

NITRATION OF AROMATIC COMPOUNDS USING ALUMINA SULFURIC ACID (ASA) AS A NOVEL HETEROGENEOUS SYSTEM AND $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ AS NITRATING AGENT IN WATER*

M. HOSSEINI-SARVARI**, M. TAVAKOLIAN AND S. ASHENAGAR

Department of Chemistry, Shiraz University, Shiraz, I. R. of Iran
Email: hossaini@shirazu.ac.ir

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

1. INTRODUCTION

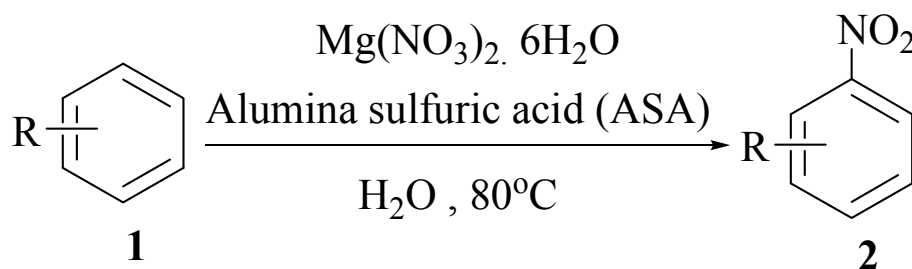
Organic reactions in aqueous media are interesting because water is a relatively green and cheap media for organic reactions [1]. However, using water for organic reactions is not always practical because of the poor solubility of organic molecules in water, and also water could inhibit the catalyst's 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 sulfuric 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 $\text{VO}(\text{NO}_3)_3$ [13], $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ [14], $(\text{Me}_4\text{N})\text{NO}_3$ [15], $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ [16], NaNO_3 [12b, 17], and $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ [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.

*Received by the editor December 8, 2010 and in final revised form February 14, 2011

**Corresponding author



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 ^1H -NMR spectroscopy (Table 1). When 1 equiv of 1a and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (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, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 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_2Cl_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 $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 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) / $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ / 80°C / H_2O	2.5	95
2	ASA (0.05 g) / $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ / 80°C / H_2O	4	85
3	ASA (0.025 g) / $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ / 80°C / H_2O	8	50
4	ASA (0.15 g) / $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ / 80°C / H_2O	2.5	95
5	ASA (0.1 g) / $\text{Cd}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ / 80°C / H_2O	4	52 ^{b,c}
6	ASA (0.1 g) / $\text{Ni}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ / 80°C / H_2O	24	30 ^{b,c}
7	ASA (0.1 g) / $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ / 80°C / H_2O	24	50 ^{b,c}
8	ASA (0.1 g) / $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ / 80°C / H_2O	24	60 ^{b,c}
9	ASA (0.1 g) / $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ / reflux / CH_2Cl_2	24	trace
10	ASA (0.1 g) / $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ / reflux / PhCH_3	24	trace
11	ASA (0.1 g) / $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ / r.t. / H_2O	24	0
12	ASA (0.1 g) / $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ / 80°C	24	0
13	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ / 80°C / H_2O	24	0

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

Table 2. Nitration of aromatic compounds with $\text{Mg}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ as nitrating agent and ASA as catalyst in water

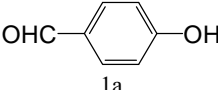
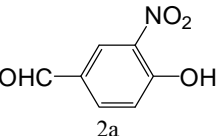
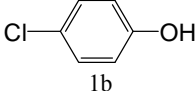
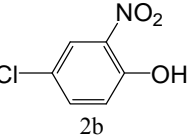
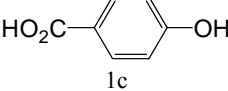
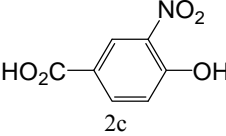
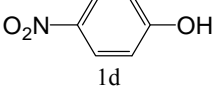
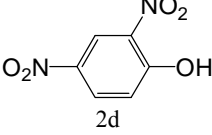
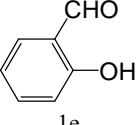
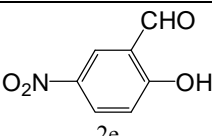
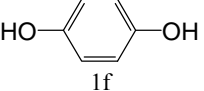
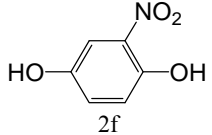
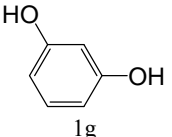
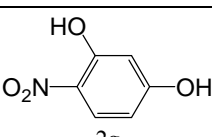
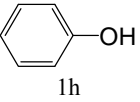
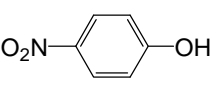
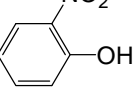
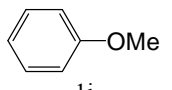
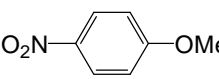
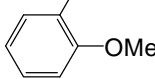
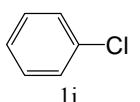
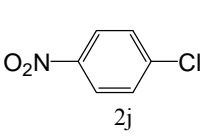
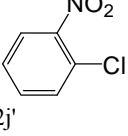
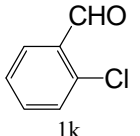
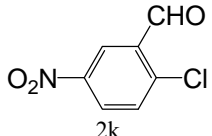
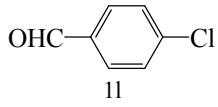
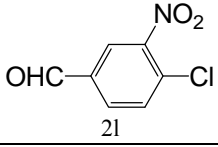
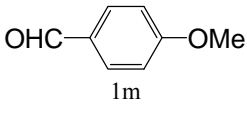
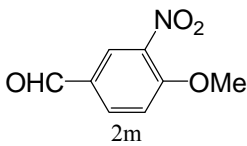
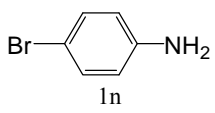
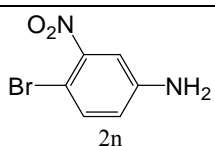
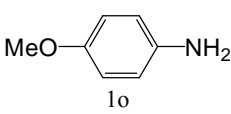
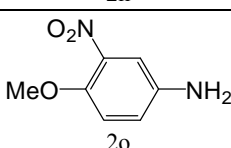
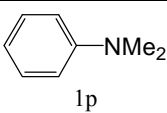
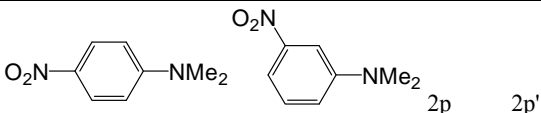
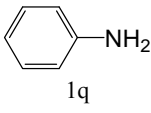
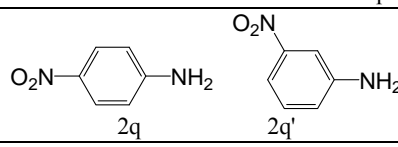
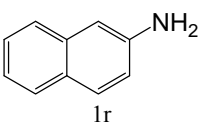
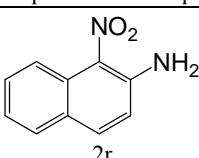
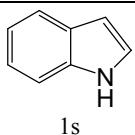
Entry	Aromatic compounds	Nitrated compound	Time (h)	Yield ^{a,b} %	M.p./°C (Lit.)
1	 1a	 2a	3.5	95	138-140 (140-41)[21]
2	 1b	 2b	.5	95	84-86 (85-89)[21]
3	 1c	 2c	5	90	179-182 (184)[21]
4	 1d	 2d	5	95	107-110 (118-12)[21]
5	 1e	 2e	3.5	82	127-129 (1129-130)[21]
6	 1f	 2f	2.5	75	130-132 (133)[22]
7	 1g	 2g	3	85	120-123 (122)[21]
8	 1h	  2h 2h'	3	2h: 2h' 15:85	2h: 112-114 (114)[23] 2h': 42-44 (45)[23]
9	 1i	  2i' 2i	3	2i : 2i' 30: 70 ^b	2i: 50-52 (53)[23] 2i': liq. (9-12)[21]
10	 1j	  2j 2j'	20	2j : 2j' 30:70 ^b	2j: 82-84 (84-86)[10b] 2j': 30-32 (32)[23]
11	 1k	 2k	24	85	72-74 (75-77)[21]

Table 2. (Continued)

12			10	90	140-147 (148-150)[21]
13			8	87	99-101 (97-100)[21]
14			6	90	125-128 (128-132)[21]
15			6	92	55-57(56-58)[21]
16			5	2p : 2p' 25:75 ^b	2p:162-165 (163-165)[21] 2p': 60-62 (60)[24]
17			5.5	2q : 2q' 15:85 ^b	2q: (146-149)[21] 2q': (70-73)[21]
18			6	83	125-125 (127)[25]
19		--	8	0	--

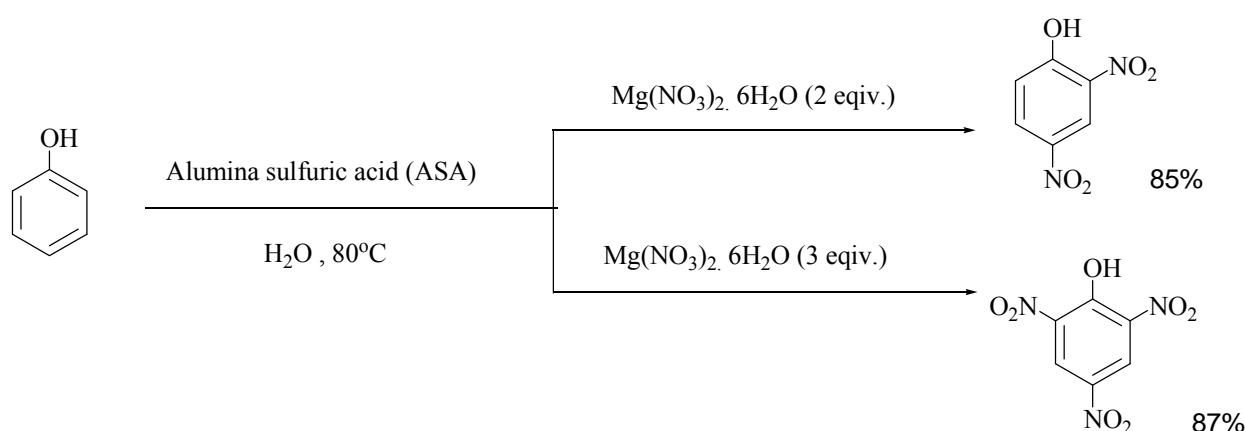
^a)Yields are the isolated compounds. ^b)The ratio of two regioisomers was determined by ¹H NMR of the crude products mixture before isolation by column chromatography.

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), *meta* 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 ₂ O/ 80°C/H ₂ O	3	85	15
2	Cr (NO ₃) ₃ .9H ₂ O/ rt / THF[8b]	24	37	60
3	Cr (NO ₃) ₃ .2N ₂ O ₄ /rt/THF[8b]	Immed.	40	59
4	Mg (NO ₃) ₂ .6H ₂ O /reflux/Et ₂ O[16]	10	40	49
5	Mg (NO ₃) ₂ .6H ₂ O[16]	20	25	21
6	Silica sulfuric acid/Al (NO ₃) ₃ .9H ₂ O.wet SiO ₂ /r.t./CH ₂ Cl ₂ [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 Nicolet 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 $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (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°C , 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 ^1H 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 $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (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°C , 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 $138\text{--}140^\circ\text{C}$ (lit [22] $140\text{--}141^\circ\text{C}$); IR (KBr) ($\nu_{\text{max}}/\text{cm}^{-1}$): 3236, 2816, 1693, 1620, 1562, 1423, 1334, 1269, 1126; ^1H 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 $84\text{--}86^\circ\text{C}$ (lit [22] $85\text{--}89^\circ\text{C}$); IR (KBr) ($\nu_{\text{max}}/\text{cm}^{-1}$): 3490, 1631, 1531, 1469, 1384, 1346, 1238; ^1H 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 $179\text{--}182^\circ\text{C}$ (lit. [22] 184°C); IR (KBr) ($\nu_{\text{max}}/\text{cm}^{-1}$): 3309, 3089, 2842, 1689, 1627, 1539, 1434, 1342; ^1H NMR (250 MHz, DMSO): δ 11.73 (brs, 1H, -CO₂H), 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 $107\text{--}110^\circ\text{C}$ (lit. [22] $108\text{--}112^\circ\text{C}$); IR (KBr) ($\nu_{\text{max}}/\text{cm}^{-1}$): 3587, 3529, 1608, 1569, 1531, 1523, 1438, 1357, 1280; ^1H 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 $127\text{--}129^\circ\text{C}$ (lit. [22] $129\text{--}130^\circ\text{C}$); IR (KBr) ($\nu_{\text{max}}/\text{cm}^{-1}$): 3460, 3074, 2935, 1666, 1620, 1477, 1334, 1323; ^1H 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 $130\text{--}132^\circ\text{C}$ (lit. [23] 133°C); IR (KBr) ($\nu_{\text{max}}/\text{cm}^{-1}$): 3462, 3075, 2924, 1670, 1623, 1478, 1324, 1320; ^1H 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) ($\nu_{\max}/\text{cm}^{-1}$): 3388, 3300, 1628, 1592, 1525, 1511, 1444, 1327, 1284; ^1H 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) ($\nu_{\max}/\text{cm}^{-1}$): 3331, 1614, 1592, 1500, 1346; ^1H 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) ($\nu_{\max}/\text{cm}^{-1}$): 3241, 1623, 1606, 1593, 1538, 1479; ^1H 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) ($\nu_{\max}/\text{cm}^{-1}$): 3041, 1619, 1584, 1495, 1342; ^1H 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) ($\nu_{\max}/\text{cm}^{-1}$): 3045, 1621, 1658, 16003, 1545, 1489; ^1H 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) ($\nu_{\max}/\text{cm}^{-1}$): 3106, 1604, 1578, 1519, 1477, 1344; ^1H NMR (250 MHz, DMSO): δ 8.24 (d, 2H, $J=8.5$ Hz, Ar-H), 7.52 (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) ($\nu_{\max}/\text{cm}^{-1}$): 3096, 1688, 1550, 1467; ^1H 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) ($\nu_{\max}/\text{cm}^{-1}$): 2930, 1666, 1620, 1477, 1334, 1323; ^1H 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) ($\nu_{\max}/\text{cm}^{-1}$): 3101, 2873, 2715, 2596, 1701, 1593, 1431, 1330; ^1H 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) ($\nu_{\max}/\text{cm}^{-1}$): 3487, 3001, 2623, 1697, 1620, 1539, 1431, 1357, 1288; ^1H 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) ($\nu_{\max}/\text{cm}^{-1}$): 3475, 3363, 1639, 1531, 1346; ^1H 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, -NH₂); 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) ($\nu_{\max}/\text{cm}^{-1}$): 3474, 3354, 1632, 1531, 1346; ^1H NMR (250 MHz, DMSO): δ 7.28 (s, 1H, Ar-H), 6.74-6.81 (m, 2H, Ar-

H), 6.40 (brs, 2H, -NH₂), 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) ($\nu_{\max}/\text{cm}^{-1}$): 1593, 1510, 1346; ¹H NMR (250 MHz, CDCl₃): 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, -NMe₂); 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 °C), IR(KBr) ($\nu_{\max}/\text{cm}^{-1}$): 1606, 1592, 1534, 1471; ¹H NMR (250 MHz, CDCl₃): δ 7.52 (m, 2H, Ar-H), 7.34 (m, 1H, Ar-H), 6.98 (m, 1H, Ar-H), 2.92 (s, 6H, -NMe₂); GC-MS/ EI: m/z (%) = 166 (M⁺, 14), 109 (35), 65 (60), 53 (38), 39 (100).

4-nitroaniline (2q) Yellow powder; mp (146-148 °C (lit [22] 146-149°C); IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 3475, 3363, 1601, 1530, 1348; ¹H NMR (250 MHz, CDCl₃): 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, -NH₂); GC-MS/ EI: m/z (%) = 138 (M⁺, 45).

3-nitroaniline (2q') Yellow powder; mp 69-71 °C (lit. [22] 70-73°C), IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 3477, 3362, 1609, 1592, 1532, 1469; ¹H NMR (250 MHz, DMSO): δ 8.84 (s, 1H, Ar-*H*), 7.62-8.61 (m, 3H), 4.05 (brs, 2H, -NH₂); 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) ($\nu_{\max}/\text{cm}^{-1}$): 3472, 3364, 1600, 1529; ¹H NMR (250 MHz, CDCl₃): 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, -NH₂); 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.

Acknowledgement- We gratefully acknowledge the support of this work by Shiraz University.

REFERENCES

- (a) Grieco, P. A. (1998). *Organic Synthesis in Water*. London, Blacky Academic Professional. (b) Li, C. J. & Chan, T. H. (1997). *Organic Reactions in Aqueous Media*. New York, John Wiley & Sons. (c) Cornils, B. & Herrmann, W. A. (1998). *Aqueous-Phase Organometallic Chemistry*. Weinheim, Concepts and Applications, Wiley-VCH. (d) Li, C. J. (2005). Organic Reactions in Aqueous Media with a Focus on Carbon–Carbon Bond Formations: A Decade Update. *Chem. Rev.* 105, 3095. (e) Lindstrom, U. M. (2002). Stereoselective Organic Reactions in Water. *Chem. Rev.* 102, 2751. (f) Anastas, P. & Warner, J. C. (1998). *Green Chemistry: Theory and Practice*. Oxford, Oxford University Press. (g) Firouzabadi, H., Iranpoor, N. & Jafari, A. A. (2005). Micellar Solution of Sodium Dodecyl Sulfate (SDS) Catalyzes Facile Michael Addition of Amines and Thiols to α,β -Unsaturated Ketones in Water under Neutral Conditions. *Adv. Synth. Catal.* 347, 655. (h) Chankeshwara, S. V. & Chakraborti, A. K. (2006). Catalyst-Free Chemoselective *N*-tert-Butyloxycarbonylation of Amines in Water. *Org. Lett.*, 8, 3259. (i) Firouzabadi, H., Iranpoor, N. & Garzan, A. (2005). Pronounced Catalytic Effect of Micellar Solution of Sodium Dodecyl Sulfate (SDS) for Regioselective Iodination of Aromatic Compounds with a Sodium Iodide/Cerium (IV) Trihydroxide Hydroperoxide System. *Adv. Synth. Catal.* 347, 1925.
- Olah, G. A. & Kuhn, S. J. (1964). *Friedel-Crafts and Related Reactions*. Vol. 2, New York, Wiley-Interscience.

3. (a) Hoggett, J. G., Moodie, R. B., Penton J. R. & Schofield, K. (1971). *Nitration and Aromatic Reactivity*. London, Cambridge University Press. (b) Schofield, K. (1980). *Aromatic Nitration*. London, Cambridge University Press.
4. Laszlo, P. & Pennetreau, P. (1987). Vastly improved para preference in the nitration of halobenzenes. *J. Org. Chem.*, 52, 2407.
5. Kwok, T. J. & Jayasuriya, K. (1994). Application of H-ZSM-5 Zeolite for Regioselective Mononitration of Toluene. *J. Org. Chem.*, 59, 4939.
6. Smith, K., Musson, A. & Deboos, G. A. (1998). A Novel Method for the Nitration of Simple Aromatic Compounds. *J. Org. Chem.*, 63, 8448.
7. (a) Samajdar, S., Becker, F. F. & Banik, B. K. (2000). Surface-mediated highly efficient regioselective nitration of aromatic compounds by bismuth nitrate. *Tetrahedron Lett.*, 41, 8017. (b) Sun, H. B., Hua, R., & Yin, Y. (2005). Highly Efficient Nitration of Phenolic Compounds in Solid Phase or Solution Using $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ as Nitrating Reagent. *J. Org. Chem.*, 70, 9071.
8. (a) Waller, F. J., Barrett, A. G. M., Braddock, D. C. & Ramprasad, D. (1998). Hafnium (IV) and zirconium (IV) triflates as superior recyclable catalysts for the atom economic nitration of o-nitrotoluene. *Tetrahedron Lett.*, 39, 1641. (b) Firouzabadi, H., Iranpoor, N. & Zolfigol, M. A. (1998). Efficient and Selective Mono and Dinitration of Phenols With $\text{Cr}(\text{NO}_3)_3 \cdot 2\text{N}_2\text{O}_4$ as a New Nitrating Agent. *Synth. Commun.*, 28, 2773.
9. (a) Waller, F. J., Barrett, A. G. M., Braddock, D. C. & Ramprasad, D. (1997). Lanthanide (iii) triflates as recyclable catalysts for atom economic aromatic nitration. *Chem. Commun.*, 613. (b) Barrett, A. G. M., Braddock, D. C., Ducray, R., McKinnell, R. M. & Waller, F. J. (2000). Lanthanide Triflate and Triflide Catalyzed Atom Economic Nitration of Fluoroarenes. *Synlett*, 57.
10. (a) Frost, C. G., Hartley, J. P. & Griffin, D. (2002). Counterion effects in indium-catalysed aromatic electrophilic substitution reactions. *Tetrahedron Lett.*, 43, 4789. (b) Yin, W. P. & Shi, M. (2006). Indium triflate as a recyclable catalyst for the nitration of aromatic compounds without a halogenated solvent. *J. Chem. Res.*, 549.
11. (a) Gigante, B., Prazeres, A. O., Marcelo-Curto, M. J., Cornelis, A. & Laszlo, P. (1995). Mild and Selective Nitration by Claycop. *J. Org. Chem.*, 60, 3445. (b) Rodrigues, J. A. R., Filho, A. P., Moran, P. J. S. & Custodio, R. (1999). Regioselectivity of the nitration of phenol by acetyl nitrate adsorbed on silica gel. *Tetrahedron*, 55, 6733. (c) Iranpoor, N., Firouzabadi, H. & Heydari, R. (1999). Ionic Complex of N_2O_4 with 18-Crown-6: A Highly Efficient and Selective Reagent for Nitration of Phenols. *Synth. Commun.*, 29, 3295. (d) Tasneem, A. M. M., Rajanna, K. C., & Saiparakash, P. K. (2001). Ammonium nickel sulphate mediated nitration of aromatic compounds with nitric acid. *Synth. Commun.*, 31, 1123. (e) Bahulayan, D., Narayan, G., Sreekumar, V. & Lalithambika, M. (2002). Natural bentonite clay-dilute HNO_3 (40%)— A mild, efficient, and reusable catalyst/reagent system for selective mono nitration and benzylic oxidations. *Synth. Commun.*, 32, 3565. (f) Tanemura, K., Suzuki, T., Nishida, Y., Satsumabayashi, K. & Horaguchi, T. (2003). A mild and efficient method for the mononitration of aromatic compounds by cerium (III) ammonium nitrate in acetic anhydride. *J. Chem. Res. Synop.*, 497. (g) Muathen, H. A. (2003). Selective Nitration of Aromatic Compounds with Bismuth Subnitrate and Thionyl Chloride. *Molecules*, 8(7), 593. (h) Iranpoor, N., Firouzabadi, H. & Heydari, R. (2003). Silica-Acetate Complex of N_2O_4 : A Heterogeneous Reagent for the Selective Nitration of Phenols and Nitrosation of Thiols. *Synth. Commun.*, 33, 703. (i) Lancaster, N. L. & Liopis-Mestre, V. (2003). Aromatic nitrations in ionic liquids: the importance of cation choice. *Chem. Commun.*, 2812. (j) Prakash, G. K. S., Panja, C., Mathew, T., Surampudi, V., Petasis, N. A., & Olah, G. A. ipso-Nitration of Arylboronic Acids with Chlorotrimethylsilane–Nitrate Salts (2004). *Org. Lett.*, 6, 2205. (k) Ramana, M. M. V., Malik, S. S. & Parihar, J. A. (2004). Guanidinium nitrate: a novel reagent for aryl nitrations. *Tetrahedron Lett.*, 45, 8681. (l) Strazzolini, P., Giumanini, A. G. & Runcio, A. (2001). Nitric acid in dichloromethane solution. Facile preparation from potassium nitrate and sulfuric acid. *Tetrahedron Lett.*, 42, 1387. (m) Peng, X., Suzuki, H. & Lu, C. (2001). Zeolite-assisted nitration of neat toluene and chlorobenzene with a nitrogen dioxide/molecular oxygen system.

- Remarkable enhancement of para-selectivity. *Tetrahedron Lett.*, 42, 4357. (n) Bharadwaj, S. K., Hussain, S., Kar, M. & Chaudhuri, M. K. (2008). Al (H_2PO_4)₃: An efficient catalyst for nitration of organic compounds with nitric acid. *Catalysis Commun.* 9, 919. (o) Ghorbani-Choghamarani, A., Goudarziafshar, H., Nikoorazm, M. & Yousefi, M. (2009). Aluminum nitrate and silica sulfuric acid as efficient nitrating media for the mononitration of phenols under mild and heterogeneous conditions. *Can. J. Chem.* 87, 1144.
12. (a) Riego, J. M., Sedin, Z., Zaldivar, J. M., Marziano, N. C. & Tortato, C. (1996). Sulfuric acid on silica-gel: an inexpensive catalyst for aromatic nitration. *Tetrahedron Lett.*, 37, 513.
13. Zolfigol, M. A., Ghasemi, E. & Madrakian, E. (2003). Trichloroisocyanuric Acid/ NaNO_2 as a Novel Heterogeneous System for the Selective Mononitration of Phenols under Mild Conditions. *Synlett*, 191.
14. Rajagopal, R. & Srinivasan, K. V. (2003). Regio-selective Mono Nitration of Phenols with Ferric Nitrate in Room Temperature Ionic Liquid. *Synth. Commun.*, 33, 961.
15. Shackelford, S. A., Anderson, M. B., Christie, L. C., Goetzen, T., Guzman, M. C., Hananel, M. A., Kornreich, W. D., Li, H., Pathak, V. P., Rabinovich, A. K., Rajapakse, R. J., Truesdale, L. K., Tsank, S. M. & Vazir, H. N. (2003). Electrophilic Tetraalkylammonium Nitrate Nitration. II. Improved Anhydrous Aromatic and Heteroaromatic Mononitration with Tetramethylammonium Nitrate and Triflic Anhydride, Including Selected Microwave Examples. *J. Org. Chem.*, 68, 267.
16. Zolfigol, M. A., Ghaemi, E. & Madrakian, E. (2000). A Convenient Method for Selective Mono or Dinitration of Phenol under Mild Conditions. *Synth. Commun.*, 30, 1689.
17. Zolfigol, M. A., Ghaemi, E. & Madrakian, E. (2001). Nitration Of Phenols Under Mild And Heterogeneous Conditions. *Molecules*, 6, 614.
18. (a) Hosseini Sarvari, M. (2005). $\text{ZnO}/\text{CH}_3\text{COCl}$: A New and Highly Efficient Catalyst for Dehydration of Aldoximes into Nitriles Under Solvent-Free Condition. *Synthesis*, 5, 787. (b) Hosseini-Sarvari, M. & Sharghi, H. (2007). A Novel Method for the Synthesis of N-Sulfonylaldimines by ZnO as a Recyclable Neutral Catalyst Under Solvent-Free Conditions. *Phos. Silicon. Sulf.* 182, 2125. (c) Hosseini-Sarvari, M. (2007). Titania (TiO_2)-Catalyzed Expedient, Solventless and Mild Synthesis of Bis(Indolyl)Methanes. *Acta. Chim. Slov.* 54, 345. (d) Hosseini-Sarvari, M., Sharghi H. & Etemad, S. (2007). Solvent-free Knoevenagel Condensations over TiO_2 . *Chin. J. Chem.*, 25, 1563. (e) Hosseini-Saravri, M. (2008). Synthesis of Bis (indolyl) methanes using a Catalytic Amount of ZnO under Solvent-Free Conditions. *Synth. Commun.*, i6, 832. (f) Hosseini-Sarvari, M. (2008). Synthesis of Bis (indolyl) methanes using a Catalytic Amount of ZnO under Solvent-Free Conditions. *Can. J. Chem.* 86, 65. (g) Hosseini-Sarvari, M. (2008). TiO_2 as a new and reusable catalyst for one-pot three-component syntheses of α -aminophosphonates in solvent-free conditions. *Tetrahedron*, 5459. (h) Hosseini-Sarvari, M., & Etemad, S. (2008). Nanosized zinc oxide as a catalyst for the rapid and green synthesis of b-phosphono malonates. *Tetrahedron* 5519. (i) Hosseini-Sarvari M. (2008). Synthesis of β -aminoalcohols Catalyzed by ZnO. *Act. Chim. Slov.* 440. (j) Hosseini-Sarvari, M., Sharghi, H. & Etemad S. (2008). Nanocrystalline ZnO for Knoevenagel Condensation and Reduction of the Carbon,Carbon Double Bond in Conjugated Alkenes. *Helv. Chim. Acta*, 91, 715.
19. Sharghi, H., Hosseini Sarvari, M. & Eskandari, R.; (2005). Alumina sulfuric acid as a novel heterogeneous system for esterification of carboxylic acids in solvent free conditions. *J. Chem. Res.(s)*, 482.
20. Hosseini-Sarvari, M. & Sharghi, H. (2006). Alumina sulfuric acid mediated solvent-free and one-step Beckmann rearrangement of ketones and aldehydes and a useful reagent for synthesis of keto- and ald'oximes. *J. Chem. Res.(s)*, 205.
21. Vogels (1986). *Text Book of Practical Organic Chemistry 4th Edn.* London & New York, Longman.
22. (a) www.sigmaaldrich.com. (b) www.chemexper.com. (c) www.rdchemicals.com.
23. Zhang, P., Cedilote, M., Cleary, T. P. & Pierce, M. E. (2007). Mono-nitration of aromatic compounds via their nitric acid salts. *Tetrahedron Lett.*, 8659.
24. (2002-2003) *CRC Handbook of Chemistry and Physics. 83rd Edition.*

25. Saunders Cliff, C. R. & Hamilton, S. (1932). Isomeric nitro- and amino naphthalene-1-sulfonic acids. *J. Am. Chem. Soc.*, 54(2), 636.