NITRATION OF AROMATIC COMPOUNDS USING ALUMINA SULFURIC ACID (ASA) AS A NOVEL HETEROGENEOUS SYSTEM AND Mg (NO$_3$)$_2$.6H$_2$O AS NITRATING AGENT IN WATER[*]

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Abstract – A novel and safe method for nitration of phenols, anilines and other aromatic compounds has been found to be feasible with alumina sulfuric acid (ASA) as catalyst and Mg (NO$_3$)$_2$.6H$_2$O as nitrating agent in neat water as solvent. The use of water makes this method compatible with the green chemistry approach.

Keywords – Alumina sulfuric acid, nitration, Mg (NO$_3$)$_2$.6H$_2$O, water, heterogeneous
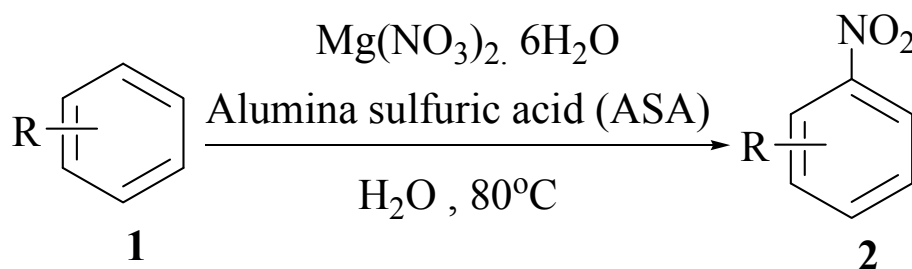
1. INTRODUCTION

Organic reactions in aqueous media are interesting because water is a relatively green and cheap media for organic reactions [1]. However, using water for organic reactions is not always practical because of the poor solubility of organic molecules in water, and also water could inhibit the catalyst's activity [1d, e]. So, it is necessary to further develop and design a novel catalyst/reagent system for use in water.

Nitration of aromatic compounds is a fundamental reaction of great industrial importance and the nitro aromatic compounds are key organic intermediated. A mixture of concentrated or fuming nitric acid with sulfric acid has been used as the most common nitrating reagent for the nitration of benzene, alkyl benzene and less reactive aromatic compounds [2], but highly reactive aromatic compounds, such as phenols and anilines are easily oxidized. Recently, a wide variety of nitrating reactions have been developed including the use of Fe (III) [3] or Cu (II) [4], montmorillonite clay [5], zeolites [6], bismuth (III) salts [7], group IV and VI metal salts [8], lanthanide (III) salts [9], indium salts [10] and so on [11]. However, the majority of the reported methods for nitration of aromatic compounds suffer from disadvantages such as strongly acidic media, over nitration, tedious work-up, and safety problems (storage, handling, using toxic transition metal cations such as Hg^{+2}, and using organic solvents). These disadvantages have encouraged researchers to develop procedures using solid acids [7a, 11n, e, 12], and using nitrate salts such as VO (NO$_3$)$_3$ [13], Fe (NO$_3$)$_3$.9H$_2$O [14], (Me$_4$N) NO$_3$ [15], Mg (NO$_3$)$_2$.6H$_2$O [16], NaNO$_3$ [12b, 17], and Bi (NO$_3$)$_3$.5H$_2$O [7b].

According to our previous works which were concerned with the safety of new methodologies for organic reactions in solvent-free conditions [18], we have found that alumina sulfuric acid (ASA), which is an effective reagent for esterification [19], and Beckmann rearrangement [20] are also good inorganic acidic resins for nitration of aromatic compounds under simple and green conditions using water as solvent (Scheme 1). ASA can be readily prepared *via* the previous reported procedure by reaction of acidic type alumina with chlorosulfonic acid [19, 20]. ASA is a white solid which could be stored for a long period of time without a decrease in activity.

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$$ \text{Mg(NO}_3)_2 \cdot 6\text{H}_2\text{O} $$

$$ R \underset{\text{1}}{\text{—}} \xrightarrow[\text{H}_2\text{O , 80}^o\text{C}]{\text{Alumina sulfuric acid (ASA)}} R \underset{\text{2}}{\text{—}} \text{NO}_2 $$

Scheme 1

2. RESULTS AND DISCUSSION

In order to optimize the reaction condition, *para*-hydroxy benzaldehyde 1a was chosen as a model compound and the nitration reaction was considered under a variety of conditions *via* TLC and ^{1}H-NMR spectroscopy (Table 1). When 1 equiv of 1a and Mg(NO$_3$)$_2$.6H$_2$O (1 mmol) as nitrating agent were carried out in water as solvent (1 mL) in the presence of ASA (0.1 g, 0.3 mmol), a higher yield of nitrated compound 2a could be isolated (Entry 1). We also carried out the same reaction by using other nitrated salts. Amongst the nitrate salts tested, Mg (NO$_3$)$_2$. 6H$_2$O turned out to be the most effective nitrating agent for this purpose (Entries 5-8). The reaction proceeded with low yields in solvents such as toluene or CH$_2$Cl$_2$ under reflux conditions (Entries 9, 10). No yields were obtained when the reaction was carried out at room temperature or without water (Entry 11, 12). A similar reaction in the absence of catalyst (ASA) did not lead to the formation of the desired product 2a, even after 24 h (Entry 13). Based on these results, and in order to generalize the procedure, the nitration of aromatic compounds using ASA as catalyst and Mg (NO$_3$)$_2$.6H$_2$O as nitration reagent in the presence of water as solvent was examined. The results are summarized in Table 2.

Table 1. Nitration of *para*-hydroxy benzaldehyde 1a in various reaction conditions

Entry	Condition	Time (h)	Yield (%)[a]
1	ASA (0.1 g) /Mg (NO$_3$)$_2$.6H$_2$O/ 80°C/H$_2$O	2.5	95
2	ASA (0.05 g)/ Mg (NO$_3$)$_2$.6H$_2$O/ 80°C/H$_2$O	4	85
3	ASA (0.025 g)/ Mg (NO$_3$)$_2$.6H$_2$O/ 80°C/H$_2$O	8	50
4	ASA (0.15 g)/ Mg (NO$_3$)$_2$.6H$_2$O/ 80°C/H$_2$O	2.5	95
5	ASA (0.1 g) /Cd (NO$_3$)$_2$.6H$_2$O/ 80°C/H$_2$O	4	52[b,c]
6	ASA (0.1 g) /Ni (NO$_3$)$_3$.9H$_2$O/ 80°C/H$_2$O	24	30[b,c]
7	ASA (0.1 g) /Cu (NO$_3$)$_2$.3H$_2$O/ 80°C/H$_2$O	24	50[b,c]
8	ASA (0.1 g) /Zn (NO$_3$)$_2$.6H$_2$O/ 80°C/H$_2$O	24	60[b,c]
9	ASA (0.1 g)/ Mg (NO$_3$)$_2$.6H$_2$O/ reflux/CH$_2$Cl$_2$	24	trace
10	ASA (0.1 g)/ Mg (NO$_3$)$_2$.6H$_2$O/ reflux/PhCH$_3$	24	trace
11	ASA (0.1 g)/ Mg (NO$_3$)$_2$.6H$_2$O/ r.t. /H$_2$O	24	0
12	ASA (0.1 g)/ Mg (NO$_3$)$_2$.6H$_2$O/ 80°C	24	0
13	Mg (NO$_3$)$_2$.6H$_2$O/ 80°C/H$_2$O	24	0

[a] Isolated yields. [b] A mixture of nitrated and oxidized products was obtained. [c] The yields were determined by ^{1}H NMR.

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Table 2. Nitration of aromatic compounds with Mg (NO$_3$)$_3$.6H$_2$O
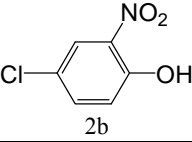as nitrating agent and ASA as catalyst in water
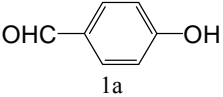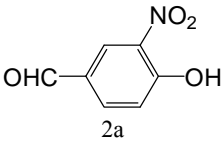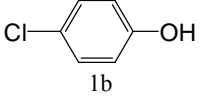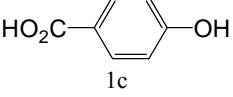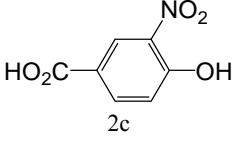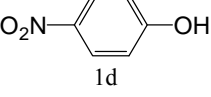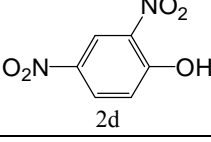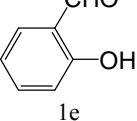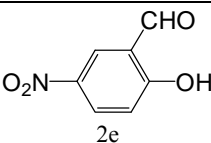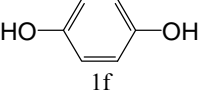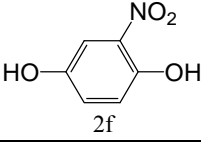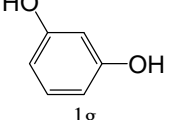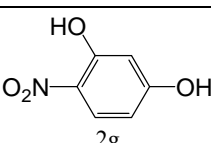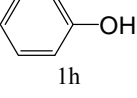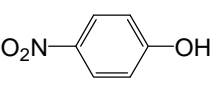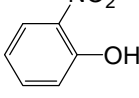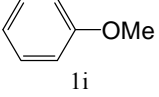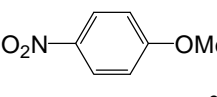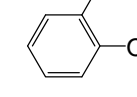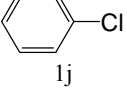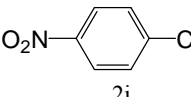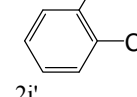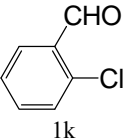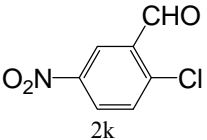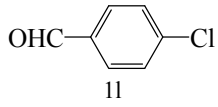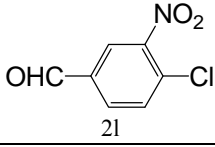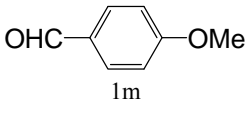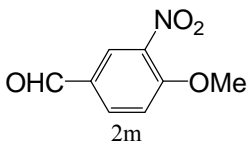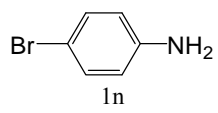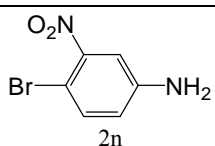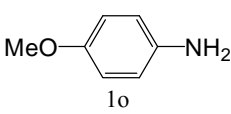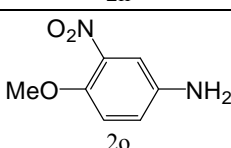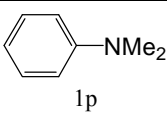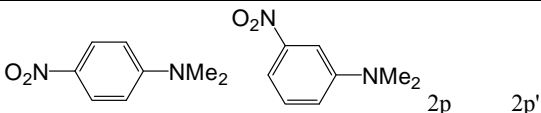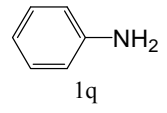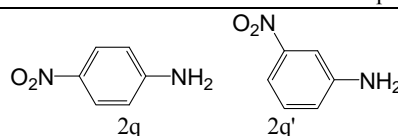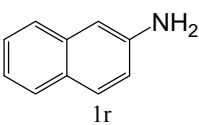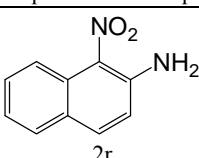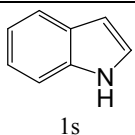
Entry	Aromatic compounds	Nitrated compound	Time (h)	Yield[a,b] %	M.p./°C (Lit.)
1	OHC—C$_6$H$_4$—OH (para) **1a**	OHC—C$_6$H$_3$(NO$_2$)—OH **2a**	3.5	95	138-140 (140-41)[21]
2	Cl—C$_6$H$_4$—OH (para) **1b**	Cl—C$_6$H$_3$(NO$_2$)—OH **2b**	.5	95	84-86 (85-89)[21]
3	HO$_2$C—C$_6$H$_4$—OH (para) **1c**	HO$_2$C—C$_6$H$_3$(NO$_2$)—OH **2c**	5	90	179-182 (184)[21]
4	O$_2$N—C$_6$H$_4$—OH (para) **1d**	O$_2$N—C$_6$H$_3$(NO$_2$)—OH **2d**	5	95	107-110 (l18-12)[21]
5	CHO, OH (ortho) **1e**	CHO, O$_2$N—, OH **2e**	3.5	82	127-129 (l129-130)[21]
6	HO—C$_6$H$_4$—OH (para) **1f**	HO—C$_6$H$_3$(NO$_2$)—OH **2f**	2.5	75	130-132 (133)[22]
7	HO, OH (meta) **1g**	HO, O$_2$N—, OH **2g**	3	85	120-123 (122)[21]
8	C$_6$H$_5$—OH **1h**	O$_2$N—C$_6$H$_4$—OH **2h**; (NO$_2$)—C$_6$H$_4$—OH **2h'**	3	2h: 2h' 15:85	2h: 112-114 (114)[23] 2h': 42-44 (45)[23]
9	C$_6$H$_5$—OMe **1i**	O$_2$N—C$_6$H$_4$—OMe **2i'**; (NO$_2$)—C$_6$H$_4$—OMe **2i**	3	2i : 2i' 30: 70[b]	2i: 50-52 (53)[23] 2i': liq. (9-12)[21]
10	C$_6$H$_5$—Cl **1j**	O$_2$N—C$_6$H$_4$—Cl **2j**; (NO$_2$)—C$_6$H$_4$—Cl **2j'**	20	2j : 2j' 30:70[b]	2j: 82-84 (84-86)[10b] 2j': 30-32 (32)[23]
11	CHO, Cl (ortho) **1k**	CHO, O$_2$N—, Cl **2k**	24	85	72-74 (75-77)[21]

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Table 2. (Continued)

12	OHC—⬡—Cl 1l	OHC—⬡(NO₂)—Cl 2l	10	90	140-147 (148-150)[21]
13	OHC—⬡—OMe 1m	OHC—⬡(NO₂)—OMe 2m	8	87	99-101 (97-100)[21]
14	Br—⬡—NH₂ 1n	O₂N Br—⬡—NH₂ 2n	6	90	125-128 (128-132)[21]
15	MeO—⬡—NH₂ 1o	O₂N MeO—⬡—NH₂ 2o	6	92	55-57(56-58)[21]
16	⬡—NMe₂ 1p	O₂N—⬡—NMe₂ 2p O₂N ⬡—NMe₂ 2p'	5	2p : 2p' 25:75[b]	2p:162-165 (163-165)[21] 2p': 60-62 (60)[24]
17	⬡—NH₂ 1q	O₂N—⬡—NH₂ 2q O₂N ⬡—NH₂ 2q'	5.5	2q : 2q' 15:85[b]	2q: (146-149)[21] 2q': (70-73)[21]
18	⬡⬡—NH₂ 1r	⬡⬡(NO₂)—NH₂ 2r	6	83	125-125 (127)[25]
19	⬡⬡N H 1s	--	8	0	--

[a]Yields are the isolated compounds. [b]The ratio of two regioisomers was determined by ^{1}H NMR of the crude products mixture before isolation by column chromatography.

According to Table 2, various aromatic compounds with an electron-donating and electron-withdrawing group were nitrated by ASA as catalyst in the presence of water. Nitrophenols are very important organic synthesis intermediates, and as such, various phenolic compounds nitrated by ASA (Entries 1-8). Phenol (Entry 8) undergoes predominant, *ortho*-selective nitration in good yield. However, other phenolic compounds containing an electron-withdrawing group at *para* position were obtained regioselectively at the *ortho* position related to the OH group (entries 1-4). In the case of *ortho* substituted phenol such as *ortho*-hydroxy benzaldehyde, the nitration reaction afforded selectively only a 5-nitro-2-hydroxy benzaldehyde in 82% yield (Entry 5).

Recently, Sun and co-workers[7b] reported that the nitration reaction of 1, 4-benzenediol failed, but as shown in Table 2, (Entry 6, 7), *metha* and *para* dihydroxybenzene were nitrated to give 4-nitro-1, 3-benzenediol and 2-nitro-1, 4-benzene diol in 85% and 76% yields respectively. However, under the same reaction conditions, *ortho* dihydroxybenzene gave a mixture of nitrated and oxidized products.

In the case of simple aromatic compounds such as anisole and chlorobenzene, two nitrated products were obtained (Entries 9, 10). In addition, substituted benzaldehydes were also nitrated and the corresponding products formed in good to high yields (Entries 11-13). In addition, ASA is suitable for the nitration of aromatic compounds with oxidizable functional groups like amino groups (Entries 14-17). It is interesting to note that the amino group in the presence of ASA (as an acidic media) was protonated and therefore acted as a deactivating group. Thus, other activating groups on the aromatic rings dictated the regioselectivity (Entries 14, 15).However, in the cases where no other groups were presented in the aromatic ring (Entries 16, 17), the reactions produced mixtures of *meta* and *para* isomer. These results are similar to other observed previous methods [23].

We have also tried di-nitration and tri-nitration of phenol with in the presence of ASA. Di-nitration and tri-nitration of phenol with two and three equivalent amounts of nitrating agent were easily performed and 2, 4-dinitrophenol and 2, 4, 6-trinitrophenol were obtained in good yields, respectively (Scheme 2).
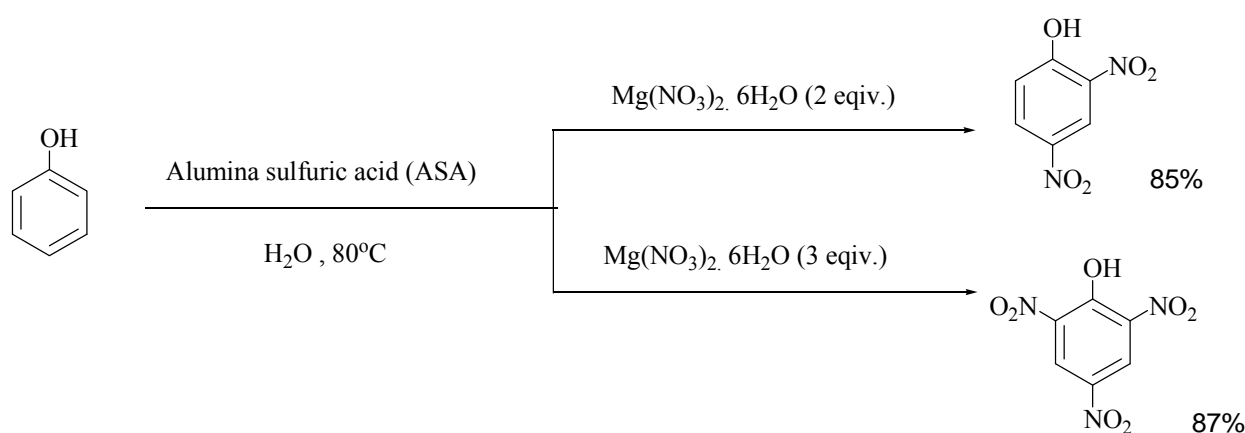
Scheme 2

Mechanistically we proposed that in the presence of ASA, in situ formation of HNO_3 and nitronium ions is a major factor for effective nitration of aromatic compounds with magnesium nitrate.

Reactions were carried out under the same reaction conditions for a comparative evaluation of the efficacy of our methods with some other methods reported for the nitration of aromatic compounds (Table 3).

Table 3. Comparison of mononitration of phenol by our method with other reported methods

Entry	Reagent/temp./solvent	Time (h)	%Ortho	%Para
1	ASA (0.1 g) /Mg $(NO_3)_2.6H_2O$/ 80^oC/H_2O	3	85	15
2	Cr $(NO_3)_3.9H_2O$/ rt / THF[8b]	24	37	60
3	Cr $(NO_3)_3.2N_2O_4$/rt/THF[8b]	Immed.	40	59
4	Mg $(NO_3)_2.6H_2O$ /reflux/Et_2O[16]	10	40	49
5	Mg $(NO_3)_2.6H_2O$[16]	20	25	21
6	Silica sulfuric acid/Al $(NO_3)_3.9H_2O$.wet SiO_2/r.t./CH2Cl2[11o]	0.5	36	43

3. EXPERIMENTAL

Progress of the reactions was monitored by the use of silica gel polygrams SIL G/UV 254 plates. IR spectra were recorded on Perkin Elmer 781 and on Impact 400 D Nickolet FTIR spectrometers. NMR spectra were recorded on Bruker DPX 250 MHz instrument and mass spectra on Shimadzu QP 1100 EX spectrometer using EI 70 eV modes. Microanalyses were performed on a PerkinElmer 240-B microanalyzer.

3.1. GENERAL PROCEDURE

a) General procedure for mononitration of aromatic compounds

Aromatic compound (1 mmol) and Mg $(NO_3)_2.6H_2O$ (1 mmol) were added to ASA (0.1 g, 0.3 mmol) in a test tube by adding water (1 mL). The mixture was stirred in an oil bath at 80^oC, and TLC monitored the progress of the reaction. At the end of the reaction (see Table 2) the resulting mixture was mixed with ethyl acetate/water and filtered to remove ASA. The filtrate was washed with water (2 × 10 ml), dried over Na_2SO_4 and the solvent removed under reduced pressure to give the product, which was recrystallised from a suitable solvent or purified by column chromatography (ethyl acetate-hexane). All products are known and were characterized by ^{1}H NMR, IR and mass spectral data, which were found to be identical with those described in ref. 7, 10b, 22-24.

b) General procedure for di- and tri- nitration of aromatic compounds

Aromatic compound (1 mmol) and Mg $(NO_3)_2.6H_2O$ (2 mmol for di and 3 mmol for tri-nitration) were added to ASA (0.1 g, 0.3 mmol) in a test tube by adding water (2-3 mL). The mixture was stirred in an oil bath at 80^oC, and TLC monitored the progress of the reaction. At the end of the reaction, the resulting mixture was mixed with ethyl acetate/water and filtered to remove ASA. The filtrate was washed with water (2 × 10 ml), dried over Na_2SO_4 and the solvent removed under reduced pressure to give the product, which was recrystallised from a suitable solvent or purified by column chromatography (ethyl acetate-hexane).

4-Hydroxy-3-nitrobenzaldehyde (2a) Yellow powder; mp 138-140^oC (lit [22] 140-141^oC); IR (KBr) (v_{max}/cm^{-1}): 3236, 2816, 1693, 1620, 1562, 1423, 1334, 1269, 1126; ^{1}H NMR (250 MHz, CDCl$_3$): δ 11.01 (brs, 1H, -OH), 9.94 (s, 1H, -CHO), 8.63 (s, 1H, Ar-*H*), 8.14 (d, 1H, *J*=3.5 Hz), 7.33 (d, 1H, *J*=3.5 Hz, Ar-*H*); GC-Ms/ EI: m/z (%) = 167 (M+, 10), 149 (25), 129 (11), 111 (11), 85 (23), 69 (100).

4-Chloro-2-Nitrophenol (2b) Yellow powder; mp 84-86^oC (lit [22] 85-89^oC); IR (KBr) (v_{max}/cm^{-1}): 3490, 1631, 1531, 1469, 1384, 1346, 1238; ^{1}H NMR (250 MHz, DMSO): δ 11.33 (brs, 1H, -OH), 7.90 (s, 1H, Ar-*H*), 7.54 (d, 1H, *J*=8.9 Hz), 7.14 (d, 1H, *J*=8.9 Hz, Ar-*H*); GC-Ms/ EI: m/z (%) = 173 (M+, 16), 156 (7), 143 (26), 128 (10), 115 (41), 99 (39), 73 (29), 63 (100), 51 (20), 37 (13), 30 (26).

4-Hydroxy-3-Nitrobenzoic acid (2c) Yellow powder; mp 179-182^oC (lit. [22] 184^oC); IR (KBr) (v_{max}/cm^{-1}): 3309, 3089, 2842, 1689, 1627, 1539, 1434, 1342; ^{1}H NMR (250 MHz, DMSO): δ 11.73 (brs, 1H, -CO$_2$H), 10.23 (brs, 1H, -OH), 8.33 (s, 1H, Ar-*H*), 7.98 (d, 1H, *J*=7.9 Hz), 7.16 (d, 1H, *J*=7.9 Hz, Ar-*H*); GC-Ms/ EI: m/z (%) = 183 (M+, 7), 149 (22), 129 (17), 97 (38), 57 (100).

2, 4-Dinitrophenol (2d) Yellow powder; mp 107-110^oC (lit. [22] 108-112^oC); IR (KBr) (v_{max}/cm^{-1}): 3587, 3529, 1608, 1569, 1531, 1523, 1438, 1357, 1280; ^{1}H NMR (250 MHz, DMSO): δ 11.02 (brs, 1H, -OH), 8.65 (s, 1H, Ar-*H*), 8.26 (d, 1H, *J*=9.3 Hz), 7.22 (d, 1H, *J*=9.2 Hz, Ar-*H*); GC-Ms/ EI: m/z (%) = 184 (M+, 4), 167 (10), 129 (10), 111 (12), 85 (22), 69 (100).

2-Hydroxy-5-nitrobenzaldehyde (2e) Yellow powder; mp 127-129^oC (lit. [22] 129-130^oC); IR (KBr) (v_{max}/cm^{-1}): 3460, 3074, 2935, 1666, 1620, 1477, 1334, 1323; ^{1}H NMR (250 MHz, DMSO): δ 11.5 (brs, 1H, -OH), 9.91 (s, 1H, -CHO), 8.49 (s, 1H, Ar-*H*), 8.32 (d, 1H, *J*=9.1 Hz, Ar-*H*), 7.05 (d, 1H, *J*=9.1 Hz, Ar-*H*); GC-Ms/ EI: m/z (%) = 167 (M+, 11), 149 (13), 129 (7), 111 (12), 85 (24), 69 (100).

4-Hydroxy-2-nitrophenol (2f) Yellow powder; mp 130-132 ^oC (lit. [23] 133 ^oC); IR (KBr) (v_{max}/cm^{-1}): 3462, 3075, 2924, 1670, 1623, 1478, 1324, 1320; ^{1}H NMR (250 MHz, DMSO): δ 11.8 (brs, 2H, -OH), 8.65 (s, 1H, Ar-*H*), 8.42 (d, 1H, *J*=9.1 Hz, Ar-*H*), 7.15 (d, 1H, *J*=9.1 Hz, Ar-*H*); GC-Ms/ EI: m/z (%) = 155 (M+, 16), 149 (23), 129 (8), 111 (12), 69 (100).

4-Nitro-1, 3-benzenediol (2g) Yellow powder; mp 120-123°C (lit. [22] 122°C); IR (KBr) (v_{max}/cm^{-1}): 3388, 3300, 1628, 1592, 1525, 1511, 1444, 1327, 1284; ^{1}H NMR (250 MHz, CDCl$_3$): δ 10.2 (brs, 1H, -OH), 8.13 (d, 1H, *J*=9.2 Hz, Ar-*H*), 7.25 (s, 1H, Ar-*H*), 6.62 (d, 1H, *J*=9.2 Hz, Ar-*H*), 6.44 (brs, 1H, -OH); GC-Ms/ EI: m/z (%) = 155 (M+, 7), 139 (31), 121 (10), 109 (74), 77 (12), 65 (47), 51 (19), 39 (48), 30 (25), 28 (100).

4-Nitrophenol (2h) Yellow powder; mp 112-114°C (lit. [21] 114°C); IR (KBr) (v_{max}/cm^{-1}): 3331, 1614, 1592, 1500, 1346; ^{1}H NMR (250 MHz, CDCl$_3$): δ 8.18 (d, 2H, *J*=5.50 Hz, Ar-*H*), 7.00 (d, 2H, *J*= 5.49 Hz, Ar-*H*), 6.35 (s, 1H, -OH); GC-Ms/ EI: m/z (%) = 139 (M+, 14), 109 (50), 81 (33), 65 (84), 53 (31), 46 (22), 39 (100), 30 (77), 28 (41).

2-Nitrophenol (2h') Yellow powder; mp 42-44°C (lit. [21] 45°C); IR (KBr) (v_{max}/cm^{-1}): 3241, 1623, 1606, 1593, 1538, 1479; ^{1}H NMR (250 MHz, CDCl$_3$): δ 10.5 (s, 1H, -OH), 8.10 (d, 1H, *J*=8.50 Hz, Ar-*H*), 7.59 (m, 1H, Ar-*H*), 7.16 (d, 1H, *J*=8.4 Hz, Ar-H), 7.00 (m, 1H, Ar-H); GC-Ms/ EI: m/z (%) = 139 (M+, 40), 109 (35), 81 (55), 65 (60), 53 (38), 39 (100), 30 (66).

4-Nitroanisole (2i) **Yellow powder; mp 50-52 (lit. [21] 53°C); IR (KBr) (v_{max}/cm^{-1}): 3041, 1619, 1584, 1495, 1342; ^{1}H NMR (250 MHz, CDCl$_3$): δ 8.12 (d, 2H, *J*=5.50 Hz, Ar-*H*), 6.86 (d, 2H, *J*= 5.49 Hz, Ar-*H*), 3.73 (s, 3H, -OMe); GC-Ms/ EI: m/z (%) = 153 (M+, 11), 109 (54), 81 (27), 65 (12), 53 (31), 39 (100).**

2-Nitroanisole (2i') Yellow powder; liq. (lit. [22] 9-12°C); IR (KBr) (v_{max}/cm^{-1}): 3045, 1621, 1658, 16003, 1545, 1489; ^{1}H NMR (250 MHz, CDCl$_3$): δ 8.0 (d, 1H, *J*=8.50 Hz, Ar-*H*), 7.54 (m, 1H, Ar-*H*), 7.16 (d, 1H, *J*=8.4 Hz, Ar-H), 7.00 (m, 1H, Ar-H); GC-Ms/ EI: m/z (%) = 153 (M+, 140, 109 (51), 81 (50), 39 (100).

4-Nitrochlorobenzene (2j) Yellow powder; mp 82-84°C (lit. [10b] 84-86°C); IR (KBr) (v_{max}/cm^{-1}): 3106, 1604, 1578, 1519, 1477, 1344; ^{1}H NMR (250 MHz, DMSO): δ 8.24 (d, 2H, *J*=8.5 Hz, Ar-*H*), 752 (d, 2H, *J*=8.5 Hz, Ar-*H*); GC-Ms/ EI: m/z (%) = 157 (M+, 15), 129 (21, 127 (19), 111 (84), 99 (33), 75 (100).

2-Nitrochlorobenzene (2j') Yellow powder; mp 30-32°C (lit. [21] 32°C); IR (KBr) (v_{max}/cm^{-1}): 3096, 1688, 1550, 1467; ^{1}H NMR (250 MHz, DMSO): δ 7.32-7.87 (m, 4H, Ar-*H*); GC-Ms/ EI: m/z (%) = 157 (M+, 15), 129 (21, 127 (20), 111 (83), 99 (33), 75 (100).

2-Chloro-5-nitrobenzaldehyde (2k) Yellow powder; mp 72-74°C (lit. [22] 75-77°C); IR (KBr) (v_{max}/cm^{-1}): 2930, 1666, 1620, 1477, 1334, 1323; ^{1}H NMR (250 MHz, DMSO): δ 9.91 (s, 1H, -CHO), 8.49 (s, 1H, Ar-*H*), 8.32 (d, 1H, *J*=9.1 Hz, Ar-*H*), 7.05 (d, 1H, *J*=9.1 Hz, Ar-*H*); GC-Ms/ EI: m/z (%) = 185 (M+, 11), 69 (100).

4-Chloro-3-nitrobenzaldehyde (2l) Yellow powder; mp 140-147°C (lit. [22] 148-150°C); IR (KBr) (v_{max}/cm^{-1}): 3101, 2873, 2715, 2596, 1701, 1593, 1431, 1330; ^{1}H NMR (250 MHz, DMSO): δ 10.1 (s, 1H, -CHO), 8.22 (s, 1H, Ar-*H*), 7.90 (d, 1H, *J*=3.1 Hz, Ar-*H*), 7.55 (d, 1H, *J*=3.1 Hz, Ar-*H*); GC-Ms/ EI: m/z (%) = 185 (M+, 9), 167 (10), 149 (22), 129 (15), 97 (19), 73 (45), 57(100).

4-Methoxy-3-nitrobenzaldehyde (2m) Yellow powder; mp 99-101°C (lit. [22] 97-100°C); IR (KBr) (v_{max}/cm^{-1}): 3487, 3001, 2623, 1697, 1620, 1539, 1431, 1357, 1288; ^{1}H NMR (250 MHz, DMSO): δ 9.84 (s, 1H, -CHO), 8.10 (s, 1H, Ar-*H*), 8.07 (d, 1H, *J*=8.7 Hz, Ar-*H*), 7.45 (d, 1H, *J*=8.7 Hz, Ar-*H*), 3.96 (s, 3H, -OMe); GC-Ms/ EI: m/z (%) = 181 (M+, 6), 167 (11), 149 (11), 129 (8), 111 (8), 85 (13), 69 (100).

4-Bromo-3-nitroaniline (2n) Yellow powder; mp 125-128°C (lit. [22] 128-132°C); IR (KBr) (v_{max}/cm^{-1}): 3475, 3363, 1639, 1531, 1346; ^{1}H NMR (250 MHz, DMSO): δ 9.00 (s, 1H, Ar-*H*), 8.75 (d, 1H, *J*=9.0 Hz, Ar-*H*), 8.50 (d, 1H, *J*=9.0 Hz, Ar-*H*), 6.41 (brs, 2H, -NH$_2$); GC-Ms/ EI: m/z (%) = 217 (M+, 3), 213 (6), 185 (7), 149 (22), 129 (14), 97 (23), 73 (49), 57 (100).

4-Methoxy-3-nitroaniline (2o) Yellow powder; mp 55-57°C (lit. [22] 56-58°C); IR (KBr) (v_{max}/cm^{-1}): 3474, 3354, 1632, 1531, 1346; ^{1}H NMR (250 MHz, DMSO): δ 7.28 (s, 1H, Ar-*H*), 6.74-6.81 (m, 2H, Ar-

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H), 6.40 (brs, 2H, -NH$_2$), 3.73 (s, 3H, -OMe); GC-Ms/ EI: m/z (%) = 168 (M+, 12), 213 (23), 185 (9), 149 (22), 57 (100).

N,N-dimethyl-4-nitroaniline (2p) Yellow powder; mp 162-165°C (lit. [22] 163-165°C); IR (KBr) (ν_{max}/cm^{-1}): 1593, 1510, 1346; ^{1}H NMR (250 MHz, CDCl$_3$): δ 8.08 (d, 2H, *J*=5.50 Hz, Ar-*H*), 6.86 (d, 2H, *J*= 5.49 Hz, Ar-*H*), 2.75 (s, 6H, -NMe$_2$); GC-Ms/ EI: m/z (%) = 166 (M+, 12), 109 (56), 65 (81), 53 (65), 39 (100).

N,N-dimethyl-3-nitroaniline (2p') Yellow powder; mp 60-62 (lit. [24] 60 ^{o}C), IR(KBr) (ν_{max}/cm^{-1}): 1606, 1592, 1534, 1471; ^{1}H NMR (250 MHz, CDCl$_3$): δ 7.52 (m, 2H, Ar-H), 7.34 (m, 1H, Ar-H), 6.98 (m, 1H, Ar-*H*), 2.92 (s, 6H, -NMe$_2$); GC-Ms/ EI: m/z (%) = 166 (M+, 14), 109 (35), 65 (60), 53 (38), 39 (100).

4-nitroaniline (2q) Yellow powder; mp (146-148 ^{o}C (lit. [22] 146-149°C); IR (KBr) (ν_{max}/cm^{-1}): 3475, 3363, 1601, 1530, 1348; ^{1}H NMR (250 MHz, CDCl$_3$): δ 7.94 (d, 2H, *J*=5.50 Hz, Ar-*H*), 6.76 (d, 2H, *J*= 5.49 Hz, Ar-*H*), 4.25 (brs, 2H, -NH$_2$); GC-Ms/ EI: m/z (%) = 138 (M+, 45).

3-nitroaniline (2q') Yellow powder; mp 69-71 ^{o}C (lit. [22] 70-73°C), IR (KBr) (ν_{max}/cm^{-1}): 3477, 3362, 1609, 1592, 1532, 1469; ^{1}H NMR (250 MHz, DMSO): δ 8.84 (s, 1H, Ar-*H*), 7.62-8.61 (m, 3H), 4.05 (brs, 2H, -NH$_2$); GC-Ms/ EI: m/z (%) = 138 (M+, 44).

1-nitronaphthalen-2-amine (2r) Yellow powder; mp 125-125°C (lit. [25] 127°C); IR (KBr) (ν_{max}/cm^{-1}): 3472, 3364, 1600, 1529; ^{1}H NMR (250 MHz, CDCl$_3$): δ 8.16 (d, 1H, *J*=7.85 Hz, Ar-*H*), 7.88 (d, 1H, *J*=7.78 Hz, Ar-*H*), 7.75 (d, 1H, *J*=7.80 Hz, Ar-*H*), 7.43-.7.62 (m, 1H, Ar-*H*), 7.26-7.34 (m, 1H, Ar-*H*), 6.84-6.97 (m, 1H, Ar-*H*), 4.01 (brs, 2H, -NH$_2$); GC-Ms/ EI: m/z (%) = 188 (M+, 11).

4. CONCLUSION

In conclusion, an efficient electrophilic substitution reaction of aromatic compounds, specially phenols and anilines with magnesium nitrate as the nitrating agent in the presence of ASA has been developed as a new, mild and safety catalyst. The method offers several advantages including high yields, simple experimental work-up procedure, and using a cheap and environmental solvent (water); hence, it is a useful addition to the existing methods.

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