# OPTIMIZATION OF THE ISOMERIZATION REACTION OF *ENDO*-TETRAHYDRODICYCLOPENTADIENE INTO *EXO*-TETRAHYDRODICYCLOPENTADIENE

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**Abstract**

The key ingredient in JP-10 fuel (Jet Propellant 10), known as *Exo*-tetrahydrodicyclopentadiene (*exo*-THDCPD), played a crucial role in powering high-performance cruise missiles, rockets, and supersonic aircraft. This essential component was synthesized by converting *endo*-tetrahydrodicyclopentadiene (*endo*-THDCPD). In this study, *exo*-THDCPD was synthesized through the isomerization reaction of *endo*-THDCPD using an $AlCl_3$ catalyst. The optimal conditions for the isomerization reaction have been thoroughly investigated such as the influence of the solvent, reaction time, temperature reaction, and mass ratio of starting materials. In these conditions, the desired product was obtained up to the conversion rate of 98.5% and the selectivity of 99.5%. Moreover, the specific properties of *exo*-THDCPD were also thoroughly studied in this article.

***Keywords:*** *Exo-tetrahydrodicyclopentadiene; endo-tetrahydrodicyclopentadiene; isomerization reaction.*

## 1. Introduction

High-speed flights of hypersonic vehicles face challenges with heat management, requiring onboard fuels with strong heat absorption capabilities for regenerative cooling systems [1, 2]. Fuels with high density tend to have excellent heat absorption properties due to their high energy content per unit volume. Additionally, high-density fuels enable aircraft to carry more fuel in a limited space, giving them an advantage for long-distance journeys. These fuels are typically made up of either pure synthetic hydrocarbons or a combination of different synthetic hydrocarbons, all designed to meet the specific requirements of the system in use [3, 4].

JP-10, a blend of three hydrocarbons - *exo*-tetrahydrodicyclopentadiene, endo-tetrahydrodicyclopentadiene, and adamantane, is the leading candidate for current and future propulsion systems (Fig. 1). The primary component in JP-10 is *exo*-THDCPD, giving it a single-component fuel status. This fuel has a unique molecular structure with

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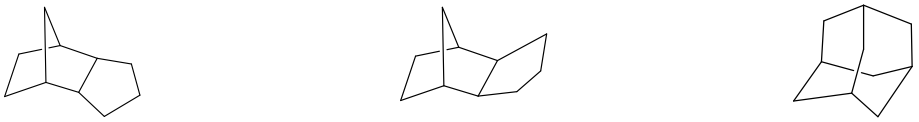
three interconnected rings, providing it with a higher volumetric energy density of 39.6 MJ/L. In comparison to traditional jet engine fuels like Jet-A with lower volumetric energy density of 34.1 MJ/L, JP-10 offers superior performance with lower freezing (-79°C) and higher flash (54°C) points [5-7]. Furthermore, JP-10 is known for its impressive specific impulse of 297.4 s [8]. These exceptional physical and chemical characteristics make JP-10 a popular choice for various advanced propulsion systems [9, 10].



*endo*-THDCDP *exo*-THDCPD adamantane

*Fig. 1. Structural formula of the components of JP-10 fuel.*

*Exo*-THDCPD servers not only as a component in JP-10 fuel but also as a crucial precursor in the synthesis of adamantane and a potent fuel diluent with exceptional viscosity characteristics [11]. As a result, researchers in the field have shown keen interest in studying the synthesis of this compound. A current area of interest in the synthesis of *exo*-THDCPD involves studying the isomerization process of *endo*-THDCPD into its isomer form [12, 13].

In this article, we studied the modulation of *exo*-THDCPD through the isomerization reaction of *endo*-THDCPD using an $AlCl_3$ catalyst. Specifically, our research focuses on optimizing conditions for the isomerzation process, such as reaction temperature, reaction time, reaction solvents, and catalyst ratio. Additionally, properties related to fuel characteristics of *exo*-THDCPD were also presented in this article.

## 2. Experiment

### *2.1. Materials*

*Endo*-THDCPD (self-synthesized, purity ≥ 98%); $AlCl_3$ anhydrous used was of AR grade from Sigma Aldrich; cyclohexane, dichloromethane, chloroform, acetone, n-heptane, toluene used were of AR grade from Aladdin.

### *2.2. Characterization techniques*

Infrared spectra were recorded on Spectrum Two, Perkin Elmer at Le Quy Don Technical University. The nuclear magnetic resonance (NMR) spectra have been recorded with Brucker Avance 500 MHz spectrometers at Institute of Chemistry, Vietnam Academy of Science and Technology. $^1$H-NMR spectra: δ (H) are given in ppm relative to tetramethylsilane (TMS), using δ ($CDCl_3$) = 7.26 ppm as an internal reference. $^{13}$C- NMR spectra: δ (C) are given in ppm relative to TMS, using δ ($CDCl_3$) = 77.0 ppm as an internal reference. The gas chromatography-mass spectrometry (GC-MS) analysis was conducted on the GC-456 instrument at University of Science.

The density was measured by hydrometer method according to the international standard ASTM D1298-12b(2017)e1 "Standard Test Method for Density, Relative Density, or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method". The freezing point was measured according to the international standard ASTM D97-17b "Standard Test Method for Pour Point of Petroleum Products". The volumetric energy value was measured by bomb calorimeter according to the internatonal standard ASTM D240-19 "Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter". The flash point was measured according to the international standard ASTM D93-20 "Standard Test Methods for Flash Point by Pensky-Martens Closed Cup Tester". The concentrations of ingredients and products were determined using the external standard method by GC-456 gas chromatograph equipped with MS-1 capillary column (30 m × 0.25 mm × 0.25 μm) (50$^{o}$C for 3 min, 8 $^{o}$C/min until 280$^{o}$C). The conversion and selectivity of the reaction were calculated as follows:

Conversion (%): [1 - (amount of remained *endo*-THDCPD/ initial amount *endo*-THDCPD) x 100%.

Selectivity (%): [amount of formed *exo*-THDCPD/ amount of consumed *endo*-THDCPD] x 100%.

***2.3. General procedure***

The reaction vessel consists of a three-necked flask with a capacity of 250 ml, fitted with a reflux condenser in the central neck and sampling equipment, and a temperature sensor installed in the other two necks. The reaction vessel was placed on a magnetic stirrer with temperature and stirring speed control. For reactions conducted at temperatures below room temperature, the temperature was maintained using a circulating refrigeration system. In a typical reaction, *endo*-THDCPD was dissolved in various solvents at a predetermined ratio and then added to the reaction vessel under a nitrogen atmosphere. Once the *endo*-THDCPD was completely dissolved, the reaction mixture was heated (or cooled) to the reaction temperature. Subsequently, a quantity of anhydrous aluminum chloride catalyst was added to the reaction vessel, and the reaction commenced. With a stirring speed of 800 rpm, the entire reaction was conducted over a period ranging from 30 minutes to 5 hours. The reaction products were periodically collected during the reaction. Specifically, at specified time intervals, 5 ml of the liquid solution was withdrawn from the reaction medium and washed with a 10% $NaHCO_3$ aqueous solution until reaching pH = 7. The resulting solution was then dried using anhydrous $MgSO_4$, the solvent was evaporated, and the resulting product was analyzed by gas chromatography using a GC-456 instrument.

## 3. Results and discussion

### *3.1. Effect of isomerization time*

The extent of *endo*-THDCPD conversion was contingent upon the reaction time. To refine this timeframe, the isomerization reaction of *endo*-THDCPD was conducted by using $AlCl_3$ as a catalyst in dichloromethane solvent at 20°C, with the mass ratio of $AlCl_3$, *endo*-THDCPD, and solvent at 0.15, 1.0, and 1.0, respectively.

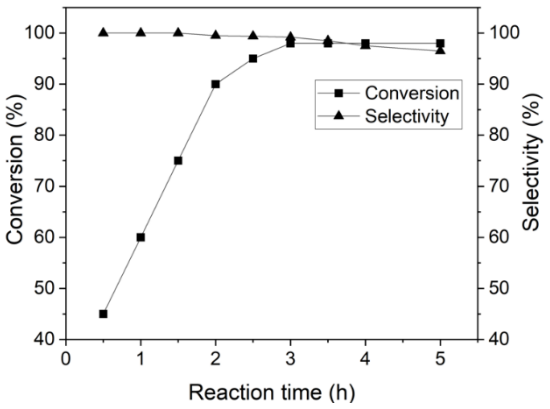



*Fig. 2. Effect of reaction time on conversion and selectivity.*

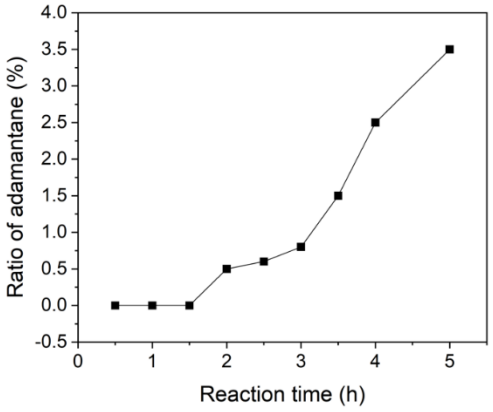



*Fig. 3. The amount of adamantane formed over time.*

The obtained results showed that the conversion and selectivity of the desired product were significantly affected by reaction time (Fig. 2). After increasing the isomerization time to 3 hours, the conversion rate reached 98% and did not change with longer times. However, the selectivity showed an increase from 0.5 hours to 3 hours, but then slightly decreased after surpassing the 3-hour mark. This was due to some *exo*-THDCPD converting into adamantane, reducing selectivity. The formation of adamantane over time was shown in Fig. 3. Therefore, it was concluded that the best duration for isomerization was 3 hours.

### *3.2. Effect of solvents on conversion and selectivity*

The influence of solvent on conversion and selectivity of *exo*-THDCPD was needed to investigate. In the isomerization reaction, inert solvents were employed to dissolve *endo*-THDCPD. The solvents were carefully chosen to dissolve the solid *endo*-THDCPD and aid in the isomerization process until enough *exo*-THDCPD was produced to dissolve its *endo*-precursor. It was crucial for the inert solvent selected to be unreactive with the raw material, final product, and $AlCl_3$ catalyst. Suitable inert solvents included chlorinated paraffins like dichloromethane and chloroform, as well as paraffins such as cyclohexane, heptane, acetone, and toluene. Therefore, the choice of solvent played a vital role in determining the speed of *endo*-THDCPD conversion. The research team conducted an isomerization

reaction using a 15% $AlCl_3$ catalyst for 3 hours in various solvents. The specific results of this reaction were detailed in Table 1.

The results showed that used solvents, except toluene, promoted isomerization, with dichloromethane being the most effective in enhancing the process. Isomerization with the $AlCl_3$ catalyst follows the pathway of carbonium ion chain transmission [14]. Solvents like dichloromethane interact with the $AlCl_3$ catalyst to produce the carbonium ion, which initiates the isomerization reaction. The carbonium ion then continues the chain reaction by generating hydrogen ions, leading to increased reaction conversion. On the other hand, toluene tends to hinder the chain reaction by capturing the carbonium ion through alkylation reactions. Additionally, since the isomerization reaction releases mild heat, solvents that act as heat sinks can improve conversion efficiency. Therefore, dichloromethane is deemed the most suitable solvent for the isomerization reaction of *endo*-THDCPD using an $AlCl_3$ catalyst. The volume of solvent used also plays a significant role in the reaction rate. Hence, extensive studies have been carried out to optimize the solvent volume. Specifically, the solvent volume was varied from 50% to 150% by weight relative to *endo*-THDCPD (Fig. 4).

*Table 1. Effect of solvents on conversion and selectivity*

| Solvents | Selectivity (%) | Conversion (%) |
|---|---|---|
| Cyclohexane | 99.5 | 30.3 |
| n-Heptane | 99.5 | 20.5 |
| Dichloromethane | 99.5 | 98.5 |
| Chloroform | 99.5 | 45.6 |
| Acetone | 99.3 | 36.2 |
| Toluene | 98.2 | 8.1 |

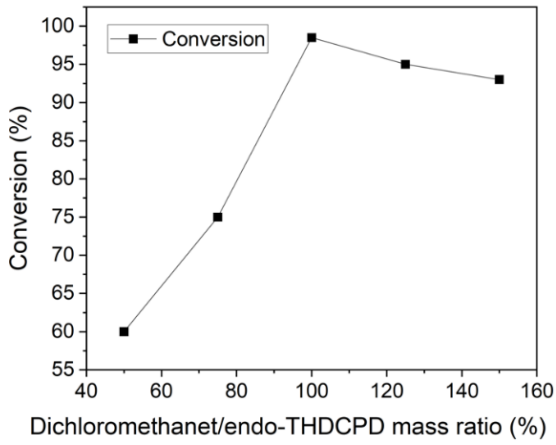



*Fig. 4. Effect of quantity of solvent on conversion.*

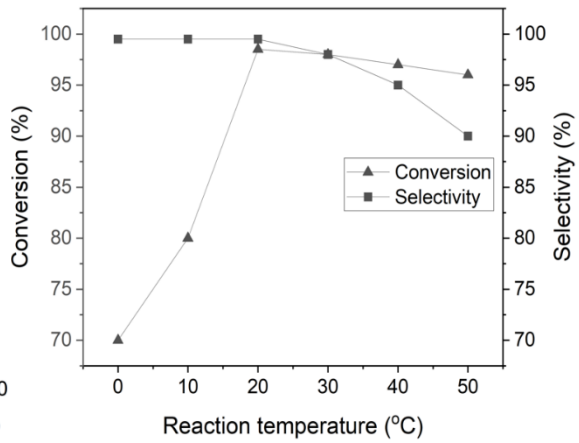



*Fig. 5. Effect of reaction temperature on conversion and selectivity.*

The results illustrated in Fig. 4 indicate that as the mass ratio between $CH_2Cl_2$ and *endo*-THDCPD was increased from 0.5 to 1, the conversion rate nearly doubled. However, with further increases in this ratio, the conversion experienced a slight decrease. These observed results were mainly due to the heterogeneous nature of the isomerization reaction, where the presence of the solvent played a crucial role in influencing the reaction kinetics. In cases where there was a low amount of solvent, the poor dispersion of reactants and catalysts hindered the conversion rate. On the other hand, an excess of solvent reduced the interaction between reactants and catalysts, ultimately leading to lower conversion rates. Therefore, the optimal mass ratio of dichloromethane to *endo*-THDCPD for this isomerization reaction was found to be 1:1.

### *3.3. The effect of isomerization temperature*

It was found that the conversion and selectivity of the desired product were significantly affected by the temperature. The isomerization reaction of *endo*-THDCPD to *exo*-THDCPD also forms the by-product amadatane at high temperature. The reaction was conducted across a temperature range from 0°C to 50°C (Fig. 5). At low temperatures ($0^oC$ and $10^oC$), the conversion rate was low due to the slow reaction rate. However, temperatures exceeding 30°C led to decreased selectivity, primarily due to the increased formation of amadatane. So the optimal temperature for this isomerization reaction was 20°C.

### *3.4. The influence of quantity of catalyst*

Aluminum (III) chloride serves as a prevalent Lewis acid catalyst for this isomerization reaction. It was found that the conversion and selectivity of *exo*-THDCPD was significantly affected by the catalyst concentration of $AlCl_3$ (Fig. 6). With an increase in catalyst loading, a corresponding rise in the conversion rate was observed and the optimal catalyst loading was determined to be 15% quantitatively. It seemed that the reaction might reach a dynamic equilibrium after increasing the mass ratio of catalyst more than 15%.

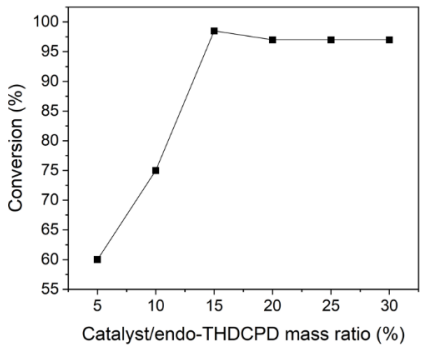



*Fig. 6. Effect of quantity of catalyst on conversion.*

### *3.5. Characterization of exo-THDCPD*

The synthesized *exo*-THDCPD was characterized as a colorless oil, possessing a density of 0.937 g/cm$^3$ (20$^o$C), a flash point of 56°C, a viscosity of 2.752 mPa.s (25$^o$C) and a freezing temperature of -79°C. It exhibits a calorific value of 41.84 MJ/L and demonstrates a high purity of 99%. Furthermore, the product's characterization is supported by the GC, FTIR, and NMR spectra, as illustrated in Figures 7-11.

FTIR spectroscopy of *exo*-THDCPD (Fig. 9) was carried out to further characterize the *exo*-THDCPD structure. FTIR spectra showed characteristic bands of the –$CH_2$ functional groups. Specifically, stretching vibration and bending vibration of –$CH_2$ groups with wavenumber ranges in the 2942-2864 cm$^{-1}$, and 1468-549 cm$^{-1}$, respectively.

Furthermore, $^1$H and $^{13}$C-NMR signals are observed for all protons and carbon atoms in the formula of *exo*-THDCPD (Fig. 7, 8, and Table 2).

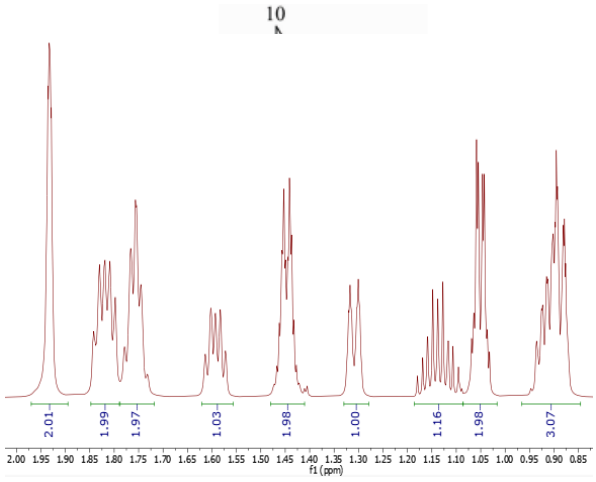



*Fig. 7. $^1$H-NMR spectrum of exo-THDCPD.*

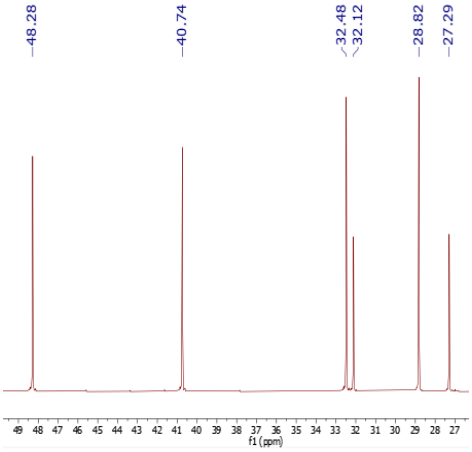



*Fig. 8. $^{13}$C-NMR spectrum of exo-THDCPD.*

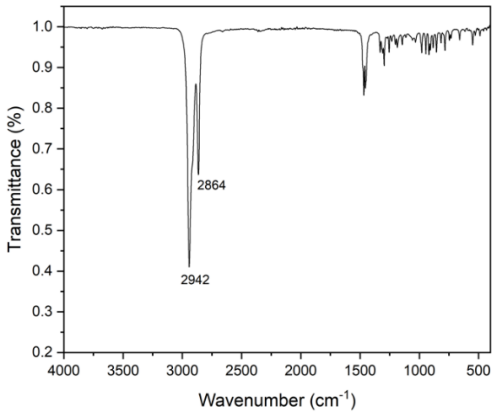



*Fig. 9. FTIR spectrum of exo-THDCPD.*

*Table 2. $^{1}H$, $^{13}C$ - NMR spectrum data of exo-THDCPD*

| No. | $\delta_H$ (ppm) | $\delta_C$ (ppm) | Groups |
|---|---|---|---|
| 1 | 1.45; 1.05 | 28.82 | $CH_2$ |
| 2 | 1.93 | 40.74 | CH |
| 3 | 1.45; 1.05 | 28.82 | $CH_2$ |
| 4 | 1.93 | 40.74 | CH |
| 5 | 1.75 | 48.28 | CH |
| 6 | 1.75 | 48.28 | CH |
| 7 | 1.82; 0.90 | 32.48 | $CH_2$ |
| 8 | 1.82; 0.90 | 32.48 | $CH_2$ |
| 9 | 1.59; 1.13 | 27.29 | $CH_2$ |
| 10 | 1.31; 0.90 | 32.12 | $CH_2$ |

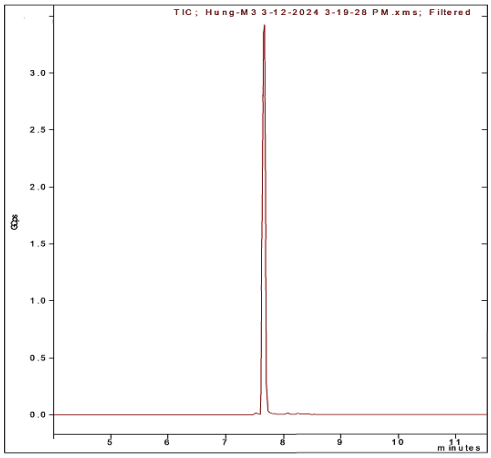



*Fig. 10. GC spectrum of exo-THDCPD.*

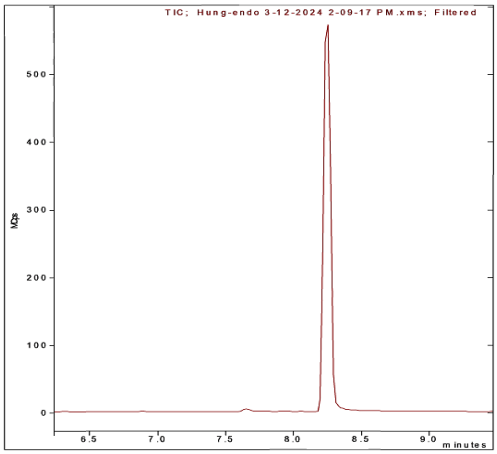



*Fig. 11. GC spectrum of endo-THDCPD.*

The GC spectra exhibit distinct peaks for *endo*-THDCPD and *exo*-THDCPD, with retention times of 7.670 minutes and 8.255 minutes, respectively.

## 4. Conclusion

*Exo*-THDCPD was successfully synthesized through the isomerization of *endo*-THDCPD, achieving a conversion rate of 98.5% and a selectivity of 99.5%. The reaction was conducted in dichloromethane solvent at a temperature of 20°C for 3 hours, with a mass ratio of catalyst to *endo*-THDCPD to dichloromethane set at 0.15:1:1, respectively. Furthermore, specific properties of *exo*-THDCPD fuel were investigated, revealing its suitability as an excellent fuel for rocket engines.

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# TỐI ƯU HÓA PHẢN ỨNG ĐỒNG PHÂN HÓA *ENDO*-TETRAHYDRODICYCLOPENTADIENE TẠO THÀNH *EXO*-TETRAHYDRODICYCLOPENTADIENE

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**Tóm tắt:** Thành phần chính trong nhiên liệu JP-10 (nhiên liệu phản lực thế hệ thứ 10), được gọi là *Exo*-tetrahydrodicyclopentadiene (*exo*-THDCPD), đóng vai trò quan trọng trong việc cung cấp năng lượng cho tên lửa hành trình, tên lửa và máy bay siêu thanh hiệu suất cao. Thành phần thiết yếu này được tổng hợp bằng cách chuyển đổi *endo*-tetrahydrodicyclopentadiene (*endo*-THDCPD). Trong nghiên cứu này, *exo*-THDCPD được tổng hợp thông qua phản ứng đồng phân hóa *endo*-THDCPD sử dụng chất xúc tác $AlCl_3$. Các điều kiện tối ưu cho phản ứng đồng phân hóa đã được nghiên cứu kỹ như ảnh hưởng của dung môi, thời gian phản ứng, nhiệt độ phản ứng và tỉ lệ khối lượng của nguyên liệu ban đầu. Trong điều kiện tối ưu này, sản phẩm mong muốn thu được với tỉ lệ chuyển đổi là 98,5% và độ chọn lọc là 99,5%. Hơn nữa, các tính chất đặc trưng của *exo*-THDCPD cũng đã được nghiên cứu trong bài báo này.

***Từ khóa**: Exo-tetrahydrodicyclopentadien; endo-tetrahydrodicyclopentadien; phản ứng đồng phân hóa.*

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