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## ARTICLE TYPE

# Dihydrobenzofurans production from catalytic tandem Claisen rearrangement–intramolecular hydroaryloxylation of allyl phenyl ethers in subcritical water

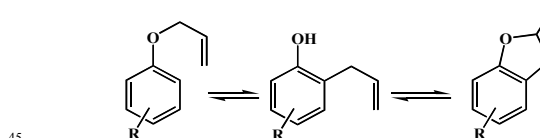
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We herein report a mild method for the preparation of dihydrobenzofurans through hydrothermal catalytic tandem Claisen rearrangement-intramolecular hydroaryloxylation of allyl phenyl ethers. This reaction provides a new method for constructing dihydrobenzofurans, a process that is potentially applicable to natural product synthesis. SBA-15, TS-1, HZSM-5 were chosen as catalysts in a hydrothermal reaction medium between 200 and 320 °C. HZSM-5 catalyst showed the highest catalytic activity, and the effects of molar ratio of allyl phenyl ether/water, time, pressure, temperature and catalyst on the claisen hydroaryloxylation in hydrothermal condition were investigated. The latter two process variables had the greatest influence on the product yields and distribution. A series of allyl phenyl ether derivatives were also treated in hydrothermal condition with HZSM-5 catalyst to offer high yield of corresponding dihydrobenzofurans.

## 1. Introduction

Dihydrobenzofuran is the key structure moiety of many highly biologically active materials, constructing pharmaceuticals (furan), lignans <sup>[1]</sup>, and other biologically natural compounds (pterocarpan) <sup>[2]</sup>. Pterocarpan have a 2,3-dihydrobenzofuran skeleton, which could be response to fungi infections and biological activities against, such as HIV, central nervous system (CNS) injury and malaria <sup>[3]</sup>. Hence, many effective methods for the construction of dihydrobenzofurans have been proposed during the past several decades <sup>[4]</sup>. Traditional methods such as oxidative coupling reaction <sup>[5]</sup>, Lewis acids catalyzed Schmidt reaction <sup>[6]</sup>, radical-based cyclizations <sup>[7]</sup>, Pummerer reactions <sup>[8]</sup>, directed  $\alpha$ -metalations <sup>[9]</sup>, and transition metal-mediated reactions <sup>[10]</sup>, have been developed for the synthesis of dihydrobenzofuran and its derivatives. While the above methods provide the desired heterocycles, few can be universally applied and several produce a variety of side products. Recently, a new and milder method for the preparation of dihydrobenzofurans was proposed, which consists of two tandem steps: Claisen rearrangement and intramolecular hydroalkoxylation as shown in Scheme 1 <sup>[11]</sup>. Catalysts such as transition-metal complexes (Cu(OTf)<sub>2</sub>), Lewis acid, Brønsted acid have been prepared to accelerate the reaction rate <sup>[12]</sup>. However, drawbacks such as toxic reagent (DMF, CH<sub>3</sub>CN, methallyl chloride) <sup>[12]</sup>, catalyst recycling <sup>[13]</sup>, and moderate targeted product yield <sup>[14]</sup> also accompanied with this method. Therefore, increasing attentions are being shifted to the method development of preparing dihydrobenzofuran and its derivatives in a more efficient and environmental-friendly way.



Scheme 1. The tandem Claisen rearrangement-intermolecular hydroalkoxylation of allyl phenyl ethers.

Water above its boiling point and below its critical point is usually defined as subcritical water (SBW) which exhibits properties that are very different from that of water at ambient temperature. SBW was employed as reaction medium in organic and inorganic syntheses, biomass conversion, biopolymer degradation, and aqueous waste stream remediation due to its abundance, low cost, and ease of product isolation <sup>[15]</sup>. The physicochemical characteristics of water are greatly changeable only by varying the pressure or temperature <sup>[16]</sup>. Moreover, SBW behaves like many organic solvents so that most of small organic compounds are completely miscible with it. Grieco et al <sup>[17]</sup> for the first time demonstrated the benefit of water for the rearrangement of allyl vinyl ethers. An et al <sup>[18]</sup> suggested that acid facilitated the hydroaryloxylation reaction in SBW condition. To date, however, no study on the production of dihydrobenzofuran from the tandem Claisen rearrangement and intermolecular hydroaryloxylation and its derivatives under hydrothermal conditions in the presence of potential heterogeneous catalysts was reported.

Herein we report a new dihydrobenzofuran ring-forming process via tandem Claisen rearrangement-intermolecular hydroaryloxylation. Reactions of allyl phenyl ether were carried out in SBW at a temperature range of 200–320 °C in the presence

of three different heterogeneous zeolite catalysts (SBA-15, TS-1, and HZSM-5). These three zeolite catalysts have mesoporous pore, high specific surface area, and uniform size and shape of the pores over micrometer length scales<sup>[19]</sup>. High thermal stability and the advantage of tuning the pore size make these materials interesting for use as supports and catalysts for various heterogeneously catalyzed reactions<sup>[19, 20]</sup>. Furthermore, the application of zeolites, as catalysts, also relies on their intrinsic acidity for processes such as cracking, isomerization and alkylation<sup>[21]</sup>. In this present study, we examine the effect of reaction time, temperature, catalyst type and allyl phenyl ether to water molar ratio on the yields and selectivity of liquid products, aiming to maximize the desired product yield. Next, a series of allyl phenyl ether derivatives were treated under hydrothermal condition in the presence of HZSM-5 catalyst. Finally, a reaction network was proposed based on the experimental results.

## 2. Experimental Section

### 2.1. Materials and chemicals

TS-1, SBA-15, HZSM-5 were prepared strictly based on the procedure described in reference<sup>[22,23]</sup>. Four different types of catalysts were prepared and denoted as TS-1, SBA-15, HZSM-5(Si:Al=22:1) and HZSM-5(Si:Al=200:1). The compounds including allyl phenyl ether(APE), allyl p-tolyl ether, allyl o-tolyl ether, allyl m-tolyl ether, 1-(allyloxy)naphthalene, allyl phenyl ethers with NO<sub>2</sub>, NH<sub>2</sub>, Cl, Br, C(CH<sub>3</sub>)<sub>3</sub> and OCH<sub>3</sub> in para position and S, methallyl and crotyl system, were synthesized from the corresponding phenols with allyl bromide according to the modified method<sup>[24-26]</sup>.

All other chemicals, such as solvents, were obtained from Sigma-Aldrich in high purity (≥99%). Freshly double-distilled water was used throughout the experiments. All solutions were prepared with double-distilled water. The reactors, which were welded by stainless-steel Swagelok type tube fitting, were used in most experiments. The assembled reactors had an internal volume of 17.5 ml. The body of the reactor consisted of 1-inch port connector sealed with two 1-inch caps at both ends.

### 2.2. Procedure

Before used in reactions, all reactors were firstly washed with acetone and air dried, and then loaded with 10 ml of duplicate distilled water and heated to 380 °C for 8 h to expose the reactor walls to a hydrothermal environment. These reactors were then cleaned with acetone and dried by air, waiting for use.

In a typical run, APE and water was directly loaded into the reactor with or without catalyst. Reactions were carried out by placing the loaded reactors in an isothermal molten-salts bath preheated to the desired temperature which was controlled by using an Omega type temperature controller. Molten-salts bath was controlled to 180-380 ±3 °C<sup>[27]</sup>. The preheating time is between 1 and 3 min within the temperature range examined. After the desired holding time, the reactors were removed out of the molten-salts bath and placed into cold water bath. After reaching room temperature, the reactors were taken out of the water and dried. The reactors were opened and most of the aqueous-phase products including catalysts were transferred into a beaker. The dumped reactor was washed several times with additional 10-20 ml dichloromethane (DCM) to ensure that all

contents were recovered. All the collected contents were subjected to filtration for the liquid and catalyst separation. Product molar yields were calculated as the moles of products formed by per mole of all initially loaded into the reactor.

Duplicated independent runs were conducted under identical conditions to determine the uncertainties in the experimental results. Results reported herein represent the mean values for the two independent trials.

### 2.3. Analysis of products

Products quantification was performed in a Gas-Chromatograph (6890N, Agilent) equipped with an autosampler, autoinjector, mass spectrometric detector, and an Agilent HP-5 nonpolar capillary column (50m × 200µm × 0.33µm). A volume of 2µl was injected for each sample, and the inlet temperature and split ratio were 300 °C and 3:1, respectively. The detector temperature was set at 250 °C. The column was initially held at 60°C. The temperature was ramped to 250°C at 15°C/min and held isothermally for 2 minutes, giving a total runtime of about 15 min. Helium served as the carrier gas (1 ml/min). The compositions of compounds were obtained from electronic integration measurements using flame ionization detection. The sample also was identified by GC (6890-5973, Agilent), which was operated at 70Ev (condition:EI) under the same conditions as GC-MS analysis. Quantification of products was carried out on an Agilent Technologies 7890 gas chromatograph with a flame ionization detector (GC-FID) at the same conditions as described above.

### 2.4. Characterization of catalysts

X-ray diffraction patterns (XRD) of the catalysts were performed on a Bruker D8 diffractometer with Cu Kα radiation from 0.5 to 90° with a scan speed 1°/min. X-ray photoelectron spectroscopy (XPS) measurements were obtained on a PHI-5500 spectrometer with Al Kα X-ray radiation as the X-ray source for excitation.

Temperature programmed desorption (TPD) was conducted by Chembet 3000 chemical adsorbed instrument from Quantachrom. Before adsorption, the sample (0.1g) was dried in flowing He (99.99%, 30 ml/min) at 500 °C for 30 min. The adsorption of catalyst was performed by passing a gas mixture, containing NH<sub>3</sub> with N<sub>2</sub> as balance gas, through the sample bed at 100 °C for 2 h with a total flow rate of 100 ml/min<sup>[22]</sup>. TPD measurements were carried out from 100 to 650 °C in a heating rate of 10 °C/min, with He as the carrying gas. The effluent stream was monitored continuously with a thermal conductivity detector (TCD) to determine the rate of ammonia desorption.

## 3. Results and Discussion

### 3.1. Products identification

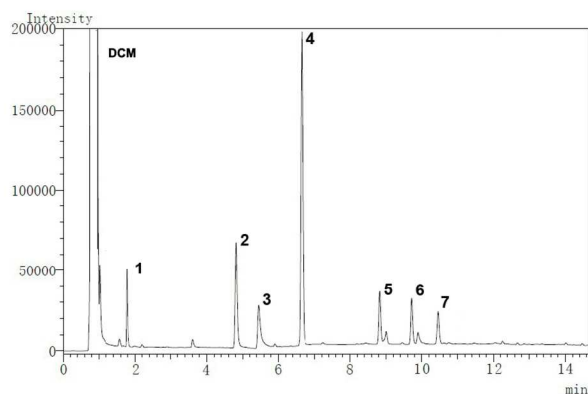
Fig. 1 shows the total ion chromatogram from the tandem Claisen rearrangement-intramolecular hydroaryloxylation (CR-IH) of APE in SBW at 260 °C for 20 min. The peaks in Fig. 1 were identified by using a National Institute of Standards and Technology (NIST) mass spectral database with the GC-MS. Table 1 provides the detailed information about the compound identification and peak area % of the major components in the reaction products. Table 1 shows that 2-methyl-2,3-dihydrobenzofuran (peak 4 in Fig.1) is by far the most abundant

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products from catalytic the CR-IH of APE in SBW. 2-Allylphenol (peak 2 in Fig.1) is an abundant intermediate product (peak 3 in Fig.1) could be resulted from migration of the double bond in product 2 with the aromatic ring<sup>[28]</sup>, which was less stable likely and would undergo thermal cyclization to form product 3 and 2-methylbenzofuran (peak 6 in Fig.1). 3-(2-Hydroxyphenyl)-2-propanol (peak 7 in Fig.1) was formed by the hydration of the allylic double bond of product 2. Obviously, those compounds could be decomposed into phenol (peak 1 in Fig.1) in SBW.



**Fig. 1** Total ion chromatogram for the major products from the CR-IH of APE in SBW at 260 °C for 20 min.

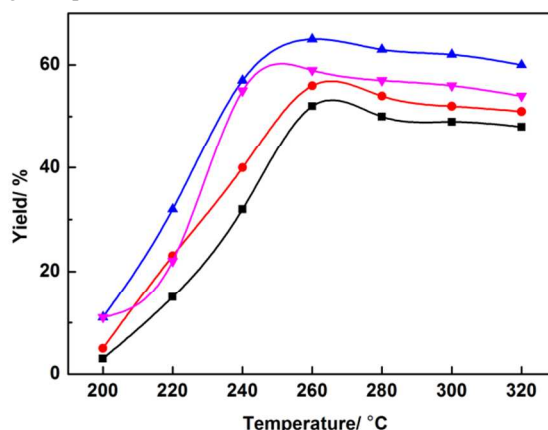
**Table 1** Tentative identities and area % of major peaks in total ion chromatograms

Peak no.	Compound Name	Structure	Area/ %	RT/ min
1	phenol		8.64	1.63
2	2-allylphenol		10.42	4.80
3	(E,Z)-2-propenylphenol		4.51	5.31
4	2-methyl-2,3-dihydrobenzofuran		63.24	6.12
5	allyl phenyl ether		4.20	7.17
6	2-methylbenzofuran		3.23	7.48
7	3-(2-hydroxyphenyl)-2-propanol		4.76	7.65

## 3.2. Effects of temperature

Previous study<sup>[28]</sup> suggested that temperature was the most influential parameter upon the products yield from the reaction of APE in high temperature. Therefore, temperature was selected as the first parameter rather than other variables to investigate its influence on the conversion of APE and yield of dominant product of 2-methyl-2,3-dihydrobenzofuran.

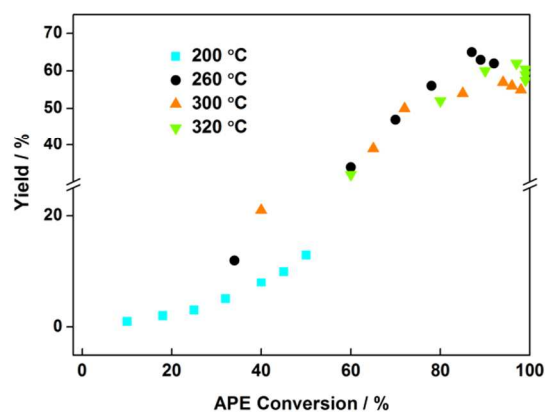
The reactions were conducted at a fixed reaction time of 15 min with varying temperature from 200 to 320 °C. Yield of 2-methyl-2,3-dihydrobenzofuran are plotted as a function of temperature in Fig. 2. The yield of 2-methyl-2,3-dihydrobenzofuran increased with increasing temperature and hit the highest value at 260 °C. Thereafter, the yield of 2-methyl-2,3-dihydrobenzofuran decreased due to its further reaction or the promotion of side reactions at more severe temperatures. For example, 2-methyl-2,3-dihydrobenzofuran could partially decompose to 2-allylphenol and 2-propenylphenol from the ring opening reaction at high temperature water<sup>[29]</sup>.



**Fig. 2** Effect of temperature on the yield of 2-methyl-2,3-dihydrobenzofuran at different APE/water mole ratios of: 1 : 20(■), 1 : 40(●), 1 : 60(▲), and 1 : 80(▼) at a reaction time of 15 min.

Fig. 3 shows the yield of selected product 4 and the corresponding conversion of APE at four different temperatures without catalysts. It shows that the conversion of APE is always the lowest at 200 °C. Increasing temperature improved the conversion of APE and the yield of 2-methyl-2,3-dihydrobenzofuran. The yield of 2-methyl-2,3-dihydrobenzofuran is very low (<5%) as the conversion of APE is less than 20%, suggesting that formation of 4 was a multiple step reaction which was difficult to occur at low temperatures.



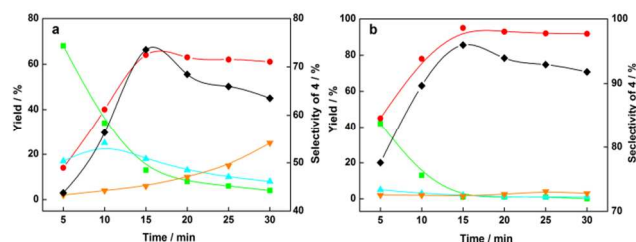


**Fig. 3** Yield of 2-methyl-2,3-dihydrobenzofuran and conversion of APE under different temperatures.

In the CR-IH of APE, changes of APE/ water molar ratio also affected the yield of 2-methyl-2,3-dihydrobenzofuran. At different APE/water molar ratios, the highest yield of 2-methyl-2,3-dihydrobenzofuran was always observed at a temperature of 260 °C. Fig. 2 shows that the yield of 2-methyl-2,3-dihydrobenzofuran increased with increasing the APE/water molar ratio. The highest yield (65%) of 2-methyl-2,3-dihydrobenzofuran was achieved at 260 °C.

### 3.3. Effect of time

Batch experiments in two different mediums, i.e., with and without HZSM-5 catalyst were carried out with the reactor at 260 °C for a reaction time ranging from 5 to 30 min. The conversion of APE, the contents of products and selectivity from these two medium systems are displayed in Fig. 4a and Fig. 4b, respectively.



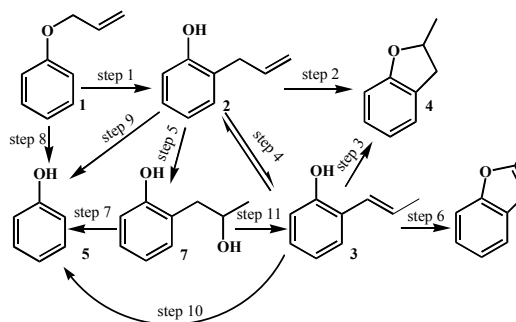
**Fig. 4** CR-IH of APE at 260 °C without (a) and with (b) HZSM-5(Si:Al=22:1), the yield of APE (■), 2-methyl-2,3-dihydrobenzofuran (●), 2-allylphenol (▲), other products (▼) and selectivity of 2-methyl-2,3-dihydrobenzofuran 4 (◆).

At a reaction time of 15 min, addition of HZSM-5 increased the conversion from 87 % without catalyst to 95% in the presence of HZSM-5. Higher yield and selectivity of 2-methyl-2,3-dihydrobenzofuran was also observed in the presence of HZSM-5 relative to the uncatalyzed reaction. The yield of 2-allylphenol and other products also decreased in the presence of catalyst. These result suggested that addition of catalyst is necessary if one expect to achieved higher yield and selectivity of 2,3-dihydrobenzofuran.

### 3.4. Reaction paths

Based on the products distribution from the reaction of APE under hydrothermal conditions, we propose a possible reaction network of APE which can provide possible method on how to

suppress by-products formation and how to improve the yield of dihydrobenzofuran through process optimization and catalyst screening study.



**Scheme. 2** Possible reaction network for the reaction of APE under hydrothermal condition.

Steps 1-3 are the main reaction paths of the CR-IH of APE. Step 1 involves Claisen rearrangement to form 2-allylphenol (2). Then two parallel reaction pathways are available for 2-methyl-2,3-dihydrobenzofuran (4) in this hydrothermal environment: undergoes C-O bond ring closure to form 4 (step 2) or isomerization to form (E,Z)-2-propenylphenol (3) (step 4) then hydroalkoxylation (step 3). Apart for the main reactions, there exist some side reactions. 2 could proceed in Markovnikov fashion with addition of water (step 5) into 3-(2-hydroxyphenyl)-2-propanol (7) [30]. On the other hand, 7 could also eliminate water to give 3 in step 11. Substrate 3 was also cyclized to furnish benzofuran (6) in step 6. Those compounds could decompose through steps 7-10 into phenol (5).

### 3.5 Effect of catalyst

#### 3.5.1. Catalyst activity

**Table 2** Different catalysts on the tandem Claisen hydroaryloxylation of APE.

Entry <sup>a</sup>	Conversion/ %	Yield of 4/ %	Selectivity of 4/ %	Yield of other products/ %
Without catalyst	87	65	73	23
SBA-15	90	65	72	20
TS-1	94	78	82	12
HZSM-5 (Si:Al=200)	94	85	90	2
HZSM-5 (Si:Al= 22)	96	91	95	1-2

<sup>a</sup> General reaction conditions: 260 °C, APE / water =1:40, 15 min, 10mg catalyst.

Table 2 shows the Claisen rearrangement-intermolecular hydroaryloxylation of using SBA-15, TS-1, HZSM-5(Si:Al=22:1) and HZSM-5(Si:Al=200:1) as catalysts in hydrothermal condition under 260 °C. 10 mg catalysts were employed into each reaction, respectively. The acidity of catalysts was also determined by NH<sub>3</sub>-TPD experiment and the NH<sub>3</sub>-TPD patterns were shown in Fig. 5. In Table 2, the conversion using SBA-15 as the catalyst is almost the same as the conversion without catalyst, which indicates that the SBA-15's catalytic activity could be negligible in the selective reaction. The conversion TS-1 and different ratio of Si:Al catalysts of HZSM-5 could get range from 94-96%. Nevertheless, the selectivity only reach 82% with TS-1 compared

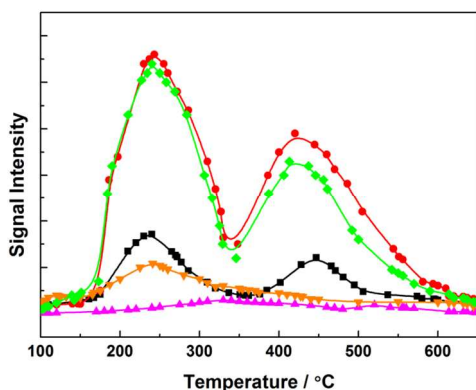
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with 95% HZSM-5(Si:Al=22:1). Simultaneously, only trace amounts of by-products (<2%) was detected in the reaction with HZSM-5 catalyst (Si:Al=22:1), exhibiting the high activity.

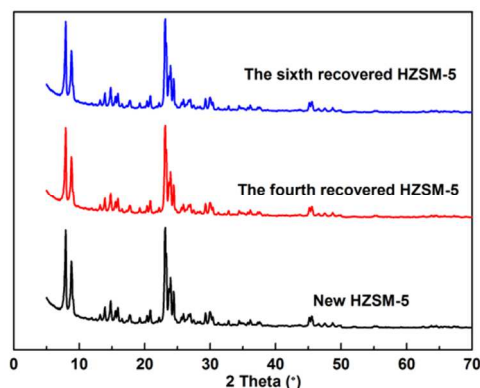
Due to the framework of crystalline microporous aluminosilicates in zeolites, the charge-compensating protons of the oxygen anions bridging between Al and Si give rise to strong Brønsted acidity<sup>[31]</sup>. Zeolites usually offer good selectivity owing to the shape selective characteristics. They have been broadly applied in industry, i.e., product shape, reactant shape, and restricted transition state shape selectivity. In order to investigate the relationship between zeolites and selectivity, the acidity of zeolites should be investigated. As shown in Fig. 5, there are no evident peaks in the TPD profile of pure silica SBA-15 material, indicating that SBA-15 material has no acid site. HZSM-5 with different Si/Al ratios shows two desorption peaks, one focused at the range of 150-250 °C and the other at 350-450 °C, representing the Brønsted acid sites<sup>[32]</sup>. Only one desorption peak was observed in the NH<sub>3</sub>-TPD profile of TS-1, which is very weak compared with that of HZSM-5. To the different ratios of Si:Al in HZSM-5 catalysts, the higher Si/Al ratio has weaker acid sites corresponding to weaker acidity<sup>[34]</sup>. Compared the results in Table 2 and Fig. 5, we can get the conclusion that HZSM-5 with stronger acidity (low Si/Al ratio) can accelerate the tandem Claisen hydroaryloxylation reaction more effectively than HZSM-5 with weaker acidity (high Si/Al ratio) in subcritical water condition process.



**Fig. 5** NH<sub>3</sub>-TPD curves of different zeolites, HZSM-5(Si:Al=200:1) (■), HZSM-5(Si:Al=22:1) (●), TS-1 (▼), SBA-15 (▲), sixth recovered HZSM-5(Si:Al=22:1) (◆).

### 3.5.2. Recycling of catalyst

It is important to point out that all of the catalysts were separated from the products through filtration and could be easily reused. Fig. 6 shows the XRD patterns of the samples before and after the reaction. As shown in Fig. 6, the structure did not change after the reactions; the crystal structure of HZSM-5 was maintained after the reactions.



**Fig. 6** XRD patterns of original HZSM-5, fourth recovered HZSM-5 and sixth recovered HZSM-5 catalysts.

The results of the repeated use of the catalyst HZSM-5 (Si:Al=22:1) for the Claisen hydroaryloxylation of APE were summarized in Table 3. The use of the recovered catalyst also produced an excellent yield (run 6, 88%). The NH<sub>3</sub>-TPD curve for the sixth recovered catalyst was shown in Fig. 5, which was similar to the fresh HZSM-5 catalyst. These results clearly indicate that the catalyst is low deactivation in hydrothermal condition and can be used repeatedly without loss of activity.

**Table 3** Recycled use of the HZSM-5 catalyst in using Claisen hydroaryloxylation of APE

Run	Yield (%) <sup>a</sup>	Run	Yield (%)
1	91	4	88
2	89	5	89
3	90	6	88

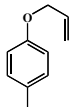
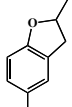
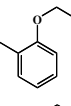
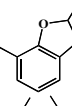
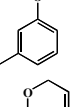
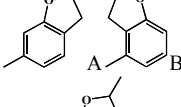
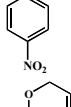
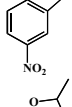
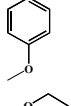
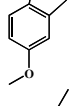
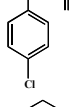
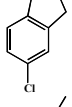
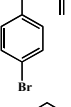
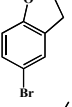
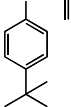
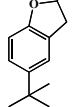
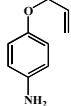
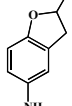
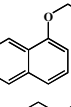
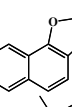
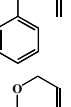
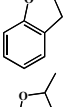
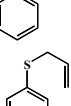
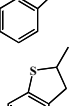
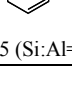
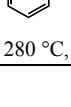
<sup>a</sup> Reaction condition: 260 °C, APE / water =1:40, 10 min, 10mg catalyst.

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## ARTICLE TYPE

**Table 4** HZSM-5 catalyzed CR-IH of APE under hydrothermal conditions.

Entry <sup>a</sup>	Substrate	Product	Yield
1			93%
2			91%
3			A 61% B 26%
4			95%
5			87%
6			93%
7			91%
8			91%
9			90%
10 <sup>b</sup>			82%
11			85%
12			90%
13			87%

<sup>a</sup> Reaction conditions: 260 °C, 15min, 10 mg HZSM-5 (Si:Al=22:1) (entry 1-9 and 11-13); <sup>b</sup> 280 °C, 20min, 10 mg HZSM-5 (Si:Al=22:1) (entry 10).

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## ARTICLE TYPE

## 3.4. CR-IH of different substrates with catalyst

CR-IH reactions with a wide range of APE derivatives were tested. Table 4 shows the results. High yields are obtained from the reactions of allyl p-tolyl ether and allyl o-tolyl ether (95% and 91%, entries 1-2). The APE with meta position of CH<sub>3</sub> was also employed in the Claisen hydroaryloxylation. 2,6-dimethyl-2,3-dihydrobenzofuran and 2,5-dimethyl-2,3-dihydrobenzofuran were obtained as two major products, with 63% and 30% reaction yield, respectively (entry 3). The reactions of APE bearing electron-withdrawing groups such as NO<sub>2</sub>, OCH<sub>3</sub>, Cl and Br at the para position, respectively, with proceeded smoothly to furnish in good yields (87-95%, entries 4-7). Even APE bearing C(CH<sub>3</sub>)<sub>3</sub> or NH<sub>2</sub>, as electron-donating group, at the para position, the reaction also gives excellent yield (90% and 91%, entries 8-9). Then, 1-(allyloxy)naphthalene is treated in the subcritical water to offer the desired yield (83%, entry 10), which was higher yield and less time than reported<sup>[11]</sup>. Finally, methallyl phenyl ether, 3-methyl-allyloxybenzene and allyl(phenyl)sulfane are conducted in the hydrothermal condition, which acquire excellent yields (85%, 90% and 87%, entries 11-13). The presence of S and dimethyl systems in the products is very useful for further synthetic elaborations, which could be synthesized to pharmaceuticals for injury, antioxidant, and hepatopathy<sup>[33]</sup>. All of the products are analyzed by <sup>1</sup>H NMR and their data were consistent with those reported in the literature<sup>[34]</sup>.

## Conclusion

In summary, the current investigations have demonstrated that Claisen rearrangement-intermolecular hydroaryloxylation was successfully treated in the hydrothermal condition between 200-320 °C. The presence of temperature and HZSM-5 catalyst significantly affected the product yields. The reaction can have a lot of by-products in high temperature. Then, the moderate temperature examined (260 °C) appears to be the best for producing dihydrobenzofuran in excellent yield. The higher acidity of HZSM-5 with low ratio of Si/Al can effectively improve the selectivity. A range of allyl phenyl ether derivatives exhibit desired yield (83-95%) via subcritical water. These results clearly indicate that the mild procedure is easy to set up and allows the transformation of various substituted allyl phenol ethers in the hydrothermal condition with HZSM-5 catalyst.

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## Notes and references

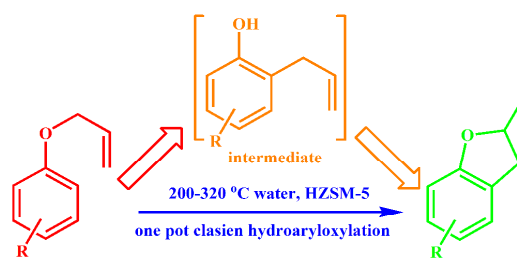
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- 1 Y. Romero, F. Richard, Y. Renème, S. Brunet, *Appl Catal A: Gen.* 2009, **353**(1), 46-53; J. M. Ketcham, B. Biannic, A. Aponick, *Chem. Commun.*, 2013, **49**, 4157-4159.
- 2 P. Xie, Y. Huang, R. Chen, *Org. Lett.*, 2010, **12** (17), 3768-3771.
- 3 G. L. Milligan, C. J. Mossman, J. Aube, *J. Am. Chem. Soc.*, 1995, **117**(42), 10449-10459; J. S. Bose, V. Gangan, R. Prakash, S. K. Jain, S. K. Manna, *J. Med. Chem.*, 2009, **52** (10), 3184-3190.
- 4 M. Uyanik, H. Okamoto, T. Yasui, K. Ishiara, *Science*, 2010, **328**(5984), 1376-1379.
- 5 C. Ericsson, L. Jovanovic, S. Michael, *Organ. Lett.*, 2010, **12** (9), 1976-1979.
- 6 S. Wang, B. D. Gates, J. S. Swenton, *J. Org. Chem.*, 1991, **56**(6), 1979-1981; C. Robert, K. Fahey, F. Aldabbagh, *Org. Biomol. Chem.* 2013, **11**, 1672-1682; H. Zhang, E. M. Ferreira, B. M. Stoltz, *Angew. Chem. Int. Edit.*, 2004, **43**(45), 6144-6148.
- 7 K. Inoue, A. Sawada, I. Shibata, A. Baba, *J. Am. Chem. Soc.*, 2002, **124** (6), 906-907.
- 8 S. Akai, N. Kawashita, H. Satoh, Y. Wada, K. Kakiguchi, Y. Kita, *Org. Lett.*, 2004, **6**(21), 3793-3796; S. W. Youn, J. Eom, *J. Org. Chem.*, 2006, **71** (17), 6705-6707.
- 9 E. D. Coy, L. Jovanovic, M. Sefkow, *Org. Lett.*, 2010, **12**(9), 1976-1979; D. Zhou, L. Zhang, S. Zhang, H. Fu, J. Chen, *Energ. Fuel.*, 2010, **24**, 4054-4061; M. Beller, J. Seayad, A. Tillack and H. Jiao, *Angew. Chem., Int. Ed.*, 2004, **43**, 3368-3398.
- 10 B. D. Kelly, J. M. Allen, R. E. Tundel, T. H. Lambert, *Org. Lett.*, 2009, **11**(6), 1381-1383.
- 11 V. H. Grant, B. Liu, *Tetrahedron. Lett.*, 2005, **46**(8), 1237-1239; X. Li, A. R. Chianese, T. Vogel, *Org. Lett.*, 2005, **7**(24), 5437-5440; R. T. Durand, L. B. Gobbi, B. L. Gray, *Org. Lett.*, 2002, **4**(22), 3847-3850; B. Douglas, C. R. Larsen, *J. Am. Chem. Soc.*, 2012, **134**(25), 10357-10360. H. Sajiki, S. Mori, T. Ohkubo, T. Ikawa, A. Kume, T. Maegawa, Y. Monguchi, *Chem. Eur. J.*, 2008, **14**(17), 5109-5111.
- 12 A. M. Martin Castro, *Chem. Rev.*, 2004, **104**, 2939-3002. K. Chiba, M. Fukuda, S. Kim, Y. Kitano, M. Tada, *J. Org. Chem.*, 1999, **64**(20), 7654-7656.
- 13 Y. Yamamoto, K. Itonaga, *Org. Lett.*, 2009, **11**(3), 717-720.
- 14 P. E. Savage, *J. Supercrit. Fluids.*, 2009, **47**, 407-414; M. C. Clark, B. Subramaniam, *AIChE J.*, 1999, **45**, 1559-1565. P. E. Savage, *Chem. Rev.*, 1999, **99**(2), 603-622.
- 15 T. Razzaq, T. N. Glasnov, C. O. Kappe, *Chem. Eng. Tech.*, 2009, **32**(11), 1702-1716. C. Liu, G. X. Hu, *Rsc. Adv.*, 2013, **3**, 20877-20882. P. G. Duan, P. E. Savage, *Energ. Environ. Sci.*, 2011, **4**(4), 1447-1456.
- 16 I. Yutaka, K. Hataeda, O. Sata, T. Yokoyama, M. Arai, *Angew. Chem. Int. Edit.*, 2001, **40**(1), 210-213.
- 17 P. A. Grieco, J. D. Clark, C. T. Jagoe, *J. Am. Chem. Soc.*, 1991, **113** (14), 5488-5489.
- 18 J. An, L. Bagnell, T. Cablewski, C. R. Struss, R. W. Trainor, *J. Org. Chem.*, 1997, **62** (8), 2505-2511.
- 19 L. Shirazi, E. Jamshidi, M. R. Ghasemi, *Cryst. Res. Technol.*, 2008, **43**(12), 1300-1306.
- 20 D. Zhao, J. Sun, Q. Li, G. D. Stucky, *Chem. Mater.*, 2000, **12**(2), 275-279; J. Zhou, Z. Hua, X. Cui, Z. Ye, F. Cui, J. Shi, *Chem. Commun.*, 2010, **46**, 4994-4996.
- 21 G. J. Kramer, R. A. Santan, C. A. Emels, A. K. Nowak, *Nature*, 1993, **363**, 529-531.
- 22 L. Chen, X. Li, G. Tian, Y. Li, J. C. Rooke, G. Zhu, S. Qiu, X. Yang, B. Su, *Angew. Chem. Int. Ed.*, **50**, 11156-11161.
- 23 P. Wu, T. Tatsumi, *Chem. Mater.*, 2002, **14**(4), 1657-1664. D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka, G. D. Stucky, *Science*, **279**(5350), 548-552.



- 24 B. Kiumars, K. Mohammad, K. Mohammad, *Chem. Lett.*, 2007, **36(11)**, 1324-1325. L. H. Chen, X. Y. Li, G. Tian, *Angew. Chem. Int. Edit.*, 2011, **50(47)**, 11156-11161; H. Staub, N. R. Nicolas, N. Even, *Chem. Eur. J.*, 2011, **17(15)**, 4254-4265. P. Duan, P. E. Savage, *Bioresource. Technol.*, 2011, **102(2)**, 1899-1906
- 5 25 H. Wu, J. J. Lai, *Ind. Eng. Chem. Res.*, 1995, **34(5)**, 1536-1538.
- 26 J. Luo, Y. Xu, L. Zhao, C. Hu, *Bioresource. Technol.*, 2010, **101(22)**, 8873-8880.
- 27 C. K. Krishnan, T. Hayashi, M. Ogura, *Adv. Mater.*, 2008, **20(11)**, 2131-2136.
- 10 28 N. T. Mathew, S. Khair, S. Mayadevi, R. Jha, S. Sivasanker, *J. Catal.*, 2005, **229**, 105-113.
- 29 L. Bagnell, T. Cablewski, C. R. Strauss, *J. Org. Chem.*, 1996, **61(21)**, 7355-7359.
- 15 30 K. Y. Lee, H. K. Lee, S. K. Ihm, *Top. Catal.*, 2010, **53(3-4)**, 247-253.
- 31 L. Shirazi, E. Jamshidi, M. R. Ghasemi, *Cryst. Res. Technol.*, 2008, **43(12)**, 1300-1306.
- 32 H. V. Grant, B. Liu, *Tetrahedron. Lett.*, 2005, **46**, 1237-1240; W. N. Reich, C. G. Yang, Z. Shi, C. He, *Syn. Lett.*, 2006, **8**, 1278-1280; K. Hori, H. Kitagawa, A. Miyoshi, T. Ohta, I. Furukawa, *J. Organomet. Chem.* 2007, **692**, 671-677.
- 20 33 W. N. Reich, C. G. Yang, Z. Shi, C. He, *Syn. Lett.*, 2006, **8**, 1278-1280; K. Hori, H. Kitagawa, A. Miyoshi, T. Ohta, I. Furukawa, *J. Organomet. Chem.*, 2007, **692**, 671-677.
- 25 34 T. Adschiri, R. Shibata, T. Sato, M. Watanabe, K. Arai, *Ind. Eng. Chem. Res.*, 1998, **37**, 2634-2638.



The one pot rapid and high-yielding clasién hydroaryloxylation of allyl phenyl ethers in subcritical water is described (see scheme).