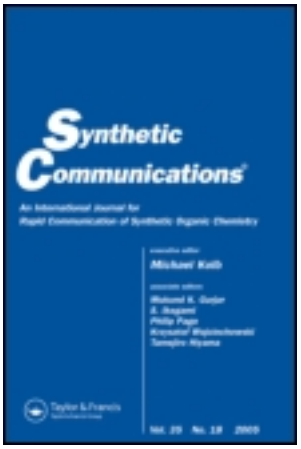

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Aqueous-Phase Synthesis of α-Hydroxyphosphonates Catalyzed by β-Cyclodextrin

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AQUEOUS-PHASE SYNTHESIS OF α-HYDROXYPHOSPHONATES CATALYZED BY β-CYCLODEXTRIN

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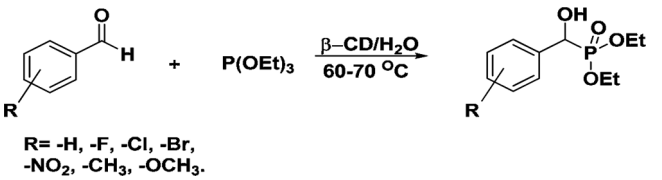
Organic Chemistry Division I, Indian Institute of Chemical Technology, Hyderabad, India

GRAPHICAL ABSTRACT



Abstract *α-Hydroxyphosphonates were synthesized from aromatic/heteroaromatic aldehydes with triethyl phosphite in the presence of β-cyclodextrin in an aqueous medium. The β-cyclodextrin can be recovered and reused without loss of catalytic activity.*

Keywords Aromatic/heteroaromatic aldehydes; β-cyclodextrin; α-hydroxyphosphonate; triethyl phosphate; water

INTRODUCTION

α-Hydroxyphosphonate derivatives are important organophosphorus compounds associated with a wide variety of biological and pharmaceutical activities.[1] These derivatives are extensively used as synthetic intermediates[2] with iterative manipulation of functional groups to 1,2-diketones[3] and α-ketophosphonates.[4] The hydrolyzed products of α-hydroxyphosphonates exhibit a wide range of medicinal properties such as antiviral,[5] antibacterial,[6] and anticancer activities.[7]

In the past, there have been reports on the synthesis of α-hydroxyphosphonates from the corresponding aldehydes by the reaction of dialkyl (or) trialkyl phosphates, catalyzed by bases such as ethyl magnesium bromide,[8] potassium fluoride on alumina,[9] quinine,[10] lithium diisopropylamine (LDA),[11] MgO,[12] NH_4VO_3,[13] and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU),[14] as well as acids such as

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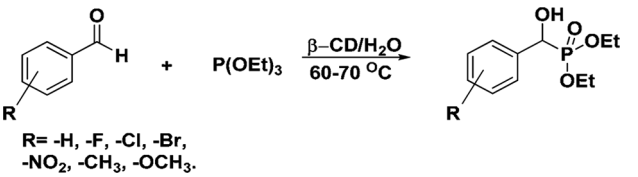
alumina,[15] $Ti(OPri)_2$,[16] $LiClO_4 \cdot Et_2O$, TMSCl,[17] and guanidine hydrochloride.[18] Most of these catalysts are very expensive and moisture sensitive, and all the reported methods involve usage of volatile and flammable organic solvents and extensive reaction times, resulting in poor yields. However, with increasing environmental concerns, an environmentally benign method under neutral conditions is highly desirable.

Presently, organic reactions in the aqueous phase have attracted attention because of the advantages of water, an environmentally benign and economically affordable solvent. However, the fundamental problem in performing the reaction in water is that many organic substrates are hydrophobic and insoluble in water. In continuation of our efforts to develop greener chemical approaches for the synthesis of novel reaction intermediates and heterocyclic moieties,[19] herein we disclose the synthesis of α-hydroxy phosphonates using β-cyclodextrin as a reusable catalyst under supramolecular catalysis.

RESULTS AND DISCUSSION

Cyclodextrins (CDs) are cyclic oligosaccharides possessing hydrophobic cavities, which bind substrates selectively and catalyze chemical reactions with high selectivity. They catalyze the reactions by supramolecular catalysis involving reversible formation of host–guest complexes by noncovalent bonding as seen in enzymes. We describe herein the remarkable catalytic activity of β-cyclodextrin in the reaction of aldehydes toward a variety of triethyl phosphites to give exclusively substituted α-hydroxy phosphonates.

In this study, a model reaction was conducted by reacting benzaldehyde with triethyl phosphite in H_2O to obtain the corresponding α-hydroxy phosphonate in poor yield due to poor solubility of the aldehyde in H_2O. When the same reaction was conducted using β-CD at room temperature, the product was obtained in moderate yield (65%). In a controlled reaction using β-CD as a supramolecular catalyst, at 70 °C the product was obtained in excellent yield (Scheme 1). This encouraging result made us expand the scope of the reaction by reacting various aromatic and heteroaromatic aldehydes with triethyl phosphite to obtain the corresponding α-hydroxyphosphonates in quantitative yields. In general, all the reactions were clean and resulted in good yields (80–93%). Substitution on aromatic aldehyde played a crucial role in governing the product yield as it can be seen from the Table 1. Electron-withdrawing group on benzaldehyde gave a good yield (Table 1, entry 2), whereas electron-donating group on benzaldehyde gave a lower yield (Table 1, entry 8) in comparison with benzaldehyde (Table 1, entry 1).



Scheme 1.

Table 1. β-CD-II catalyzed synthesis of α-hydroxyphosphonates

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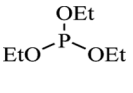
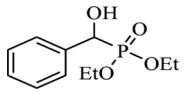
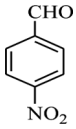
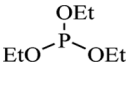
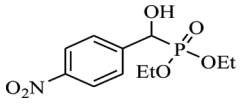
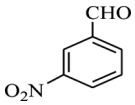
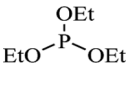
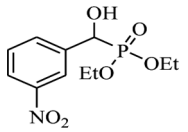
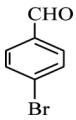
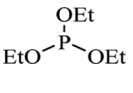
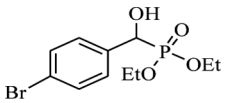
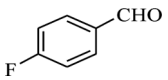
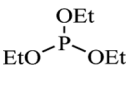
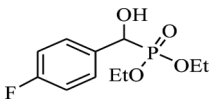
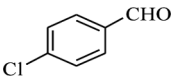
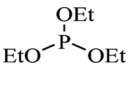
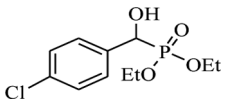
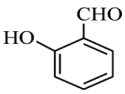
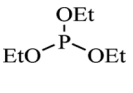
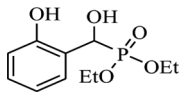
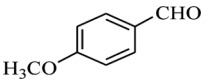
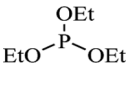
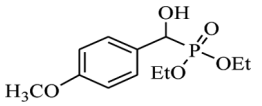
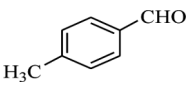
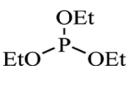
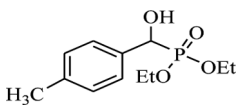
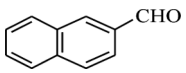
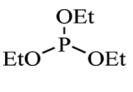
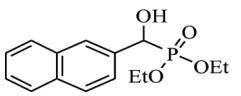
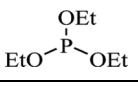
1				10 h	89
2				8 h	93
3				9 h	90
4				10 h	88
5				9.5 h	86
6				10 h	87
7				12 h	90
8				11 h	81
9				10.5 h	80
10				10 h	89
11				10.5 h	85

(*Continued*)

Table 1. Continued

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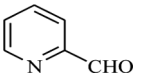
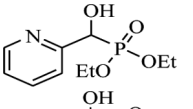
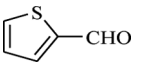
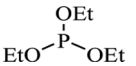
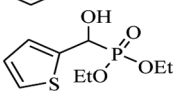
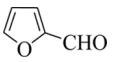
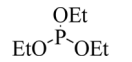
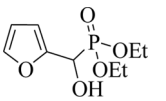
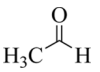
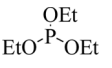
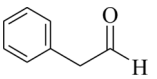
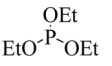
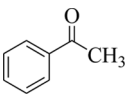
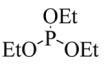
					
12				10.5 h	81
13				10 h	83
14			No reaction	12 h	
15			No reaction	14 h	
16			No reaction	16 h	

Notes. Reaction conditions: β-cyclodextrin (1.0 equiv), aldehyde (1 equiv), and triethyl phosphite (1 equiv) at 60–70 °C for 8–12 h. All products were confirmed by ^{1}H and ^{13}C NMR and direct comparison with authentic samples.

[a]Yields of the isolated product.

When we reacted salicylaldehyde with triethyl phosphite, an enhancement of product yield was observed. With optimized reaction conditions on hand, we attempted to synthesize α′-methyl-α -hydroxy phosphonates by reacting acetophenone with triethyl phosphate, but no reaction was observed even after prolonged reaction times. All the products were characterized by ^{1}H and ^{13}C NMR, infrared (IR) spectrometry, and mass spectrometry and compared with literature reports.

The catalytic activity of β-cyclodextrin for these reactions was established by the fact that no reaction was observed in the absence of cyclodextrin. Evidence for complexation between the aldehyde and cyclodextrin is supported by ^{1}H NMR studies. ^{1}H NMR spectra (dimethylsulfoxide, DMSO) of β-CD, β-CD-benzaldehyde complex were examined, and it was observed that there was an upfield shift of H-C (3) (0.02 ppm) and H-C (5) (0.02 ppm) protons of cyclodextrin in the β-CD-benzaldehyde complex when compared to β-CD, indicating the formation of an inclusion complex of aldehyde with β-CD. The complexation with β-CD increases the reactivity of aldehyde carbonyl functionality because of intermolecular hydrogen bonding with the CD-hydroxyl groups, facilitating the addition of phosphite. Here, β-CD not only forms the inclusion complex with aldehyde but is also involved in the intermolecular hydrogen bonding with the guest molecule to promote the reaction.

The generality of this reaction was investigated for the synthesis of various α-hydroxyphosphonate derivatives by using different substituted aldehydes with triethyl phosphite at optimal conditions. The reaction proceeded smoothly to afford the corresponding α-hydroxyphosphonates.

EXPERIMENTAL

Thin-layer chromatography (TLC) was carried out using silica-gel 60 F_{254} precoated plates. Visualization was accomplished with an ultraviolet (UV) lamp or I_2 stain. All products were characterized by their NMR and MS spectra. ^1H and ^{13}C NMR were recorded on 200 MHz in $CDCl_3$ using tetramethylsilane (TMS) as an internal standard; chemical shifts were reported in parts per million (ppm, δ).

General Procedure

β-Cyclodextrin (1 mmol) was dissolved in water (20 mL). Aldehyde (1.0 mmol) was added to this clear solution and stirred for 10 min, and then triethylphosphite (2.0 mmol) was added, after which the reaction was heated at 60–70 °C until completion of the reaction as indicated by TLC. The reaction mixture was extracted with ethyl acetate (3 × 10 mL). The organic layers were washed with water and a saturated brine solution and dried over anhydrous Na_2SO_4. The combined organic layers were evaporated under reduced pressure, and the resulting crude product was purified by column chromatography by using ethyl acetate and hexane (3:7) as eluent. The aqueous layer was cooled to 5 °C to recover β-CD (Table 1). The products were confirmed by comparison with authentic samples.

Spectral Data of Principal Compounds

Diethyl hydroxy(phenyl)methylphosphonate (Table 1, Entry 1).[20] Solid, mp, 76–78 °C; IR: 3251, 2987, 1730, 1621, 1473; ^1H NMR (200 MHz) δ 1.10–1.54 (m, 6H), 3.0 (s, OH), 3.85 (s, 1H), 3.99–4.49 (m, 4H), 6.89–6.94 (m, 2H), 7.12 (s, 1H), 7.24–7.34 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 16.07, 63.18, 64.81, 112.44, 123.92, 125.72, 130.69, 138.61; MS m/z (ESI); 267 $(M + Na)^+$. Anal. calcd. for ($C_{11}H_{17}O_4P$): C, 54.10; H, 7.02. Found: C, 54.02; H, 6.95.

Diethyl hydroxy(4-nitrophenyl)methylphosphonate (Table 1, Entry 2).[20] IR: 3179, 2991, 2114, 1751, 1627, 1523, 1342 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.02–1.75 (m, 6H), 3.2 (s, OH), 3.85–4.58 (m, 4H), 6.88–6.97 (m, 2H), 8.18–8.44 (m, 2H), 4.74 (s, 1H);^{13}C NMR (75 MHz, $CDCl_3$) δ 15.72, 29.68, 64.99, 71.79, 110.43, 122.00, 127.46, 136.29. 159.25, 170.25; MS m/z (ESI); 312 $(M + Na)^+$. Anal. calcd. for ($C_{11}H_{16}NO_6P$): C, 45.68; H, 5.58; N, 4.84. Found: C, 45.62, H, 5.51; N, 4.79.

Diethyl (4-bromophenyl)hydroxy methylphosphonate (Table 1, Entry 4).[20] IR: 3250, 2990, 2854, 1736, 1631, 1484, 1233 cm^{-1}, ^1H NMR (200 MHz, $CDCl_3$) δ 1.05–1.44 (m, 6H), 3.25 (s, OH), 3.87 (s, 1H), 4.06–4.32 (m, 4H),

6.51–6.59 (m, 2H), 6.66–7.03 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.5, 62.3, 71.1, 124.5, 125.9, 130.4, 132.0, 134.2; MS m/z (ESI); 345 $(M + Na)^+$. Anal. calcd. for ($C_{11}H_{16}BrO_4P$): C, 40.89; H, 4.99. Found: C, 40.83; H: 4.92.

Diethyl (4-flurophenyl)(hydroxy)methylphosphonate (Table 1, Entry 5).[20] IR: 3341, 2924, 2854, 1735, 1631, 1485; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.07–1.4 (m, 6H), 3.7 (s, OH), 3.89 (s, 1H), 4.00–4.32 (m, 4H), 6.75 (m, 2H), 7.19–7.25 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.6, 61.8, 69.9, 114.9, 127.8, 130.0, 131.8, 156.2; MS *m/z* (ESI); 263 $(M + H)^+$. Anal. calcd. for ($C_{11}H_{16}FO_4P$): C, 50.39; H, 6.15. Found C, 50.35; H, 6.11.

Diethyl (4-chlorophenyl)(hydroxy)methylphosphonate (Table 1, Entry 6)[20]**.** Solid, mp, 67–68 °C; IR: 3245, 2923, 2854, 1738, 1620, 1036 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.99–1.52 (m, 6H), 3.9 (s, OH), 3.86 (s, 1H), 4.12–4.24 (m, 4H), 6.74–6.79 (m, 2H), 7.17–7.26 (m, 2H); MS *m/z* (ESI); 301 $(M + Na)^+$. Anal. calcd. for ($C_{11}H_{16}ClO_4P$): C, 47.41; H, 5.79. Found: C, 47.32; H, 5.74.

Diethyl hydroxy(2-hydroxy phenyl)methylphosphonate (Table 1, Entry 7). White solid, mp 96–97 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.41 (m, 6H), 3.5 (s, OH), 3.88 (s, 1H), 4.12–4.36 (m, 4H), 5.96–6.20 (m, 2H), 6.89 (m, 2H), 8.01 (s, OH); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 14.2, 61.5, 65.4, 115.3, 120.8, 128.1, 128.8, 129.1, 140.5; MS *m/z*: 283 $(M + Na)^+$. Anal. calcd. for ($C_{11}H_{17}O_5P$): C, 50.77; H, 6.58. Found: C, 5.71; H, 6.52.

Diethyl hydroxy(4-methoxyphenyl)methylphosphonate (Table 1, Entry 8).[20] White solid, mp 119–120 °C; IR (KBr): 3268, 1225, 1051 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.39 (dd, 2H, $J = 8.7$, 2.8 Hz, Ar-H), 6.87 (d, 2H, $J = 8.5$ Hz, Ar-H), 4.97 (d, 1H, $J = 10$ Hz, P-CH), 3.91 (m, 4H, O–CH_2), 3.82 (s, 3H, Ar-O–CH3), 1.26 (t, 3H, J = 7.8 Hz, CH_3), 1.21 (t, 3H, $J = 7.8$ Hz, CH_3); MS *m/z* 275 $(M + H)^+$. Anal. calcd. for ($C_{12}H_{19}O_5P$): C, 52.55; H, 6.98. Found: C, 52.49; H, 6.93.

Diethyl hydroxy(p-tolyl)methylphosphonate (Table 1, Entry 9).[20] Solid, mp 94–95 °C; IR: 3253, 2985, 2858, 1733, 1627, 1492, 1247, 1035 cm^{-1}, ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.88–1.51 (m, 6H), 2.07 (s, 3H), 4.73 (d,1H), 3.93–4.28 (m, 4H), 6.56–6.99 (m, 2H), 7.07–7.49 (m, 2H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 15.96, 20.98, 29.67, 64.61, 71.65, 110.03, 126.97, 130.90, 132.80, 138.73, 169.16; MS *m/z* (ESI); 281 $(M + Na)^+$. Anal. calcd. for ($C_{12}H_{19}O_4P$): C, 55.81; H, 7.42. Found: C, 55.78; H, 7.38.

Diethyl hydroxyl(naphthalen-2-yl)methylphosphonate (Table 1, Entry 10).[20] IR: 3351, 2974, 2844, 1735, 1631, 1485; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.05–1.2 (m, 6H), 3.82 (s, OH), 4.01 (s, 1H), 4.10–4.32 (m, 4H), 7.15–7.29 (m, 2H), 7.58–7.75 (m, 3H), 7.90–8.12 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 61.9, 71.0, 124.1, 125.8, 126.5, 127.1, 127.4, 127.9, 131.0, 133.9; MS *m/z* (ESI): 295 $(M + H)^+$. Anal. calcd. for ($C_{15}H_{19}O_4P$): C, 61.22; H, 6.51. Found: C, 61.18; H, 6.48.

Diethyl hydroxyl(pyridyin-2-yl)methylphosphonate (Table 1, Entry 11). Colorless oil; IR: 3351, 2957, 1630, 1621, 1373; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.09–1.24 (m, 6H), 3.12 (s, OH), 3.89–4.39 (m, 4H), 4.78 (s, 1H), 6.79–6.84 (m,

2H), 7.12–7.24 (t, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.6, 63.28, 69.81, 120.44, 124.91, 135.21, 145.69, 156.61; MS m/z (ESI); 268 $(M + Na)^+$. Anal. calcd. for ($C_{10}H_{16}O_4P$): C, 48.98; H, 6.58; N, 5.71. Found: C, 48.90; H, 6.51; N, 5.68.

Diethyl hydroxy(thiophene-2-yl)methylphosphonate (Table 1, Entry 12).[20] IR: 3350, 2890, 2848, 1726, 1611, 1484, 1230 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.03–1.34 (m, 6H), 3.84 (s, OH), 3.89 (s, 1H), 4.16–4.32 (m, 4H), 6.51–6.69 (m, 2H), 7.03 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.6, 61.5, 72.3, 124.5, 126.8, 127.5, 135.8; MS m/z (ESI): 273 $(M + Na)^+$. Anal. calcd. for ($C_9H_{15}O_4PS$): C, 43.20; H, 6.04. Found: C, 43.16; H, 6.02.

Diethyl furan-2-yl(hydroxyl)methylphosphonate (Table 1, Entry 13).[20] IR: 3265, 2973, 2884, 1738, 1620 cm^{-1}, ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.2–1.42 (m, 6H), 3.85 (s, OH), 4.12 (s,1H), 4.22–4.44 (m, 4H), 6.04–6.20 (m, 2H), 7.26 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.6, 62.0, 71.9, 110.1, 112.5, 138.9, 153.4; MS m/z (ESI): 257 $(M + Na)^+$. Anal. calcd. for ($C_9H_{15}O_5P$): C, 46.16; H, 6.46. Found: C, 46.10; H, 6.39.

CONCLUSION

In conclusion, we have developed an environmentally friendly method to synthesize α-hydroxy phosphonates in good yields under neutral conditions involving supramolecular catalysis in H_2O. This method has the additional advantage that the reaction excludes highly flammable organic solvents, moisture-sensitive catalysts, and elevated reaction temperatures.

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REFERENCES

1. Dingwall, J. G.; Campell, C. D.; Baylis, E. K. Amino alkane phosphorous acids. U.K. Patent Appl. 1 542 938 **1979**; *Chem. Abstr.* **1978**, 88, 105559j.
2. Engel, R. Phosphonates as analogues of natural phosphonates. *Chem. Rev.* **1977**, *77*, 349–367.
3. Oiah, G. A.; Wu, A. Synthetic methods and reactions. 159. Preparation of 1,2-diketones from nonenolizable aliphatic and aromatic acyl chlorides with diethyl 1-alkyl(aryl)-1-(trimethylsiloxy)-methanephosphonates. *J. Org. Chem.* **1991**, *56*, 902–904.
4. Iorga, B.; Eymery, F.; Savignac, P. Controlled monohalogenation of phosphonates: A new route to pure α-monohalogenated diethyl benzylphosphonates. *Tetrahedron* **1999**, *55*, 2671–2686.
5. Ishiguri, Y.; Yamada, Y.; Kato, Y. Y.; Sasaki, M.; Mukai, K. Fungicidal composition comprising α-substituted ethylphosphinic acids or their salts, and method of preventing or curing plant diseases using them. Eur. Patent Appl. EP 82–301905, **1982**; *Chem. Abstr.* **1983**, *98*, 102686u.

6. Pokalwar, R. U.; Hangarge, R. V.; Maske, P. V.; Shingare, M. S. Synthesis and antibacterial activities of α-hydroxyphosphonates and α-acetyloxyphosphonates derived from 2-chloroquinoline-3-carbaldehyde. *Arkivoc.* **2006**, *11*, 196.
7. Patel, D. V.; Rielly-Gauvin, K.; Ryono, D. E. Preparation of peptidic α-hydroxy phosphonates a new class of transition state analog renin inhibitors. *Tetrahedron Lett.* **1990**, *31*, 5587–5590.
8. Gawron, O.; Grelecki, C.; Reilly, W.; Sands, J. Bromomagnesium salts of dialkyl phosphites as intermediates in the synthesis of substituted hydroxymethyl phosphonic acid esters. *J. Am. Chem. Soc.* **1953**, *75*, 3591–3592.
9. Texier-Boullet, F.; Lequitte, M. An unexpected reactivity of simple heterogeneous mixture of γ-alumina and potassium fluoride: 1-hydroxyalkane phosphonic esters synthesis from non-activated ketones in "dry media." *Tetrahedron Lett.* **1986**, *27*, 3515–3516.
10. Smaardijk, A. A. B.; Noorda, S.; Bolhuis, F.; Wynberg, H. The absolute configuration of α-hydroxyphosphonate. *Tetrahedron Lett.* **1985**, *26*, 493–496.
11. Blazis, V. J.; Koeller, K. J.; Spilling, C. D. Reactions of chiral phosphorous acid diamines: The asymmetric synthesis of chiral α-hydroxy phosphonamides, phosphonates, and phosphonic acids. *J. Org. Chem.* **1995**, *60*, 931–940.
12. Sardarian, A. R.; Kaboudin, B. Surface-mediated solid phase reactions: Preparation of diethyl 1-hydroxyarylmethylphosphonates on the surface magnesia. *Synth. Commun.* **1997**, *27*, 543–551.
13. Sonar, S. S. Niobium (V) Chloride catalyzed Abramov reaction: An efficient protocol for the preparation of α-hydroxy phosphonate. *Bull. Korean Chem. Soc.* **2008**, *29*, 1781–1783.
14. Pamies, O.; Backvall, J. E. An efficient route to chiral α- and β-hydroxyalkanephosphonates. *J. Org. Chem.* **2003**, *6*, 4815–4818.
15. Texier-Boullet, F.; Foucaud, A. Synthesis of 1-hydroxyalkanephosphonic esters on alumina. *Synthesis* **1982**, 916.
16. Yokomatsu, T.; Yamagishi, T.; Shibuya, S. Enantioselective synthesis of α-hydroxyphosphonates through asymmetric Pudovik reactions with chiral lanthanoid and titaniumalkoxide. *J. Chem. Soc. Perkin Trans. 1* **1997**, 1527–1534.
17. Azizi, N.; Saidi, M. R. Lithium perchlorate diethyl ether solution: A highly efficient media for the abramov reaction. *Phosphorus, Sulfur, Silicon Relat. Elem.* **2003**, *178*, 1255–1259.
18. Heydari, A.; Arefi, A.; Khaksar, S.; Tajbakhsh, M. Hydrophosphonylation of aldehydes catalyzed byguanidine hydrochloride in water. *Catal. Commun.* **2006**, *7*, 982–984.
19. Murthy, S. N.; Madhav, B.; Reddy, V. P.; Nageswar, Y. V. D. One-pot synthesis of 2-amino-4H-chromen-4-yl phosphonate derivatives using β-cyclodextrin as reusable catalyst in water. *Tetrahedron Lett.* **2010**, *51*, 3649–3653.
20. Zhou, X.; Liu, X.; Yang, X.; Shang, D.; Xin, J.; Feng, X. Highly enantioselective hydrophosphonylation of aldehydes catalyzed by tridentate schiff base aluminum(III) complexes. *Angew. Chem. Int. Ed.* **2008**, *47*, 392–394.