Journal of Saudi Chemical Society (2016) **20**, 530–535

King Saud University

Journal of Saudi Chemical Society

www.ksu.edu.sa
www.sciencedirect.com

ORIGINAL ARTICLE

Polymer supported sulphanilic acid – A novel green heterogeneous catalyst for synthesis of benzimidazole derivatives

Umesh P. Tarpada, Bhautik B. Thummar, Dipak K. Raval *

Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar 388 120, Gujarat, India

Received 21 May 2012; accepted 8 July 2012
Available online 7 September 2012

KEYWORDS

Heterogeneous catalyst;
Epoxy modification;
Polymer supported sulphanilic acid;
o-Phenylenediamine;
Araylaldehydes;
Benzimidazole

Abstract Polymer supported sulphanilic acid was synthesized and used as green, reusable and heterogeneous catalyst and duly characterized using chemical methods like determination of free hydroxyl content, epoxy equivalent weight and free sulphonic acid content as well as infrared spectroscopy and thermogravimetric analysis. The prepared catalyst was applied for one-pot synthesis of 2-substituted benzimidazoles from *o*-phenylenediamine and various aromatic aldehydes in absolute ethanol under thermal condition. Catalyst was separated from the product by simple filtration and could be reused for at least five times with almost retention in its efficiency. Due to three dimensional network structures, it shows high thermal stability and can be reused without any further purification.

1. Introduction

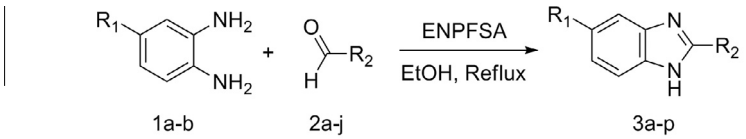
Epoxy resins are important thermosetting polymers. They are currently used in advanced composites (Guo et al., 2008), nanocomposite, coatings (Lin et al., 2007), structural adhesives (Wang et al., 2008), matrices for fiber composite and microelectronics (Liu et al., 2008), due to their high stiffness, high strength, good chemical resistance and dimensional stability (Zhang et al., 2002). The primary requirement for high-temperature performance necessitates the selection of polyfunctional epoxy resins and curing agents which are capable of creating high crosslink densities. Thus, novolac epoxy resin, can produce a more firmly crosslinked three-dimensional network compared to epoxy diglycidyl ether of bisphenol A and hence can give enhanced adhesive strength retention at elevated temperatures (Gouri et al., 2000). Epoxy resins are extensively investigated and widely used in the electronic/electrical instruments because of their great versatility, good chemical and electrical properties and excellent adherence to many substrates (Kinjo et al., 1989). As alternatives to halogen-containing epoxy resin, phosphorus-containing epoxy resins (Cheng et al., 2002a,b) have been investigated. Although they exhibit high flame retardance, its industrialization is difficult for its complex synthesis and high cost, as well as debating environmental problems (Shieh and Wang, 2002). Nitrogen-

* Corresponding author. Tel.: +91 02692 226856x211; fax: +91 02692 236475.
E-mail address: dipanalka@yahoo.com (D.K. Raval).

Peer review under responsibility of King Saud University.

ELSEVIER Production and hosting by Elsevier

http://dx.doi.org/10.1016/j.jscs.2012.07.014
1319-6103



ENPFSA: Epoxidized novolac phenol formaldehyde resin modified using sulfanilic acid

Scheme 1 General synthetic pathway for the synthesis of benzimidazole derivatives.

containing epoxy resins have excellent thermal stability and good flame retardance and are suitable materials for high-quality electronic/electrical instruments. Herein, we have synthesized epoxy novolac phenol formaldehyde resin (ENPFR) with reactive epoxy groups. This was modified by sulphanilic acid to develop network polymeric structure having free $-SO_3H$ group and it was applied as a solid heterogeneous catalyst for the synthesis of benzimidazole and its derivatives.

Benzimidazole and its derivatives have been the area of much research interest due to their importance in various applications and its widespread biochemical significance (Alexander et al., 1966). Benzimidazole structure is found in several classes of drugs based on the substituents present at different positions (Velık et al., 2004). Benzimidazole derivatives find many applications in several therapeutic area such as antimicrobial agents (Fonseca et al., 2001), antiviral agent against several viruses such as HIV (Roth et al., 1997), influenza (Migawa et al., 1998),and herpes (HSV-1) (Migawa et al., 1998), antitumor (Denny et al., 1990), anti-inflammatory (Sondhi et al., 2006), anthelmintic agents (Yang et al., 2005) as well as antiprotozoal agents (Valdez-Padilla et al., 2009). The amino ketone derivatives of imidazo [1,2-a]-benzimidazoles are potent adrenoblockers, spasmolytics, antiarrhythmogens, and antimicrobial agents (Anisimova et al., 2002). Benzimidazoles are also important intermediates in organic synthesis (Bai et al., 2001; Hasegawa et al., 1999). A number of methods have been adopted for the synthesis of benzimidazoles from different reactants and reaction conditions such as reaction between *o*-phenylenediamine and aldehyde under oxidative conditions (Lombardy et al., 1996; Middleton and Wibberley, 1980; Pätzold et al., 1992; Stephens and Bower, 1949), *o*-phenylenediamine and carboxylic acid (Geratz et al., 1979; Middleton and Wibberley, 1980; Wright, 1951) in the presence of catalyst such as H_2O_2/HCl (Bahrami et al., 2007), $Sc(OTf)_3$ (Itoh et al., 2004; Nagata et al., 2003), $Cu(OTf)_2$ (Chari et al., 2010), $KHSO_4$ (Ma et al., 2006), ionic liquids (Ma et al., 2007), *p*-TsOH (Han et al., 2007), SiO_2 as solid support (Ben-Alloum et al., 1998) and under microwave irradiation using Poly phosphoric acid as catalyst (Lu et al., 2002). However many of these methodologies suffer one or more disadvantages like low yields, lack of easy availability of the starting materials, prolonged reaction time, high temperature, excess requirement of catalysts, special apparatus, harsh reaction conditions, extraction of product, formation of byproduct etc. Thus there is a need of simple and efficient protocol for the synthesis of benzimidazole derivatives. Herein, we report a method for the synthesis of benzimidazole derivatives by using polymer supported recyclable heterogeneous catalyst to obtain product with high yield in moderate reaction time and easy extraction of catalyst for reuse with high efficiency (Scheme 1).

The heterogenicity of catalyst has avoided number of reported disadvantages for the synthesis of benzimidazole by different reagents and reaction conditions (Hein et al., 1957).

2. Experimental

2.1. Chemicals and reagents

All chemicals used were of laboratory reagent grade and used without further purification. Phenol, formaldehyde and epichlorohydrin were obtained from Sd. Fine Chem. Pvt. Ltd., Mumbai, India. *o*-phenylenediamine, sodiumhydroxide and sulphanilic acid were obtained from Samir Tech Chem. Pvt. Ltd., Vadodara, India. Various aldehydes, ethyl acetate and *n*-hexane were used as received from Merck, Mumbai, India. 1,4-Dioxane was supplied by Sisco Chem. Pvt. Ltd., Mumbai, India.

2.2. Analytical methods

Melting points were determined by open capillary method and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer operating at 400 MHz for ^{1}H NMR, and 100 MHz for ^{13}C NMR, as solutions in DMSO-*d6*. Chemical shifts (δ) are expressed in parts per million (ppm) and referenced to the residual protic solvent. FT-IR spectra were recorded on Shimadzu FT-IR 8401 spectrometer using KBr disc, and are expressed in wavenumbers (cm^{-1}). The mass spectra (ESI-MS) were recorded on Shimadzu LCMS-2010 spectrometer. Thermogravimetric analysis (TGA) data were recorded on a TGA/DTA (TA instrument Model 5000/2960 thermogravimetric analyser, USA) and Carbon, Hydrogen and Nitrogen were estimated on a PerkinElmer 2400 Series II CHNS/O Elemental Analyzer. All the reactions were monitored by thin-layer chromatography (TLC) performed on Silica Gel 60 F_{254} precoated plates (Merck).

2.3. General procedure for the synthesis of catalyst ENPFSA

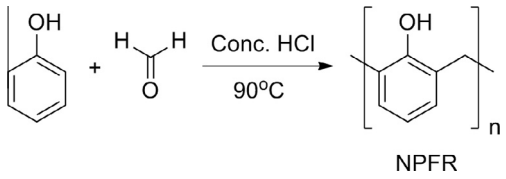
2.3.1. Preparation of novolac phenol formaldehyde resin (NPFR)

NPFR was prepared by condensation reaction between phenol and formaldehyde under acidic condition by following a reported method (Scheme 2) (Motawie et al., 2008).

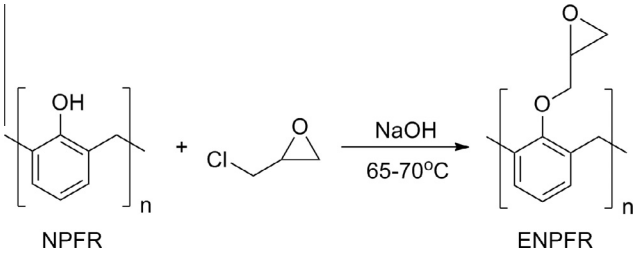
The IR spectrum of the prepared NPFR exhibited absorption bands of –OH at 3134 cm^{-1}, C═C aromatic at 1600 cm^{-1} and CH_2 at 1405 cm^{-1}.

2.3.2. Epoxidation of NPFR

ENPFR was prepared by condensation reaction between above prepared NPFR and epichlorohydrine in the presence of sodium hydroxide (Scheme 3) as per the procedures described elsewhere (Motawie and Sadek, 1998).



Scheme 2 General synthetic pathway for the synthesis of NPFR.



Scheme 3 General synthetic pathway for the synthesis of ENPFR.

The FT-IR spectrum of prepared ENPFR exhibited absorption bands for C–H alkane at 2925 cm^{-1}, C=C aromatic at 1510 cm^{-1}, CH_2 at 1460 cm^{-1}, C–O at 1170 cm^{-1} and epoxy group at 910 cm^{-1}.

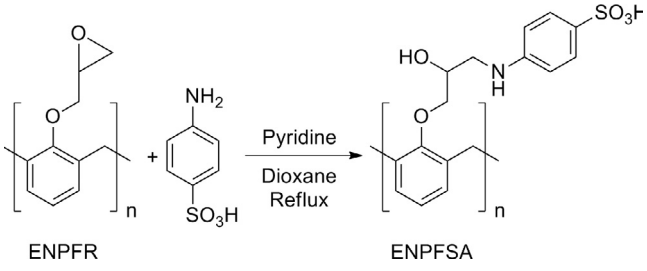
2.3.3. Modification of ENPFR by sulphanilic acid

Mixture of ENPFR and sulphanilic acid (equiv. mole) was refluxed in dioxane in the presence of catalytic amount of pyridine in a three neck RB flask equipped with a mechanical stirrer for 3–4 h. Mixture was cooled to room temperature. Formation of epoxidized novolac phenol formaldehyde resin modified using sulphanilic acid (ENPFSA) was indicated by pH change from 8 to 4. The prepared catalyst was cured with resole phenol formaldehyde resin and washed with hot water followed by ethanol, diethyl ether and finally dried (Scheme 4).

The IR spectrum of ENPFSA exhibited absorption bands for N–H at 3400 cm^{-1}, C–H alkane at 2927 cm^{-1}, C=C aromatic at 1520 cm^{-1}, CH_2 at 1470 cm^{-1}, S–O at 1200 cm^{-1}, and C–O at 1175 cm^{-1}.

2.4. General experimental procedure for the synthesis of benzimidazoles **3a-p**

To a refluxing solution of aldehyde (1 mmol) and *o*-phenylenediamine (1.05 mmol) in ethanol (10 mL) in a 250 mL RB flask, sulphonic acid functionalized polymer supported catalyst ENPFSA (20% w/w with respect to *o*-phenylenediamine) was added. The progress of the reaction was monitored by TLC. After completion of reaction, the catalyst was recovered by filtration and filtrate was extracted with ethyl acetate. The extract was dried over anhydrous Na_2SO_4, residue of product was obtained in excellent yield with high purity by adding *n*-hexane to the extracted filtrate. The recovered catalyst was washed with ethanol, chloroform, diethyl ether and subsequently dried at 80 °C for recycling.



Scheme 4 General synthetic pathway for the synthesis of ENPFSA.

2.5. Spectral data analysis of selected compounds

2.5.1. 2-(4-chlorophenyl)-1H-benzo[d]imidazole **3a**

IR (KBr): 3044 (w), 1455, 1404, 1270, 970, 749 cm^{-1}; ^1H NMR (DMSO-*d6*, δ ppm): 12.98 (s, 1H, NH), 8.20 (d, 2H, J = 8.4 Hz, Ar–H), 7.22–7.73 (m, 6H, Ar–H); ^{13}C NMR (DMSO-*d6*, δ ppm): 150.63 (C-2), 135.50 (C-8, C-9), 134.95 (C-4′), 129.52 (C-1′), 129.39 (C-3′, C-5′), 128.61 (C-2′, C-6′), 123.23 (C-5, C-6), 119.44 (C-4, C-7); ESI-MS: m/z 229.53 $(M + H)^+$; Anal. Calcd. for $C_{13}H_9ClN_2$: C, 68.28; H, 3.97; N, 12.25; Found: C, 68.58; H, 4.01; N, 12.31.

2.5.2. 2-phenyl-1H-benzo[d]imidazole **3c**

IR (KBr): 3433 (w), 3050, 1446, 1412, 1280, 970, 750 cm^{-1}; ^1H NMR (DMSO-*d6*, δ ppm): 12.94 (s, 1H, NH), 8.21 (d, 2H, J = 7.6 H_Z, Ar–H), 7.62–7.21 (m, 7H, Ar–H); ^{13}C NMR (DMSO-*d6*, δ ppm): 151.72 (C-2), 140.1 (C-8, C-9), 130.68 (C-4′), 130.28 (C-1′), 129.40 (C-3′, C-5′), 126.92 (C-2′, C-6′), 122.57 (C-5, C-6), 116.4 (C-4, C-7); ESI-MS: m/z 195.10 $(M + H)^+$; Anal. Calcd. for $C_{13}H_{10}N_2$: C, 80.39; H, 5.19; N, 14.42; Found: C, 80.69; H, 5.16; N, 14.46.

2.5.3. 5-methyl-2-(3-nitrophenyl)-1H-benzo[d]imidazole **3k**

(KBr): 3431 (w), 3054, 1450, 1420, 1281, 972, 748 cm^{-1}; ^1H NMR (DMSO-*d6*, δ ppm): 13.13 (s, 1H, NH), 8.99–7.07 (m, 7H, Ar–H), 2.45 (s, 3H, CH_3); ^{13}C NMR (DMSO-*d6*, δ ppm): 154.53 (C-2), 148.84 (C-3′), 136.12 (C-6′), 134.48 (C-8), 132.84 (C-6), 132.37 (C-9), 131.12 (C-1′), 130.20 (C-5′), 124.47 (C-5), 122.77 (C-4′), 121.14 (C-2′), 119.53 (C-7), 117.44 (C-4), 21.84 (CH_3); Mass spectrum (ESI-MS): m/z 254.15 $(M + H)^+$; Anal. Calcd. for $C_{14}H_{11}N_3O_2$: C, 66.40; H, 4.38; N, 16.59; Found: C, 66.35; H, 4.34; N, 16.57.

3. Results and discussion

3.1. Characterization of ENPFSA

ENPFR was characterized by determining epoxy equivalent weight by the reported method (Guo et al., 2008) and determination of free hydroxyl group in NPFR and in ENPFR (Ahluwalia and Aggarwal, 2000). It was observed that free –OH content in epoxy resin was found to become zero from 16.43% –OH content for parent NPFR. It indicates that the –OH groups were converted into epoxy groups. ENPFSA was characterized by determination of free sulphonic acid group and free –OH content (Ahluwalia and Aggarwal, 2000). An increase in –OH content was observed upon modification of ENPFR with sulphanilic acid. The % –OH content and moles of $–SO_3H$ groups per gram for ENPFSA were found to be 34 and 20, respectively. It was observed that epoxy equivalent weight was found to decrease compared to ENPFR

Table 1 % Weight loss as a function of temperature for NPFR, ENPFR and ENPFSA from thermogravimetric study.

Resin	% Weight loss at °C										
	100	150	200	250	300	350	400	450	500	550	600
NPFR	1.68	6.90	9.62	12.34	14.25	16.17	17.97	21.14	26.19	32.11	37.34
ENPFR	1.46	5.87	9.90	19.64	28.54	38.58	50.41	55.25	58.13	60.57	62.61
ENPFSA	2.23	2.48	3.13	8.93	22.66	31.74	42.73	48.93	52.72	55.76	58.04

Table 2 Model reaction of o-phenylenediamine (1.0 mmol) with benzaldehyde (1.05 mmol) by using different amounts of catalyst ENPFSA in absolute ethanol under reflux.

Entry	Amount of catalyst (%)	Reaction time (h)[a]	Yield (%)[b]
1	0	4	–
2	10	4	70
3	15	4	80
4	20	3	88
5	25	4.5	75

[a] Reaction was monitored by TLC.
[b] Isolated yields.

with increasing hydroxyl content as equimol to free $–SO_3H$ group. This indicates that epoxy ring gets opened up by sulphanilic acid leaving free –OH group equivalent to opening of each epoxy ring. Formation of ENPFR was characterized by IR spectroscopy, appearance of characteristic band at 910 cm^{-1} due to epoxy group. The formation of ENPFSA was characterized by appearance of characteristic band at 3400 cm^{-1} due to N–H along with disappearance of band at 910 cm^{-1} for epoxy group. Formation of catalyst could also be confirmed by comparing thermogram of ENPFR and ENPFSA. It was found that % of weight loss in ENPFR at temperature 200 °C showed 9.90% where as at same temperature the ENPFSA showed 3.13% only and at temperature 250 °C ENPFSA showed 8.93% of weight loss due to the removal of sulphanilic acid (Table 1).

3.2. Optimization of the reaction condition

Reaction was optimized by varying the amount of catalyst. We chose the reaction between *o*-phenylenediamine **1a** and benzaldehyde **2c** as the model reaction. First we carried out model reaction in the absence of catalyst (Table 2, entry 1), and found that the reaction did not proceed. Next, the amount of catalyst was varied with respect to **1a** (Table 2, entries 2–5). It was found that only 70% and 75% yields were obtained by taking 10% and 25% amounts of catalyst ENPFSA (Table 2, entry 2 & 5) respectively. The best result (88% yield of product **3c**) was obtained by using 20% amount of catalyst (Table 2, entry 4). By using this optimized conditions, various benzimidazole derivatives **3a-p** were synthesized in shorter time as well as in high yields using ENPFSA as the catalyst.

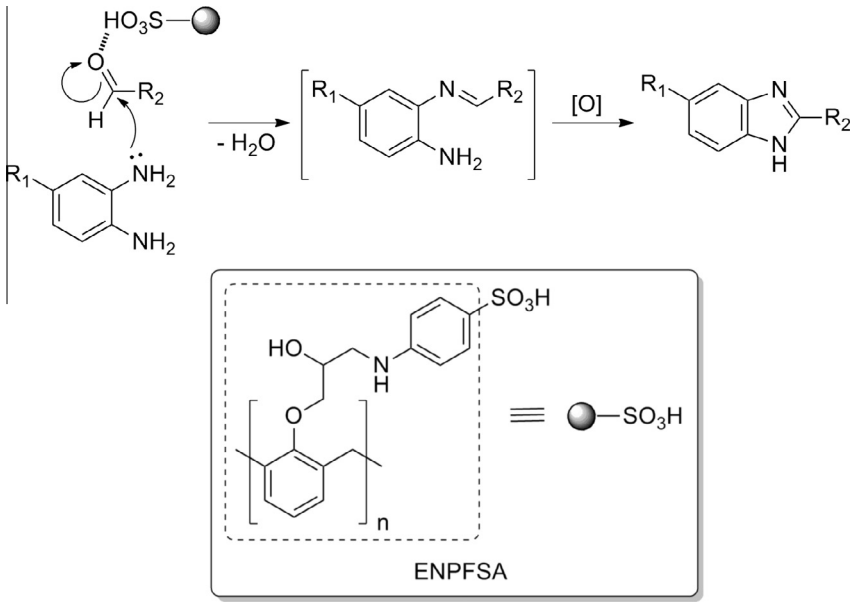
It was observed that the aromatic aldehyde bearing an electron withdrawing substituent underwent the conversion smoothly as compared to that bearing an electron donating substituent (Table 3). We have synthesized compounds **3e-g** bearing an electron withdrawing substituent ($–NO_2$) in 3 h with high yields where as compounds **3b & 3i** bearing an electron donating substituent (–OH & $–OCH_3$, respectively) in 4 h.

All prepared products were well characterized by ^1H NMR, ^{13}C NMR and IR spectroscopy. In ^1H NMR spectra of compounds **3a-p**, the N–H proton of benzimidazole moiety reso-

Table 3 Synthesis of benzimidazole **3a-p** by using polymer supported sulphanilic acid as heterogeneous catalyst.

Compd.	R_1	R_2	Time (h)[a]	Yield (%)[b]	Melting point (°C)	
					Observed	Reported
3a	H	4-Chlorophenyl	3	80	290	289–291 (Lu et al. (2002))
3b	H	4-Hydroxy-3-methoxphenyl	4	70	224	224.7–225.4 (Navarrete-Vázquez et al. (2007))
3c	H	Phenyl	3	88	290	292–293 (Lu et al. (2002))
3d	H	4-Hydroxy phenyl	3.5	78	253	254.1–256.6 (Navarrete-Vázquez et al. (2007))
3e	H	4-Nitro phenyl	3	90	312	308–310 (Han et al. (2007))
3f	H	2-Nitro phenyl	3	84	211	210 (Alloum et al. (2003))
3g	H	3-Nitro phenyl	3	90	200	200–202 (Han et al. (2007))
3h	H	Furfuryl	3	85	284	284–286 (Han et al. (2007))
3i	H	4-Methoxy phenyl	4	78	225	224–225 (Lu et al. (2002))
3j	H	2-Hydroxy phenyl	3.5	78	241	241–243 (Sharghi et al. (2008))
3k	CH_3	3-Nitro phenyl	3	80	212	–
3l	CH_3	4-Hydroxy phenyl	3.5	77	300	300.1–302.6 (Navarrete-Vázquez et al. (2007))
3m	CH_3	2-Nitro phenyl	3.5	81	213	212.1–215 (Navarrete-Vázquez et al. (2007))
3n	CH_3	Phenyl	3.5	85	246	246 (Sharghi et al. (2008))
3o	CH_3	4-Hydroxy-3-methoxphenyl	4	76	225	225.3–227.1 (Navarrete-Vázquez et al. (2007))
3p	CH_3	2-Hydroxy phenyl	3.5	78	240	240–242 (Navarrete-Vázquez et al. (2007))

[a] Reaction was monitored by TLC.
[b] Isolated yields.



Scheme 5 Plausible mechanism for the formation of benzimidazole.

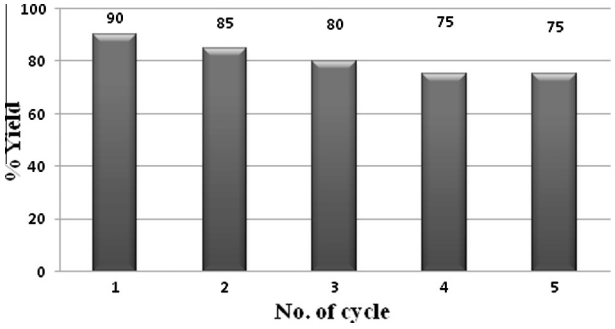


Figure 1 Recyclability study of catalyst.

nates in more down field region i.e. around δ 13 ppm. The plausible mechanism for the formation of benzimidazole derivative is suggested in Scheme 5.

The first step may involve H-bond formation between the catalyst and aldehyde followed by intramolecular oxidative cyclization via imine to produce benzimidazole. Advantages of this method are its simplicity, and easy isolation of the product from the reaction mixture with high yields. The catalyst could be recovered easily by simple filtration because of its heterogenicity. It has high thermal stability as evident from the thermogravimetric analysis (Table 1). It could be recycled and reused five times with almost comparable efficiency without loss in amount as shown in Fig. 1. The reaction of *o*-phenylenediamine **1a** with benzaldehyde **2c** was repeated five times using the same portion of catalyst recovered from the previous batch.

4. Conclusion

Herein we report a high-yielding, one-pot synthesis of 2-substituted benzimidazole derivatives from readily available *o*-phenylenediamines and aromatic aldehydes, under simple and convenient conditions. The conditions are mild, and a wide range of functional groups can be tolerated. ENPFSA as catalyst offers advantages including simplicity of operation, easy workup procedure, product obtained in high yields with excellent purity, less time consuming and the recyclability of the catalyst.

Acknowledgments

Authors thank the Head, Department of Chemistry, Sardar Patel University for providing research facilities and SICART, Vallabh Vidyanagar for TGA and IR facilities on concessional charges. UPT is grateful to UGC, New Delhi for providing research fellowship in science for meritorious students for the academic years 2010–2012.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jscs.2012.07.014.

References

Ahluwalia, V.K., Aggarwal, R., 2000. Comprehensive Practical Organic Chemistry: Preparations and Quantitative Analysis. Universities Press, India Pvt. Ltd.

Alexander, F.P., Alexander, D.G., Simonov, A.M., 1966. Advances in the chemistry of imidazole. Russ. Chem. Rev. 35, 122.

Alloum, A.B., Bougrin, K., Soufiaoui, M., 2003. Synthèse chimiosélective des benzimidazoles sur silice traitée par le chlorure du thionyle. Tetrahedron Lett. 44, 5935–5937.

Anisimova, V.A., Avdyunina, N.I., Spasov, A.A., Barchan, I.A., 2002. Synthesis and pharmacological activity of aminoketones and aminoalcohols of the imidazo[1,2-a]benzimidazole series. Pharm. Chem. J. 36, 377–381.

Bahrami, K., Khodaei, M.M., Kavianinia, I., 2007. A simple and efficient one-pot synthesis of 2-substituted benzimidazoles. Synthesis 2007 (547), 50.

Bai, Y., Lu, J., Shi, Z., Yang, B., 2001. Synthesis of 2,15-hexadecanedione as a precursor of muscone. Synlett 2001 (0544), 46.

Ben-Alloum, A., Bakkas, S., Soufiaoui, M., 1998. Benzimidazoles: oxydation hétérocyclisante par le nitrobenzène ou le diméthylsulfoxyde sur silice et sous irradiation micro-ondes ou ultra-violet. Tetrahedron Lett. 39, 4481–4484.

Chari, M.A., Sadanandam, P., Shobha, D., Mukkanti, K., 2010. A simple, mild, and efficient procedure for high-yield synthesis of benzimidazoles using coppertriflate as catalyst. J. Heterocycl. Chem. 47, 153–155.

Cheng, K.-C., Yu, S.-Y., Chiu, W.-Y., 2002a. Thermal properties of main-chain phosphorus-containing epoxide cured with amine. J. Appl. Polym. Sci. 83, 2733–2740.

Cheng, K.-C., Yu, S.-Y., Chiu, W.-Y., 2002b. Thermal properties of side-chain phosphorus-containing epoxide cured with amine. J. Appl. Polym. Sci. 83, 2741–2748.

Denny, W.A., Rewcastle, G.W., Baguley, B.C., 1990. Potential antitumor agents. 59. Structure-activity relationships for 2-phenylbenzimidazole-4-carboxamides, a new class of minimal DNA-intercalating agents which may not act via topoisomerase II. J. Med. Chem. 33, 814–819.

Fonseca, T., Gigante, B., Gilchrist, T.L., 2001. A short synthesis of phenanthro[2,3-d]imidazoles from dehydroabietic acid. Application of the methodology as a convenient route to benzimidazoles. Tetrahedron 57, 1793–1799.

Geratz, J.D., Stevens, F.M., Polakoski, K.L., Parrish, R.F., Tidwell, R.R., 1979. Amidino-substituted aromatic heterocycles as probes of the specificity pocket of trypsin-like proteases. Arch. Biochem. Biophys. 197, 551–559.

Gouri, C., Ramaswamy, R., Ninan, K.N., 2000. Studies on the adhesive properties of solid elastomer-modified novolac epoxy resin. Int. J. Adhes. Adhes. 20, 305–314.

Guo, Q., Liu, J., Chen, L., Wang, K., 2008. Nanostructures and nanoporosity in thermoset epoxy blends with an amphiphilic polyisoprene-block-poly(4-vinyl pyridine) reactive diblock copolymer. Polymer 49, 1737–1742.

Han, X.M., Ma, H.Q., Wang, Y.L., 2007. P-TsOH catalyzed synthesis of 2-arylsubstituted benzimidazoles. Arkivoc, 150–154.

Hasegawa, E., Yoneoka, A., Suzuki, K., Kato, T., Kitazume, T., Yanagi, K., 1999. Reductive transformation of α, β-epoxy ketones and other compounds promoted through photoinduced electron transfer processes with 1,3-dimethyl-2-phenylbenzimidazoline (DMPBI). Tetrahedron 55, 12957–12968.

Hein, D.W., Alheim, R.J., Leavitt, J.J., 1957. The use of polyphosphoric acid in the synthesis of 2-aryl- and 2-alkyl-substituted benzimidazoles, benzoxazoles and benzothiazoles 1. J. Am. Chem. Soc. 79, 427–429.

Itoh, T., Nagata, K., Ishikawa, H., Ohsawa, A., 2004. Synthesis of 2-arylbenzothiazoles and imidazoles using scandium triflate as a catalyst for both a ring closing and an oxidation steps. Heterocycles 63, 2769–2783.

Kinjo, N., Ogata, M., Nishi, K., Kaneda, A., 1989. Epoxy Molding Compounds as Encapsulation Materials for Microelectronic Devices Speciality Polymers/Polymer Physics. Springer, Berlin, Heidelberg.

Lin, Z., Wu, W., Wang, J., Jin, X., 2007. Studies on swelling behaviors, mechanical properties, network parameters and thermodynamic interaction of water sorption of 2-hydroxyethyl methacrylate/novolac epoxy vinyl ester resin copolymeric hydrogels. React. Funct. Polym. 67, 789–797.

Liu, C.-L., Ying, Y.-G., Feng, H.-L., Dong, W.-S., 2008. Microwave promoted rapid curing reaction of phenolic fibers. Polym. Degrad. Stab. 93, 507–512.

Lombardy, R.L., Tanious, F.A., Ramachandran, K., Tidwell, R.R., Wilson, W.D., 1996. Synthesis and DNA interactions of benzimidazole dications which have activity against opportunistic infections. J. Med. Chem. 39, 1452–1462.

Lu, J., Yang, B., Bai, Y., 2002. Microwave irradiation synthesis of 2-substituted benzimidazoles using PPA as a catalyst under solvent-free conditions. Synth. Commun. 32, 3703–3709.

Ma, H.Q., Wang, Y.L., Li, J.P., Wang, J.Y., 2007. Selective synthesis of 2-aryl-1-arylmethyl-1H-1,3-benzimidazoles promoted by ionic liquid. Heterocycles 71, 135–140.

Ma, H.Q., Wang, Y.L., Wang, J.Y., 2006. A simple KHSO4 promoted synthesis of 2-arylsubstituted benzimidazoles by oxidative condensation of aldehydes with *o*-phenylenediamine. Heterocycles 68, 1669–1673.

Middleton, R.W., Wibberley, D.G., 1980. Synthesis of imidazo[4,5-b]- and [4,5-c]pyridines. J. Heterocycl. Chem. 17, 1757–1760.

Migawa, M.T., Girardet, J.-L., Walker, J.A., Koszalka, G.W., Chamberlain, S.D., Drach, J.C., Townsend, L.B., 1998. Design, synthesis, and antiviral activity of α-nucleosides: D- and L-isomers of lyxofuranosyl- and (5-deoxylyxofuranosyl)benzimidazoles. J. Med. Chem. 41, 1242–1251.

Motawie, A.M., Badr, M.M., Amer, M.S., Moustafa, H.Y., Ali, I.M., 2008. Some coating studies on phenolic epoxy/poly(vinyl acetal)s resins. J. Appl. Sci. Res., 1043–1051.

Motawie, A.M., Sadek, E.M., 1998. Adhesives and coatings based on poly(vinyl acetal)s. J. Appl. Polym. Sci. 70, 1769–1777.

Nagata, K., Itoh, T., Ishikawa, H., Ohsawa, A., 2003. Synthesis of 2-substituted benzimidazoles by reaction of *o*-phenylenediamine with aldehydes in the presence of Sc(OTf)(3). Heterocycles 61, 93.

Navarrete-Vázquez, G., Moreno-Diaz, H., Estrada-Soto, S., Torres-Piedra, M., León-Rivera, I., Tlahuext, H., Muñoz-Muñiz, O., Torres-Gómez, H., 2007. Microwave-assisted one-pot synthesis of 2-(substituted phenyl)-1H-benzimidazole derivatives. Synth. Commun. 37, 2815–2825.

Pätzold, F., Zeuner, F., Heyer, T., Nielas, H.J., 1992. Dehydrogenations using benzofuroxan as oxidant. Synth. Commun. 22, 281–288.

Roth, T., Morningstar, M.L., Boyer, P.L., Hughes, S.H., Buckheit, R.W., Michejda, C.J., 1997. Synthesis and biological activity of novel nonnucleoside inhibitors of HIV-1 reverse transcriptase. 2-Aryl-substituted benzimidazoles. J. Med. Chem. 40, 4199–4207.

Sharghi, H., Asemani, O., Khalifeh, R., 2008. New one-pot procedure for the synthesis of 2-substituted benzimidazoles. Synth. Commun. 38, 1128–1136.

Shieh, J.-Y., Wang, C.-S., 2002. Effect of the organophosphate structure on the physical and flame-retardant properties of an epoxy resin. J. Polym. Sci. A: Polym. Chem. 40, 369–378.

Sondhi, S.M., Singh, N., Kumar, A., Lozach, O., Meijer, L., 2006. Synthesis, anti-inflammatory, analgesic and kinase (CDK-1, CDK-5 and GSK-3) inhibition activity evaluation of benzimidazole/benzoxazole derivatives and some Schiff's bases. Bioorg. Med. Chem. 14, 3758–3765.

Stephens, F.F., Bower, J.D., 1949. 626. The preparation of benziminazoles and benzoxazoles from Schiff's bases. Part I. J. Chem. Soc. (Resumed), 2971–2972.

Valdez-Padilla, D., Rodríguez-Morales, S., Hernández-Campos, A., Hernández-Luis, F., Yépez-Mulia, L., Tapia-Contreras, A., Castillo, R., 2009. Synthesis and antiprotozoal activity of novel 1-methylbenzimidazole derivatives. Bioorg. Med. Chem. 17, 1724–1730.

Velík, J., Baliharová, V., Fink-Gremmels, J., Bull, S., Lamka, J., Skálová, L., 2004. Benzimidazole drugs and modulation of biotransformation enzymes. Res. Vet. Sci. 76, 95–108.

Wang, D.-C., Chang, G.-W., Chen, Y., 2008. Preparation and thermal stability of boron-containing phenolic resin/clay nanocomposites. Polym. Degrad. Stab. 93, 125–133.

Wright, J.B., 1951. The chemistry of the benzimidazoles. Chem. Rev. 48, 397–541.

Yang, D., Fokas, D., Li, J., Yu, L., Baldino, C.M., 2005. A versatile method for the synthesis of benzimidazoles from o-nitroanilines and aldehydes in one step via a reductive cyclization. Synthesis 2005 (47), 56.

Zhang, Z., Liu, Y., Huang, Y., Liu, L., Bao, J., 2002. The effect of carbon-fiber surface properties on the electron-beam curing of epoxy-resin composites. Compos. Sci. Technol. 62, 331–337.