ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

# An facile and efficient route catalyzed by Copper (II) Triflate for the synthesis of α-hydroxy phosphonates under solvent less condition.

**Kabeer A Shaikh[1], and Yogesh B Salve[2]*.**

[1]P.G. Department of Chemistry, Sir Sayyed College of Arts, Commerce and Science, Roshangate, Aurangabad-431001, Maharashtra, India.
[2]Department of Chemistry, Shri Dnyaneshwar Mahavidyalaya Newasa, Tal-Newasa, Dist- Ahmednagar-414603, Maharashtra, India.

**ABSTRACT**

A very easy, simple and highly useful approach was developed for one pot synthesis of α-hydroxy phosphonates using substituted aromatic aldehyde, diethyl phosphite catalyzed by copper triflate under solvent less condition. The reaction works out at elevated temperature. The present approach supports important key features such as simple, mild and solvent free reaction condition, eco-friendly and inexpensive catalyst and easy work-up procedure in addition to shorter reaction time, high yield with no formation of side products. The products were confirmed by IR, $^{1}H$ NMR, $^{13}C$ NMR and mass spectroscopic techniques.

**Keywords**: simple and clean approach, short reaction time, high yield, low-cost chemicals

https://doi.org/10.33887/rjpbcs/2024.15.5.4

***Corresponding author***

ISSN: 0975-8585

## INTRODUCTION

The organophosphorus chemistry is branch of chemistry that deals with study of organophosphorus compounds with their synthesis, characteristics and application in various field such as industrial, agricultural, pharmacological and medical sector [1, 2]. The phosphorus containing compounds found in complex organic compounds in blood, muscles, nerves and in teeth and bones as calcium phosphate. The phosphorus is present in energy rich compounds i.e. Adenosine triphosphate (ATP) which is key molecule of source of energy [3] (Fig. 1). Phosphate compounds are important in living system and play crucial role in different biological processes such as maintenance of cell membrane integrity and nucleic acid, cellular metabolism, regulation of subcellular processes, maintenance of acid-base homeostasis and bone mineralization [4, 5]. The α-hydroxy phosphonates are integral part of many natural compounds which largely present and biologically important in freshwater and marine ecosystems and can be synthesized by so many different types of microorganisms [6] (including protozoa, bacteria, archaea).

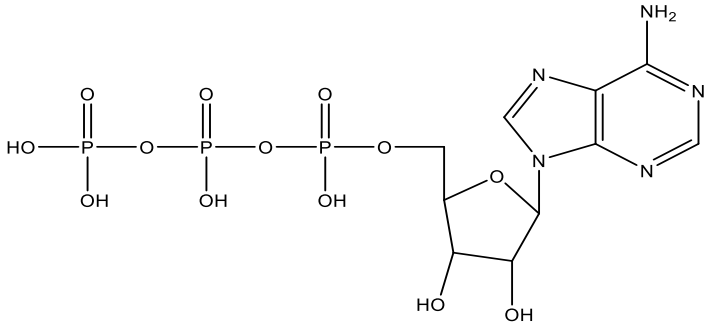



**Figure 1: Adenosine tri phosphate (energy rich compound)**

Over the last decade, synthesis of α-hydroxy phosphonates received noticeable attention due to its pharmacologically potent activities such as antibacterial [7-9], antifungal [10], antioxidant [11, 12], anticancer [13, 14], anti-HIV [15], enzyme inhibitor [16] properties. In addition to these, α-hydroxy phosphonates play important role of precursor for synthesis of α-keto [17], α-amino [18], α-halo [19], α-acetoxy phosphonates [20] and 1-2 diketone [21]. The α-hydroxy phosphonates are firstly synthesized by the Pudovik reaction, in which the C–P bond is composed by the integration of a dialkyl phosphite to an unsaturated system and the Abramov reaction in which the C–P bond is composed by the integration of a trialkyl phosphite to an unsaturated system. A literature survey reveals that synthesis of α-hydroxy phosphonates involves reaction between substituted aromatic aldehyde and diethyl phosphite with different catalysts such as, $Et_3N$ [22], $Ba(OH)_2$ [23], $K_2CO_3$ [24], $Na_2CO_3$ [25], nano-$TiO_2$ [26], nBuLi [24], [bmIm]OH [28], STA [29], Na@FAP [30], Piperazine [31]. Along with this, reaction of substituted aldehyde and ketones with trialkyl phosphite in presence of catalyst such as $LiClO_4.Et_2O$ [32], guanidine hydrochloride [33], Ch/Cl [33], $KHSO_4$ [34], $Bi(NO_3)_3.5H_2O$ [35] yields α-hydroxy phosphonates. Among these, variety of catalyst are suffered from drawbacks such as elevated reaction temperature, long reaction time, forceful reaction conditions, low yield, low selectivity, tedious work-up, use of toxic and expensive reagents. In order to circumvent these difficulties Hence currently, there is much emphasis on design and development of green, sustainable and eco-friendly catalyst for organic conversions [36-38].

So, the development of an affordable protocol with facile accessibility, a lower toxic solid acid catalyst and the capability to work under neat conditions is highly appreciated for the synthesis of α-hydroxy phosphonates. This may be achieved by utilization of solid acid catalysts for synthesis of organic compounds produce environmentally favourable condition and help to minimize liberation of toxic reaction residues into the environment [39-41]. The utilization of copper triflates as catalyst for organic synthesis of most bioactive heterocycles has been proven to be fortunate in many reactions [42-45]. The mechanism of interaction between metal triflate and organic moieties has been investigated by mass spectrometry [46].

ISSN: 0975-8585

## MATERIAL AND METHODS

### General

All the chemicals, reagents and solvents were purchased from Merk, Loba and Avra make. They are utilized without further purification. The melting point were recorded on digital melting/boiling point apparatus of Labtronics make which expressed in degree centigrade ($^oC$) and found uncorrected. Thin layer chromatography was accomplished on precoated plates of TLC silica gel 60 F254. 20% ethyl acetate in hexane solvent was used for TLC. Visualization was made with UV light (254 or 365nm). IR spectra were obtained on Shimatzu Infra-Red Spectrophotometer and absorptions ($\nu_{max}$) were reported in wave numbers ($cm^{-1}$). The $^1H$ NMR spectra were recorded using Bruker- 500 MHz spectrometer in $CDCl_3$ solvent using TMS as an internal standard and chemical shifts were measured in δ parts per million (ppm) and coupling constants (J) were measured in hertz (Hz).

**The spectral analysis of some of the representative compounds were given here: Compound 3a: Diethyl hydroxyl (phenyl) methyl phosphonates**:
**$^1H$ NMR** (400 MHz, $CDCl_3$) δ ppm: 7.26-7.49 (m, 5H, Ar-H), 5.00-5.03 (d, 1H, J= 10.8 Hz, CH-PO-), 3.94-4.10 (m, 4H, $OCH_2$), 1.19-1.28 (m, 6H, $OCH_2CH_3$); **$^{13}C$ NMR** (125 MHz, $CDCl_3$): 16.3, 16.3, 63.0, 63.1, 76.7, 127.0, 127.0, 128.1, 128.2, 128.2, 136.5; **MS m/z** (ESI); 245 $(M+H)^+$

**Compound 3b: Diethyl hydroxyl (4-methyl phenyl) methyl phosphonates**:
$^1H$ NMR (400 MHz, $CDCl_3$) δ ppm: 7.16-7.37 (m, 4H, Ar-H), 4.95-4.98 (d, 1H, J=10.4 Hz CH-PO-), 3.93-4.09 (m, 4H, $OCH_2$), 2.34 (s, 3H, Ar-$CH_3$), 1.20-1.29 (m, 6H, $OCH_2CH_3$);
**$^{13}C$ NMR** (125 MHz, $CDCl_3$): 16.3, 16.3, 21.2, 63.0, 63.0, 76.7, 126.9, 127.0, 128.8, 128.9, 133.4, 137.9; **MS m/z** (ESI); 259 $(M+H)^+$

**Compound 3c: Diethyl hydroxyl (4-methoxy phenyl) methyl phosphonates**:
$^1H$ NMR (400 MHz, $CDCl_3$) δ ppm: 6.89-7.41 (m, 4H, Ar-H), 4.93-4.96 (d, 1H, J=10Hz, CH-PO-), 3.91-4.10 (m, 4H, $OCH_2$), 3.81 (s, 3H, $OCH_3$), 1.20-1.30 (m, 6H, $OCH_2CH_3$); **$^{13}C$ NMR** (125 MHz, $CDCl_3$): 16.4, 16.4, 55.2, 63.0, 63.0, 76.7, 113.7, 113.7, 128.4, 128.4, 128.4, 159.5; **MS m/z** (ESI): 274.25 $(M+H)^+$

**Compound 3d: Diethyl hydroxyl (3-nitro phenyl) methyl phosphonates**:
$^1H$ NMR (400 MHz, $CDCl_3$) δ ppm: 7.53-8.37 (m, 4H, Ar-H), 5.13-5.16 (d, 1H, J=11.2 Hz, CH-PO-), 4.08-4.14 (m, 4H, $OCH_2$), 3.59 (s, 1H, OH), 1.25-1.57 (m, 6H, $OCH_2CH_3$); **$^{13}C$ NMR** (125 MHz, $CDCl_3$): 16.3, 16.3, 62.5, 62.5, 79.4, 122.8, 123.5, 129.8, 133.2, 136.8, 148.1; **MS m/z** (ESI): 290.37 $(M+H)^+$

**Compound 3e: Diethyl hydroxyl (2-fluoro phenyl) methyl phosphonates**:
$^1H$ NMR (400 MHz, $CDCl_3$) δ ppm: 7.02-7.68 (m, 4H, Ar-H), 5.36-5.39 (d, 1H, J=11.2 Hz, CH-PO-), 3.99-4.22 (m, 4H, $OCH_2$), 1.21-1.31 (m, 6H, $OCH_2CH_3$); **$^{13}C$ NMR** (125 MHz, $CDCl_3$): 16.3, 16.3, 62.5, 62.5, 73.6, 115.7, 124.5, 127.9, 128.7, 129.2, 159.6; **MS m/z** (ESI): 263.58 $(M+H)^+$

**Compound 3f: Diethyl hydroxyl (4-fluoro phenyl) methyl phosphonates**:
$^1H$ NMR (400 MHz, $CDCl_3$) δ ppm: 7.44-7.48 (m, 2H, Ar-H), 7.02-7.07 (m, 2H, Ar-H), 4.98- 5.01 (d, 1H, J=10.4 Hz, CH-PO-), 3.97-4.10 (m, 4H, $OCH_2$), 1.21-1.29 (m, 6H, $OCH_2CH_3$); **$^{13}C$ NMR** (125 MHz, $CDCl_3$):16.4, 16.4, 62.5, 62.5, 80.4, 115.7, 115.7, 128.7, 128.7, 131.5, 161.8; **MS m/z** (ESI): 263.04 $(M+H)^+$

**Compound 3g: Diethyl hydroxyl (4-chloro phenyl) methyl phosphonates**:
$^1H$ NMR (400 MHz, $CDCl_3$) δ ppm: 7.23-7.46 (m, 4H, Ar-H), 4.81-4.79 (d, 1H, J=10.8 Hz, CH-PO-), 3.99-4.26 (m, 4H, $OCH_2$), 1.24-1.35 (m, 6H, $OCH_2CH_3$); **$^{13}C$ NMR** (125 MHz, $CDCl_3$): 16.3, 16.3, 62.4, 62.4, 80.3, 128.5, 128.5, 129.0, 129.0, 134.0, 133.2; **MS m/z** (ESI): 279.74 $(M+H)^+$

### General procedure for the synthesis of derivatives of α-hydroxy phosphonates

In a 50 ml round bottom flask, the mixture of substituted aromatic aldehyde (1.0 mmol), diethyl phosphite (1.0 mmol) and $Cu(OTf)_2$ (20 mol%) was heated at $65^oC$ for half hrs under solvent free condition and the progress of reaction was monitored by TLC. After completion of reaction, water was discharged to the reaction mixture and extracted with ethyl acetate, then organic layer was dry over an. $Na_2SO_4$ and concentrated under reduced pressure to obtain desired product. The crude product was recrystallized in ethanol solvent to afford the pure product which was characterized by spectroscopic methods.

ISSN: 0975-8585

## RESULT AND DISCUSSION

At first endeavour, the reaction was carried out utilizing 3-nitro benzaldehyde (1 mmol) and diethyl phosphite (1 mmol) in absence of catalyst under solvent free condition at room temperature as well as heating at 65$^0$C but progress of reaction was not visually examined on TLC even stirring for 2 hrs (Table-1, Entry 1 and 2). Furthermore, similar reaction was performed with 5 mol% of $Cu(OTf)_2$ at room temperature, no product visualised on TLC even stirring for 2 hrs. (Table-1, Entry 3), then same reaction mixture was heated at 65$^0$C for next half hrs, surprisingly product was formed with 35% of yield (Table-1, Entry 4). Afterwards, we tried for improvement in yield of desired product by selecting similar reactant with increasing concentration of catalyst $Cu(OTf)_2$ from 10, 15, 20 mol%. It was observed that, yield of desired product was increases as catalyst concentration increases (**Table-1 Entry 5, 6 and 7**).

**Table 1: Optimization of concentration of catalyst[a]**

| Entry | Catalyst conc. (mol %) | Time (hrs.) | Yield[b] (%) |
|---|---|---|---|
| 1[c] | - | 2 | NP |
| 2 | - | 2 | NP |
| 3[c] | 5 | 2 | NP |
| 4 | 5 | 0.5 | 35 |
| 5 | 10 | 0.5 | 75 |
| 6 | 15 | 0.5 | 80 |
| 7 | 20 | 0.5 | 90 |

[a]Reaction condition: 3-nitro benzaldehyde, (1mmol), diethyl phosphite, (1 mmol) heating at 65$^0$C under solvent free condition, [b]Isolated yields, [c]room temperature, NP- No Product

To find out effect of solvent for synthesis of Diethyl hydroxyl (3-nitro phenyl) methyl phosphonates, we screened different solvent such as toluene, THF, 1,4-dioxane, acetonitrile and ethanol for nucleophilic addition of diethyl phosphite towards 3-nitro benzaldehyde in presence of 20 mol% of $Cu(OTf)_2$ catalyst at 65$^o$C. The reaction performed very well with faster rate and excellent yield under neat condition. (**Table-2, Entry 6**). It may be due to under neat conditions, the concentration of catalyst leads to higher reaction rates than the same reaction performed in the presence of solvent. So, all other derivatives are synthesized using different substituted aldehydes and diethyl phosphite with excellent yield in presence of 20 mol% amount of catalyst $Cu(OTf)_2$ under solvent free condition at 65$^o$C and the results are summarized in **Table-3**

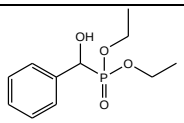
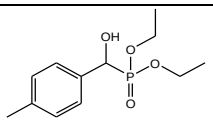
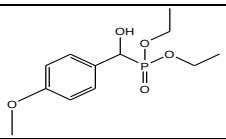
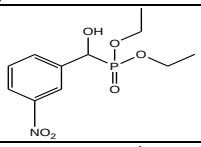
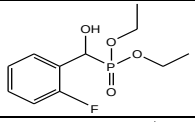
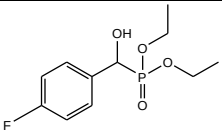
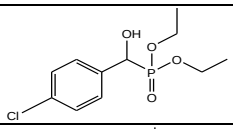
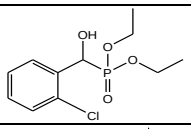
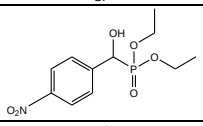
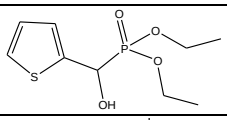
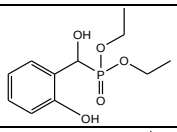
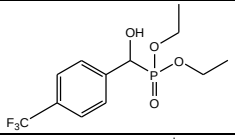
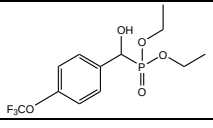
**Table 2: Screening of solvent[a]**

| Entry | Solvent | Time (hrs) | Yield (%)[b] |
|---|---|---|---|
| 1 | Toluene | 0.5 | 55 |
| 2 | THF | 0.5 | 66 |
| 3 | 1,4-dioxane | 0.5 | 72 |
| 4 | Acetonitrile | 0.5 | 80 |
| 5 | Ethanol | 0.5 | 85 |
| **6** | **Neat** | **0.5** | **90** |

[a]Reaction condition: 3-nitro benzaldehyde, (1 mmol), diethyl phosphite, (1 mmol), $Cu(OTf)_2$ (20 mol%) heating at 65$^0$C, [b]Isolated yields

ISSN: 0975-8585

**Table 3: Synthesis of α -hydroxy phosphonates derivatives using aromatic aldehyde and diethyl phosphite under solvent free condition at 65°C temperature[a]**

| Entry | Aldehyde | Compound | M.P. °C found | Yield[b] (%) |
|---|---|---|---|---|
| 1 | Benzaldehyde |  | 74-75 | 85 |
| 2 | 4-Methyl benzaldehyde |  | 95-96 | 86 |
| 3 | 4-Methoxy benzaldehyde |  | 120-122 | 90 |
| 4 | 3-Nitro benzaldehyde |  | 80-82 | 90 |
| 5 | 2-Fluro benzaldehyde |  | 88-89 | 84 |
| 6 | 4- Fluro benzaldehyde |  | 78-79 | 88 |
| 7 | 4-Chloro benzaldehyde |  | 68-70 | 90 |
| 8 | 2-Chloro benzaldehyde |  | 75-77 | 88 |
| 9 | 4- Nitro benzaldehyde |  | 88-90 | 90 |
| 10 | Thiophene 2-aldehyde |  | 67-68 | 80 |
| 11 | Salicyldehyde |  | 70-72 | 85 |
| 12 | 4-trifluromethyl benzaldehyde |  | 90-92 | 88 |
| 13 | 4-trifluromethoxy benzaldehyde |  | 97-99 | 86 |

[a]Reaction condition : aromatic aldehyde (1 mmol), diethyl phosphite, (1 mmol), $Cu(OTf)_2$ (20 mol%) heating at 65°C under solvent free condition, [b]Isolated yields

ISSN: 0975-8585

## CONCLUSION

In conclusion, we have developed facile, more efficient and straightforward protocol for one pot synthesis of α-hydroxy phosphonates using different substituted aromatic aldehyde (1.0 mmol) and diethyl phosphite (1.0 mmol) in presence of copper triflate (20 mol%) as a catalyst under solvent free condition at $65^0$C temperature. With comparison of earlier reported methodologies, the present synthetic protocol is mild, solvent free, eco-friendly and inexpensive catalyst and easy work-up procedure.

## ACKNOWLEDGEMENT

Authors are thankful to SAIF, Indian Institute of Science Bangalore for providing NMR facilities. We are also grateful to Principal, Shri Dnyaneshwar Mahavidyalaya Newasa Tal: Newasa, Dist: Ahmednagar, Maharashtra (India) for providing necessary facilities to carry out present work.

## REFERENCES

[1] Jakub A. Special Issue "Organophosphorus Chemistry: A New Perspective". Molecules 2023; 28, 4752.
[2] Mazzacurati M, Baccolini G, Boga C. Advanced Studies on the Synthesis of Organophosphorus Compounds, Chapter-1 2007; pp 3-15.
[3] Behboudian MH, Pickering AH, Dayan E. Encyclopedia of Applied Plant Sciences 2016; 1: 219-224.
[4] Penido MG MG, Alon US. Phosphate homeostasis and its role in bone health. Pediatric Nephrology 2012; 27: 2039-2048.
[5] Jastrzab R, Nowak M, Zabiszak M, Odani A, Kaczmarek MT. Significance and properties of the complex formation of phosphate and polyphosphate groups in particles present in living cells. Coordination Chemistry Reviews 2021; 435: 1-22.
[6] Ruffolo F, Dinhof T, Murray L, Zangelmi E, Chin JP, Pallitsch K, Peracchi A. The Microbial Degradation of Natural and Anthropogenic Phosphonates. Molecules 2023; 28: 1-29.
[7] Battula S, Battini N, Singh D, Ahmed Q N. 2-Oxo Promoted Hydrophosphonylation & Aerobic Intramolecular Nucleophilic Displacement Reaction. Org Biomol Chem 2015; 13: 8637-8641.
[8] Gundluru M, Reddy Malllu KK, Sarva S, Cirandur SR. Green and eco-friendly synthesis of α-hydroxyphosphonates as antioxidant and antimicrobial agents. J Molecular Structure 2022; 1256: 1-13.
[9] Reddy GS, Syama Sundar C, Prasad SS, Dadapeer E, Raju CN, Reddy CS. Synthesis, spectral characterization and antimicrobial activity of α-hydroxyphosphonates. Der Pharma Chemica 2012; 4; (6) 2208-2213.
[10] Patil NS, Deshmukh GB, Patil SV, Bholay AD, Gaikwad ND. Synthesis and biological evaluation of novel N-aryl maleimide derivatives clubbed with α-hydroxyphosphonates. Euro J Med Chem 2014; 83: 490-497.
[11] Sampath C, Naga Raju C, Venkata Rao C. An efficient synthesis, spectral characterization, anti-microbial and anti-oxidant activities of novel α-hydroxyphosphonates and α-hydroxyphosphinates. Phosphorus Sulfur Silicon Relat Elem 2016; 191: 95–99.
[12] Uma Maheswara Rao K, Syama Sundar C, Siva Prasad S, Radha Rani C, Suresh Reddy C. Neat synthesis and anti-oxidant activity of α-hydroxy phosphonates Bull Korean Chem Soc 2011; 32: 3343–3347.
[13] Radai Z, Windt T, Nagy V, Furedi A, Kiss NZ, Randelovic I, Tovari J, Keglvich G, Szakacs G, Toth S. Synthesis and anticancer cytotoxicity with structural context of an α-hydroxyphosphonate based compound library derived from substituted benzaldehydes. New J Chemi 2019; 43: 14028-14035.
[14] Sowery RD, So AI, Gleave ME. Therapeutic options in advanced prostate cancer: present and future. Curr Urol Rep 2007; 8: 53-59.
[15] Pokrovsky AG, Pronayeva TR, Fedyuk NV, Shirokova EA, Khandazhinskaya AL, Tarusova NB, Karpenko IL, Krayevsky AA. Anti-HIV activity of novel phosphonate derivatives of AZT, d4T, and ddA. Nucleosides, Nucleotides & Nucleic Acids 2001; 20: (4–7) 767–769.
[16] Patel DV, Riclly-Gauvin K, Ryono DE. Peptidic α-hydroxy phosphmyls c-terminal modification methodology. Tetrahedron Letters 1990; 31: (39) 5591-5594.
[17] Habib F, Naseer I, Sara S. Preparation of α-ketophosphonates by oxidation of α-hydroxy phosphonates with neutral alumina supported potassium permanganate (NASPP) under solvent free condition and potassium permanganate in dry benzene. Tetrahedron lett 2002; 43: 477-480.

[18] Babak K, A Convenient synthesis of 1-aminophosphonates from 1- hydroxyphosphonates. Tetrahedron letters 2003; 44: 1051-1053.
[19] Bogdan I, Frederic E, Phillippe S. Controlled monohalogenation of phosphonates: A new route to pure α-monohalogenated diethyl benzylphosphonates. Tetrahedron 1999; 55: 2671-2686.
[20] Habib F, Naseer I, Sara S, Zohreh A. Facile and high yielding preparation of α-acetoxyphosphonates from α-hydroxyphosphonates assisted by microwave irradiation. Synthesis 2004; 11: 1771-1774.
[21] Geoge AO, An-hsiang W. Preparation of 1,2-diketones from nonenolizable aliphatic and aromatic acyl chlorides with diethyl 1-alkyl (aryl)-1-(trimethylsiloxy)- methanephosphonatesl. J Org Chem 1991; 56: 902-904.
[22] Zehuai M, Yinjun W, Xi M. An efficient and green method to prepare bis-α-hydroxy phosphonates using triethylamine as catalyst. Phosphorus Sulfur Silicon Relat. Elem. 2021; 196: (2) 195-199.
[23] Pandi M, Chanani PK, Govindasamy S. An efficient synthesis of α-hydroxy phosphonates and 2-nitroalkanols using $Ba(OH)_2$ as catalyst. Appl Catal A Gen 2012; 441–442: 119–123.
[24] Sun YM, Xin N, Xu ZY, Liu LJ, Meng FJ, Zhang H, Fu BC, Liang QJ, Zheng HX, Sun LJ, Zhao CQ, Han LB. Addition of Optically Pure H-Phosphinate to Ketones: the Selectivity, Stereochemistry and Mechanism. Org Bimol Chem 2014; 12: (46) 9457-9465.
[25] Kong DL, Liu RD, Li GZ, Zhang PW, Wu MS. A Rapid, Convenient, Solventless Green Approach for the Synthesis of α-hydroxyphosphonates by Grinding. Asian J Chemistry 2014; 26: (4) 1246-1248.
[26] Prasad SS, Jayaprakash SH, Rao KU, Reddy NB, Kumar PCR, Reddy CS. Nano-TiO2 catalyzed microwave synthesis of α-hydroxyphosphonates. Org Commun 2014; 7: (3) 98-105.
[27] Liu C, Zhang Y, Qian Q, Yuan D, Yao Y. n-BuLi as a Highly Efficient Precatalyst for Hydrophosphonylation of Aldehydes and Unactivated Ketones. Org Lett 2014; 16: 6172–6175.
[28] Li X, Jin C, Gu L. C–H Hydroxylation of Phosphonates with Oxygen in [bmIm]OH to Produce Quaternary α-Hydroxy Phosphonates. J Organic Chemistry 2015; 80: 2443–2447.
[29] Santhisudha S, Sreelakshmi P, Jayaprakash SH, Vijaya Kumar B, Suresh Reddy C. Silica-Supported Tungstic Acid Catalyzed Synthesis and Antioxidant Activity of α-Hydroxyphosphonates. Phosphorus Sulfur Silicon Relat. Elem 2015; 190: 1479-1488.
[30] Ramananarivo HR, Solhy A, Sebti J, Smahi A, Zahouily M, Clark J, Sebti S. An Eco-Friendly Paradigm for the Synthesis of α-Hydroxyphosphonates Using Sodium-Modified Fluorapatite under Solventless Conditions. ACS Sustain Chem Eng 2013; 1: 403-409.
[31] Suresh Kumar K, Bhupendra Reddy C, Veera Narayana Reddy M, Radha Rani C, Suresh Reddy C. Green chemical synthesis of α-hydroxyphosphonates. Org. Commun 2012; 5: (2) 50-57.
[32] Najmedin A, Mohammad RS. Lithium Perchlorate Diethyl Ether Solution: A Highly Efficient Media for the Abramov Reaction. Phosphorus, Sulfur, and Silicon 2003; 178: 1255–1259.
[33] Tidke VA. Green Synthesis of α-hydroxyphosphonates by using DES Catalyst. Ijsrst 2021; 9: (6) 310-315.
[34] Babak K, Payam D, Samaneh F, Hesam E. Hydroxy and amino phosphonates and bisphosphonates: Synthetic method and their biological applications. Frontiers in Chemistry 2022; 10: 1-17.
[35] Kumar A, Jamwal S, Khan S, Singh N, Rai VK. $Bi(NO_3)_3.5H_2O$ catalyzed phosphonylation of aldehydes: an efficient route to α-hydroxyphosphonates Phosphorus Sulfur Silicon Relat Elem 2017; 192: (3) 381-385.
[36] Rongxian B, Jian Y, Lijun M, Changhui L, Fengtian W, Yanlong G. Facile synthesis of 3,4-fused tricyclic indoles with a seven-membered ring through a three-component reaction of 4-hydroxyindole, aldehyde, and malonodinitrile or ethyl cyanoacetate. Tetrahedron 2016; 72: (17) 2170-2177.
[37] Palanisamy R, Bingbing L, Yanlong G. Aldo-X Bifunctional Building Blocks for the Synthesis of Heterocycles. Chem Rec 2017; 17: (2) 142-183.
[38] Anshu D, Sarika B, Ruchi S, Vijay P. Water-Triggered Metal-Free Synthesis of Pyranopyrazoles via One-Pot Oxidation / Michael Addition / Cyclization / Dehydration Sequence. ChemistrySelect 2018; 3: 9785 –9789.
[39] Karen W, James HC. Solid acids and their use as environmentally friendly catalysts in organic synthesis. Pure Appl Chem 2000; 72: (7) 1313–1319.
[40] Princy G, Satya P. Solid acids: Green alternatives for acid catalysis. Catalysis Today 2014; 236: (Part B) 153-170.
[41] Leena R, Solid Acid Catalysts in Green Chemistry. Resonance 2007; 30-36.
[42] Saghir A, Abu TK. Copper (II) triflate catalyzed three-component reaction for the synthesis of 2,3-diarylquinoline derivatives using aryl amines, aryl aldehydes and styrene oxides. Org Biomol Chem 2021; 19: 3255–3262.

[43] Rafael FAG, Nuno RE, Jaime ASC, Carlos AMA. Copper (II) Triflate As a Reusable Catalyst for the Synthesis of trans-4,5-Diamino-cyclopent-2-enones in Water. J. Org Chem 2018; 83: 7509−7513.
[44] Rameshwar PP, Yong RL. Copper (II) triflate-catalyzed reactions for the synthesis of novel and diverse quinoline carboxylates. RSC Adv 2013; 3: 22039-22045.
[45] Reddy MR, Reddy NG, Mehmood U, Ibnelwaleed AH, Rahman SU, Khalil H, Basireddy VSR. Copper (II) Triflate Catalyzed Synthesis of 2,4-Disubstituted Oxazoles from α-Diazoketones. Synthesis 2015; 47: 1-6.
[46] Lionel M, Jean-Francois G, Elisabet D. Metal Triflates as Catalysts in Organic Synthesis: Determination of Their Lewis Acidity by Mass Spectrometry. Chem Plus Chem 2022; 87: (6) 1-13.