Polymer supported sulfanilic acid: A highly efficient and recyclable green heterogeneous catalyst for the construction of 4,5 dihydropyrano[3,2-c]chromenes under solvent free condition.

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## Abstract

Polystyrene divinylbenzene supported sulfanilic acid was prepared, characterized and tested as an acidic catalyst in multicomponent organic synthesis. This is the first report focusing on the development of one-pot solvent free synthesis of 4,5-dihydropyrano [3,2-c]chromenes under acidic conditions. It proved to be a versatile catalyst for microwave assisted synthesis of 4,5dihydropyrano[3,2-c]chromenes. This methodology is mild, high yielding, green and the catalyst could be easily recycled for several times.

Keywords Heterogeneous catalyst; microwave; chromenes; solvent free; multicomponent

## **1. Introduction**

The development of multi-component reactions (MCRs) designed to produce multifaceted biologically active compounds. It has become an important area of research in organic and medicinal chemistry.<sup>1-4</sup> Dihydropyrano [3,2-c]chromenes and their derivatives are of considerable interest as they possess a broad spectrum of biological and pharmaceutical

properties<sup>5</sup> such as antidyslipidemic,<sup>6</sup> anticancer,<sup>7</sup> antimalarial,<sup>8</sup> molluscicidal,<sup>9</sup> antiinflammatory<sup>10</sup>. These derivatives widely employed as pigments<sup>11</sup> and potential biodegradable agrochemicals<sup>12</sup>.

To date, a wide variety of lewis base or basic catalyst have been efficiently promoted the synthesis of 4,5-dihydropyrano[3,2-c]chromenes such as nano ZnO,<sup>13</sup> Diammonium hydrogen phosphate,<sup>14</sup> DBU,<sup>15</sup> TBAB,<sup>16</sup> KAl(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O,<sup>17</sup> TMGT,<sup>18</sup> MgO,<sup>19</sup> K<sub>2</sub>CO<sub>3</sub>,<sup>20</sup> pyridine,<sup>21</sup> [bmim]OH,<sup>22</sup> Morpholine<sup>23</sup>. More recently, a one-pot three component reaction of 4,5-dihydropyrano[3,2-c]chromenes promoted by DMAP<sup>24</sup> was also reported.

Recently the use of heterogeneous catalyst has received considerable attention due to their operational advantages such as insolubility in organic solvent as well as in water. It can be easily recovered from reaction media and creates least hazard to environment. However, certain limitations of heterogeneous catalysis are frequently encountered, such as lower efficiency or selectivity compared to that of homogeneous systems.<sup>25-27</sup> To improve these properties, a variety of polymer-supported heterogeneous catalysts have been devised in recent years.<sup>28-30</sup>

Despite of extensive studies on the reported reactions in the literature, to the best of our knowledge, there is no report focusing on the development of one-pot solvent free synthesis of Dihydropyrano [3,2-c]chromenes under acidic conditions using polymer supported acid catalyst. During the course of our studies on catalytic reactions<sup>31-40</sup> here in this letter, we disclose a simple method for surface modification and functionalization of cross-linked polystyrene-divinyl benzene with sulfanilic acid and used as a catalyst in microwave assisted rapid, high yielding, and green synthetic protocol for synthesis of pyran annulated heterocycles (Scheme 1).

## <Scheme 1>

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