Plastic waste to drug intermediate: targeted cleavage of C–O bonds in polyphenylene oxide to 3,5–dimethyl phenol

Bo Feng⊥, Yaxuan Jing⊥, Yong Guo, Xiaohui Liu, Yanqin Wang*

Shanghai Key Laboratory of Functional Materials Chemistry, Research Institute of Industrial Catalysis, School of Chemistry and Molecular Engineering, East China University of Science and Technology, Shanghai 200237, P. R. China.

E-mail: wangyanqin@ecust.edu.cn

⊥ Both authors contributed equally to this work.

Experimental procedures

Chemicals

$RuCl_3 \cdot 3H_2O$ was purchased from Aladdin Reagent Co., Ltd (Shanghai, China). TiO_2 were purchased from Macklin Reagent Co., Ltd (Shanghai, China). Hydroxyapatite were purchased from Macklin Reagent Co., Ltd (Shanghai, China). PPO was purchased from Sigma Aldrich. 3,5-dimethylphenol was purchased from Macklin. Both o-cresol and m-cresol were purchased from Bailingwei(J&K). Decane was purchased from Maryer. Pentadecane was purchased from Macklin. The mPPO was purchased from Shanghai Xingyu Suhua. All purchased chemicals were of analytical grade and used without further purification.

Catalyst preparation

Nb_2O_5 was synthesized according to our previous reported procedures[1]. Typically, 19.2 g of prepared niobium oxalate and 0.711 g of ammonium oxalate were dissolved in 50 mL deionized water, and then the transparent solution was aged in a Teflon-lined autoclave for 24 h at 180 °C. After cooling down, the solid was filtered, washed with distilled water and then dried at 50 °C overnight. Finally, the Nb_2O_5 sample was obtained by calcination at 400 °C for 4 h in air with a linear heating ramp of 10 °C min^{-1}.

The Ru/ Nb_2O_5 catalysts were prepared by incipient wetness impregnation of Nb_2O_5

with aqueous solution of $RuCl_3$. The metal loading in Ru/Nb_2O_5 catalyst was 2wt%, 0.5wt%, 0.05wt% respectively. Typically, take 0.05wt%Ru/Nb_2O_5 for example, 0.6g Nb_2O_5 power was quickly add to 0.9g $RuCl_3$ solution (4.83 μmol/g) under strring. After that, the mixture was ultrasonically treated for 0.5h to ensure that the solid was uniformly dispersed. Then the obtained samples were dried at 60 °C for 12 h and then calcined at 773K in air atmosphere and at last reduced in a 10% H_2/Ar flow at 500 °C for 4 h. Other supports ($MgAl_2O_4$, TiO_2 and hydroxyapatite(HAP)) loaded Ru catalysts were also prepared with the incipient wetness impregnation method and executed the same procedure.

Catalytic test and product analysis.

The detailed reaction conditions are described in the figure captions and table footnotes. In a typical reaction with PPO conversion as example, catalyst (0.1 g), PPO (50 mg) and decane (5 g) were loaded into a stainless-steel autoclave reactor. After the reactor was purged with H_2 three times and charged to the target H_2 pressure (2 MPa), the reaction was conducted at target temperature (280 °C) with a magnetic stirring speed of 600 r.p.m. After the reaction, the reactor was quenched to ambient temperature in an ice-water bath, and after cooling, 0.2 g of ethyl acetate and 150μl pentadecane (115mg) were added and stirred for 10 min to ensure that the phenols in the product were completely dissolved in decane. Then the organic products were analyzed by gas chromatography (GC) and GC–MS on an Agilent 7890B gas chromatograph with flame ionization detector and an Agilent 7890A GC-MS instrument, both equipped with HP-5 capillary columns (30m*250mm). The liquid solution was separated from the solid catalyst by centrifugation and was directly analyzed. Pentadecane was used as an internal standard for the quantification of liquid products. The mass yield of products was calculated by using the equation:

$$\text{Yield(Y)} = (\text{mass of product}) / (\text{mass of substrate}) \times 100\%.$$

It should be noted that, if the substrate is not deoxygenated, the mass yield is approximately equal to the molar yield, otherwise, the mass yield will be significantly less than the molar yield and the true yield of the substance is underestimated.

The production distribution in the liquid phase were calculated by using the equation:

$$\text{Selectivity(S)} = \text{Y(product)} / \text{(total yield)} \times 100\%.$$

And the selectivity of aromatic monomers in liquid were calculated by using the equation:

$$S_{\text{(aromatic monomer)}} = (\text{Y(3,5-DMP)} + \text{Y(2,6-DMP)} + \text{Y(m-xylene)} / \text{(total yield)} \times 100\%.$$

The kinetic study of deoxidization of 3,5-DMP was conducted at a H_2 pressure range of 0.5−3 MPa in reaction conditions. The 3,5-DMP conversions were limited to lower than 10 %. The initial rate of deoxidization of 3,5-DMP was calculated based on the formation rate of 1,3-dimethylcyclohexane plus m-xylene.

The stability test of $0.05Ru/Nb_2O_5$. After the reaction, the product was separated by centrifugation and the liquid was collected for quantitative analysis of the product by chromatography. The collected solids were first treated with 5 g of toluene for 1 h to dissolve the unreacted plastic, and then centrifuged to collect the solids and dried in a vacuum oven at 60° C for 12 h. The dried sample were directly subjected to the next reaction or regenerated. The regeneration procedure of the catalyst was to reduce the dried sample in a 10% H_2/Ar flow at 400 °C for 3h. Since a few solids are lost after each treatment, all cyclic tests were performed keeping the same value of mass(catalyst) /mass(substrate) and other reaction conditions as the first, and all cyclic tests were no fresh catalyst additions.

Characterization

The powder XRD patterns were recorded with a Rigaku D/max–2550VB/PC diffractometer by using Cu Kα (L=0.15406 nm) radiation that was operated at 40 kV and 40 mA. The actual Ru loading in the sample was detected by inductively coupled plasma–atomic emission spectroscopy (ICP-AES) on a Perkin-Elmer Optima 2100 DV spectrometer.

Infrared (IR) spectra of pyridine adsorption were recorded on Nicolet NEXUS 670 FT–IR spectrometer. The samples were pressed into self-supporting disks and placed in an IR cell attached to a closed glass–circulation system. The disk was dehydrated by heating at 400 °C, for 1 h under vacuum to remove the physically adsorbed water. After the cell was cooled to room temperature, the IR spectrum was recorded as background. Pyridine vapor was then introduced into the cell at room–temperature until equilibrium was reached, and then a second spectrum was recorded. The subsequent evacuation was performed at 100 °C, for 10 min followed by spectral acquisitions. The spectra presented were obtained by subtracting the spectra recorded before and after pyridine adsorption.

Temperature programmed desorption of carbon dioxide as a probe molecule (CO_2-TPD) was carried out on a Micromeritics ChemiSorb 2720 equipped with TCD detector. 80 mg of the catalyst was placed in a quartz sample tube. Before TPD experiments the catalysts were outgassed at 400 °C for 1 h in a flow of helium. Subsequently, the catalysts were cooled down to 50 °C and treated under a CO_2 flow for 30 min. Weakly adsorbed CO_2 was removed by flushing with He at 50 °C for 30 min. The desorption of CO_2 was measured by heating the catalyst from 50 °C to 600 °C at a heating rate of 10 °C min−1 in a He flow. The desorbed products were analyzed by TCD detector.

Temperature programmed desorption of hydrogen as a probe molecule (H_2-TPD) was carried out on a Micromeritics ChemiSorb 2720 equipped with TCD detector. Before TPD experiments the catalysts (80mg) were pretreatment at 400 °C for 1 h in a flow of 10%H_2/Ar. Subsequently, the catalysts were cooled down to 50 °C and treated under a H_2 flow for 30 min. Weakly adsorbed H_2 was removed by flushing with Ar at 50 °C for 30 min. The desorption of H_2 was measured by heating the catalyst from 50 °C to 600 °C at a heating rate of 10 °C min^{-1} in an Ar flow. The desorbed products were analyzed by TCD detector. The Ru dispersion was calculated assuming a stoichiometry of 1:1 for H_2 released on Ru.

DRIFTS of o-cresol adsorption were collected with a NICOLET iS50 FT–IR spectrometer equipped with an MCT/A detector. Firstly, the catalysts were pretreated *in situ* in the cell in Ar at 400 °C for 40 min and background spectra were recorded at 250 °C, 30 °C, respectively. Then o-cresol with Ar was bubbled into the *in situ* cell for 40 min. Next, the cell was purged with Ar at 30 °C for 30 min and the adsorption spectra of acetone were recorded. Finally, the temperature was increased to 250 °C and the adsorption spectra of acetone were recorded at increasing temperature.

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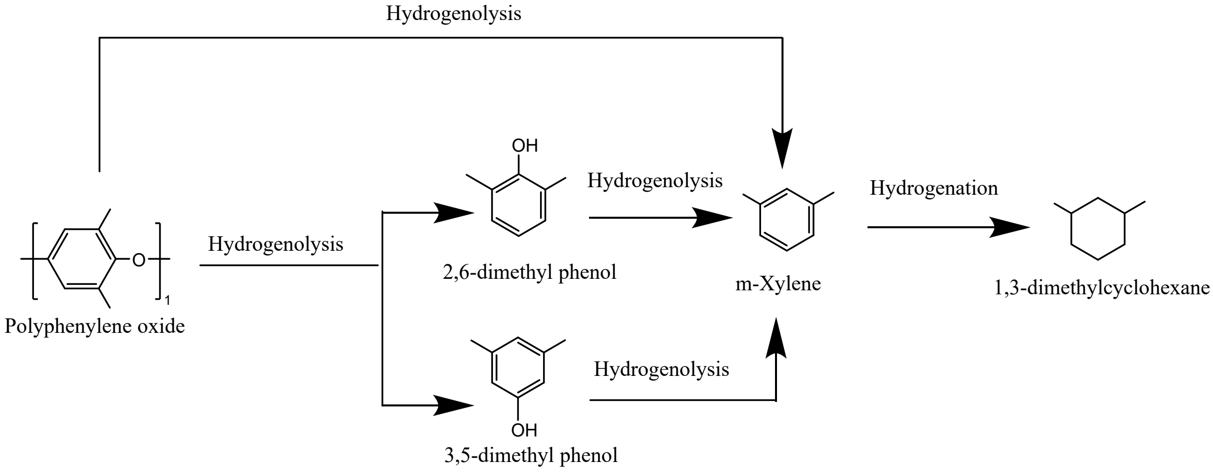


Figure S1. Reaction pathways of the conversion of PPO over Ru/Nb_2O_5 catalysts.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 4.49 – 4.66 (s, 1H), 6.51 – 6.67 (s, 1H), 2.19 – 2.36 (s, 5H), 6.38 – 6.54 (s, 2H).

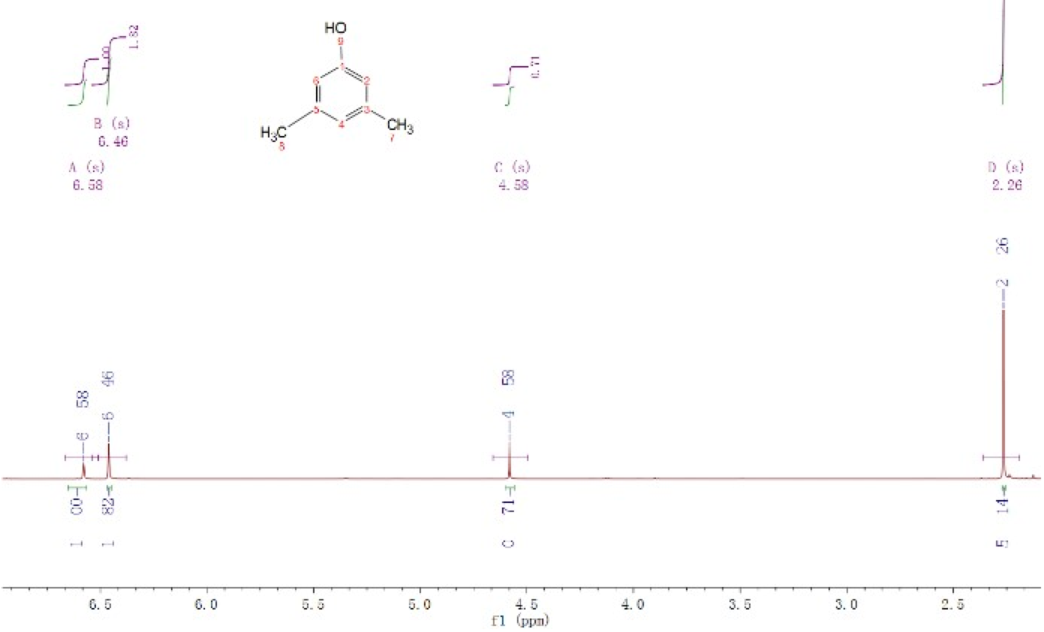


Figure S2: ^{1}H NMR spectrum of 3,5-DMP.

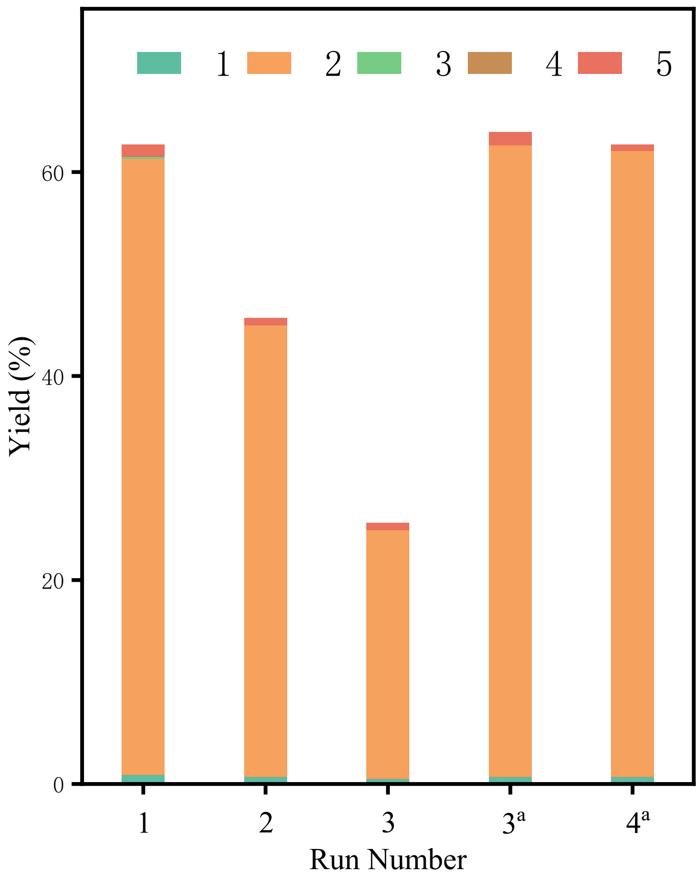
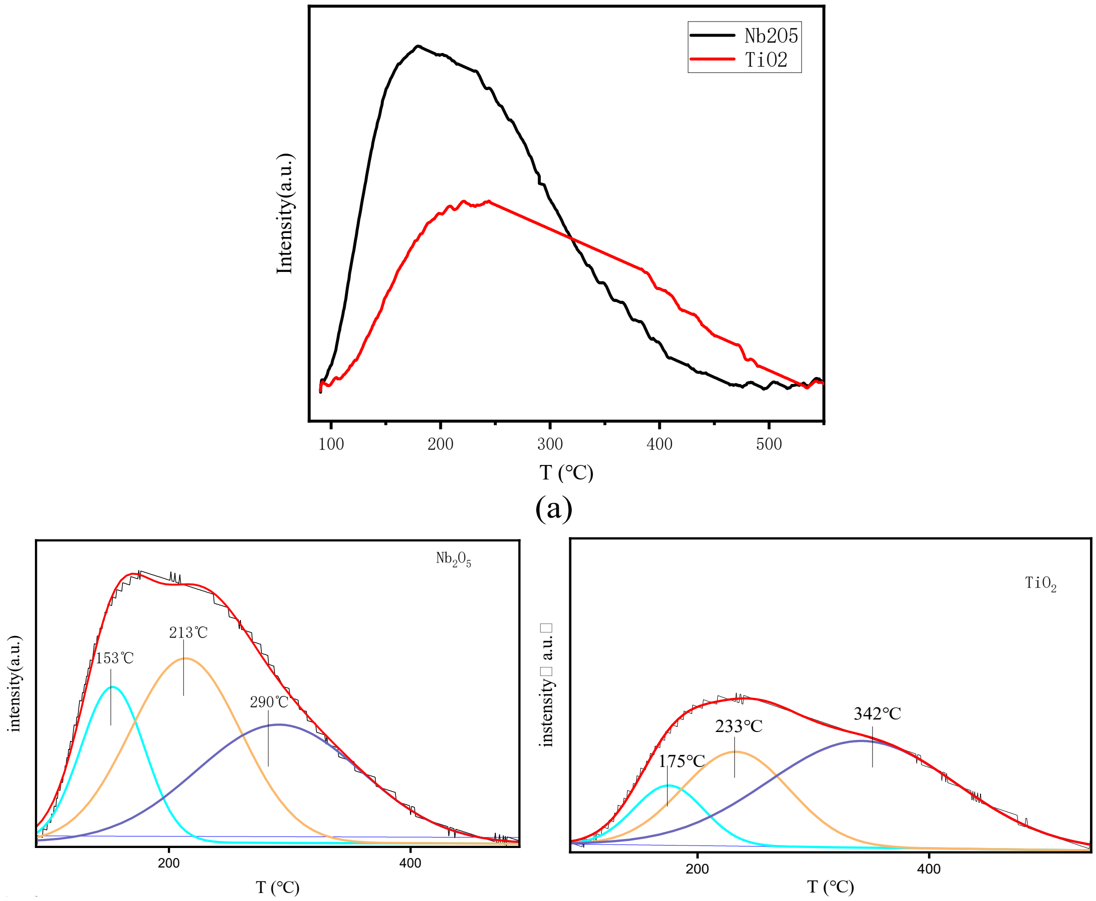


Figure S3. Recycling tests of PPO over 0.05Ru/Nb2O5 catalyst. Reaction conditions: PPO 50 mg, 0.05Ru/Nb2O5 100 mg, 5 g decane, temperature= 280 °C, pressure(H2)= 2 MPa, reaction time= 4 h. ‘a’ means that the catalyst was regenerated.



(a)

(b) (c)

Figure S4. The NH_3-TPD result of Nb_2O_5 and TiO_2 (a), and results of split-peak fitting of NH_3-TPD curves for Nb_2O_5 (b) and TiO_2 (c).

The acid strength had been evaluated for Nb_2O_5 and TiO_2 by NH_3-TPD (Figure S4). From the results (Figure S4. a), TiO_2 has stronger acid strength than Nb_2O_5, and the total acid amount of Nb_2O_5 was significantly greater than TiO_2, indicating the hydrolytic activity of PPO does not correlate with the acid strength but the amount of weak and medium acid. Moreover, the result of Split-peak fitting (Figure S4. b and c) also supports this.

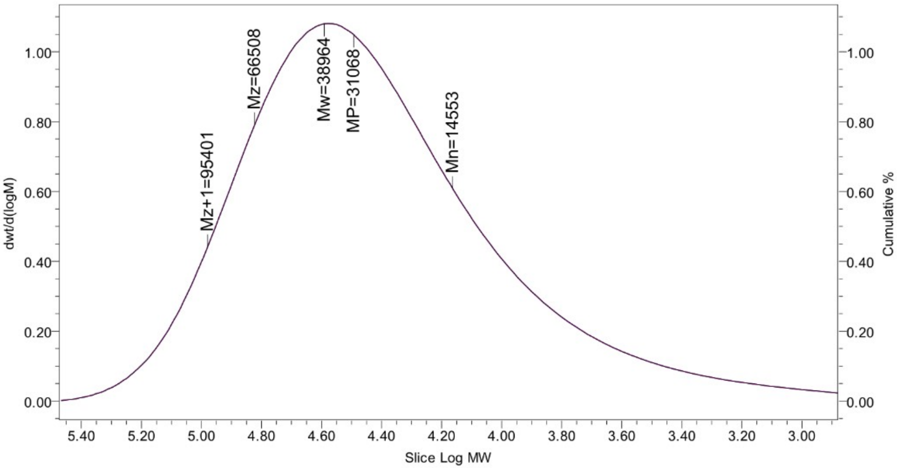


Figure S5. The GPC result of　PPO（from Sigma Aldrich）

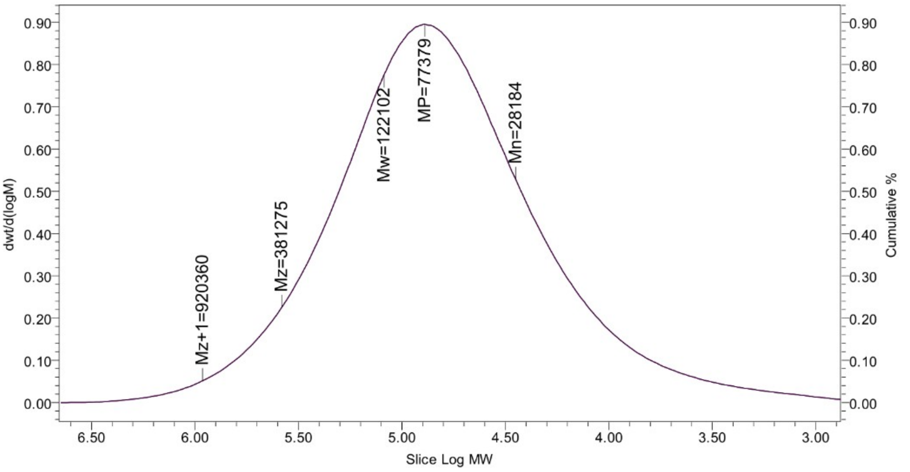


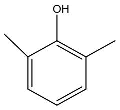
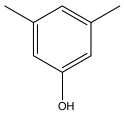
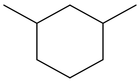
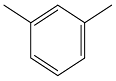
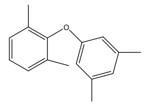
Figure S6. The GPC result of　the common PPO（MPPO）

The Mw=38964 (Figure S5) of PPO plastic from Sigma Aldrich and the common PPO (MPPO) used in our system has Mw=122102 (Figure S6).

Table S1. Elemental analysis results of various PPO plastics.

Substrates	Percentage content (wt %)		Elemental analysis (wt %)		Plastics composition (wt %)	
	Water	Ash	C	H	PPO	PS
Frire resistant mPPO	2.8	9.4	75.7	6.7	60.2	39.8

Table S2. Production of 3,5-DMP from MPPO over 0.05 %Ru/Nb_2O_5 catalyst.

Substrate	*Yield/%				
					
MPPO	0.8	40.7	0.9	4.5	0

Condition: 50mg MPPO, 100mg 0.05 %Ru/Nb_2O_5, 5g decane, 280°C, 2MPa H_2, 24h.

*The quantitative yield results are based on the PPO content in MPPO.

Table S3. The Bronsted and Lewis acid amounts of various catalysts calculated from pyridine adsorption infrared (Py-FTIR) spectra.

Entry	Sample	Brønsted acid (μmol/g)	Lewis acid (μmol/g)	Brønsted acid/ Total acid	Total acid (μmol/g)
1	Nb_2O_5	219.5	463.2	0.32	682.7
2	TiO_2	18.9	155.2	0.11	174.1

Table S4. Ru contents, BET surface area and Ru dispersion of different catalysts.

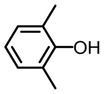
Catalyst	Ru content (wt%)	BET surface area ($m^2 \bullet g^{-1}$)	Ru dispersion (%)
$0.05Ru/Nb_2O_5$	0.055	156.41	69.7
$0.05Ru/MgAl_2O_4$	0.077	68.07	57.7
0.05Ru/HAP	0.071	13.76	48.0
$0.05Ru/TiO_2$	0.054	59.78	56.3

The mental contents in the catalysts were measured by ICP-OES.

The metal dispersions were calculated based on the H_2-TPD data.

Ru contents, BET surface area and Ru dispersion are measured, and those result（Table S4），indicated that all samples had a good dispersion of Ru metal (48.0%-69.7%). Combined with the loading of Ru, we believe that the size of Ru species in these samples are very small.

Table S5. Depolymerization of PPO over $0.05Ru/Nb_2O_5$ at N_2 atmosphere.



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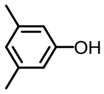

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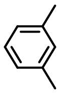

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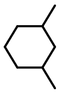

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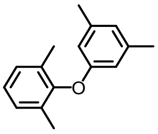

5

catalyst	Yield (wt.%)					
	1	2	3	4	5	Total
$0.05Ru/Nb_2O_5$	<1	9.6	-	-	1.7	11.3

Reaction conditions: substrate 50 mg, catalyst 100 mg, decane 5.0 g, $P(N_2)$ = 2 MPa, T= 280 ºC, t= 4 h.

We also check the experiment under N2 atmosphere, and the results (Table S5) showed that a few amounts of 3,5-DMP were detected in the product, which supports our proposed mechanism.

References

1. Y. Xin, L. Dong, Y. Guo, X. Liu, Y. Hu and Y. Wang, *Journal of Catalysis*, 2019, **375**, 202-212.