

Molybdate-Catalyzed Oxidative Bromination of Aromatic Compounds Using Mineral Acids and H₂O₂

Sushil Kumar Sharma* and Prof. D.D Agarwal**

*Ph.D research Scholar, Department of Chemistry, JJTU Rajasthan, India

** Ex-Vice Chancellor JJTU Rajasthan, India

Abstract- A facile, efficient, simple, environmentally safe, regioselective, controllable and economical method for the oxybromination of aromatic compounds using sodium molybdate in presence of mineral acids and H₂O₂. The use of sodium molybdate as catalyst accelerates the rate of reaction in presence of mineral acids and hydrogen peroxide.

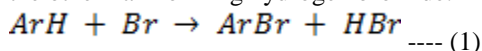
Index Terms- Halogenation, Bromination, Anilines, Sodium Chlorate, Aqueous medium, Oxidative Bromination

I. INTRODUCTION

The insertion of bromine atom into the organic molecule with its simultaneous oxidation is called oxybromination. The bromonium ion (Br⁺) along with counter ion (mainly OH⁻) is the main active species in oxybromination reactions. The bromonium ion provided directly in the solution by brominating reagent or alternately it is generated in-situ from the oxidation of bromide (Br⁻) using suitable oxidant in particular reaction conditions. The later strategy is more favorable than former one and it is widely utilized. The oxybromination reactions are vital for the synthesis of various important bromoderivatives: bromohydrins, α-bromoketones and α,α-dibromoketones as well as for other useful organic synthesis.

Bromination of organic compound is one of the popular industrial process due to multiple uses like: In water purification, agriculture, healthcare, photography etc.

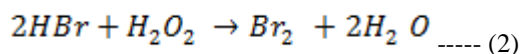
Organic compounds are brominated by either addition or substitution reactions. Bromine undergoes addition to the unsaturated hydrocarbons (alkenes and alkynes) via a cyclic bromonium intermediate. In non-aqueous solvents such as carbon disulfide, it gives di-bromo products. For example, reaction of bromine with ethylene will produce 1,2-dibromoethane as product. When bromine is used in presence of water, a small amount of the corresponding bromohydrin will form along with desired dibromo compounds. Bromine also gives electrophilic nuclear bromination of phenols and anilines. Due to this properties, bromine water was employed as a qualitative reagent to detect the presence of alkenes, phenols and anilines in a particular system. Like the other halogens, bromine also participates in free radical reactions. Classical bromination of aromatics, for example, utilizes only 50% of the halogen, with the other half forming hydrogen bromide.



Though bromine has many application in chemistry as a reagent, it has some disadvantages also whenever dispersed to

environment. Some bromine-related compounds have been evaluated to have an ozone depletion potential or bio accumulate in living organisms. As a results, many industrial bromine compounds are no longer manufactured and are being banned.

Theoretically, it is possible to reoxidise the Hydrogen Bromide, e.g. with H₂O₂, and achieve high bromine utilization, between 90 and 95%.



Thus, activated aromatic, like as phenols, anisols, and anilines, may be oxybrominated without catalyst, while inactive (benzene, toluene) but not deactivated ones, have been oxybrominated in the presence of quaternary ammonium salts. Practically, however HBr recycling is rarely performed in industrial processes, as the additional step and the corrosiveness of HBr necessitate reactor costs that exceed those of purchasing more Br₂.

Oxidation of bromides to bromine according to this invention typically takes place in a commercial setting in a packed column with addition of the reagents and steam in a continuous system using hydrogen peroxide as an oxidant for bromine production; however, variations are possible as will be familiar to those skilled in the art.

This invention provides that bromine can be derived from about 0.01 wt % to about 60 wt % HBr, about 3 wt % to about 70 wt % H₂O₂, about 0.03 wt % to about 0.5 wt % catalyst according to this invention and about 5 wt % to about 20 wt % HCl, all based on the sum of the weights of the HBr, the H₂O₂, the catalyst, and the HCl prior to each being used in the bromine derivation. Typically, the bromide source, the oxidant, and the catalyst, and when included, the hydrogen chloride or mineral acid, are in aqueous solution. This invention also provides that the molar ratio of bromide source to catalyst according to this invention can be from about 150:1 to about 1200:1, or about 200:1 to about 1000:1, or about 400:1 to about 900:1, or about 600:1 to about 850:1, or about 858:1 to about 831:1.

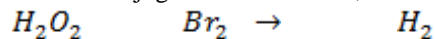
The major issue is transportation and storage of large quantities of molecular bromine and HBr is extremely hazardous. These risk can be reduced by bromide recycling. Several recent publications cite toxicity of as the incentive to investigate various complex oxybromination reagents. Neurocardiogenic syncope is a well-defined cardiovascular condition, its cause, however is still poorly understood. Although several pathophysiologic interpretations regarding its cause have been proposed, various mechanism may contribute to the cause in

different subjects or even simultaneously in one subject. But in real life two situations have to be distinguished:

(a) When molecular bromine is available on site, it is the cheapest and most environmental friendly brominating



reagent. used in conjugation with , the stoichiometry would



then be $+ 2Ar + 2ArBr + 2 O$.

(b) When a bromine containing reagent has to shipped to the site, only four reagents are cheap enough to matter for large-scale



manufacturing: , HBr, KBr and NaBr.

II. IDENTIFY, RESEARCH AND COLLECT IDEA

All the melting points are uncorrected and are presented in degree celcius. FT-IR spectra was recorded on a Bomem Hartmann and Barun MB-series FT-IR spectrometer. ACS grade chemicals were purchased from commercial firms (Sigma Aldrich) (> 99% pure) and used without further purification. Common reagent grade chemicals were procured from SD Fine Chemicals Ltd. (Mumbai, India) and also used without further purification. Gas Chromatograph were performed using an HP-5890, with the HP1 capillary column. Mass spectra were measured on an LC-MSD-Trap-XCT instrument. High-resolution mass spectra were measured on a MALDI-FTMS.

Sodium Molybdate specification:

(CAS No. 10102-40-6)

Assay	99.5%
P ^H of a 5% solution at 25 degree celcius	7.0 – 10.5
Insoluble Matter	0.0005%
Chloride (Cl)	0.0005%
Plosphate (PO ₄)	2 ppm
Sulphate (SO ₄)	0.005%
Ammonium (NH ₄)	0.0001%
Heavy Metal (as Pb)	2 ppm
Iron (Fe)	0.0001%

Table 4.3 : Composition of reagent

Test: By oxidative titration after reduction of Mo^{VI}. Weigh accurately about 0.3g, and dissolve in to 10 mL of water in a 150 mL beaker. Activate the zinc amalgam of a Jones redactor by passing 100 mL of 1N sulphuric acid, through the column. Discard this acid, and place 25 mL of ferric ammonium sulphate in the receiver under the column to the sample solution, add 100 mL of 1N sulphuric acid and pass this mixture through the

redactor, followed by 100 mL of 1N sulphuric acid and then 100 mL of water. Add 5 mL of phosphoric acid of the solution in the receiver, and titrate with 0.1N KMnO₄ volumetric solution. Run a blank and make any necessary correction. One mL of 0.1 N KMnO₄ corresponds to 0.008066g of sodium molybdate.

$$\frac{[mL(Sample) - mL(Blank)] * N KMnO_4}{Sample\ wt\ (g)} * 8.066(g)$$

% Na₂MoO₄.2H₂O

Sodium Molybdate FTIR spectra:

FTIR spectrum of pure sodium molybdate is given in Figure xyz. The Mo-O stretching frequency appears at 826 cm-1.

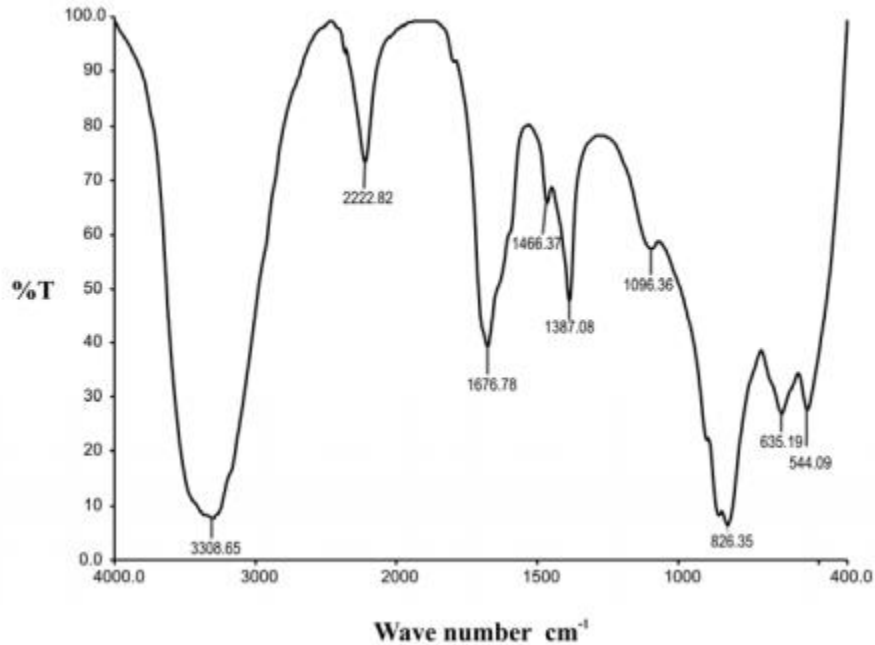
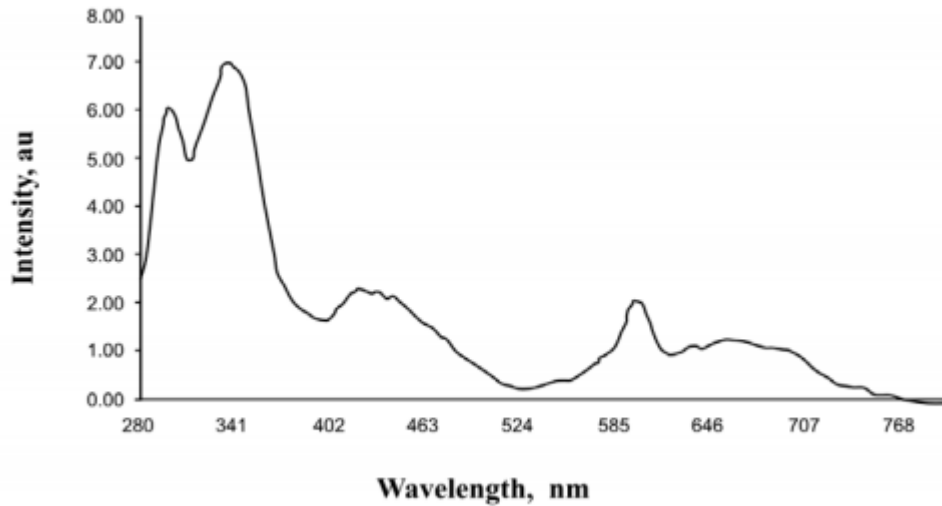


Figure 4.3a FTIR spectrum of pure sodium molybdate (SM)



a) SM solution

Figure 4.3b FTIR spectrum of sodium molybdate solution

Sodium molybdate (SM) effectiveness over a wide P^H range:

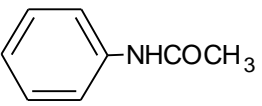
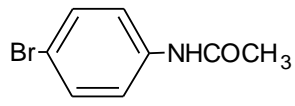
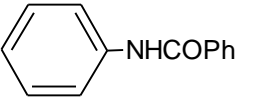
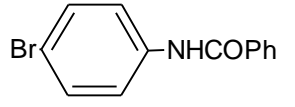
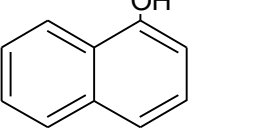
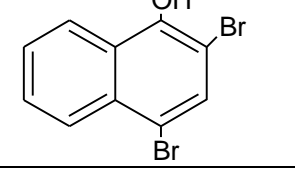
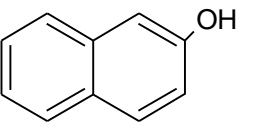
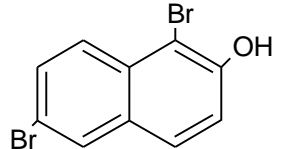
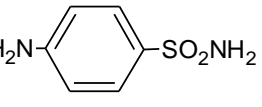
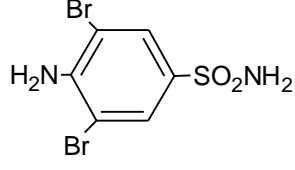
It is environmentally safe and nontoxic. It is effective over a wide pH range. Due to increasing environmental constrains,

molybdate represents a logical, environmentally acceptable alternative. In *appendix I figures* describe the detailed summary of of the pH dependence of reagent and shows the admittance of sodium molybdate at different pH ranges.

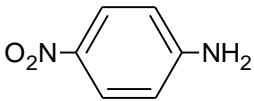
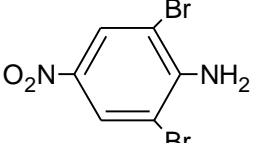
Elemental composition and mass composition by element (g/mol) of NaMoO₄:

Symbol	Element	Atomic weight	Number of atoms	Mass percent
Na	Sodium	22.989769282	1	12.5662%
Mo	Molybdenum	95.962	1	52.4527%
O	Oxygen	15.99943	4	34.9811%

Bromination of various aromatics with sodium molybdate using mineral acids and hydrogen peroxide at room temp.^a

Entry	Substrate	Product	Time/min	Yield (%) ^b	Mp/°C (lit.)
1.			10	98	167(165-169)
2.			25	92	200(200-202)
3.			15	93	105(105-107)
4.			20	95	104(105-107)
5.			20	95	235(235-237)

6.			15	96	80(80-84)
7.			20	90	183(181-185)
8.			15	98	200(198-200)
9.			15	91	92(92-94)
10.			25	93	120(120-121)
11.			20	95	114(116-117)
12.			15	94	108(110-113)
13.			20	97	127(127-130)
14.			20	96	102(100-103)
15.			15	92	166(164-166)
16.			15	90	102(102-104)

17.			20	94	204-208 (206-208)
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III. STUDIES AND FINDINGS

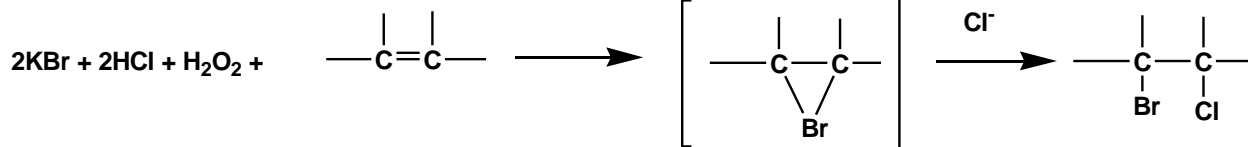
- I- All commercially available chemicals and reagents were used without further purification unless otherwise indicated. All reactions were carried out in air without any special precautions. ¹H and ¹³C NMR spectra were recorded on a Bruker F113V spectrometer operating at 500/200, and 125/50 MHz, respectively. Chemical shifts are reported in ppm relative to TMS as an internal standard, for ¹H and ¹³C NMR spectra. FT-IR spectra were recorded on Perkin Elmer GX-2000 spectrometer. Gas chromatograms were recorded on ThermoTrace-GC-Ultra. Melting points were recorded on Veego- capillary instrument as well as on Mettler Toledo FP62 melting point apparatus with open capillary tubes and are uncorrected. Progress of the reactions was monitored by thin layer chromatography (TLC) using Aluchrosep Silica Gel 60/UV254 plates of Merck, Germany or on TLC's prepared from silica-gel fine powder coated on glass plates. Compounds were purified by column chromatography over silica gel 100-200 mesh size and neutral alumina wherever necessary using hexane/ethyl acetate as eluent. (Note: The peak appeared in ¹H-NMR spectra around 1.6 -1.7 and 3.3 ppm is corresponding to the residual H₂O from the deuterated solvent CDCl₃ and DMSO respectively).
- II- Potassium bromide is used in some photographic developers to inhibit the formation of fog (undesired reduction of silver). Bromine is also used to reduce mercury pollution from coal-fired power plants. This can be achieved either by treating activated carbon with bromine or by injecting bromine compounds onto the coal prior to combustion. Soft drinks containing brominated vegetable oils are sold in the US (2011). Various bromine containing compounds are used in various pharmaceutical applications such as brompheniramine, bromocriptine (parkinsons disease), citalopram hydrobromide (antidepressant), homatropine methyl bromide (anticholinergic), propantheline.
- III- Spectral data (¹H NMR, IR and MS) of of brominated compounds is given below:
- IV- **4-bromoacetanilide (2)**: White crystals; ¹H NMR (400 MHz, DMSO): δ 2.1 (3H, s), 7.25

- (2H, d, J= 8.4 Hz), 7.52 (2H, d, J = 8.8 Hz), 9.73 (1H, s); IR (KBr): 3293, 3260, 3186, 3115, 3052, 1668, 1644, 1601, 1586, 1532, 1487, 1394, 1309, 1290, 1255, 1007, 831, 819, 740, 687, 504 cm⁻¹; MS m/z calcd. for C₈H₈BrNO: 216.07, FOUND 216.
- V- **4-Bromobenzanilide (3)**: Light grayish powder; ¹H NMR (400 MHz, CDCl₃): δ 7.29-7.74 (9H, m); IR (KBr): 3339, 3054, 1661, 1589, 1411, 1196, 946, 893, 750, 714, 509 cm⁻¹; MS m/z calcd. for C₁₃H₁₀BrNO: 276.132, FOUND 276.
- VI- **2,4,6-Tribromoaniline (4)**: White-shining fine needles; ¹H NMR (400 MHz, CDCl₃): δ 7.49 (s, 2H, ArH), 5.21 (bs, 2H, NH₂); IR (KBr): 3414, 3293, 1452, 1383, 1285, 1225, 1063, 858, 729, 706, 673, 546, 486 cm⁻¹; MS m/z calcd. for C₆H₄Br₃N: 329.816, found 327.
- VII- **2,4-Dibromo-1-naphthol (6)**: Grayish-brown powder; ¹³C NMR (100 MHz, CDCl₃): 148.02, 131.73, 130.93, 127.97, 126.97, 126.74, 124.92, 122.66, 113.27, 103.09; IR (KBr): 3412, 3075, 1961, 1934, 1720, 1616, 1583, 1548, 1502, 1449, 1374, 1330, 1266, 1230, 1209, 1146, 1057, 1030, 966, 870, 851, 766, 716, 671, 646, 602, 580 cm⁻¹; MS m/s calcd. for C₁₀H₆Br₂O: 302, found 300.
- VIII- **1,6-Dibromo-2-naphthol (7)**: Light brown solid; ¹H NMR (400 MHz, CDCl₃): δ 6.20 (1 H, brs), 7.40-7.78 (2H, dd, J=66 and 9Hz), 8.15-8.36 (2H, dd, J =33 and 9 Hz), 8.76 (1H, s); IR (KBr): 3485, 3444, 1617, 1586, 1381, 1210, 1183, 928, 871, 805, 645, 536, 512 cm⁻¹.
- IX- **5,7-Dibromo-8-hydroxyquinoline (9)**: Light beige powder; ¹H NMR (400 MHz, DMSO): δ 8.90 (dd, 1H, arom), 8.46 (dd, 1H, arom), 7.89 (s, 1H, arom) 7.65 (t, 1H, arom); IR (KBr): 3071, 1738, 1583, 1491, 1459, 1389, 1333, 1273, 1202, 1138, 1045, 934, 868, 808, 787, 725, 686, 652, 617, 594, 563, 500 cm⁻¹; MS m/z calcd. for C₉H₅Br₂NO: 302.95, found 302.2.
- X- **3,5-Dibromosalicylaldehyde (10)**: Pale-yellow crystalline powder; ¹H NMR (400 MHz, CDCl₃): δ 7.68 (d, 1H, J=2.12 Hz, ArH), 7.90(d, 1 H, J= 2.60 Hz, ArH), 9.81 (S, 1h, COOH), 11.51 (s, 1H, OH); IR(KBr): 3184, 1682, 1662, 1653, 1449, 1410, 1375, 1362, 1327, 1281, 1255, 1200, 1153, 1134, 877, 866, 735, 712, 692, 679, 505 cm⁻¹; MS m/z calcd. for C₇H₄Br₂O₂:279.9, found 280.

XI- **2,6-Dibromo-4-nitroaniline (18)** : Yellow powder; $^1\text{H NMR}$ (400 MHz, DMSO): δ 8.21 (2h,s), 6.79 (1H,s); IR(KBr): 3480, 3372, 3084, 2922, 2666, 2363, 1605, 1501, 1474, 1383, 1300, 1270, 1126, 943, 897, 821, 737, 695, 575, 532, 457 cm^{-1} ; MS m/z calcd. for $\text{C}_6\text{H}_4\text{Br}_2\text{N}_2\text{O}_2$: 295.9, found 295.2.

IV. RESULTS AND DISCUSSION

Our initial exploratory studies probed the best reaction conditions and for that we choose salicylic acid (10 mmol) as a typical compound which was first reacted with molecular bromine (20 mmol) in CH_3CN (10 ML) at room temperature for 50 minutes. Workup of the reaction resulted under-brominated



Na_2MoO_4 - Catalysed Generation of Br_2 using Potassium Bromide and Mineral Acids. It was claimed that sodium molybdate (Na_2MoO_4) catalyses the oxidative bromination of various activated aromatics, without the need for stoichiometric amounts of acid. We found, however, that the Na_2MoO_4 , which dictates the acidic environment (pH 2-3) is required for the reaction to proceed.

The present review gives short glance on various reagents reported in the literature for oxidative bromination of various substrates using various oxidative reagents with new catalysts and new non catalyst methods.

However, Na_2MoO_4 may be used to catalyse oxidative bromination in the presence of dilute mineral acids, which may solve problems arising from the corrosiveness of 49% HBr, or other combinations of bromide with concentrated acids. This is important, because, although the productivity of the processes employing concentrated acids is higher, it is partly due to corrosiveness that recycling of bromide is shunned by the chemical industries.

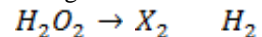
Halogenation reactions are gained considerable importance from their discovery. The halides are important in organic synthesis due to their use for synthesis of various commercially important compounds. Among the halides chlorides and bromides are of commercially important over fluoride and iodide. Organic bromides are widely used as synthetic precursors for various coupling reactions in organic and pharmaceutical synthesis. They can be used as potent antitumor, antibacterial, antifungal, antineoplastic, antiviral, and anti-oxidizing agents and also as industrial intermediates in the manufacture of pharmaceuticals, agrochemicals, and other specialty products, for instance, flame-retardants. The traditional bromination using elemental bromine shows a maximum of 50% atom efficiency in terms of bromine consumption. The bromination reaction has been still attracting attention to develop the more practical method without the use of hazardous and highly toxic elemental bromine. Oxidative bromination is a process which generates electrophilic bromine using various oxidants with or without

off-white 3,5-dibromosalicylic acid (3,5-DBSA) which melts over a range 190-221 $^\circ\text{C}$ (Table 1, entry 1). Other solvents such as CH_3COOH , CH_3OH , CAN, H_2O and CH_2Cl_2 were also tested but the results were unsatisfactory, yielding 3,5-dibromosalicylic acid in lower yields with low melting points where the crude product is contaminated by significant quantities of impurities particularly the monobrominated salicylic acid or decarboxylated brominated phenol.

As this study mainly deals with application of dilute acids, the term acid refers to a dilute acid of $\sim 1\text{M}$ in water. Where concentrated acid is used, the concentration is specified. Similarly, the amount of Na_2MoO_4 used in all reactions, are 1-2 mol % relative to substrate unless noted otherwise. Reagent productivity will be in terms of amount of substance produced per unit reactor volume per unit time.

using catalyst. (An exception is fluorination, since it is too difficult to oxidize fluoride.) In the laboratory as well Industrial scale, however, bromination is generally carried out with hazardous, toxic, and corrosive molecular bromine mostly in combination with chlorinated solvents. A growing ecological awareness among chemists has coincided with an increased understanding of oxidative bromination in biological systems, which has boosted research in the field of oxidative bromination. From Green chemistry point of view Hydrogen peroxide and oxygen are considered as best agent for oxidative halogenation as the waste generated is water only^{6,7}. In the literature various oxidative halogenation methods are reported, where various oxidants like metals, persulphate, mineral acids and hyper valent iodine are used for generation of electrophilic bromine.

Using HCl for bromination is interesting, as it seems possible that companies engaged in chlorination processes may also be interested in bromination, and might have waste HCl streams available on production sites. As chlorine is less soluble than bromine in water, it seems reasonable to suppose that the absence of chlorinated products indicates either that no chlorine gas is formed when HCl is used as the source of protons. With the use of this system, ex situ bromination of 1-octene gave >99%. Selectivity to 1,2-dibromooctane, indicating that the sodium



molybdate- catalysed reaction $2\text{HX} + \quad + 2 \quad \text{O}$. Moreover, an ex situ process is advantageous in this case, because in a one-pot reaction using HCl + KBr, attack of chloride on the cyclic bromonium cation would result in formation of a vic-bromo-chloro-product in above reaction in presence of 1 mol% sodium molybdate.

V. CONCLUSION

Molybdate-catalysed oxidative bromination is a cost effective and safe system, the risk factor for the known reagents like molecular bromine is very high. Furthermore, this method

has the advantages of low transportation and storage risk is less. The drawback of the system is high prices and low productivity (compared to using Br_2), and the fact that concurrent unwanted decomposition of H_2O_2 in the reagent system. A comparison of

the brominating ability of the present system with those of published methods shows that the present protocol is inexpensive, simpler, faster and more efficient than other catalytic bromination systems used for this purpose.

APPENDIX

Characterization of Representative Brominated Compounds:

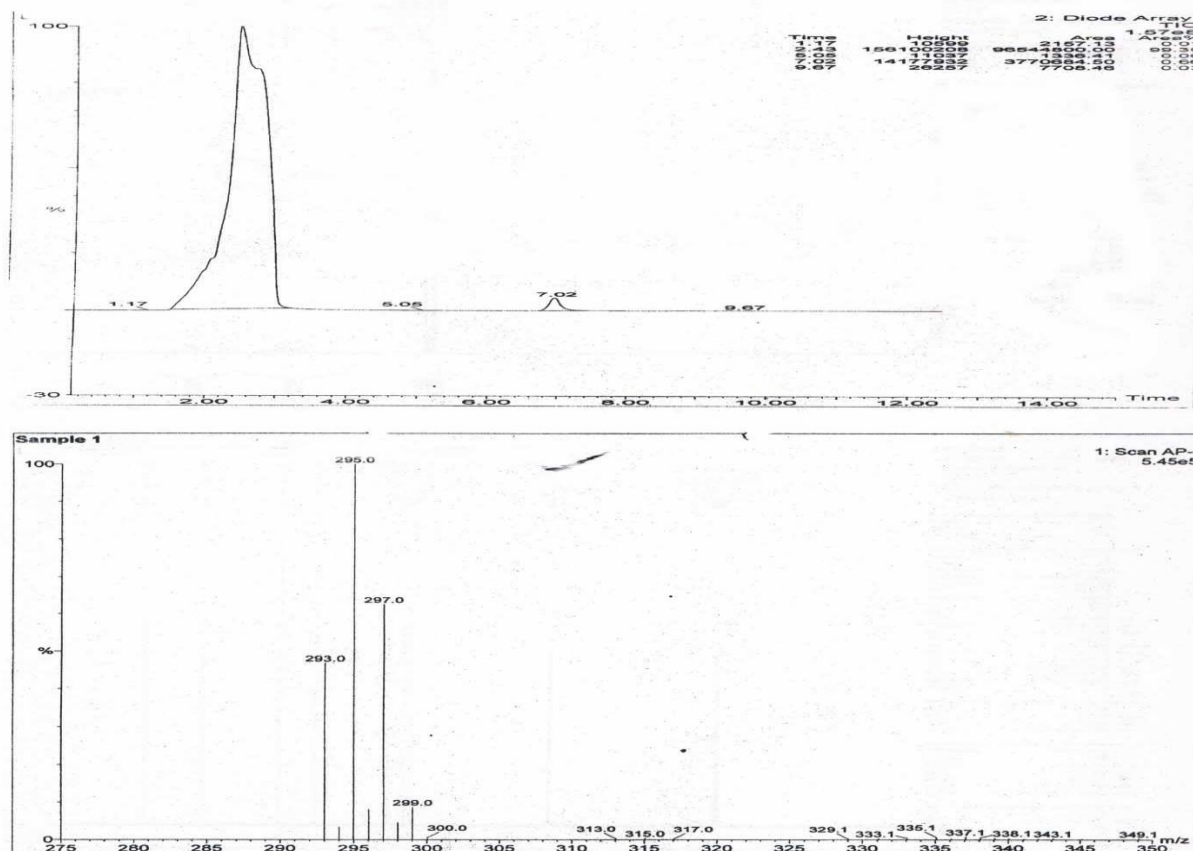


Figure 1. LC-MS of 3,5-dibromosalicylic acid (1)

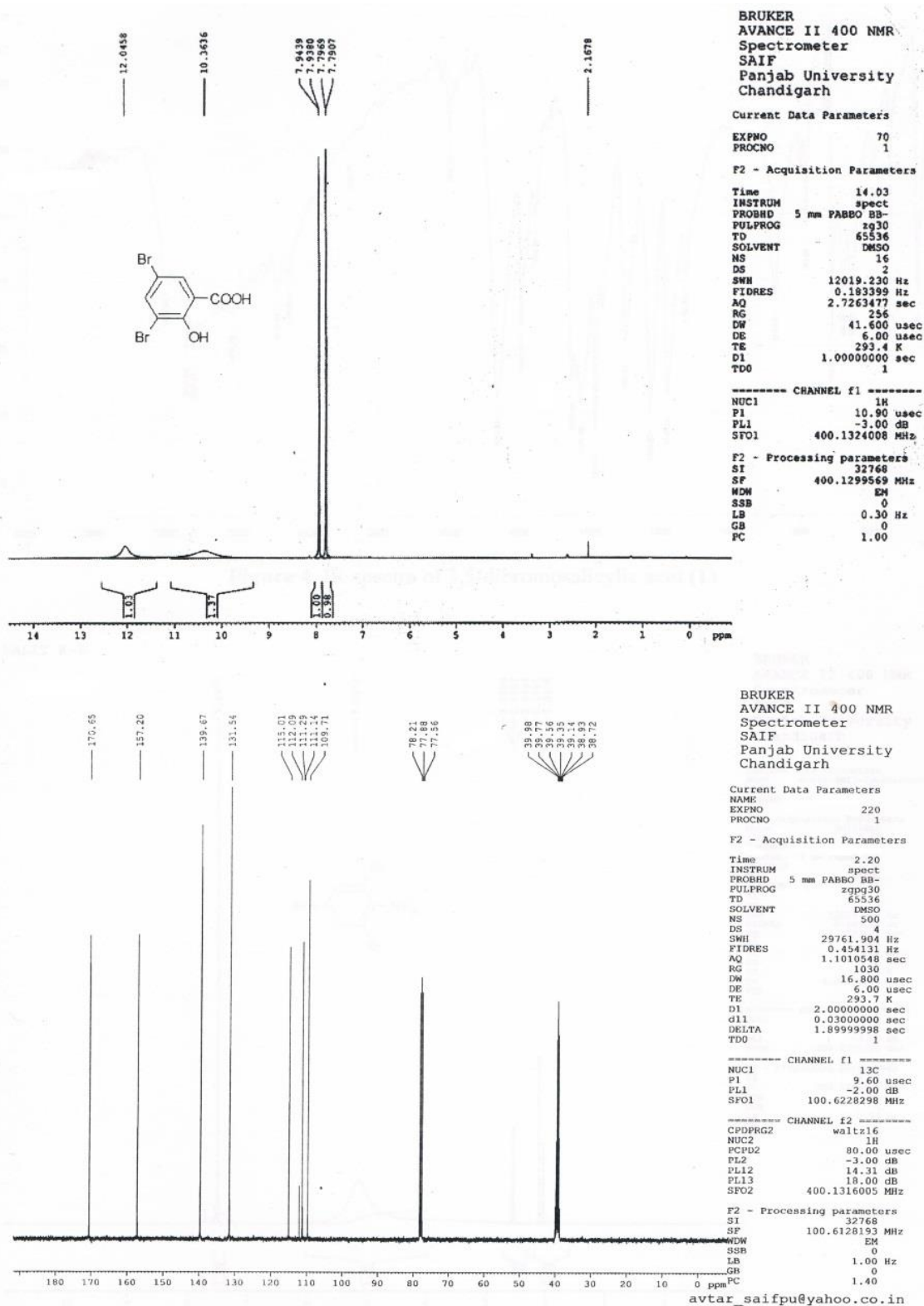


Figure 2. ¹H and ¹³C-NMR spectra of 3,5-dibromosalicylic acid (1)

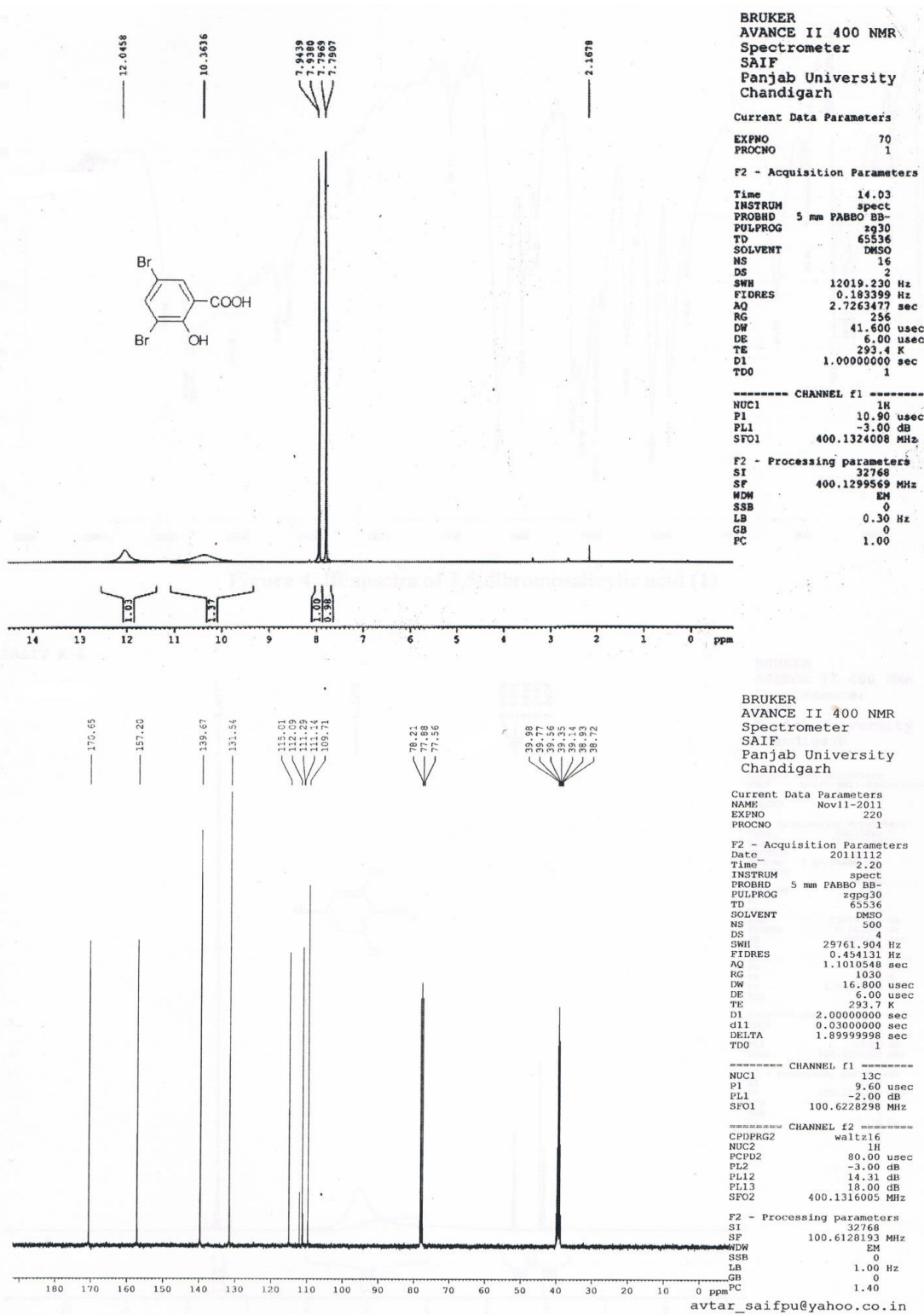


Figure 3. ¹H and ¹³C-NMR spectra of 3,5-dibromosalicylic acid (1)

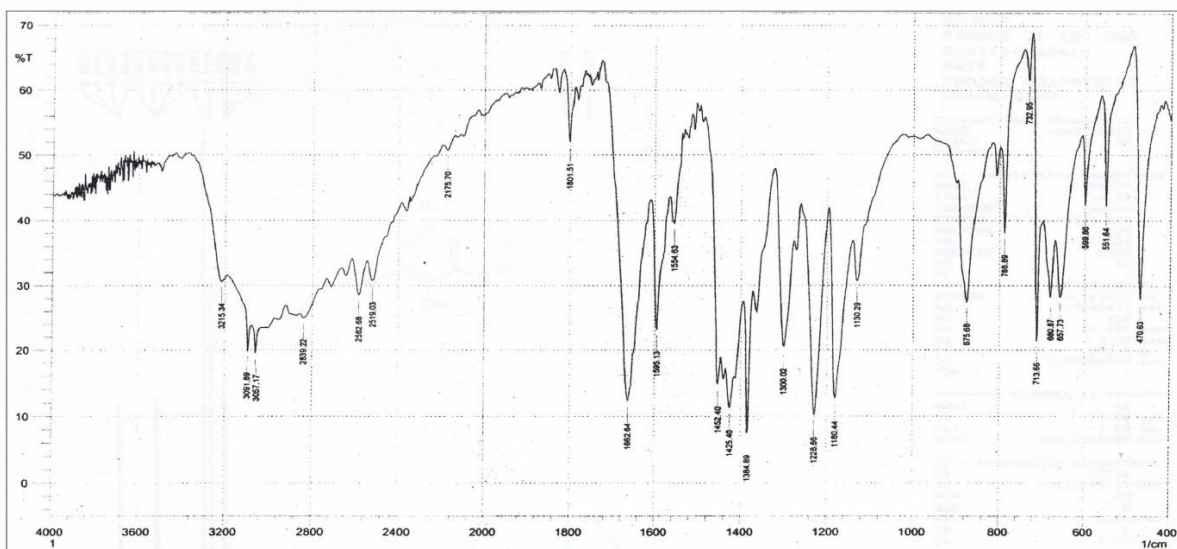


Figure 4. IR spectra of 3,5-dibromosalicylic acid (1)

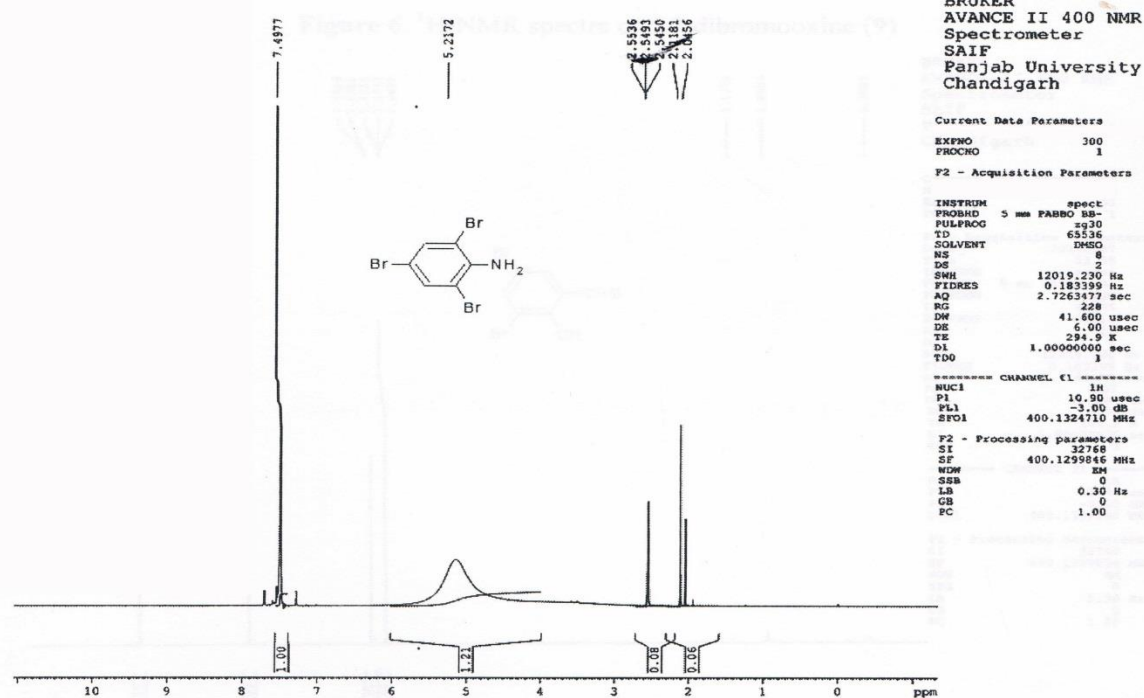


Figure 5. ¹H-NMR spectra of 2,4,6-tribromoaniline (4)

ACKNOWLEDGMENT

I owe my deep sense of gratitude to Almighty God Ganesha for his blessing, mercy, guidance and strength that made it possible for me to complete my studies and enabling me to accomplish research work. At this moment of accomplishment, first of all I pay homage to my guide, Prof. Dr. D.D. Agarwal. This work would not have been possible without his guidance, support and encouragement. Under his guidance I successfully overcame many difficulties and learned a lot. I can't forget his hard times. Despite of his busy schedule, he used to review my thesis progress, give his valuable suggestions and made corrections. His unflinching courage and conviction will always

inspire me, and I hope to continue to work with his noble thoughts. I can only say a proper thanks to his through my future work. It is to his that I dedicate this work.

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AUTHORS

First Author – Sushil Kumar Sharma, Ph.D research Scholar,
Department of Chemistry, JJTU Rajasthan, India

Second Author – Prof. D.D Agarwal, Ex-Vice Chancellor JJTU
Rajasthan, India