



## General Synthesis Method of Hantzsch dihydropyridine Using Scrap Automobile Catalyst (SAC)

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**Abstract:** 1,4-Dihydropyridine (DHP) derivatives are an important class of organic compounds known for their broad biological and pharmacological activities, particularly as calcium channel blockers, which make them valuable in medicinal chemistry. Given their significance, developing efficient and sustainable synthetic methods for these derivatives is crucial. In this study, we present a green, one-pot Hantzsch synthesis of 1,4-dihydropyridines using a Scrap Automobile Catalyst (SAC) as a sustainable and reusable heterogeneous catalyst. The multicomponent reaction was carried out under mild conditions using ammonium acetate in ethanol (EtOH) with various aldehydes and 1,3-diketones. The results demonstrate that the SAC-catalysed reaction proceeds efficiently, with electron-withdrawing substituents accelerating the reaction, achieving completion in just 1.5–2 hours. In contrast, reactions involving benzaldehyde required longer reaction times (up to 4 hours) but still afforded a high yield of 88%. This approach not only offers a rapid, high-yielding, and environmentally benign synthetic route but also provides an innovative solution for the valorisation of difficult-to-recycle automotive waste, aligning with the principles of green chemistry. The SAC catalyst proved to be reusable, further enhancing the sustainability of the process. This study highlights the potential of waste-derived catalysts in organic synthesis, offering a cost-effective and eco-friendly alternative to conventional methods.

**Keywords:** Hantzsch Reaction, Sustainable Catalysis, Scrap Automobile Catalysts, PGM metals

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### 1. INTRODUCTION

The increase in population density in the world increases the need for all kinds of needs for living life in direct proportion. This situation has made it difficult to meet the life on earth with the amount of production from scratch and has shown that it is no longer possible to evaluate waste products completely as garbage. It is an increasingly recognised fact that the use of waste-based catalysts in sustainable chemical synthesis is a potential solution to minimising environmental impact and enhancing the efficiency of chemical processes. The integration of waste-derived materials into catalytic systems has been shown to address issues of waste management in addition to promoting the principles of green chemistry by utilising abundant and often underutilised resources. A significant benefit of waste-based catalysts is their capacity to enable chemical reactions under milder conditions, a crucial aspect for sustainable synthesis (Rostamnia & Xin, 2014). Metal-organic frameworks (MOFs) derived from waste materials have exhibited notable catalytic activity in reactions such as the Hantzsch coupling reaction, underscoring their efficiency and reusability. The potential for these catalysts to be isolated and reused multiple times is significant, given that it reduces the need for fresh materials and minimises waste generation (Rostamnia & Xin, 2014). The development of heterogeneous catalysts from agricultural waste is a promising avenue for biodiesel production, as evidenced by the dual benefits of waste valorisation and sustainable energy generation. This has been

demonstrated in the study by Khan et al. (Khan et al., 2021). In addition, the application of catalysts derived from waste materials is congruent with the principles of a circular economy, wherein the valorisation of waste materials is achieved through the repurposing process. For instance, geopolymer microspheres synthesised from slag have been employed as low-cost catalysts for CO<sub>2</sub> hydrogenation, thereby exemplifying the capacity of industrial waste to be converted into effective catalytic materials (Deng et al., 2022). This method not only mitigates the environmental impact of chemical synthesis but also enhances resource efficiency by utilising materials that would otherwise be discarded, thus promoting a sustainable and circular approach to chemical production.

In other words, the materials that provide the reusable condition have been very important for ensuring sustainable development and reducing the negative situation on the environment that occurs while maintaining human life. In other words, humanity has now started to look for ways to reuse waste. One of the most important examples of this situation is the catalytic converters on the cars. Because it has been a mandatory part on all cars since 1993 (Searles, 2002). These critical parts are in high demand in various sectors such as recycling, jewellery, electronics and automotive. Because PGM metals (such as platinum, palladium and rhodium) from used catalytic converters are known to be precious metals. These metals can be easily reused in many applications in science, industry and industry. However, recycling of catalytic converters is a very long, difficult and costly sector (Xu et al., 2022). Since catalytic converters are a combination of chemical and mechanical processes such as melting, roasting and refining, the number of companies making them is also small. Whether this difficult and long process can be used in new sectors with fewer processes has been the subject of important studies in the scientific world in recent years. One of these is the utilisation as a catalyst through synthesis in organic chemistry. After 2000s, citronellal has been successfully applied on monofunctional reactions such as sequential cyclisation (Cova et al., 2019; Zuliani et al., 2020), wet air oxidation of Malathion (Isgoren et al., 2023), hydrogenation of alkenes (Zengin et al., 2011), nitroarenes (Genc, 2015) and Vegetable Oils (Sonmez et al., 2013). However, studies on its effect on multicomponent methods are scarce. To conclude, the significance of waste-based catalysts in sustainable chemical synthesis cannot be overestimated (Yuan et al., 2022). They provide a route through which the chemical industry can reduce its waste output, enhance its resource efficiency, and promote environmentally friendly practices in its manufacturing processes. By leveraging waste materials as catalysts, chemical manufacturers can transition towards more sustainable business practices that align with global efforts to mitigate environmental degradation and promote a circular economy (Tickner et al., 2022).

In the world of organic chemistry, there are many examples of reactions that take place over multiple reactants. These compounds, especially as a result of technological developments in the field of medicine and the widespread use of their effects on health treatment, a significant increase in their pharmacological use has been recorded. The most important of these are indoles, pyridines, pyrimidines and other nitrogen-containing compounds (Ulloora et al., 2013). 1, 4 Dihydropyridines are one of the best-known drug active ingredients in this field. Although 1, 4-Dihydropyridine (1, 4-DHP) was first discovered in 1882, it became famous when nifedipine, a member of the 1, 4-DHP family, was used as an antianginal and antihypertensive drug (Raj et al., 2025). In addition, it also affects non-diabetic nephropathies (Wilmer et al., 2003), angiotensin-converting enzyme inhibition (Brown & Vaughan, 1998; Raj et al., 2025), and human cytochrome P450 enzyme inhibition (M. et al., 2000; Sakamuru et al., 2025). More recently, felodipine and nicardipine have been utilised as cardiovascular drugs and Camiglibose for diabetes and Lobeline-126 as a respiratory stimulant (Zheng & Crooks, 2015). This widespread use has led to the development of various synthesis methods for this type of compound. Traditionally, the Hantzsch technique has been used for the synthesis of dihydropyridine, which involves the condensation of 1, 3-diketones, different aldehydes and a nitrogen source in methanol (Conrad & Guthzeit, 1882). Nowadays, the realisation of this process over the catalyst for shorter and higher yields is being investigated and SBA-15 (Rajabi et al., 2015), manganese (III)-porphyrin complex (El-Remaily et al., 2021), SeO<sub>2</sub>/Hap (Madhavi et al., 2022), nicotinic acid (Patel et al., 2013), CuI Nanoparticles (Cahyana et al., 2020), Glutathione coated mag. Nanoparticles (Maleki et al., 2021), volcanic based hybrid nanocomposites (Valadi et al., 2020), and alumina sulphuric acid (ASA) (Besoluk et al., 2008) and the others are known studies (Chand et al., 2025; Ong et al., 2025; Sakamuru et al., 2025; Soni et al., 2025).

In this study, Hantzsch reaction was carried out over dimedone, ethyl acetoacetate, various aldehydes and ammonium acetate with a small amount of PGM as catalyst. The application of a multicomponent synthesis as well as single-component hydrogenation and oxidation was investigated using temperature, time, catalyst ratio, and suitable solvent parameters.

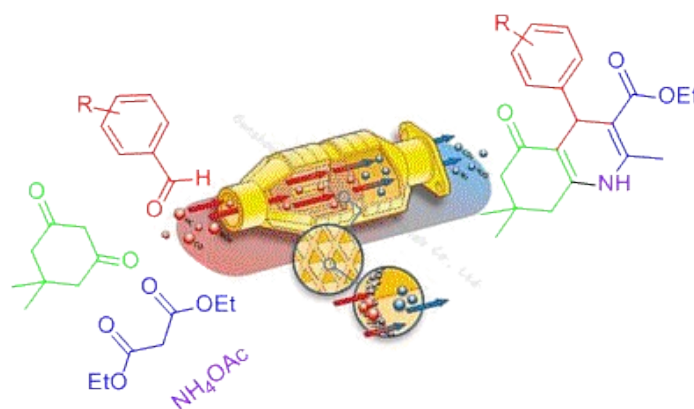
## 2. EXPERIMENTAL SECTION

### 2.1. Chemicals and Reagents

The STUART SMP50 was used to do melting point analysis. A VARIAN Infinity NMR spectrometer (at 75 Hz. and 300 Hz.) was used to determine  $^{13}\text{C}$  and  $^1\text{H}$  NMR measurements, respectively. The Perkin Elmer Avio 200 was used to measure ICP-OES. FEI Quanta 250 FEG was used for analyses of SEM-EDX.

### 2.2. Synthesis Procedure

Synthesis methods of 1,4 dihydropyridine Using SAC (Figure 1): Dimedone (1 mmol) / ethyl acetoacetate (1 mmol) or ethyl acetoacetate (2 mmol), aldehyde (1 mmol), ammonium acetate (4 mmol), and SAC were mixed in ethanol at 80 °C. The reaction was finished and cooled. The SAC was then separated from the fluid by centrifugation (6000 rpm) and cleaned with ethanol. After combining the raw solution with 25 mL of ice-cold water, it was filtered. The product was dried at 105 °C.



**Figure 1:** The method for the synthesis of 1, 4 dihydropyridine has been developed in the presence of SAC.

**Diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (1):**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 1.20 (t,  $J=7.00$  Hz, 6H,  $2\times\text{CH}_3$ ), 2.25 (s, 6H,  $2\times\text{CH}_3$ ), 4.00-4.15 (q,  $J=6.5$  Hz, 4H,  $2\times\text{OCH}_2$ ), 4.95 (s, 1H, -CH), 5.75 (s, 1H, NH), 7.10-7.25 (m, 5H,  $\text{C}_6\text{H}_5$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 14.0, 19.5, 39.5, 60.5, 103.5, 126.0, 128.5, 128.0, 144.0, 147.0, 167.5. IR (ATR,  $\text{cm}^{-1}$ ): 3375 (N-H, amine stretching vibration), 2980 (C-H, aliphatic stretching), 1720 (C=O, ester carbonyl stretching), 1585 (C=C, aromatic stretching), 1340 (C-H, bending vibrations of methyl groups).

**Diethyl 4-(4-bromophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (2):**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 1.18 (t,  $J=7.0$  Hz, 6H,  $2\times\text{CH}_3$ ), 2.30 (s, 6H,  $2\times\text{CH}_3$ ), 3.80-4.10 (q,  $J=6.7$  Hz, 4H,  $2\times\text{OCH}_2$ ), 4.90 (s, 1H, CH), 5.58 (s, 1H, NH), 7.14 (d,  $J=8.5$  Hz, 2H, Ar-H), 7.24 (d,  $J=8.5$  Hz, 2H, Ar-H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 14.2, 19.7, 39.3, 59.8, 103.2, 119.8, 129.8, 130.8, 143.8, 146.8, 166.8. IR (ATR,  $\text{cm}^{-1}$ ): 3328 (N-H, amine stretching vibration), 2970 (C-H, aliphatic stretching), 1725 (C=O, ester carbonyl stretching), 1582 (C=C, aromatic stretching), 1345 (C-H, bending vibrations from methyl groups).

**Diethyl 2,6-dimethyl-4-(4-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (3):**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 1.21 (t,  $J=6.9$  Hz, 6H,  $2\times\text{CH}_3$ ), 2.33 (s, 6H,  $2\times\text{CH}_3$ ), 4.07-4.11 (q,  $J=6.4$  Hz, 4H,  $2\times\text{OCH}_2$ ), 5.26 (s, 1H, CH), 6.01 (s, 1H, NH), 7.39 (d, 2H,  $J=8.7$  Hz, Ar-H), 8.05 (d, 2H,  $J=8.7$  Hz).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 14.1, 20.3, 39.4, 58.9, 113.0, 123.6, 128.3, 143.7, 146.3, 152.9, 166.8. IR (ATR,  $\text{cm}^{-1}$ ): 3348 (N-H, amine stretching vibration), 2973 (C-H, aliphatic stretching), 1732 (C=O, ester carbonyl stretching), 1581 (C=C, aromatic stretching), 1338 (C-H, bending vibrations of methyl groups).

**Diethyl 4-(4-cyanophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (4):**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 1.17 (t,  $J=6.8$  Hz, 6H,  $2\times\text{CH}_3$ ), 2.37 (s, 6H,  $2\times\text{CH}_3$ ), 4.03-4.11 (q,  $J=6.6$  Hz, 4H,  $2\times\text{OCH}_2$ ), 5.02 (s, 1H, CH), 5.88 (s, 1H, NH), 7.41 (d, 2H,  $J=8.5$  Hz, Ar-H), 7.49 (d, 2H,  $J=8.5$  Hz, Ar-H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 14.0, 19.5, 40.6, 59.6, 104.9, 109.6, 119.3, 128.9, 131.9, 144.0, 152.3, 166.9. IR (ATR,  $\text{cm}^{-1}$ ): 3356 (N-H, amine stretching vibration), 2979 (C-H, aliphatic stretching), 1734 (C=O, ester carbonyl stretching), 1583 (C=C, aromatic stretching), 1349 (C-H, bending vibrations of methyl groups).

**Diethyl 4-(phenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (5):** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 0.94 (s, 3H, CH<sub>3</sub>, methyl group), 1.08 (s, 3H, CH<sub>3</sub>, methyl group), 1.23 (t, *J* = 7.4 Hz, 3H, CH<sub>3</sub>), 2.15-2.28 (m, 2H, CH<sub>2</sub>), 2.41 (s, 3H, CH<sub>3</sub>), 4.12 (m, 2H, CH<sub>2</sub>), 5.07 (s, 1H, CH), 5.85 (s, 1H, NH), 6.88-7.33 (m, 5H, Ar-H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 14.6, 19.7, 27.5, 29.9, 33.1, 36.7, 41.2, 51.2, 60.2, 106.3, 112.3, 126.4, 128.3, 128.4, 144.2, 147.5, 149.4, 167.9, 196.2. IR (ATR, cm<sup>-1</sup>): 3382 (N-H, amine stretching vibration), 2982 (C-H, aliphatic stretching), 1727 (C=O, ester carbonyl stretching), 1592 (C=C, aromatic stretching), 1342 (C-H, bending vibrations of methyl groups).

**Ethyl 4-(4-bromophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,7,8-hexahydroquinoline-3-carboxylate (6):** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 0.94 (s, 3H, CH<sub>3</sub>), 1.08 (s, 3H, CH<sub>3</sub>), 1.21 (t, *J* = 7.3 Hz, 3H, CH<sub>3</sub>), 2.15-2.34 (m, 2H, CH<sub>2</sub>), 2.37 (s, 3H, CH<sub>3</sub>), 4.11 (m, 2H, CH<sub>2</sub>), 5.02 (s, 1H, CH), 6.55 (s, 1H, NH), 7.22 (d, 2H, *J* = 7.8 Hz, Ar-H), 7.33 (d, 2H, *J* = 7.9 Hz, Ar-H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 14.6, 19.8, 27.5, 29.9, 33.1, 36.7, 41.3, 51.1, 60.3, 106.0, 112.0, 120.2, 130.2, 131.3, 144.3, 146.6, 149.2, 167.7, 196.1. FTIR (ATR, cm<sup>-1</sup>): 3354 (N-H, amine stretching vibration), 2971 (C-H, aliphatic stretching), 1730 (C=O, carbonyl stretching), 1600 (C=C, aromatic stretching), 1345 (C-H, bending vibrations of methyl groups).

**Ethyl 2,7,7-trimethyl-4-(4-nitrophenyl)-5-oxo-1,4,5,6,7,7,8-hexahydroquinoline-3-carboxylate (7):** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 0.93 (s, 3H, CH<sub>3</sub>), 1.11 (s, 3H, CH<sub>3</sub>), 1.85 (t, *J* = 7.2 Hz, 3H, CH<sub>3</sub>), 2.18-2.38 (m, 4H, CH<sub>2</sub>), 2.43 (s, 3H, CH<sub>3</sub>), 4.03-4.08 (m, 2H, CH<sub>2</sub>), 5.17 (s, 1H, CH), 6.34 (s, 1H, NH), 7.53 (d, 2H, *J* = 7.9 Hz, Ar-H), 8.12 (d, 2H, *J* = 7.9 Hz, Ar-H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 14.4, 19.1, 27.2, 29.7, 32.7, 37.5, 41.0, 50.9, 59.9, 103.9, 110.4, 123.3, 129.2, 146.2, 146.4, 150.4, 155.4, 167.3, 195.6. FTIR (cm<sup>-1</sup>): 3432 (N-H, amine stretching), 2952 (C-H, aliphatic stretching), 1732 (C=O, carbonyl stretching), 1602 (C=C, aromatic stretching), 1373 (C-H, bending vibrations of methyl group), 1313 (NO<sub>2</sub>, asymmetric stretching of nitro group).

**Ethyl 4-(4-cyanophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,7,8-hexahydroquinoline-3-carboxylate (8):** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 0.92 (s, 3H, CH<sub>3</sub>), 1.10 (s, 3H, CH<sub>3</sub>), 1.19 (t, *J* = 7.4 Hz, 3H, CH<sub>3</sub>), 2.21-2.33 (m, 4H, CH<sub>2</sub>), 2.42 (s, 3H, CH<sub>3</sub>), 4.08-4.17 (m, 2H, CH<sub>2</sub>), 5.11 (s, 1H, CH), 6.24 (s, 1H, NH), 7.44 (d, 2H, *J* = 8.0 Hz, ArH), 7.54 (d, 2H, *J* = 8.0 Hz, ArH). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 14.3, 19.9, 27.5, 29.7, 33.1, 37.6, 41.4 (C, sp<sup>3</sup> carbon in quinoline ring), 50.9, 60.4, 105.3, 110.0, 111.6, 119.7, 129.3, 132.3, 144.4, 148.8, 152.7, 167.2, 196.1. IR (cm<sup>-1</sup>): 3432 (N-H, amine stretching), 2958 (C-H, aliphatic stretching), 2226 (C≡N, nitrile stretching), 1716 (C=O, carbonyl stretching), 1604 (C=C, aromatic stretching), 1152 (C-H, methyl and methoxy bending vibration).

### 3. RESULTS AND DISCUSSION

#### 3.1. Characterisation

A scrap automobile catalyst was first separated from carbon and dust particles as a whole (50 x 50 mm). This was done by washing with ultrapure water, chromic acid, and ultrapure water. Finally, it was dried at 105 °C for 4 hours. The dried catalyst was crushed with the help of a mortar and passed through a 100-micron sieve. Compounds containing metals such as platinum (Pt), palladium (Pd) and rhodium (Rh) in catalytic converters are usually found in zero valence (neutral) or low oxidation states. The structure of the catalytic converter usually consists of a ceramic or metallic carrier material (substrate). This material has fine honeycomb-shaped channels so that the area of contact of the exhaust gases with the surface is maximised. Metals such as Pt, Pd and Rh are placed on the surface of this substrate as a very thin coating (usually on the micron level). Very small particles tend to aggregate due to the high surface energy. This can cause the particles to stick together to form larger aggregates, which reduces the effectiveness of the surface area. Aggregation can reduce the effectiveness of the catalyst because the reactant is less likely to contact the entire surface. The catalyst particles should be uniformly dispersed on the carrier material, which ensures a better performance and prevents the loss of particles. Therefore, instead of crushing them small, it is tried to separate them from the honeycomb channels as much as possible. The ready-to-use catalyst was analysed by SEM-EDX and inductively coupled plasma atomic emission spectroscopy (ICP-OES) in Table 1. In Figure 2, Platinum 4.34%, Rhodium 0.46% were found as catalyst content before the reaction process, while quartz (SiO<sub>2</sub>) 11.01% Si, alumina (Al<sub>2</sub>O<sub>3</sub>) 36.39% Al and magnesia (MgO) 0.35% Mg were found.

#### 3.2. Solvent Behaviour of Reaction

The effect on the various solvents utilised in the Hantzsch synthesis varies significantly in terms of performance in Figure 3. Following four hours of reaction, ethanol (EtOH) yielded 88%, whereas methanol (MeOH) yielded 78%. However, the yields of ethanol-water mixture and methanol-water mixture were found to be 60% and 63%, respectively, indicating that these solvents are less efficient

than individual applications. Other solvents, such as acetone and tetrahydrofuran (THF), produced lower yields of 65% and 45%, respectively. The results presented suggest that the type of solvent applied and the reaction time have an enormous effect on the rate of Hantzsch synthesis. Protic solvents, such as ethanol and methanol, were shown to have the potential for higher yields, whereas apolar solvents, such as THF and acetone, which require longer reaction durations, lowered the efficiency. These findings highlight the importance of solvent selection and reaction conditions in understanding how they affect the efficiency of multicomponent reactions using waste vehicle catalyst.

**Table 1.** ICP-OES and SEM-EDX results.

<i>Element (%)</i>	<i>Pt</i>	<i>Rh</i>	<i>Al</i>	<i>Si</i>	<i>Mg</i>	<i>Cr</i>	<i>Fe</i>	<i>Ni</i>
Before Reactions	4,3	0,5	36,9	13,2	1,3	0,2	0,1	0,4
After Reusability	4,1	0,2	25,3	15,0	2,1	0,9	0,2	0,1

<b>Before Reaction</b>			<b>After Reusability</b>		
<b>Element</b>	<b>Wt. %</b>	<b>At %</b>	<b>Element</b>	<b>Wt. %</b>	<b>At %</b>
<b>C K</b>	10.52	17.63	<b>C K</b>	20.47	31.52
<b>O K</b>	36.93	46.49	<b>O K</b>	35.39	40.90
<b>MgK</b>	0.35	0.29	<b>MgK</b>	2.36	1.80
<b>AlK</b>	36.39	27.16	<b>AlK</b>	22.53	15.44
<b>SiK</b>	11.01	7.89	<b>SiK</b>	14.65	9.64
<b>RhL</b>	0.46	0.09	<b>P K</b>	0.51	0.30
<b>PtL</b>	4.34	0.45	<b>PtM</b>	4.08	0.39

### 3.3. The Effect of Temperature

The SAC, the study of the effect of temperature on the activity of the catalyst is largely known to vary directly with the reaction temperature. Because the interaction of reactants over the catalyst surface directly affects the collision rate and the activation energy required for the formation of the final product with kinetic energy connection. In our study, we did not observe sufficient product conversion in ethanol for 24 hours at ambient temperature, but it gave 65% yield after 8 hours at 50 °C. The main yield was synthesised at 80 °C in 85% yield in one and a half to four hours depending on the functional groups on the aldehyde. Since the increase in temperature did not cause any change in yield, it was not continued at very high temperatures. All results are presented in Figure 4.

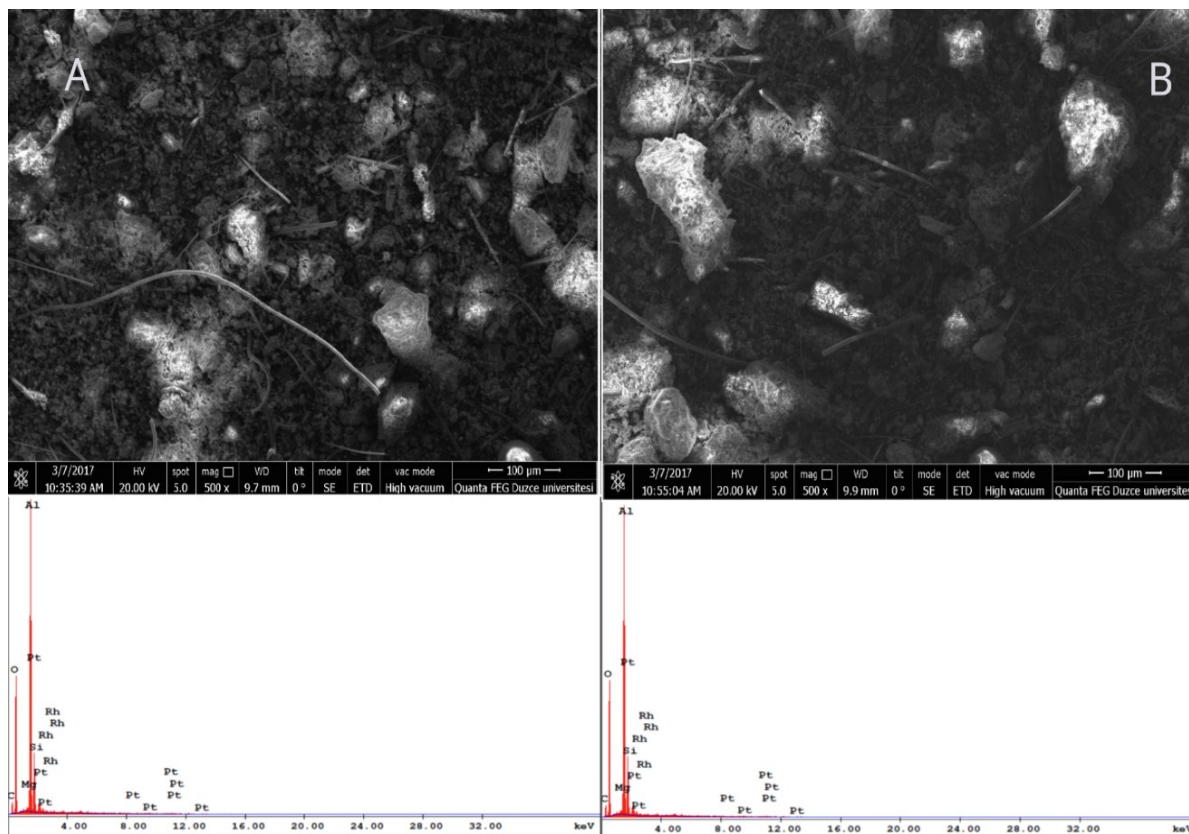


Figure 2. SEM images before reaction (A), after reaction (B)

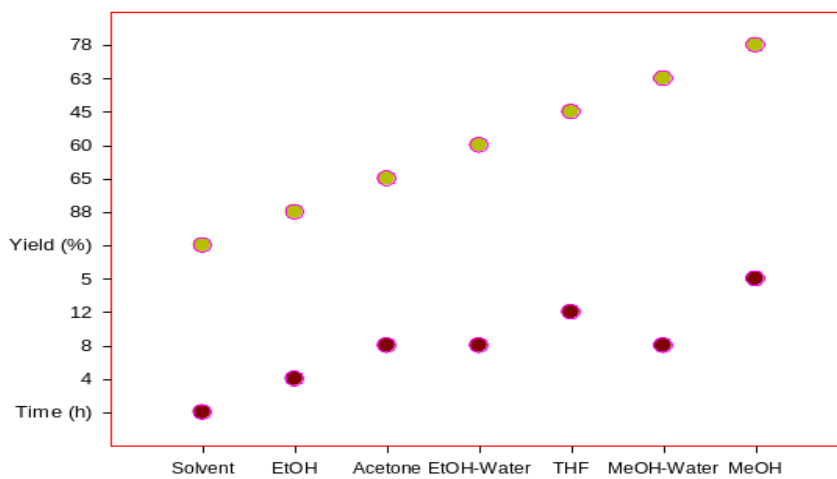
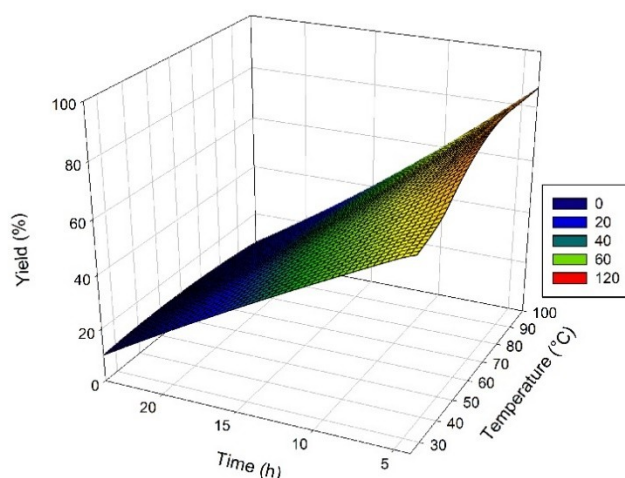


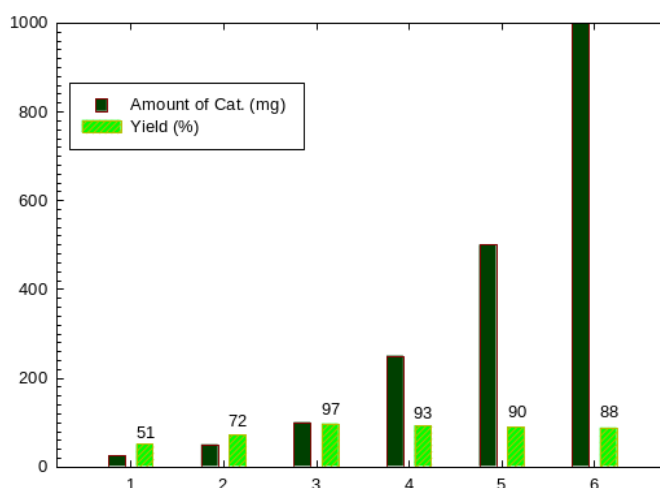
Figure 3: Solvent Selection Analysis of Synthesis.



**Figure 4:** Temperature effect analysis of synthesis.

### 3.4. Effect of Catalyst Dosage

Catalyst dosage regulation is important in organic reactions involving catalysts because the amount of catalyst used can significantly affect the outcome of the reaction in Figure 5. Using too little or too much catalyst can result in inefficient or undesirable reactions. Using too much catalyst can be wasteful and increase the cost of the reaction, while using too little can result in lower yields. The amount of SAC used in the reactions was calculated and the results are listed in Table 5. The reactions were carried out in smaller volumes with very low reaction yields. When higher amounts of SAC (250 mg- 500 mg- 1000 mg) were used, there was no noticeable acceleration of the reaction rate. As a result, the solvent-containing product was absorbed onto the surface of the catalyst when the catalyst was used in larger amounts. As a result, the yield of the reactions decreased.



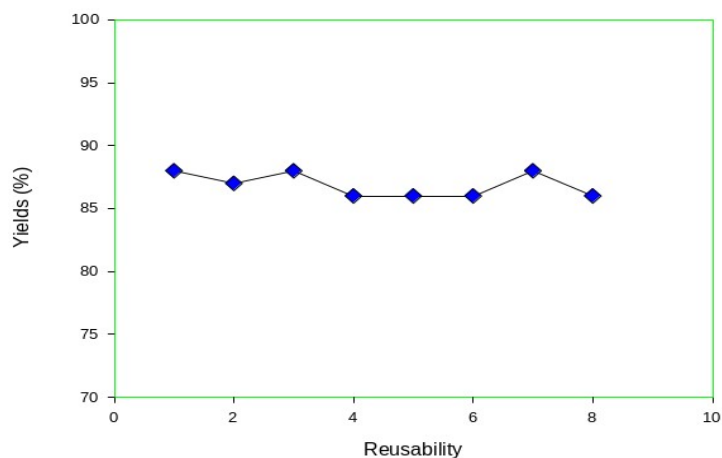
**Figure 5:** Amount of Catalysis Selection.

### 3.5. Reusability of Catalyst

The potential for reuse of SAC was thoroughly tested to determine its efficiency across several cycles of use. As shown in Figure 6, the SAC displayed outstanding stability and efficacy when used repeatedly in Hantzsch synthesis procedures. After purification and washing with methanol, water, and ether, followed by drying, the catalyst maintained its catalytic activity for eight consecutive reaction cycles. The yield was generally stable over the cycles, ranging from 86% to 88%. Notably, the



catalyst's performance did not drop significantly, indicating its high reusability. This consistent yield underlines the recycled vehicle catalyst's potential for extended usage in catalytic processes without considerable loss of efficiency, making it a viable option for sustainable and cost-effective applications in chemical synthesis.



**Figure 6:** Reusability of Scrap Automobile Catalysis.

### 3.5. The Catalytic Performance of SAC On the Hantzsch Reaction

The findings show that the SAC catalyst efficiently supports the Hantzsch reaction, resulting in good yields and appropriate reaction times. Notably, reactions with reactants 7 and 10 produced the highest yields (97%) in 1.5 hours, confirming the SAC's catalytic effectiveness. The products' melting points (m.p.) matched the given values, indicating the purity and success of the reactions. This result demonstrates SAC's practical utility as a catalyst for effective and repeatable chemical reactions in the Hantzsch method (Table 2).

**Table 2:** Hantzsch synthesis, showing the results of the synthesis of dihydropyridine.

Code	Reactant	Reactant	Yield b (%)	Time (h)	Reported m.p (°C)	Found m.p. (°C)
1			88	4	156-158 (Arslan et al., 2009)	158
2			89	3	141-142 (Demirci et al., 2016)	144
3			91	2.5	200-202 (Arslan et al., 2009)	202
4			92	2.5	200-202 (Kaya et al., 2024)	201
5			94	2	214-216 (Arslan et al., 2009)	215
6			95	2	252-254 (Arslan et al., 2009)	253
7			97	1.5	241-243 (Kaya et al., 2024)	243
8			97	1.5	222-223 (Demirci, 2011)	222

The Hantzsch synthesis, known for its versatility in the production of 1,4-DHPs, was performed using aromatic aldehyde derivatives and two diketone systems EAA-EAA (ethyl acetoacetate-ethyl



acetoacetate) and Dimedone-EAA (5,5-dimethyl-1,3-cyclohexanedione-ethyl acetoacetate) in the presence of a sustainable catalytic system derived from SAC. The SAC, containing platinum (Pt) and palladium (Pd), acted as an efficient heterogeneous catalyst, facilitating the reaction via its exceptional redox and adsorption properties. The role of Pt and Pd in SAC, widely recognised for their catalytic activity in industrial processes, was instrumental in enhancing the reaction efficiency by stabilising intermediates and lowering activation energy. The SAC often contain precious metals such as platinum (Pt), palladium (Pd), and rhodium (Rh). These metals are critical to ensure that the catalysts work effectively. However, these precious metals in SAC are present at zero valence and this property is important in understanding their role in the reaction mechanism. Zero valence precious metals generally refer to the situation where the metal atoms are in a free state and do not share electrons. In this case, the metal atoms interact with reactants through an oxidation state or covalent bonds, but do not exhibit oxidation or reduction properties on their own. This zero-valence state allows metals to remain stable in catalysis processes and effectively participate in various chemical reactions. These precious metals on SAC form active centers on the surface of the catalyst, increasing the speed and efficiency of reactions. Thanks to these properties, the recycling and utilisation of SAC is considered as part of sustainable chemical processes.

The interplay between aldehyde substituents, diketone systems, and the SAC catalyst significantly influenced product yields, reaction times, and melting points. Reactions involving EAA-EAA generally exhibited moderate yields and melting points due to the symmetrical and less sterically hindered nature of the diketone. In contrast, Dimedone-EAA reactions yielded structurally more stable products with higher melting points, attributed to the rigidity and bulkiness of the dimedone ring. The Pt and Pd in SAC were crucial in maintaining high catalytic efficiency and selectivity, ensuring that the desired DHPs were obtained in high purity.

The aldehyde derivatives used in this study included benzaldehyde, 4-Br benzaldehyde, 4-NO<sub>2</sub> benzaldehyde, and 4-CN benzaldehyde. These substituents played a critical role in dictating the reaction's progression and efficiency. Aromatic aldehydes with electron-withdrawing substituents, such as 4-Br, 4-NO<sub>2</sub>, and 4-CN, exhibited higher reactivity compared to the unsubstituted phenyl group. The electron-withdrawing nature of these substituents increased the electrophilicity of the aldehyde carbonyl carbon, enhancing the rate of nucleophilic attack by the enamine intermediate. For instance, while the reaction involving benzaldehyde and EAA-EAA required 4 hours to achieve an 88% yield, the reaction with 4-CN benzaldehyde completed in 2.5 hours, yielding 92%. Similarly, the 4-NO<sub>2</sub> derivative, with a strong electron-withdrawing nitro group, achieved a high yield of 91% in the same duration. These results underscore the accelerating effect of substituents that enhance the electrophilic character of the aldehyde.

The comparison between EAA-EAA and Dimedone-EAA systems highlighted significant differences in product yields, melting points, and reaction times. The EAA-EAA system, which involves two molecules of ethyl acetoacetate, produced DHPs with yields ranging from 88% to 92%, and melting points in the range of 156-202 °C. In contrast, reactions involving Dimedone-EAA exhibited markedly higher yields (94-97%) and shorter reaction times (1.5-2 hours). The products also had higher melting points (214-254 °C), indicating enhanced structural stability and crystallinity. The steric and electronic effects imparted by the rigid cyclic structure of dimedone contributed to these improvements. The Pd and Pt nanoparticles within SAC likely played a dual role, acting as both adsorption sites for reactants and redox centres to facilitate the enamine formation and subsequent cyclisation steps.

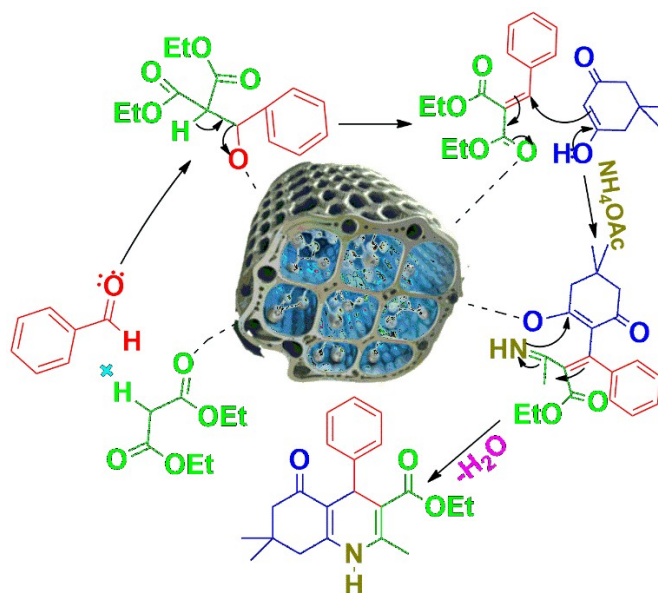
The Hantzsch reaction mechanism proceeds through three primary stages in Figure 2:

- (1) Knoevenagel condensation between the aldehyde and one molecule of the active methylene compound,
- (2) enamine formation with the second molecule of the diketone,
- (3) cyclisation and subsequent aromatisation to yield the final DHP product.

The SAC catalyst, rich in Pt and Pd, provided a favorable surface for these transformations. The metallic sites on SAC likely stabilised the reaction intermediates, particularly the  $\alpha$ ,  $\beta$ -unsaturated carbonyl species and enamine, by coordinating with lone pairs on oxygen and nitrogen atoms. Additionally, the redox capability of Pt and Pd facilitated proton transfer steps, reducing the overall energy barrier for cyclisation. The SAC system also demonstrated excellent recyclability and stability, further enhancing its suitability as a green catalyst. After five cycles, the catalyst retained over 90% of its original activity, showcasing its robustness and alignment with sustainability principles.

This study highlights the integration of SAC as a sustainable and efficient catalyst in the Hantzsch reaction, demonstrating its capability to enhance reaction efficiency and selectivity. The systematic evaluation of aldehyde substituents and diketone systems underscores the importance of molecular

structure and electronic effects in determining reaction outcomes. The results not only expand the applicability of Hantzsch synthesis but also promote green chemistry practices through the valorisation of waste-derived catalysts. In conclusion, the kinetics and yields of the reaction are greatly influenced by the selection of the aldehyde and diketone molecules. While the presence of several aromatic groups and differences in the acidity of the diketone might impact the efficacy of the reaction, electron-withdrawing groups on the aldehyde speed up the process by stabilising the positive charge on the carbonyl carbon. These results emphasise how crucial reactant selection is to maximising SAC's effectiveness throughout the 1,4-dihydropyridine synthesis (Figure 7).



**Figure 7:** Plausible mechanism of the formation of DHP.

The predicted mechanism of the reaction carried out in the Hantzsch synthesis using SAC starts with aldehydes being protonated in the acidic environment of SAC to form carbonyl carbon which gains a positive charge, which enhances the electrophilic character of aldehydes ( Hamasaka et al., 2019). Then, 1,3-diketone (e.g., dimedone) performs a nucleophilic attack and reacts with the protonated aldehyde, in this step intermediate 1,4-dihydropyridine species are formed (Krishna et al., 2022; Neto et al., 2021). Finally, a second nucleophilic molecule, usually an aldehyde or ketone, condenses with this intermediate, thus yielding the desired 1,4-dihydropyridine product. SAC improves the efficiency of the reaction by effectively activating the reactants in this process and supporting their stability in the reaction medium. The reusability of SAC reduces environmental impacts while increasing process efficiency and highlights the potential of waste-based catalysts in sustainable chemical processes (Wilson & Clark, 2000).

#### 4. CONCLUSION

The work highlights the sustainable use of Pt and Pd rich SAC as an effective and reusable catalyst for the Hantzsch synthesis of 1,4-dihydropyridine (DHP). By reusing SAC - a waste material - the research adheres to the principles of Green Chemistry, which focuses on transforming industrial by-products into valuable tools for organic synthesis. The catalytic system provided high yields (88-97%) for a range of aldehyde derivatives and diketone combinations, with significantly reduced reaction times (1.5-4 hours). Pt and Pd within the SAC played a key role in catalysing critical reaction steps such as Knoevenagel condensation, enamine formation and cyclisation. The efficiency and sustainability of the SAC as a heterogeneous catalyst is underlined by its ability to stabilise intermediates and facilitate proton transfer.

The Pt and Pd in SAC acted as versatile catalytic centres, stabilising intermediates and facilitating redox processes. Demonstrating the advanced catalytic capabilities of SAC, these interactions reduced activation energies and increased reaction selectivity. SAC retained over 90% of its catalytic activity over five cycles, reflecting its robustness and alignment with sustainable chemistry principles. These studies demonstrate that SAC can be used as a cost-effective and sustainable catalyst for organic reactions. Through the conversion of industrial waste into high performance catalysts, the study provides a model for the integration of waste valorisation with chemical synthesis. The results have

implications for wider applications of SAC in other transformations, as a contribution to green chemistry and the circular economy. Overall, the research demonstrates the potential of recycled materials to drive innovation and sustainability in organic synthesis, bridging the gap between waste management and advanced catalysis.

## 5. CONFLICT OF INTEREST

The author declare that they have no conflicts of interest.

## 6. ACKNOWLEDGMENTS

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