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Highly Effective Opening of Epoxides with Aromatic Amines in Presence of β-Cyclodextrin in Water

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This paper reports a simple, mild, and convenient method to synthesize β-amino alcohols. These β-amino alcohols were achieved in excellent yields (80-96 %) by ring-opening reaction of oxiranes with aromatic amines catalyzed by β-cyclodextrin at 30 ºC in water. β-cyclodextrin as the catalyst greatly accelerated the reactions and can be recovered and reused.

Keywords: Oxiranes, β-Cyclodextrin, β-Amino alcohols, Ring-opening

INTRODUCTION

β-Amino alcohols are versatile intermediates in the synthesis of a wide range of biologically active natural and synthetic products such as unnatural amino acids [1,2] and chiral auxiliaries [3]. The classical approach for the preparation of β-amino alcohols involves the ring opening of epoxides at elevated temperatures in an excess amount of amines [4]. These reactions are accompanied by poor regioselectivity and long reaction time. To avoid these drawbacks, other methods were reported recently, which involved the use of metal amides [5-7], metal triflates [8-10], metal halides [11-14], organobismuth triflate complex [15], copper(II) tetrafluoroborate [16], ionic liquid [17], phosphomolybdic acid-Al_2O_3 [18], thiourea [19] and Hβ zeolite [20]. However, most of these methods involve the use of expensive reagents, air- and/or moisture-sensitive catalysts, hazardous organic solvents and suffering from poor regioselectivity. In view of these limitations, inexpensive, environmentally benign and highly efficient catalysts are expected to be developed for the ring-opening of epoxides directly with anilines.

Having hydrophobic cavities, cyclodextrins form host-guest complexes with substrates *via* non-covalent bonding. The complexation depends on the size, shape and hydrophobicity of the guest molecule. β-Cyclodextrin catalyzes chemical reactions by supramolecular catalysis with high efficiency. No investi-gations of ring opening of epoxides with aromatic amines in the presence of β-cyclodextrin in water have been reported. Our earlier study on ester hydrolysis successfully catalyzed by β-cyclodextrin derivatives [21-23] promoted us to attempt ring opening of aromatic epoxides with aromatic amines in the presence of β-cyclodextrin in water.

EXPERIMENTAL

All the reactions were carried out without any special precautions in an atmosphere of air. Oxiranes and amines were purchased from Sigma-Aldrich. β-Cyclodextrin (β-CD, reagent grade) was recrystallized twice from H_2O and dried *in vacuo* for 12 h at 100 ºC. Water used as the solvent in all reactions was double distilled. ^{1}H NMR, ^{13}C NMR and HMBC spectra were recorded on BRUKER 500- or 400-MHz spectrometers. High-resolution mass spectra (HRMS) were observed on Bruker LC-Q-TOF spectrometer.

Synthesis of β-amino alcohols: β-Cyclodextrin (0.50 mmol) was dissolved in water (15 mL) by warming to 50 ºC until a clear solution was formed; then oxirane (0.50 mmol) dissolved in acetone (2 mL) was added and the mixture was allowed to reach reaction temperature. Amine (0.50 mmol) was added and the mixture was stirred at reaction temperature until the reaction was complete (TLC). The organic material was extracted with ethyl acetate. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. The resulting crude product was further purified by silica-gel (60-120 mesh) column chromatography with petroleum ether:ethyl acetate (4:1) as eluent. The filtrate was evaporated to dryness under reduced pressure. The resulting residue was dissolved in a small amount of hot water and the aqueous solution was poured into ethyl acetate (25 mL) to give precipitate and

filtrated to recover β-cyclodextrin (> 95 %), and recovered β-cyclodextrin was dried for 12 h at 95 ºC before reuse. NMR spectra of all compound β-amino alcohols were recorded in $CDCl_3$ solvent. The new compounds **16B**, **17B**, **18B**, **19B**, **20B** and **21B** were characterized by ^{1}H NMR, ^{13}C NMR, HMBC and HRMS spectra.

Spectral data

1-Phenoxy-3-(phenylamino)propan-2-ol (1A) [Ref. 13]**:** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29 (dd, *J* = 8.5, 7.5 Hz, 2H), 7.18 (dd, *J* = 8.4, 7.5 Hz, 2H), 6.98 (t, *J* = 7.4 Hz, 1H), 6.91 (d, *J* = 7.9 Hz, 2H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.67 (d, *J* = 7.7 Hz, 2H), 4.24 (ddt, *J* = 8.4, 7.1, 4.2 Hz, 1H), 4.04 (qd, *J* = 9.4, 5.1 Hz, 2H), 3.42 (dd, *J* = 13.0, 4.3 Hz, 1H), 3.28 (dd, *J* = 13.0, 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.69, 148.34, 129.85, 129.60, 121.61, 118.33, 114.84, 113.57, 70.32, 69.10, 46.91 ppm.

1-(*o*-Toluidino)-3-phenoxypropan-2-ol (2A) [Ref. 24]**:** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 (dd, *J* = 21.1, 12.8 Hz, 2H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 7.3 Hz, 1H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 2H), 6.72 (dd, *J* = 17.4, 7.7 Hz, 2H), 4.46-4.22 (m, 1H), 4.13 (qd, *J* = 9.4, 5.0 Hz, 2H), 3.52 (dd, *J* = 12.8, 4.4 Hz, 1H), 3.38 (dd, *J* = 12.8, 7.0 Hz, 1H), 2.61 (brs, 1H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.41, 146.00, 130.26, 129.61, 127.17, 122.71, 121.37, 117.65, 114.55, 110.11, 70.21, 68.76, 46.60, 17.52 ppm.

1-(*p*-Toluidino)-3-phenoxypropan-2-ol (3A) [Ref. 24]**:** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 - 7.30 (m, 2H), 7.02 (dd, *J* = 15.0, 7.7 Hz, 3H), 6.98 - 6.92 (m, 2H), 6.64 (d, *J* = 8.4 Hz, 2H), 4.29 (ddt, *J* = 8.3, 7.2, 4.2 Hz, 1H), 4.09 (qd, *J* = 9.4, 5.1 Hz, 2H), 3.44 (dd, *J* = 12.9, 4.3 Hz, 1H), 3.31 (dd, *J* = 12.9, 7.2 Hz, 1H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.46, 145.79, 129.84, 129.59, 127.39, 121.33, 114.59, 113.55, 70.11, 68.87, 47.10, 20.40 ppm.

1-(2-Methoxyphenylamino)-3-phenoxypropan-2-ol (4A) [Ref. 24]**:** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 (dd, *J* = 8.4, 7.6 Hz, 2H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.97 (d, *J* = 7.9 Hz, 2H), 6.91 (td, *J* = 7.7, 1.2 Hz, 1H), 6.85-6.78 (m, 1H), 6.77-6.69 (m, 2H), 4.32 (ddd, *J* = 10.9, 6.3, 4.6 Hz, 1H), 4.11 (qd, *J* = 9.4, 5.1 Hz, 2H), 3.88 (s, 3H), 3.49 (dd, *J* = 13.1, 4.6 Hz, 1H), 3.37 (dd, *J* = 13.1, 6.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.50, 147.18, 138.01, 129.57, 121.29, 121.28, 117.20, 114.60, 110.27, 109.63, 70.09, 68.89, 55.45, 46.56 ppm.

1-(4-Methoxyphenylamino)-3-phenoxypropan-2-ol (5A) [Ref. 25]**:** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 (dd, *J* = 8.5, 7.5 Hz, 2H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.95 (d, *J* = 7.9 Hz, 2H), 6.86- 6.80 (m, 2H), 6.71-6.65 (m, 2H), 4.28 (tt, *J* = 8.1, 4.2 Hz, 1H), 4.09 (qd, *J* = 9.4, 5.1 Hz, 2H), 3.78 (d, *J* = 4.0 Hz, 3H), 3.41 (dd, *J* = 12.8, 4.2 Hz, 1H), 3.28 (dd, *J* = 12.8, 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.45, 152.68, 142.18, 129.59, 121.33, 114.97, 114.84, 114.58, 70.14, 68.86, 55.82, 47.81 ppm.

1-(2-Chlorophenylamino)-3-phenoxypropan-2-ol (6A) [Ref. 24]**:** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42-7.29 (m, 3H), 7.22-7.12 (m, 1H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.96 (d, *J* = 7.9 Hz, 2H), 6.81-6.74 (m, 1H), 6.69 (td, *J* = 7.7, 1.3 Hz, 1H), 4.77 (brs, 1H), 4.32 (d, *J* = 3.6 Hz, 1H), 4.12 (qd, *J* = 9.4, 5.0 Hz, 2H), 3.47 (ddd, *J* = 19.9, 13.0, 5.5 Hz, 2H), 2.58 (d, *J* = 4.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.33, 143.93, 129.64, 129.32, 127.87, 121.43, 119.73, 117.85, 114.55, 111.49, 69.93, 68.68, 46.35 ppm.

1-(2-Nitrophenylamino)-3-phenoxypropan-2-ol (7A) [Ref. 24]**:** ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (brs, 1H), 8.19 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.50-7.40 (m, 1H), 7.37-7.27 (m, 2H), 7.03-6.90 (m, 4H), 6.68 (ddd, *J* = 8.4, 7.0, 1.1 Hz, 1H), 4.32 (d, *J* = 16.6 Hz, 1H), 4.10 (qd, *J* = 9.4, 5.0 Hz, 2H), 3.71-3.59 (m, 1H), 3.59-3.48 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.16, 145.52, 136.26, 129.66, 127.02, 121.59, 115.79, 114.55, 113.75, 69.68, 68.61, 45.58 ppm.

2-Phenyl-2-(phenylamino)ethanol (8B) [Ref. 26]**:** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (dt, *J* = 15.1, 7.4 Hz, 4H), 7.30-7.20 (m, 1H), 7.09 (t, *J* = 7.8 Hz, 2H), 6.67 (t, *J* = 7.3 Hz, 1H), 6.56 (d, *J* = 7.9 Hz, 2H), 4.48 (dd, *J* = 6.8, 4.3 Hz, 1H), 3.91 (dd, *J* = 11.1, 4.2 Hz, 1H), 3.73 (dd, *J* = 11.1, 7.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.86, 140.45, 129.14, 128.26, 126.79, 117.92, 113.90, 67,38, 59.87 ppm.

2-Phenyl-2-(*o*-tolylamino)ethan-1-ol (9B) [Ref. 27]**:** ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.32 (m, 4H), 7.31-7.26 (m, 1H), 7.08 (d, *J* = 7.3 Hz, 1H), 6.99-6.90 (m, 1H), 6.65 (td, *J* = 7.4, 0.9 Hz, 1H), 6.39 (d, *J* = 7.9 Hz, 1H), 4.56 (dd, *J* = 7.0, 4.2 Hz,1H), 3.99 (dd, *J* = 11.1, 4.2 Hz, 1H), 3.80 (dd, *J* = 11.1, 7.0 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.13, 140.20, 130.13, 128.88, 127.65, 127.01, 126.70, 122.61, 117.54, 111.51, 67.55, 59.80, 17.72 ppm.

2-Phenyl-2-(*p*-tolylamino)ethan-1-ol (10B): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49-7.18 (m, 5H), 6.94 (d, *J* = 8.1 Hz, 2H), 6.53 (d, *J* = 8.3 Hz, 2H), 4.51 (dd, *J* = 7.1, 4.2 Hz, 1H), 3.96 (dd, *J* = 11.1, 4.2 Hz, 1H), 3.77 (dd, *J* = 11.1, 7.2 Hz, 1H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.93, 140.33, 129.79, 129.68, 128.81, 127.56, 127.16, 126.76, 115.39, 114.08, 67.37, 60.20, 20.38 ppm.

2-[(2-Methoxyphenyl)amino]-2-phenylethan-1-ol (11B) [Ref. 28]**:** ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.30 (m, 4H), 7.26 (ddd, *J* = 9.4, 3.9, 1.7 Hz, 1H), 6.79 (dd, *J* = 7.7, 1.5 Hz, 1H), 6.75-6.60 (m, 2H), 6.42 (dd, *J* = 7.7, 1.7 Hz, 1H), 4.54 (dd, *J* = 7.3, 4.3 Hz, 1H), 3.95 (dd, *J* = 11.1, 4.3 Hz, 1H), 3.90 (s, 3H), 3.80 (dd, *J* = 11.1, 7.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.17, 140.25, 137.02, 128.81, 127.59, 126.75, 121.14, 117.17, 111.52, 109.46, 67.51, 59.81, 55.50 ppm.

2-[(4-Methoxyphenyl)amino]-2-phenylethan-1-ol (12B) [Ref. 25]**:** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45-7.23 (m, 7H), 6.68 (ddd, *J* = 8.4, 7.0, 1.1 Hz, 1H), 6.60 (d, *J* = 8.6 Hz, 1H), 4.71 (dd, *J* = 10.4, 6.0 Hz,1H), 4.18-4.00 (m, 1H), 3.93 (dd, *J* = 11.1, 6.2 Hz, 1H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.43, 141.32, 140.32, 128.81, 128.57, 128.04, 127.59, 126.75, 126.07, 115.31, 114.78, 67.37, 60.87, 55.71 ppm.

2-[(2-Chlorophenyl)amino]-2-phenylethan-1-ol (13B) [Ref. 29]**:** ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.20 (m, 6H), 6.96 (td, *J* = 8.2, 1.5 Hz, 1H), 6.61 (td, *J* = 7.7, 1.4 Hz, 1H), 6.44 (dd, *J* = 8.2, 1.3 Hz, 1H), 4.56 (dd, *J* = 6.5, 4.3 Hz, 1H), 3.99 (dd, *J* = 11.1, 4.1 Hz, 1H), 3.83 (dd, *J* = 11.1, 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.06, 139.52, 129.14, 128.95, 127.82, 127.68, 126.68, 119.76, 117.86, 112.86, 67.38, 59.67 ppm.

2-[(2-Nitrophenyl)amino]-2-phenylethan-1-ol (14B) [Ref. 24]**:** ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (d, *J* = 5.0 Hz, 1H), 8.19 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.41-7.28 (m, 5H), 6.78-6.52 (m, 2H), 4.73 (dt, *J* = 10.5, 5.3 Hz, 1H), 4.04 (dd, *J* = 11.1, 4.0 Hz, 1H), 3.94 (dd, *J* = 11.1, 6.3 Hz, 1H). ^{13}C NMR (100 MHz,

$CDCl_3$): δ 144.59, 138.68, 136.02, 129.13, 128.15, 126.82, 126.62, 115.97, 115.10, 67.12, 59.26 ppm.

2-(4-Chlorophenyl)-2-(phenylamino)ethanol (15B) [Ref. 19]**:** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28 (d, J = 27.6 Hz, 4H), 7.10 (dd, *J* = 8.4, 7.5 Hz, 2H), 6.69 (t, *J* = 7.3 Hz, 1H), 6.53 (d, *J* = 7.7 Hz, 2H), 4.46 (dd, *J* = 7.0, 4.1 Hz, 1H), 3.92 (dd, *J* = 11.1, 4.1 Hz, 1H), 3.71 (dd, *J* = 11.1, 7.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.45, 138.58, 132. 8, 129.23, 128.16, 118.16, 113.88, 67.19, 59.34 ppm.

1-(Phenylamino)hexan-2-ol (22A) [Ref. 13]**:** ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.14 (m, 2H), 6.73 (t, *J* = 7.3 Hz, 1H), 6.65 (dd, *J* = 8.6, 0.9 Hz, 2H), 3.97-3.59 (m, 1H), 3.26 (dd, *J* = 12.9, 3.2 Hz, 1H), 3.00 (dd, *J* = 12.9, 8.6 Hz, 1H), 1.65-1.19 (m, 6H), 0.93 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.33, 129.33, 117.91, 113.31, 70.41, 50.34, 34.83, 27.83, 22.78, 14.08 ppm.

2-(4-Chlorophenyl)-2-(*o*-tolylamino)ethan-1-ol (16B): m.f. $C_{15}H_{16}NOCl$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.30 (m, 4H), 7.09 (d, *J* = 7.3 Hz, 1H), 7.01-6.94 (m, 1H), 6.67 (td, *J* = 7.4, 0.9 Hz, 1H), 6.32 (d, *J* = 7.9 Hz, 1H), 4.50 (dd, *J* = 7.2, 4.1 Hz, 1H), 3.96 (dd, *J* = 11.1, 4.1 Hz, 1H), 3.75 (dd, *J* = 11.1, 7.2 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.89, 138.86, 133.30, 130.23, 129.05, 128.12, 127.03, 122.74, 117.81, 111.52, 67.34, 59.33, 17.70 ppm. HRMS (ESI) calculated for $C_{15}H_{16}NOCl$ $(M+H)^+$ 262.0999, found $(M+H)^+$ 262.0995.

2-(4-Chlorophenyl)-2-(*p*-tolylamino)ethan-1-ol (17B): m.f. $C_{15}H_{16}NOCl$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (m, 4H), 6.93 (d, *J* = 8.0 Hz, 2H), 6.47 (d, *J* = 8.4 Hz, 2H), 4.44 (dd, *J* = 7.3, 4.1 Hz, 1H), 3.90 (dd, *J* = 11.1, 4.1 Hz, 1H), 3.69 (dd, *J* = 11.1, 7.3 Hz, 1H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.63, 138.93, 133.26, 129.75, 129.00, 128.17, 127.45, 114.09, 67.22, 59.66, 20.42 ppm. HRMS (ESI) calculated for $C_{15}H_{16}NOCl$ $(M+H)^+$ 262.0999, found $(M+H)^+$ 262.0994.

2-(4-Chlorophenyl)-2-[(2-methoxyphenyl)amino]ethan-1-ol (18B): m.f. $C_{15}H_{16}NO_2Cl$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (s, 4H), 6.79 (dd, *J* = 7.5, 1.8 Hz, 1H), 6.75-6.63 (m, 2H), 6.34 (dd, *J* = 7.5, 1.9 Hz, 1H), 4.49 (dd, *J* = 7.3, 4.3 Hz, 1H), 3.93 (dd, *J* = 11.1, 4.2 Hz, 1H), 3.90 (s, 3H), 3.76 (dd, *J* = 11.1, 7.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.18, 138.89, 136.72, 133.25, 128.98, 128.15, 121.12, 117.43, 111.50, 109.51, 67.31, 59.31, 55.50 ppm. HRMS (ESI) calculated for $C_{15}H_{16}NO_2Cl$ $(M+H)^+$ 278.0948, found $(M+H)^+$ 278.0945.

2-(4-Chlorophenyl)-2-[(4-methoxyphenyl)amino]ethan-1-ol (19B): m.f. $C_{15}H_{16}NO_2Cl$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (s, 4H), 6.79-6.61 (m, 2H), 6.55-6.43 (m, 2H), 4.39 (dd, *J* = 7.5, 4.1 Hz, 1H), 3.89 (dd, *J* = 11.1, 4.1 Hz, 2H), 3.70 (s, 3H), 3.69-3.64 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.53, 141.03, 138.97, 133.28, 129.00, 128.19, 115.32, 114.80, 67.22, 60.31, 55.73 ppm. HRMS (ESI) calculated for $C_{15}H_{16}NO_2Cl$ $(M+H)^+$ 278.0948, found $(M+H)^+$ 278.0944.

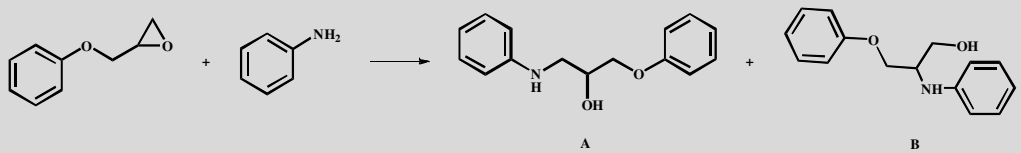
2-(4-Chlorophenyl)-2-[(2-chlorophenyl)amino]ethan-1-ol (20B): m.f. $C_{14}H_{13}NOCl_2$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 (dt, *J* = 11.3, 8.6 Hz, 5H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.65 (t, *J* = 7.5 Hz, 1H), 6.40 (d, *J* = 8.0 Hz, 1H), 5.19 (s, 1H), 4.54 (s, 1H), 4.20-3.92 (m, 1H), 3.82 (dd, *J* = 10.8, 7.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.79, 138.17, 133.53, 129.20, 129.10, 128.06, 127.66, 119.84, 118.11, 112.80, 67.14, 59.15 ppm. HRMS (ESI) calculated for $C_{14}H_{13}NOCl_2$ $(M+H)^+$ 282.0452, found $(M+H)^+$ 282.0449.

2-(4-Chlorophenyl)-2-[(2-nitrophenyl)amino]ethan-1-ol (21B): m.f. $C_{14}H_{13}N_2O_3Cl$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (d, *J* = 5.4 Hz, 1H), 8.21 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.47- 7.26 (m, 4H), 6.69 (ddd, *J* = 8.4, 7.0, 1.1 Hz, 1H), 6.60 (d, *J* = 8.6 Hz, 1H), 4.71 (dd, *J* = 10.5, 6.0 Hz, 1H), 4.18-4.00 (m, 1H), 3.93 (dd, *J* = 11.1, 6.2 Hz, 1H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 144.29, 137.36, 136.07, 129.31, 128.02, 126.89, 116.23, 114.96, 99.99, 66.90, 58.68 ppm. HRMS (ESI) calculated for $C_{14}H_{13}N_2O_3Cl$ $[M+Na]^+$ 315.0512, found $[M+Na]^+$ 315.0510.

RESULTS AND DISCUSSION

Initially, for the model study, the ring opening reaction of 1,2-epoxy-3-phenoxy propane was carried out with aniline in water using β-cyclodextrin as the catalyst (Table-1). The yield was only 78 % after stirring for 8 h under 20 °C (Table-1, entry 1). While the yield was up to 96 % when the temperature was 30 °C and the yields were more than 95 % when the temperature was higher than 30 °C (Table-1, entries 2-6). However, the ratio of the major isomer A decreased as the temperature increased. The higher regioselectivity was achieved at 20 and 30 °C (Table-1, entries 2, 3). In order to understand the role of catalyst, control reaction was proceeded at 30 °C (Table-1, entry 7) and only 9 % of the product was obtained even with prolonged reaction time in the absence of catalyst.

TABLE-1
RING-OPENING REACTION OF 1,2-EPOXY-3-PHENOXY PROPANE WITH ANILINE IN THE PRESENCE OF CYCLODEXTRIN AT DIFFERENT REACTION CONDITIONS



A B

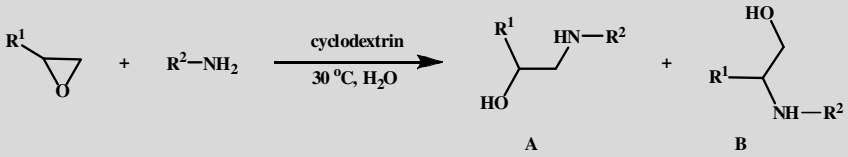
Entry	Temperature (°C)	Time (h)	Yield (%)[b]	Ratio (A:B)[c]
1	20	8	78	85:15
2	30	8	96	85:15
3	40	8	95	82:18
4	50	8	96	73:27
5	60	6	95	72:28
6	80	5	96	65:35
7	30[a]	16	9	84:16

[a]No cyclodextrin; [b]Isolated yield; [c] The ratio of isomers was calculated by ^{1}H NMR

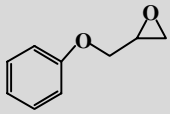
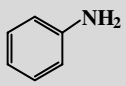
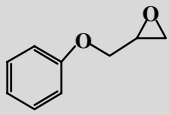
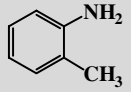
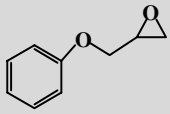
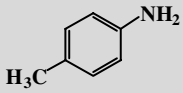
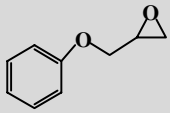
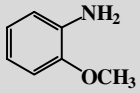
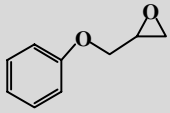
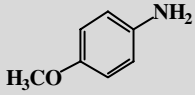
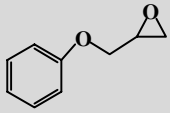
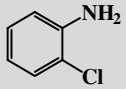
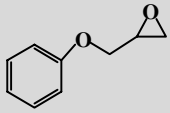
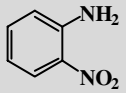
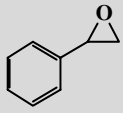
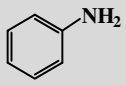
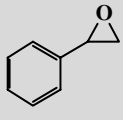
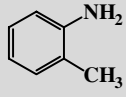
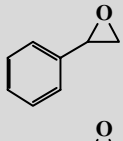
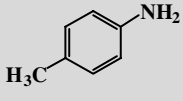
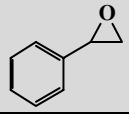
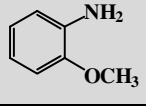
With the optimized reaction conditions, the scope of the reactions was investigated at 30 °C with the styrene oxide, 4-chlorostyrene oxide, 1,2-epoxy-3-phenoxy propane and 1,2-epoxyhexane as the substrates and series of aromatic amines with electron-donating and electron-withdrawing groups as the nucleophiles. As listed in Table-2, β-amino alcohols were obtained in high yield (80-96 %). For amines with an electron-withdrawing group, moderate yields were obtained (Table-2, entries 6, 13, 20). However, for 2-nitroaniline, the yields were low even after prolong the reaction time (Table-2, entries 7, 14, 21). Similar to 1,2-epoxy-3-phenoxy propane, the yields of ring-opening of Styrene oxide, 4-chlorostyrene oxide and 1,2-epoxyhexane with aniline were also very low (< 10 %) in the absence of cyclodextrin.

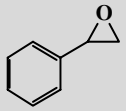
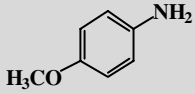
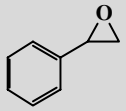
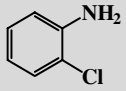
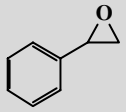
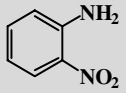
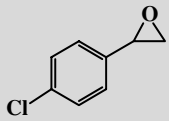
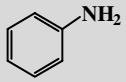
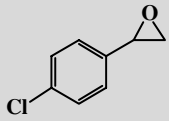
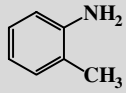
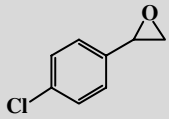
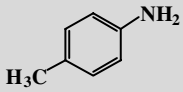
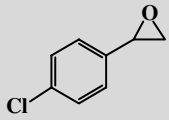
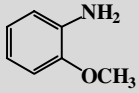
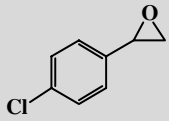
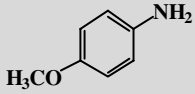
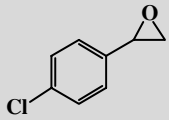
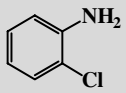
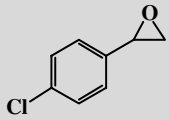
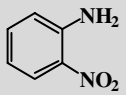
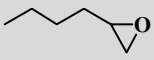
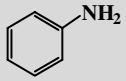
Unsymmetrical alkyl oxiranes such as 1,2-epoxy-3-phenoxy propane and 1,2-epoxyhexane afforded β-amino alcohols with preferential attack at the terminal position. For anilines with *ortho*-substituents, only one isomer was obtained (Table-2,

TABLE-2
RING-OPENING REACTION OF EPOXIDES WITH AROMATIC AMINES IN THE PRESENCE OF β-CYCLODEXTRIN



A B

Entry	Epoxide	Amine	Time (h)	Yield (%)[a,b]	Ratio (A:B)[c]
1			8	96	85:15
2			7	84	100:0
3			7	87	83:17
4			6	86	100:0
5			6	90	82:18
6			24	70	100:0
7			24	20	100:0
8			7	90	7:93
9			7	83	3:97
10			11	88	0:100
11			8	93	10:90

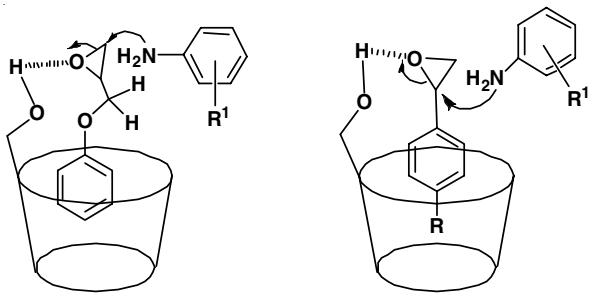
12			9	94	0:100
13			24	74	8:92
14			24	21	7:93
15			6	84	12:88
16			8	84	9:91
17			8	86	0:100
18			10	91	15:85
19			10	93	0:100
20			24	76	5:95
21			26	15	6:94
22			16	71	100:0

[a]All products were characterized by ^{1}H NMR and ^{13}C NMR; [b]Isolated yield; [c]The ratio of isomers were calculated by ^{1}HNMR

entries 2, 4, 6, 7, 22). In the case of aniline, 4-methylaniline and 4-methoxyaniline, a mixture of two regioisomers was isolated in ratios of 85:15, 83:17 and 82:18, respectively. (Table-2, entries 1, 3, 5).Alkenyl oxiranes such as styrene oxide and (*p*-chlorophenyl) styrene oxide have been treated with various amines in the presence of β-cyclodextrin. For most of the amines, only one isomer was obtained (Table-2, entries 10, 12, 13, 14, 17, 19) and for anilines,anilines with *ortho*-substituents, a mixture of two regioisomers was produced (Table-2, entries 8, 9, 11, 15, 16, 18, 20, 21).

According to the literature [30], benzyl ring of the epoxides insert into the cavity of β-cyclodextrin partially from the secondary rim and the epoxides are fixed through supramolecular interaction. Moreover, hydrogen bond is formed between the hydroxyl group of β-cyclodextrin and the oxygen atom of epoxides. Hydrogen bond favours nucleophiles to attack the C-O bond of epoxide. For alkyl oxirane 1,2-epoxy-3-phenoxy propane, terminal carbon atom is attacked more preferentially. Steric effect may play important roles on the ring-opening reaction. As the anilines with bukly *ortho*-substituents, only one isomer was obtained. In the case of smaller steric-hindrance of aniline and *para*-substituent anilines, mixed products were obtained. For styrene oxide and (*p*-chlorophenyl) styrene oxide, the C-O is activated by the hydrogen bond. Benzylic carbon atom is attacked easily due to its high activity. So electronic effect may affect this transformation deeply. Aromatic amines with the substituent on the *para*-position attack the benzylic carbon completely. The reaction intermediates of the ring-opening catalyzed by β-cyclodextrin were proposed in **Scheme-I**.

In order to evaluate the recycling capability of β-cyclodextrin, the ring opening of 1,2-epoxy-3-phenoxy propane with aniline was carried out with recovered catalyst. As revealed in



R=H, Cl; R^1=H, CH_3, OCH_3, Cl, NO_2

Scheme-I

Table-3, the recovered catalyst showed almost equal efficiency in consecutive four cycles under identical reaction conditions and all the ratios of two regioisomers A:B are 85:15, which indicated that the catalyst was stable and suitable to be reused for several times.

TABLE-3
REUSE OF CYCLODEXTRIN FOR THE RING-OPENING REACTION OF 1,2-EPOXY-3-PHENOXY PROPANE WITH ANILINE

Cycle	1	2	3	4
Yield (%)[a]	96	95	95	94

[a]Isolated yield.

Conclusion

In conclusion, β-cyclodextrin is a highly efficient and reusable catalyst for the ring-opening of epoxides containing benzene group with different aniline derivatives. Excellent yields were achieved for this reaction along with high regio-selectivity. This method is simple, economic, environmental and efficient, which would be a useful way to modern synthetic methodology in green chemistry.

ACKNOWLEDGEMENTS

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