



## Research Article

# Bismuth Oxychloride as an Efficient Heterogeneous Catalyst for Aldol Condensation Reaction between Aldehydes and Ketones

Nguyen Thi Kim Oanh<sup>1,2,\*</sup>, Nguyen Vinh Huu<sup>1,2</sup>, Linh Xuan Nong<sup>1,2</sup><sup>1</sup>*Institute of Applied Technology and Sustainable Development, Nguyen Tat Thanh University, 298A-300A Nguyen Tat Thanh, Ward 13, District 4, Ho Chi Minh City, 700000, Vietnam.*<sup>2</sup>*Faculty of Environmental and Food Engineering, Nguyen Tat Thanh University, Ho Chi Minh City, Vietnam.*

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## Abstract

The aldol reaction is a cornerstone of modern synthetic organic chemistry in which the  $\beta$ -hydroxyketone was formed by the reaction of an enol or an enolate and a carbonyl compound. Benzalacetone is one of the fundamental building blocks of benzalacetone synthase structure that play an important role for construction of a variety of medically crucial phenylbutanoids, such as anti-inflammatory glucoside lindleyin in rhubarb and gingerol. The non-transition metal material attracted much attention from research groups on the world, such a potential catalyst as BiOCl for organic reaction due to its remarkably chemical and physical properties as relative stability, resistance of air and moisture, low toxicity. The BiOCl material was synthesized by the solvothermal method. The structure features of material were defined by modern analytic methods such as X-ray diffraction (XRD), Fourier Transform infrared spectroscopy (FT-IR), Scanning Electron Microscope (SEM), and Nitrogen Adsorption-Desorption Isotherms. The BiOCl material was successfully utilized as a catalyst for the aldol condensation reaction of benzaldehyde and acetone. The reaction was performed in the mild condition with the presence of 10 mol% catalyst and 2 equivalent of  $\text{Cs}_2\text{CO}_3$  as base without by-product in very short reaction times and good yields. The benzalacetone product obtained around 85% yield at 120 °C for 24 h. The BiOCl material after reaction was recovered and reused many times without significant reducing of catalytic activity.

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**Keywords:** Aldol condensation; benzalacetone; Bismuth Oxychloride; heterogeneous catalyst

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## 1. Introduction

Benzalacetone has been known as an  $\alpha,\beta$ -unsaturated ketone compound that boasts bio-pharmaceutical properties, including its role as anti-inflammatory coumarin skeleton compound [1]. Recently, benzalacetone and its derivatives

have been reported to be radical scavengers with antioxidant properties [2–4]. Various methods for synthesizing these compounds have been reported in the literature [5–7]. The simplest method involves the Claisen-Schmidt condensation reaction, which is typically carried out with the presence of  $\text{AlCl}_3$  or HCl as an acid catalyst or with base catalyst without a solvent at room temperature. However, this reaction often leads to a dehydration reaction of  $\beta$ -

\* Corresponding Author.

Email: [ntkoanh@ntt.edu.vn](mailto:ntkoanh@ntt.edu.vn) (N.T.K. Oanh);  
Telp: +84-392073898, Fax: +(08)-39404759

hydroxycarbonyl compounds that yields the corresponding arylidene product with a decrease in yield due to side reactions under most conditions [8,9]. To avoid by-products and improve reaction efficiency, various homogeneous catalysts have been used, including  $\text{InCl}_3$  salt [10], bismuth(III) chloride [11],  $\text{TiCl}_3(\text{SO}_3\text{CF}_3)$  [12],  $\text{Yb}(\text{OTf})_3$  [13], and  $\text{FeCl}_3$  [14]. However, these homogeneous catalysts cannot be recoverable or reusable after performing the reaction.

The utilization of non-transition metal catalysts in organic reactions has garnered widespread attention [15]. Bismuth(III) salts, such as  $\text{Bi}(\text{OTf})_3$ ,  $\text{Bi}(\text{NO}_3)_3$ ,  $\text{BiBr}_3$  and  $\text{BiCl}_3$  are considered promising catalysts due to their stability, air and moisture resistance, and low toxicity [16]. These bismuth(III) salts have been utilized as catalysts in various organic reactions, including Mukaiyama-type reactions [17], hydroamination [18], alkylation [19], benzannulation [20], oxidation [21], and other reactions [22–25]. However, the use of  $\text{BiOCl}$  as a catalyst for organic reactions has received limited attention until recently, when it is reported to be effective as a catalyst for selective benzyl alcohol oxidation reactions [26].

Our ongoing studies on the  $\text{BiOCl}$  material have shown its effectiveness in catalyzing the aldol condensation reaction of aromatic benzaldehyde and the formation of the benzalacetone compound. A key advantage of this material is its ability to be recovered and reused multiple times with little to no loss in catalytic performance.

## 2. Materials and Methods

### 2.1 Reagents

In this study, the following chemicals were utilized: Bismuth(III) nitrate pentahydrate ( $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ , 99%, Sigma Aldrich), N,N-dimethylformamide (DMF, 99.5%, Xilong Chemical, China), dichloromethane (DCM, 99.5%, Xilong Chemical, China), acetone

(99.5%, Xilong Chemical, China), benzaldehyde (99%, China), ethyl acetate (99.6%, Xilong Chemical, China), hexane (99.5%, Xilong Chemical, China). All materials are of analytical graded and utilized without further purification prior to the synthesis process.

### 2.2 $\text{BiOCl}$ Fabrication Procedures

The  $\text{BiOCl}$  material was synthesized by the solvothermal method (Figure 1) based on the previous literature [27,28]. Firstly,  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  (6 mmol) and dichloromethane (DCM) (30 mL) were dissolved in 30 mL of DMF. The mixture was then stirred on a magnetic stirrer for 30 min at room temperature and formed a transparent homogenous mixture. The mixture is poured into a Teflon tube with a stainless steel sheath. The reaction was carried out in a furnace at  $150^\circ\text{C}$  for 16 h. After the reaction, the white solid was separated from the suspension by centrifugation at 6000 rpm for 10 min. The obtained material was dried in a vacuum oven at  $60^\circ\text{C}$  after 24 h. XRD pattern and FT-IR spectra of  $\text{BiOCl}$  material were suitable with the previous reports.

### 2.3 Synthesis of Benzalacetone Compound

A reaction mixture was prepared by combining benzaldehyde (0.4 mmol, 0.0424 g), acetone (1.5 mL) and 20 mol%  $\text{BiOCl}$  (Scheme 1). The mixture was placed in a 10 mL pressure ball bottle, and stirred at  $120^\circ\text{C}$  for 24 h. After the reaction, a certain amount of reaction mixture was then extracted, mixed with 1 mL of water and 2 mL of ethylacetate, and dried using  $\text{Na}_2\text{SO}_4$ . The extracted solution was analyzed by GC using n-octane as the standard. The organic matter was condensed upon reducing pressure. The product was purified using column chromatography with a 1/3 ethylacetate/hexane solvent system to obtain a colorless liquid benzaldehyde. Product structures were determined using GC-MS and  $^1\text{H}$  NMR (Figure S5, S6, Supplementary Information (SI)).

To assess the reusability of the  $\text{BiOCl}$  catalyst, the reaction mixture was centrifuged to

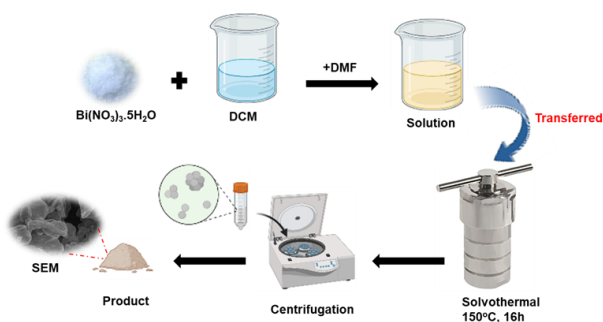
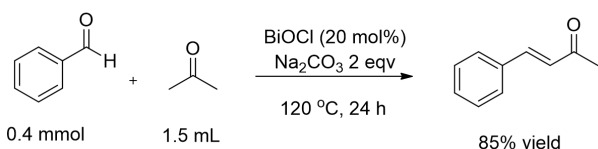


Figure 1. Schematic illustration of the solvothermal method for  $\text{BiOCl}$  synthesis.



Scheme 1. Synthesis of benzalacetone compound from benzaldehyde.

separate the catalyst, washed several times with DMF and exchanged with methanol, then activated at 150 °C under vacuum pressure for 6 h. After the leaching test, the BiOCl catalyst was separated by centrifugation and the resulting liquid phase was placed in a new reaction ball bottle. A new reagent was added to the solution without a catalyst, and the reaction was repeated under the same conditions. The reaction stages were monitored using GC.

### 3. Results and Discussion

#### 3.1 Structural Analysis of BiOCl Material

The XRD patterns of BiOCl is shown in Figure S1 (SI). The results suggested a highly pure tetragonal structure for BiOCl, as the diffraction peaks matched those of the standard reference material (JCPDS No. 06-0249) [29,30]. The strong characteristic peak are observed at 11.75°, which is indexed as (001) and related to the [Cl–Bi–O–Bi–Cl] stacking structure along the *c*-axis [31]. The diffraction peaks of BiOCl at 2 $\theta$  of 24.16°, 25.88°, 32.56°, 33.52°, 36.72°, 40.9°, 46.76°, 49.84°, 55.16°, and 58.68° corresponded to crystal planes (002), (101), (110), (102), (003), (112), (200), (113), (104), and (212), respectively, and are consistent with standard card (JCPDS no. 06-0249), indicating the tetragonal crystal structure of BiOCl [32]. Besides, there are some impurity peaks at 17° and 20° attributed to the remains Bi(NO<sub>3</sub>)<sub>3</sub> on the synthesized samples [33], due to it not being completely removed after the sample washing process.

The existence of BiOCl material is verified using FT-IR spectra (Figure S2, SI). The presence of small amount of mixed solvent (DMF and DCM) in the preparation process is indicat-

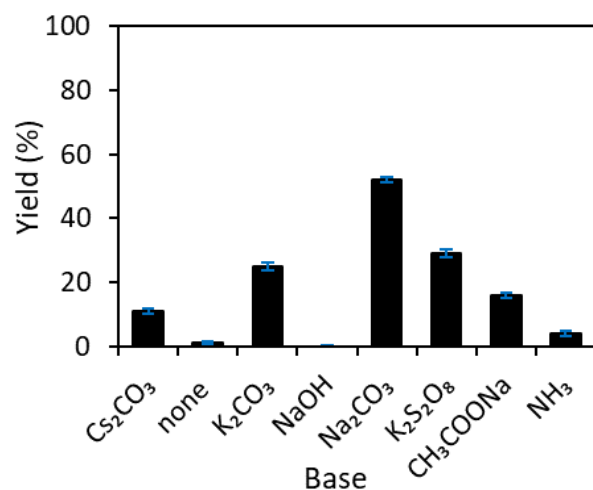


Figure 2. Effect of the base types to reaction yield.

ed by strong bands of C–H stretching vibration in –CH<sub>2</sub>– and –CH<sub>3</sub> group at 2900–2800 cm<sup>-1</sup>, 1415–1465 cm<sup>-1</sup>, and 949 cm<sup>-1</sup> [34,35], the C–Cl vibration (738 cm<sup>-1</sup>) [36]. Besides, conjugation will somewhat affect the position of the C=O stretch, moving it to a lower wavenumber [37,38]. The peaks at 1400, 1155, 1040 cm<sup>-1</sup> may be assigned as the asymmetric and symmetric stretching vibration peaks of Bi–Cl band in BiOCl structure [39]. Besides, the band at 528 cm<sup>-1</sup> is assigned to the Bi–O stretching mode [40].

Figure S3 (SI) displays SEM images of the BiOCl at various magnifications. The images reveal that sample is composed of numerous nanoflakes with diameters ranging from 0.1–1  $\mu$ m [41]. These ultra-thin nanoflakes have a large surface area and high surface energy, causing them to easily aggregate. This aggregation process also leads to the creation of mesopores or macropores. This is consistent with previous studies [42,43].

The physical properties of BiOCl were verified through N<sub>2</sub> adsorption/desorption measurement (Figure S4, SI). The results showed that the isotherm in Figure S4a (SI) is attributed to Type IV physisorption and a H3 hysteresis loop is observed [44,45], indicating that the nano-sheet particles may aggregate to form slit-shaped pores. The pore size distribution (Figure S4b, SI), is mesoporous with an average pore diameter of 7.93 nm. SBET is calculated from the slope and the intercept of the linear relation of 1/[Q(P/P<sub>0</sub>–1)] against P/P<sub>0</sub> (BET plot), where Q is the amount of adsorbed at P/P<sub>0</sub>, as shown for BiOCl material in Figure S4c (SI). BET plot for a mesoporous material shows a linear relation in the P/P<sub>0</sub> range of 0.00–0.17 and gives a small SBET value of about 4 m<sup>2</sup>/g. This result is also suitable with other reported values about BiOCl material [46,47].

#### 3.2 Investigation of the Catalytic Activity of BiOCl Material for Aldol Condensation Reaction

To determine the optimal reaction conditions, we studied the impact of various base types on the reaction between benzaldehyde and acetone in the presence of Cs<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, NaOH, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, CH<sub>3</sub>COONa, and NH<sub>3</sub>, respectively. The reaction was conducted at 120 °C for 24 h, with 20 mol% BiOCl as a catalyst, 2 eqv of base and acetone as the solvent. The results indicate that using bases (Figure 2) such as Cs<sub>2</sub>CO<sub>3</sub>, CH<sub>3</sub>COONa and NH<sub>3</sub> in the synthesis of benzalacetone yields less than 16%, 11%, and 4% reaction efficiency, respec-

tively. Bases, such as  $K_2CO_3$  and  $K_2S_2O_8$ , are also not suitable, with yields of only 25% and 29%, respectively.  $Na_2CO_3$  provides the best results, with a yield of 51%. Acid and base species are considered "hard" if they have a high charge density and are difficult to polarize. Larger and smaller species are higher up on the periodic table. As a result, it's easy to see why the yield of the aldol condensation reaction with  $Na_2CO_3$  is higher than with  $K_2CO_3$ , because  $Na_2CO_3$  is harder or stronger than  $K_2CO_3$  [48–50]. No reaction occurs when the base is omitted or replaced with NaOH. This demonstrates the significance of the base in the reaction process, as previously reported [51,52].

In organic synthesis reactions, the amount of base used can significantly impact reaction efficiency. To determine its effect, we conducted the reaction at 120 °C with 20 mol% BiOCl as the catalyst and  $Na_2CO_3$  as a base, in air, for 24 h. The base amount is varied from 0.5 to 3 equivalents, and the results of the impact on

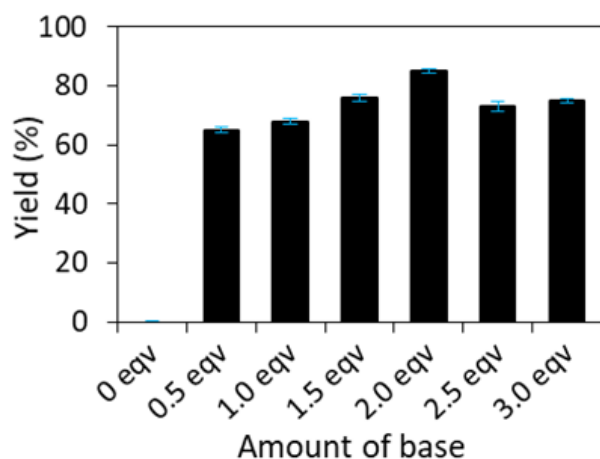


Figure 3. Effect of the amount of base to reaction yield.

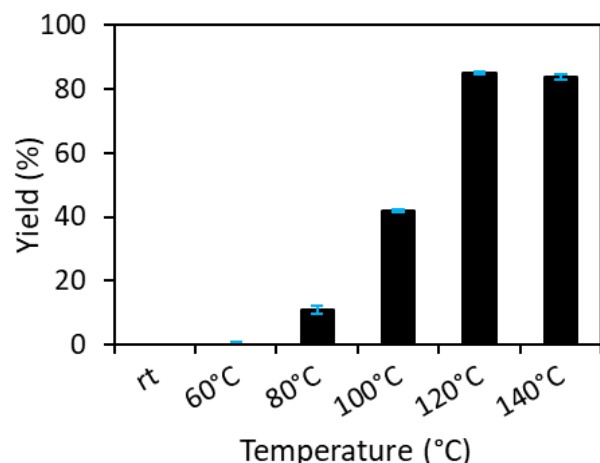


Figure 4. Effect of the temperature parameter to reaction yield.

the reaction yield are presented in Figure 3. The base amount has a significant impact on the reaction yield. This highlights the crucial role that the base plays in the synthesis of benzalacetone. The reaction does not occur in the absence of base. With the addition of 0.5 equivalent of base, the reaction yield is 65%. As the base amount increases to 2 equivalents, the yield reaches 85%. However, further increase in base amount to 3 equivalents resulted in a decrease in reaction efficiency to 75%. This demonstrates that the appropriate amount of base is necessary for optimal reaction effectiveness.

To study the impact of temperature on the reaction, we performed the reaction using acetone and benzaldehyde (0.4 mmol), 20 mol% BiOCl as a catalyst, and  $Na_2CO_3$  (2 eqv) as a base. The experiments were conducted in an air environment for 24 h. We evaluated the reaction at temperatures of 30, 60, 80, 100, 120, and 140 °C, respectively. The result of the temperature's effect on the reaction's efficiency is presented in Figure 4. The results indicate that the reaction does not proceed at temperatures below 80 °C. The synthesis efficiency reaches 42% at 100 °C and shows the highest yield of 85% at 120 °C. When the temperature is raised to 140 °C, there is a slight decrease in efficiency to 84%. Therefore, the results demonstrate that the reaction only occurs at a relatively high temperature, and the optimal temperature for further investigation of other factors is 120 °C. The pace of a chemical reaction accelerates as the temperature rises. Heat causes the reactant particles to travel more quickly, increasing the likelihood of collisions. The fact that the collisions happen more violently as the

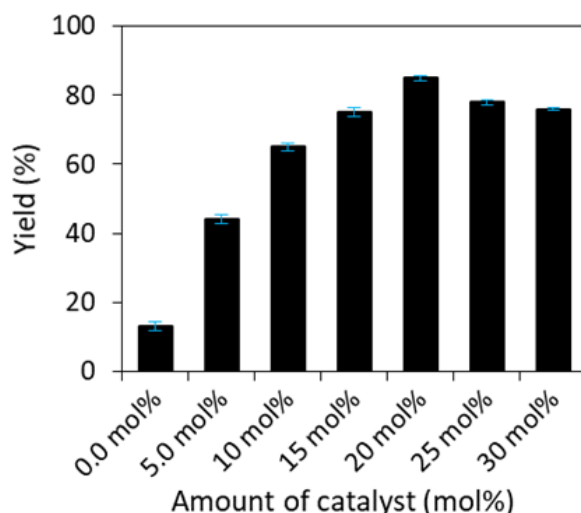


Figure 5. Effect of the catalyst amount to reaction yield.



temperature rises have an even more significant effect since it increases the likelihood that the reactants will overcome the activation energy barrier and proceed to create products. Besides, the effect of raising the temperature has been ascribed to decreasing adsorption of water for catalyst [53–55], as well as an increase in conventional heterogeneous catalytic reactions occurring on the BiOCl catalyst.

The amount of catalyst also has a significant effect on the reaction yield. The experiments were performed at 120 °C, Na<sub>2</sub>CO<sub>3</sub> (2 eqv.) as a base, and using acetone as the solvent and reactant, with varying amounts of BiOCl catalyst (0, 5, 10, 15, 20, 25, and 30 mol%). The impact of BiOCl catalyst content on reaction efficiency is displayed in Figure 5. The results shows that the reaction yield is low without a catalyst at 13%. With 5 mol% catalyst, the reaction efficiency increases to 44%. As the catalyst content increases, the reaction efficiency improves, reaching 85% with 20 mol% catalyst. However, further increases in catalyst content above 20 mol% led to a gradual decrease in efficiency, with 78% and 76% for 25 mol% and 30 mol% catalyst, respectively. Catalysts speed up chemical reactions. However, if just enough catalyst is supplied to keep it from becoming overly active, any additional catalyst will merely idly float around and the rate of the reaction won't grow any further. Thus, the best conditions for the reaction should involve 20 mol% BiOCl catalyst content for further investigation of other factors.

The reaction rate in the liquid phase using solid catalysts is heavily influenced by the amount of solvent used due to mass transfer processes. Our study examines the impact of solvent volume on reaction yield. The reaction was carried out at 120 °C with acetone as both

the solvent and reactant, using 20 mol% BiOCl as a catalyst in air conditions for 24 h. The amount of acetone solvent was varied from 0.5 to 3 mL (Figure 6). Results shows that as the solvent volume increases, the reaction efficiency improves, reaching a maximum of 85% at 1.5 mL. However, further increase in solvent led to a sharp decrease in efficiency, thus 1.5 mL is selected as the optimal amount for further investigation.

To evaluate the catalytic performance of BiOCl against other homogeneous catalysts, we conducted reactions under optimal conditions of 120 °C, using acetone as solvent and reactant, and 20 mol% catalysts in air for 24 h. The homogeneous catalysts tested were BiCl<sub>3</sub> (0.08 mmol, 25.2 mg) and Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (0.08 mmol, 38.8 mg) salts, while the heterogeneous catalyst was BiOCl under different conditions. Figure 7 compares the catalytic ability of BiOCl with the homogeneous catalysts. The results shows that BiCl<sub>3</sub> has a low reaction efficiency of 7%, while the use of Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O as a catalyst resulted in a yield of 43%. In contrast, BiOCl outperforms the homogeneous catalysts, achieving the highest efficiency of 85% when using 20 mol% BiOCl. The Bi(III) cation [56,57] is considered a borderline element by the hypothesis of hard and soft acids and bases (HSAB) [58]. As soft Lewis acids, Bi(III) salts with electron-withdrawing groups combine with hard atoms in Lewis bases to generate weak complexes (such as the carbonyl group) [59]. Additionally, while the 6s orbital (inert pair) is stabilized as a result of relativistic effects, the Lewis acid behavior of Bi(III) salts can be attributed to the availability of unoccupied orbitals (d and/or Bi–X s\*), with the latter property being accentuated by strong withdrawing groups like oxychloride (–OCl) [59].

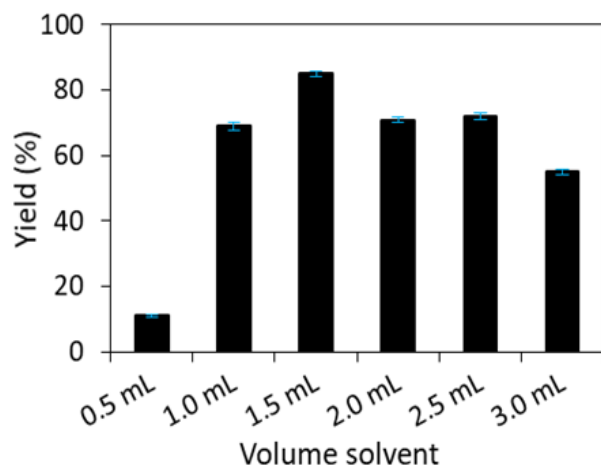


Figure 6. Effect of the solvent volume to reaction yield.

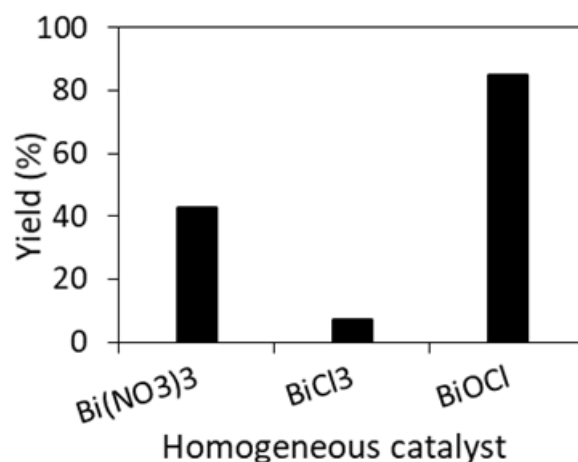


Figure 7. The comparison of heterogeneous catalyst with homogeneous catalysts.

Besides, BiOCl material can survive long in the reaction environment leading to high catalytic efficiency. These results demonstrate the effectiveness of BiOCl as a catalyst for the synthesis of benzalacetone.

To ensure that the reaction does not occur in conditions of non-catalyst or reaction media that have some active metal centers separated from the solid phase during the reaction, leading to incomplete reactions under heterogeneous catalytic conditions, a "leaching test" was performed on the coupling reaction between acetone and benzaldehyde. The reaction was run at 120 °C using 1.5 mL of solvent and 20 mol% BiOCl as a catalyst in air for 24 h. The reaction was stopped after 4 h, analyzed by GC, and then centrifuged to remove the solid catalyst. The solution was stirred for another 24 h under the same reaction conditions without the solid catalyst. Further samples were taken every 4 h and analyzed by GC to monitor the change in

yield. Figure 8 shows the results of the heterogeneity test. The reaction yield reaches around 85% after 24 h and increases insignificantly to 84% after 28 h. Therefore, the optimal reaction time is set at 24 h to save energy. The leaching test showed that after 4 h, the yield was 19%. After removing the catalyst, the reaction yield remains almost unchanged, indicating that the C–C coupling reaction between acetone and benzaldehyde mainly occurs due to the solid catalyst and the catalyst is stable in the reaction environment.

The use of heterogeneous catalysts has an advantage over homogenous catalysts due to their ease of recovery and reuse. The recovery process involved separating the BiOCl material via centrifugation and washing it with DMF and acetone, followed by drying at 85 °C under vacuum for 24 h. The results from the reuse of the recovered catalyst shows a reaction efficiency of 83% after the fourth run (Figure 9), indicating stable performance. XRD patterns of BiOCl in Figure 10 further confirmed its stability in the reaction media.

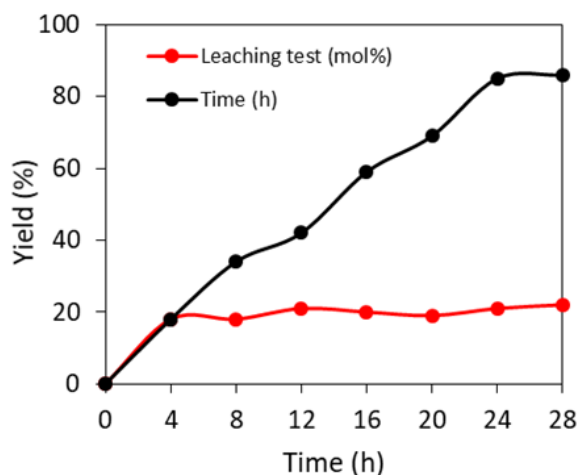


Figure 8. Leaching test.

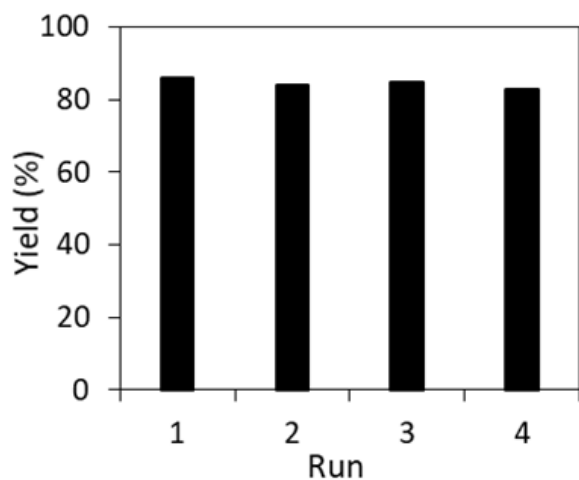


Figure 9. The recovery and reuse of BiOCl material.

#### 4. Conclusions

BiOCl has been found to be an effective catalyst for C–C coupling reactions between acetone and benzaldehyde to produce benzalacetone derivatives in the medium atmosphere. With an efficiency of 85% after 24 h at 120 °C, using acetone as both reactant and solvent in the presence of 20 mol% BiOCl catalyst, the results are comparable to some homogeneous catalysts. Additionally, the BiOCl catalyst can be recovered and reused 4 times without

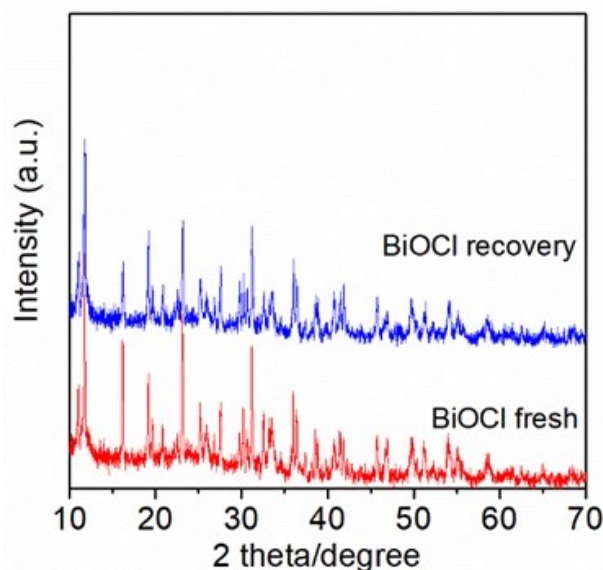


Figure 10. XRD patterns of BiOCl fresh and recovery.

significant reduction in efficiency, suggesting its stability in the reaction. These results highlight the potential of BiOCl as a heterogeneous catalyst for use in organic synthesis reactions.

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### CRedit Author Statement

Author Contributions: Oanh T. K. Nguyen: Experiment, Methodology, Investigation, Resources, Data Curation, Writing, Review and Editing, Supervision; Vinh Huu Nguyen: Experiment, Methodology, Formal Analysis, Data Curation, Writing Draft Preparation, Visualization, Software, Project Administration; Linh Xuan Nong: Validation, Writing, Review and Editing, Data Curation. All authors have read and agreed to the published version of the manuscript.

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**General information:** All reactions were performed under air atmosphere. All chemicals were obtained from commercial sources and used directly without further treatment. Solvents used in the experiment have been prior treated following standard procedure. The reaction process was monitored by TLC. The NMR spectra were recorded in 400 MHz apparatus using  $\text{CDCl}_3$  as solvent, and the frequencies  $^1\text{H}$  NMR measurement were 500 MHz. Chemical shifts were recorded in ppm by employing TMS or the solvent peak of  $\text{CDCl}_3$  as internal standard. GC analyses were carried out utilizing HP HP 5890 GC system, DB-624 column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.5  $\mu\text{m}$ ) and FID detector. GC-MS analyses were performed using a Hewlett Packard GC-MS 5972 with a RTX-5MS column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.5  $\mu\text{m}$ ). The temperature program for GC-MS analysis heated samples from 60 to 280  $^\circ\text{C}$  at 10  $^\circ\text{C}/\text{min}$  and held them at 280  $^\circ\text{C}$  for 2 min. Inlet temperature was set constant at 280  $^\circ\text{C}$ . MS spectra were compared with the spectra gathered in the NIST library.

**Catalyst characterization:** Physical and chemical methods are used to determine the characteristic properties of  $\text{BiOCl}$ . X-ray diffraction (XRD) analysis to determine the material structure was carried out on the Bruker AXS D8 Advantage with the source being  $\text{Cu K}\alpha$ . Physical adsorption to determine the specific surface of the catalyst was performed on Nova Quantachrome 2200e. Samples were activated in a vacuum at 150  $^\circ\text{C}$  for 6 h, followed by nitrogen adsorption at 77  $^\circ\text{C}$  and low pressure. Infrared spectrum (FT-IR) was performed on a Bruker TENSOR37, with a KBr-compressed sample used to determine functional groups in the material. The SEM images of catalyst were obtained by scanning electron microscope (SEM) on a JSM 7401F device (JEOL).

Material properties

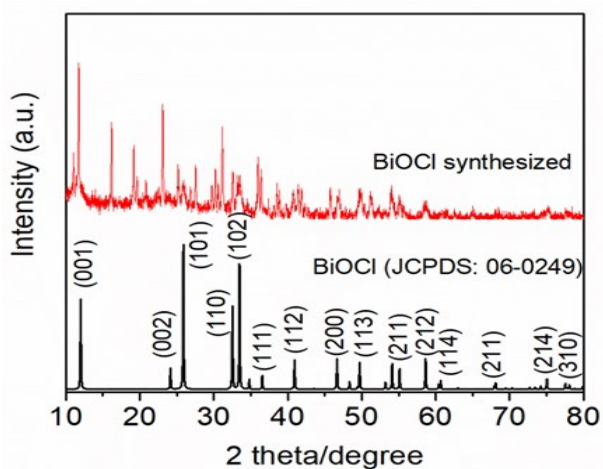


Figure S1. XRD pattern of  $\text{BiOCl}$  material.

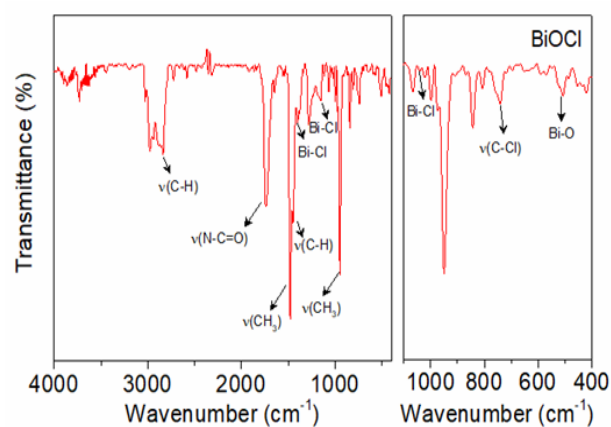


Figure S2. FT-IR spectra of  $\text{BiOCl}$  material.

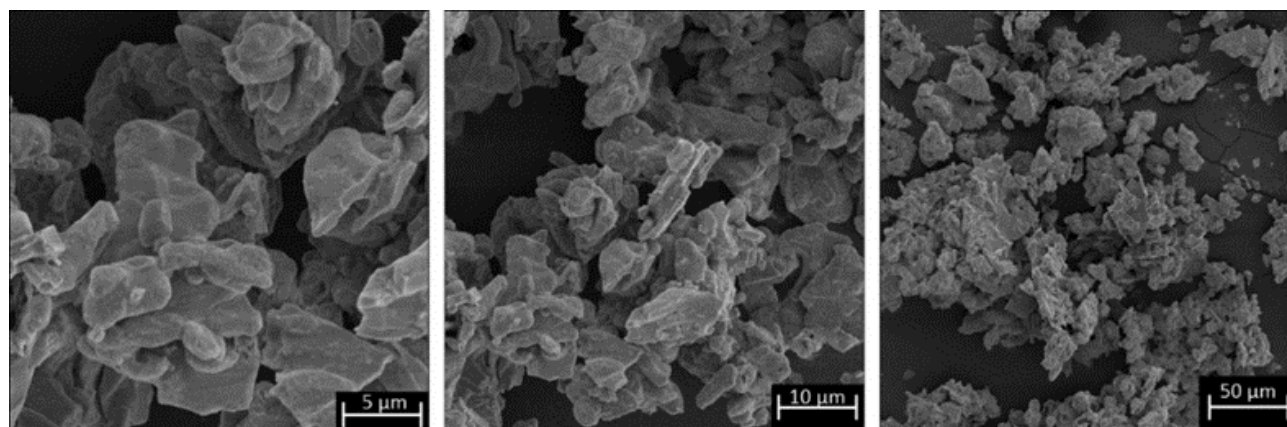


Figure S3. The SEM images of  $\text{BiOCl}$  material at different magnification.

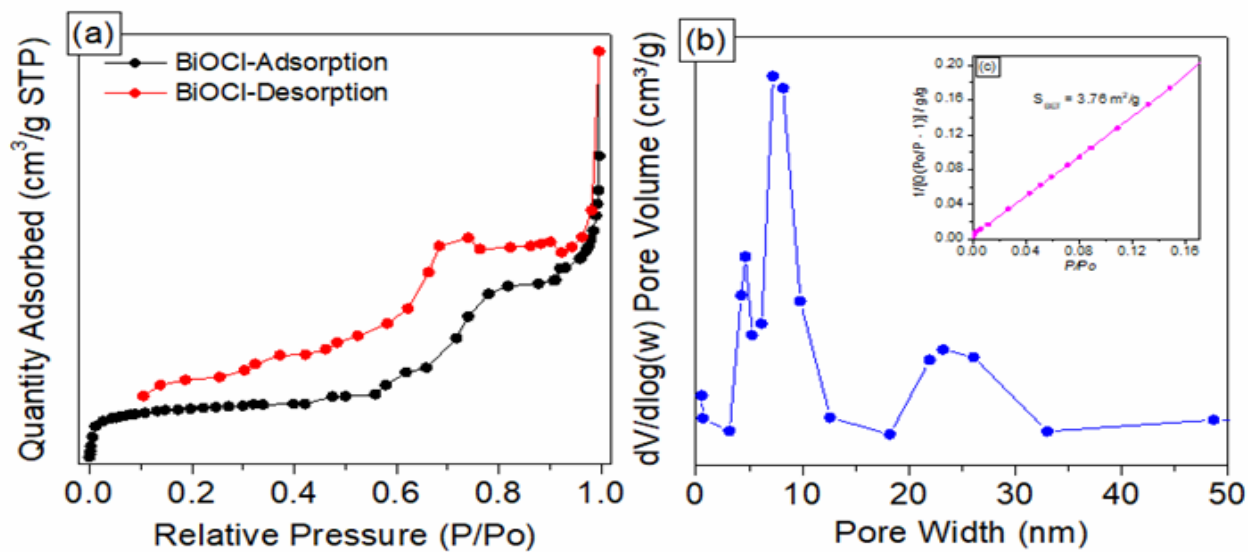


Figure S4. N<sub>2</sub> adsorption/desorption isotherms (a), pore size distribution (b), and BET plot (c) of BiOCl material.

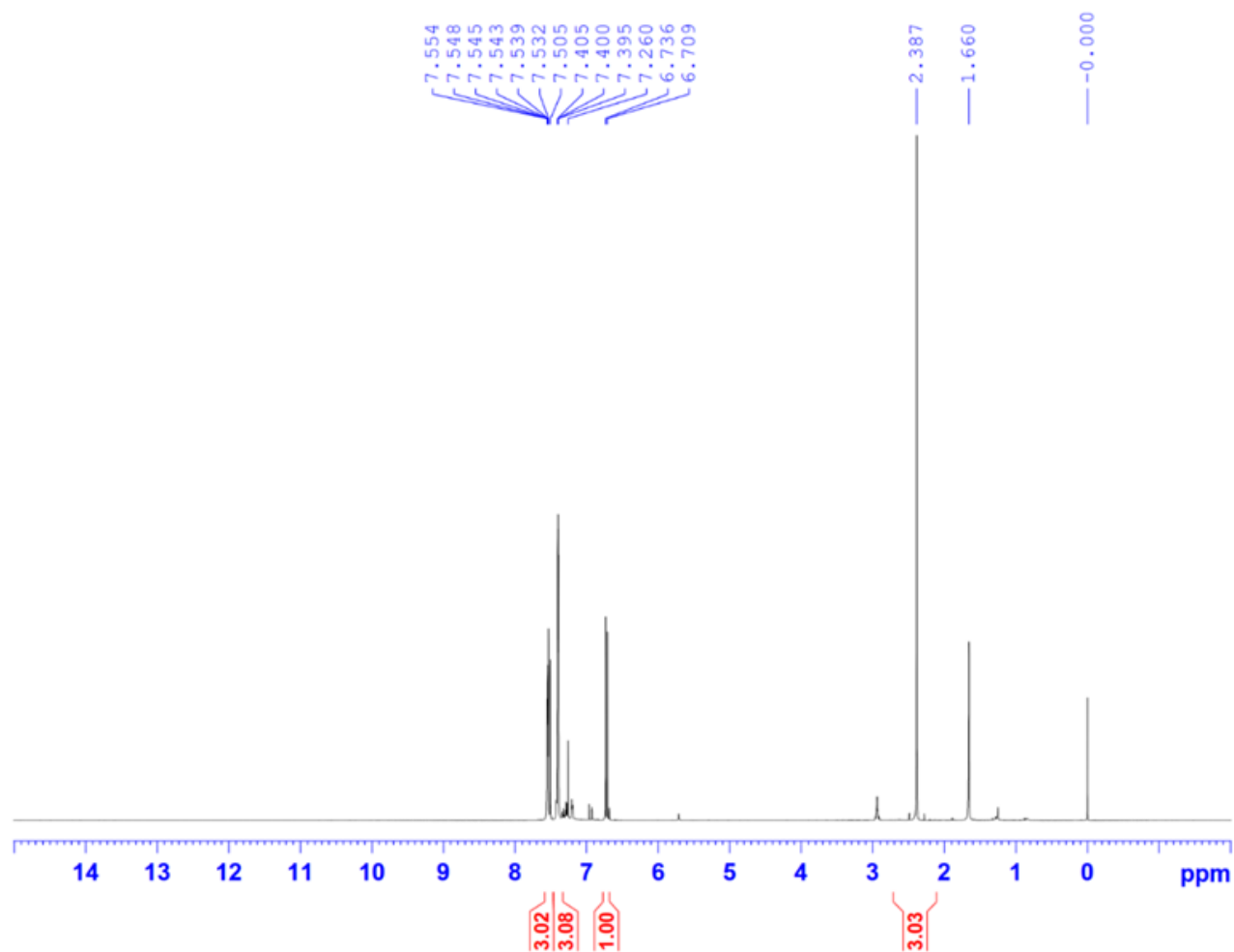


Figure S5. <sup>1</sup>H NMR spectra of benzalacetone.

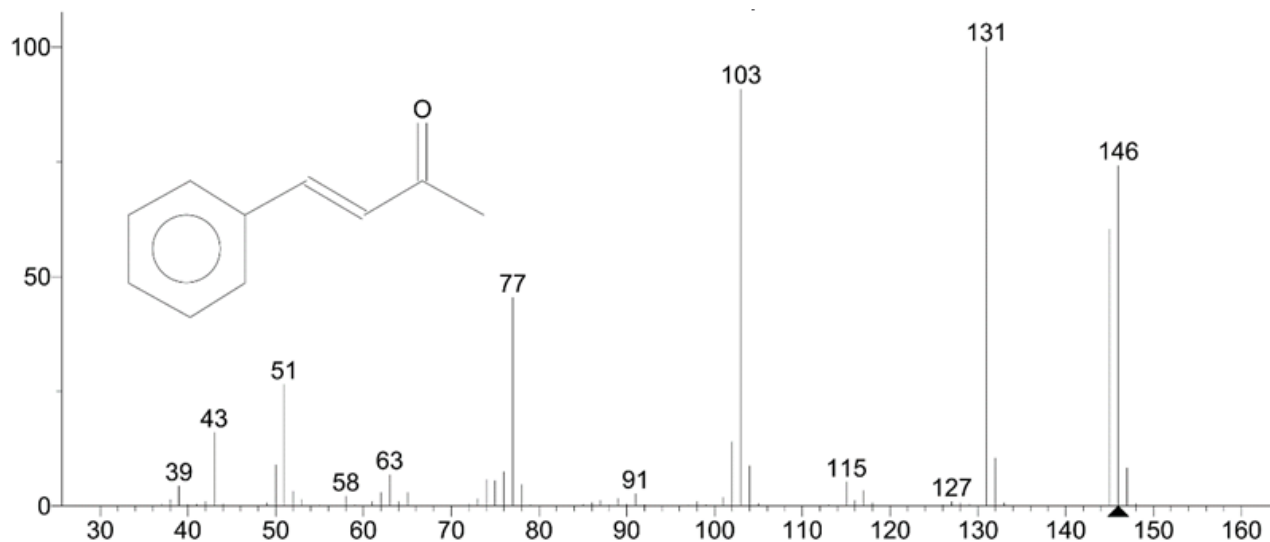


Figure S6. MS spectra of benzalacetone.

#### Characterization data for benzalacetone (Fig. S5, Fig. S6).

Prepared as shown in the general experimental procedure and purified on silica gel (ethyl acetate/hexane = 1:3): colorless liquid, 85% yield. This compound is known [1].  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.554-7.505 (m, 3H), 7.405-7.395 (m, 3H), 6.721 (d,  $J = 13.5$  Hz, 1H).  $m/z = 146$ .

#### Reference

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