

# Green Synthesis of $\alpha$ -acetoxyphosphonate Derivatives by using ChCl/ 2ZnCl<sub>2</sub> Assolvent from 2-chloro Quinolines 3-carbaldehyde and Triethylphosphite

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**Abstract:** A series of bioactive  $\alpha$ -hydroxyphosphonate (2a-i) and  $\alpha$ -acetoxyphosphonate (3a-i) derivatives have been synthesized for the first time by applying green approach benign choline chloride based ZnCl<sub>2</sub> a deep eutectic mixture was employed as an efficient and green ionic liquid catalyst for solvent free condition at room temperature. The current approach to generate sustainable solvent / catalyst in place of volatile organic compounds to 2-chloroquinoline-3-carbaldehyde (1a-i) with triethylphosphite. The reaction is furnished in short time and products were obtained in good yield. Elemental analysis, IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and mass spectral data elucidated the structures of all newly synthesized compounds.

**Keywords:**  $\alpha$ -hydroxyphosphonates,  $\alpha$ -acetoxyphosphonate, deep eutectic mixture, volatile organic compounds.

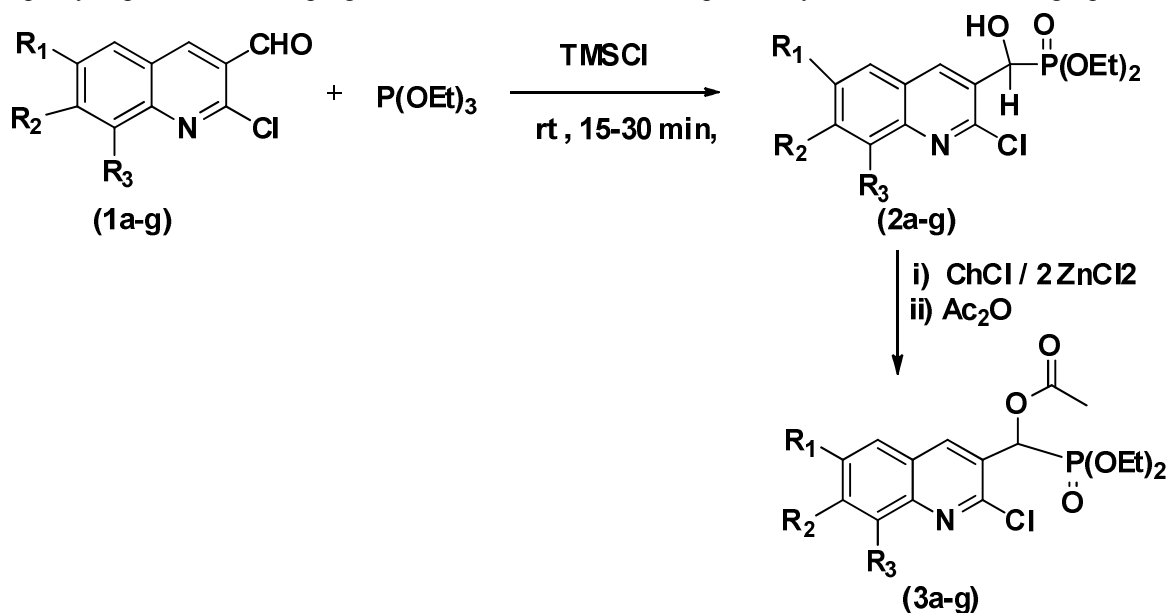
## I. INTRODUCTION

Organo phosphorous compounds are of extraordinary importance with regard to their versatile applications in pharmaceutical industries<sup>[1]</sup>, functionalized materials<sup>[2]</sup> and synthetic chemistry<sup>[3]</sup>. A broad array of natural phosphorus constructed biologically active composites which works important roles as metabolic intermediates as common regulatory knobs for proteins and as a fortitude for the genetic acquaintance.<sup>[4]</sup> Particularly, hydroxyphosphonates have elicited considerable interest of chemists due to their capable pharmacological effects as inhibitors of human rennin<sup>[5a]</sup> and HIV protease<sup>[5b]</sup>, antitumor<sup>[5c]</sup>, antibacterial<sup>[5d]</sup>, antiviral<sup>[5e]</sup> and antioxidant agents.<sup>[5f]</sup> Much of these activities has been credited to the relatively passive nature of the C-P bond and to the physical and structural resemblance of phosphonic and phosphonic acids to the biologically important phosphate ester and carboxylic acid functionality.<sup>[6]</sup> Furthermore,  $\alpha$ -hydroxy phosphonates are valuable precursors for the preparation of  $\alpha$ -functionalized phosphonates, for instance amino, keto, halo, and acetoxy phosphonates.<sup>[7a-d]</sup> The quinoline nucleus are significant components of pharmacologically efficient synthetic compounds can also be frequently known in the structure of several naturally occurring alkaloids with broad spectrum of biological activities.<sup>[8a-b]</sup>  $\alpha$ -acetoxyphosphonates are considered as vital and valuable phosphorus compounds for the synthesis of optically active  $\alpha$ -hydroxyphosphonates.

DESs are counta new class of ionic liquid referents, and they can typically be derived from inexpensive, commercially available raw materials. DESs can potentially be less costly and more environmentally benign when compared with traditional ionic liquids.<sup>[9 a-b]</sup> A DES composed of choline chloride (ChCl) and oxalic acid dihydrate was able to achieve the partial dissolution of the non-crystalline parts of cellulose and liberated cellulose nanocrystals after mechanical treatment. An effective O-acetylation of cellulose and chitin was also studied using a Lewis acid DES of ChCl-ZnCl<sub>2</sub>.<sup>[10]</sup> Therefore, many synthetic methods for the construction  $\alpha$ -acetoxyphosphonate in the presence of DES choline chloride in ZnCl<sub>2</sub> have been proposed in present research report.

## II. EXPERIMENTAL SECTION GENERAL PROCEDURES

2-Chloroquinoline-3-carbaldehydes were prepared in the laboratory by the reported method.<sup>[11]</sup>  $\text{CHCl}_3\text{-SnCl}_4[\text{DES}]^{[12]}$  triethylphosphite, were procured from Sigma- Aldrich. All melting points were determined in open capillaries on Kumar's melting point apparatus. The products were characterized by their spectral data.  $^1\text{H}$  NMR spectra were recorded on Varian INOVA-500 (500 MHz) spectrometer. Chemical shifts are reported in ppm from the solvent resonance as the TMS as an internal standard. IR spectra were recorded on a Perkin-Elmer FTIR. Mass spectra were recorded on Micro mass Quattro using electrospray Ionization technique, showing (m+1) peak as a base peak. The test for the purity of products and the progress of the reactions were accomplished by TLC on Merck silica gel plates.



### Scheme: Synthesis of [ 3a-j ] and (2a-j) from [1a-j] by using DES

**General procedure. Diethyl (2 -chloro-quinolin-3-yl) (hydroxy) methylphosphonate (2a).** A mixture of 2-chloroquinoline-3-carbaldehyde (0.95 gm, 5 mmol) and triethylphosphite (1.66 gm, 10 mmol) in 40ml  $\text{CHCl}_3\text{-2ZnCl}_2$  was at room temperature few drops of chloro(trimethyl)silane (0.05 gm, 3mmol) was added to the solution. Progress of reaction was monitored on TLC. After completion of reaction (20 min.), the mixture was concentrated on rotary-evaporator under reduced pressure, to obtain an oily residue. The oily residue was dissolved in methanol for the removal of TMSCl. This methanolic solution was concentrated, dissolved in dichloromethane and reprecipitated with hexane. Thus, obtained solid was filtered, washed with hexane and dried in oven at  $40^\circ\text{C}$  (1.41 gm) IR (KBr),  $\text{cm}^{-1}$ : 3249 (- OH); 1217 (- P=O); 1017 (-P-O-C).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$  ppm: 1.1 (t, 3H, O- $\text{CH}_2\text{-CH}_3$ ); 1.2 (t, 3H, O- $\text{CH}_2\text{-CH}_3$ ); 2.0 (s, 1H, -CH-OH); 4.3 (m, 4H, O- $\text{CH}_2\text{-CH}_3$  and OCH $_2\text{-CH}_3$ ); 5.5 (d, 1H, -CH-P=O); 7.6 (t, 1H, Ar-H, C $_6$ ); 7.8 (t, 1H, Ar-H, C $_7$ ); 7.7 (d, 1H, Ar-H, C $_5$ ); 8.2 (d, 1H, Ar-H, C $_8$ ); 8.7 (s, 1H, Ar-H, C $_4$ ). ES-MS: m/z 330 (m+1) base peak and 331.9 (m+3). Elemental analysis:  $\text{C}_{14}\text{H}_{17}\text{ClNO}_4\text{P}$  Calcd.: C: 51.25 %, H: 5.15 %, N: 4.27 %; Found: C: 51.36 %, H: 5.72 %, N: 4.523 %.

| Sr. NO | R $_1$   | R $_2$  | R $_3$  | Yield (%) | MP ( $^\circ\text{C}$ )  | Sr. NO | Yield (%) | MP ( $^\circ\text{C}$ ) |
|--------|----------|---------|---------|-----------|--------------------------|--------|-----------|-------------------------|
| 2a     | H        | H       | H       | 93.2      | 128-130 $^\circ\text{C}$ | 3a     | 96.2      | 91-93 $^\circ\text{C}$  |
| 2b     | CH $_3$  | H       | H       | 88.8      | 145-147 $^\circ\text{C}$ | 3b     | 93.5      | 83-85 $^\circ\text{C}$  |
| 2c     | H        | CH $_3$ | H       | 92.2      | 141-143 $^\circ\text{C}$ | 3c     | 94.3      | 87-89 $^\circ\text{C}$  |
| 2d     | H        | H       | CH $_3$ | 86.5      | 172-174 $^\circ\text{C}$ | 3d     | 89.5      | 98-100 $^\circ\text{C}$ |
| 2e     | OCH $_3$ | H       | H       | 94.1      | 156-160 $^\circ\text{C}$ | 3e     | 92.1      | 96-98 $^\circ\text{C}$  |

|    |   |                  |                  |      |            |    |      |          |
|----|---|------------------|------------------|------|------------|----|------|----------|
| 2f | H | OCH <sub>3</sub> | H                | 91.2 | 166-170 °C | 3f | 88.5 | 98-99 °C |
| 2g | H | H                | OCH <sub>3</sub> | 84.2 | 149-151 °C | 3g | 78.6 | 82-85 °C |

**Diethyl(2-chloro-6-methylquinolin-3-yl)(hydroxy)methylphosphonate (2b).** IR (KBr), cm<sup>-1</sup>: 3255 (-OH); 1229 (-P=O); 1045 (-P-O-C). <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ ppm: 1.2 (t, 3H, O-CH<sub>2</sub>-CH<sub>3</sub>); 1.3 (t, 3H, O-CH<sub>2</sub>-CH<sub>3</sub>); 2.4 (s, 1H, -CH-OH); 2.6 (s, 3H, ArCH<sub>3</sub>); 4.2 (q, 2H, O-CH<sub>2</sub>-CH<sub>3</sub>); 4.3 (q, 2H, O-CH<sub>2</sub>-CH<sub>3</sub>); 5.7 (d, 1H, CH-P=O); 7.4 (s, 1H, Ar-H, C<sub>5</sub>); 7.5 (d, 1H, Ar-H, C<sub>7</sub>); 7.8 (d, 1H, Ar-H, C<sub>8</sub>); 8.5 (s, 1H, Ar-H, C<sub>4</sub>). ES-MS: m/z 344 (m+1) base peak and 345.9 (m+3). Elemental analysis: C<sub>15</sub>H<sub>19</sub>ClNO<sub>4</sub>P Calcd.: C: 52.41 %, H: 5.57 %, N: 4.07 %; Found: C: 52.431 %, H: 5.470%, N: 4.157 %.

**Diethyl(2-chloro-8-methylquinolin-3-yl)(hydroxy)methylphosphonate (2c).** IR (KBr) cm<sup>-1</sup>: 3242 (-OH); 1221 (-P=O); 1035 (-P-O-C). <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ ppm: 1.1 (t, 3H, O-CH<sub>2</sub>-CH<sub>3</sub>); 1.2 (t, 3H, O-CH<sub>2</sub>-CH<sub>3</sub>); 2.3 (s, 1H, -CH-OH); 2.6 (s, 3H, ArCH<sub>3</sub>); 4.1 (q, 2H, O-CH<sub>2</sub>-CH<sub>3</sub>); 4.2 (q, 2H, O-CH<sub>2</sub>-CH<sub>3</sub>); 5.7 (d, 1H, CH-P=O); 7.3 (t, 1H, Ar-H, C<sub>6</sub>); 7.5 (d, 1H, Ar-H, C<sub>5</sub>); 7.7 (d, 1H, Ar-H, C<sub>7</sub>); 8.6 (s, 1H, Ar-H, C<sub>4</sub>). ES-MS: m/z 344 (m+1) base peak and 346 (m+3). Elemental analysis: C<sub>15</sub>H<sub>19</sub>ClNO<sub>4</sub>P Calcd.: C: 52.42 %, H: 5.58 %, N: 4.05 %; Found: C: 52.61 %, H: 5.63 %, N: 4.18 %.

**Diethyl (2-chloro-6-methoxyquinolin-3-yl)(hydroxy)methylphosphonate (2d).** IR (KBr) cm<sup>-1</sup>: 3271 (-OH); 1225 (-P=O); 1038 (-P-O-C). <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ ppm: 1.2 (t, 3H, O-CH<sub>2</sub>-CH<sub>3</sub>); 1.3 (t, 3H, O-CH<sub>2</sub>-CH<sub>3</sub>); 2.6 (s, 1H, -CH-OH); 3.8 (s, 3H, ArO-CH<sub>3</sub>); 4.1 (q, 2H, O-CH<sub>2</sub>-CH<sub>3</sub>); 4.2 (q, 2H, O-CH<sub>2</sub>-CH<sub>3</sub>); 5.6 (d, 1H, CH-P=O); 7.0 (s, 1H, ArH, C<sub>5</sub>); 7.4 (d, 1H, Ar-H, C<sub>7</sub>); 7.9 (d, 1H, Ar-H, C<sub>8</sub>); 8.5 (s, 1H, Ar-H, C<sub>4</sub>). ES-MS: m/z 360 (m+1) base peak and 362 (m+3). Elemental analysis: C<sub>15</sub>H<sub>19</sub>ClNO<sub>5</sub>P Calcd.: C: 50.08 %, H: 5.32 %, N: 3.89 %; Found: C: 50.22 %, H: 5.41 %, N: 3.97 %.

**Diethyl(2-chloro-7-methoxyquinolin-3-yl)(hydroxy)methylphosphonate (2e).** IR (KBr) cm<sup>-1</sup>: 3258 (-OH); 1226 (-P=O); 1037 (-P-O-C). <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ ppm: 1.2 (t, 3H, O-CH<sub>2</sub>-CH<sub>3</sub>); 1.3 (t, 3H, O-CH<sub>2</sub>-CH<sub>3</sub>); 2.6 (s, 1H, -CH-OH); 3.8 (s, 3H, ArO-CH<sub>3</sub>); 4.2 (q, 2H, O-CH<sub>2</sub>-CH<sub>3</sub>); 4.3 (q, 2H, O-CH<sub>2</sub>-CH<sub>3</sub>); 5.7 (d, 1H, CH-P=O); 7.3 (d, 1H, Ar-H, C<sub>6</sub>); 7.5 (s, 1H, Ar-H, C<sub>8</sub>); 7.7 (d, 1H, Ar-H, C<sub>5</sub>); 8.5 (s, 1H, Ar-H, C<sub>4</sub>). ES-MS: m/z 343.9 (m+1) base peak and 346 (m+3). Elemental analysis: C<sub>15</sub>H<sub>19</sub>ClNO<sub>5</sub>P Calcd.: C: 50.08 %, H: 5.32 %, N: 3.89 %; Found: C: 50.188 %, H: 5.445 %, N: 4.312%.

**Diethyl (2-chloro-6-ethoxyquinolin-3-yl)(hydroxy)methylphosphonate (2f).** IR (KBr) cm<sup>-1</sup>: 3261 (-OH); 1243 (-P=O); 1051 (-P-O-C). <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ ppm: 1.2 (t, 3H, O-CH<sub>2</sub>-CH<sub>3</sub>); 1.3 (t, 3H, O-CH<sub>2</sub>-CH<sub>3</sub>); 1.4 (t, 3H, Ar-O-CH<sub>2</sub>-CH<sub>3</sub>); 3.3 (bs, 1H, -CH-OH); 4.3 (q, 2H, O-CH<sub>2</sub>-CH<sub>3</sub>); 4.5 (q, 2H, O-CH<sub>2</sub>-CH<sub>3</sub>); 4.4 (q, 2H, O-CH<sub>2</sub>-CH<sub>3</sub>); 5.6 (d, 1H, CH-P=O); 7.0 (s, 1H, Ar-H, C<sub>5</sub>); 7.5 (d, 1H, Ar-H, C<sub>7</sub>); 7.9 (d, 1H, Ar-H, C<sub>8</sub>); 8.4 (s, 1H, ArH, C<sub>4</sub>). ES-MS: m/z 374 (m+1) base peak and 376 (m+3). Elemental analysis: C<sub>16</sub>H<sub>21</sub>ClNO<sub>5</sub>P Calcd.: C: 51.41 %, H: 5.66 %, N: 3.75 %; Found: C: 51.535 %, H: 5.789 %, N: 3.92 %.

**Diethyl (2-chloro-8-ethylquinolin-3-yl)(hydroxyl)methylphosphonate (2g).** IR (KBr) cm<sup>-1</sup>: 3259 (-OH); 1229 (-P=O); 1048 (-P-O-C). <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ ppm: 1.2 (t, 3H, O-CH<sub>2</sub>-CH<sub>3</sub>); 1.35 (m, 6H, O-CH<sub>2</sub>-CH<sub>3</sub> and Ar-CH<sub>2</sub>-CH<sub>3</sub>); 2.3 (s, 1H, -CHOH); 3.25 (q, 2H, Ar-CH<sub>2</sub>-CH<sub>3</sub>); 4.2 (m, 4H, O-CH<sub>2</sub>-CH<sub>3</sub> and O-CH<sub>2</sub>-CH<sub>3</sub>); 5.6 (d, 1H, CH-P=O); 7.4 (t, 1H, Ar-H, C<sub>6</sub>); 7.6 (d, 1H, Ar-H, C<sub>7</sub>); 7.8 (d, 1H, Ar-H, C<sub>8</sub>); 8.4 (s, 1H, Ar-H, C<sub>4</sub>). ES-MS: m/z 358 (m+1) base peak and 360 (m+3). Elemental analysis: C<sub>16</sub>H<sub>21</sub>ClNO<sub>4</sub>P Calcd.: C: 53.71 %, H: 5.92 %, N: 3.92 %; Found: C: 53.92 %, H: 5.75 %, N: 4.10 %.

**Diethyl acetoxyl(2-chloro-quinolin-7-yl)methylphosphonate (3a).** To the stirring mixture of diethyl (2-chloro-quinolin-3-yl) (hydroxy) methylphosphonate (0.49 gm, 1.5 mmol) and acetic anhydride (0.45 gm, 4.5 mmol), 15ml CHCl<sub>3</sub>-2ZnCl<sub>2</sub> was added the reaction mixture was stirred at room temperature. Progress of reaction was monitored on TLC. After completion of reaction (7 min.), reaction mixture was poured on crushed ice and stirred to get a solid product. The obtained solid was filtered and washed with water, dried in oven at 40 °C (0.53gm) IR (KBr) cm<sup>-1</sup>: 1769cm<sup>-1</sup> (-O-CO-CH<sub>3</sub>); 1227cm<sup>-1</sup> (-P=O); 1018cm<sup>-1</sup> (-P-O-C). <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ ppm: 1.2 (t, 3H, OCH<sub>2</sub>-CH<sub>3</sub>); 1.3 (t, 3H, O-CH<sub>2</sub>-CH<sub>3</sub>); 2.2 (s, 3H, O-CO-CH<sub>3</sub>); 4.1 (q, 2H, O-CH<sub>2</sub>-CH<sub>3</sub>); 4.2 (q, 2H, O-CH<sub>2</sub>-CH<sub>3</sub>); 6.5 (d, 1H, -CH-P=O); 7.5 (t, 1H, Ar-H, C<sub>6</sub>); 7.7 (t, 1H, Ar-H, C<sub>7</sub>); 7.8 (d, 1H, Ar-H, C<sub>5</sub>); 8.1 (d, 1H, Ar-H, C<sub>8</sub>); 8.4 (s, 1H, Ar-H, C<sub>4</sub>). ES-MS: m/z

372 (m+1) base peak and 374 (m+3). Elemental analysis: C<sub>16</sub>H<sub>19</sub>ClNO<sub>5</sub>P Calcd.: C: 51.65 %, H: 5.15 %, N: 3.772 %; Found: C: 51.851 %, H: 5.312 %, N: 3.912 %.

**Diethyl acetoxy(2-chloro-6-methylquinolin-3-yl)methylphosphonate (3b).** IR (KBr) cm<sup>-1</sup>: 1749 (-O-CO-CH<sub>3</sub>); 1214 (-P=O); 1019(-P-O-C). <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ ppm: 1.2 (t, 3H, O-CH<sub>2</sub>-CH<sub>3</sub>); 1.3 (t, 3H, O-CH<sub>2</sub>-CH<sub>3</sub>); 2.2 (s, 3H, O-CO-CH<sub>3</sub>); 2.5 (s, 3H, ArCH<sub>3</sub>); 4.2 (q, 2H, O-CH<sub>2</sub>-CH<sub>3</sub>); 4.2 (q, 2H, O-CH<sub>2</sub>-CH<sub>3</sub>); 6.6 (d, 1H, -CH-P=O); 7.5 (d, 1H, ArH, C<sub>7</sub>); 7.6 (s, 1H, Ar-H, C<sub>5</sub>); 7.9 (d, 1H, Ar-H, C<sub>8</sub>); 8.4 (s, 1H, Ar-H, C<sub>4</sub>). ES-MS: m/z 386 (m+1) base peak and 388 (m+3). Elemental analysis: C<sub>17</sub>H<sub>21</sub>ClNO<sub>5</sub>P Calcd.: C: 52.93 %, H: 5.49 %, N: 3.63 %; Found: C: 53.728 %, H: 5.46 %, N: 3.162 %.

**Diethyl acetoxy(2-chloro-8-methylquinolin-3-yl)methylphosphonate (3c).** IR (KBr) cm<sup>-1</sup>: 1758 (-O-CO-CH<sub>3</sub>); 1215 (-P=O); 1046(-P-O-C). <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ ppm: 1.2 (t, 3H, O-CH<sub>2</sub>-CH<sub>3</sub>); 1.3 (t, 3H, O-CH<sub>2</sub>-CH<sub>3</sub>); 2.2 (s, 3H, O-CO-CH<sub>3</sub>); 2.7 (s, 3H, Ar-CH<sub>3</sub>); 4.2 (q, 2H, O-CH<sub>2</sub>-CH<sub>3</sub>); 4.5 (q, 2H, O-CH<sub>2</sub>-CH<sub>3</sub>); 6.8 (d, 1H, -CH-P=O); 7.5 (t, 1H, Ar-H, C<sub>6</sub>); 7.6 (d, 1H, Ar-H, C<sub>7</sub>); 7.7 (d, 1H, Ar-H, C<sub>5</sub>); 8.5 (s, 1H, Ar-H, C<sub>4</sub>). ES-MS: m/z 386 (m+1) base peak and 388.1 (m+3). Elemental analysis: C<sub>17</sub>H<sub>21</sub>ClNO<sub>5</sub>P Calcd.: C: 52.93 %, H: 5.49 %, N: 3.63 %; Found: C: 52.981 %, H: 5.615 %, N: 3.820 %.

**Diethyl acetoxy(2-chloro-6-methoxyquinolin-3-yl)methylphosphonate (3d).** IR (KBr) cm<sup>-1</sup>: 1749 (-O-CO-CH<sub>3</sub>); 1234(-P=O); 1046 (-P-O-C). <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ ppm: 1.2 (t, 3H, O-CH<sub>2</sub>-CH<sub>3</sub>); 1.3 (t, 3H, O-CH<sub>2</sub>-CH<sub>3</sub>); 2.1 (s, 3H, O-CO-CH<sub>3</sub>); 3.8 (s, 3H, Ar-O-CH<sub>3</sub>); 4.1(q, 2H, O-CH<sub>2</sub>-CH<sub>3</sub>); 4.3 (q, 2H, O-CH<sub>2</sub>-CH<sub>3</sub>); 6.7 (d, 1H, -CH-P=O); 7.2 (s, 1H, Ar-H, C<sub>5</sub>); 7.5 (d, 1H, Ar-H, C<sub>7</sub>); 7.8 (d, 1H, Ar-H, C<sub>8</sub>); 8.3 (s, 1H, Ar-H, C<sub>4</sub>). ESMS: m/z 402 (m+1) base peak and 405(m+3). Elemental analysis: C<sub>17</sub>H<sub>21</sub>ClNO<sub>6</sub>P Calcd.: C: 50.82 %, H: 5.27 %, N: 3.49 %; Found: C: 51.247 %, H: 5.748 %, N: 3.412%.

**Diethyl acetoxy(2-chloro-7-methoxyquinolin-3-yl)methylphosphonate (3e).** IR (KBr) cm<sup>-1</sup>: 1765 (-O-CO-CH<sub>3</sub>); 1207 (-P=O); 1051 (-P-O-C). <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ ppm: 1.2 (t, 3H, O-CH<sub>2</sub>-CH<sub>3</sub>); 1.3 (t, 3H, O-CH<sub>2</sub>-CH<sub>3</sub>); 2.2 (s, 3H, O-CO-CH<sub>3</sub>); 4.2 (s, 3H, Ar-O-CH<sub>3</sub>); 4.3 (q, 2H, O-CH<sub>2</sub>-CH<sub>3</sub>); 4.5 (q, 2H, O-CH<sub>2</sub>-CH<sub>3</sub>); 6.7 (d, 1H, -CH-P=O); 7.3 (d, 1H, Ar-H, C<sub>6</sub>); 7.5(s, 1H, Ar-H, C<sub>8</sub>); 7.8(d,1H, Ar-H, C<sub>5</sub>); 8.5 (s, 1H, Ar-H, C<sub>4</sub>). ES-MS: m/z 402 (m+1) base peak and 403.9 (m+3). Elemental analysis: C<sub>17</sub>H<sub>21</sub>ClNO<sub>6</sub>P Calcd.: C: 50.82 %, H: 5.27 %, N: 3.49 %; Found: C: 50.855 %, H: 5.446 %, N: 3.13

**Diethyl acetoxy(2-chloro-6-ethoxyquinolin-3-yl)methylphosphonate (3f).** IR (KBr) cm<sup>-1</sup>: 1765 (-O-CO-CH<sub>3</sub>); 1224 (-P=O); 1030 (-P-O-C). <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ ppm: 1.2 (t, 3H, O-CH<sub>2</sub>-CH<sub>3</sub>); 1.3 (m, 6H, O-CH<sub>2</sub>-CH<sub>3</sub> and Ar-O-CH<sub>2</sub>-CH<sub>3</sub>); 2.2 (s, 3H, O-CO-CH<sub>3</sub>); 3.1 (q, 2H, Ar-O-CH<sub>2</sub>-CH<sub>3</sub>); 4.1 (q, 2H, O-CH<sub>2</sub>-CH<sub>3</sub>); 4.3 (q, 2H, O-CH<sub>2</sub>-CH<sub>3</sub>); 6.5 (d, 1H, -CH-P=O); 7.3 (t, 1H, Ar-H, C<sub>6</sub>); 7.5 (d, 1H, Ar-H, C<sub>7</sub>); 7.8 (d, 1H, Ar-H, C<sub>5</sub>); 8.3(s, 1H, Ar-H, C<sub>4</sub>). ES-MS: m/z 416 (m+1) base peak and 418 (m+3). Elemental analysis: C<sub>18</sub>H<sub>23</sub>ClNO<sub>6</sub>P Calcd.: C: 51.99 %, H: 5.58 %, N: 3.37 %; Found: C: 52.42 %, H: 5.45 %, N: 3.74 %.

**Diethyl acetoxy (2-chloro-8-ethylquinolin-3-yl) methylphosphonate (3g).** IR (KBr) cm<sup>-1</sup>: 1762 (-O-CO-CH<sub>3</sub>); 1232(-P=O); 1041(-P-O-C). <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ ppm: 1.2 (t, 3H, O-CH<sub>2</sub>-CH<sub>3</sub>); 1.3 (m, 6H, O-CH<sub>2</sub>-CH<sub>3</sub> and Ar-CH<sub>2</sub>-CH<sub>3</sub>); 2.3 (s, 3H, O-CO-CH<sub>3</sub>); 3.2 (q, 2H, Ar-CH<sub>2</sub>-CH<sub>3</sub>); 4.0 (q, 2H, O-CH<sub>2</sub>-CH<sub>3</sub>); 4.4 (q, 2H, O-CH<sub>2</sub>-CH<sub>3</sub>); 6.6 (d, 1H, -CH-P=O); 7.4 (t, 1H, Ar-H, C<sub>6</sub>); 7.6 (d, 1H, Ar-H, C<sub>7</sub>); 7.7 (d, 1H, Ar-H, C<sub>5</sub>); 8.4 (s, 1H, Ar-H, C<sub>4</sub>). ES-MS: m/z 400.1 (m+1) base peak and 402 (m+3). Elemental analysis: C<sub>18</sub>H<sub>23</sub>ClNO<sub>5</sub>P Calcd.: C: 54.07 %, H: 5.80 %, N: 3.50 %; Found: C: 54.313 %, H: 5.991 %, N: 3.624 %.

### III. RESULT AND DISCUSSION

DESs can potentially be less costly and more environmentally benign when compared with traditional ionic liquids. A DES composed of choline chloride (ChCl) and ZnCl<sub>2</sub> an effective O-acetylation of cellulose and chitin was reported earlier. α-acetoxyphosphonate in the presence of DES choline chloride in ZnCl<sub>2</sub> have been reported with excellent yield, short Time duration and especially eco- friendly catalyst/solvent

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