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# SYNTHESIS OF BIOACTIVE POLYHYDROQUINOLINES USING SULFATED TIN OXIDE AS AN EFFICIENT SOLID SUPERACID CATALYST

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**ABSTRACT**

A novel synthetic scheme has been designed for the synthesis of polyhydroquinoline derivatives via one-pot condensation of aromatic aldehydes, EAA, dimedone, and $NH_4OAc$ by employing synthesized STO as a heterogeneous solid acid catalyst in ethanol under reflux condition. FTIR, XRD, and SEM EDX were used to confirm the sulfated tin oxide. BET plots were used to analyze the surface area of the catalyst. The reactions were assessed for diverse solvents and catalyst loading. The yields of all the polyhydroquinoline derivatives were found to range between 80 to 92%. All the synthesized polyhydroquinolines were validated by spectral data. This exercise is efficient and green as it uses an environmentally friendly catalyst, has a significant atom economy, is cost-effective and easy to work up.

**Keywords:** STO, Aromatic Aldehydes, Ethyl Acetoacetate, Dimedone, Ethanol, Polyhydroquinolines, Reflux.
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## INTRODUCTION

In current synthetic organic chemistry, multi-component reactions have appeared as effective and stunning techniques that provide the spectacular creation of many new bonds in a single pot. It also provides substantial advantages over orthodox linear type synthesis having extraordinary atom economy, ease of implementation, and broad application character. Research in academia and industry has highly accentuated the use of MCRs for a comprehensive range of products.[1] For the synthesis of 1,4-dihydropyridine, the Hantzsch reaction is trademarked as a one-pot, three and four-component procedure. Symmetrical and unsymmetrical 1,4-DHP compounds were produced using a range of substituted 1,3-dicarbonyl and β-ketoesters compounds.[2-3] Among those 1,4-DHP compounds, substituted polyhydroquinoline derivatives have piqued the curiosity of chemists due to their amazing biological properties, such as being calcium antagonists.[4] 2, 4-disubstituted PHQs exhibit potential as lipid modulating and anti-hyperglycemic agents.[5] Polyhydroquinoline is an essential structural design in the formulation of medications for the treatment of hypertension and other cardiovascular disorders. These molecules reveal antibacterial, antifungal, antituberculosis, and anticoagulant properties.[6] PHQ derivatives exhibit assets such as antiatherosclerotic, antitumor, vasodilator, bronchodilator, hepatoprotective activity, and geroprotective.[7] Additionally, it has been demonstrated that polyhydroquinolines reduce cellular tau levels, suggesting that they may be useful in the search for Alzheimer's disease treatments.[8] Recognizing the significance of polyhydroquinoline derivatives in the production of several drugs, numerous protocols were reported. A reformed Hantzsch reaction comprising the multi-component combination of an aldehyde with a β-ketoester, a diketone, and ammonium acetate is the most popular method for producing polyhydroquinolines.

The synthetic methodologies stated involving the catalyst such as ceric ammonium nitrate,[9] Baker's yeast,[10] Metal triflates,[11] zeolites,[12] organocatalysts,[13] thiourea dioxide,[14] thiazolium ion,[15] triphenyl phosphine,[16] $GaCl_3$,[17] $Al_2(SO_4)_3$,[18] $I_2$[19] and metal oxide NPs.[20] PHQs synthesis without a catalyst has been reported, although the processes take a very long time to respond.[21] There have also been described solvent and catalyst-free processes that involve grinding the reaction mixtures.[22] However, these methods are not


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always effective and need the consumption of a solvent for product segregation. PHQs have also been produced using microwave irradiation.[23] The enantioselective synthesis PHQs have been proposed using an organocatalyst derived from phosphoric acid.[24]

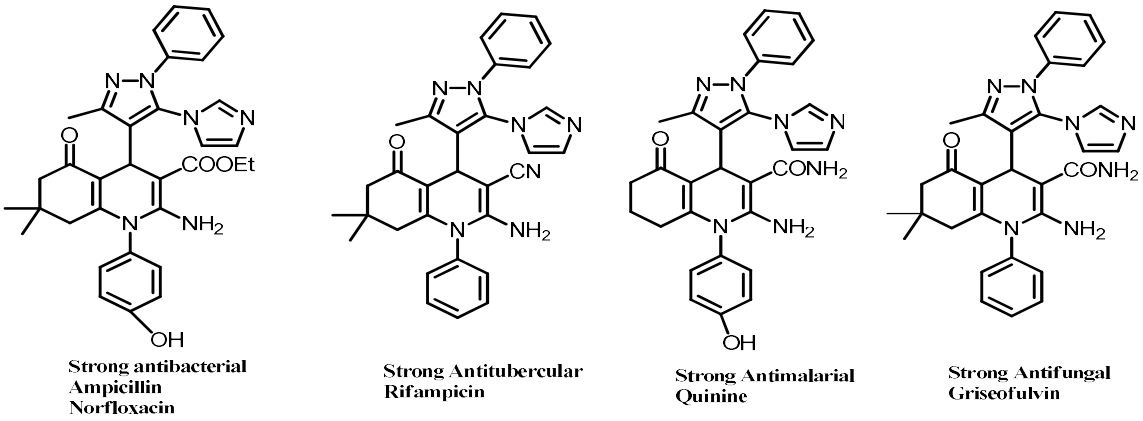
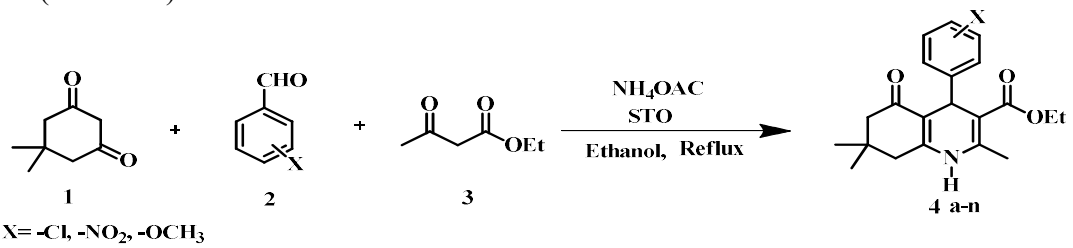



Fig.-1: Drug Scaffolds Comprising of PHQ Nucleus

The sulfated tin oxide (STO) catalyst has a number of benefits, including sample preparation, nontoxicity, affordability, excellent selectivity, environmental friendliness, good yield, and stability in air, moisture, and heat.[25] In spite of the above efforts to progress the polyhydroquinolines synthesis, a number of shortcomings have been noticed like low yield, extended reaction time, tedious workup practice, and perilous solvents. We have synthesized sulfated tin oxide NPs and investigated their potential for use in synthetic processes as part of our research on the formulation of environmentally friendly synthetic techniques and taking into account the catalytic benefits of STO. We have designed a practical and green approach for the production of polyhydroquinolines employing STO as a solid heterogeneous superacid catalyst in ethanol under reflux conditions (Scheme-1).




Scheme-1: Synthesis of PHQ Derivatives

## EXPERIMENTAL

### Material and Methods

The reagents used were all obtainable from stores. Distillation was used to clean up the solvents used in chromatography. Aluminum plates covered with silica gel were used to perform the TLC analysis on the reactions. We measured the melting points of the synthesized goods. IR and $^1$H NMR spectroscopy was used to identify every molecule that was produced. Tetramethylsilane was used as a reference in $CDCl_3$ and $^1$H NMR measurements were taken using a Bruker Advance II 400 MHz Spectrometer. A Perkin Elmer Spectrum RX FTIR instrument invaded IR spectrum. Using the Nova Nano sem NPEP303, SEM pictures were captured. Brucker X flash 6I30 was used to obtain ESD maps.

### Synthesis of STO

The procedure proposed in the literature was used to produce sulfated tin oxide.[25] 100 g of stannous chloride was dissolved in 300 ml of water. With steady stirring and progressive addition of 25% ammonia, the pH of the solution was kept at 8. 400 ml of a cold, and 1 to 5% ammonium acetate solution was added to the precipitate. The produced solid was recovered using filtration and dried for 24–30 hours at 100 °C. The resulting tin oxide was treated slowly with 40 ml of concentrated $H_2SO_4$ and it was then left to stand for an

hour. The end product was purified, desiccated at 100°C, heated again for 4 hours at 500°C, and then stored in the sealed sample bottle.

**Synthesis of Polyhydroquinoline Derivatives**

An aryl aldehyde (5 mmol), EAA (5 mmol), dimedone (5 mmol), and $NH_4OAc$ (6.5 mmol) were added to a round bottom flask with 20 ml of ethanol. Sulfated tin oxide (20 mg) was introduced to this reaction mixture. The reaction mixture was heated to reflux and continuously stirred till the completion of the reaction (monitored by TLC using a 7:3 pet ether: ethyl acetate system) before being cooled to room temperature. To extract the solid catalyst, the crude solid was diluted filtered, and cleaned with ethyl acetate. The solid product was obtained by evaporating the filtrate. The pure product was extracted by recrystallizing the generated solid in hot ethanol. Using $^1$HNMR, IR, mass spectrometry, and melting points along with data from the literature, the structures of pure compounds were validated. The isolated catalyst was washed three times in succession with ethanol and then DI water followed by drying in a vacuum oven, utilized in further efforts at reactions. The recyclability of the STO catalyst was investigated across five successions. For the first three cycles, there was no discernible decline in the yield or selectivity of the product, but for the fourth and fifth cycles, the yield significantly decreased.

## RESULTS AND DISCUSSION

**Characterization of Synthesized STO**

FTIR, XRD, and SEM-EDS were among the analytical techniques used to describe the produced sulfated tin oxide. FTIR was used to illustrate the type of chemical functionalities present in the synthesized STO. The sulphate groups that have a bidentate attachment to tin are clearly visible in the IR bands of the STO catalyst at wavelengths 1390, 1190, 1165, 1035, and 941 $cm^{-1}$. Sulfated groups are responsible for the STO's strong acidic character. The $SnO_2.2H_2O$ formula for the STO catalyst was discovered using XRD analysis. Tin oxide's crystalline tetragonal structure is not broken down by sulphate groups, which leads to a lower crystal size and proliferation of surface area. At 2ɵ=27.20, 35.25, and 52.80, the XRD patterns show a characteristic of pure $SnO_2$ with a tetragonal structure. The SEM analysis shows that STO has a cubic crystalline shape, with particles that range in size from 27 to 72 nm. The S, O, and Sn components are dispersed throughout the catalyst, according to the EDS. The weight-to-percentage ratio determined by EDS is in good agreement with the predicted stoichiometry.[26]

**Optimization of Reaction Conditions**

In order to synthesize bioactive nitrogen-containing heterocycles, we have designed a reliable, inexpensive one-pot approach for producing PHQ derivatives via condensing substituted benzaldehyde, EAA, dimedone, and $NH_4OAc$ with STO in ethanol under reflux conditions. For preliminary conclusions, benzaldehyde, EAA, dimedone, and $NH_4OAc$ (1:1:1:1) as expressive reactants, and 10 mg of sulfated tin catalyst were chosen for optimization of the reaction. We discovered that the ethyl acetoacetate was not completely reacted at the specified ratio as determined by TLC, Petroleum ether: Ethyl acetate-7:3), resulting in a poor yield of 1, 4-DHP. As a result, we used an extra amount of ammonium acetate (1:1:1:1.3), exhibiting complete depletion of EAA with an enhanced yield of product. This could be because the ammonia concentration has risen. The impact of reaction temperature was studied (Table-1). The yield of the product (4a) greatly depends on temperature. Even with a long response time, low-temperature product development is not advantageous. With an increase in temperature, we discovered that the reaction period shortens and the product yield rises. Because of the rise in temperature, the condensation process and the release of ammonia from ammonium acetate may be improved.

Table-1: Temperature Influence on PHQ (4a) Synthesis

| Entry | Reaction Temperature($^0$C) | Time (h) | Yield [b] (%) |
|---|---|---|---|
| 1 | R.T. | 7.0 | 67 |
| 2 | 50 | 5.2 | 78 |
| 3 | 70 | 4.5 | 85 |
| 4 | Reflux | 3.8 | 92 |

[a]Reaction condition: benzaldehyde (5 mmol), EAA (5 mmol), dimedone (5 mmol), $NH_4OAc$ (6.5 mmol), and STO nanocatalyst in EtOH (20 ml) at a different temperature, [b]Yields of the products.

The different loading of the catalyst was studied (Table-2). It was observed that STO Nanocatalyst functioned worthy for 20 mg (entry 6, Table-2). It might be because a larger quantity of catalyst allows for more Bronsted acidic sites and a larger surface area to start the reaction.

Table-2: Effect of Catalyst Quantity on the Synthesis of PHQ (4a)

| Entry | Quantity of STO (mg) | Time (h) | Yield [b] (%) |
|---|---|---|---|
| 1 | None | 7 | 68 |
| 2 | 2 | 5.5 | 78 |
| 3 | 5 | 5.2 | 81 |
| 4 | 10 | 4.7 | 84 |
| 5 | 15 | 3.8 | 88 |
| 6 | 20 | 3.8 | 92 |

[a]Reaction condition: benzaldehyde (5 mmol), EAA (5 mmol), dimedone (5 mmol), $NH_4OAC$ (6.5 mmol), and quantity of STO nanocatalyst in EtOH (20 ml) at reflux, [b]Yields of the products.

Furthermore, 20 mg of catalyst per 5 mmol of the substrate was used to test the impact of several solvents, from non-polar to polar on catalytic action. Table-3 shows that the product was given in lower to moderate yields by the various solvents (both polar and non-polar), with ethanol providing the best yield (92%). Although the reaction was also run at reflux in clean water, the yield of 4a was only moderate (68%).

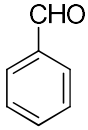
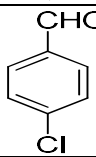
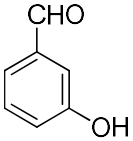
Table-3: Study of Solvent Screening for Synthesis of PHQ (4a)

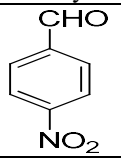
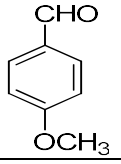
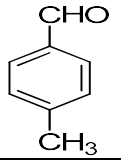
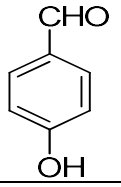
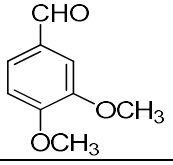
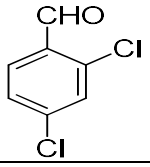
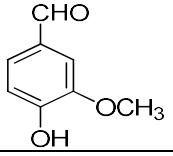
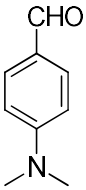
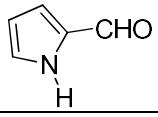
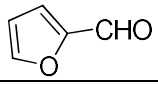
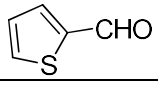
| Entry | Solvent | Time (h) | Yield[b] (%) |
|---|---|---|---|
| 1 | Hexane | 5.2 | 48 |
| 2 | $CCl_4$ | 4.9 | 51 |
| 3 | THF | 4.6 | 65 |
| 4 | DMF | 4.2 | 62 |
| 5 | $CH_3CN$ | 4.2 | 59 |
| 6 | $CHCl_3$ | 4.1 | 71 |
| 7 | Water | 4.0 | 68 |
| 8 | Ethanol | 3.8 | 92 |

[a]Reaction condition: benzaldehyde (5 mmol), EAA (5 mmol), dimedone (5 mmol), $NH_4OAc$ (6.5 mmol), and solvents, using 20 mg STO nanocatalyst at reflux, [b]Yields of the products.

The influence of aryl aldehyde substituents on reaction yield was investigated and is displayed in Table- 4 i.e., with aldehydes abiding electron-withdrawing groups (Table-4, entries 2, 4, 9) as well as electron donating groups (Table-4, entries 5-8) and also heteroaryl aldehydes (Table-4, entries 12, 13, 14). The protocol works effectively for each type of aryl aldehyde.

Table-4: STO Catalyzed Synthesis of PHQ Derivatives

| Entry | Aldehyde | Product | Time (h) | Yield[b] (%) | Melting Point ($^0$C) |
|---|---|---|---|---|---|
| 1 |  | 4 a | 3.8 | 92 | 204-206 |
| 2 |  | 4 b | 3.9 | 90 | 208-210 |
| 3 |  | 4 c | 4.2 | 86 | 200-202 |

| Entry | Aldehyde | Product | Time (h) | Yield[b] (%) | Melting Point ($^0$C) |
|---|---|---|---|---|---|
| 4 |  | 4 d | 3.5 | 94 | 242-244 |
| 5 |  | 4 e | 4.2 | 82 | 254-256 |
| 6 |  | 4 f | 4.4 | 82 | 260-262 |
| 7 |  | 4 g | 4.5 | 84 | 230-232 |
| 8 |  | 4 h | 4.7 | 80 | 204-206 |
| 9 |  | 4 i | 4.0 | 85 | 202-204 |
| 10 |  | 4 j | 4.3 | 88 | 214-216 |
| 11 |  | 4 k | 4.6 | 85 | 234-236 |
| 12 |  | 4 l | 3.8 | 86 | 230-232 |
| 13 |  | 4 m | 3.9 | 86 | 244-246 |
| 14 |  | 4 n | 3.9 | 88 | 224-226 |

[a]Reaction condition: substituted aryl aldehyde (5 mmol), EAA (5 mmol), dimedone (5 mmol), $NH_4OAc$ (6.5 mmol), in ethanol at reflux using 20 mg catalyst, [b]Yields of the products.

Being a heterogeneous catalyst, sulfated tin oxide is easily dissociated from the reaction combination and reused. In order to determine the possibility for STO to be reused for a model reaction, the catalytic activity of sulfated tin oxide was examined for 5 reaction cycles following the first reaction (Fig.-2). The yields of the products slightly decrease with each reuse.

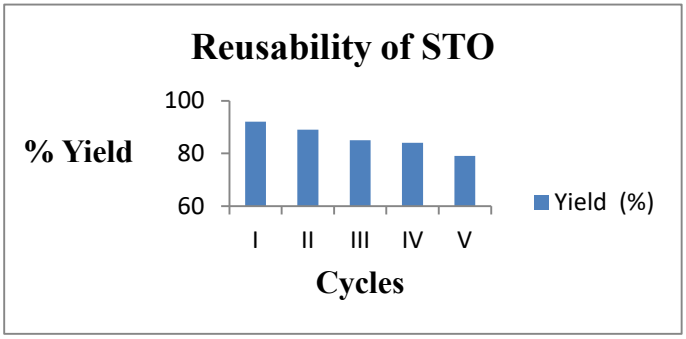
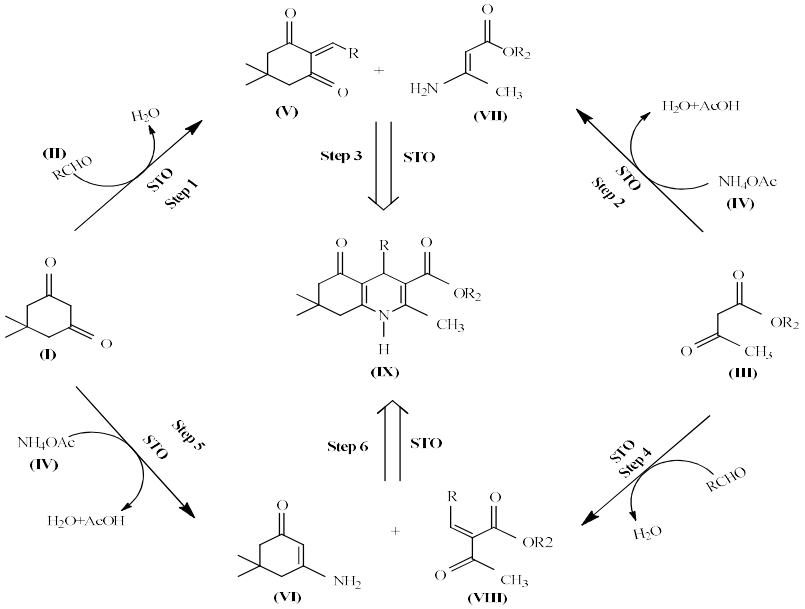



Fig.-2: Reusability of STO Nanocatalyst




Scheme-2: Plausible Mechanism of PHQ Synthesis

**Spectroscopic Analysis**

**Ethyl 2,7,7-trimethyl-5-oxo-4-phenyl-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (4a)**

IR ($cm^{-1}$) (KBr): 690, 735, 1073, 1169, 1227, 1382, 1435, 1490, 1643, 1686, 2957, 3070, 3282, 3434; $^1H$ NMR (400 MHz, $CDCl_3$) δ ppm: 0.92 (s, 3H), 1.06 (s, 3H), 1.15-119 (t, J=7.1Hz, 3H), 2.12-2.31 (m, 4H), 2.25 (s, 3H), 4.01-4.06 (q, J=7.1Hz, 2H), 5.04 (s, 1H), 6.67 (s, 1H), 7.05 (t, 1H), 7.15-7.27 (m, 4H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ ppm: δ 14.19, 19.33, 27.98, 29.30, 32.71, 37.24, 40.94, 50.10, 60.00, 105.00, 110.90, 1242, 129.0, 144.5, 146.2, 149.4, 154.5, 166.85, 195.43; Mass: ($M^+$) = m/z = 339.

**Ethyl 4-(4-chlorophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (4b)**

IR ($cm^{-1}$) (KBr Pellets): 980, 1004, 1073, 1139, 1153, 1169, 1382, 1435, 1452, 1603, 1643, 1686, 2929, 2957, 3070, 3189, 3283; $^1H$ NMR (400 MHz, $CDCl_3$) δ ppm: δ 0.92 (s, 3H), 1.06 (s, 3H), 1.15-118 (t, J=7.1Hz, 3H), 2.12-2.24 (m, 4H), 2.38 (s, 3H), 4.00-4.06 (q, J=7.1Hz, 2H), 4.96 (s, 1H), 6.53 (s, 1H), 7.14-7.22 (m, 4H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ ppm: δ 14.1, 19.2, 27.1, 29.3, 32.7, 36.6, 40.8, 50.6, 59.9, 105.5, 111.3, 126.32, 128.0, 129.0, 133.6, 144.1, 149.1, 149.5, 154.5, 167.2, 195.6; Mass: ($M^+$) = m/z = 373.

**Plausible Mechanism**

The Bronsted acidity of STO catalyzed the reaction via forming H-bonding with the carbonyl groups of aldehydes. The dimedone (I) or β-ketoester (III) reacted with an aldehyde (II) via Knoevenagel

condensation to form intermediate (V) or (VI). The β-ketoester (III) reacted with ammonium acetate to yield intermediate (VII) or (VIII). Both these intermediates undergo cyclization to generate desired product (IX).

## CONCLUSION

We have mechanized an affluent and competent methodology for the one pot condensation of four components, including aromatic aldehydes, EAA, dimedone, and $NH_4OAC$, with sulfated tin oxide serving as a solid heterogeneous superacid nanocatalyst, affording a high-yield of biologically active polyhydroquinoline derivatives. The catalyst is inexpensive and easily producible. The work is also noteworthy for its excellent product yields, simple workup, clean reactions, short reaction times, and moderate reaction conditions.

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## CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

## AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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[RJC- 8183/2022]