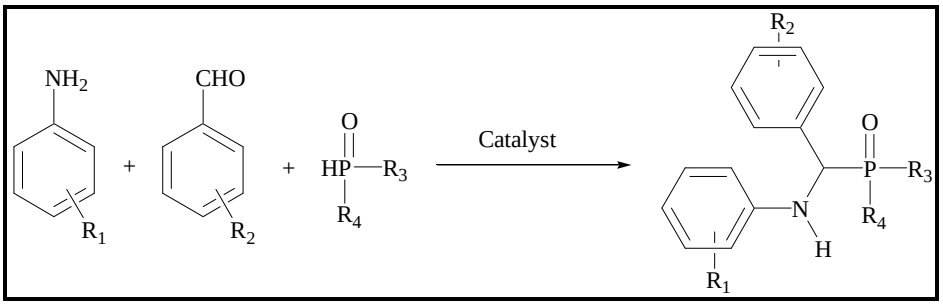
IV. Nano Ceria catalyzed synthesis of α-Aminophosphonates under ultrasonication

4.1 Introduction

Phosphonic acids and their phosphonate derivatives are of immense interest in synthetic organic chemistry due to their biological activities [1]. Organo phosphorous compounds have found a wide range of applications in the areas of agriculture, chemical and pharmaceutical industries [2-4]. They are used as inhibitors of synthase, HIV protease [5], antibiotics, enzyme inhibitors [6], anti-thrombotic agents [7], herbicides [8], fungicides [9], insecticides [10], plant growth regulators [11,12] and as substrates in the synthesis of phosphonopeptides [13-14].

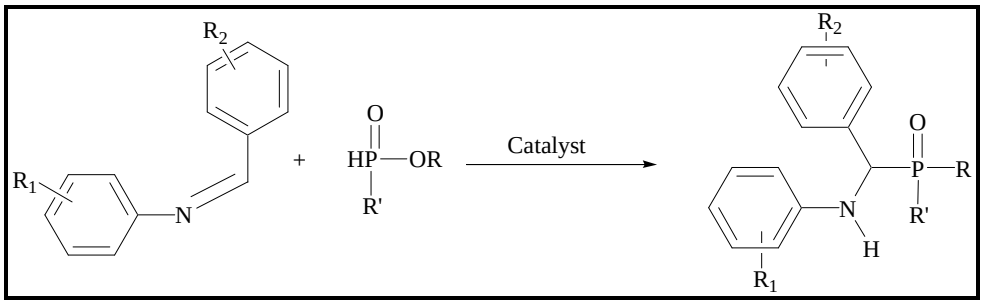
Thus, a variety of synthetic approaches are desirable to synthesize α-amino phosphonates. The two major pathways for the synthesis of α-amino phosphonates are given below. However, a one-pot protocol (Kabachnik-Fields reaction) represents a convenient route for the synthesis of α-amino phosphonates as many imines are hygroscopic and are not sufficiently stable for isolation.

(a) Kabachnik-Fields reaction: In this the amine, aldehyde and di or trialkylphosphite are reacted in a single-pot in the presence of catalyst to afford the corresponding products (Scheme 4.1) [15,16].



Scheme 4.1 Lewis acid or base promoted Kabachnik-Fields reaction

(b) Pudovik reaction: In this transformation, dialkylphosphites are reacted with preformed imines in presence of a base or a Lewis acid catalyst (Scheme 4.2) [17].



Scheme 4.2 Lewis acid or base promoted Pudovik reaction

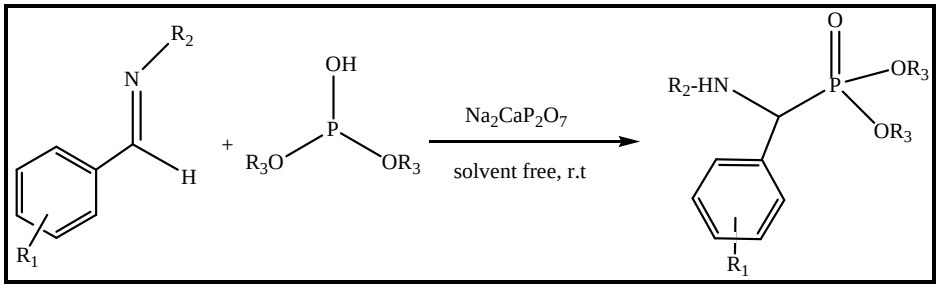
Various Lewis acid catalysts used for such reaction are tin(IV) chloride [18], zirconium(IV) chloride [19] and boron trifluoride–diethyl ether complex [20]. $H_3PW_{12}O_{40}$ [21], magnesium perchlorate [22], trimethylanilinium Chloride [23], bismuth nitrate pentahydrate [24], scandium tris(dodecyl)sulphate [25.26], indium(III) chloride [27], samarium(II) iodide [28], metal triflates [29] [M(OTf)n, M = La, Li, Mg, Al, Cu, Ce], lithium perchlorate [30,31], tantalum(V) chloride–silicon dioxide [32], alumina [33], trifluoroacetic acid [34], montmorillonite KSF [35], stannous chloride [36] and (bromodimethyl) sulfonium bromide [37]. These approaches are satisfactory for a one-pot synthesis of α-aminophosphonates.

Table 4.1 Literature reports for synthesis of α-amino phosphonates.

Catalyst	**Solvent**	**Temp. (^oC)**	**Time (h)**	**Yield (%)**	**Reference**
$BiCl_3$	ACN	Reflux	5-28	70-88	38
TsCl	DCM	RT	2-4	65-85	39
$LiClO_4$	Diethyl ether	RT	0.5	85-98	40
$In(OTf)_3$	THF	Reflux	12-54	16-99	41
$Sc(OTf)_3$	$[BMIM]PF_6$	20	2	93-99	42

$SbCl_3$-Al_2O_3	ACN	Reflux	2.5-5.5	68-92	43
GaI_3	DCM	Reflux	2.5-6	74-95	44
Yr_2O_3-ZrO_2	ACN	60	2-11	55-99	45
CAN	ACN	RT	3-3.5	76-90	46
[BMIM]PF_6 [BMIM]BF_4	--	RT	5-12	75-91	47
Alum	--	RT	5-90 min	82-97	48
$FeCl_3$	THF	60 ^oC	0.75	92	49
$AlCl_3$	ACN	RT	8.5	72-85	50

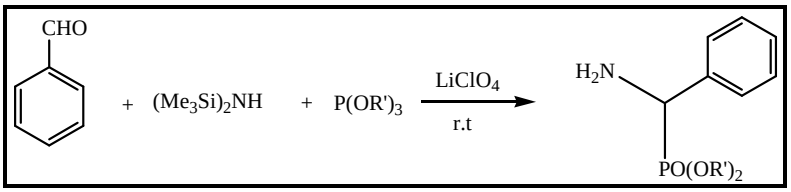
Elmakssoudi et al. demonstrated the synthetic diphosphate $Na_2CaP_2O_7$ to be an efficient reagent for the synthesis of α-amino phophonates from imines and dialkyl phosphates [51]. The catalyst was very stable and could be reused several times with high catalytic activity (Scheme 4.3).



Scheme 4.3 $Na_2CaP_2O_7$ catalyzed synthesis of α-amino phosphonates.

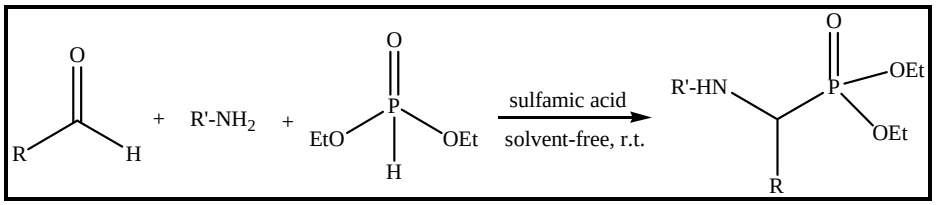
Azizi et al. [52] developed a novel and mild protocol for the one-pot, three-component synthesis of primary α-amino phosphonates from an aldehyde,

hexamethyldisilazane and a trialkyl phosphite in a short reaction time using solid $LiClO_4$ as a catalyst (Scheme 4.4).



Scheme 4.4 $LiClO_4$ catalyzed synthesis of α-amino phosphonates.

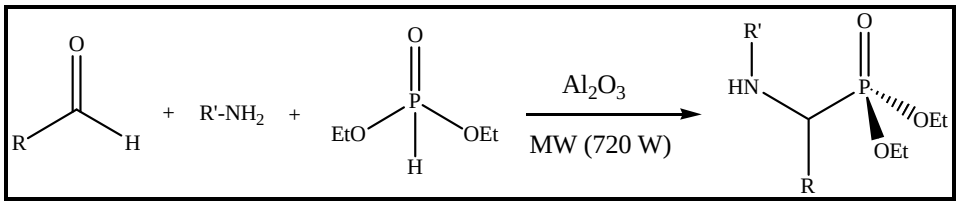
Mitragotri et al. [53] developed an efficient multicomponent reaction protocol for the synthesis of α-aminophosphonates using sulfamic acid as a commercially available and cost effective solid acid catalyst. Simple work-up procedure, general applicability, ambient temperature and solvent-free conditions have made this protocol distinctly superior over many other protocols reported earlier (Scheme 4.5).



Scheme 4.5 $SbCl_3/Al_2O_3$ catalyzed synthesis of α-amino phosphonates.

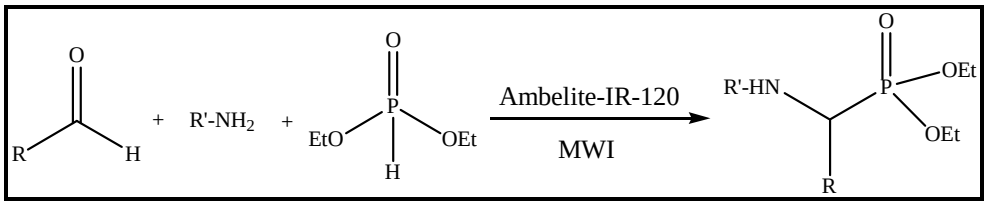
Apart from these methodologies, the use of non-conventional techniques like microwave has also been reported for the synthesis of α-amino phosphonates.

Kaboudin et al. [33] developed a simple, efficient and general method for the synthesis of 1-aminoalkyl phosphonates through a one-pot reaction of aldehydes with amines in the presence of acidic alumina under solvent-free conditions using microwave irradiation as a promoter (Scheme 4.6).



Scheme 4.6 Al_2O_3 catalysed synthesis of α-amino phosphonates.

Bhattacharya et al. [54] have reported Amberlite-IR 120 catalyzed synthesis of α-amino phosphonates reaction under microwave irradiation. The method was simple, efficient, and environmentally benign for three-component reaction of an amine, an aldehyde or a ketone, and diethyl phosphite within a short reaction time under solvent-free reaction conditions. The major advantages of this protocol were good yields, inexpensive, ecofriendly and reusable catalyst, mild and solvent-free reaction conditions and tolerance towards various functionalities present in the substrates (Scheme 4.7).



Scheme 4.7 Amberlite IR-120 catalyzed synthesis of α-amino phosphonates.

Although significant advances have been made in this direction; there still exist some limitations such as use of solvents, expensive and toxic catalyst, longer reaction time and elevated temperature thereby limiting their applications. Also in many cases, a two step protocol is employed wherein a preformed imine is used, which is not preferred since some imines are hygroscopic and are not stable for isolation. Thus, an efficient protocol was desired for the synthesis of α-aminophosphonates which could overcome the above disadvantages and facilitate the direct addition of phosphites to imines in a one pot fashion under mild reaction conditions.

In recent years, solvent-free reactions have gained considerable attention since the method was valuable not only for ecological and economical reasons but

also for simplicity in procedures and high yields of products. Emphasis was also done towards the development of clean and green chemical processes.

Maximum work has been done on synthesis of α-aminophosphonates by using acid catalyst. Hence there is a scope to synthesis the α-aminophosphonates by use of base catalyst. In this context, Ceria have gained much importance because of its high basicity [55]. The catalytic activity of ceria is well known for CO_2 fixation and transalkylation [56-58].

Ultrasonication has increasingly been used in organic synthesis in the last three decades. It has been demonstrated as an alternative energy source for organic reactions ordinarily accomplished by heating. A great number of organic reactions can be carried out in short reaction time, high yields and mild reaction conditions under ultrasonication. The use of ultrasound-irradiation technique for activating various reactions is well documented in the literature such as oxidation reaction [59], Pinacol–pinacolone reaction [60], Ullmann condensation [61] and Suzuki cross-coupling [62]. Moreover ultrasound assisted reactions are believed to satisfy the demands of “green chemistry” allowing for solvent-free conditions to be employed.

In all above reported work, the synthesis of α - aminophosphonates can be carried out by using various Lewis and Bronsted acid catalysts under various temperature ranges and with or without solvent. In this paper, we carried out the synthesis of α - aminophosphonates under solvent free condition and under ultrasonication by use of base catalyst such as CeO_2. We had synthesised nano CeO_2 and explore its catalytic activity for α - aminophosphonates. The catalyst was characterized by using various analytical techniques. The present work also contributes towards heterogeneous catalysis with respect to recovery and reuse which is extremely important for industrial application.

4.2 Experimental

4.2.1 Materials

Cerium nitrate were purchased from M/S S.D. Fine Chemical, Mumbai, India. All the chemicals were purchased from firms of repute with their highest purity available and were used without further purification.

4.2.2 Methods

4.2.2.1 Synthesis of nano CeO_2

CeO_2 nanoparticles were prepared by adding ammonia solution to an aqueous solution of cerium (III) nitrate in presence of CTAB. In a typical procedure, added 1 g of $Ce(NO_3)_3$ in solution of CTAB dissolved in 100 cm^3 of water. Mole ratio of Ce/CTAB was kept at unity. pH of the solution was adjusted between 10-11 by adding 25% ammonia solution under vigorous stirring for 2-3 h. The resulting mixture was ultrasonicated for 10 min and then filtered off. The obtained precipitate was thoroughly washed with water for three time and subsequently with acetone. The precipitate was dried at 120^oC for 12 h. It was then calcined at 500^oC for 3 h. The prepared catalyst was then characterized with various techniques such as X-ray diffractograms (XRD), EDAX, Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM).

4.2.2.2 General procedure for synthesis of α-aminophosphonates

A mixture of benzaldehyde (1 mmol, 0.106 g), aniline (1 mmol, 0.92 g) and triethyl phosphite (1 mmol, 0.166g) was taken in 10 mL round bottom flask. 5 mol % of catalyst was added to the reaction mixture. The reaction mixture was ultrasonicated in ultrasonic bath (30 KHz, 150 W) for an appropriate time. The progress of the reaction was monitored by TLC. After completion of the reaction the catalyst was separated by centrifugation and subsequently washed with dichloromethane. The reaction mixture was diluted with water and the product was extracted by dichloromethane (3 × 10 cm^3). Organic layer was dried over anhydrous sodium sulphate and was evaporated under reduced pressure to give the product.

The product was purified by column chromatography by using pet ether and ethyl acetate (95:05) solvent system. The purified product was then confirmed by its spectral analysis after analyzing by IR, ^{1}H NMR and mass spectra.

Following parameters were optimized for synthesis of α-aminophosphonates

1) Catalyst : ZnO, MgO, CeO_2
2) Effect of Solvents : Water, Ethanol, Toluene, DCM, ACN, without solvent
3) Effect of Catalyst conc. : 02 to 10 mg

The optimised reaction conditions are summarised in table 4.3

4.2.3 Characterization of Nano CeO_2

4.2.3.1 X-Ray Diffraction

The X-ray diffractograms were obtained (XRD, MINI FLEX RIGAKU MODEL) with Cu K-α radiation (1.5418 A°) with scanning rate of 2^o per min from 2^o to 80^o. The X-ray diffraction spectrum (XRD) of the prepared CeO_2 is shown in fig. 4.1. The fluorite phase of ceria was observed. The diffraction peaks displayed almost all the characteristic diffractions corresponding to the face-centred cubic (FCC) CeO_2, matching with the JCPDS pattern (Powder Diffraction File No 34-394). It was found that the CeO_2 nanoparticles show good crystallinity. The crystallite size of CeO_2 powder was around 4-5nm, calculated from the X-ray line broadening by applying full width half maximum (FWHM) of characteristic peak (111) to the Scherrer equation.

$$D = 0.9 \lambda / \beta \cos \theta$$

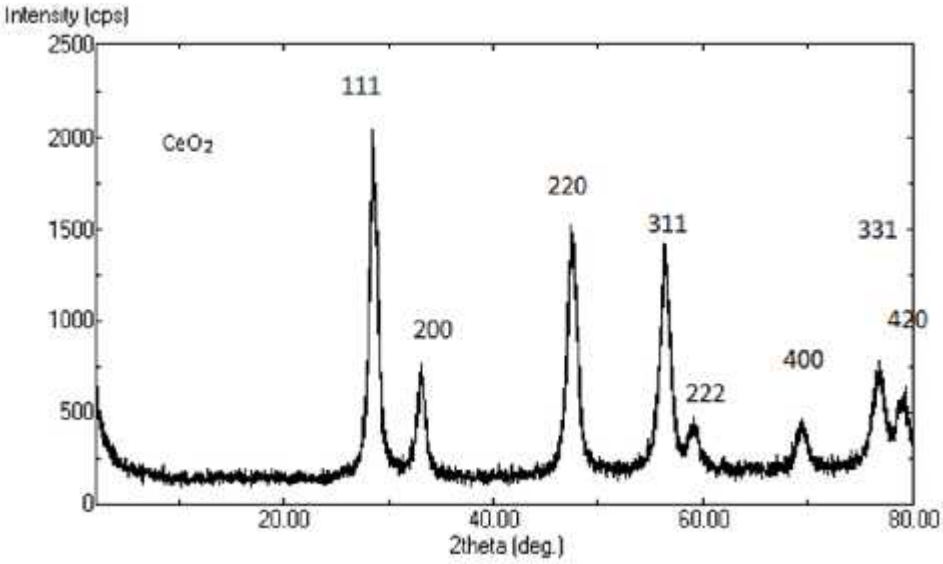


Figure 4.1 XRD of Nano Ceria

4.2.3.2 Transmission Electron Microscope

Particle size and external morphology of the prepared particles were observed on a Transmission Electron Microscope (TEM) (Philips CM 200, operating at 20 – 200 kV accelerating voltage and having resolution upto 2.4 A^o). It can be seen from fig. 4.2 (A) that the size of CeO_2 nanoparticles was in the range of 4 -5 nm and the shape of the particles was mostly spherical. The size of nano CeO_2 obtained from TEM was in well agreement with the crystal size from the XRD data. The TEM image shows well crystallites and their lattice images for all particles (fig. 4.2.B). The 220 and 311 reflections were clearly observed. [63]

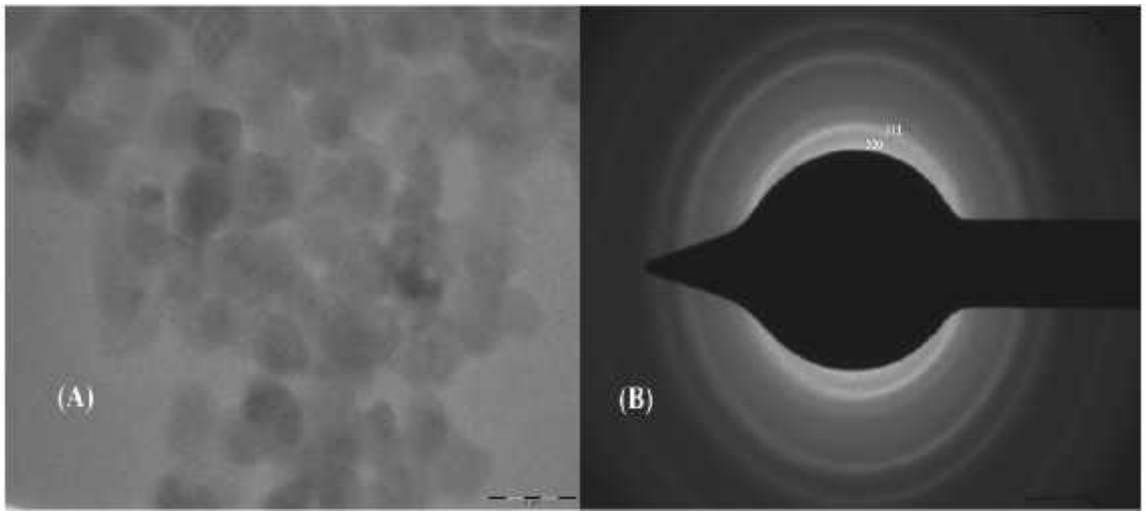


Figure 4.2 TEM image of Ceria (A) and crystalline image by TEM of Ceria (B)

4.2.3.3 Scanning Elwctron Micreoscope and EDAX

Surface morphology and EDAX (Energy Dispersive X-Ray Spectroscopy) analysis was done by using Field Emission Gun-Scanning Electron Microscopes (FEG-SEM) JSM-7600F model operating at accelerating voltage 0.1 to 30 kV, Magnification x25 to 1,000,000 and having resolution 1.0 nm - 1.5 nm (15kV). SEM image of CeO_2 (fig. 4.3-A) shows the result in support of the TEM image having agglomerated spherical particles. EDAX analysis shown in Fig. 4.3-B shows presence of only cerium and oxygen elements in prepared CeO_2.

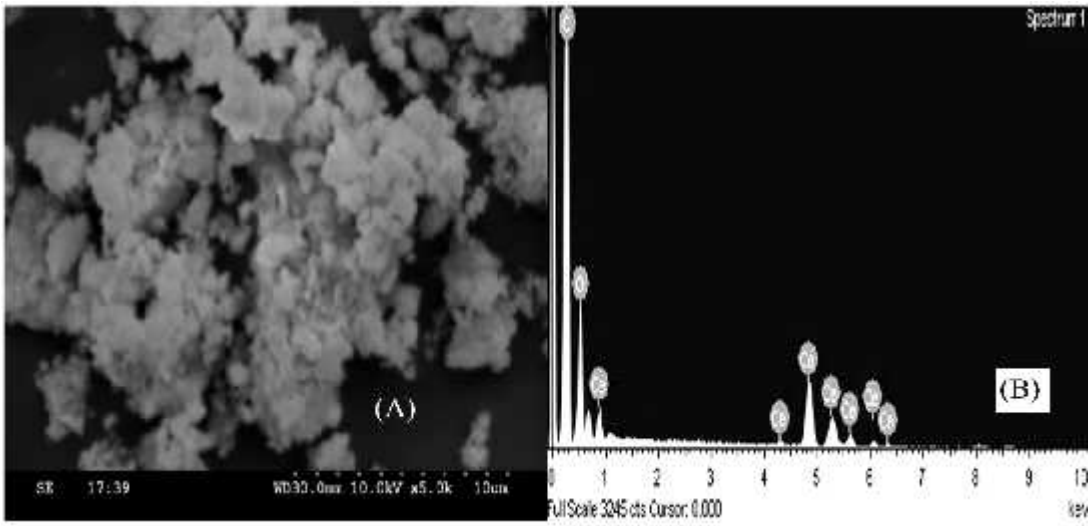
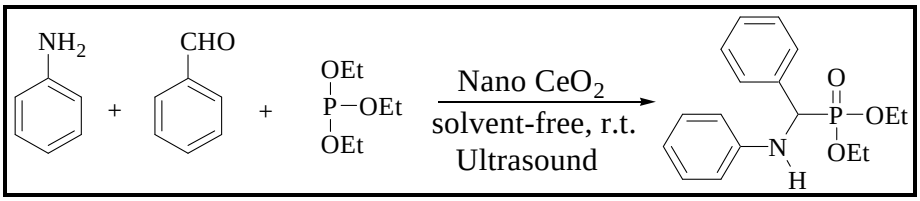


Fig. 4.3. A- SEM Spectra of Nano Ceria, B- EDAX spectra of nano Ceria

4.3 Result and Discussion

The present work reports an efficient protocol for one pot synthesis of α-amino phosphonates using CeO_2 as a catalyst under ultrasonication and solvent-free conditions (Scheme 4.11).



Scheme 4.8 One pot synthesis of α-amino phosphonates using nano CeO_2

Initially aniline, benzaldehyde and diethyl phosphite was chosen as a starting material for model reaction and the role of various reaction parameters such as catalyst, solvent and catalyst loading were studied (Table 4.2, entries 1-17). Basic catalysts such as ZnO (amphoteric), MgO and CeO_2 were used for the above reaction. It was observed that ZnO, MgO and CeO_2 gave good yields of desired product. Whereas CeO_2 (gave 60%) gave lower yield of the desired product as compare to the ZnO and MgO. Since our focus was to investigate the catalytic activity of CeO_2. We have prepared nano CeO_2. It was interestingly observed that after reducing the particle size of CeO_2 from bulk to nano size, CeO_2 gave 99% yield of the α-amino phosphonates in 5 min (Table 4.2, entry 1-4). The influence of various solvents such as water, ethanol, dichloromethane, acetonitrile and toluene on the reaction system was investigated and it was observed that excellent yield of the product was obtained when the reaction was carried out under solvent-free conditions (Table 4.2, entries 5-10).

Table 4.2 Influence of catalyst, solvent and catalyst loading[a]

Entry	Catalyst	Solvent	Catalyst loading (mol %)	Yield (%)[b]
Influence of catalyst				
1	ZnO	Solvent Free	10	72
2	MgO	Solvent Free	10	66
3	CeO_2 (bulk)	Solvent Free	10	60
4	CeO_2 (nano)	Solvent Free	10	99
Influence of solvent				
5	CeO_2 (nano)	Solvent Free	10	99
6	CeO_2 (nano)	Water	10	70
7	CeO_2 (nano)	Ethanol	10	72
8	CeO_2 (nano)	Toluene	10	52
9	CeO_2 (nano)	dichloromethane	10	71
10	CeO_2 (nano)	Acetonitrile	10	97
Influence of catalyst concentration				
11	CeO_2 (nano)	Solvent Free	10	99
12	CeO_2 (nano)	Solvent Free	8	99
13	CeO_2 (nano)	Solvent Free	6	99
14	CeO_2 (nano)	Solvent Free	5	99
15	CeO_2 (nano)	Solvent Free	4	90

16	CeO_2 (nano)	Solvent Free	2	74
17	CeO_2 (nano)	Solvent Free	0	30

[a] Reaction conditions: aniline (1 mmol), benzaldehyde (1 mmol), triethyl phosphite (1 mmol), solvent (1 mL) for 5 min. under ultrasonication.

[b] Isolated Yields.

The CeO_2 has both Lewis and Bronsted basic sites [55] which are strong and widely distributed over the CeO_2 surface [57]. In addition to this it has smaller particle size and hence has high surface area due to which nano CeO_2 shows better catalytic activity for the synthesis of α-aminophosphonate. The probable reason may be that under solvent-free conditions the concentration of catalyst was more leading to high reaction rates as compared to the reaction in solvent. Catalyst concentration was also affect the yield of the product. Table 4.3, entries 11-17 showed that 5 mol % of the catalyst was enough to give maximum yields of the product.

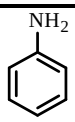
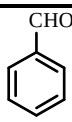
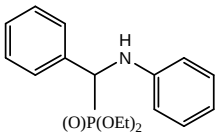
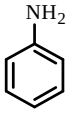
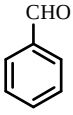
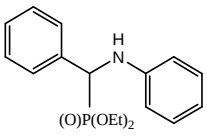
Table 4.3 Optimized reaction conditions for synthesis of α-amino phosphonates are

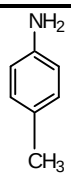
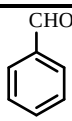
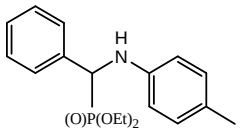
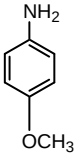
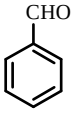
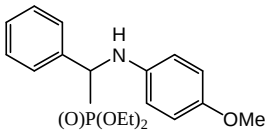
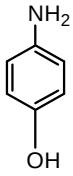
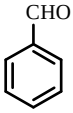
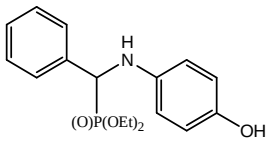
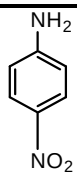
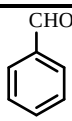
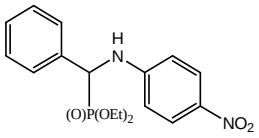
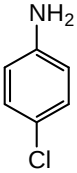
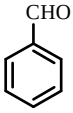
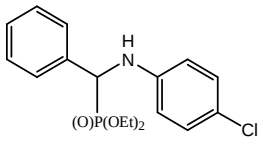
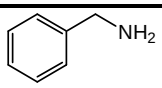
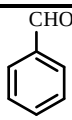
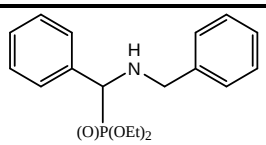
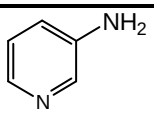
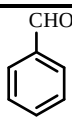
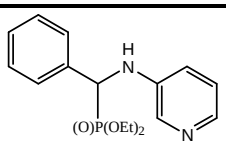
Conditions	**Optimized Parameters**
Catalyst	CeO_2
Solvent	Solvent free
Catalyst Concentration	5 mol%

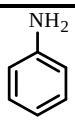
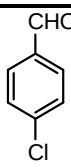
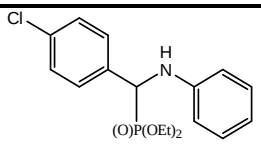
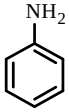
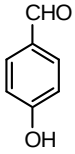
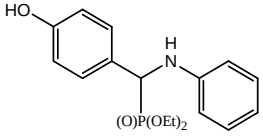
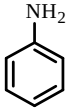
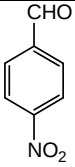
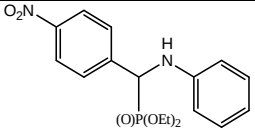
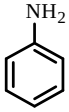
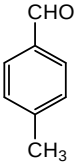
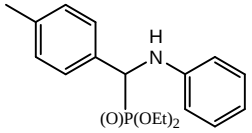
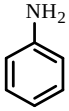
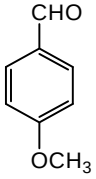
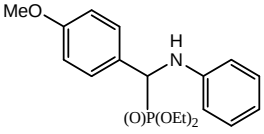
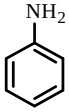
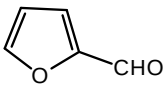
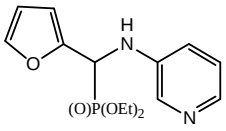
Thus, using CeO_2 as catalyst of choice, the one pot reaction of structurally and electronically different amines/aldehydes and triethyl phosphite was studied at ambient temperature under ultrasonicationss (Table 4.4, entries 1-15). The reaction of aniline, benzaldehyde and diethylphosphite in presence of nano CeO_2 (5 mol %) as a catalyst gave 99% yield of diethyl [aniline(phenyl)methyl] phosphonate (entry 1).

Various aromatic and heteroaromatic aldehyde containing electron donating or electron withdrawing functional groups are treated with various aliphatic, aromatic and heteroaromatic amines and did not show any remarkable difference in the yield of desired products. The results are given in Table 4.4 which shows that all reactions proceeded cleanly to give the corresponding α-aminophosphonate. Amine substituted with electron withdrawing group required less time than the amine substituted with electron donating group (Table 4.4, entry 3-7). Similar observation is noticed in case of aromatic aldehyde when they are attached with electron withdrawing and electron donating groups (Table 4.4, entry 10-14).

Table 4.3 CeO_2 catalyzed one pot synthesis of α-aminophosphonates[a]

Entry	Amine	Aldehyde	Product	Time in min.	Yield[b] (%)
1				5	99
2[C]				30	60

3				10	97
4				10	90
5				10	90
6				30	87
7				10	92
8				20	93
9				30	85

10				15	94
11				15	84
12				20	95
13				10	87
14				15	91
15				20	85

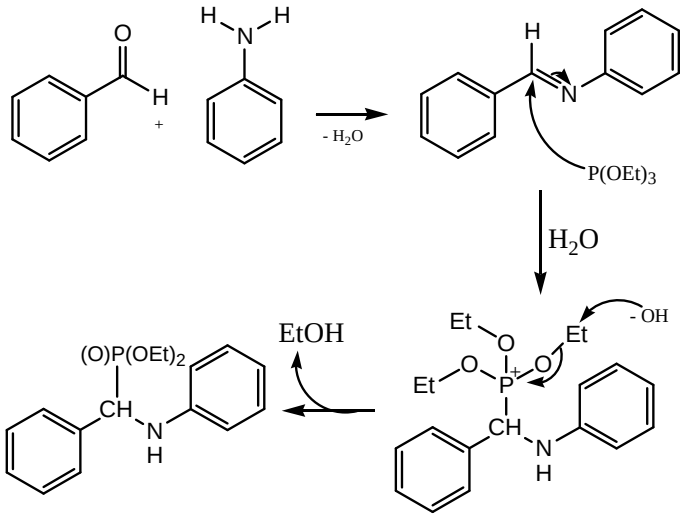
[a] Reaction conditions: amine (1 mmol), aldehyde (1 mmol), triethyl phosphite (1 mmol), CeO_2 (5 mol%).

[b] Isolated Yields determined by GC. Yields in parentheses are of isolated compounds.

[C] under stirring

Reaction Mechanism

The mechanism of the reaction is similar to that reported in the literature and involves two steps in which the first step was the reaction of an amine with aldehyde to generate an imine which then gets activated by the catalyst. The basic CeO_2 activate the imine formation due to which addition of phosphite is facilitated to give a phosphonium intermediate. This phosphonium intermediate undergoes reaction with water to give the α-aminophosphonate and ethanol as shown in (Scheme 4.9).



Scheme 4.9 Mechanism of the synthesis of α-aminophosphonate

Catalyst Reusability

The catalyst was separated from the reaction mixture by centrifugation, washed with dichloromethane and dried. Table 4.4 indicates the reusability of the catalyst. It clearly reveals that the catalyst can be used for three cycles without much loss in the yield of desired product.

Table 4.4 Recyclability of nano CeO_2[a]

Run	Fresh	Run 1	Run 2	Run 3
% Yield[b]	99	98	98	97.5

[a] Reaction Condition: Benzaldehyde (1 mmol), Aniline (1 mmol), Triethyl phosphite (1 mmol) and 5 mol% recycled CeO_2 under Ultrasonication for 5 min.

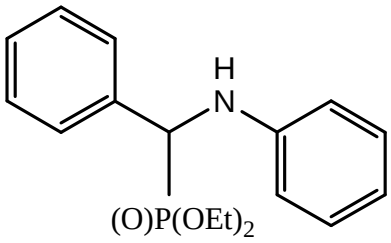
[b] Isolated yield.

4.4 Conclusion

- Nano CeO_2 was found to be an efficient catalyst for one pot synthesis of α-aminophosphonates under ultrasound.
- The catalytic system tolerates a wide range of functional groups providing excellent yields of desired products.
- The present study can be considered as the green protocol for synthesis of α-aminophosphonates, having advantages like solvent-free condition, high yields of desired products, good selectivity and hence environmentally benign methodology.
- The present catalytic system afforded high yields of desired product within a short reaction time.
- Recyclability of the catalyst is the added advantages of the system.
- The protocol was found to be general in nature.

4.5 Spectral Data

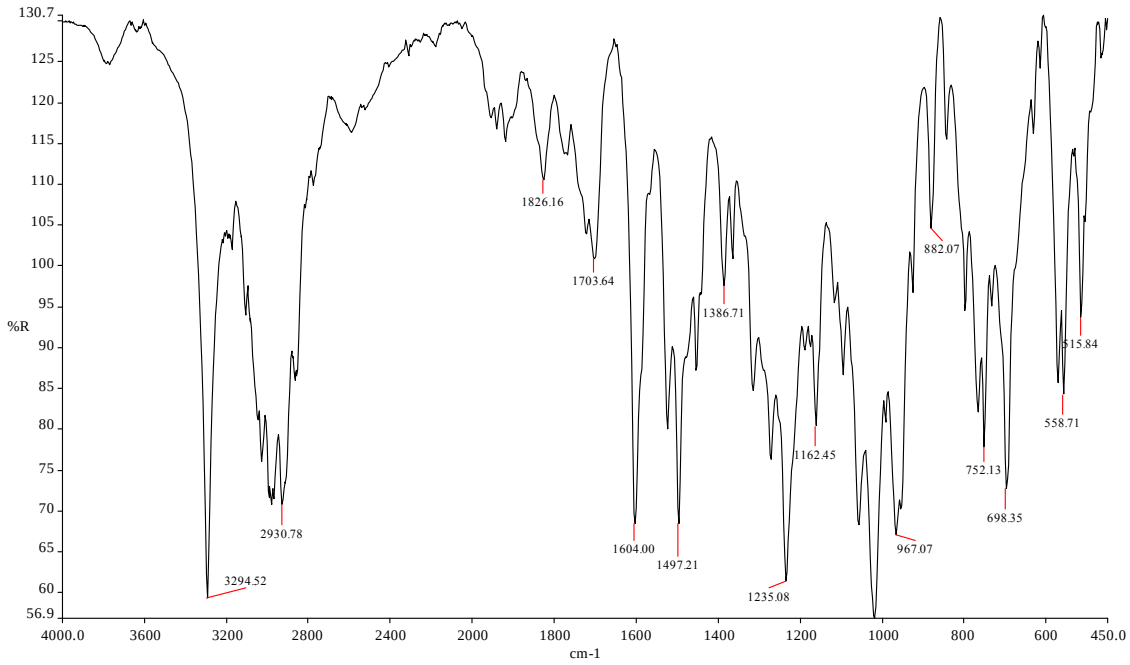
IR, Mass and H^1- NMR of entry 1, Table 4.3



(Phenyl-phenylamino-methyl)-phosphonic acid diethyl ester

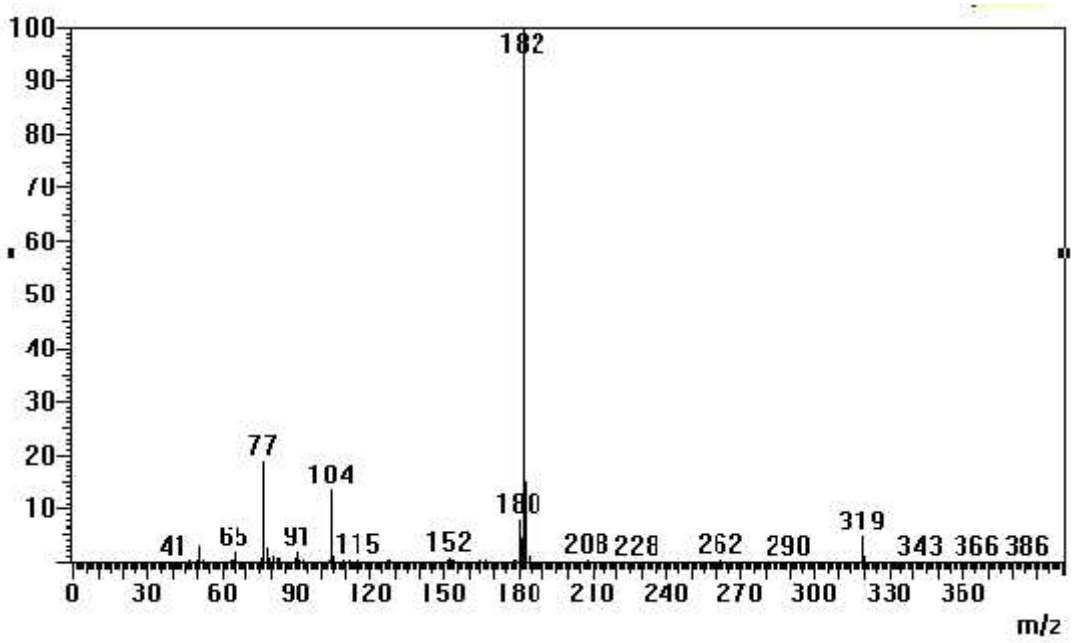
IR Spectra

IR (KBr) cm^{-1}: 3294 (–NH), 3000 (=CH), 2930 (–CH), 1162 (C-N), 1235 (P–O), 1103–997 (P–O–Et).



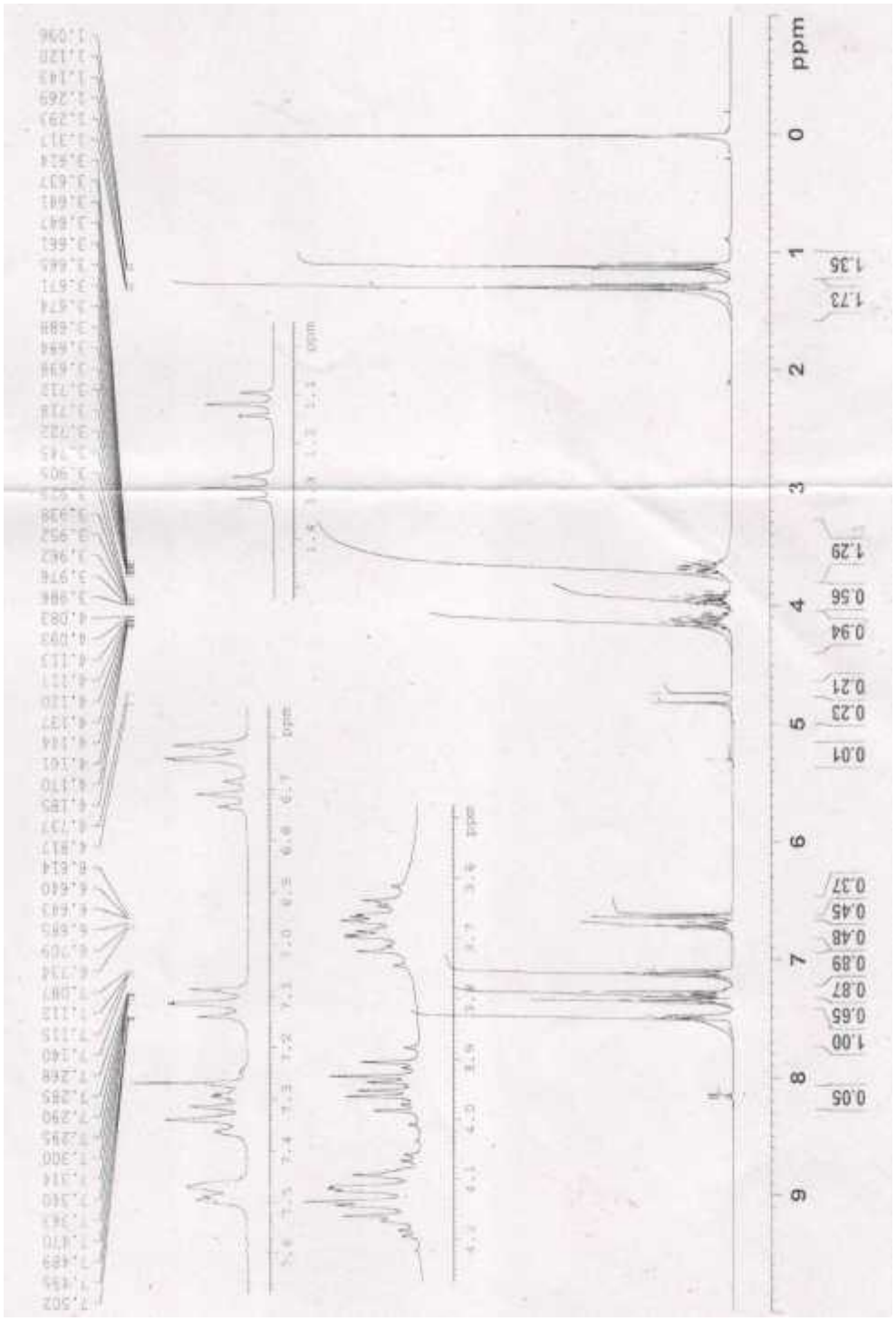
Mass Spectra

GC–MS (EI, 70 eV): m/z (%) = 77(20%), 104(15%), 182(100%) [M]+, 319(5%).



H^1-NMR Spectra (300 MHz,CDCl3):

δ 1.1 (t, 3H, OCH2CH3), 1.3 (t, 3H, OCH2CH3), 3.6–3.8 (m, 1H, OCH2CH3), 3.8–4.0 (m, 1H, OCH2CH3), 4.0–4.3 (m, 2H, OCH2CH3), 4.7 (d, 1H, CH), 4. 8 (s, 1H, NH), 6.62 (d, 2H, C6H5), 6.70 (t, 1H, C6H5), 7.11 (t, 2H, C6H5), 7.26–7.36 (m, 3H, C6H5), 7.51 (d, 2H, C6H5) ppm.



4.6 References

1. R. P. Sheridan, J. Chem. Inf. Comput. Sci. 42 (2002) 103-108.
2. R. Engel, Chem. Rev. 77 (1977) 349.
3. K. A. Schug, W. Lindner, Chem. Rev. 105 (2005) 64.
4. F. Palacios, C. Alonso, J. M. De los Santos, Curr. Org. Chem. 8 (2004) 1481.
5. J. A. Sikosrki, M. J. Miller, D. S. Braccolino, D. G. Cleary, S. D. Corey, J. E. Ream, D. Schnur, A. Shah, M. C. Walker, Phosphorus Sulfur Silicon Relat. Elem. 76 (1993) 375-378.
6. B. Stowasser, K. H. Budt, L. Jian- Qi, A. Peyman, D. Ruppert, Tetrahedron Lett. 33 (1992) 6625-6628.
7. F. R. Atherton, C. H. Hassall, R. W. Lambert, J. Med. Chem. 29 (1986) 29-40.
8. A. Peyman, K. H. Budt, J. S. Paning, B. Stowasser, D. Ruppert, Tetrahedron Lett. 33 (1992) 4549-4552.
9. J. H. Meyer, P. A. Barlett, J. Am. Chem. Soc.120 (1998) 4600-4609.
10. L. Maier, Phosphorus, Sulfur Silicon Relat. Elem.53 (1990) 43-67.
11. L. Maier, H. Spoerri, Phosphorus, Sulfur Silicon Relat. Elem. 61 (1991) 69-75.
12. J. Emsley, D. Hall, In Chemistry of Phosphorus; Harper & Row: London, 1976, pp 494.
13. L. Maier, P. Lea, J. Phosphorus Sulfur, Silicon Relat. Elem. 17 (1983) 1-19.
14. P. P. Giannousis, P. A. Bartlett, J. Med. Chem. 30 (1987) 1603-1609.
15. M. I. Kabachnik, T. Y. Medve, Dokl. Akad. Nauk. SSSR 83 (1952) 689; Chem. Abstr. 47 (1953) 2724b.
16. E. K. Fields, J. Am. Chem. Soc. 74 (1952) 1528.
17. A. N. Pudovik, Dokl. Akad. Nauk. SSSR 83 (1952) 865; Chem. Abstr. 47 (1953) 4300.
18. S. Laschat, H. Kunz, Synthesis 1/2 (1992) 90-95;.
19. J. S. Yadav, B. V. S. Reddy, S. Raj, K. B. Reddy, A. R. Prasad, Synthesis 15 (2001) 2277-2280.

20. H. J. Ha, G. S. Nam, Synth. Commun. 22 (1992) 1143-1148.
21. A. Heydari, H. Hamadi, M. Pourayoubi, Catal. Commun. 8 (2007) 1224-1226.
22. S. Bhagat, A. K. Chakraborti, J. Org. Chem. 72 (2007) 1263-1270.
23. A. Heydari, A. Arefi, Catal. Commun. 8 (2007) 1023-1026.
24. A. K. Bhattacharya, T. Kaur, Synlett 5 (2007) 745-748.
25. K. Manabe, S. Kobayashi, Chem. Commun. 8 (2000) 669-670.
26. C. Qian, T. Huang, J. Org. Chem. 63 (1998) 4125-4128.
27. B. C. Ranu, A. Hajra, J. Jana, Org. Lett. 1 (1999) 1141-1143.
28. F. Xu, Y. Luo, M. Deng, Q. Shen, Eur. J. Org. Chem. 24 (2003) 4728-4730.
29. H. Firouzabadi, N. Iranpoor, S. Sobhani, Synthesis 16 (2004) 2692-2696.
30. N. Azizi, M. R. Saidi, Eur. J. Org. Chem. 23 (2003) 4630-4633.
31. A. Heydari, A. Karimian, J. Ipaktschi, Tetrahedron Lett. 39 (1998) 6729-6732.
32. S. Chandrasekhar, S. J. Prakash, V. Jagadeshwar, C. Narsihmulu, Tetrahedron Lett. 42 (2001) 5561-5563.
33. B. Kaboudin, R. Nazari, Tetrahedron Lett. 42 (2001) 8211-8213.
34. T. Akiyama, M. Sanada, K. Fuchibe, Synlett 10 (2003) 1463-1464.
35. J. S. Yadav,B. V. S. Reddy, C. Madan, Synlett 7 (2001) 1131-1133.
36. R. Gallardo-Macias, K. Nakayama, Synthesis 1 (2010) 57–62.
37. B. Kaboudin, E. Jafari, Synlett (2008) DOI: 10.1055/s-2008-1078509.
38. Z. -P. Zhan, J. -P. Li, Synth. Commun. 35 (2005) 2501.
39. J. Wu, W. Sun, H. -G. Xia, X. Suna, Org. Biomol. Chem. 4 (2006) 1663.
40. M. R. Saidi, N. Azizi, Synlett (2002) 1347.
41. R. Ghosh, S. Maiti, A. Chakraborty, D. K. Maiti, J. Mol. Catal. A: Chem. 210 (2004) 53.
42. S. Lee, J. H. Park, J. Kang, J. K. Lee, Chem. Commun. (2001) 1698.
43. Ambica, S. Kumar; S. C. Taneja, M. S. Hundal, K. K. Kapoor, Tetrahedron Lett. 49 (2008) 2208.
44. P. Sun, Z. Hu, Z. Huang, Synth. Commun. 2004, 43, 4293.

45. Ramalingam, P. Kumar, Catal. Lett. (2008) doi:10.1007/s10562-008-9562-x.
46. K. Ravinder, A. Vijender Reddy, P. Krishnaiah, G. Venkataramana, V. L. Niranjan Reddy, Y. Venkateswarlu, Synth. Commun.34 (2004) 1677.
47. J. S. Yadav, B. V. S. Reddy, P. Sreedhar, Green Chem. 4 (2002) 436.
48. S. S. Sonar, K. F. Shelke, G. K. Kakade, B. B. Shingate, M. S. Shingare, Chinese Chemical Letters 20 (2009) 1042–1046.
49. Z. Rezaei, H. Firouzabadi, N. Iranpoor, A. Ghaderi, M. R. Jafari, A. A. Jafari, H. R. Zare,E uropean Journal of Medicinal Chemistry 44 (2009) 4266–4275.
50. A. Manjula; B. V. Rao; P. Neelakantana, Synthetic Communications, 33 (2003) 2963 — 2969.
51. A. Elmakssoudi, M. Zahouily, A. Mezdar, A. Rayadh, S. Sebti, C. R. Chimie, 8 (2005) 1954.
52. N. Azizi, F. Rajabi, M. R. Saidi, Tetrahedron Lett. 45 (2004) 9233.
53. S. D. Mitragotri, D. M. Pore, U. V. Desai, P. P. Wadgaonkar, Catal. Commun. (2008) doi:10.1016/j.catcom.2008.02.011.
54. A. K. Bhattacharya, K. C. Rana, Tetrahedron Lett. 49 (2008) 2598.
55. Trovarelli, A. In Catalysis by Ceria and Related Materials; Imperial College Press, 2002; catalytic science series, Vol. 2, pp 409.
56. R. Juarez, P. Concepcion, A. Corma, H. Garcia, Chem. Commun. 46 (2010) 4181–4183.
57. B. M. Bhanage, S. Fujita, Y. Ikushima, M. Arai, Appl. Catal., A 219 (2001) 259–266.
58. R. Juarez, A. Corma, H. Garcia, Green Chem. 11 (2009) 949–952.
59. V. Singh, V. Sapehiyia, G.L. Kad, Synthesis 2 (2003) 198.
60. A. Gaplovsky, M. Goplosky, S. Toma, J.L. Luche, J. Org. Chem. 65 (2000) 8444.
61. M. Robin, V. Pique, R. Faure, J.P. Glay, J. Hetero. Chem. 39 (2002) 1083.
62. R. Rajagopal, D.V. Jarikote, K.V. Srinivasan, Chem. Commun. 6 (2002) 616.

63. T. Masui, H. Hirai, N. Imanaka, G. Adachi, J of Mater Sci. Lett. 21 (2002) 489– 491.