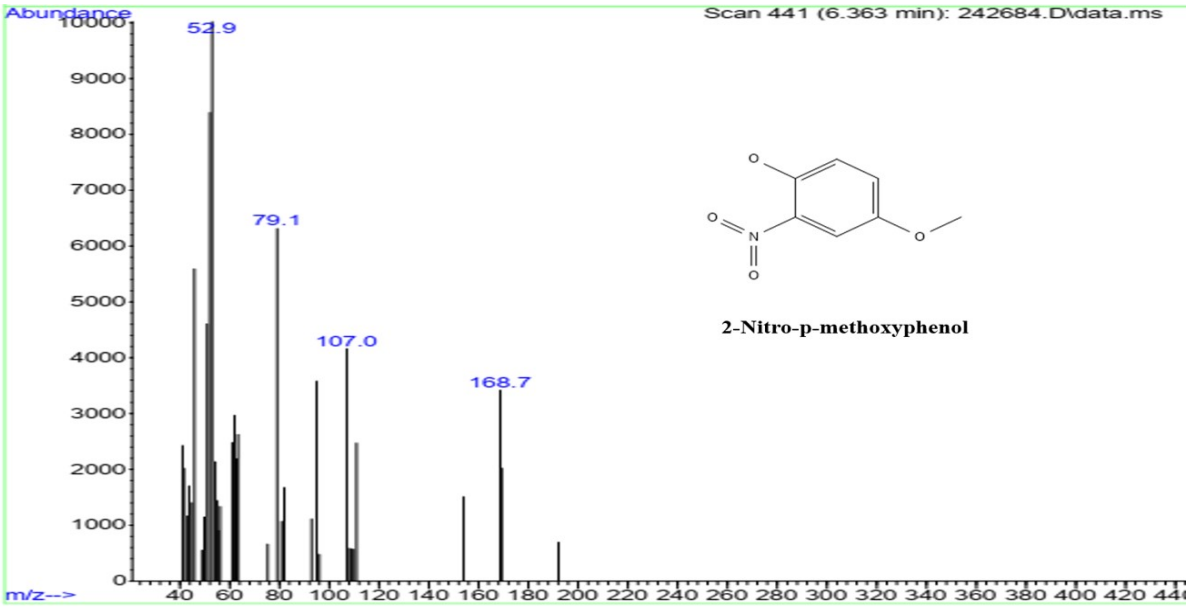
2,5-dimethyl-4-nitrophenol



MW= 167

Figure S 6: MS spectrum of 2,5-Dimethyl-4-nitrophenol

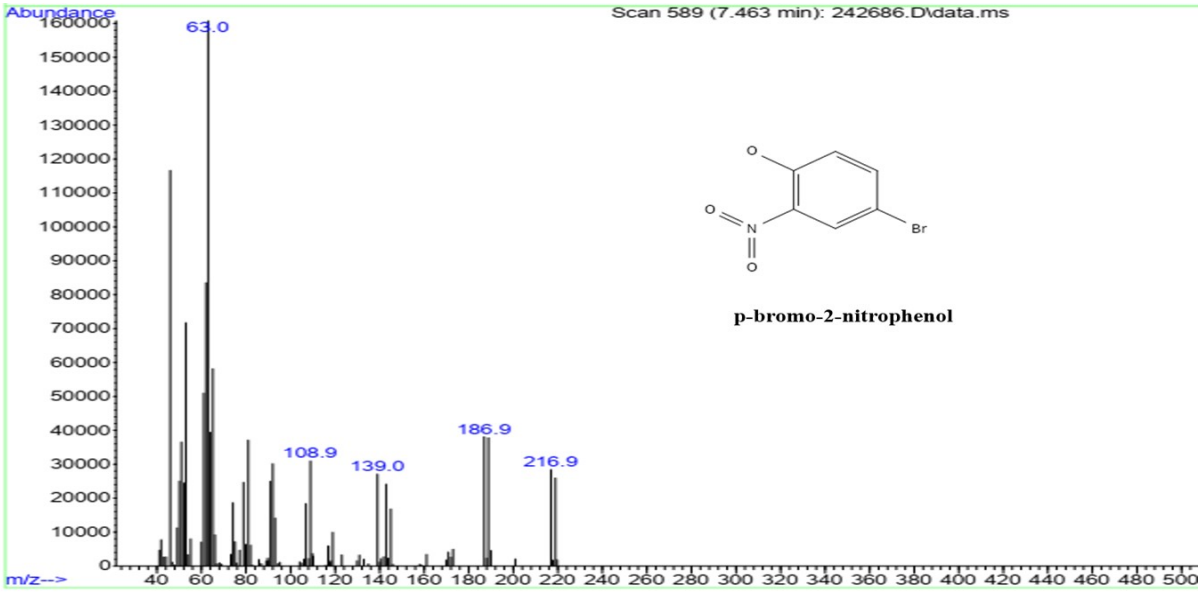
2-Nitro-p-methoxyphenol



MW= 169

Figure S 7: MS spectrum of 2-Nirto-p-methoxyphenol

p-bromo-2-nitrophenol



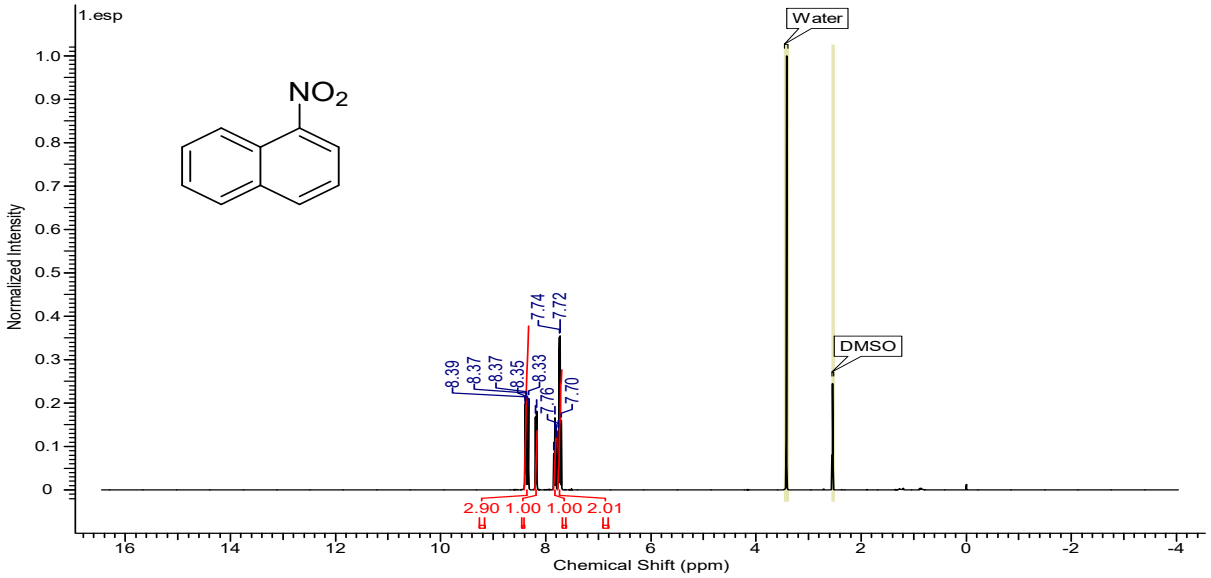
MW= 216.8

Figure S 8: MS spectrum of p-bromo-2-nitrophenol

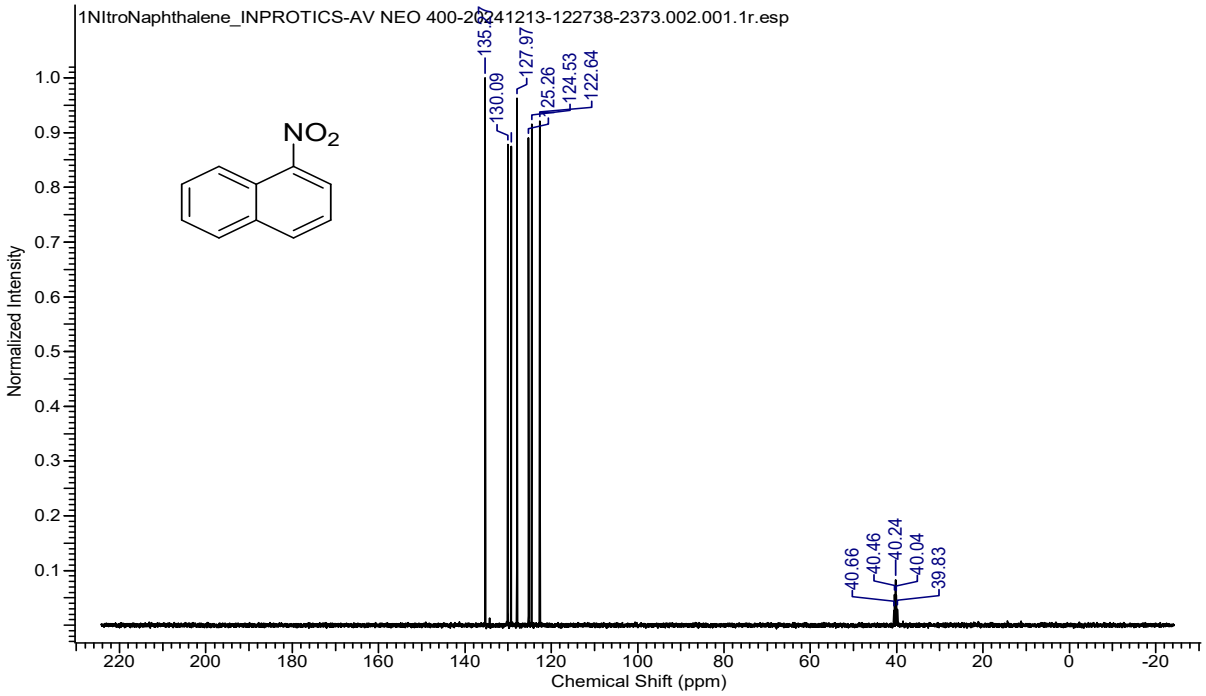
S3: 1H, 13C NMR of the products.

1-Nitronaphthalene

^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 7.70 - 7.77 (m, 2 H) 7.82 (ddd, *J*=8.57, 7.00, 1.31 Hz, 1 H) 8.17 - 8.20 (m, 1 H) 8.32 - 8.41 (m, 3 H)

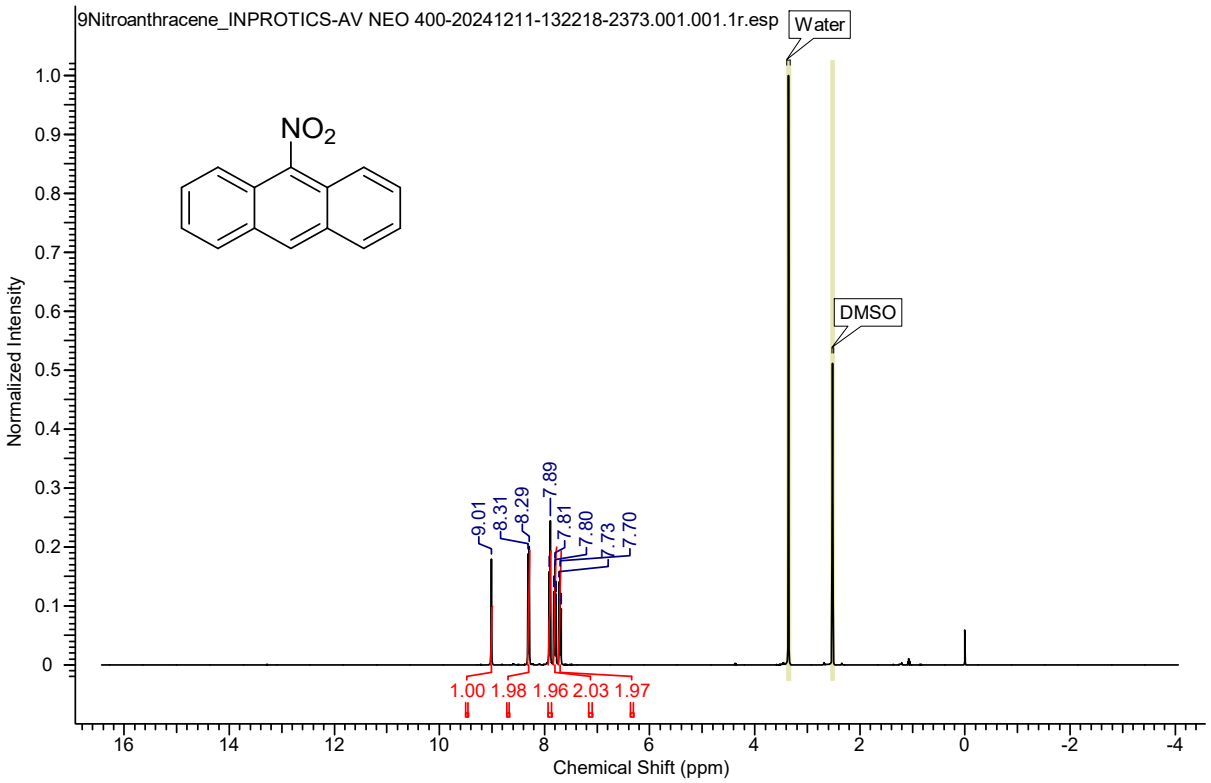


^{13}C NMR (101 MHz, DMSO-d_6) δ ppm 122.64 (s) 124.53 (s) 125.26 (s) 127.97 (s) 129.31 (s) 130.09 (s) 135.27 (s)

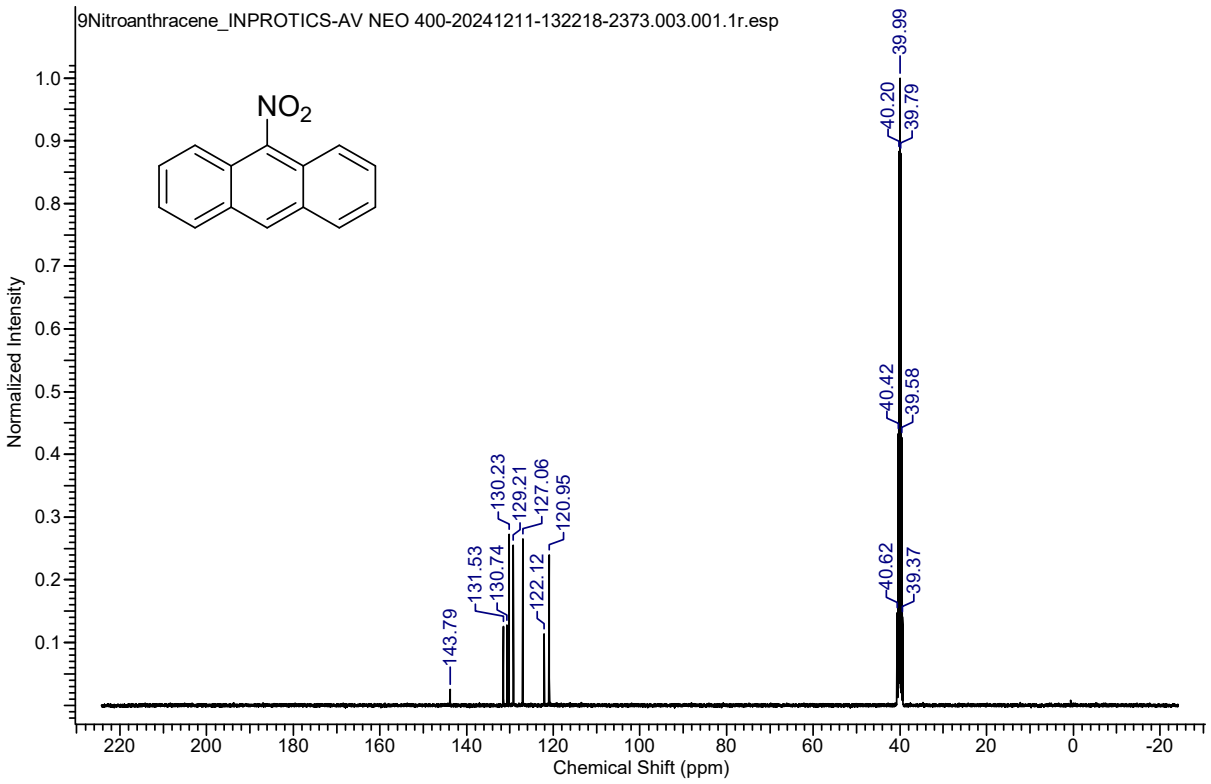


9-Nitroanthracene

^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 7.68 - 7.73 (m, 2 H) 7.77 - 7.83 (m, 2 H) 7.87 - 7.93 (m, 2 H) 8.30 (d, *J*=8.50 Hz, 2 H) 9.01 (s, 1 H)

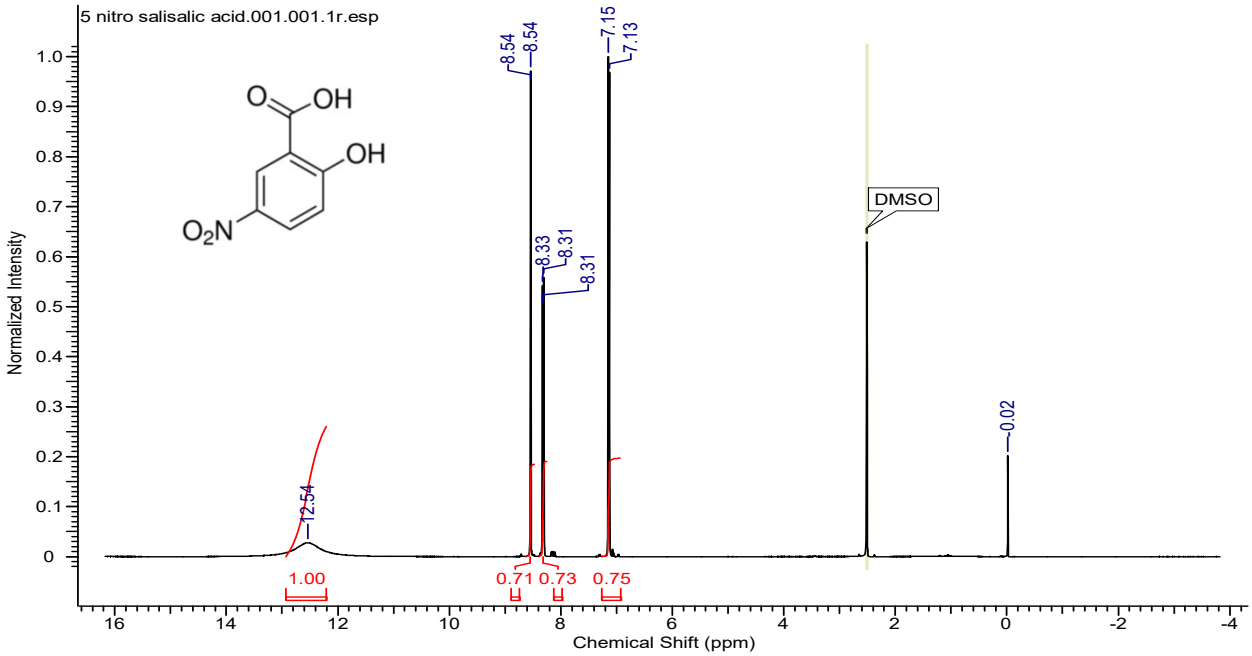


^{13}C NMR (101 MHz, DMSO-d_6) δ ppm 95 (s) 122.12 (s) 127.06 (s) 129.21 (s) 130.23 (s) 130.74 (s) 131.53 (s) 143.79 (s)

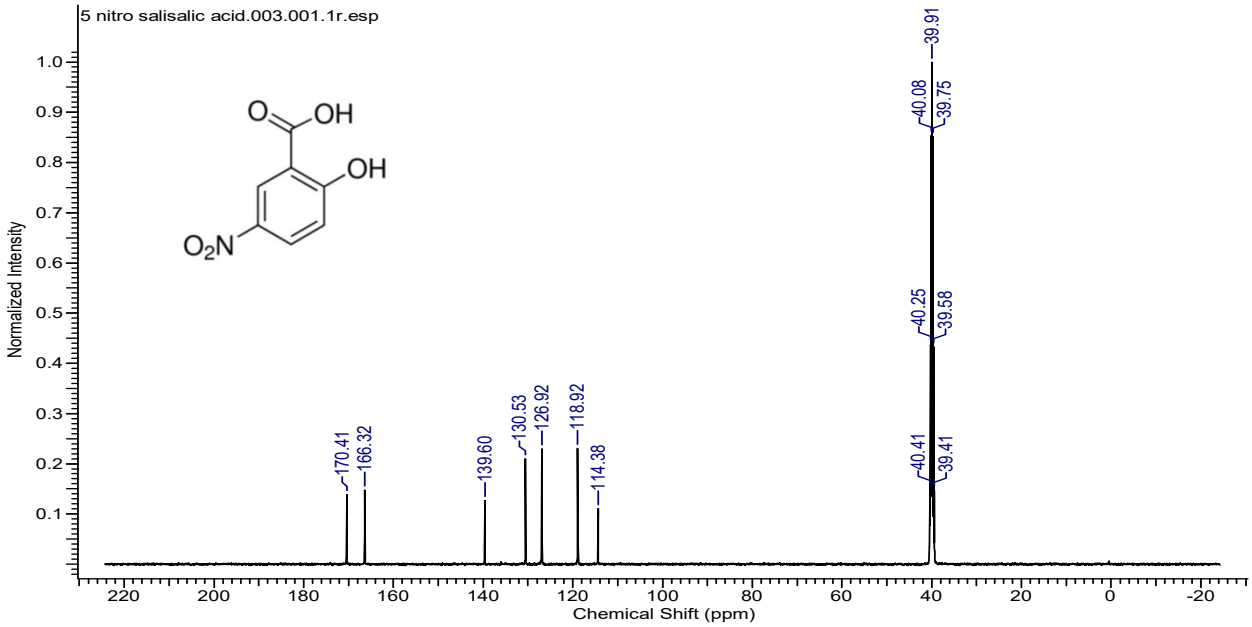


5-Nitro-salicylic acid

^{1}H NMR (500 MHz, DMSO-d_6) d ppm 7.14 (d, *J*=9.16 Hz, 1 H) 8.32 (dd, *J*=9.31, 2.90 Hz, 1 H) 8.54 (d, *J*=3.05 Hz, 1 H) 12.54 (br. s., 1 H)

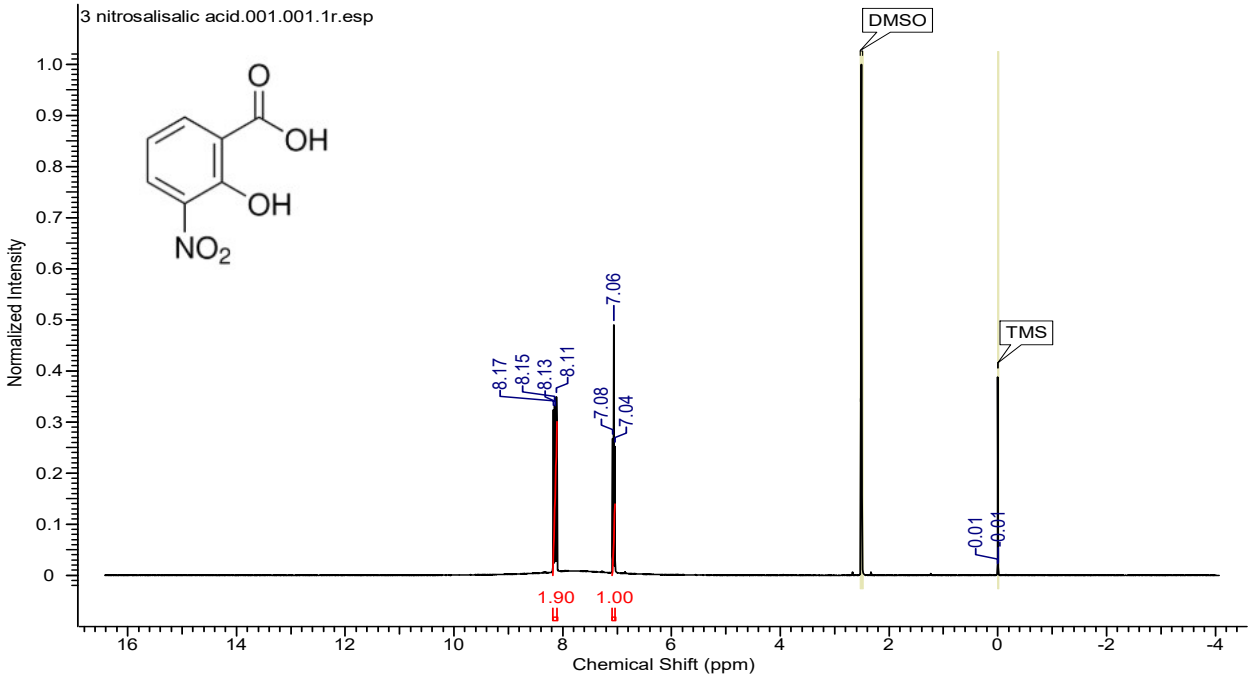


^{13}C NMR (126 MHz, DMSO-d_6) d ppm 114.38, 118.92, 126.92, 130.53, 139.60, 166.32, 170.41 .

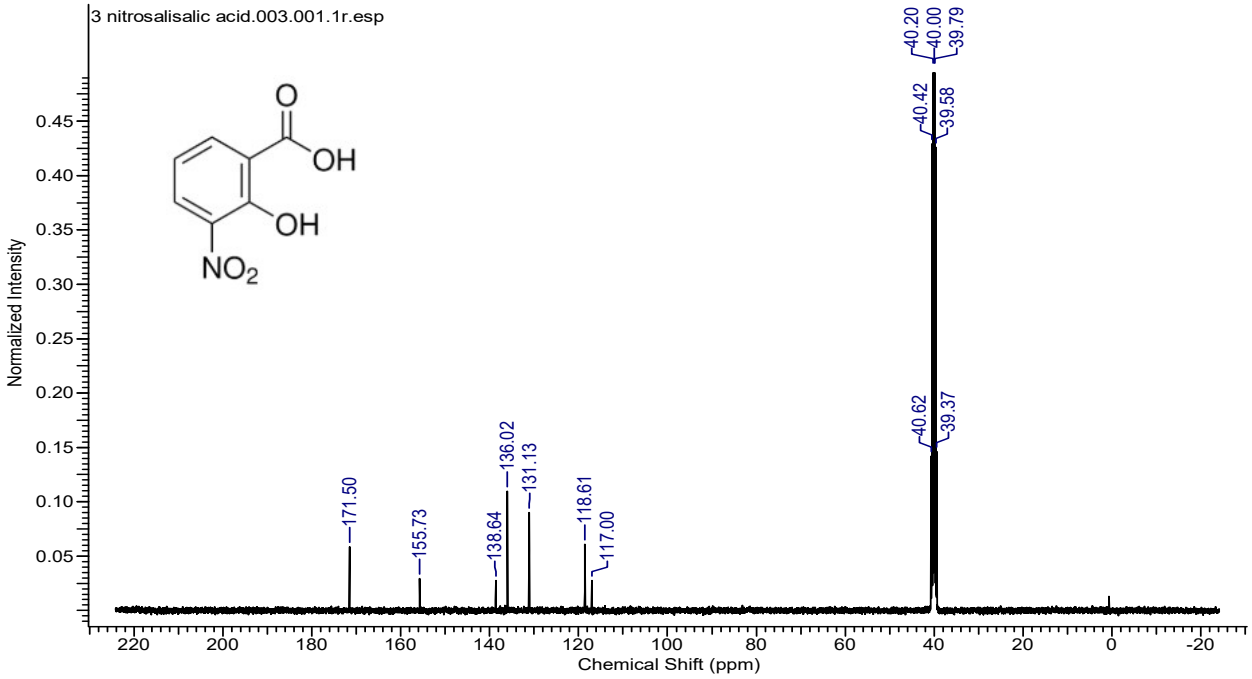


3-Nitro-salicylic acid

^{1}H NMR (400 MHz, DMSO-d_6) d ppm 7.06 (t, J=8.00 Hz, 1 H) 8.10 - 8.18 (m, 2 H)

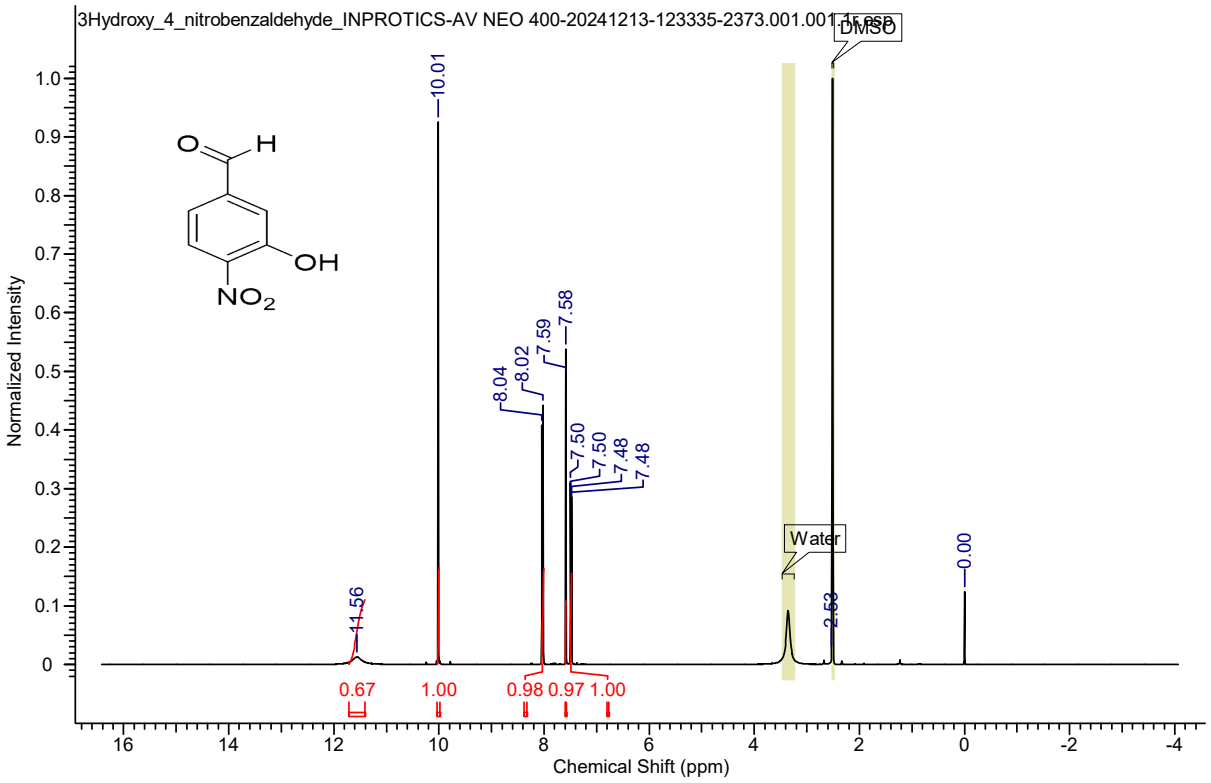


^{13}C NMR (101 MHz, DMSO-d_6) d ppm 117.00, 118.61, 131.13, 136.02, 138.64, 155.73, 171.50

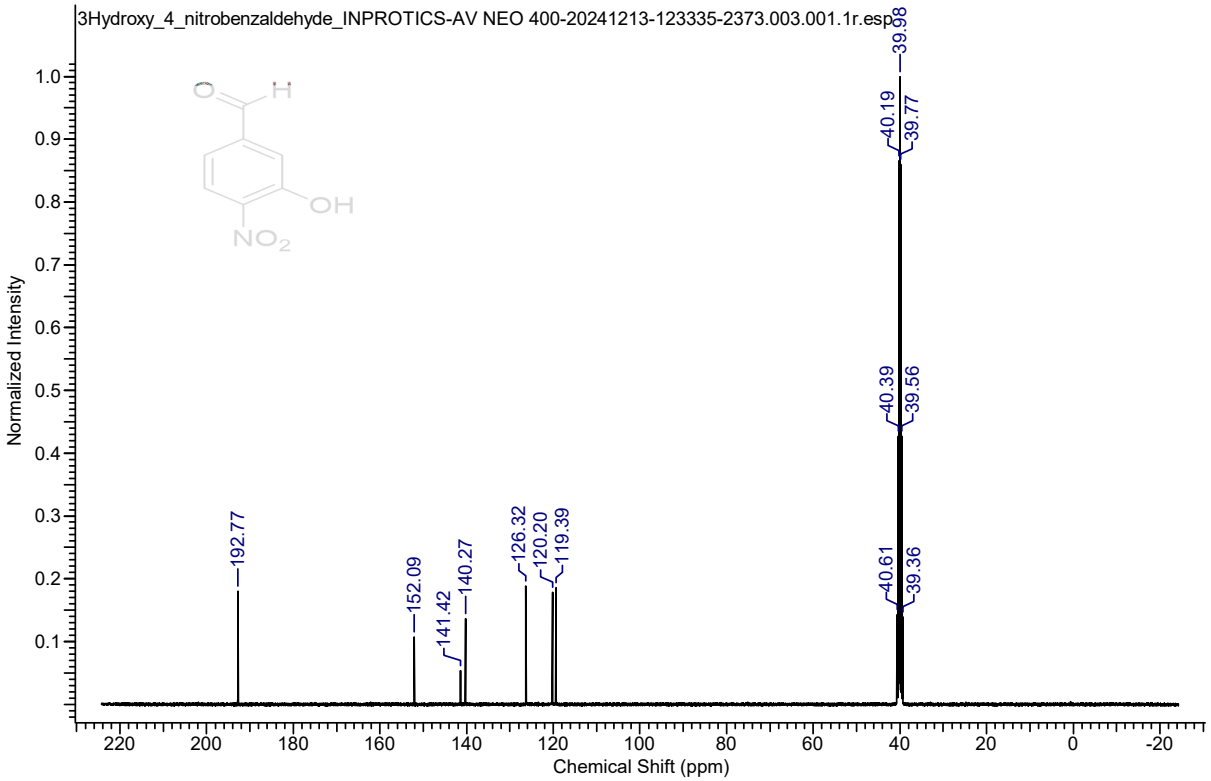


3-Hydroxy-4-nitrobenzaldehyde

^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 7.49 (dd, *J*=8.25, 1.63 Hz, 1 H) 7.59 (d, *J*=1.63 Hz, 1 H) 8.03 (d, *J*=8.25 Hz, 1 H) 10.01 (s, 1 H) 11.56 (br. s., 1 H)

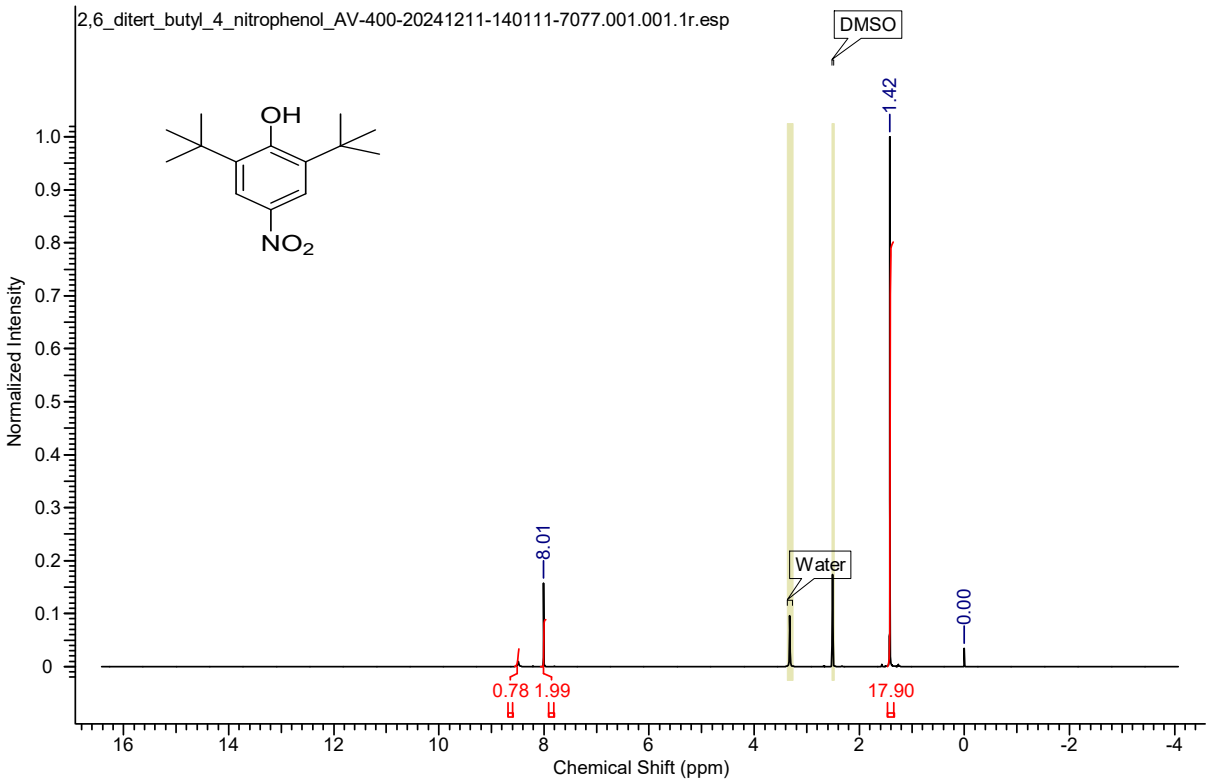


^{13}C NMR (101 MHz, DMSO-d_6) δ ppm 39.36 (s) 39.56 (s) 39.77 (s) 39.98 (s) 40.19 (s) 40.39 (s) 40.61 (s) 119.39 (s) 120.20 (s) 126.32 (s) 140.27 (s) 141.42 (s) 152.09 (s) 192.77 (s)

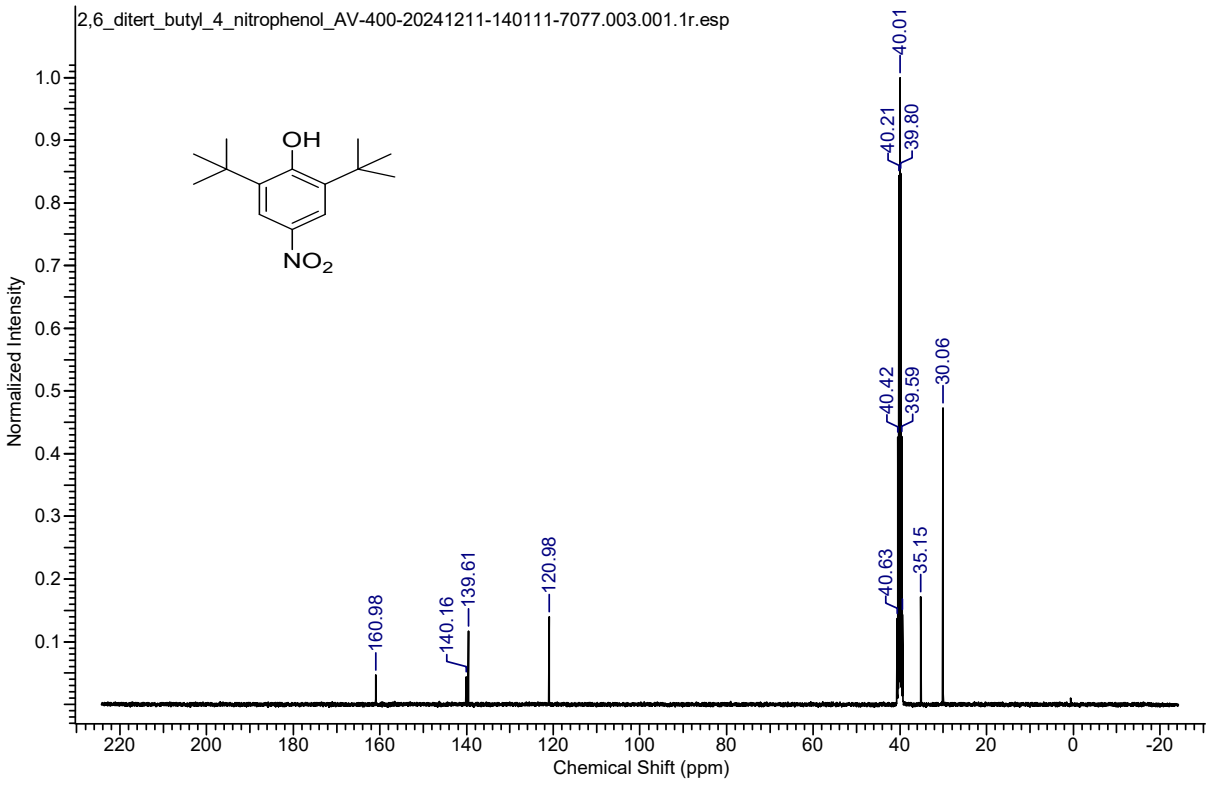

3Hydroxy_4_nitrobenzaldehyde_INPROTICS-AV NEO 400-20241213-123335-2373.003.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
192.77
152.09
141.42
140.27
126.32
120.20
119.39
40.61
40.39
40.19
39.98
39.77
39.56
39.36
OH
NO2

2,6-Ditertbutyl-4-nitrophenol

^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 1.42 (s, 18 H) 8.01 (s, 2 H)

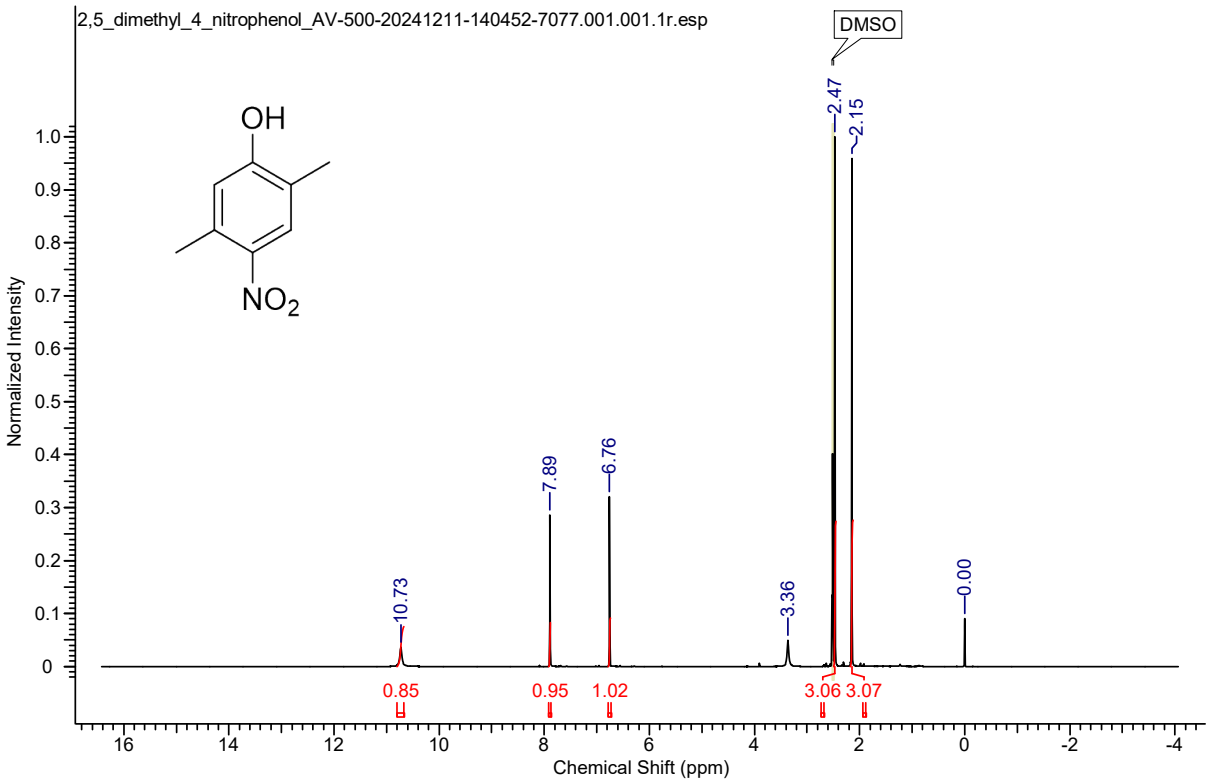


^{13}C NMR (101 MHz, DMSO-d_6) δ ppm 30.06 (s) 35.15 (s) 120.98 (s) 139.61 (s) 140.16 (s) 160.98 (s)

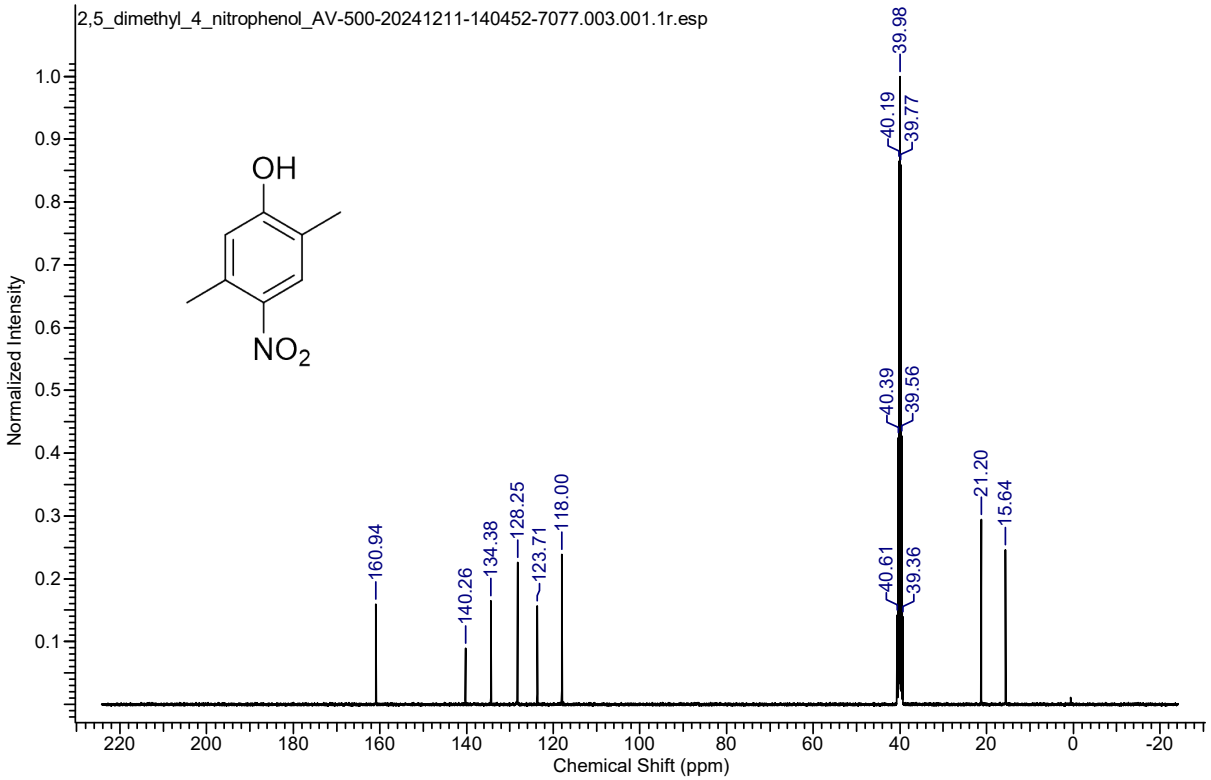


2,5-dimethyl-4-nitrophenol

^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 2.15 (s, 3 H) 2.47 (s, 3 H) 6.76 (s, 1 H) 7.89 (s, 1 H) 10.73 (br. s., 1 H)

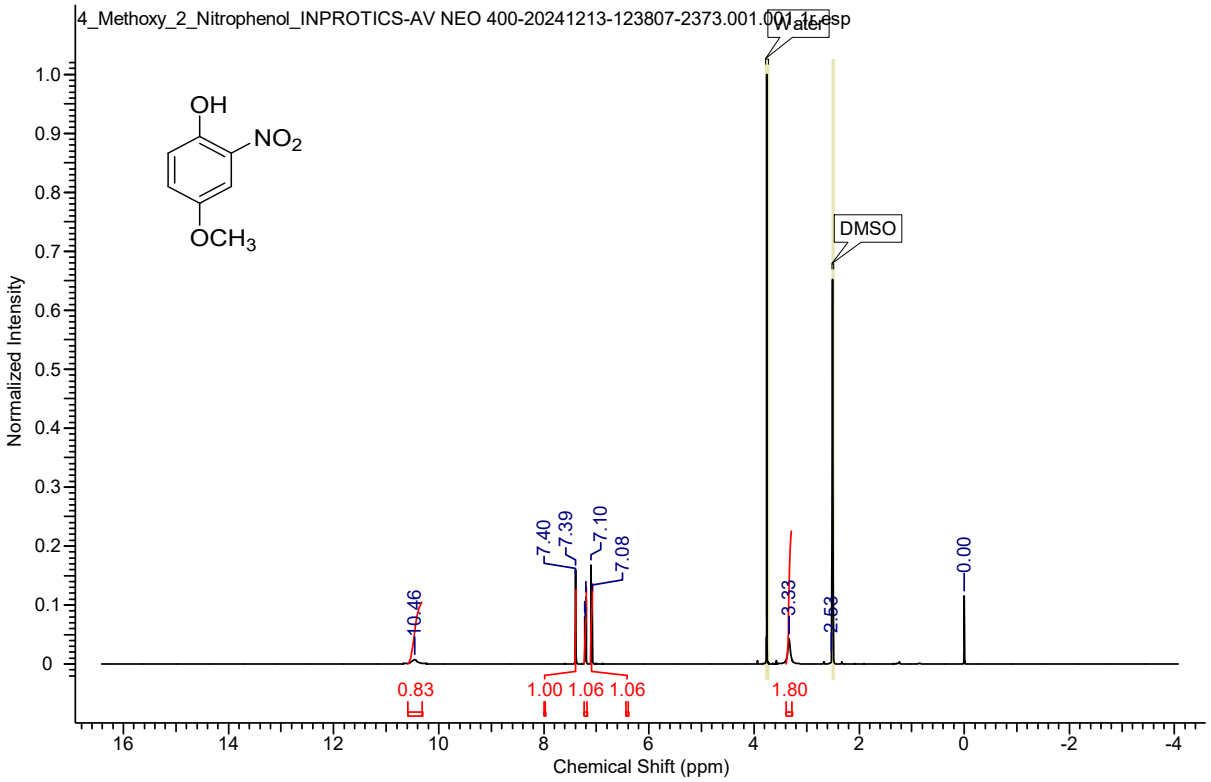


^{13}C NMR (101 MHz, DMSO-d_6) δ ppm 15.64 (s) 21.20 (s) 118.00 (s) 123.71 (s) 128.25 (s) 134.38 (s) 140.26 (s) 160.94 (s)

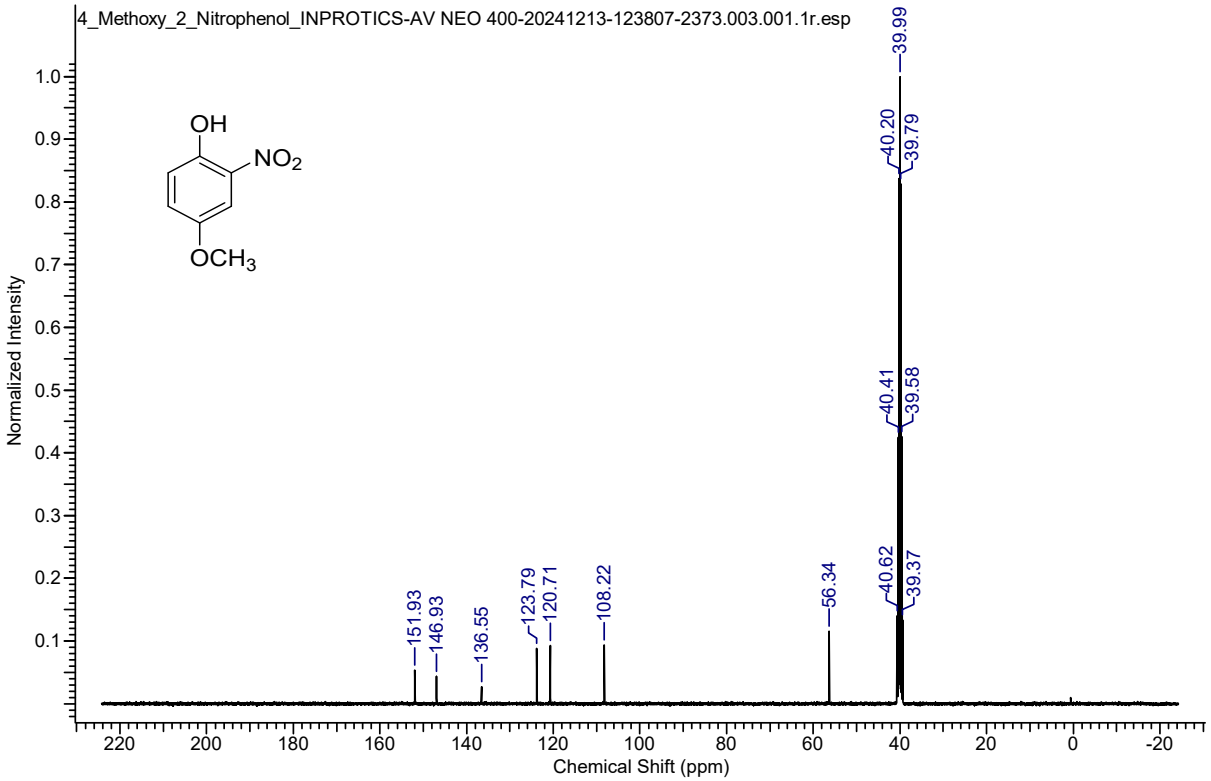


4-Methoxy-2-nitrophenol

^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 3.33 (br. s., 2 H) 7.09 (d, *J*=9.13 Hz, 1 H) 7.21 (dd, *J*=9.13, 3.13 Hz, 1 H) 7.40 (d, *J*=3.13 Hz, 1 H) 10.46 (br. s., 1 H)

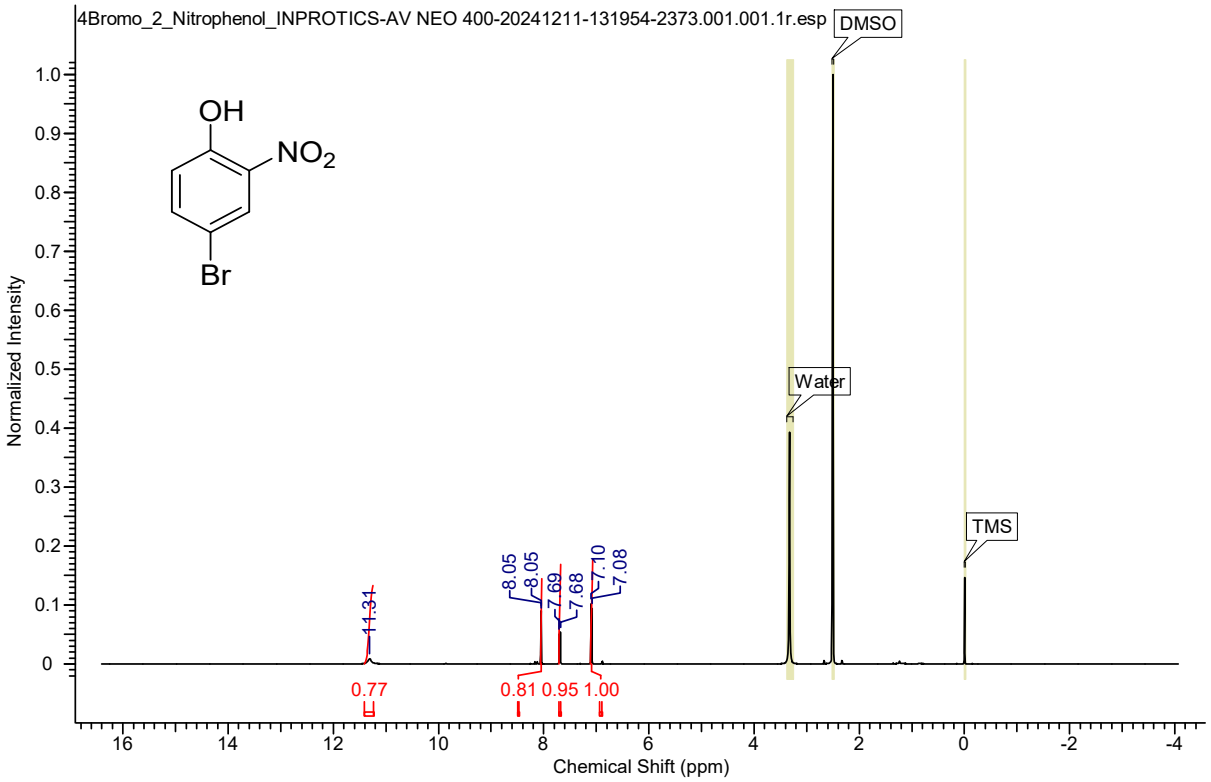


^{13}C NMR (101 MHz, DMSO-d_6) δ ppm 56.34 (s) 108.22 (s) 120.71 (s) 123.79 (s) 136.55 (s) 146.93 (s) 151.93 (s)

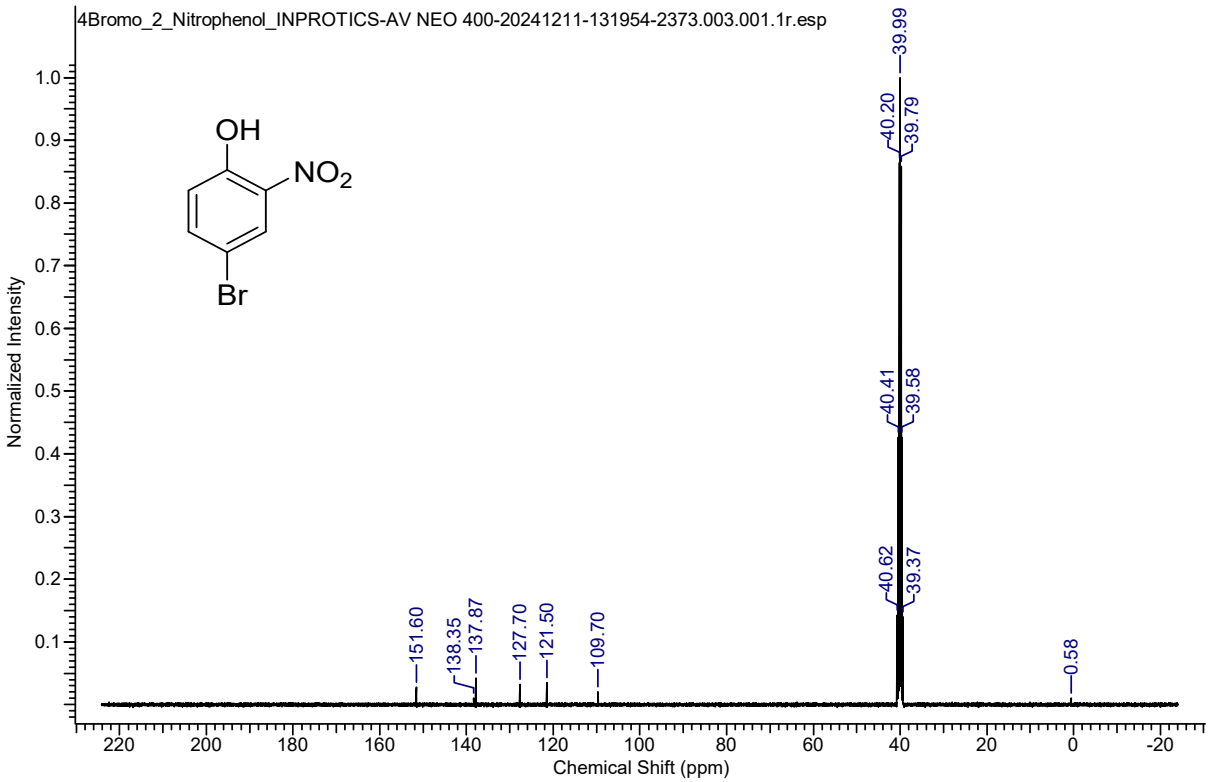


4-Bromo-2-nitrophenol

^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 7.09 (d, *J*=8.88 Hz, 1 H) 7.70 (dd, *J*=8.94, 2.56 Hz, 1 H) 8.05 (d, *J*=2.50 Hz, 1 H) 11.31 (br. s., 1 H)

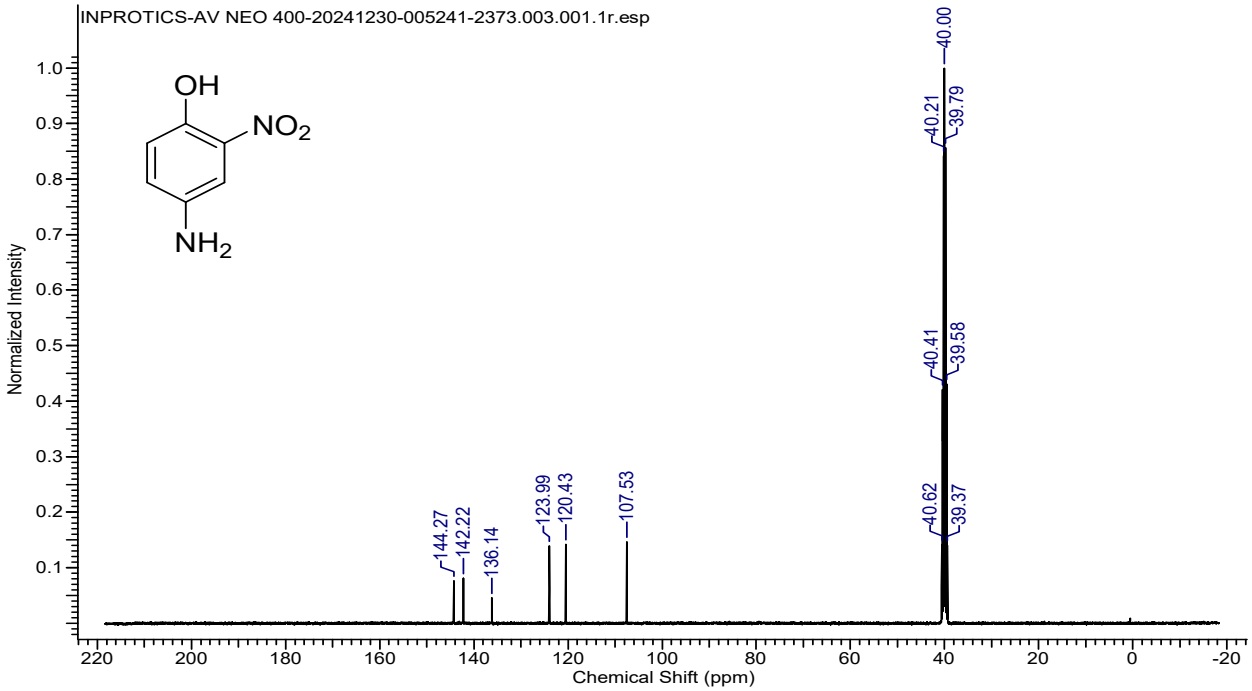


^{13}C NMR (101 MHz, DMSO-d_6) δ ppm) 109.70 (s) 121.50 (s) 127.70 (s) 137.87 (s) 138.35 (s) 151.60 (s)



4-Amino-2-nitrophenol

^{1}H NMR (400 MHz, DMSO-d_6) d ppm 5.11 (br. s., 2 H) 6.83 - 6.93 (m, 2 H) 7.10 (dd, *J*=1.94, 1.06 Hz, 1 H) 9.82 (s, 1 H)



^{13}C NMR (101 MHz, DMSO-d_6) d ppm 107.53 (s, 1 C) 120.43 (s, 1 C) 123.99 (s, 1 C) 136.14 (s, 1 C) 142.22 (s, 1 C) 144.27 (s, 1 C)

S4: Images taken during the experiments.

The nitrating agent is pumped using syringe pump and solid substrate was added from the other side. In addition, the colour change was observed and confirmed the reactions.

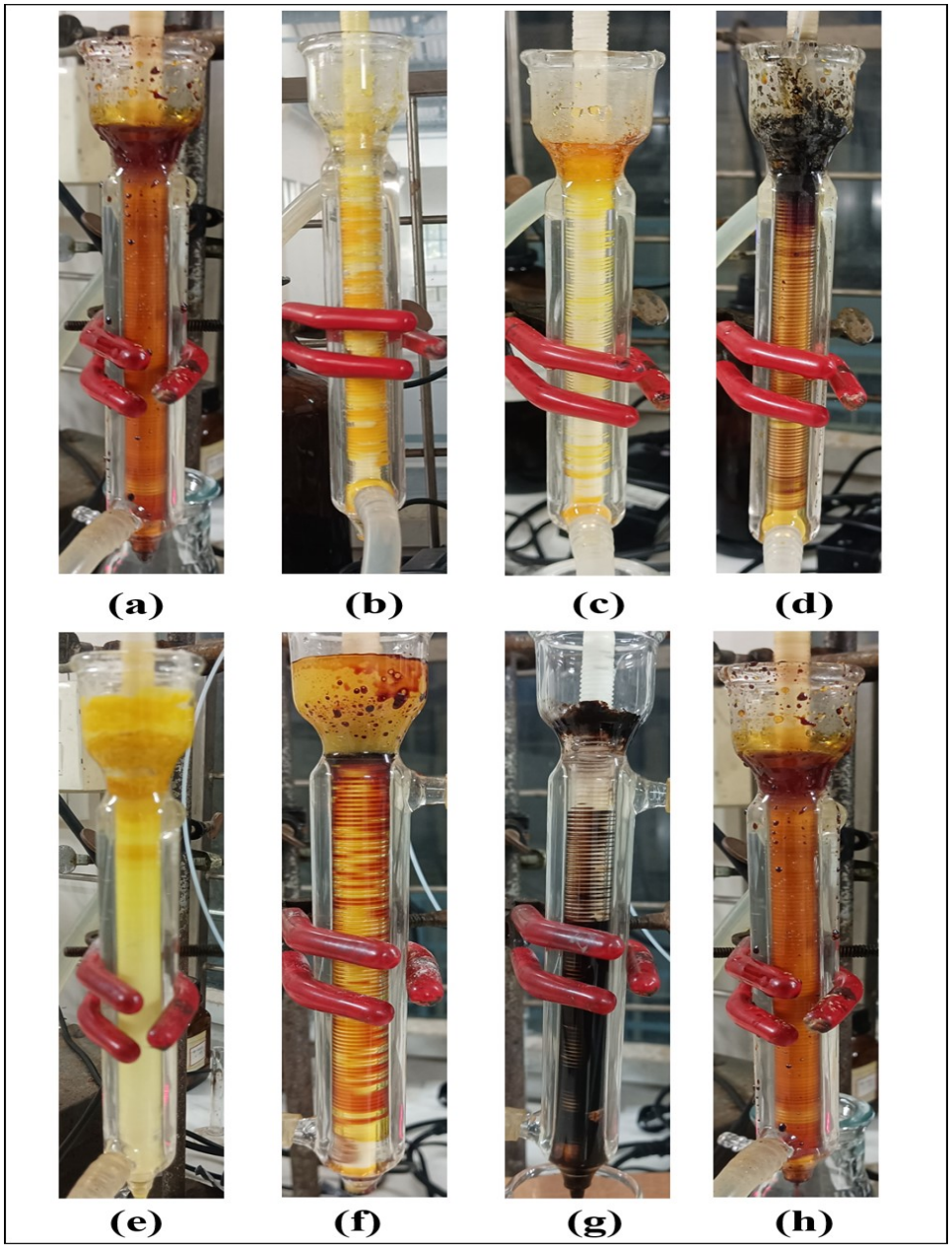


Figure S 10: Images taken during the reaction (a) Naphthalene Nitration, (b) Anthracene Nitration, (c) Salicylic acid Nitratin, (d) 4-Methoxyphenol Nitration, (e) 2,5-dimethylphenol, (f) 3-Hydroxybenzaldehyde, (g) 4-Aminophenol and (h) 4-Bromophenol