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A VERSATILE AND REGIOSELECTIVE SYNTHESIS OF VICINAL AZIDOALCOHOLS USING CROSS-LINKED POLY(4-VINYLPYRIDINE) SUPPORTED AZIDE ION UNDER SOLVENT-FREE CONDITIONS

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Abstract A new polymeric reagent, cross-linked poly(4-vinylpyridine) supported azide ion, [P_4-VP]N_3, was introduced as polymeric reagents for efficient and regioselective conversion of epoxides to azidohydrins in the presence of cross-linked poly(4-vinylpyridine) supported sulfuric acid, [P_4-VP]H_2SO_4, as a solid proton source and as catalyst under solvent-free conditions. The advantages of this polymeric reagent over some of those reported in the literature are easy work-up procedure and regeneration of the reagent.

Keywords: Ring opening of epoxide; *β*-Azidoalcohols; Poly(4-vinylpyridine); Solvent-free conditions; Regioselectivity.

INTRODUCTION

Polymer supported reagents and catalysts have been widely applied in organic synthesis[1−7]. These heterogeneous reagents are becoming popular in organic transformations since they offer advantages such as easy work up and recyclability. Since these reagents are easily isolated by simple filtration in most cases, they lend themselves well to lessen environmental pollution. These polymeric reagents are generally used in single step reactions. The reactions can often be driven to completion by using an excess of these reagents without the fear of separating the unspent reagent from the desired products. The spent polymeric reagents can usually be removed quantitatively and regenerated. Solid phase synthesis, in particular, polymer supported nucleophiles, has been widely used in organic synthesis mainly because of the ease of separation of products[1−18].

Ring opening reactions of epoxides with nucleophiles are very useful approach in organic synthesis for preparation of functionalized oxygenated compounds. Epoxides are versatile intermediates in organic synthesis and a variety of reagents such as electrophiles, nucleophiles, acids, bases, reducing agents and some oxidizing agents are known for the ring opening and are widely studied[19]. The reactions of nucleophiles, such as oxygen compounds (water, alcohols and phenols)[20−24], nitrogen compounds (amine and derivatives of amines, azide, nitrate, isocyanides)[25−27], halides[28] and various carbon nucleophiles[29], have been performed in both organic and aqueous solvents.

Vicinal azidoalcohols are precursors of aminoalcohols[30], which are well known as *β*-blockers and present in various natural products and different bioactive compounds[31]. They are also useful for the synthesis of vicinal aminoalcohols, carbohydrates, nucleosides, lactams and oxazolines[25, 32−34].

Since the *β*-amino alcohols are very important in both organic and medical chemistry[35], the ring opening of epoxides with azide[36] and nitro compounds presents[37] an effective synthetic route of *β*-amino alcohols. Azidation of epoxides with azide compounds is often carried out under either alkaline or acidic conditions.

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Several different methods have been devised in order to obtain the direct azidolysis of epoxides in the presence of sodium azide[25, 38], such as $NaN_3/LiClO_4$[39], NaN_3/CAN (ceric ammonium nitrate)[40], NaN_3/halohydrin dehalogenase[41], $NaN_3/CeCl_3$[42], NaN_3/oxone[43], $NaN_3/LiBF_4$[44], $NaN_3/(TBA)_4PFeW_{11}O_{39}{\cdot}3H_2O$[45], NaN_3/PEG-300 (polyethylene glycol)[46] and NaN_3/PVA or PAA, poly(vinylamine) or poly(allylamine)[47]. These conditions usually require high temperatures and/or long reaction times, and as side reactions, isomerization, epimerization, and rearrangement may be induced by alkaline conditions of the reactions with alkali azides in these systems. Furthermore, many new methods have been introduced for this kind of transformation, for example, it has been found that sodium azide impregnated on a calcium cation exchange Y-type zeolite induced the nucleophilic ring opening of epoxides in aprotic solvents affording azidohydrins[48]. Several other reported reagents are tributyltin azide without solvent and promoter[49], dibutyltin azide in dimethyl formamide[50], triethylaluminium/hydrogen azide as a mild and efficient reagent for medium to large ring cyclic epoxides[51], diethylaluminium azide for the regio-and stereoselective ring opening of 2,3-epoxyalcohols[52], trimethylsilylazide in the presence of a Lewis acid[53] and also trimethylsilylazide in presence of Cr (salen)[54]. In addition, it has been reported that simple salts, such as lithium or magnesium perchlorate, zinc or lithium triflate and ammonium chloride can be used as efficient catalysts for the azidolysis of epoxides in acetonitrile[55]. Use of phase transfer catalysts has also been reported for the preparation of azidohydrins[56]. Amberlite supported azide system, for promoting the reaction of polycyclic aromatic hydrocarbon epoxides with azides, has also been described[57].

However, many of these methods involve the use of expensive and stoichiometric amounts of reagents or catalysts, suffer from poor regioselectivity, strongly acidic conditions and also require extended reaction times. Therefore, the development of a new and efficient protocol for this transformation under mild and more convenient conditions is still needed.

Cross-linked poly(4-vinylpridine) supported sulfuric acid, $[P4\text{-}VP]H_2SO_4$, would be a proton source similar to all of the reported acidic solid supports or acidic resins such as polystyrene sulfonic acid and Nafion-H[58]. Therefore, the use of this solid acidic resin as a new proton source and as a new polymeric phase transfer catalyst for ring opening of epoxides using cross-linked poly(4-vinylpyridine) supported azide ion, $[P_4\text{-}VP]N_3$, was studied. However, any reduction in the amount of strong inorganic acids needed and any simplification in handling procedures are required for risk reduction, economic advantage and economic protection[59]. In addition, there is current research and general interest in heterogeneous systems because such systems have importance in industry and in developing technologies[60]. On the other hand polymeric reagents would be particularly attractive since they can be recovered by filtration and can be used again.

In continuation of our studies on the development of application of cross-linked poly(4-vinylpyridine) supported azide ion, $[P_4\text{-}VP]N_3$, in organic synthesis[61–65], herein we wish to report an improved, fast and regioselective ring opening of epoxides by using $[P_4\text{-}VP]N_3/[P_4VP]H_2SO_4$, and consequently the corresponding β-azidoalcohols are prepared under solvent-free conditions at 65 °C.

EXPERIMENTAL

Materials and Instruments

The chemicals were either prepared in our laboratory or were purchased from Fluka (Buchs, Switzerland), Aldrich (Milwaukee, WI) and Merck (Germany) chemical companies. Poly(4-vinylpyridine) cross-linked with 2% divinyl benzene (DVB), $[P_4\text{-}VP]$ 2% DVB; (white powder, 100–200 mesh) was purchased from Fluka. Cross-linked poly(*N*-methyl-4-vinylpyridinium) iodide ($[P_4\text{-}VP]I$) was synthesized according to our reported procedures[8–10]. The progress of the reaction was monitored by thin-layer chromatography (TLC) with silica gel PolyGram SIL G/UV 254 plates. All products were characterized by comparison of their melting points, Fourier transform infrared (FTIR) spectroscopy, and ^{1}H-NMR spectral data with those of known samples, and all yields refer to the isolated pure products. The melting points were determined with a Buchi melting point B-540 B. V. CHI apparatus. The FTIR spectra were obtained with a Bruker Equinox (model 55), Germany, and the NMR spectra were recorded on a Bruker AC 400 Avance DPX spectrophotometer, Germany at 400 MHz in $CDCl_3$ solutions.

Preparation of [P_4-VP]N_3

Cross-linked poly(*N*-methyl-4-vinylpyridinium) azide, [P_4-VP]N_3, was synthesized and its capacity was determined according to our reported procedure (Scheme 2)[61].

Poly(4-vinylpyridine) cross-linked with 2% DVB (white powder, 100–200 mesh; 1.0 g) was added to a solution of methyl iodide (20 mmol, 3.24 g) in acetonitrile (10 mL), and the mixture was slowly stirred for 24 h at room temperature. The yellow quaternized polymer, [P4-VP]I, was filtered and was washed with distilled water and acetonitrile. It was then dried under vacuum in the presence of P_2O_5 at 40 °C overnight (Scheme 2, step 1).

The obtained [P_4-VP]I was added to 40 mL of a 3 mol/L aqueous solution of sodium azide and the mixture was stirred slowly for 24 h. The prepared resin, [P_4-VP]N_3, was filtered off and was washed rapidly with distilled water (3 × 8 mL). It was then washed with diethyl ether and dried under vacuum in the presence of P_2O_5 at 40 °C overnight. The activity of the polymer was determined by potentiometric titration of the filtrates with a 0.1 mol/L aqueous solution of silver nitrate, and it was found to be 3.4 mmol of azide ion per gram of the polymer.

Preparation of [P_4-VP]HCl

To a solution of 0.6 mL of concentrated hydrochloric acid (12 mol/L) in distilled water (10 mL), [P_4-VP] 2% DVB (1 g) was added, and stirred for 24 h. The mixture was filtered and washed with distilled water until the filtrate gave a negative test for HCl. Then it was dried in vacuum at 50 °C for 5 h to give 1.2 g of [P_4-VP]HCl. The capacity of the polymer was determined by gravimetric method and potentiometric titration with a 0.1 mol/L solution of sodium hydroxide. The obtained capacity of polymer was 4.6 mmol/g of the polymer.

Preparation of [P_4-VP]H_2SO_4

To a solution of 0.6 mL of concentrated sulfuric acid (16 mol/L) in distilled water (10 mL), [P_4-VP] 2% DVB (1 g) was added, and stirred for 24 h. The mixture was filtered and washed with distilled water until the filtrate gave a negative test for H_2SO_4. Then it was dried in vacuum at 50 °C for 5 h to give 2.2 g of [P_4-VP]H_2SO_4. The capacity of the polymer was determined by gravimetric method and potentiometric titration with a 0.1 mol/L solution of sodium hydroxide. The obtained capacity of polymer was 5.6 mmol/g of the polymer.

General Procedure for Azidolysis of Epoxides Using [P_4-VP]N_3/[P_4-VP]H_2SO_4 under Solvent-free Conditions

In a mortar a mixture of epoxide (1mmol), [P_4-VP]N_3 (0.5 g, 1.7 mmol) and [P_4-VP]H_2SO_4 (0.5 g, 2.7 mmol) was pulverized for 3–5 min. The mixture was stirred at 65 °C in a water bath for the appropriate time as indicated in Table 2. The progress of the reaction was monitored by TLC using *n*-hexane/ethyl acetate (80:20) as eluent. After completion of the reaction, the suspension was filtered and washed with $CHCl_3$ (3 × 5 mL). The combined organic layer was dried over anhydrous $CaCl_2$ and filtered. The solvent was evaporated to obtain β-azidoalcohols in good to high isolated yields (80%–90%). If further purification is needed, preparative TLC or column chromatography on silica gel provides highly pure products.

Azidolysis of Phenylglycidyl Ether Using [P_4-VP]N_3/[P_4-VP]H_2SO_4 under Solvent-free Conditions as a Typical Procedure

In a mortar a mixture of phenylglycidyl ether (1 mmol) [P_4-VP]N_3 (1 g, 3.4 mmol) and [P_4-VP]H_2SO_4 (0.5 g, 2.8 mmol) was pulverized for 3–5 min. The mixture was stirred at 65 °C in a water bath for 15 min. The progress of the reaction was monitored by TLC using *n*-hexane/ethyl acetate (80:20) as eluent. After completion of the reaction, the suspension was filtered and washed with $CHCl_3$ (3 × 5 mL). The combined organic layer was dried over anhydrous $CaCl_2$ and filtered. The solvent was evaporated to obtain 2-azido-3-phenoxypropanol in high isolated yield (180 mg, 95%).

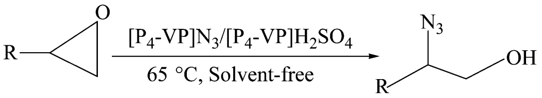
Regeneration of [P_4-VP]N_3

The spent cream-colored polymer (1 g) was added to a solution of methyl iodide (20 mmol, 3.24 g) in acetonitrile (10 mL) and was stirred for 10 h. The mixture was filtered and the separated polymer was added to a 40 mL of a 3 mol/L aqueous solution of sodium azide, and was slowly stirred for 24 h. The mixture was filtered and washed with distilled water (3 × 8 mL), and dried under vacuum in the presence of P_2O_5 at 40 °C overnight.

The capacity of the regenerated polymer was determined and it was found that, it had the same capacity as the original form (3.4 mmol of azide ion per gram of polymer). The regenerated polymer reused several times did not show losing its activity (Table 2, entries 3–6).

RESULTS AND DISCUSSION

In connection with our organic program to develop environmentally friendly methods using polymer-supported reagents[8–18, 61–65], herein we wish to report an extremely convenient and efficient method for regioselective ring opening of epoxides using cross-linked poly(4-vinylpyridinie) supported azide ion [P_4-VP]N_3 in the presence of cross-linked poly(4-vinylpyridinie) supported sulfuric acid, [P_4-VP]H_2SO_4, or cross-linked poly(4-vinylpyridinie) supported hydrochloric acid, [P_4-VP]HCl, as solid proton source and as new polymeric phase transfer catalyst under solvent-free conditions at 65 °C. A good range of epoxides were also subjected to azidolysis in the presence of [P_4-VP]N_3/[P_4-VP]H_2SO_4 under solvent-free conditions (Scheme 1).

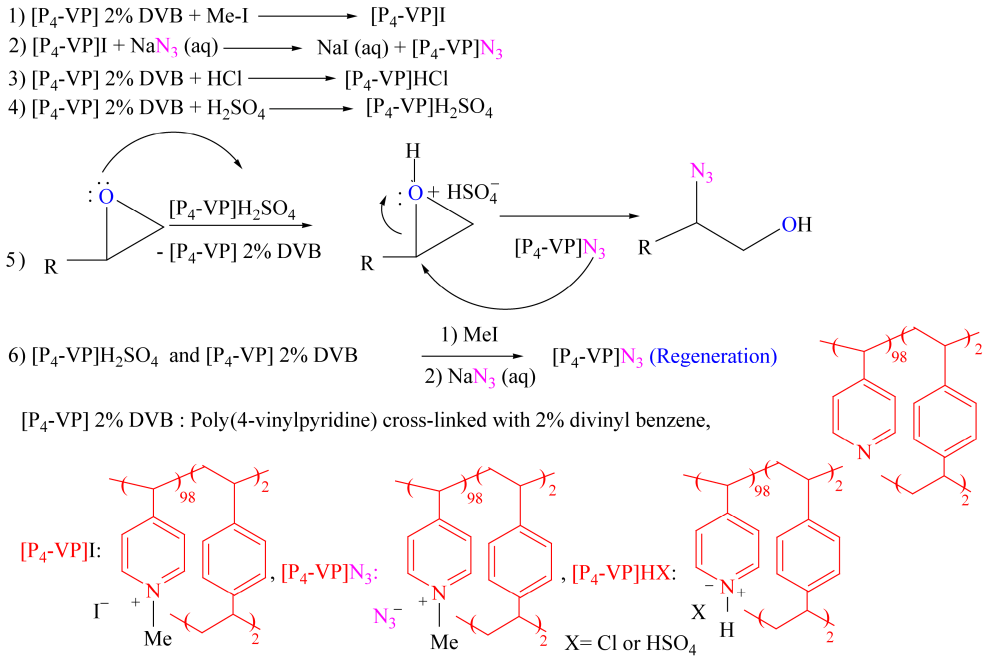


Scheme 1 Regioselective azidolysis of epoxides

[P_4-VP]N_3, is easily prepared by ion exchange reaction between cross-linked poly(*N*-methyl-4-vinylpyridinium) iodide with excess amount of sodium azide under solvent-free conditions (Scheme 2, steps 1 and 2)[61–65]. Cross-linked poly(4-vinylpyridinie) supported hydrochloric acid, [P_4-VP]HCl, (Scheme 2, Step 3) and cross-linked poly(4-vinylpyridinie) supported sulfuric acid, [P_4-VP]H_2SO_4, (Scheme 2, Step 4) are easily prepared by the reaction of [P_4-VP] 2% DVB with HCl or H_2SO_4, respectively. Preparation stages of [P_4-VP]N_3, [P_4-VP]HCl and [P_4-VP]H_2SO_4 and the plausible reaction pathway of ring opening of epoxides and regeneration of the polymeric reagent are given in Scheme 2. It is important to note that this polymeric reagent was stable and could be stored for a long time (months) without losing its activity, so it could be readily used for azidolysis of epoxides. This polymeric reagent is used in a single step reaction, its main advantage over non-polymeric reagents is its insolubility in the reaction medium and consequently its easier work-up by a simple filtration. The reactions can be driven to completion using excess amounts of reagent without the fear of excess of reagent separating from the products. One of the most disadvantages of the polymeric reagents is their high cost and chemical suitability as given in step 6 of Scheme 2.

[P_4-VP]N_3 can be used as a mild and efficient polymeric reagent for regioselective ring opening of epoxides in the presence of a solid polymeric acid, such as [P_4-VP]HCl or [P_4-VP]H_2SO_4 and consequently the corresponding β-azidoalcohols are prepared (Scheme 2).

In order to increase the yields of β-azidoalcohols optimization of the reaction conditions was accomplished. Phenylglycidyl ether (1 mmol) was chosen as a model substrate and was converted to the corresponding β-azidoalcohol in different solvents, such as water, ethanol, acetonitrile, dichloromethane, carbon tetrachloride and chloroform, at different temperatures and under solvent-free conditions. Also, we have investigated a number of different reaction conditions for synthesis of β-azidoalcohol and the results are summarized in Table 1. It was observed that, a molar ratio of 1/3.4/2.8 of phenylglycidyl ether/[P_4-VP]N_3/[P_4-VP]H_2SO_4 under solvent-free conditions at 65 °C was the best to achieve the highest yield of the product as indicated in Table 1 (entry 17).



Scheme 2 Preparation stages of [P4-VP]N3, [P4-VP]HCl and [P4-VP]H2SO4 and the plausible reaction pathway of ring opening of epoxides and regeneration of the polymeric reagent

Table 1. Optimization of the reaction conditions for ring opening of phenylglycidyl ether (1 mmol) under different conditions

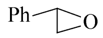
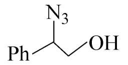
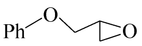
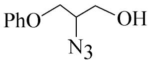
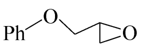
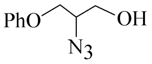
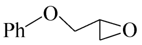
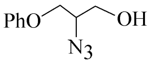
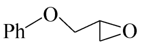
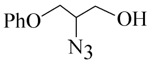
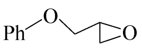
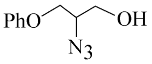
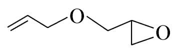
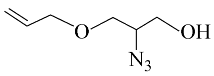
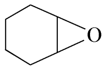
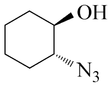
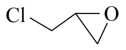
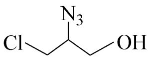
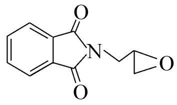
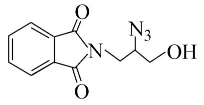
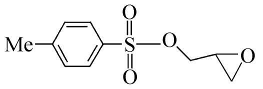
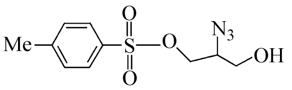
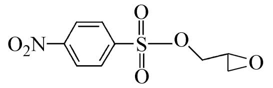
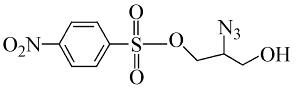
Entry	Solvent	Catalyst (mmol)	Temp (°C)	$[P_4\text{-VP}]N_3$ (mmol)	Time (h)	Yield [a](%)
1	CCl_4	CAN [b] (0.1)	r.t.	3.4	20	70
2	$CHCl_3$	CAN (0.1)	45	3.4	20	70
3	CH_3CN	CAN (0.1)	45	3.4	15	75
4	CH_2Cl_2	CAN (0.1)	45	3.4	15	70
5	C_2H_5OH	CAN (0.1)	45	3.4	4	85
6	H_2O	CAN (0.1)	45	3.4	2	88 [c]
7	C_2H_5OH	$[P_4\text{-VP}]H_2SO_4$ (2.8)	r.t	3.4	12	30
8	H_2O	$[P_4\text{-VP}]H_2SO_4$ (2.8)	r.t	3.4	8	50 [c]
9	CH_2Cl_2	$[P_4\text{-VP}]H_2SO_4$ (2.8)	45	3.4	18	78
10	C_2H_5OH	$[P_4\text{-VP}]H_2SO_4$ (2.8)	45	3.4	2.5	87
11	H_2O	$[P_4\text{-VP}]H_2SO_4$ (2.8)	45	3.4	1	85 [c]
12	Solvent-Free	CAN (0.1)	65	3.4	40 min	85
13	Solvent-Free	$[P_4\text{-VP}]HCl$ (2.3)	65	3.4	30 min	90
14	Solvent-Free	$[P_4\text{-VP}]HCl$ (3.2)	65	1.7	0.5	71
15	Solvent-Free	$[P_4\text{-VP}]HCl$ (3.2)	65	0.85	0.5	63
16	Solvent-Free	$[P_4\text{-VP}]HCl$ (2.3)	65	1.7	0.5	70
17	Solvent-Free	$[P_4\text{-VP}]H_2SO_4$ (2.8)	65	3.4	15 min	95
18	Solvent-Free	$[P_4\text{-VP}]H_2SO_4$ (2.8)	65	1.7	30 min	75
19	Solvent-Free	$P_4\text{-VP}]H_2SO_4$ (1.4)	65	3.4	30 min	80
20	Solvent-Free	$[P_4\text{-VP}]H_2SO_4$ (2.8)	r.t.	3.4	15 h	40

[a] Isolated yields; [b] CAN: Ceric ammonium nitrate; [c] In water as solvent, H_2O was also reacted as nucleophile and 1,2-diol product was also obtained and the yield refers to the obtained 1,2-diol product.

We then applied these conditions in ring opening of different epoxides to prepare the corresponding β-azidoalcohols and the results are given in Table 2.

This new, simple method can be successfully applied for the synthesis of a wide range of β-azidoalcohols starting from the corresponding epoxides. We have also successfully applied this new method on a nearly large scale for example; up to 15 mmol of phenylglycidyl ether (Table 2, Entry 1) could be converted into the 2-azido-3-phenoxypropanol.

Table 2. Ring opening of epoxides using [P_4-VP]N_3/[P_4-VP]H_2SO_4 under solvent-free conditions at 65 °C

Entry	Epoxide	Product	Time (min)	Yield (%)
1			15	95
2			15	95
3[a]			15	90
4[a]			15	85
5[a]			20	80
6[a]			20	78
7			15	90
8			15	92
9			15	92
10			30	85
11			30	80
12			30	80

[a] The entries 3–6 refer to the use of the [P_4-VP]N_3 that is recycled first, second, third and fourth time, respectively, under identical conditions.

The β-azidoalcohol products were characterized by FTIR, and ^{1}H- and ^{13}C-NMR spectroscopy, and physical properties were compared with literature values of known compounds. In this respect, the appearance of a strong band in the region 2095–2105 cm^{-1} for stretching vibration of the $-N{=}N{=}N$ and another strong band in the region 3362–3502 cm^{-1} for stretching vibration of the $O-H$ group indicates the formation of corresponding β-azidoalcohol products. Characteristic spectral data of some β-azidoalcohol products are summarized below and the FTIR, ^{1}H- and ^{13}C-NMR spectra of 2-azido-3-phenoxypropanol are given in Figs. 1–3 respectively.

2-Azido-2-phenylethanol

FTIR (neat); υ max (cm^{-1}): 3361.6, 2929.8, 2102.7, 1602.5, 1493, 1453.8, 1069, 700; ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 3.36 (s, 1H, $CH_2O\underline{H}$), 3.62 (dd, 1H, $C\underline{H_2}OH$), 3.70 (dd, 1H, $C\underline{H_2}OH$), 4.72 (t, 1H, CHN_3), 7.32–7.39 (m, 5H, Ph); ^{13}C-NMR (100 MHz, $CDCl_3$, δ): 66.3, 67.6, 127.9, 128.8, 129.3, 138.

2-Azido-3-phenoxypropanol

FTIR (neat); υ max (cm^{-1}): 3412.8, 2930.5, 2103.6, 1599, 1496, 1245.6, 1173.3, 1046, 755.3, 691.7, 510;

^{1}H-NMR (400 MHz, $CDCl_3$, *δ*): 2.6 (s, 1H, $CH_2O\underline{H}$), 3.77 (dd, 1H, $C\underline{H}_2OH$), 3.85 (dd, 1H, $C\underline{H}_2OH$), 4.1 (d, 2H, CH_2OPh), 4.29 (m, 1H, CHN_3), 6.9 (d, 2H, Ar-H), 7.1 (t, H, Ar-H), 7.3 (m, 2H, Ar-H); ^{13}C-NMR (100 MHz, $CDCl_3$, *δ*): 54, 68.8, 70, 115, 121.9, 130, 158.6.

2-Azido-3-allyloxopropanol

FTIR (neat); *υ* max (cm^{-1}): 3412, 2864, 2102.3, 1646, 1421, 1276.7, 1108, 1000, 930; ^{1}H-NMR (400 MHz, $CDCl_3$, *δ*): 2.75 (s, 1H, OH), 3.50–3.61 (d, 2H, OCH_2), 3.61 (dd, 1H, CH_2OH), 3.70 (dd, 1H, CH_2OH), 4.01 (m, 1H, CHN_3), 4.1 (d, 2H, CH_2O), 5.2 (d, 1H, $H_2C{=}CH$), 5.3 (d, 1H, $H_2C{=}CH$), 5.8–5.9 (m, 1H, $H_2C{=}CH$); ^{13}C-NMR (100 MHz, *δ*): 53, 70.6, 71, 72.8, 117.9, 134.6.

2-Azido-3-N-phetalimidopropanol

FTIR (neat); *υ* max (cm^{-1}): 3502, 2945, 2094.5, 1777, 1704.8, 1395.8, 1259.8, 1008, 924.7, 874, 723.6, 580, 530; ^{1}H-NMR (400 MHz, $CDCl_3$, *δ*): 2.89 (s, 1H, $CH_2O\underline{H}$), 3.41–3.46 (dd, 1H, $C\underline{H}_2OH$), 3.47–3.70 (dd, 1H, $C\underline{H}_2OH$), 3.8–3.9 (t, 2H, NCH_2), 4.1 (m, 1H, CHN_3); ^{13}C-NMR ($CDCl_3$): 7.4 (d, 2H, Ar-H), 7.8 (d, 2H, Ar-H); ^{13}C-NMR (100 MHz, $CDCl_3$, *δ*): 55, 69.8, 70, 123.9, 132.2, 134.7, 169.

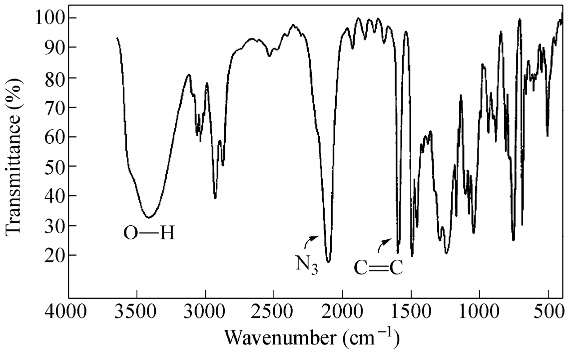


Fig. 1 FTIR spectrum of 2-azido-3-phenoxypropanol

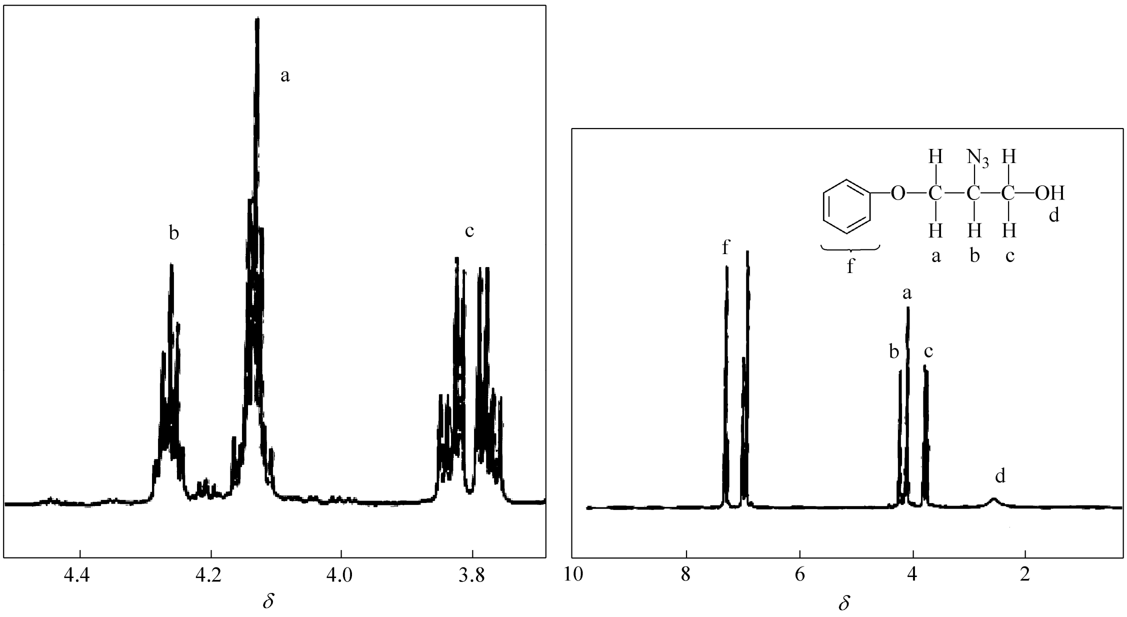


Fig. 2 ^{1}H-NMR spectra of 2-azido-3-phenoxypropanol

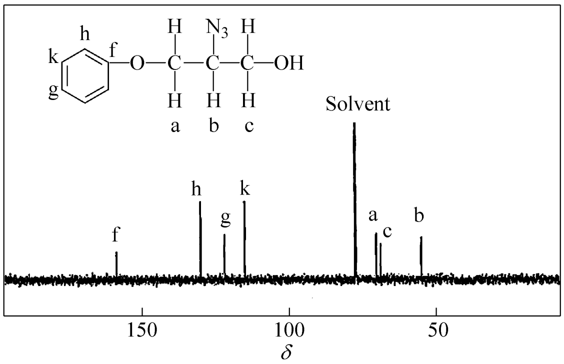


Fig. 3 ^{13}C-NMR spectrum of 2-azido-3-phenoxypropanol

In Table 3, other reported methods for preparation of *β*-azidoalcohols are compared with the present method. As it is demonstrated, the reaction times of the reactions in the present method are shorter than those in the previously reported methods[30, 39, 42, 45, 46, 56]. This can probably be attributed to the high local concentration of azide ion species inside the pores.

The advantages of this method over conventional classical methods are mild reaction conditions, safe handling, rapid, mildness of polymeric reagent and very simple work-up. In addition, there are current research and general interest in heterogeneous systems because such systems are important in industry and developing technologies[60].

Table 3. Comparison of different methods for synthesis of *β*-azidoalcohols

Entry	Reagents and reaction conditions	Time	Isolated yield (%)	Ref.
1	$[P_4\text{-VP}]N_3/[P_4\text{-VP}]H_2SO_4$, solvent-free, 65 °C	15 min	95	a
2	NaN_3/PEG-300, 60 °C	1.5 h	85	[46]
3	LiN_3/CH_3CN, 80 °C	20 h	94	[39]
4	$NaN_3/NH_4Cl/MeOH\text{-}H_2O$, reflux	5 h	90	[39]
5	$NaN_3/Mg(ClO_4)_2/CH_3CN$, 80 °C	2 h	78	[39]
6	$NaN_3/LiClO_4/CH_3CN$, 80 °C	5 h	92	[39]
7	$NaN_3/CeCl_3\cdot 7H_2O/CH_3CN\text{-}H_2O$, reflux	3 h	96	[42]
8	NaN_3/DMSO, 80 °C	3 h	92	[30]
9	NaN_3/functionalized cross-linked polyacrylamide/EtOH, 50 °C	1 h	30	[56]
10	$NaN_3/(TBA)_4PFeW_{11}O_{39}\cdot 3H_2O/CH_3CN\text{-}H_2O$, 80 °C	4.5 h	85	[45]

[a] Present method (Table 2, entry 2)

CONCLUSIONS

We have developed an efficient, rapid and experimentally simple method for the synthesis of *β*-azidoalcohols from various epoxides *via* regioselective ring opening of epoxides using a polymer supported azide ion, $[P_4\text{-VP}]N_3$, as nucleophile and a polymer supported sulfuric acid, $[P_4\text{-VP}]H_2SO_4$, as a solid proton source and as a catalyst under solvent-free conditions. $[P_4\text{-VP}]N_3$ and $[P_4\text{-VP}]H_2SO_4$ have readily prepared from commercially available cross-linked poly(4-vinylpyridine). The spent polymeric reagent was easily separated by filtration and was easily regenerated by treatment with NaN_3 and reused for several times.

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