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Efficient method for ring opening of epoxides with amines by NaY zeolite under solvent-free conditions

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Abstract

NaY zeolite was used as a recyclable catalyst for the ring opening of epoxides using aliphatic and aromatic amines as nucleophile under solvent-free conditions to give the corresponding β-amino alcohols in high yields (up to 92%) with regioselectivity (100%).

Keywords: Epoxides; Ring opening; Amines; Solvent-free; Zeolites

1. Introduction

β-Amino alcohols are versatile intermediates in synthesis of a wide range of biologically active natural and synthetic products, unnatural aminoacids, β-blockers in pharmaceuticals and insecticides [1]. The ring opening of epoxides by amines is an important route for the preparation of β-amino alcohols [2]. The classical approach for the synthesis of β-amino alcohols, involves the ring opening of epoxides using excess amounts of amine as nucleophile at elevated temperatures. However, this process is not suitable particularly when dealing with thermally sensitive epoxides due to occurrence of side reactions [3]. To overcome these problems, variety of protocols have been introduced for the cleavage of epoxides with amines in presence of metal halides [4], metal triflates [5], metal alkoxides [6], metal amides and triflamide [7], transition metal salts [8], hexafluoro-2-propanol under reflux (HFIP) [9], ionic liquid [10], zirconium sulfophenyl phosphonate [11], montmorillonite clay under microwave irradiation [12a] and solvent-free condition [12b], silica [13] and alumina/modified alumina [14]. However, there are still limitations with existing methods; for example less basic amines fail to open these epoxides under ambient condition and require high temperature. Further, many of these catalysts used are either corrosive or expensive.

Therefore, it is required to develop an improved catalyst for the activation of epoxides, which renders them to be more susceptible to nucleophilic attack under milder condition. In view of emerging importance of efficient and environment friendly processes, we undertook new synthetic methodologies that have intrinsic advantages such as environmentally benign catalyst, easy product separation, catalyst reuse, no generation of salts/waste products and elimination of the use of corrosive/hazardous acids and organic solvents [4j,8b,11,13b,15]. We, therefore, focused our attention on an environment friendly heterogeneous catalysts such as zeolites [16]. Zeolites are particularly attractive because these are thermally stable, highly crystalline in nature and are commercially available. We have explored the possibility of using different zeolites likes ZSM-5 (Si/Al = 25), ZSM-5 (Si/Al = 900), Naβ, NaY, Na Mordenite 060 and powdered A and X as catalyst for the ring opening reaction of epoxides under solvent-free conditions.

2. Experimental

All zeolites were purchased from M/S. Zeocat, Uetikon, Switzerland. Morpholine, piperidine, (distilled before use) was purchased from s.d. Fine Chemicals, India. Styrene oxide and substituted styrene oxides were synthesized by reported methods [20]. 1-Propene oxide, 1-hexene oxide, 1-octene oxide,

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cyclohexene oxide, epichlorohydrin and aniline (Aldrich, USA) were used as received. Microanalysis of the products was carried out on a Perkin-Elmer CHN Analyzer 2400. ^{1}H NMR spectra were recorded in $CDCl_3$ (Bruker F113V 200 MHz). Product distribution and purity was determined from analysis using a HPLC (Shimadzu SCL-10AVP) having a Luna 5μ C18 (2) column in water: acetonitrile (20:80) as eluent at a flow rate of 0.5 ml/min and at λ_{max} = 220 nm on PDA detector.

2.1. Typical experimental procedure

A mixture of styrene oxide (2 mmol), aniline (2 mmol) and zeolites (50 mg, 25%, w/w) was magnetically stirred initially under solvent-free condition at 5 °C, which was gradually raised to room temperature (35 °C) at a specified time. Zeolites were activated at 250 °C under nitrogen gas purge for 3 h prior to their use. The reaction progress was monitored on TLC using hexane-ethyl acetate (9:1) as mobile phase till epoxide is fully consumed. The reaction mixture was then treated with 10 ml of diethyl ether and catalyst was filtered, washed with additional 5 ml of diethyl ether and dried at 250 °C for 3 h which was ready for further use. The filtrate was dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash column chromatography using hexane-ethyl acetate as mobile phase (9:1). The recovered catalyst was used five times for ring opening of propylene oxide with aniline with retention of activity and regioselectivity.

3. Products characterizations

All products were characterized by ^{1}H NMR, ^{13}C and LCMS. 2-Phenylamino-2-phenyl-ethanol (entry 9) [4h,4i], 1-phenyl-2-piperidin-1-yl-ethanol (entry 23) [21], 1-phenylamino-3-chloro-2-propanol (entry 27) [13b], anti-1,2-diphenyl-2-(phenylamino)-ethanol (entry 28) [11] trans-2-(phenylamino) cyclohexanol (entry 29) [4f,4j,11] and 1-phenoxy-3-phenylamino-propan-2-ol (entry 32) [10,13b] were known compounds compared with literature. The other unknown compounds characterization was given in Table 1.

4. Crystal data collection and refinement

The diffraction experiments were carried out on a Bruker AXS SMART APEX CCD diffractometer at room temperature (300 K). The SMART [17] program was used for collecting data frames, indexing reflection, and determination of lattice parameters; SAINT [17] program for integration of the intensity of reflections and scaling. The SADABS [18] program for absorption correction and the SHELXTL [19] program for space group, structure determination, and least-squares refinements on F^2. The structure was solved by direct methods. The non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed by full matrix least squares. In all three compounds, H atoms attached to the nitrogen was located from the difference electron density map and refined

Table 1
Characterization of new products obtained by the ring opening of epoxides by aniline

Compound	^{1}H NMR (δ ppm)	^{13}C NMR (δ ppm)	LCMS $[M+H]^+$
1-Phenylamino-propan-2-ol	1.22 (d, 3H, J = 6.3 Hz), 2.93 (dd, 1H, J = 8.5 Hz, J = 12.9 Hz), 3.18 (dd, 1H, J = 3.3 Hz, J = 12.9 Hz), 3.39–4.00 (m, 1H), 6.60–6.78 (m, 3H), 7.10–7.20 (m, 2H)	20.6, 51.4, 66.0, 113.1, 117.5, 129.0, 148.0	152.1
2-(3-Nitrophenyl)-2-phenylaminoethanol	3.74 (dd, 1H, J = 6.9 Hz, J = 10.9 Hz), 3.96 (1H, dd, J = 3.7 Hz, J = 10.9 Hz), 4.45 (1H, dd, J = 4.3 Hz, J = 6.9 Hz), 6.49–7.25 (m, 9H)	66.7, 71.3, 113.9, 118.9, 121.8, 122.7, 129.5, 133.3, 143.4, 147.5, 148.5	259.1
1-Phenylamino-propan-2-ol	1.22 (d, 3H, J = 6.3 Hz), 2.93 (dd, 1H, J = 8.5 Hz, J = 12.9 Hz), 3.18 (dd, 1H, J = 3.3 Hz, J = 12.9 Hz), 3.39–4.00 (m, 1H), 6.60–6.78 (m, 3H), 7.10–7.20 (m, 2H)	20.6, 51.4, 66.0, 113.1, 117.5, 129.0, 148.0	152.1
2-(4-Chlorophenyl)-2-phenylaminoethanol	3.48 (dd, 1H, J = 7.9Hz, J = 11.0 Hz), 3.70 (dd, 1H, J = 3.7 Hz, J = 11.0 Hz), 4.30 (dd, 1H, J = 4.0 Hz, J = 6.9 Hz), 6.4–7.3 (m, 9H)	59.2, 66.7, 113.7, 117.9, 127.9, 128.6, 129.0, 138.6, 146.8	248.2
2-Morpholin-4-yl-1 phenyl-ethanol	2.45–2.52 (m, 4H), 2.68–2.78 (m, 2H), 3.71–3.77 (m, 4H), 4.74 (dd, 1H, J = 4.5 Hz, J = 9.4 Hz), 7.34–7.36(m, 5H)	53.4, 66.6, 66.9, 68.6, 125.7, 127.5, 128.3, 139.2	208
1-Phenylamino-2-hexanol	1.1 (t, 3H, J = 6.6 Hz), 1.33–1.55 (m, 6H), 2.92 (dd, 1H, J = 8.6 Hz, J = 12.7 Hz), 3.21 (dd, 1H, J = 3.1 Hz, J = 12.7 Hz), 3.77–3.87 (m, 1H), 6.6–7.10 (m, 5H)	14.0, 22.7, 27.8, 34.8, 50.4, 70.4, 113.4, 117.9, 129.3, 148.5	216
1-Phenylamino-2-octanol	0.90 (t, 3H, J = 6.6 Hz), 1.33–1.51 (m, 8H), 2.92 (dd, 1H, J = 8.6 Hz, J = 12.8 Hz), 3.22 (dd, 1H, J = 3.1 Hz, J = 12.6 Hz), 3.6–3.8 (m, 1H), 6.5–7.10 (m, 5H)	14.6, 23.4, 26.1, 29.9, 32.3, 35.7, 50.7, 70.7, 113.8, 118.2, 129.7, 148.9	244
1-(4-Chloro-phenoxy)-3-phenylamino-propan-2-ol	3.04–3.15 (dd, 1H, J = 7.4 Hz, J = 12.9 Hz), 3.21–3.29 (dd, 1H, J = 3.6 Hz, J = 12.8 Hz), 3.80 (d, 2H, J = 5.0 Hz), 4.02–4.10 (m, 1H), 6.55 (d, 2H, J = 8.0 Hz), 6.6–6.74 (m, 3H), 7.10–7.16 (m, 4H)	46.3, 68.3, 70.1, 113.0, 115.5, 117.7, 125.0, 129.0, 147.7, 156.7	278

Table 2
Crystallographic data for three compounds

	Compound **3B**	Compound **4B**	Compound **5**
Empirical formula	$C_{13}H_{19}NO$	$C_{12}H_{17}NO_2$	$C_{20}H_{19}NO$
M	205.29	207.27	289.36
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*P*21/*c*	*C*2/*c*	*P*21/*c*
Crystal dimensions (mm)	0.18 × 0.10 × 0.06	0.20 × 0.12 × 0.08	0.12 × 0.08 × 0.04
a(Å)	12.225(4)	18.289(14)	12.511(3)
b(Å)	5.9855(19)	5.986(4)	5.9775(12)
c(Å)	17.102(6)	22.438(16)	24.230(5)
α(°)	90	90	90
β(°)	108.372(7)	112.79(3)	119.534(9)
γ(°)	90	90	90
U(Å^3)	1187.6(7)	2265(3)	1576.6(6)
Z	4	8	4
D_c (g cm^{-3})	1.148	1.216	1.219
F(0 0 0)	448	896	616
Total reflections	4373	5349	5892
Observed reflections [$I > 2\sigma(I)$]	1547	1990	2067
Parameters refined	137	137	205
Final (R1) (on *F*)	0.0753	0.0678	0.0814
Final (*w*R2) (on F^2)	0.1796	0.1499	0.1408

isotropically. All the other hydrogen atoms were located by geometric placing.

The single crystal of compound **3B**, **4B**, **5** suitable for X-ray analysis was grown with the equal amount of petroleum ether (40–60) and diethyl ether, hexane and CH_2Cl_2 and toluene, respectively. Summary of crystallographic data for all the three compounds are given in Table 2, ORTEP diagrams with atom numbering scheme are shown in Figs. 2–4, respectively. All three catalytic products obtained from the above cited catalytic reactions, crystallizes in centro-symmetric space group clearly indicating that they are racemic compounds. Compounds **3B** and **4B** exist in racemic form with only one asymmetric carbon C7, the structural data show presence of equimolar amounts of *R* and *S* enantiomer. Structural data revealed individual molecule present in **5** is anti conformation (*R* and *S* conformation around the asymmetric carbon atom C7 and C8, respectively) and equimolar amount of *S* and *R* form constitute racemic mixture for compound **5**.

Crystallographic data for all the three compounds (**5**, **3B**, **4B**) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 281038-281040. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Fax: +44 1233 336033, e-mail: deposit@ccdc.cam.ac.uk.

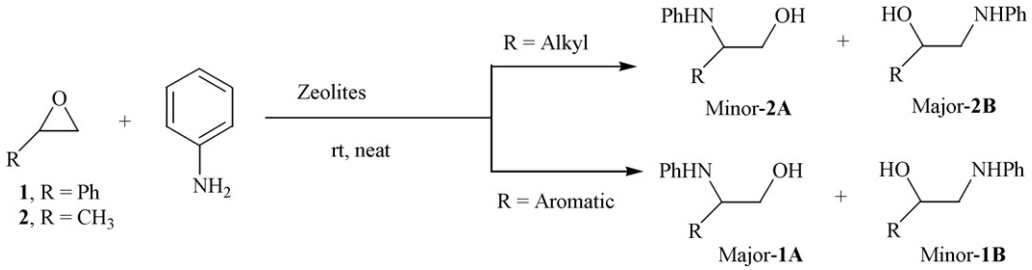
5. Results and discussion

The ring opening reaction of epoxides of styrene and propene with aniline in the presence of activated zeolites at 250 °C prior to use, viz., Zeolite 4A, Zeolite 5A, Zeolite X, Zeolite Naβ, Zeolite NaY, Zeolite Na Mordenite 060, ZSM-5 (Si/Al = 25) and ZSM-5 (Si/Al = 900) as a catalyst was carried out under solvent-free condition and the results are summarized in Table 3 (Scheme 1). Isolated yields of the corresponding amino alcohols were obtained between 25 and 92%. The activity of the catalyst is correlated with the Lewis acidity (aluminum content)

Table 3
Ring opening of epoxides with aniline using different zeolites as a catalyst under solvent-free conditions

Entry[a]	R	Zeolites	Time (h)	Isolated yield (%)	Ratio of 1A:1B (2A:2b)[b]
1 (2)	Ph (CH_3)	Zeolite 4A	8 (6)	70 (75)	90:10 (0:100)
3 (4)	Ph (CH_3)	Zeolite 5A	8 (6)	72 (73)	90:10 (0:100)
5 (6)	Ph (CH_3)	Zeolite X	8 (6)	75 (76)	91:9 (0:100)
7 (8)	Ph (CH_3)	Zeolite Naβ	8 (6)	85 (80)	90:10 (0:100)
9 (10)	Ph (CH_3)	Zeolite NaY	8 (6)	90 (92)	92:8 (0:100)
11	3-NO_2Ph	Zeolite NaY	10	92	70:30
12	4-ClPh	Zeolite NaY	10	90	80:20
13 (14)	Ph (CH_3)	Zeolite Mordenite	8 (6)	30 (25)	90:10 (0:100)
15 (16)	Ph (CH_3)	ZSM-5 (25)	8 (6)	60 (65)	91:9 (0:100)
17 (18)	Ph (CH_3)	ZSM-5 (900)	8 (6)	75 (78)	90:10 (0:100)

[a] Epoxides (2 mmol) were treated with aliphatic amines (2 mmol) in the presence of zeolites (25%, w/w) at room temperature (35 °C) under solvent-free condition.
[b] Regioisomeric ratio was determined by ^{1}H NMR analysis of crude sample and compared by literature data.



Scheme 1.

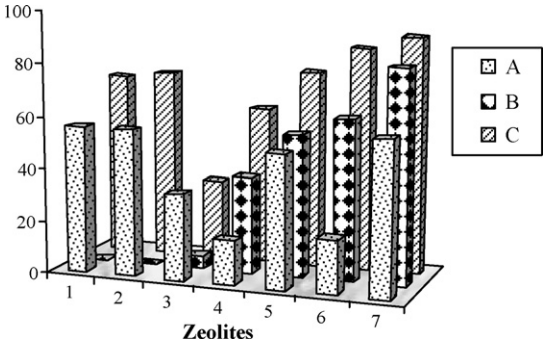


Fig. 1. Effect of Al content and surface area of different zeolites (1 = 4A, 2 = 5A, 3 = Na Mordenite 060, 4 = Na ZSM-5 (25), 5 = NaX, 6 = Naβ, 7 = NaY) on ring opening of styrene oxide with aniline. (A) % Al content (10^1), (B) surface area (10^1 m^2 g^{-1}) and (C) % yield of amino alcohol **2A**.

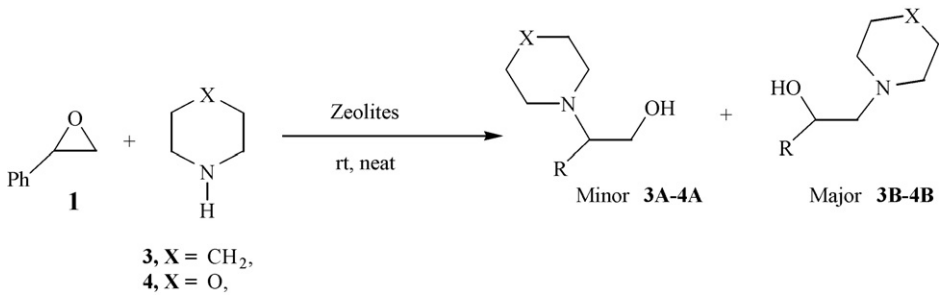
Table 4
Ring opening of styrene oxide with piperidine and morpholine using different zeolites as a catalyst under solvent-free conditions

Entry[a]	Amines	Zeolites	Time (h)	Isolated yield (%)	Ratio of A:B[b]
19	3	Zeolite 4A	10	65	20:80
20	3	Zeolite 5A	10	68	18:82
21	3	Zeolite X	10	75	15:85
22	3	Zeolite NaB	10	85	15:85
23	3	Zeolite NaY	10	93	4:96
24	4	Zeolite NaY	8	90	6:94
24	3	Zeolite Mordenite	10	40	20:80
25	3	ZSM-5 (25)	10	55	16:85
26	3	ZSM-5 (900)	10	70	15:85

[a] Epoxides (2 mmol) were treated with piperidine (2 mmol) in the presence of zeolites (25%, w/w) at room temperature (35 °C) under solvent-free condition.
[b] Regioisomeric ratio was determined by ^{1}H NMR analysis of crude sample and compared by literature.

and surface area (Fig. 1). It was observed that the zeolite NaY having high aluminum content and surface area is most active for the ring opening of styrene and propylene oxide with aniline (Table 3, entries 9 and 10). Likewise, when zeolite Na mordenite was used as catalyst the reactivity was found to be poor (entries 13 and 14) as it has both low surface area and low aluminum content. However, in the case of zeolites 4A, 5A where the surface area is very low but the Al content is comparable to NaY the activity was found to be moderate (entries 1–4). Selective formation of the regioisomeric product **1A** as a major product arising from nucleophilic attack of aniline at benzylic carbon was observed with epoxides of styrene [20] (entries 9, 11, 12) while in the case of aliphatic epoxides (propylene oxide) formation of regioisomeric product **2B** as a major product was obtained by nucleophilic attack on the less hindered terminal carbon (entry 10).

The ring opening of styrene oxide with piperidine as representative aliphatic amine (Scheme 2) using all the zeolites gave similar pattern of activity and selectivity (Table 4) as it was found for aniline, suggesting the general applicability of the method. Previously, various metal salts have been used for the ring opening of epoxides, however, this method is applicable for aromatic amines only and is not suitable for aliphatic amines due to strong Lewis acid property of the salts used [4a,4e–h]. Aliphatic amine form strong bonding with these metal salts causing catalyst poisoning making the method unsuitable for ring opening reaction. Among all the zeolites used, NaY zeolite was found to be excellent catalyst for the ring opening of styrene oxide with piperidine in terms of reactivity and regioselectivity (entry 23). Aliphatic amines exhibited a preference for the nucleophilic attack at terminal carbon of epoxide to give corresponding β-amino alcohol, product **3B–4B** (entries 23 and 24) and the best selectivity (**3A**:**3B**::4:96 and **4A**:**4B**::6:94) was observed with piperidine and morpholine (entries 23 and



Scheme 2.

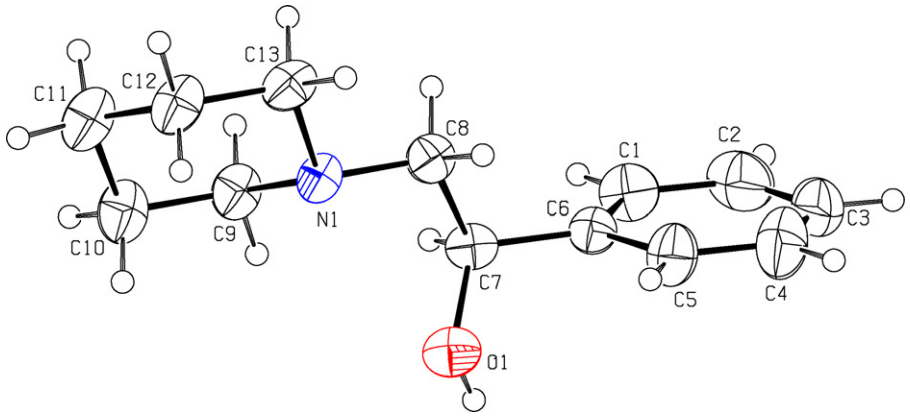


Fig. 2. ORTEP diagram (40% probability factor for thermal ellipsoids) with atom numbering scheme for compound **3B** (1-phenyl-2-piperidin-1-yl-ethanol).

24) with NaY zeolite. The regioselectivity of the ring opening products, 1-phenyl-2-piperidin-1-yl-ethanol (**3B**) and 1-phenyl-2-morpholin-1-yl-ethanol (**4B**), respectively, were determined by single crystal X-ray. ORTEP diagrams for the compounds **3B** and **4B** are given in Figs. 2 and 3. In the case of aliphatic amines such as morpholine and piperidine [21] two regioisomers could not be physically separated by column chromatography, hence the ratio of the two regioisomers were determined by integrating the benzylic proton of A and B appeared at δ ~3.9 and 4.7 ppm, respectively in ^{1}H NMR.

In order to evaluate the general applicability of the method, the catalyst NaY was used for the ring opening of the various epoxides by aniline under identical experimental conditions (Table 5). In case of *trans*-stilbene oxide reaction was carried out at 80 °C yielding only *anti* regio-isomer (entry 28) which on crystallization in toluene gave single crystal Fig. 4. Further, a *trans* stereospecificity was observed in the epoxide ring opening during the reaction of cyclohexene oxide with aniline (entry 29). Furthermore, excellent chemoselectivity was achieved with epichlorohydrin (entry 27) resulting in a 90% yield of amino alcohol and no product arising from nucleophilic displacement of chlorine [22] was detected by HPLC, ^{1}H and ^{13}C NMR.

In absence of zeolites, the epoxide ring opening reaction of styrene oxide with aniline under similar reaction conditions does not occur even after 20 h, indicating that the zeolites have an important role as catalyst for the opening of epoxide ring. Zeolites are a crystalline aluminosilicates in which silica and alumina tetrahedrons are joined together by sharing of oxygen atoms having large cavities in range of 5.6–12.0 Å diameter and uniform pore openings having size in the range of 4.1–7.4 Å (Table 6). The catalytic activity of the zeolites observed in the present case can be explained in terms of the reaction occurring on the Lewis acid sites of the zeolites located on both external surface and inside the cage depending upon the dimensions of channel size and epoxide/amines. For example, in the case of zeolites NaA and NaZSM-5 the substrate and product dimensions are greater than their channel size, hence the reaction is largely taking place on the external surface of the zeolites.

To evaluate the recycling capability of the catalyst (NaY zeolite), ring opening of propylene oxide with aniline was used as a representative reaction. After completion of the reaction, 10 ml of diethyl ether was added to the reaction mixture and filtered. The recovered catalyst was further washed with an additional 5 ml portion of diethyl ether and dried for 2 h at 250 °C before

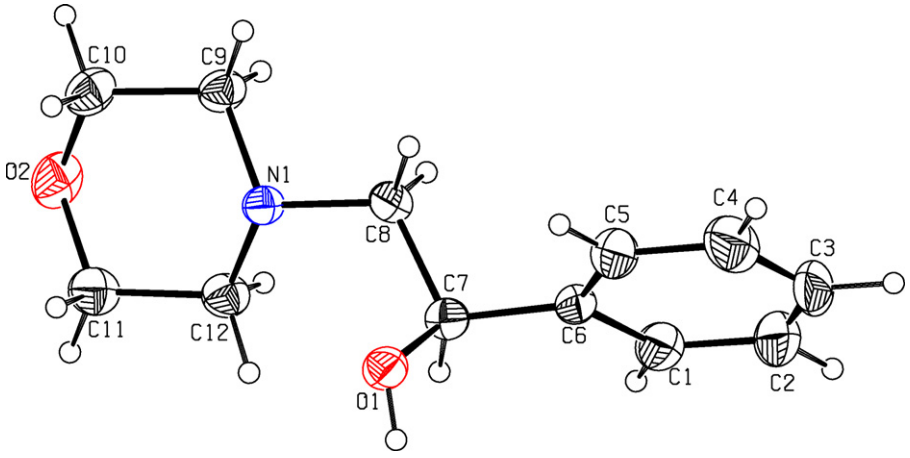
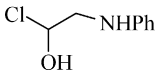
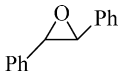
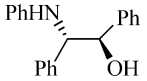
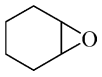
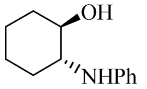
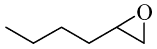
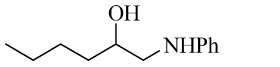
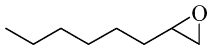
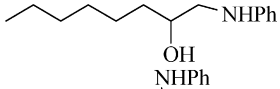
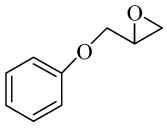
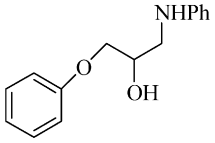
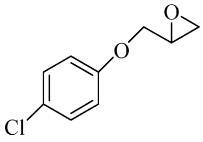
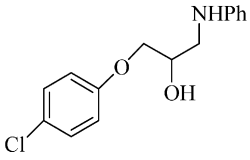


Fig. 3. ORTEP diagram (40% probability factor for thermal ellipsoids) with atom numbering scheme for compound **4B** (2-morpholin-4-yl-1-phenyl-ethanol).

Table 5
Ring opening of different epoxides with aniline using zeolite NaY as a catalyst under solvent-free conditions

Entry[a]	Epoxide	Major product	Time (h)	Isolated yield (%)
27			5	70
28			12	50[b,c]
29			10	40
30			6	92
31			6	90
32			5	95
33			10	75

[a] All epoxides (2 mmol) were reacted with aniline (2 mmol) in the presence of NaY zeolite (25%, w/w) at (35 °C) in solvent-free condition.
[b] Similar condition except that reaction carried out at 80 °C.
[c] Single crystal of the product was obtained and *anti* product was observed completely by ^{1}H NMR and HPLC.

reuse. The reactivity and regioselectivity was retained in the subsequent five test runs.

In conclusion, zeolites under solvent-free conditions are efficient, recyclable, eco-friendly and industrially applicable catalyst for the epoxide ring opening reaction. The reaction proceeds rapidly to give β-amino alcohol in excellent yield. An aromatic amine such as aniline exhibits excellent regioselectivity via preferential nucleophilic attack of the amine at the benzylic carbon to give terminal alcohol as major product with epoxide of styrenes. On the other hand, aliphatic amines selectively attack the terminal carbon of the epoxides to give β-amino alcohol as the major product. Further, a *trans* stereospecificity was observed in the ring opening of cyclohexene oxide during the reaction with aromatic amines.

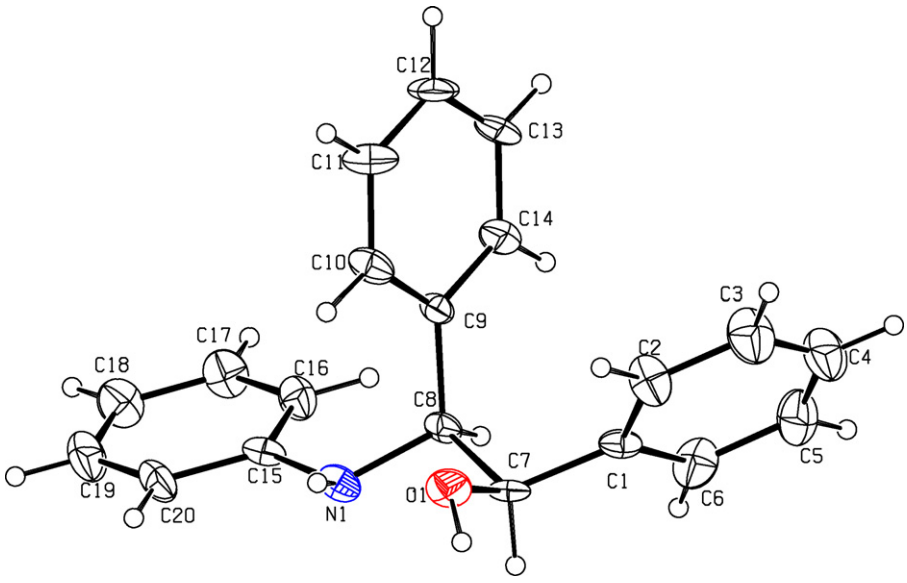


Fig. 4. ORTEP diagram (40% probability factor for thermal ellipsoids) with atom numbering scheme for compound **5** (*anti*-1,2-diphenyl-2-(phenylamino)-ethanol).

Table 6
Physical characterization of different zeolites

Zeolite	Channel size (Å)	Channel/cavity diameter (Å)	BET surface area ($m^2\ g^{-1}$)	Chemical composition on anhydrous basis (wt%)			
				Na_2O	Al_2O_3	SiO_2	Al content
NaA	4.1 × 4.1	11.4	–	27.3	21.1	51.5	5.59
NaX	7.4 × 7.4	12.0	542	24.6	19.0	56.4	5.04
NaY	7.4 × 7.4	12.0	810	3.0	22.0	71.0	5.83
Naβ	6.6 × 6.7; 5.6 × 5.6	6.7	612	1.2	7.8	91.0	2.06
Na Mordenite 060	6.5 × 7.0; 2.6 × 5.7	7.0	50	7.5	12.4	80.1	3.29
Na ZSM-5 (25)	5.1 × 5.5; 5.3 × 5.6	5.6	371	3.0	6.4	90.8	1.69
Na ZSM-5 (900)	5.1 × 5.5; 5.3 × 5.6	5.6	315	1.5	0.2	98.1	0.05

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