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ORIGINAL PAPER

One-pot synthesis of 2-arylbenzimidazole, 2-arylbenzothiazole and 2-arylbenzoxazole derivatives using vanadium(IV)–salen complex as homogeneous catalyst and vanadium(IV)–salen complex nanoparticles immobilized onto silica as a heterogeneous nanocatalyst

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Abstract The efficient synthesis of 2-arylbenzimidazole, 2-arylbenzothiazole and 2-arylbenzoxazole derivatives is described by condensation of aryl aldehydes and *o*-phenylenediamines, 2-aminothiophenol and 2-aminophenol in a single pot using a catalytic amount of vanadium(IV)–salen complex or vanadium–salen nanoparticles supported on silica (5.0 mol%) in excellent isolated yields. The immobilized catalyst was characterized by powder X-ray diffraction, scanning electron microscopy, atomic force microscopy, transmission electron microscopy, inductively coupled plasma analysis, thermogravimetric instrument for analysis of nitrogen adsorption and FT-IR spectroscopy.

Keywords Vanadium(IV)–salen complexes · Nanoparticle heterogeneous catalyst · Benzimidazole · Benzothiazole · Benzoxazole

Introduction

Benzo-fused heterocyclic systems such as benzimidazole, benzothiazole, and benzoxazole derivatives are present in natural products and in synthetic pharmaceutical and agrochemical compounds [1–8]. These compounds have been extensively studied due to their wide ranges of application, e.g., biological and therapeutic activities (such as an anticancer agent [9], an orexin-1 receptor antagonist [10], a HIV reverse transcriptase inhibitor [11], to name just a few), enzyme inhibitors [12], in vivo imaging [13], fluorescence material [14], plant growth regulator [15] and dyes [16].

While many reports are available for the synthesis of benzimidazoles, benzothiazoles and benzoxazoles, the most popular approaches generally involve condensation–dehydration of *o*-phenylenediamines, 2-aminothiophenol and 2-aminophenol with either carboxylic acid derivatives under strong acid/high temperature conditions [17–19], or aldehydes with subsequent oxidation using various oxidative reagents such as nitrobenzene (high-boiling point oxidant/solvent) [20–24], 1,4-benzoquinone [25], I_2 [26], Fe(III)/Fe(II) [27], air [28, 29], $In(OTf)_3$ [31], $PhI(OAc)_2$ [32], Zn praline [33], $Sc(OTf)_3$ [34, 35], $Yb(OTf)_3$ [36], heteropoly acids [37], thionyl chloride-treatment [38], DDQ [39, 40], electron-deficient olefins [41], benzofuroxan [42], MnO_2 [43], $Pb(OAc)_4$ [44], oxone [45], $NaHSO_3$ [46, 47], H_2O_2/HCl [48], $Na_2S_2O_5$ [49], potassium persulfate–$CuSO_4$ [50], potassium ferricyanide [51], H_2O_2/CAN [52], $H_2O_2/Fe(NO_3)_3$ [53], cobalt(III)–salen complex supported on activated carbon [54], Cu(II) complex [55], porphyrinatoiron(III) complex supported on activated silica [56], NH_4OAc [57], and 4-methoxy-TEMPO [8] for the synthesis of benzimidazoles, air [30], $Sc(OTf)_3$ [34], potassium persulfate–$CuSO_4$ [50], H_2O_2/CAN [52], $H_2O_2/Fe(NO_3)_3$ [53], on water [58] and 4-methoxy-TEMPO [8] for the synthesis of benzothiazoles and air [29], MnO_2 [43], $Pb(OAc)_4$ [44], potassium persulfate–$CuSO_4$ [50], potassium ferricyanide [51] and 4-methoxy-TEMPO [8] for the synthesis of benzoxazoles have been employed in the synthesis of these products. Nevertheless, there are rare examples for preparation of all types of these classes of compounds under similar conditions. Most conditions led

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to the formation of one or two classes of these products and they failed to form other types.

In accordance with the *green* chemistry principles, the immobilization of homogeneous metal coordination complexes is a very useful methodology in organic synthesis. Heterogeneous catalysts are easily separated from the reaction mixture and can be recovered and reused [59, 60]. Inorganic solids have been widely used as solid supports of chiral salen complexes [61, 63]. The use of inorganic solid supports has some advantages over other types of supports, such as mechanical resistance, chemical and thermal stability [62].

Supported heterogeneous vanadium catalysts have shown wide applicability; such as oxidative desulfurization of model fuel diesel [64], oxidation of sulfides [65], enantioselective cyanosilylation of aldehydes [60] oxidation and oxidative bromination of organic substrates [66], epoxidation of geraniol [67], and oxidation of cyclohexane [68].

In this paper, we report an efficient, simple and one-pot, synthesis of 2-arylbenzimidazoles, 2-arylbenzothiazoles and 2-arylbenzoxazole from various *o*-phenylendiamines, 2-aminothiophenol and 2-aminophenol with aryl aldehydes, respectively, in the presence of homogeneous and heterogeneous vanadium(IV)–salen complex (5.0 mol%) under an atmospheric oxygen as a "green" oxidant in ethanol at room temperature for benzimidazoles and benzothiazoles, and in xylene at 120 °C for benzoxazole.

Experimental

Instrumentation, analysis and starting material

NMR spectra were recorded on a Bruker Avance DPX-250 (^{1}H-NMR 250 MHz and ^{13}C NMR 62.9 MHz) spectrometer in pure deuterated solvents with tetramethylsilane as an internal standard. IR spectra were obtained using a Shimadzu FT-IR 8300 spectrophotometer. Mass spectra were determined on a Shimadzu GCMS-QP 1000 EX instruments at 70 or 20 eV. Scanning electron micrographs were obtained by scanning electron microscopy (SEM) instrumentation (SEM, XL-30 FEG SEM, Philips, at 20 kV). An atomic forced microscope (AFM, DME-SPM, version 2.0.0.9) was also used for AFM images. Melting points determined in open capillary tubes in a Büchi-535 circulating oil melting point apparatus. X-ray diffraction (XRD, D8, Advance, Bruker, axs) were obtained for characterization of the heterogeneous catalyst. TEM image was obtained using a transmission electron microscopy (TEM, CN-10, Philips, 100 kV). The thermogravimetry (TG) of the samples was analyzed using a lab-made TGA instrument. The ICP analysis data were obtained using a Varian Vista-pro analyzer. The purity determination of the substrates and reaction monitoring were accomplished by TLC on silica gel PolyGram SILG/UV 254 plates. Chemical materials were purchased from Fluka, Aldrich and Merck Companies. The used aminopropyl silica gel was also purchased from Fluka. The Schiff base *N*,*N*′-(salicylaldehyde)ethylenediamine (Salen) was prepared by reported procedures [69–71]. The catalysts, VO–salen **1** and VCl_2–salen **2**, were synthesized following a reported procedure [69, 72]. In a typical reaction for preparation of VO–salen **1**, the salen (1.55 g in 5 mL ethanol) was added to an ethanolic solution of $VOSO_4$ (1.25 g in 50 mL ethanol). The reaction mixture was maintained in reflux for 2 h. After the reaction was completed the solid was filtered and recrystallized in ethanol. Also, for the preparation of VCl_2–salen **2**, a suspension of VO–salen **1** (2.1 g, 6.30 mmol) in toluene (50 mL) was added to $SOCl_2$ (0.53 mL, 7.22 mmol) and the reaction mixture was kept under reflux during 30 min. After the reaction was completed the solid was filtered and washed with toluene.

Anchoring of VCl_2(salen) complexes onto silica

3-Aminopropyl functionalized silica gel (1.0 g) and VCl_2–salen **2** (1.5 mmol) were added to CH_2Cl_2 under stirring at 25 °C and kept stirring for 24 h. The solid products were separated by centrifuging and washed several times with CH_2Cl_2. The solid products then dried at 60 °C in vacuum.

General procedure for the preparation of 2-substituted benzimidazoles in the presence of vanadium(IV)–salen complex

A mixture of *o*-phenylenediamine (1.0 mmol) and aryl aldehyde (1.0 mmol) was stirred in 10.0 mL of EtOH in the presence of VCl_2–salen (5.0 mol%) at room temperature for the appropriate time as mentioned in Table 2. After the reaction was completed the solvent was evaporated to give the crude product, which was purified by silica gel column chromatography employing *n*-hexane/ethyl acetate (8:1) as eluent.

General procedure for the preparation of 2-substituted benzothiazoles in the presence of vanadium(IV)–salen complex

A mixture of 2-aminothiophenol (1.0 mmol) and aryl aldehyde (1.0 mmol) was stirred in 5.0 mL of EtOH in the presence of VCl_2–salen (5.0 mol%) at room temperature for the appropriate time as mentioned in Table 2. After the reaction was completed the solvent was evaporated to give the crude product, which was purified by silica gel column chromatography employing *n*-hexane/ethyl acetate (10:1) as eluent.

General procedure for the synthesis of 2-substituted benzoxazoles in the presence of vanadium(IV)–salen complex

A mixture of 2-aminophenol (1.0 mmol) and aryl aldehyde (1.0 mmol) was stirred in 1.0 mL of xylene in the presence of VCl_2–salen catalyst (5.0 mol%) at 120 °C for the appropriate time as mentioned in Table 2. After the reaction was completed the solvent was evaporated to give the crude product, which was purified by silica gel column chromatography employing *n*-hexane/ethyl acetate (20:1) as eluent.

General procedure for the preparation of 2-substituted benzimidazoles in the presence of vanadium(IV)–salen complex nanoparticles onto silica

For each reaction, *o*-phenylenediamine (1.0 mmol) with aryl aldehyde (1.0 mmol) was stirred in 10.0 mL of EtOH (96%) in the presence of 5.0 mol % vanadium(IV)–salen complex nanoparticles onto silica (the amount of catalyst has been measured via ICP results) at room temperature. Progress of reactions was monitored by TLC using *n*-hexane/ethyl acetate (8:1). After the reaction was completed the whole reaction mixture was centrifuged and rinsed with EtOH (3 × 15 mL). The recovered catalyst was dried and stored for another consecutive reaction runs and the combined centrifuge was concentrated by evaporating the solvent to give the crude product, which was purified by silica gel column chromatography employing *n*-hexane/ethyl acetate (8:1) as eluent.

General procedure for the preparation of 2-substituted benzothiazoles in the presence of vanadium(IV)–salen complex nanoparticles onto silica

For each reaction, 2-aminothiophenol (1.0 mmol) with aryl aldehyde (1.0 mmol) was stirred in 5.0 mL of EtOH (96%) in the presence of vanadium(IV)–salen complex nanoparticles onto silica (5.0 mol%) at room temperature. Progress of reactions was monitored by TLC using *n*-hexane/ethyl acetate (10:1). After the reaction was completed the whole reaction mixture was centrifuged and rinsed with EtOH (3 × 15 mL). The recovered catalyst was dried and stored for another consecutive reaction runs and the combined centrifuge was concentrated by evaporating the solvent to give the crude product, which was purified by silica gel column chromatography employing *n*-hexane/ethyl acetate (10:1) as eluent.

General procedure for the synthesis of 2-substituted benzoxazoles in the presence of vanadium(IV)–salen complex nanoparticles onto silica

2-Aminophenol (1.0 mmol) with aryl aldehyde (1.0 mmol) was stirred in 1.0 mL of xylene in the presence of 5.0 mol % vanadium(IV)–salen complex nanoparticles onto silica at 120 °C. Progress of reactions was monitored by TLC using *n*-hexane/ethyl acetate (20:1). After the reaction was completed, the whole reaction mixture was centrifuged and rinsed with EtOH (3 × 15 mL). The recovered catalyst was dried and stored for another consecutive reaction runs and the combined centrifuge was concentrated by evaporating the solvent to give the crude product, which was purified by silica gel column chromatography employing *n*-hexane/ethyl acetate (20:1) as eluent.

Spectroscopic data

2-Phenyl-1H-benzimidazole

White solid; mp 290–292 °C (Lit. [38] mp 292 °C). IR (KBr): 694 (m), 742 (s), 1,113 (m), 1,277 (m), 1,315 (m), 1,412 (s), 1,450 (s), 1,591 (w), 1,620 (m), 3,049 (w), 3,440 (w) cm^{-1}. ^1H NMR (DMSO-d_6, 250 MHz): δ 7.14–7.25 (m, 2H), 7.44–7.61 (m, 5H), 8.20 (d, $J = 7.2$ Hz, 2H), 12.94 (s, 1H). ^{13}C NMR (DMSO-d_6, 62.9 MHz): δ 122.1, 126.4, 128.4, 128.9, 129.2, 129.8, 130.1, 151.2. Mass *m/z* (%): 194 (M^+, 97.4), 149 (45.6), 115 (20.2), 97 (27.2), 73 (46.5), 57 (100.0). Anal. Calcd for $C_{13}H_{10}N_2$ (194.235): C, 80.39; H, 5.19; N, 14.42. Found: C, 80.30; H, 5.25; N, 14.39.

5-Methyl-2-phenyl-1H-benzimidazole

White solid; mp 242–243 °C (Lit. [73] mp 242–143 °C). IR (KBr): 698 (m), 1,402 (m), 1,450 (s), 2,882 (m), 3,039 (m), 3,410 (w) cm^{-1}. ^1H NMR (DMSO-d_6, 250 MHz): δ 2.35 (S, 3H), 7.00 (d, $J = 8.1$ Hz, 1H), 7.36–7.55 (m, 5H), 8.14 (d, $J = 7.6$ Hz, 2H), 12.75 (S, 1H). ^{13}C NMR (DMSO-d_6, 62.9 MHz): δ 21.3, 111.1, 118.4, 123.5, 126.2, 128.8, 129.2, 129.6, 130.3, 131.1, 150.9. Mass *m/z* (%): 209 (M^++1, 36.5), 208 (M^+, 47.4), 149 (16.1), 104 (32.1), 73 (59.1), 57 (100.0). Anal. Calcd for $C_{14}H_{12}N_2$ (208.262): C, 80.74; H, 5.81; N, 13.45. Found: C, 80.79; H, 5.77; N, 13.41.

2-Phenyl-1H-benzimidazole-5-carboxylic acid

White solid; mp 325 °C (Lit. [56] mp 325 °C). IR (KBr): 771 (m), 1,296 (s), 1,687 (s), 2,921 (br), 3,058 (m), 3,340 (m) cm^{-1}. ^1H NMR (DMSO-d_6, 250 MHz): δ 7.47–7.66 (m, 4H), 7.84 (d, $J = 8.4$ Hz, 1H), 8.17–8.20 (m, 3H), 12.79 (S, 1H), 13.19 (S, 1H). ^{13}C NMR (DMSO-d_6, 62.9 MHz): δ 122.7, 123.5, 124.0, 125.0, 126.7, 128.3, 129.2, 129.6, 130.3, 142.4, 153.7, 168.0. Mass *m/z* (%): 239 (M^++1, 8.6), 238 (M^+, 9.2), 221 (7.1), 193 (1.9), 152 (5.6), 111 (16.2), 83 (41.4), 57 (100.0). Anal. Calcd for $C_{14}H_{10}N_2O_2$ (238.244): C, 70.58; H, 4.23; N, 11.76. Found: C, 71.52; H, 4.28; N, 11.72.

Phenyl(2-phenyl-1H-benzimidazol-5-yl)methanone

Pale yellow solid; mp 221–222 °C (Lit. [73] mp 221–221.5 °C). IR (KBr): 1,282 (m), 1,321 (s), 1,614 (s), 1,639 (m), 3,116 (m), 3,398 (m) cm^{-1}. ^1H NMR (DMSO-d_6, 250 MHz): δ 7.41–7.58 (m, 11H), 8.19 (d, $J = 7.4$ Hz, 2H), 13.28 (s, 1H). ^{13}C NMR (DMSO-d_6, 62.9 MHz): δ 124.2, 126.7, 128.3, 129.0, 129.4, 129.5, 130.4, 131.0. 132.0, 138.7, 153.9.1, 195.5. Mass *m/z* (%): 299 (M^++1, 18.5), 298 (M^+, 19.2), 221 (43.7), 194 (10.5), 166 (12.6), 149 (15.8), 111 (13.9), 94 (40.8), 71 (43.5), 55 (100.0). Anal. Calcd for $C_{20}H_{14}N_2O$ (298.343): C, 80.52; H, 4.73; N, 9.39. Found: C, 80.58; H, 4.75; N, 9.25.

Ethyl 2-Phenyl-1H-benzimidazole-5-carboxylate

White solid; mp 183 °C. IR (KBr): 746 (s), 1,229 (s), 1,368 (m), 1,620 (m), 1,730 (s), 3,310 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ 1.37 (t, $J = 7.1$ Hz, 3H), 4.38 (q, $J = 7.1$ Hz, 2H), 7.26–7.43 (m, 3H), 7.57 (m, 1H), 7.95 (dd, $J = 8.5$, $J = 1.3$ Hz, 1H), 8.12–8.16 (m, 2H), 8.35 (s, 1H), 12.1 (s, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 14.3, 61.1, 124.3, 124.8, 127.1, 129.1, 129.3, 130.7, 154.9, 167.5. Mass *m/z* (%): 267 (M^++1, 11.3), 266 (M^+, 49.4), 221 (100.0), 193 (34.6), 166 (18.2), 149 (11.6), 111 (15.3), 90 (17.0), 63 (35.7). Anal. Calcd for $C_{16}H_{14}N_2O_2$ (266.298): C, 72.17; H, 5.30; N, 10.52. Found: C, 72.21; H, 5.35; N, 10.55.

2-Phenyl-1,3-benzothiazole

White solid; mp 112 °C (Lit. [8] mp 111–112 °C). IR (KBr): 686 (s), 762 (s), 962 (m), 1,431 (m), 1,472 (m), 3,060 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ 7.36–7.42 (m, 1H), 7.48–7.53 (m, 4H), 7.91 (d, $J = 8.5$ Hz, 1H), 8.08–8.13 (m, 3H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 121.7, 123.3, 125.2, 126,3, 127.6, 129.0, 131.0, 133.6, 135.1, 154.2, 168.0. Mass *m/z* (%):211(M^+, 8.2), 186 (5.3), 166 (5.5), 80 (39.2), 64 (100.0), 57 (25.8), 55 (44.1). Anal. Calcd for $C_{13}H_9NS$ (221.281): C, 73.90; H, 4.29; N, 6.63; S, 15.17. Found: C, 73.94; H, 4.32; N, 6.61; S, 15.14.

2-Phenyl-1,3-benzoxazole

White solid; mp 96–98 °C (Lit. [8] mp 96–97 °C). IR (KBr): 692 (s), 744 (s), 1,053 (s), 1,241 (s), 1,447 (s), 1,455 (m), 1,545 (s), 1,608 (m), 3,049 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): 7.23–7.37 (m, 2H), 7.51–7.57 (m, 4H), 7.75–7.85 (m, 1H), 8.25–8.28 (m, 2H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 110.6, 120.0, 124.5, 125.0, 127.1, 127.6, 128.8, 129.2, 131.0, 131.4, 142.1, 150.7, 163.0. Mass *m/z* (%):195 (M^+, 77.4), 167 (27.6), 149 (10.6), 85 (34.2), 70 (25.1), 57 (100.0). Anal. Calcd for $C_{13}H_9NO$ (195.220): C, 79.98; H, 4.65; N, 7.17. Found: C, 79.96; H, 4.68; N, 7.16.

2-(4-Methylphenyl)-1H-benzimidazole

White solid; mp: 270–272 °C (Lit. [73] mp 270–272 °C). IR (KBr): 744 (s), 822 (m), 964 (m), 1,273 (m), 1,393 (m), 1,431(s), 1,462 (s), 1,500 (m), 1,554 (w), 2,916 (m), 2,978 (m), 3,095 (m), 3,447 (w) cm^{-1}. ^1H NMR (DMSO-d_6, 250 MHz): δ 2.35 (s, 3H), 7.15–7.20 (m, 2H), 7.33 (d, $J = 8.1$ Hz, 2H), 7.46–7.56 (m, 2H), 8.07 (d, $J = 8.1$ Hz, 2H), 12.84 (s, 1H). ^{13}C NMR (DMSO-d_6, 62.9 MHz): δ 20.9, 121.9, 126.3, 127.4, 128.9, 129.4, 139.5, 151.3. Mass *m/z* (%): 208 (M^+, 66.5), 149 (49.1), 111 (18.0), 83 (44.9), 57 (100.0). Anal. Calcd for $C_{14}H_{12}N_2$ (208.262): C, 80.74; H, 5.81; N, 13.45. Found: C, 80.69; H, 5.90; N, 13.38.

2-(4-Methylphenyl)-1,3-benzothiazole

White solid; mp 85 °C (Lit. [74] mp 85 °C). IR (KBr): 761 (s), 816 (m), 959 (m), 1,311 (m), 1,479 (s), 1,603 (w), 2,914 (W), 3,049 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ 2.29 (s, 3H), 7.15 (d, $J = 7.9$ Hz, 2H), 7.23–7.36 (m, 2H), 7.74 (d, $J = 7.8$ Hz, 1H), 7.86 (d, $J = 8.2$ Hz, 2H), 7.94 (d, $J = 8.0$ Hz). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 21.5, 121.6, 123.1, 125.0, 126.2, 127.8, 129.7, 131.0, 135.0, 141.3, 154.3, 168.2;. Mass *m/z* (%):225 (M^+, 100.0), 224 (55.5), 223 (17.7), 190 (3.1), 148 (12.8), 108 (12.8), 91 (6.1), 89 (6.3), 82 (9.7), 69 (22.5), 63 (1.5), 58 (10.1), 57 (8.4), 55 (8.4). Anal. Calcd for $C_{14}H_{11}NS$ (225.308): C, 74.63; H, 4.92; N, 6.22; S, 14.23. Found: C, 74.64; H, 4.89; N, 6.27; S, 14.26.

2-(4-Methylphenyl)-1,3-benzoxazole

White solid; mp 113–114 °C (Lit. [75] mp 113–115 °C). IR (KBr): 760 (s), 820 (s), 1,055 (s), 1,177 (m), 1,243 (s), 1,501 (m), 1,556 (m), 1,622 (m), 2,916 (m), 3,053 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ 7. 2.43 (s, 3H), 7.20–7.36 (m, 4H), 7.55–7.59 (m. 1H), 7.74–7.78 (m, 1H), 8.15 (d, $J = 8.3$ Hz, 2H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 21.6, 110.4, 119.8, 124.3, 124.8, 127.5, 129.6, 141.9, 142.2, 150.6, 163.2. Mass *m/z* (%):209 (M^+, 100.0), 180 (9.1), 149 (22.5), 91 (27.7), 64 (35.8), 63 (45.6). Anal. Calcd for $C_{14}H_{11}NO$ (209.247): C, 80.36; H, 5.30; N, 6.69. Found: C, 80.38; H, 5.35; N, 6.72.

2-(4-Methoxyphenyl)-1H-benzimidazole

White solid; mp 226 °C (Lit. [76] mp 226–227 °C). IR (KBr): 744 (s), 1,034 (m), 1,180 (m), 1,254 (s), 1,296 (m), 1,400 (m), 1,435 (s), 1,454 (s), 1,477 (m), 1,500 (s), 1,612 (s), 2,948 (m), 3,055 (m), 3,422 (w) cm^{-1}. ^1H NMR (DMSO-d_6, 250 MHz): δ 3.78 (s, 3 H), 7.10 (d, $J =$ 8.8 Hz, 2H), 7.16 (q, $J = 3.0$ Hz, 2H), 7.50 (m, 2H), 8.12 (d, $J = 8.8$ Hz, 2H), 12.76 (s, 1H). ^{13}C NMR (DMSO-d_6,

62.9 MHz): δ 55.2, 111.0, 114.3, 118.4, 121.5, 122.0, 122.6, 128.0, 151.3, 160.5. Mass *m/z* (%): 225 (M^++1, 86.4), 224 (M^+, 92.4), 210 (51.8), 182 (51.0), 149 (30.9), 129 (17.8), 97 (30.4), 69 (100.0). Anal. Calcd for $C_{14}H_{12}N_2O$ (224.261): C, 74.98; H, 5.39; N, 12.49. Found: C, 74.93; H, 5.42; N, 12.45.

2-(4-Methoxyphenyl)-1,3-benzothiazole

White solid; mp 122 °C (Lit. [77] mp 120–121 °C). IR (KBr): 760 (s), 832 (s), 968 (m), 1,027 (m), 1,181 (m), 1,221 (m), 1,256 (s), 1,433 (m), 1,477 (s), 1,605 (s), 2,991 (w), 3,059 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ 3.78 (s, 3H,), 6.84 (d, J = 8.9 Hz, 2H), 7.25–7.39 (m, 2H), 7.78 (d, J = 7.9 Hz, 1H), 7.91–7.96 (m, 3H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 55.4, 114.3, 121.5, 122.8, 124.8, 126.2, 126.4, 129.1, 134.9, 154.2, 161.9, 167.8. Mass *m/z* (%):241 (M^+, 80.2), 240 (33.0), 226 (41.3), 210 (11.4), 198 (38.7), 165 (5.1), 149 (66.1), 73 (31.8), 71 (37.8), 69 (38.6), 57 (100.0). Anal. Calcd for $C_{14}H_{11}NOS$ (241.307): C, 69.68; H, 4.59; N, 5.80; S, 13.29. Found: C, 69.71; H, 4.60; N, 5.86; S, 13.33.

2-(4-Methoxyphenyl)-1,3-benzoxazole

White solid; mp 97–98 °C (Lit. [8] mp 97–98 °C). IR (KBr): 741 (m), 831 (m), 1,019 (m), 1,169 (m), 1,255 (m), 1,453 (m), 1,500 (s), 1,616 (s), 3,052 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ 3.85 (s, 3H), 7.01 (d, J = 8.8 Hz, 2H), 7.29–7.33 (m, 2H), 7.52–7.55 (m, 1H), 7.71–7.75 (m, 1H), 8.18 (d, J = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 55.3, 110.3, 114.3, 114.7, 119.5, 124.3, 124.5, 129.3, 142.3, 150.6, 162.2, 163.1. Mass *m/z* (%): 226 (M^++1, 11.1), 225 (M^+, 30.9), 182 (8.6), 165 (22.2), 111 (16.0), 97 (45.7), 69 (100.0). Anal. Calcd for $C_{14}H_{11}NO_2$ (225.246): C, 74.65; H, 4.92; N, 6.22. Found: C, 74.66; H, 4.97; N, 6.26.

2-(2,5-Dimethoxyphenyl)-1H-benzimidazole

White solid; mp 217–218 °C. IR (KBr): 758 (m), 1,025 (m), 1,420 (m), 1,490 (s), 1,616 (w), 3,112 (br), 3,421 (w) cm^{-1}. ^1H NMR (DMSO-d_6, 250 MHz): δ 3.78 (s, 3H), 3.95 (s, 3H), 6.99–7.20 (m, 4H), 7.65 (m, 2H), 8.01 (d, J = 3.1 Hz, 1H), 12.14 (s, 1H). ^{13}C NMR (DMSO-d_6, 62.9 MHz): δ 55.4, 56.0, 112.0, 113.3, 113.6, 117.0, 118.4, 121.5, 122.1, 134.7, 142.6, 148.7, 151.0, 153.1. Mass *m/z* (%): 255 (M^++1, 12.4), 254 (15.0), 149 (14.7), 119 (23.1), 95 (19.2), 69 (100.0). Anal. Calcd for $C_{15}H_{14}N_2O_2$ (254.284): C, 70.85 H, 5.55, N, 11.02. Found: C, 70.82, H, 5.61, N, 10.97.

2-(2,5-Dimethoxyphenyl)-1,3-benzothiazole

White solid; mp 105–107 °C. IR (KBr): 755 (m), 1,016 (m), 1,177 (m), 1,291 (s), 1,461 (m), 1,504 (s), 1,612 (m), 2,828 (w), 3,055 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ 3.90 (s, 3H), 3.98 (s, 3H), 7.00–7.02 (m, 2H), 7.37–7.41(m, 1H), 7.47–7.50 (m, 1H), 7.93 (d, J = 8.6 Hz, 1H), 8.09–8.12 (m, 2H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 55.9, 56.3, 112.7, 113.4, 118.7, 121.3, 122.7, 122.8, 124.7, 125.9, 136.3, 151.8, 152.1, 153.9, 162.9. Mass *m/z* (%): 272 (M^++1, 19.6), 271 (M^+, 67.9), 238 (47.8), 210 (14.4), 185 (30.6), 159 (13.4), 136 (100.0), 108 (18.2), 69 (37.8). Anal. Calcd for $C_{15}H_{13}NO_2S$ (271.332): C, 66.40; H, 4.83; N, 5.16; S, 11.82. Found: C, 66.45; H, 4.86; N, 5.20, S, 11.88.

2-(2,5-Dimethoxyphenyl)-1,3-benzoxazole

White solid; mp 70–72 °C. IR (KBr): 751 (m), 1,038 (m), 1,249 (m), 1,538 (m), 1,618 (m), 1,821 (w), 3,012 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ 3.88 (s, 3H), 3.93 (s, 3H), 7.037.06 (m, 2H), 7.33–7.36 (m, 2H), 7.58–7.60 (m, 1H), 7.68 (d, J = 2.8, 1H), 7.80–7.81 (m, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 55.9, 56.7, 110.5, 113.7, 115.1, 116.3, 119.0, 120.2, 124.3, 125.0, 142.0, 150.3, 152.9, 153.4, 161.4. Mass *m/z* (%): 256 (M^++1, 23.4), 255 (M^+, 93.6), 226 (72.3), 212 (31.9), 195 (12.8), 169 (35.1), 149 (38.3), 120 (94.7), 94 (100.0), 69 (92.6). Anal. Calcd for $C_{15}H_{13}NO_3$ (255.271): C, 70.58; H, 5.13; N, 5.49. Found: C, 70.61; H, 5.19; N, 5.51.

2-(4-Isopropylphenyl)-1H-benzimidazole

White solid; mp 250–251 °C (Lit. [56] mp 250–251 °C). IR (KBr): 741 (m), 1,273 (m), 1,439 (s), 1,620 (m), 2,951 (s), 3,055 (w), 3,417 (w) cm^{-1}. ^1H NMR (DMSO-d_6, 250 MHz): δ 1.22 (d, J = 6.9 Hz, 6H), 2.93 (m, 1H), 7.17 (m, 2H), 7.40 (d, J = 8.2 Hz, 2H), 7.51–7.62 (m, 2H), 8.10 (d, J = 8.2 Hz, 2H), 12.83 (s, 1H). ^{13}C NMR (DMSO-d_6, 62.9 MHz): δ 23.6, 33.3, 111.2, 118.6, 121.5, 122.3, 126.4, 127.7, 150.3, 151.3. Mass *m/z* (%): 237 (M^++1, 40.1), 236 (M^+, 67.3), 221 (100.0), 194 (11.6), 110 (17.6), 92 (29.5), 65 (31.2). Anal. Calcd for $C_{16}H_{16}N_2$ (236.316): C, 81.32; H, 6.82; N, 11.85. Found: C, 81.25; H, 6.90; N, 11.78.

2-(4-Isopropylphenyl)-1,3-benzothiazole

White solid; mp 78–79 °C. IR (KBr): 757 (s), 966 (s), 1,312 (m), 1,435 (m), 1,485 (m), 1,557 (m), 1,624 (m), 1,825 (w), 2,957 (m), 3,048 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ 1.21 (d, J = 6.7 Hz, 6H), 2.84–2.95 (m, 1H), 7.26 (d, J = 8.3 Hz, 2H), 7.28–7.40 (m, 2H), 7.81 (d, J = 7.9 Hz, 2H), 7.95 (d, J = 8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 23.5, 34.2, 121.6, 123.1, 125.0, 126.2, 126.6, 127.1, 127.6, 128.0, 131.3, 135.0, 152.2, 154.3, 168.2. Mass *m/z* (%): 253 (M^+, 52.3), 238 (100.0), 223 (23.1), 109 (22.9), 69 (18.8). Anal. Calcd for

$C_{16}H_{15}NS$ (253.361): C, 75.85; H, 5.97; N, 5.53; S, 12.65. Found: C, 75.86; H, 6.05; N, 5.57; S, 12.67.

2-(4-Isopropylphenyl)-1,3-benzoxazole

White solid; mp 76–78 °C. IR (KBr): 745 (s), 1,011 (m), 1,242 (s), 1,452 (m), 1,496 (m), 1,552 (m), 1,617 (m), 2,904 (w), 2,946 (m), 3,050 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ 1.30 (d, $J = 6.9$ Hz, 6H), 3.00 (m, 1H), 7.30–7.41 (m, 4H), 7.54–7.59 (m, 1H), 7.74–7.81(m, 1H), 8.19 (d, $J = 6.6$ Hz, 2H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 23.7, 34.2, 110.5, 119.8, 124.5, 124.7, 124.8, 127.0, 127.7, 142.2, 150.7, 152.8, 163.3. Mass *m/z* (%): 238 (M^++1, 17.6), 237 (M^+, 48.0), 222 (100.0), 207 (8.1), 193 (6.6), 130 (3.3), 65 (29.7). Anal. Calcd for $C_{16}H_{15}NO$ (237.300): C, 80.98; H, 6.37; N, 5.90. Found: C, 80.99; H, 6.42; N, 5.91.

2-(4-Chlorophenyl)-1H-benzimidazole

White solid; mp 292–293 °C (Lit. [38] mp 292 °C). IR (KBr): 744 (s), 829 (s), 964 (m), 1,014 (m), 1,088 (m), 1,273 (m), 1,319 (m), 1,427 (s), 1,470 (m), 1,489 (m), 1,626 (w), 3,051 (w) cm^{-1}. ^1H NMR (DMSO-d_6, 250 MHz): δ 7.18–7.21 (m, 2 H), 7.60 (m, 4 H), 8.17 (d, $J = 8.6$ Hz, 2H), 12.99 (s, 1 H). ^{13}C NMR (DMSO-d_6, 62.9 MHz) δ 111.4, 118.9, 121.9, 122.7, 128.1, 129.0, 134.5 150.1. Mass *m/z* (%): 230 (M^++2, 21.1), 229 (M^++1, 36.3), 228 (M^+, 54.9), 193 (13.5), 167 (7.0), 149 (25.0), 129 (11.1), 111 (15.4), 85 (33.2), 57 (100.0). Anal. Calcd for $C_{13}H_9ClN_2$ (228.681): C, 68.28; H, 3.97; N, 12.25. Found: C, 68.23; H, 4.05; N, 12.24.

2-(4-Chlorophenyl)-1,3-benzothiazole

White solid; mp 110–113 °C (Lit. [8] mp 110–112 °C). IR (KBr): 731 (m), 828 (m), 964 (m), 1,089 (s), 1,399 (m), 1,473 (s), 1,508 (m), 3,012 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ 7.31–7.43 (m, 4H), 7.82 (d, $J = 7.8$ Hz, 1H), 7.92–7.97 (m, 3H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 121.6, 123.3, 125.4, 126.5, 128.7, 129.2, 130.9, 132.1, 135.0, 137.0,154.1, 166.6. Mass *m/z* (%): 247 (M^++2, 39.3), 246 (M^++1, 27.7), 245 (M^+, 100.0), 210 (14.6), 108 (58.5), 69 (55.2). Anal. Calcd for $C_{13}H_8ClNS$ (245.726): C, 63.54; H, 3.28; N, 5.70; S, 13.05. Found: C, 63.53.28; H, 3.30; N, 5.71; S, 13.12.

2-(4-Chlorophenyl)-1,3-benzoxazole

White solid; mp 145–147 °C (Lit. [8] mp 144–145 °C). IR (KBr): 739 (s), 832 (m), 1,011 (m), 1,056 (m), 1,091 (m), 1,244 (m), 1,452 (m), 1,483 (m), 1,616 (m), 3,057 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ 7.33–7.38 (m, 2H), 7.50 (d, $J = 8.6$ Hz, 2H), 7.56–7.60 (m, 1H), 7.74–7.79 (m, 1H), 8.19 (d, $J = 8.6$ Hz, 2H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 110.6, 120.1, 124.7, 125.3, 125.6, 128.8, 129.2, 137.7, 142.0, 150.7, 162.0. Mass *m/z* (%): 231 (M^++2, 38.3), 230 (M^++1, 36.5), 229 (M^+, 100.0), 201 (27.8), 166 (17.8), 111 (10.2), 92 (21.5), 63 (79.0). Anal. Calcd for $C_{13}H_8ClNO$ (229.665): C, 67.99; H, 3.51; N, 6.10. Found: C, 67.96; H, 3.57; N, 6.12.

4-(1H-Benzimidazol-2-yl)phenyl 2-propynyl ether

White solid; mp 200–201 °C. IR (KBr): 746 (s), 835 (m), 1,025 (s), 1,178 (m), 1,229 (m), 1,450 (s), 1,495 (s), 1,610 (s), 2,859 (w), 2,919 (w), 3,270 (m), 3,417 (w) cm^{-1}. ^1H NMR (DMSO-d_6, 250 MHz): δ 3.60 (s, 1H), 4.88 (s, 2H), 7.13–7.19 (m, 4H), 7.54–7.70 (m, 2H), 8.11 (d, $J = 8.8$ Hz, 2H), 12.76 (s, 1H). ^{13}C NMR (DMSO-d_6, 62.9 MHz) δ 55.5, 78.4, 78.9, 115.2, 121.8, 123.4, 127.9, 151.2, 158.5. Mass *m/z* (%): 249 (M^++1, 15.3), 248 (M^+, 49.3), 209 (100.0), 181 (63.7), 149 (12.1), 105 (14.9), 77 (24.7), 57 (38.1). Anal. Calcd for $C_{16}H_{12}N_2O$ (248.283): C, 77.40; H, 4.87; N, 11.28. Found: C, 77.42; H, 4.91; N, 11.27.

4-(1,3-Benzothiazol-2-yl)phenyl 2-propynyl ether

White solid; mp 131–132 °C. IR (KBr): 756 (s), 841 (m), 1,015 (m), 1,226 (m), 1,245 (m), 1,485 (s), 1,602 (m), 3,277 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ 2.49 (s, 1H), 4.69 (s, 2H), 6.98–7.03 (m, 2H), 7.31–7.40 (m, 2H), 7.80 (d, $J = 8.6$ Hz, 1H), 7.94–8.00 (m, 3H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 55.9, 76.1, 78.0, 115.3, 121.5, 122.9, 124.9, 126.2, 127.2, 129.1, 134.9, 154.2, 159.7, 167.6. Mass *m/z* (%): 266 (M^++1, 3.3), 265 (M^+, 15.4), 226 (33.8), 210 (27.9), 181 (10.4), 149 (26.7), 121 (12.5), 95 (28.3), 69 (100.0). Anal. Calcd for $C_{16}H_{11}NOS$ (265.329): C, 72.43; H, 4.18; N, 5.28; S, 12.08. Found: C, 72.49; H, 4.25; N, 5.26; S, 12.13.

4-(1,3-Benzoxazol-2-yl)phenyl 2-propynyl ether

White solid; mp 121–123 °C. IR (KBr): 746 (s), 1,016 (m), 1,173 (m), 1,218 (s), 1,452 (m), 1,498 (s), 1,616 (m), 3,293 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ 2.57 (s, 1H), 4.76 (s, 2H), 7.07–7.12 (m, 2H), 7.30–7.34 (m, 2H), 7.53–7.55 (m, 1H), 7.72–7.75 (m, 1H), 8.18–8.23 (m 2H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 55.8, 76.1, 77.9, 110.4, 115.2, 119.7, 120.5, 124.4, 124.7, 129.3, 142.2, 150.6, 160.1, 162.9. Mass *m/z* (%): 250 (M^++1, 22.0), 249 (M^+, 80.6), 210 (100.0), 182 (90.9), 149 (12.9), 127 (39.2), 94 (23.7), 63 (25.9). Anal. Calcd for $C_{16}H_{11}NO_2$ (249.268): C, 77.10; H, 4.45; N, 5.62. Found: C, 77.08; H, 4.49; N, 5.60.

2-(4-{[4-(1H-Benzimidazol-2-yl)phenoxy]methyl}-1H-1,2,3-triazol-1-yl)cyclohexanol

White solid; mp: 254–256 °C. IR (KBr): 745 (m), 833 (m), 1,077 (m), 1,178 (m), 1,248 (s), 1,441 (m), 1,499 (m), 1,613 (m), 2,855 (w), 2,933 (m), 3,151 (m), 3,415 (br) cm^{-1}. ^1H NMR (DMSO-d_6, 250 MHz): δ 1.14–1.32 (m, 2H), 1.69–2.06 (m, 4H), 2.47–2.49 (m, 2H), 3.98–4.26 (m, 2H), 4.98 (s, 1H), 5.20 (s, 2H), 7.15–7.23 (m, 4H), 7.53–7.57 (m, 2H), 8.10 (d, $J = 8.7$ Hz, 2H), 8.22 (s, 1H). ^{13}C NMR (DMSO-d_6, 62.9 MHz) δ 23.7, 24.3, 31.9, 34.7, 61.3, 65.8, 71.3, 114.7, 115.0, 121.9, 122.6, 123.9, 128.0, 139.1, 141.5, 151.2, 159.5. Mass *m/z* (%): 391 (M^++2, 4.5), 390 (M^++1, 15.5), 389 (M^+, 17.4), 360 (1.3), 292 (8.7), 262 (4.5), 248 (2.4), 235 (4.4), 210 (100.0), 181 (23.9), 152 (34.5), 81 (38.6), 54 (20.8). Anal. Calcd for $C_{22}H_{23}N_5O_2$ (389.455): C, 67.85; H, 5.95; N, 17.98. Found: C, 67.88; H, 6.03; N, 17.93.

2-(4-{[4-(1,3-Benzothiazol-2-yl)phenoxy]methyl}-1H-1,2,3-triazol-1-yl)cyclohexanol

White solid; mp 196–198 °C. IR (KBr): 730 (m), 758 (s), 1,174 (m), 1,253 (s), 1,307 (m), 1,432 (m), 1,481 (s), 1,605 (m), 2,853 (w), 2,932 (m), 3,350 (br) cm^{-1}. ^1H NMR (DMSO-d_6, 250 MHz): δ 1.15–1.32 (m, 2H), 1.64–1.96 (m, 4H), 2.47–2.48 (m, 2H), 3.65–3.82 (m, 1H), 4.18–4.22 (m, 1H), 4.96 (s, 1H), 5.22 (s, 2H), 7.22 (d, $J = 8.8$ Hz, 2H), 7.37–7.53 (m, 2H), 7.98–8.10 (m, 4H), 8.24 (s, 1H). ^{13}C NMR (DMSO-d_6, 62.9 MHz) δ 23.7, 24.4, 31.9, 34.7, 61.4, 65.8, 71.3, 115.4, 122.1, 122.4, 123.9, 125.1, 125.7, 126.5, 128.8, 134.2, 141.3, 153.6, 160.6, 166.9. Mass *m/z* (%): 408 (M^++2, 5.8), 407 (M^++1, 15.9), 406 (M^+, 19.7), 389 (3.8), 292 (2.8), 279 (4.1), 227 (100.0), 210 (33.5), 180 (14.6), 152 (98.2), 134 (12.7), 108 (25.0), 81 (77.3), 55 (45.2). Anal. Calcd for $C_{22}H_{22}N_4O_2S$ (406.501): C, 65.00; H, 5.45; N, 13.78; S, 7.89. Found: C, 65.08; H, 5.49; N, 13.77; S, 7.94.

2-(4-{[4-(1,3-Benzoxazol-2-yl)phenoxy]methyl}-1H-1,2,3-triazol-1-yl)cyclohexanol

White solid; mp 182–184 °C. IR (KBr): 784 (m), 1,035 (m), 1,257 (m), 1,498 (m), 1,616 (m), 1,650 (m), 2,876 (w), 2,935 (w), 1,367 (br) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ 1.22–2.22 (m, 8H), 3.09 (s, 1H), 4.01–4.23 (m, 2H), 5.25 (s, 2H), 7.10 (d, $J = 8.9$ Hz, 2H), 7.26–7.36 (m, 2H), 7.52–7.56 (m, 1H), 7.71–7.74 (m, 2H). 8.18 (d, $J = 8.9$ Hz, 2H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 23.9, 24.7, 31.6, 33.8, 62.1, 66.9, 72.6, 110.4, 115.1, 119.6, 122.7, 124.4, 124.7, 129.4, 132.4, 143.9, 151.4, 161.8. Mass *m/z* (%) 391 (M^++1, 8.3), 290 (M^+, 18.4), 211 (78.7), 180 (20.0), 152 (85.4), 134 (13.7), 97 (15.4), 81 (100.0), 56 (45.3). Anal. Calcd for $C_{22}H_{22}N_4O_3$ (390.440): C, 67.68; H, 5.68; N, 14.35. Found: C, 67.72; H, 5.73; N, 14.42.

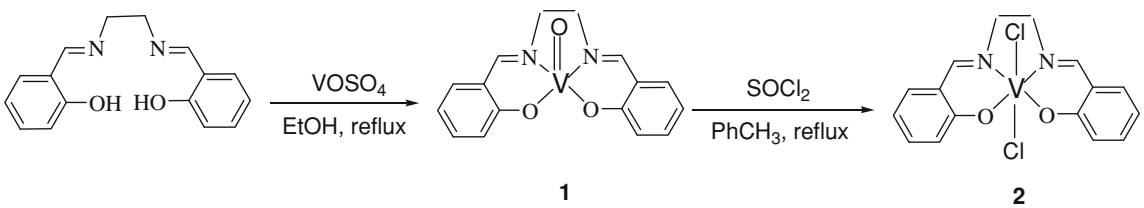
Results and discussions

Metal–salen complexes show wide applicability and are now used as catalyst for a variety of enantioselective reactions such as oxidation [78–80], sulfimidation [81], addition of TMSCN to aldehydes [82], conversion of 1,2-epoxyethanes to 2-haloethanol structures [83], sulfoxidation [84], cyclopropanation [85] and alkyne addition to ketones [86]. In conjunction with our studies on the synthesis of metal–salen complexes [54, 87–91] and our continued efforts to utilize heterogeneous catalysts for developing organic reactions [54, 56, 92–101], herein, we report a novel and efficient method for the synthesis of 2-substituted benzimidazoles, benzothiazoles and benzoxazole using a vanadium(IV)–salen complex and vanadium(IV)–salen complex nanoparticles supported on silica as the catalyst.

The catalysts, VO–salen **1** and VCl_2–salen **2**, were synthesized following a reported procedure [69, 72]. The reaction pathway for the preparation of the catalysts is shown in Scheme 1.

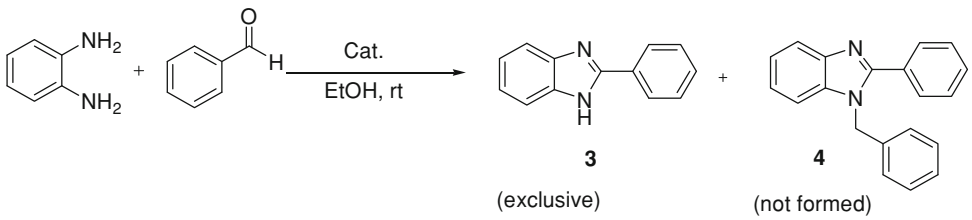
In the presence of a catalytic amount of VO(salen) **1** and VCl_2(salen) **2**, the reaction of *o*-phenylenediamine (1.0 mmol) was first examined with benzaldehyde (1.0 mmol) at room temperature in ethanol. We obtained exclusively 2-substituted product **3**, and no *N*-alkylated product **4** was observed (Scheme 2).

According to Table 1, when VO(salen) **1** and VCl_2(salen) **2** were used as catalysts in the presence of atmospheric air as a *green* oxidant, a comparison between the activity of



Scheme 1 The reaction pathway for the preparation of the catalysts

Scheme 2 Model reaction of synthesis benzimidazole derivatives



these complexes exhibits that the complex **2** results higher yield of the benzimidazole **3** than the complex **1**. While the condensation reaction of *o*-phenylenediamine with benzaldehyde without any catalyst (Table 1, entry 3) led to low yield. These observations show that vanadium–salen employs an important role in synthesis of benzimidazole. According to Table 1, the best results were obtained with the use of 5.0 mol % of VCl_2(salen) **2**. When the amount of the catalyst was lower, the yield of the product decreased, whereas raising the catalyst concentration did not lead to an appreciable increase in the yield. The product was obtained in low yield if this reaction was operated under nitrogen atmosphere (Table 1, entry 4). That is to say that O_2 plays an important role in this reaction.

During our optimization studies, the effect of solvents was also tested. We found that the solvent plays a significant role in terms of the reaction rate and the isolated yield. Among various solvents tested, ethanol clearly stands out as the solvent of choice with its fast reaction rate, high yield, cheapness, selectivity and environmental acceptability.

We proposed a mechanism for the vanadium(IV) salen complex catalyzed reaction for the synthesis of 2-substituted benzimidazole derivatives (Scheme 3). The reaction of amine with aryl aldehyde forms the imine **A**, which exists in equilibrium with the cyclic hydrobenzimidazole **B** [39–47, 54–56]. To explore a plausible mechanism for this reaction, aldehyde consumption was monitored by GC analysis and we found that the Schiff base is formed quickly and the rate-determining step (RDS) was found to be the oxidative cyclization step [56]. Furthermore, we found that it is not necessary to prepare Schiff bases in advance. The vanadium(IV)–salen complex may be oxidized under the oxidation conditions to vanadium(V)–salen complex [$V^V(O_2)$ (**C**)]. The vanadium(V)–salen complex **C** attacks the C–H bond of cyclic hydrobenzimidazole **B** and dissociates a C–H bond, forming an alkyl radical intermediate [R· HOOV (**D**)], similar to the reported experiment for the oxidation of adamantane by a VO(acac)$_2$ [102]. Then the oxidative dehydrogenation of adduct **D** affords the desired 2-arylbenzimidazole, and the simultaneous generation of H_2O_2, as shown in Scheme 3.

H_2O_2 as efficient oxidant has been shown to catalyze the oxidation of some organic reactions [52, 53, 68, 103]. We thought that, in the presence of H_2O_2, the rate of this reaction might increases. As we expected, in the presence of H_2O_2 (1.0 mmol), benzaldehyde (1.0 mmol) and *o*-phenylenediamine (1.0 mmol) 5.0 mol% of vanadium (IV)–salen complex in 10 ml ethanol, the reaction time reduced. The mechanism for the enhancement in the rate of this reaction, in the presence of H_2O_2, can be described as follows. In the presence of H_2O_2, oxidation of **B** by vanadium(V) is enhanced because of the regeneration of vanadium(V) by H_2O_2 oxidizing vanadium(IV) [104]. The redox cycling between vanadium(IV)/vanadium(V) H_2O_2 also produces a highly reactive OH radical, which can then attack to **D**, as shown in Scheme 3.

Table 1 The condensation reaction of *o*-phenylenediamine (1.0 mmol) with benzaldehyde (1.0 mmol) using either VO–salen **1** and VCl_2–salen **2** as catalysts in ethanol at room temperature

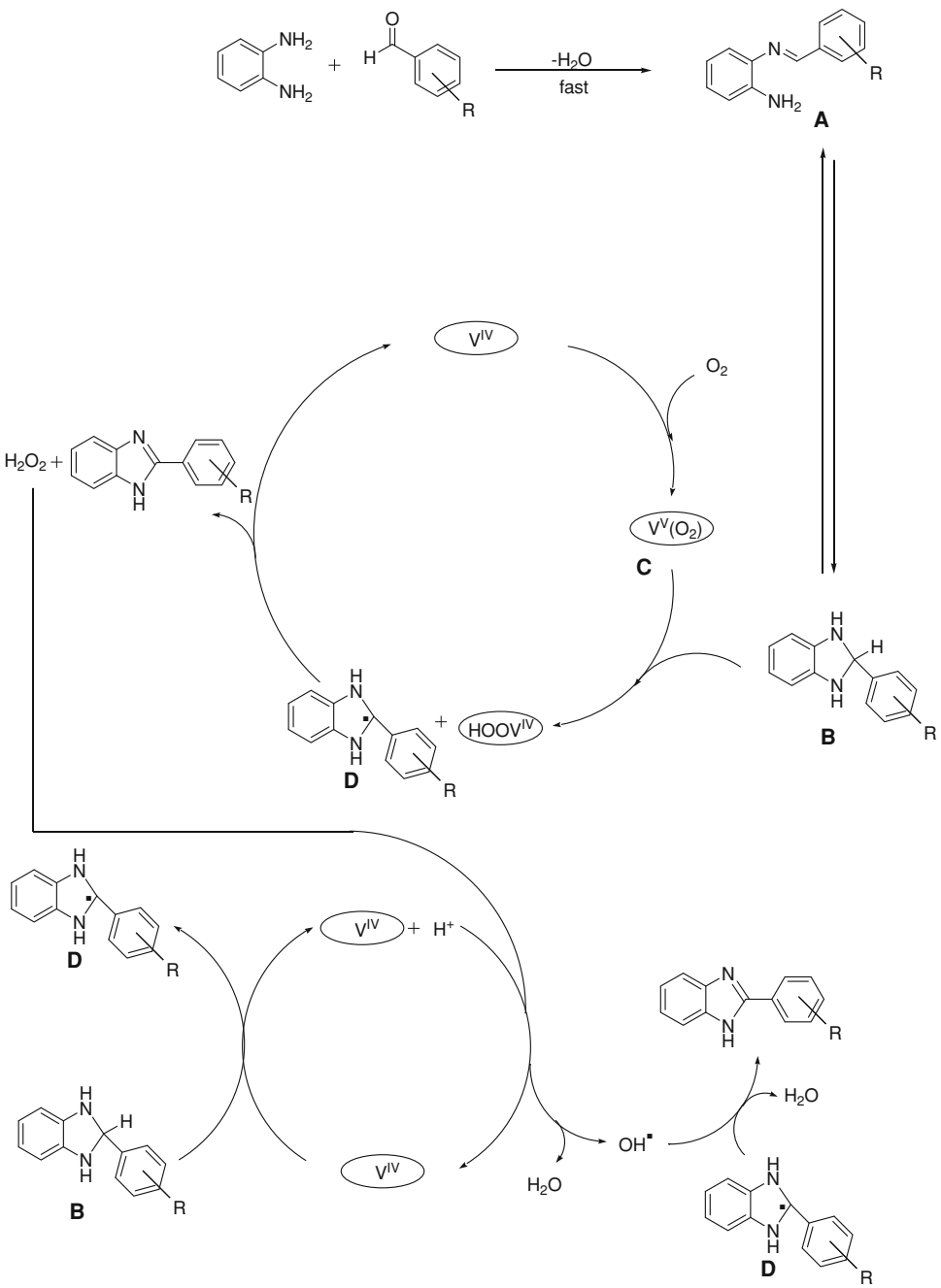
Entry	Catalyst	Catalyst (mol %)	Time (h)	Yield (%)[a]
1	**1**	5	2	89
2	**2**	5	2	93
3	–	–	12	<10
4	**2**	5	2	30[b]
5	**2**	3	2	61
6	**2**	4	2	75
7	**2**	10	2	93

[a] Isolated yield

[b] Operated under nitrogen atmosphere

Evidence related to the proposed mechanism:

To investigate the effect of oxygen on the oxidation state of vanadium–salen complex, the procedure was first followed for the synthesis of vanadium complex in both air atmosphere and under oxygen free environment such as nitrogen atmosphere. Then, to 5.0 ml of water suspension of the sample (0.1 g), synthesized under oxygen free atmosphere, ozone was bubbled with 5 ml min^{-1}. The TG analysis revealed that, in the synthesized vanadium complex, an ozone molecule was substituted with a chloride. This was evaluated based on the difference (1.3%) between the molecular weight of ozone (48 g mol^{-1}) and atomic weight of chloride (35.5 g mol^{-1}). Also, the Plato of the thermogram proved that ozone was acted as a good oxidizing agent for oxidation of V(IV) into V(V). Therefore, vanadium(V)–salen complex can be easily formed using oxidizing agents such as oxygen or ozone.



Scheme 3 The proposed mechanism for the vanadium(IV)–salen complex catalyzed the synthesis of 2-substituted benzimidazole derivatives

The synthesis of benzimidazole derivates in the presence of NaOH crystals lead to the decomposition of vanadium complex at higher temperature (228 °C) that was 43 °C higher than the result obtained in the thermogram of vanadium–salen complex. This difference also points to the formation of $NaOOV^{IV}$ as intermediate material during the synthesis of benzimidazole derivatives using vanadium–salen as catalyst.

To investigate more on the formation intermediate compounds during the catalytic activity of the catalyst, the electrochemical behaviors of both the ligand and the vanadium complex were investigated in detail as shown in Fig. 1.

According to the voltammograms the sharp peak positioned at 0.538 V is related to the conversional V(IV) complex into V(V), whereas the cathodic peak positioned at 0.485 V reveals to the reverse reduction process of vanadium complex. The difference between these two voltages is 53 mV, which reveals one electron exchange during the oxidation process of V(IV) complex. This shows that V with 5 oxidation number is considered as an intermediate during the catalytic activity of the catalyst during the synthesis of organic compounds.

In the next step, we expanded the catalytic system to the oxidative synthesis of benzothiazoles and benzoxazole

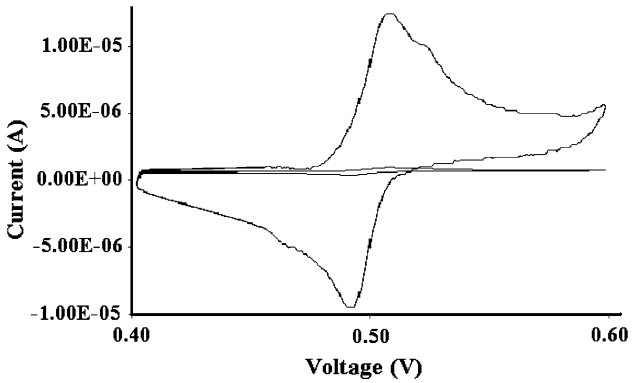


Fig. 1 Cyclic voltammograms of (A) free ligand (2×10^{-4} M) and complex (2×10^{-4} M) in EtOH (0.1 M TBTB) at glassy carbon working electrode at scan rate 50 mV s^{-1} under nitrogen atmosphere

using 2-aminothiophenol and 2-aminophenol, respectively, with aryl aldehydes as starting materials using VCl_2(salen) complex as the catalyst.

We examined the condensation reactions of benzaldehyde with 2-aminothiophenol (Scheme 4). Under the optimized reaction conditions, 2-aminothiophenol (1.0 mmol) and benzaldehyde (1.0 mmol) with VCl_2–salen complex (0.05 mmol) were taken up in ethanol, and the reaction mixture was stirred at room temperature. The reaction was completed after 3 h and 2-phenyl-1,3-benzothiazole was obtained in high yield (96%).

We have tried to develop this synthetic method for the preparation of benzoxazoles in the presence of VCl_2–salen complex as the catalyst in ethanol as solvent at room temperature, but it could not be applied for these compounds. Instead, during the research, we found that VCl_2–salen complex could catalyze the synthesis of benzoxazoles in xylene at 120 °C. Under the optimized reaction conditions, 2-aminophenol (1.0 mmol) and benzaldehyde (1.0 mmol) with VCl_2(salen) complex (0.05 mmol) was heated in xylene at 120 °C. The reaction was completed within 4 h and 2-phenyl-1,3-benzoxazole was obtained in excellent yield (95%) (Scheme 5).

Preparation of the heterogeneous supported catalyst:

One of the general trends in catalysis is to design systems that permit catalysts to be recycled and reused [63, 105, 106].

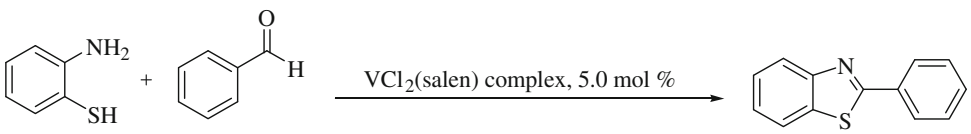
Since VCl_2–salen **2** proved to be the best catalyst among the vanadium–salens for the synthesis of 2-substitued benzimidazoles, benzothiazoles and benzoxazoles, we set out to prepare a new heterogeneous catalyst by a simple impregnation of VCl_2–salen **2** onto silica (3-aminopropyl functionalized silica gel) [107]. The route to the synthesis of the immobilized catalyst is shown in Scheme 7. First, 3-aminopropyl functionalized silica gel (1.0 g) and VCl_2–salen **2** (1.5 mmol) were added to CH_2Cl_2 under stirring at 25 °C and kept stirring for 24 h. The solid product was separated by centrifuging and washed several times with CH_2Cl_2. The solid product was then dried at 60 °C in vacuum and their vanadium nanoparticles were examined by an inductively coupled plasma (ICP) analyzer. To evaluate the quantity of vanadium nanoparticles, the supported catalyst was treated with concentrated HCl (5.0 M) and HNO_3 (5.0 M), followed by ICP analysis. The vanadium nanoparticles were determined to be 4.281% (w/w) (Scheme 6).

Characterization of vanadium complex supported on silica

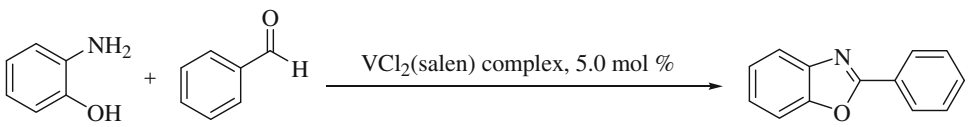
In this study, vanadium–salen complex in nano scale dimension was supported on silica substrate according to the proposed procedure.

Figure 2 shows the scanning electron microscopic (SEM) and atomic force micrograph (AFM) images of vanadium–salen nanoparticles, respectively. Good correlations were found between the average size evaluated for the vanadium nanoparticles based on AFM and SEM images. The voltage profile image (Fig. 2d) reveals that this process has capability to synthesize vanadium particles at nanoscale dimension.

Scheme 4 Synthesis of benzothiazole derivatives



Scheme 5 Synthesis of benzoxazole derivatives



Scheme 6 Preparation of immobilized VCl_2–salen catalyst with the linkage groups axially connected to vanadium atoms

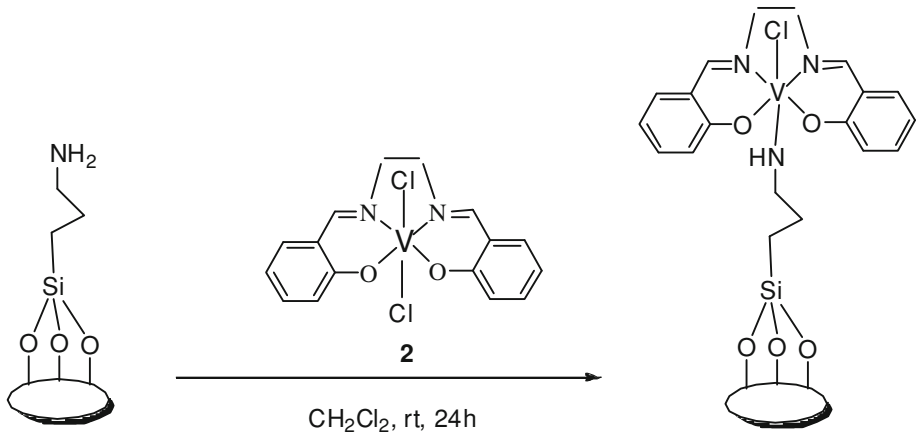
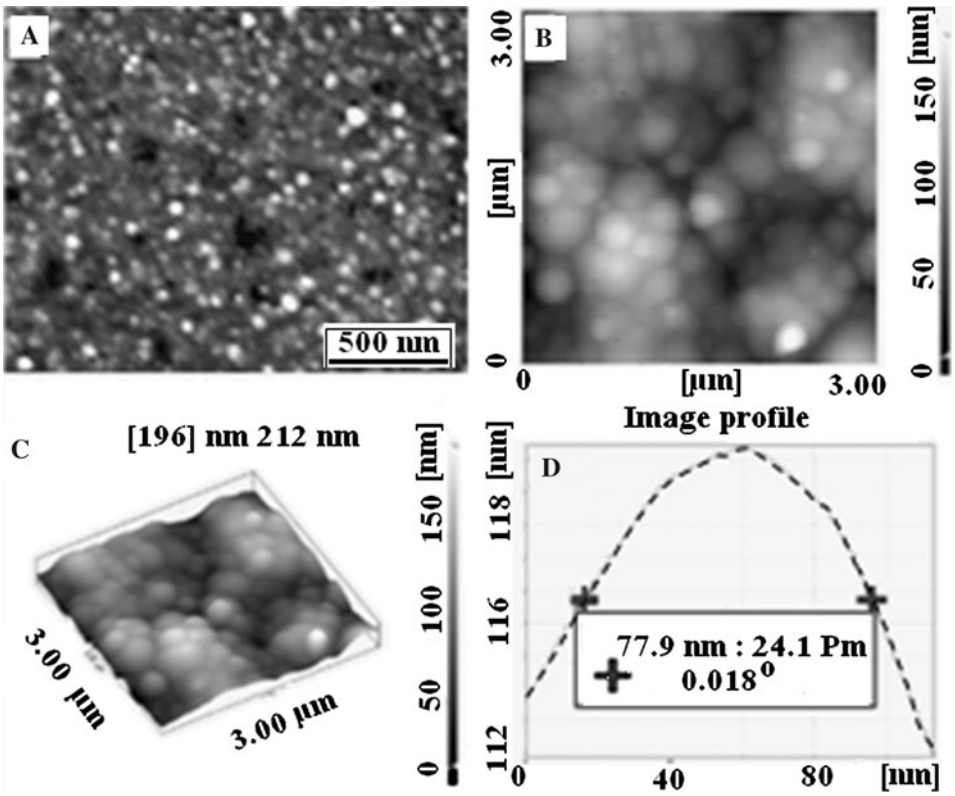


Fig. 2 **a** SEM image of vanadium–salen nanoparticles supported on silica. AFM images including: **b** two-dimensional, **c** three-dimensional and **d** voltage profile of vanadium–salen complex supported on silica



Also, the adsorption behavior of nitrogen on both silica and vanadium complex supported on silica based on thermogravimetric (TG) analysis results has been studied. Significant increase ($\sim$370 m^2 kg^{-1}) was estimated in the active surface area of silica substrate, when supported with vanadium complexes.

The thermal behavior of vanadium–salen complex on silica was also evaluated using the TG analysis. According to the thermogram, a significant decrease (11.2%) in the weight percentage of vanadium complex supported on silica at around 185 °C is related to the decomposition of vanadium–salen complex, whereas the decrease at around 820 °C is related to the decomposition of silica substrate in air atmosphere. Also, the last part (Plato) of the thermogram (7.6%) reveals the amounts of V_2O_5 formed according to the decomposition of vanadium complex.

Figure 3 shows the FT-IR spectrum of vanadium–salen complex on silica. Formation of vanadium–salen complex is approved based on the formation of V–O bond as revealed with accordance with the strong peaks positioned at $\sim$700 and 825 cm^{-1}, in the FT-IR spectrum. Also, the peak situated at $\sim$1,080 cm^{-1} is related to the formation of V–N during the supporting of the vanadium–salen complex on the modified silica [108–110].

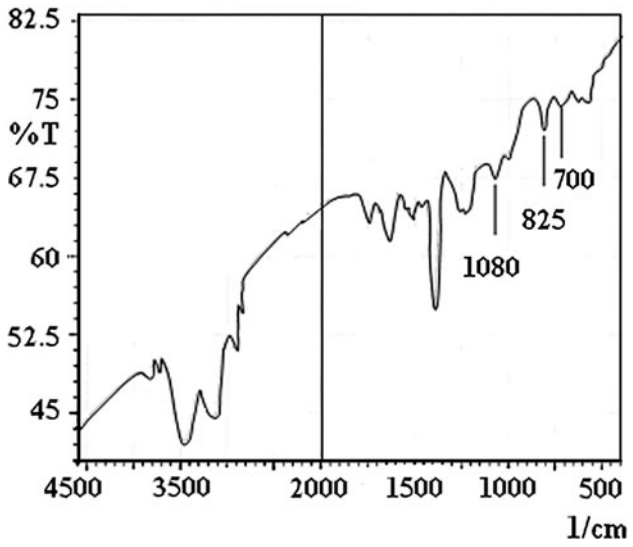


Fig. 3 FT-IR spectrum of vanadium–salen nanoparticles on silica

In this study, the amount of vanadium nanoparticles was evaluated using TG and ICP analyses. Based on the ICP results, the quantity of vanadium nanoparticles was evaluated to be 4.281%, whereas this value was ~4.3% based on the TG analysis. The small difference between ICP and TG analysis is probably related to the sample pretreatment needed for the analysis of vanadium silica sample with ICP spectrometer.

Figure 4 shows the smoothed XRD pattern on the vanadium–salen complex supported on activated silica. As clearly shown in Fig. 4, the strong peak at $2\theta = 11.9°$ is related to the activated silica. The effect of activation process is clearly revealed from the intensity of the peak. Also, the strong peaks at $2\theta = 11.9°$, 22.6°, 26.7°, 28.3°, 30.84°, 42.2°, 46.5°, 54.9°, and 60.7° are related to V(200), V(001), V(101), V(110), V(400), V(002), V(411), V(601) and (V412), respectively. In this experiment, the peak related to V(001) was investigated to estimate the theoretical average size of vanadium nanoparticles using Debye–Scherrer equation. For $\lambda = 1.504$ Å, this value was estimated to around 180 nm, which was in good agreement with the size observed on the SEM and AFM images.

A transmission electron microscopy (TEM, CM-10, Philips, 100 kV) was used for obtaining TEM images.

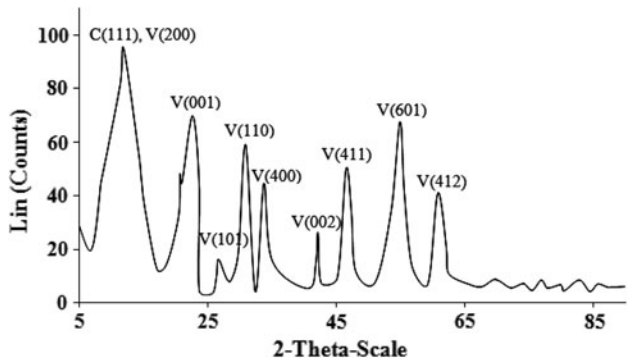


Fig. 4 Smoothed XRD pattern of vanadium–salen nanoparticles supported on silica

Homogeneous and heterogeneous catalytic benzimidazole, benzothiazole and benzoxazole synthesis

VCl_2–salen complex homogeneous and immobilized on a silica surface were tested in the catalytic synthesis of 2-substituted benzimidazoles, benzothiazoles and benzoxazoles in the presence of atmospheric oxygen as a *green* oxidant.

Supporting the VCl_2(salen) complex provided the chance of recovery of catalyst for the successive uses. The catalyst could be readily removed from the reaction mixture by simple centrifugation and be used repeatedly for several times without appreciable loss in activity.

The recovered immobilization of VCl_2(salen) complex was dried and used for another successive reaction run and the combined centrifuge was collected for product identification and quantitation. The catalytic activity of immobilized VCl_2(salen) complex remained largely unchanged even after five consecutive runs (Fig. 5).

Also, the same TEM image was observed (Fig. 6b) for the vanadium–salen nanoparticles supported on silica after synthesis by the proposed process and after at least five time use in the synthesis of organic reaction.

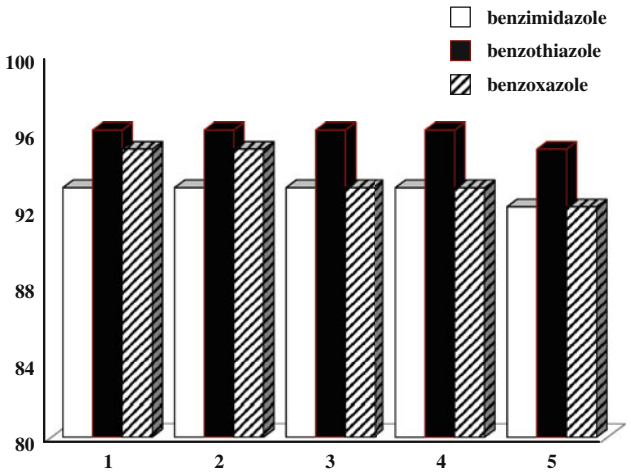


Fig. 5 Catalyst recyclability studies for 2-phenylbenzimidazole, 2-phenylbenzothiazole in ethanol at room temperature, and for 2-phenylbenzoxazole in xylene at 120 °C (time reaction for benzimidazoles, benzothiazoles and benzoxazole, respectively, are 2, 3 and 4 h)

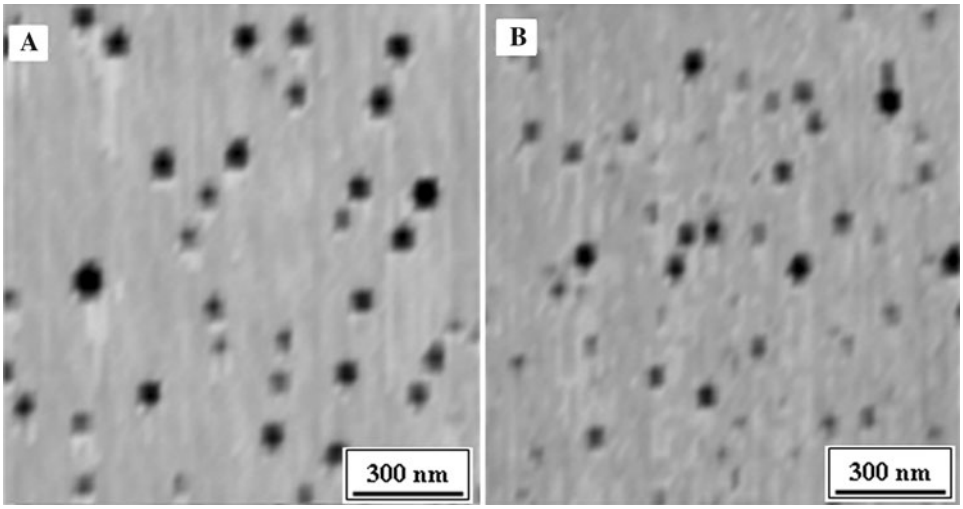
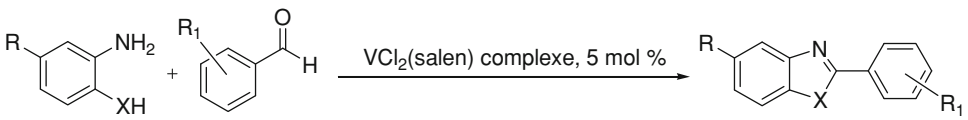


Fig. 6 TEM images of vanadium nanoparticles supported on silica **a** at initial time, **b** after at least five time use in the synthesis of organic reaction



X = NH, S, O

R = H, CH_3, COOH, PhCO, COOEt

Scheme 7 The condensation reaction of *o*-phenylendiamine, 2-aminothiophenol and 2-aminophenol with aryl aldehydes in the presence of homogeneous and heterogeneous catalysts

To check the leaching, we stirred the immobilized catalyst in EtOH at room temperature for 5 h. The immobilized catalyst was removed and the filtrate was used for the synthesis of benzimidazole under the described reaction conditions. In this case, no product was obtained after 2 h.

Finally, under the optimized conditions, the condensation of *o*-phenylenediamine, 2-aminothiophenol and 2-aminophenol with aryl aldehydes were carried out in the presence of homogeneous and heterogeneous catalysts in ethanol at room temperature for benzimidazoles and benzothiazoles, and in xylene at 120 °C for benzoxazoles (Scheme 7).

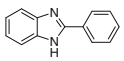
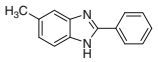
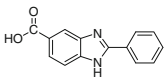
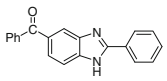
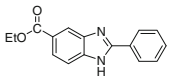
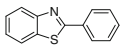
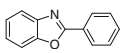
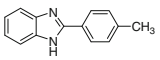
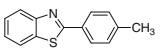
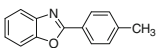
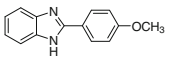
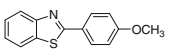
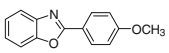
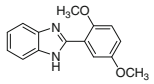
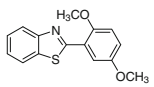
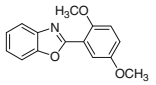
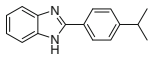
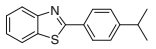
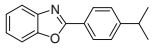
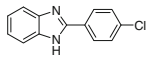
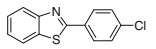
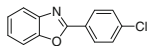
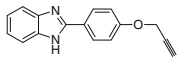
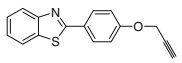
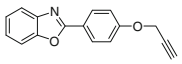
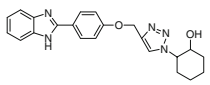
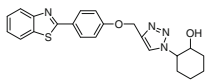
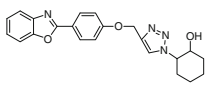
We studied the scope of the reaction by varying *o*-phenylendiamines, 2-aminothiophenol and 2-aminophenol for condensation with aryl aldehydes under the optimized condition and the results are shown in Table 2. In all cases, the reaction mixture was cleaned and carried out within 1–6 h. All products were characterized by IR, ^{1}H NMR, ^{13}C NMR and mass spectrometry.

As shown in Table 2, the presented method has the ability to tolerate other functional groups such as methyl, hydroxy, methoxy and halogen on the aryl aldehyde. Aliphatic aldehydes are not applicable for the synthesis of 2-alkylbenzimidazoles, 2-alkylbenzothiazoles and 2-alkylbenzoxazoles in the presented procedure. The reaction of 3,4-diaminotoluene, 3,4-diaminobenzoic acid, 3,4-diaminobenzophenone and ethyl 3,4-diaminobenzoate with benzaldehyde was also studied. All the substrates consistently afforded the reaction selectively to the corresponding benzimidazoles in excellent yields (Table 2, entries 2–5). Also, we have reported the synthesis of new triazole derivatives of benzimidazole, benzothiazole and benzoxazole (Table 2, entries 26–28).

To access the feasibility of applying this method on a preparative scale, we carried out the coupling of *o*-phenylenediamine with benzaldehyde in 50-mmol scale in the presence of the homogeneous and heterogeneous catalysts. As expected, the reaction proceeded smoothly, similar to the case in a smaller scale (Table 2, entry 1).

In conclusion, we have introduced a simple, mild and highly efficient method for the synthesis of 2-arylbenzimidazole and 2-arylbenzothiazole using catalytic amount (5.0 mol%) of vanadium(IV)–salen nanoparticles supported on silica as oxidant in ethanol under an atmospheric oxygen at room temperature and in xylene at 120 °C for 2-arylbenzoxazole. This catalyst can also be reused in the

Table 2 Synthesis of 2-arylbenzimidazoles, 2-arylbenzothiazoles and 2-arylbenzoxazole from various *o*-phenylendiamine, 2-aminothiophenol and 2-aminophenol (1.0 mmol) with aryl aldehydes (1.0 mmol) in the presence of homogeneous and heterogeneous VCl_2–salen catalyst (5.0 mol%) in ethanol at room temperature for benzimidazoles and benzothiazoles, and in xylene at 120 °C for benzoxazole

Entry	Product	Homogeneous catalyst		Heterogeneous catalyst	
		Time (h)	Yield (%)[a]	Time (h)	Yield (%)[a]
1		2	93	2	94
2		1.5	94	1.5	94
3		1	94	1	94
4		6	94	6	95
5		1.5	92	1.5	92
6		3	96	3	96
7		4	95	4	96
8		1.5	92	1.5	93
9		1.5	95	1.5	95
10		3	94	3	96
11		3	91	3	90
12		2.5	94	2.5	96
13		4	92	4	93
14		5	85	5	88
15		5	90	5	91
16		3	92	3	92
17		3.5	93	3.5	95
18		4	94	4	94
19		4	92	4	92
20		5.5	91	5.5	90
21		6	90	6	92
22		4	94	4	93
23		1.5	94	1.5	94
24		2	90	2	91
25		4	90	4	92
26		2	91	2	90
27		2.5	89	2.5	89
28		4	89	4	90

[a] Isolated yield

oxidation of 2-substituted benzimidazoles, benzothiazoles and benzoxazoles for several times. Hence, we believe that it will find wide application in organic synthesis as well as in industry.

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