Steric hindrance induced regio and chemo selective oxidation of aromatic amine

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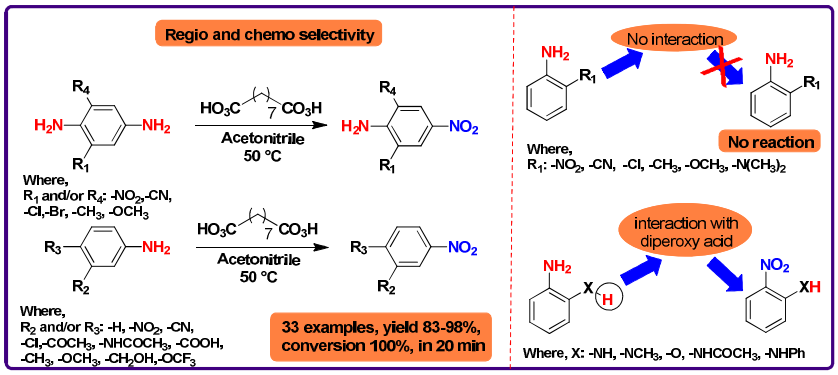


ABSTRACT

The ortho substituent hindered (except $–NH_2$, $–NHCH_3$ -OH) unusual regio and chemo selective oxidation of aromatic amine in to corresponding nitro compound is described using nonanebis(peroxoic acid). The mechanistic investigation for selective oxidation of amine ortho substituted with $–NH_2$, -OH showed the involvement of H-bonding between ortho hydrogen of adjacent –XH (-X = -NH, -NR, -O) group with oxygen atom from diperoxy acid. Various mono and diamines are oxidized into corresponding mono nitro derivatives in high yield and purity without employing any protection strategies. The protocol was also found to successful on gram scale.

INTRODUCTION

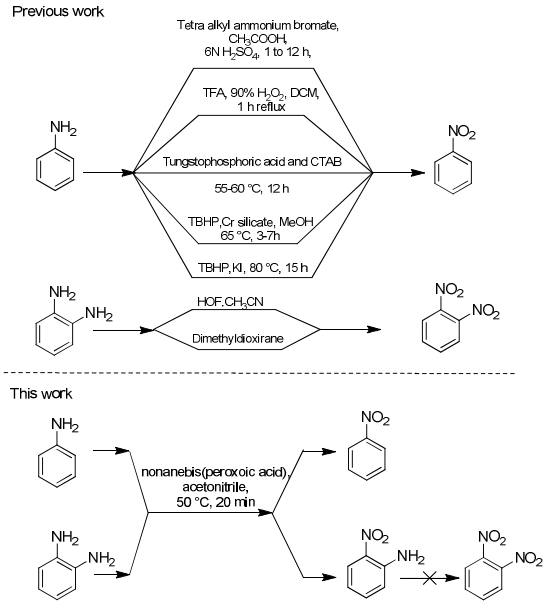
The oxidation of amines into nitro compound is considered as one of the indispensable transformations in organic synthesis as it is a direct route for the synthesis of nitro compounds. Aromatic nitro compounds are well established industrially as these compounds work as a backbone to many commercially important chemicals such as dyes,[1,2] polymers,[3,4] perfumes,[5,6] pharmaceuticals,[7] pesticide[8,9] and extensively in explosives.[8,10] They serves as important reagents for the synthesis of complex target molecules. Numerous oxidation strategies have been employed for this purpose[11] using various oxidants (Scheme 1) such as HOF-CH_3CN,[12–14] Dimethyldioxirane,[15–17] peracetic acid,[18] peroxytriflouro acetic acid,[19] *m*-CPBA,[20] oxone,[21] sodium perborate with tungstophosphoric acid and CTAB,[22] sodium perborate with acetic acid,[23] tetra alkyl ammonium bromate,[24] combination of *tert*-butyl hydroperoxide (TBHP) with various catalysts such as KI,[25] chromium silicate,[26] zirconium[27] and Fe

(III) and Mn (III) tetra aryl porphyrins,[28] superoxide and H_2O_2 mixture[29] and titanium superoxide.[30] The major short come in most of these oxidation protocol was the uncontrolled oxidation which results in to formation of multiple products such as nitroso, azo, azoxybenzene, hydroxyl amine, oxime which in turn, lack the selectivity.[11] Further some of those systems suffers various disadvantages. The hazardous halogenated solvents such as chloroform, dichloromethane and dichloroethane were most preferred to carry out this oxidation. The peracids such as peracetic acid, peroxytrifluoro acetic acid are difficult to handle in anhydrous condition. The peroxytrifluoro acetic acid, itself attack on the benzene ring to give phenol containing complex mixtures.[19] This reagent was also found to be ineffective to oxidize *p*-methoxy aniline to *p*-methoxy nitrobenzene. Whereas oxidation with *m*-CPBA in 1,2-dichloroethane occurred in 10 h under reflux condition.[20] The most studied oxidant HOF-CH_3CN required hazardous fluorine gas for the preparation as well as this reagent is quite unstable and need to prepare in situ.[11] The oxidizing systems such as KI-TBHP, Sodium perborate-tugastophosphoric acid with CTAB though follow some principles of green chemistry but reaction requires longer time (12 to 15 h) for completion with moderate to good yields. The heterogeneous catalytic system reported by Sudalai et. al. was found to be most effective not only for selective oxidation of amine to nitro as well as it gives good yield in shorter period with recycling the catalyst.[30] It is noticeable that, in all above mentioned reports attempts were made to give selective nitro as a product, but none of the chemical method successful to give chemo or regio selective oxidation. For instant, the oxidation of *o*-diamine results into formation of dinitro compounds (Scheme 1) and if mono nitro derivative is desired then one need to protect one of the amine to avoid di nitro product formation.[13] On other hand, enzymes were served as a better option to achieve chemo and regio selectivity for this transformation. [31–33] Hertweck[31] and co-workers have reported the chemo and regio selective oxidation of various para amino benzoic acid derivatives using para-aminobenzoate *N*-oxygenase (AurF) enzyme from Streptomyces thioluteus. The interaction between positively charged protein residue and anionic part of acid is responsible for higher selectivity of this protocol. Owing to this acid selective interaction, this protocol was relevant to only amines with anionic acid part at para position. Thus the need to develop a chemical method which will overcome all above short comes as well as provide certain sort of selectivity drive our attention towards this transformation. In our previous work, we have demonstrated that the long chain diperoxy acid, nonanebis(peroxoic acid) can overcome various short comes[34] of conventional peracids and can be a good alternative for them.[35] It is easy to prepare and handle, non-shock sensitive in nature and stable at room temperature.[35,36] As a part of our research to explore the applicability of diperoxy acids in the organic synthesis we decided to investigate above oxidation reaction in this peroxy acid. During this attempt we found that this diperoxy acid was not only capable to oxidize amino to nitro in shorter period and under mild conditions but also show one unusual selectivity trend which was not yet reported in the literature for any chemical oxidation method of this kind. The steric hindrance of ortho substituent and the interaction between diperoxy acids and hydrogen atom present on heteroatom (X= -N/-O) ortho to amine play vital role to induce an interesting selectivity which to the best our knowledge not yet explored in organic synthesis. This trend was also found in the other diperoxy acids we investigated here. It is noticeable that the protocol which we

report here is found to be effective to synthesize the commercially important molecules such as "Dichloran" which is widely used as a fungicide[37] from 2,6-dichlorobenzene-1,4-diamine . The molecules such as 2-amino-3-bromo-5-nitrobenzonitrile[38,39], 2-methyl-4-nitroaniline[40] which are used as intermediate to synthesize azo dyes for NLO, for dying polymers were also prepared by using present approach. 2-methoxy-4-nitroaniline which is widely used for textile dying, in the printing industry, as intermediate for the synthesis of azo dyes for tattoo inks, emulsion paints and toy enamels was also synthesized under present protocol.

Thus here we report, a metal catalyst free, mild and efficient approach for regio and chemo selective oxidation of aromatic amine to nitro using nonanebis(peroxoic acid) as a oxidant. This work highlighted the important properties of these diperoxy acids which was still remained unnoticed from their discovery.

Scheme 1. Previous report

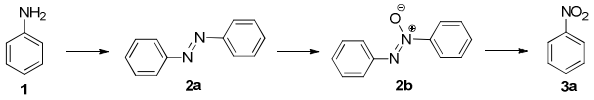


RESULTS AND DISCUSSION

The reaction conditions were optimized by taking aniline **1a** (1 equiv.) as a key substrate and nonanebis(peroxoic acid) as an oxidant at 50 °C (Table 1). The oxidant equivalent study illustrated that the formation of nitro product proceeds through azo **2a** and azoxy benzene 2b as intermediate products (Table 1, entries 1-3) and three equivalents of oxidant were required for the formation of nitro product **3a** (Table 1, entry 4). The influence of solvents for conversion studies revealed acetonitrile to be the most appropriate solvent as 100% conversion into nitro benzene was achieved within 20 min (Table 1, entry 4). On the contrary when hexane was used as a solvent, selectively azoxybenzene **2b** formation was observed (Table 1, entry 5). The other solvents gave mixture of both azoxy benzene and nitro benzene (Table 1, entries 6–13). It was also observed that the rate of formation of

nitro product increases as temperature increased from 20 °C to 50 °C (Table 1, entries 13-15). Further rise in the temperature has not shown any influence on time as well as yield (Table 1, entry 16).

Table 1. Optimization of reaction conditions[a]



Entry	Solvent	Oxidant equiv.	% conversion[b] 2a	2b	3a
1	Acetonitrile	1	41	59	-
2	Acetonitrile	2	4	55	41
3	Acetonitrile	2.5	-	39	61
4	Acetonitrile	3	-	-	100
5	Hexane	3	-	100	-
6	Toluene	3	-	71	29
7	Chloroform	3	-	56	42
8	DCM	3	-	41	59
9	Ethyl acetate	3	-	35	65
10	DMF	3	-	62	38
11	Ethanol	3	-	72	28
12	Water	3	-	75	25
13[c]	Acetonitrile	3	-	51	49
14[d]	Acetonitrile	3	-	20	80
15[e]	Acetonitrile	3	-	8	92
16[f]	Acetonitrile	3	-	-	100

Comparision with other oxidants

Entry	Oxidant	Oxidant equiv.	3a % conversion[b]
17[g]	50% H_2O_2	6	NR
18[g]	70% TBHP	6	NR
19[h]	*m*-CPBA	6	30%
20[g]	Sodium perborate	6	traces
21[h]	Oxone	6	traces
22[g]	Potassium peroxy disulphate	6	NR
23	Performic acid	6	-
24	Peracetic acid	6	-

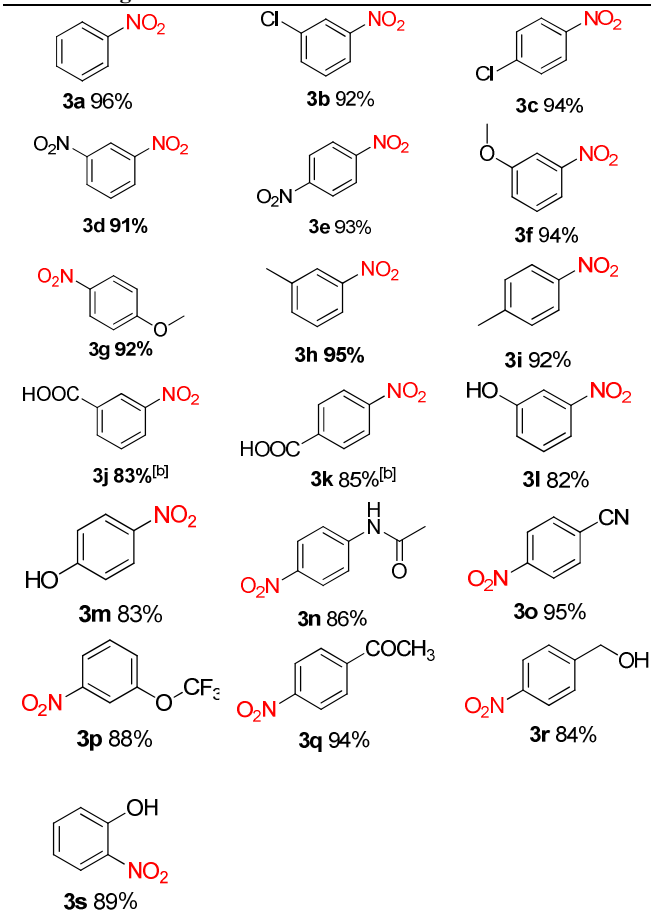
[a]Reaction conditions: **1a** (1.07 mmol), oxidant : nonanebis(peroxoic acid) , solvent 5 mL; All reactions were performed in 20 min at 50 °C unless otherwise indicated. [b]Conversion determined by GC. [c]Reaction kept for 24 h at 20 °C; [d]Reaction kept for 24 h at 30 °C; [e]Reaction kept for 1 h at 40 °C; [f]Reaction kept for 20 min at 60 °C. [g]Reaction maintanined for 2h at 50 °C. [h]Reaction maintanined for 30 min at 50 °C. NR: No Reaction.

We also examined feasibility of other commonly peroxides under present conditions (Table 1, entries 17-24). It was observed that, except *m*-CPBA (Table 1, entry 19) none other oxidants show formation of nitro benzene under optimized conditions. In case of 50% H_2O_2, 70% TBHP, and potassium peroxy disulphate only starting aniline was observed on TLC even after keeping reaction for 2 h at 50 °C (Table 1, entries 17, 18 and 22). Whereas in sodium perborate traces nitro benzene formation was observed under optimized conditions (Table 1, entry 20). The reaction with performic acid gives 6% of *N*-formylated product, 9% of **2a** and 85% of the **2b** (Table 1, entry 23). Similarly in case of peracetic acid, 10% of *N*-acylated product was formed with 90% of **2b** (Table 1, entry 24). In both peracids formation of **3a** was not observed.

Encouraged by these promising results, we applied the optimized reaction conditions to examine the substrate scope. The oxidation of various aniline derivatives under optimized reaction conditions gives corresponding nitro product in 20 min

(Table 2). It was found that the aniline derivatives with -*m* and/or - *p* substituents such as -Cl, -NO_2, -OCH_3, -CH_3, -COOH, -OH, -$NHCOCH_3$, -CN, -OCF_3, -$COCH_3$ were oxidized smoothly into corresponding nitro derivatives in 20 min (Table 2, entries **3b** to **3r**). While the *o*-substituted derivatives of aniline such as 2-chloro aniline, 2-nitro aniline, 2-anisidine, 2-toluidine, 2-amino benzonitrile failed to undergo oxidation under existing conditions even after exceeding reaction conditions for 2 h at 50 °C. In case of amino phenols no quinone formation was observed only nitro derivative was formed (Table 2, entries **3l**, **3m**, **3s**). The protocol was also found to be compatible with various functional groups such as -COOH, -$NHCOCH_3$, -CN, -OCF_3, -$COCH_3$, -CH_2OH (Table 1, entries **3j**, **3k**, **3n-3r**). The substrate which contain oxidizable groups such as -CN, -$COCH_3$ and -CH_2OH no oxidation products of respective functional group such as *N*-oxide, ester and aldehyde or acid was detected (Table 1, **3o**, **3q** and **3r**). The protocol was found to be unsuccessful when we tried competitive reaction in presence of styrene, it was found that, styrene undergoes oxidation along with aniline under present conditions to give mixture of oxidation products of both substrates. Similarly the protocol was failed with substrate containing aldehyde as reaction gives multiple products.

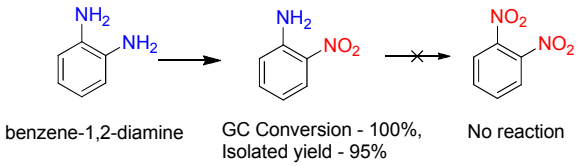
Table 2. Regio and chemo selective oxidation of various aromatic mono amine[a]



[a]Reaction conditions: amine (1 equiv.), nonanebis(peroxoic acid) (3 equiv.), acetonitrile 5 mL, All reactions were performed in 20 min. Yields given are isolated yields. [b]The reaction mass was quenched by 0.1 M sodium thiosulphate solution, extracted in ethyl acetate and purified with column chromatography using hexane: ethyl acetate as a eluting system.

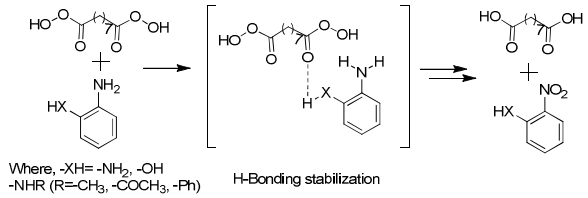
To our surprise, the oxidation of benzene-1,2-diamine under present conditions, selectively gave 2-nitro aniline as a product (**Scheme 2**). Addition of extra oxidant (3 equivalents) failed to show formation of 1,2-dinitro benzene.

Scheme 2. Selective oxidation of benzene-1,2-diamine into 2-nitroaniline



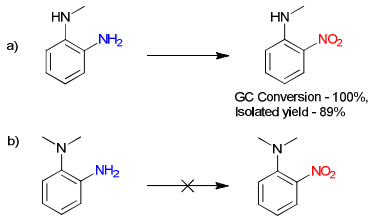
This result was further confirmed from the reaction of 2-nitro aniline which does not undergo oxidation under present conditions. From this, it was confirmed that once one of the *o*–NH_2 groups of benzene-1,2-diamine gets oxidized, it prevents further oxidation of amino group at ortho position. Again, we also understood that amine bearing hydrogen on heteroatom at ortho position only get oxidized to corresponding nitro derivative. To check feasibility, we carried out reactions with 2-amino phenol and 2-amino thiophenol. It was found that, the reaction with 2-amino phenol gave 2-nitro phenol as a product (Table 2, entry 3s). But in case of 2-amino thiophenol, the protocol was found to be unsuccessful as the reaction yields, mixture of oxidation products of both sulphur and amine instead of 2-nitro thiophenol. From the above fallouts, it was clear that, only those ortho substituted amines get oxidized to corresponding nitro derivative which possess hydrogen on heteroatom. We believe that, the reason for this selectivity could be the hydrogen bonding between hydrogen on ortho –XH group with oxygen of per acid which in turn facilitates the oxidation reaction (**scheme 3**).

Scheme 3. Hydrogen bonding between hydrogen atom on ortho –XH substituent (-NH_2/-$NHCH_3$/-OH) with carbonyl oxygen of diperoxy acid



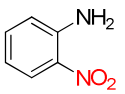
To validate this assumption, we carried out reaction on N^1-methylbenzene-1,2-diamine and N^1,N^1-dimethylbenzene-1,2-diamine (**scheme 4- a, b**). The GC analysis shows that, the former amine derivative get oxidized to *N*-methyl-2-nitroaniline whereas latter persisted as it is. This assumption was further confirmed from the reaction 2-amino phenol and 2-methoxy aniline, as former get oxidized to 2-nitro phenol whereas 2-methoxy aniline failed to undergo any oxidation reaction under present conditions. Further validation of this assumption was done by carrying out reactions with *N*-(2-aminophenyl)acetamide and 4-chloro-N^1-phenylbenzene-1,2-diamine to give **4m** 87% and **4n** 90% respectively in 20 min (Table 3, entries **4m**, **4n**).

Scheme 4. Influence of hydrogen atom of ortho –NH_2 group on oxidation of *o*-diamine

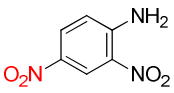


This confirmed the significant importance of hydrogen atom present on hetero atom at ortho position in the selective oxidation of diamine and amino phenol. In order to study chemo selectivity further, we carried out oxidation of various diamine in which one of the amino groups was ortho substituted with group other than –NH_2, -OH (Table 3). The results obtained shows that amine with ortho substituents (other than -NH_2 and -OH) remained unaffected under present reaction conditions. While the amine without any ortho substituents or ortho substituted with –NH_2,-OH undergo oxidation into corresponding nitro group (Table 3, entries **4a-4i**). The further advantage of this protocol was the easy synthesis of the important fungicide "Dichloran". The oxidation of 2,6-dichloro paraphenylene diamine gives 92% yield of "Dichloran" in 20 min (Table 3, entry **4e**). The reaction of benzene-1,4-diamine with 6 equiv. of peroxy acid give 1,4-dinitro benzene (Table 3, entry **4i**) but in case of benzne-1,3-diamine polar spot was observed on TLC instead of 1,3-dinitro benzene. It was noticeable that, in case of substrate like 4-nitrobenzene-1,2-diamine, with strong electron withdrawing –NO_2 group at para position, showed pronounce effect on oxidation of *p*-NH_2 group as 2,4-dinitro aniline **(4j-a)** was formed as a major product over 2,5-dinitro aniline **(4j-b)** (Table 3, entry **4j**). While in case of substrate like 4-chlorobenzene-1,2-diamine, with less electron withdrawing -Cl group, both products were obtained almost in equal amount (Table 3, entry **4l**). The oxidation of substrates bearing acyl and aryl groups on benzene-1,2-diamine further confirmed the role of hydrogen on neighbouring heteroatom in the oxidation of ortho amine to nitro (Table 3, entries **4m**, **4n**). Both substrates were smoothly oxidized in to corresponding nitro derivatives in 20 min to give 87% and 90% yield respectively.

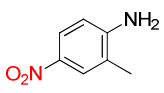
Table 3. Selective oxidation of various aromatic di-amines[a]



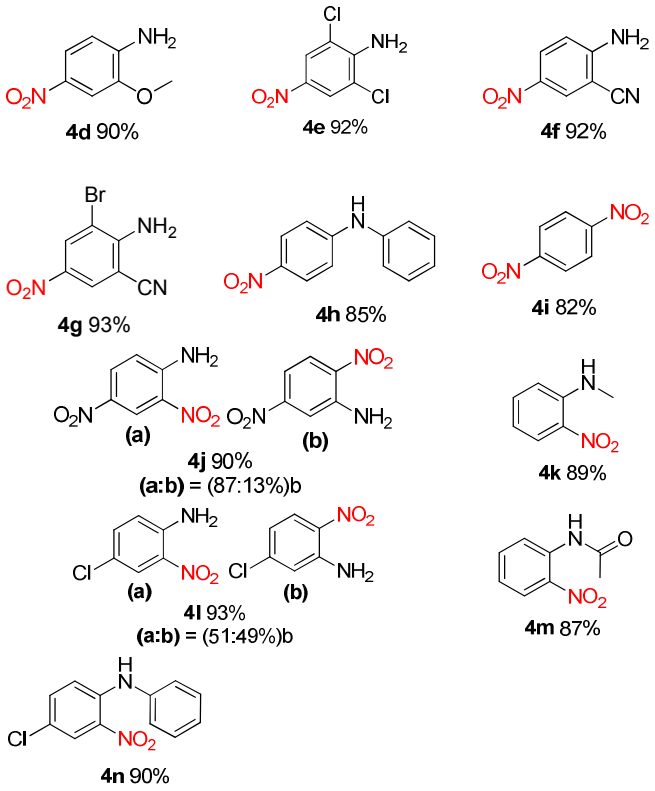
4a 95%



4b 91%



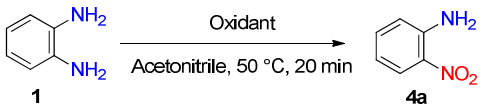
4c 94%



[a]Reaction conditions: 1 (1 equiv.), nonanebis(peroxoic acid) (3 equiv.), acetonitrile 5 mL, All reactions were Kept for 20 min. Yields given are isolated yields. [b]Conversion determined by GC analysis and products were confirmed by GC-MS analysis.

Further, when we examined conventionally used oxidizing agents for above selectivity (Table 4, entries 1-6), it was observed that except *m*-CPBA none of the oxidants show formation of ortho nitro aniline. In case of *m*-CPBA only 28% of **4a** formation was observed (Table 4, entry 6). In order to check this selectivity trend in other diperoxy acids, we carried out reaction of benzene-1,2-diamine with hexanebis(peroxoic acid) and dodecanebis(peroxoic acid) (no. of carbon atoms are 6 and 12 respectively) which also give 100% conversion in to 2-nitro aniline with 90% and 92% isolated yield respectively (Table 4, entries 1-2). Reactions of other diperoxy acids with substrates such as *o*-nitro aniline and *o*-toluidine were also failed to show any oxidation of amino group under identical conditions. This confirms the regio and chemo selective nature of diperoxy acids for oxidation of aromatic amines. The reaction of benzene-1,2-diamine **1** with aliphatic mono peroxy acids such as performic acid not shows formation of **4a** though we increased the peracid equivalents from 6 to 24 (Table 4, entry 9). In case of peracetic acid **4a** formation was not observed when 6 equivalents of Peracetic acid was used. As we increased equivalents of peracetic acid from 6 to 24, the formation of **4a** was observed. The moderate gives moderate yield of **4a** due to formation of blackish insoluble solid along with desired product which was not detected on GC-MS (Table 4, entry 10).

Table 4. Selective oxidation of benzene-1,2-diamine using conventional oxidants and other diperoxy acid's[a]



Entry	Oxidant	4a conversion[b] (%)
1	50% H_2O_2	-
2	70% TBHP	-
3	Oxone	-
4	Sodium perborate	-
5	Potassium peroxy disulphate	-
6	*m*-CPBA	28
7	Hexanebis(peroxoic acid)	100
8	Dodecanebis(peroxoic acid)	100
9[c]	Performic acid	-
10[d]	Peracetic acid	100 (58)[e]

[a] Reaction conditions: 1 (1 equiv.), Oxidant (6 equiv. for entries 1-6 and 3 equiv. for entries 7,8), Acetonitrile 5 mL, time : 2 h (entries 1-6), 20 min (for entries 7,8). [b]Conversion: determined by GC.[c]Reactions were carried out using 6, 12 and 24 equiv. of peracid. [d]Using 24 equiv. of peracetic acid.[e]islated yield.

The present approach was also examined on gram scale. We carried out oxidation of aniline and benzene-1,2-diamine on 5 g scale up of each. The reaction yields 97% nitrobenzene and 95% 2-nitro aniline in 20 min respectively. Thus it was also confirmed that the protocol can be successfully used on gram scale.

Conclusions

We have developed a simple, efficient and transition metal free protocol of oxidation of aromatic amine to nitro. The reaction selectively yields desired nitro product in shorter period, with high yield and purity irrespective of the substituents present on ring. The most exciting feature of the present approach is meta and para selective oxidation of amine whereas anilines ortho substituted with groups other than (-NH_2, -$NHCH_3$, -OH) remained unaffected. Such ortho substituent hindered selectivity plays vital role for the selective oxidation of diamine into its mono nitro derivative in which amine with ortho substituent remained unaffected. The protocol shows unexceptional selectivity for oxidation of benzne-1,2-diamine to 2-nitro aniline without further oxidizing it in to 1,3-dinitro compound. Although oxidation of amine by peroxy acid is well reported but such regio and chemo selectivity was not yet reported in any of these peroxy acids. We have also shown that the protocol was successful on gram scale.

Experimental Section

All products were confirmed by melting point, ^{1}H NMR and mass spectrometry. All melting points are uncorrected and are presented in degree Celsius. The ^{1}H NMR spectroscopic data were recorded on 400 and 500 MHz instruments in $CDCl_3$ and DMSO-d6 as a solvent and chemical shifts are expressed in δ ppm using TMS as an internal standard. GC analysis were carried out using TR-1 column, 30mX0.25mm, IDX0.25um film, FID detector and sample size 0.1 l µl. Nitrogen was used as the carrier

gas at a flow rate 2 mL/min, 80-250 °C at 10 °C/min. GC/MS was performed using Rtx-17 column, 30 m, 25 mm internal diameter, film thickness 0.25 μm, column flow: 2 mL/min, 80–250 °C at 10 °C/min.

General procedure for the synthesis of nonanebis(peroxoic acid):

Nonanebis(peroxoic acid) was synthesized as per the procedure given in literature on 10 g scale.[35,36]

General procedure for oxidation of aromatic amines using nonanebis(peroxoic acid):

In 50 mL round bottom flask, 0.1 g amine was stirred in 5 mL acetonitrile for 5 min. To this nonanebis(peroxoic acid) (3 equiv.) was added in 10 min. with constant stirring. The reaction mass was heated to 50 °C for 20 min. The reaction mass was quenched by saturated sodium thiosulphate solution (2 mL) and extracted in ethyl acetate (3 x 10 mL). The organic layer was treated with saturated sodium bicarbonate solution till acid get neutralized and then with water and were dried over anhydrous Na_2SO_4. The crude product was obtained after evaporating the solvent under vacuum which was further purified by column chromatography on silica gel with hexane/ ethyl acetate as the eluent.

Procedure for scale up reaction:

In 500 mL 3N RBF equipped with a mercury sealed stirrer 5 g amine (aniline, benzne-1,2-diamine) was taken in 250 mL acetonitrile. The reaction mass was stirred for 5 min at room temperature. To this reaction mass 6 equiv. of nonanebis(peroxoic acid) (71 g for aniline and 61 g for benzne-1,2-diamine) was carefully and slowly added over 45 to 50 min at room temperature. The reaction mass maintained at 50 °C for 20 min and then the reaction mass was quenched by saturated 50 mL sodium thiosulphate and extracted in ethyl acetate (3 x 20 mL). The organic layer was further treated with saturated sodium bicarbonate solution till it free from acids and then further with water. It was the dried over anhydrous Na_2SO_4. The solvent was evaporated under vacuum to give 97% nitro benzene and 95% 2-nitro aniline.

Spectral Data

1. **Nitrobenzene (3a)[20]:** Yellow oil ; yield 0.127 g, 96%; purity 99.4% (GC); B.P. 208-210 °C; ^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 7.54-7.58 (m, 2H), 7.69-7.72 (m, 1H), 8.23-8.25 (m, J = 8.5 Hz, J = 1 Hz 2 H). GC-MS (EI, 70 eV): m/z (%) = 123 (52.8) $[M]^+$, 93 (10.8), 77 (100).
2. **3-Chloronitrobenzene (3b)[20]:** Light yellow solid; yield 0.114 g,92%; purity 99.1% (GC); M.P. 46-47 °C; ^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 7.50-7.53 (t, J = 8 Hz, J = 8.5 Hz, 1H), 7.68-7.70 (q, J = 7.5 Hz, J = 1 Hz1H), 8.13-8.15 (q, J = 7 Hz, J = 1.5 Hz, 1H), 8.23-8.24 (t, J = 2 Hz, 1H); GC-MS (EI, 70 eV): m/z (%) = 157 (87.6) $[M]^+$, 159 (28), 127 (41.6), 129 (13.6), 113 (31), 111 (98.4), 101 (11.2), 99 (33.6), 75 (100).

3. **4-Chloronitrobenzene (3c)**[20]**:** Light yellow solid; yield 0.117 g, 94%; M.P. 82-83 °C; purity 99.0% (GC); ^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 7.52-7.53 (q, *J* = 2 Hz, *J* = 7 Hz, 2H), 8.18-8.20 (q, *J* = 2.5 Hz, *J* = 6.5 Hz, 2H); GC-MS (EI, 70 eV): m/z (%) = 157 $[M]^+$, 127, 11, 75 (100).
4. **1,3-Dinitrobenzene (3d)**[41]**:** Yellow solid; yield0.111 g 91%; M.P. 89-90 °C; purity 98.6 % (GC); ^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 7.81-7.84 (t, *J* = 8 Hz, *J* = 8 Hz, 1H), 8.58-8.60 (q, *J* = 8 Hz, *J* = 2 Hz, 2H), 9.08-9.09 (t, *J* = 8 Hz, *J* = 2 Hz, 1H); GC-MS (EI, 70 eV): m/z (%) = 168 (94.4) $[M]^+$, 122 (36.4), 92 (44.0), 76 (80), 75 (78.8), 74 (22.8).
5. **1,4-dinitrobenzene (3e)**[20]: Yellow solid; yield 0.112 g 92%; M.P. 165-166 °C; purity 98.9% (GC); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (s, 4H); GC-MS (EI, 70 eV): m/z (%) = 168 (60) $[M]^+$, 122 (20), 90 (19), 76 (46), 30 (100).
6. **1-methoxy-3-nitrobenzene (3f)**[42]**:** Yellow solid, yield 0.116 g 93%; purity 99.2% (GC); ^{1}H-NMR ($CDCl_3$, 300 MHz): δ =3.90 (s, 3H), 7.17-7.20 (d, *J* = 8.3 Hz, 1H), 7.38-743 (t, *J* = 8.1 Hz, 1H), 7.70 (s, 1H), 7.79-7.82 (d, *J* = 7.4 Hz, 1H) ; GC-MS (EI, 70 eV): m/z (%) = 153 (100) $[M]^+$, 107 (53), 92 (74), 77 (92).
7. **1-methoxy-4-nitrobenzene (3g)**[20]**:** White solid; yield 0.118 g 95%; M.P. 51-52 °C; purity 98.8% (GC); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.89 (s, 3H), 6.96 – 6.92 (m, 2H), 8.19 – 8.15 (m, 2H); GC-MS (EI, 70 eV): m/z (%) = 153 (100) $[M]^+$, 123 (47), 107 (12), 92 (56), 77 (56).
8. **3-Nitro toluene (3h)**[43,44]**:** Light yellow liquid; yield 0.119 g 95%; B.P. 230-232 °C; purity 99.5% (GC); ^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 2.47 (s, 3H,), 7.40-7.44 (t, 1H), 7.49-7.51 (d, 1H), 8.02-8.05 (t, 2H). GC-MS (EI, 70 eV): m/z (%) = 137 (75) $[M]^+$, 107 (20), 91 (100), 79 (12).
9. **4-Nitro toluene (3i)**[20]**:** Light yellow solid; yield 0.116 g 92%; M.P. 52-53 °C; purity 99.3% (GC); ^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 7.31-7.33 (d, *J* = 8.5 Hz, 2H), 8.11-8.13 (d, *J* = 8.5 Hz, 2H); GC-MS (EI, 70 eV): m/z (%) = 137 (100) $[M]^+$, 107 (32.8), 91 (90), 79 (17.6), 77 (19.6).
10. **3-Nitro benzoic acid (3j)**[42]**:** Light yellow solid; yield 0.101 g 83%; M.P. 140-142 °C; purity 98.5% (HPLC); ^{1}H-NMR (DMSO, 500 MHz): δ = 7.78-7.81 (t, *J* = 8 Hz, 1H), 8.32-8.34 (t, *J* = 7.5 Hz, 1H), 8.44-8.46 (m, 1H), 8.601-8.604 (d, *J* = 1.5 Hz, 1H). 13.6 (s, broad, 1H); EI-MS = 165.90 [M-H].
11. **4-Nitro benzoic acid (3k)**[42]: Light yellow solid; yield 0.104 g 85% yield; M.P. 235-236 °C; purity 98.8% (HPLC); ^{1}H-NMR (DMSO, 400 MHz): δ = 8.17-8.20 (m, *J* = 9.08 Hz, *J* = 1.84 Hz, 2H), 8.29-8.32 (m, *J* = 9.08 Hz, *J* = 1.88 Hz, 2H), 13.18 (s, broad, 1H); EI-MS= 165.93 [M-H].
12. **3-Nitrophenol (3l)**[45,46]**:** White solid; yield 0.105 g 82%; M.P. 96-97 °C; purity 98.6% (GC); ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 5.96 (s, 1H), 7.22-7.19 (m, 1H), 7.41 (t, *J* = 8.2 Hz, 1H), 7.72 (t, *J* = 2.0 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1 H); GC-MS (EI, 70 eV): m/z (%) = 139 (100) $[M]^+$, 93 (52.4), 81 (23.2).

13. **4-Nitrophenol (3m)**[46,47]**:** Light yellow solid; yield 0.106 g83%; M.P. 114-116 °C; purity 99.0% (GC); ^{1}H-NMR (DMSO, 500 MHz): δ = 6.065 (s, 1H), 6.935-6.953 (d, *J* = 9 Hz, 2H); 8.18-8.198 (d, *J* = 9 Hz, 2H). GC-MS (EI, 70 eV): m/z (%) = 139 (100) $[M]^+$, 93 (31.2), 81 (20), 65 (86.8).

14. ***N*-(4-nitrophenyl)acetamide (3n)**[48]**:** colorless solid; yield 0.103 g86%; M. P. 209-211; purity 98.7% (GC); ^{1}H NMR (500 MHz, DMSO) δ 2.10 (s, 3H), 7.80-7.79 (d, *J* = 5 Hz, 2H), 8.18-8.17 (d, *J* = 5 Hz, 2H), 10.52 (s, 1H). GC-MS (EI, 70 eV): m/z (%) = 180 (33) $[M]^+$, 138 (100), 122 (5.59), 108 (28.4), 92 (26.3).

15. **4-nitrobenzonitrile (*3o*)**[49,50]**:** Light yellow solid; yield 0.110 g 88%; M.P. 145-146 °C; purity 99.1% (GC); ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.87-7.91 (m, *J* = 8.0, 2H), 8.35-8.38 (m, *J* = 8.8, 2H); GC-MS (EI, 70 eV): m/z (%) = 148 (60) $[M]^+$,118 (10.6), 102 (100), 90 (29.4), 75 (47.5).

16. **1-nitro-3-(trifluoromethoxy)benzene (3p)**[51]**:** Pale yellow liquid; yield 0.105 g 90%; B.P. 208-210 °C; purity 98.1% (GC); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 15.4, 9.1 Hz, 2H), 8.28 – 8.24 (m, 1H), 8.39 – 8.35 (m, 1H); GC-MS (EI, 70 eV): m/z (%) = 207 (66) $[M]^+$, 177 (28), 161 (13), 95 (100), 92 (27), 75 (27).

17. **1-(4-nitrophenyl)ethanone (3q)**[52]: Light yellow solid; yield 0.115 g 94%; M.P. 76-78 °C; purity 99.2% (GC); ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 2.69 (s, 3H), 8.11-8.14 (m, *J* = 8.0 Hz, *J* = 2.16 Hz, 2H), 8.30-8.34 (m, *J* = 8.0 Hz, *J* = 2.24 Hz, 2H); GC-MS (EI, 70 eV); m/z (%) = 165 (17.8) $[M]^+$, 150 (100), 120 (20.8), 104 (41.6), 92 (24.9), 76 (25.9).

18. **(4-nitrophenyl)methanol (3r)**[42]**:** Pale yellow solid; yield 0.104 g 84%; M.P. 92-94 °C; purity 99.5% (GC); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.00 (d, broad 1H), 4.84 (d, *J* = 5.7 Hz, 2H), 7.54 (dd, *J* = 8.8 Hz, 2H), 8.22 (dd, *J* = 8.6 Hz, 2H); GC-MS (EI, 70 eV): m/z (%) = 153 (18) $[M]^+$, 136 (14), 107 (53), 89 (35), 77 (100), 63 (20).

19. **2-nitrophenol (3s)**[53]**:** Light yellow solid; yield 0.113g 89%; M.P. 43-44 °C; purity 99.5% (GC); ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 6.97-7.02 (m, *J* = 7.24 Hz, 1H), 7.15-7.17 (dd, *J* = 8.48 Hz, 1H), 7.57-7.61(m, *J* = 7.28 Hz, 1H), 8.10-8.12 (dd, *J* = 8.52 Hz, 1H), 10.59 (s, 1H); GC-MS (EI, 70 eV): m/z (%) = 139 (100) $[M]^+$, 122 (6.70), 109 (25.2), 93 (10), 84 (28.8), 65 (39.2), 64 (21.1), 63 (32.7).

20. **2-nitroaniline (4a)**[54]: Orange solid; yield 0.121 g 95%; M.P. 72-73 °C; 99.8% (GC); ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 6.06 (s, 2H, 6.68-6.72 (m, *J* = 8.48 Hz, 1H), 6.79-6.82 (dd, *J* = 8.4 Hz, 1H), 7.34 - 7.38(m, *J* = 8.44 Hz, 1H), 8.1- 8.13 (dd, *J* = 8.64 Hz, 1H); GC-MS (EI, 70 eV): m/z (%) = 138 (100) $[m]^+$, 108 (19.2), 92 (59.2), 80 (20.4), 65 (88.8).

21. **2,4-Dinitroaniline (4b)**[55,56]**:** Yellow orange solid; yield 0.109 g 89%; purity 99.4% (HPLC); M.P. 182-183 °C; ^{1}H-NMR (DMSO, 400 MHz): δ = 7.09-7.11 (d, *J* = 9.44 Hz, 1H), 8.09-8.12 (m, *J* = 9.4 Hz, *J* = 2.68 Hz, 1H), 8.31-8.33 (s broad, 2H), 8.801-8.808 (d, *J* = 2.64 Hz, 1H); EI-MS = 182.09 [M-H].

22. **2-Methyl-4-nitro aniline (4c)**[57,58]**:** Yellow solid; yield 0.117 g 87%; M.P. 130-132 °C; 99.3% (GC); ^{1}H-NMR ($CDCl_3$, 400 MHz): δ =2.23 (s, 3H), 3.93 (s, 2H), 7.13-7.15 (d, *J* = 8.12 Hz, 1H), 7.48-7.49 (d, *J* = 2.24 Hz, 1H), 7.51-7.54 (dd, *J* = 8.16 Hz, 1H); GC-MS (EI, 70 eV): m/z (%) = 152 (89) $[M]^+$, 122 (10.57), 106 (77.49), 94 (21.94), 77 (83.1).

23. **2-methoxy-4-nitroaniline (4d)**[59,60]**:** Yellow solid; yield 0.110 g 90%; M.P. 140-141 °C; purity 99.3% (GC); ^{1}H NMR (500 MHz, DMSO) δ 3.86 (s, 3H), 6.43 (s, 2H), 6.64 (d, *J* = 8.8 Hz, 1H), 7.56 (d, *J* = 2.2 Hz, 1H), 7.73 (dd, *J* = 8.8, 2.3 Hz, 1H); GC-MS (EI, 70 eV): m/z (%) = 168 (100) $[M]^+$, 153 (40), 122 (29), 107 (16), 95 (37), 92 (13).

24. **2,6-Dichloro-4-nitro aniline (4e)**[61]**:** Yellow solid; yield 0.108 g 92%; M.P. 189-190 °C; purity 99.1% (GC); ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 5.17 (s, 2H), 8.16 (s, 2H); GC-MS (EI, 70 eV): m/z (%) = 208 (54) $[M]^+$, 178 (54.8), 160 (51.6), 135 (17.2), 124 (100), 90 (28.4), 63 (30.8).

25. **2-Cyano-4-nitro aniline (4f)**[62,63]**:** Light yellow solid; yield 0.113 g 90%; M.P. 210-211 °C; purity 99.0% (GC); ^{1}H-NMR (DMSO, 400 MHz): δ = 6.85-6.87 (d, *J* = 9.4 Hz, 1H), 7.38 (s, 2H), 8.06-8.09 (m, *J* = 9.36 Hz, *J* = 2.68 Hz, 1H), 8.30-8.31 (d, *J* = 2.68 Hz, 1H). GC-MS (EI, 70 eV): m/z (%) = 163 (97.6) $[M]^+$, 147 (4.6), 133 (70.4), 117 (63.2), 90 (100), 78 (13.2), 63 (56).

26. **2-Bromo-6-cyano-4-nitroaniline (4g)**[64]**:** Yellow solid; yield 0.106 g 93%. M.P. 183-184 °C, purity 98.7% (HPLC); ^{1}H-NMR (DMSO, 400 MHz): δ = 7.42 (s, 2H), 8.42-8.44 (m, *J* = 2.56 Hz, 2H). GC-MS (EI, 70 eV): m/z (%) = 243 (19.79) $[M]^+$, 241 (19.93), 211 (17.90), 195 (9.04), 168-(6.01), 143 (1.23), 116 (36.98), 103 (3.06), 88 (14.45), 77 (7.04), 65 (11.95), 52-(10.63), 40 (100%).

27. **4-nitro-*N*-phenylaniline (4h)**[65,66]**:** Yellow solid; yield 0.099 g 85%; M. P. 132-134 °C; purity 99.2% (GC); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.30 (s, 1H), 6.97 – 6.93 (m, 2H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 2H), 7.42 – 7.37 (m, 2H), 8.15 – 8.11 (m, 2H); GC-MS (EI, 70 eV): m/z (%) = 214 (65) $[M]^+$, 184 (26), 167 (61), 142 (12), 77 (24).

28. ***N*-methyl-2-nitro aniline (4k)**[67,68]**:** Brown orange solid; yield 0.111 g 89%; M.P. 34-35 °C; purity 99.7% (GC); ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 2.95 (s, 3H), 6.56-6.60 (m, *J* = 8.36 Hz, 1H), 6.76-6.78 (m, *J* = 8.72 Hz, 1H), 7.37-7.41 (m, *J* = 8.0 Hz, *J* = 1.52 Hz, 1H), 7.97 (s, broad, 2H), 8.09-8.11 (m, *J* = 8.6 Hz, *J* = 1.6 Hz, 1H); GC-MS (EI, 70 eV): m/z (%) = 152 (51) $[M]^+$, 106 (33.6), 105 (53.2), 77 (100), 51 (41).

29. **4-chloro-2-nitroaniline (4l-a)**[69]**: Orange solid;** M.P. 96-97 °C; purity 99.6% (GC); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.79 (d, *J* = 8.9 Hz, 1H), 7.32 (dd, *J* = 8.9, 2.5 Hz, 1H), 8.13 (d, *J* = 2.4 Hz, 1H); GC-MS (EI, 70 eV): m/z (%) = 172 (100) $[M]^+$, 142 (92), 114 (17), 101 (19), 90 (48).

5-chloro-2-nitroaniline (4l-b)[70]**:**Yellow solid; M.P. 130-131 °C; purity 99.4% (GC); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.13 (s, 2H), 6.68 (dd, *J* = 9.1, 2.2 Hz, 1H), 6.83 (d, *J* = 2.1 Hz, 1H), 8.08 (d, *J* = 9.1 Hz, 1H); GC-MS (EI, 70 eV): m/z (%) = 172 (88) $[M]^+$, 174 (28), 142 (100), 101 (30), 114 (30), 90 (63), 78 (13).

30. ***N*-(2-nitrophenyl)acetamide (4m)**[71]: Pale yellow solid; yield 0.104 g 87%; M.P. 92-94 °C; purity 99.5% (GC); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.32 – 2.27 (m, 3H), 7.18 (dd, *J* = 8.5, 1.3 Hz, 1H), 7.67 – 7.61 (m, 1H), 8.20 (d, *J* = 8.4, 1.5 Hz, 1H), 8.78 – 8.74 (m, 1H), 10.33 (s, 1H); GC-MS (EI, 70 eV): m/z (%) = 180 (26) $[M]^+$, 138 (79), 92 (46), 65 (21), 43 (100).

31. 4-chloro-N^1-phenylbenzene-1,2-diamin (4n)[72,73]**:** Orange solid; yield 0.102 g 90%; M.P. 58-60 °C; purity 99.1% (GC); ^{1}H NMR (500 MHz, CDCl3) δ 7.17 (d, *J* = 9.2 Hz, 1H), 7.33 – 7.26 (m, 3H), 7.46 – 7.42 (m, 2H), 8.21 (d, *J* = 2.5 Hz, 2H), 9.45 (s, 1H).GC-MS (EI, 70 eV): m/z (%) =248 (100) $[M]^+$, 214 (31), 201 (59), 167 (85), 139 (26), 77 (44).

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SUPPORTING INFORMATION AVAILABLE

1H NMR and MS spectra. This material is available free of charge via the Internet at "http://pubs.acs.org."

References:

(1) Hwang, S. H.; Kim, N. K.; Koh, K. N.; Kim, S. H. *Dye. Pigment.* **1998**, *39*, 359–369.
(2) Koh, J.; Kim, S.; Kim, J. P. *Color. Technol.* **2004**, *120*, 241–246.
(3) Manabe, S.; Ito, Y. *Chem. Pharm. Bull.* **2001**, *49*, 1234–1235.
(4) Takekoshi, T. *Polym J.* **1987**, *19*, 191–202.
(5) Luckenbach, T.; Epel, D. *Environ. Health Perspect.* **2005**, *113*, 17–24.
(6) Nash, E. G.; Nienhouse, E. J.; Silhavy, T. A.; Humbert, D. E.; Mish, M. J. *J. Chem. Educ.* **1970**, *47*, 705.
(7) Belciug, M.-P.; Ananthanarayanan, V. S. *J. Med. Chem.* **1994**, *37*, 4392–4399.
(8) Ju, K.-S.; Parales, R. E. *Microbiol. Mol. Biol. Rev.* **2010**, *74*, 250–272.
(9) Mikite, G.; Jakucs, E.; Kis-Tamás, A.; Darvas, F.; Lopata, A. *Pestic. Sci.* **1982**, *13*, 557–562.
(10) Gilbert, E. E.; Leccacorvi, J. R. *Propellants, Explos. Pyrotech.* **1976**, *1*, 89–90.
(11) Yan, G.; Yang, M. *Org. Biomol. Chem.* **2013**, *11*, 2554–2566.
(12) Golan, E.; Rozen, S. *J. Org. Chem.* **2003**, *68*, 9170–9172.
(13) Kol, M.; Rozen, S. *J. Chem. Soc., Chem. Commun.* **1991**, *3*, 567–568.
(14) Rozen, S.; Bar-Haim, A.; Mishani, E. *J. Org. Chem.* **1994**, *59*, 1208–1209.
(15) Murray, R. W.; Jeyaraman, R.; Mohan, L. *Tetrahedron Lett.* **1986**, *27*, 2335–2336.
(16) Zabrowski, D. L.; Moormann, A. E.; Beck Jr., K. R. *Tetrahedron Lett.* **1988**, *29*, 4501–4504.
(17) Murray, R. W.; Rajadhyaksha, S. N.; Mohan, L. *J. Org. Chem.* **1989**, *54*, 5783–5788.
(18) Emmons, W. D. *J. Am. Chem. Soc.* **1957**, *79*, 5528–5530.
(19) Emmons, W. D. *J. Am. Chem. Soc.* **1954**, *76*, 3470–3472.
(20) Liu, J.; Li, J.; Ren, J.; Zeng, B.-B. *Tetrahedron Lett.* **2014**, *55*, 1581–1584.
(21) Webb, K. S.; Seneviratne, V. *Tetrahedron Lett.* **1995**, *36*, 2377–2378.
(22) Firouzabadi, H.; Iranpoor K. Amani, N. *Green Chem.* **2001**, *3*, 131–132.
(23) McKillop, A.; A. Tarbin, J. *Tetrahedron Lett.* **1983**, *24*, 1505–1508.
(24) Das, S. S.; Nath, U.; Deb, D.; Das, P. J. *Synth. Commun.* **2004**, *34*, 2359–2363.
(25) Reddy, K. R.; Maheswari, C. U.; Venkateshwar, M.; Kantam, M. L. *Adv. Synth. Catal.* **2009**, *351*, 93–96.
(26) Jayachandran, B.; Sasidharan, M.; Sudalai, A.; Ravindranathan, T. *J. Chem. Soc. Chem. Commun.* **1995**, 1523–1524.
(27) Krohn, K.; Küpke, J.; Rieger, H. *J. für Prakt. Chemie/Chemiker-Zeitung* **1997**, *339*, 335–339.
(28) Tollari, S.; Vergani, D.; Banfi, S.; Porta, F. *J. Chem. Soc. Chem. Commun.* **1993**, 442–444.
(29) Stuehr, D. J.; Marletta, M. A. *J. Org. Chem.* **1985**, *50*, 694–696.
(30) Dewkar, G. K.; Nikalje, M. D.; Sayyed Ali, I.; Paraskar, A. S.; Jagtap, H. S.; Sudalai, A. *Angew. Chemie Int. Ed.* **2001**, *40*, 405–408.
(31) Winkler, R.; Richter, M. E. A.; Knüpfer, U.; Merten, D.; Hertweck, C. *Angew. Chemie Int. Ed.* **2006**, *45*, 8016–8018.
(32) Lee, J.; Simurdiak, M.; Zhao, H. *J. Biol. Chem.* **2005**, *280*, 36719–36727.
(33) Lee, J.; Zhao, H. *Angew. Chem. Int. Ed. Engl.* **2006**, *118*, 638–641.
(34) P. James, A.; Phillip Sankey, J.; A. W. Johnstone, R.; McCarron, M.; Trenbirth, B. *Chem. Commun.* **1998**, 429–430.
(35) Patil, V. V.; Shankarling, G. S. *Beilstein J. Org. Chem.* **2014**, *10*, 921–928.
(36) Parker, W. E.; Witnauer, L. P.; Swern, D. *J. Am. Chem. Soc.* **1957**, *79*, 1929–1931.
(37) Henson, O. E. *Appl. Environ. Microbiol.* **1981**, *42*, 656–660.

(38) Jecs, E.; Kreicberga, J.; Kampars, V.; Jurgis, A.; Rutkis, M. *Opt. Mater. (Amst)*. **2009**, *31*, 1600–1607.
(39) Thiel, W.; Mayer, R.; Jauer, E.-A.; Modrow, H.; Dost, H. *J. für Prakt. Chemie* **1986**, *328*, 497–514.
(40) Choi, J.; Aggarwal, M. D.; Wang, W. S.; Penn, B. G.; Frazier, D. O. 1999; Vol. 3793, pp. 55–63.
(41) Xia, R.; Xie, M.-S.; Niu, H.-Y.; Qu, G.-R.; Guo, H.-M. *Green Chem.* **2014**, *16*, 1077–1081.
(42) Yang, H.; Li, Y.; Jiang, M.; Wang, J.; Fu, H. *Chem. – A Eur. J.* **2011**, *17*, 5652–5660.
(43) Manna, S.; Maity, S.; Rana, S.; Agasti, S.; Maiti, D. *Org. Lett.* **2012**, *14*, 1736–1739.
(44) González, M. P.; Toropov, A. A.; Duchowicz, P. R.; Castro, E. A. *Molecules* **2004**, *9*, 1019–1033.
(45) Thakur, K. G.; Sekar, G. *Chem. Commun.* **2011**, *47*, 6692–6694.
(46) Xiao, Y.; Xu, Y.; Cheon, H.-S.; Chae, J. *J. Org. Chem.* **2013**, *78*, 5804–5809.
(47) Ramana, M. M. V; Malik, S. S.; Parihar, J. A. *Tetrahedron Lett.* **2004**, *45*, 8681–8683.
(48) Rasheed, S.; Rao, D. N.; Reddy, A. S.; Shankar, R.; Das, P. *RSC Adv.* **2015**, *5*, 10567–10574.
(49) Yadav, A. K.; Srivastava, V. P.; Yadav, L. D. S. *RSC Adv.* **2014**, *4*, 4181–4186.
(50) Kawagoe, Y.; Moriyama, K.; Togo, H. *European J. Org. Chem.* **2014**, *2014*, 4115–4122.
(51) Ethers, T. U. S. Patent 4157344, 1979.
(52) Cai, M.; Zheng, G.; Ding, G. *Green Chem.* **2009**, *11*, 1687–1693.
(53) Zolfigol, M. A.; Khazaei, A.; Moosavi-Zare, A. R.; Zare, A.; Kruger, H. G.; Asgari, Z.; Khakyzadeh, V.; Kazem-Rostami, M. *J. Org. Chem.* **2012**, *77*, 3640–3645.
(54) Guha, N. R.; Bhattacherjee, D.; Das, P. *Tetrahedron Lett.* **2014**, *55*, 2912–2916.
(55) Harland, P. A.; Hodge, P.; Maughan, W.; Wildsmith, E. *Synthesis (Stuttg)*. **1984**, *1984*, 941–943.
(56) Yang, Y.-L.; Rajagopal, B.; Liang, C.-F.; Chen, C.-C.; Lai, H.-P.; Chou, C.-H.; Lee, Y.-P.; Yang, Y.-L.; Zeng, J.-W.; Ou, C.-L.; Lin, P.-C. *Tetrahedron* **2013**, *69*, 2640–2646.
(57) Rys, P.; Steinegger, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 4801–4806.
(58) Takahashi, T.; Yoshimura, M.; Suzuka, H.; Maegawa, T.; Sawama, Y.; Monguchi, Y.; Sajiki, H. *Tetrahedron* **2012**, *68*, 8293–8299.
(59) Van Erp, H. *J. für Prakt. Chemie* **1930**, *127*, 20–38.
(60) Burnley, J.; Carbone, G.; Moses, J. E. *Synlett* **2013**, *24*, 652–656.
(61) Mahajan, T.; Kumar, L.; Dwivedi, K.; Agarwal, D. D. *Synth. Commun.* **2012**, *42*, 3655–3663.
(62) Taylor, E. C.; Knopf, R. J.; Cogliano, J. A.; Barton, J. W.; Pleiderer, W. *J. Am. Chem. Soc.* **1960**, *82*, 6058–6064.
(63) Mąkosza, M.; Białecki, M. *J. Org. Chem.* **1998**, *63*, 4878–4888.
(64) Mrozik, H. H.; Bochis, R. J. *Chem. Abstr.* **1973**, *79*, 115333.
(65) Singh, R.; Allam, B. K.; Raghuvanshi, D. S.; Singh, K. N. *Tetrahedron* **2013**, *69*, 1038–1042.
(66) Zhang, Y.; César, V.; Lavigne, G. *European J. Org. Chem.* **2015**, *2015*, 2042–2050.
(67) Gale, D. J.; Wilshire, J. F. K. *Aust. J. Chem.* **1972**, *25*, 2145–2154.
(68) Windisch, M. P.; Jo, S.; Kim, H.-Y.; Kim, S.-H.; Kim, K.; Kong, S.; Jeong, H.; Ahn, S.; No, Z.; Hwang, J. Y. *Eur. J. Med. Chem.* **2014**, *78*, 35–42.
(69) Wang, H.; Wen, K.; Nurahmat, N.; Shao, Y.; Zhang, H.; Wei, C.; Li, Y.; Shen, Y.; Sun, Z. *Beilstein J. Org. Chem.* **2012**, *8*, 744–748.
(70) Claridge, R. P.; Millar, R. W.; Sandall, J. P. B.; Thompson, C. *Tetrahedron* **1999**, *55*, 10243–10252.
(71) Srivastava, V. P.; Yadav, A. K.; Yadav, L. D. S. *Synlett* **2014**, *25*, 665–670.
(72) Day, M.; Peters, A. T. *J. Soc. Dye. Colour.* **1967**, *83*, 137–143.
(73) Dale, B. J.; Jones, D. W.; Peters, A. T. *J. Soc. Dye. Colour.* **1974**, *90*, 101–104.