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ORIGINAL ARTICLE

V-CaHAp as a recyclable catalyst for the green multicomponent synthesis of benzochromenes

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Abstract A simple and efficient one-pot method has been developed for the synthesis of benzochromenes (**4a–k**) using V-CaHAp as a heterogeneous catalyst by the condensation of aldehydes, β-naphthol and malononitrile in ethanol as solvent at room temperature for 20 min. The reaction, with this catalyst was carried out under mild reaction conditions with very good to excellent yields (89–98%). The material can be recycled very easily and reused for at least 6 runs without substantial loss in activity, which makes this methodology environmentally benign. We achieved a feasible and cost-effective synthesis by using non-toxic materials and minimal catalyst which is easy to handle.

1. Introduction

Multicomponent Reactions (MCRs) are reactions where more than two reactants put together in a single step form a product containing all the important parts of the starting reactants (Horton et al., 2003; Cioc et al., 2014; Pirrung and Sarma, 2004). Hence, all the reactants, reagents and catalyst react sequentially to form the anticipated product which normally requires a simple and direct method. MCR addresses the principles of synthetic efficiency and reaction design. These types of reactions are flexible, convergent and atom efficient in nature, which makes them eco-friendly and sustainable (Pirrung and Sarma, 2004; Slobbe et al., 2012; Domling et al., 2012). Moreover, diversity can be obtained easily by tuning the reacting components. Even more eco-friendly reactions are achievable if they are promoted by heterogeneous catalyst. MCRs are important and are applied in pharmaceuticals, agrochemicals and among other applications (Slobbe et al., 2012; Domling et al., 2012).

Heterogeneous catalysis has been in use since the start of organic chemistry (Marc-Olivier and Chao-Jun, 2012; Herrmann and Kohlpaintner, 1993). The activity and selectivity of these catalysts are enhanced by the surface of a support. Hence, the effective surface area of the reagent is increased significantly. The catalyst can be reused

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when recycled, although after some time it gets deactivated depending on its half-life (Maddila et al., 2015a, 2015b, 2015c). The main advantages of heterogeneous catalysts are the relative ease of catalyst separation from the product, recyclability, non-corrosiveness and tolerance of extreme operating conditions which makes them environmentally friendly.

Hydroxyapatites (HAps) have gained an ample attention due to their high chemical stability, cation exchange ability and adsorption capacity (Mori et al., 2004; Kaneda et al., 2006). HAps materials have both acidic and basic sites in crystal lattice and they are anticipated to perform as an acidic/basic catalyst (Tsuchida et al., 2008). HAps and supported materials are of significance due to their potential effectiveness in organic transformations, water purification, fertilizer production and effectiveness as controlled drug delivery systems in medical treatments (Koutsopoulos, 2002). Herein, we describe the synthesis and characterization of new classes of hydroxyapatite-bound transition metal catalysts and their prominent catalytic performances for the synthesis of heterocyclic molecules and carbon–carbon bond-forming reactions.

Chromenes are an important group of heterocyclic compounds due to their significant functions in nature and their pharmacological applications (Conti and Desideri, 2009). Their derivatives are most valuable pharmacologic compounds possessing various significant biological properties such as anti-microbial (Kidwai et al., 2005), anticancer (Kheirollahi et al., 2014), anti-inflammatory (Dong-Oh et al., 2007), antiviral and central nervous system activities (Smith et al., 1998). They can also be used in industry as antioxidants (Ahmed et al., 2012; Koneni et al., 2008; Maddila et al., 2015c). Because of their importance, the synthesis of substituted chromenes has become a focus of synthetic organic chemistry. Some of the protocols have been developed for the synthesis of benzochromene derivatives via the condensation of benzaldehydes, β-naphthol and malononitrile with the use of various catalysts, such as ceric ammonium nitrate (CAN) (Kumar et al., 2010), disodium hydrogen phosphate (Na_2HPO_4) (Meng et al., 2011), Mg/Al Hydrotalcite (Surpur et al., 2009), MgO (Kumar et al., 2007), cetyltrimethylammonium bromide (Jin et al., 2004), Tetrabutylammonium bromide (TBABr) (Paesha and Jayashankara, 2007), I_2/K_2CO_3 (Ren and Cai, 2008), Preyssler heteropolyacid ($H_{14}[NaP_5W_{30}O_{110}]$) (Heravi et al., 2007), thiourea dioxide ($N_2H_4CSO_2$) (Verma and Jain, 2012), $[Cu(bpdo)_2$š$2H_2O]^{2+}$/SBA-15 (Malakooti et al., 2013), Poly(4-vinylpyridine) (PVPy) (Albadi et al., 2013), Silica tungstic acid (STA) (Farahi et al., 2014), Nanozeolite clinoptilolite (Baghbanian et al., 2013), Potassium phthalimide (PPI) (Kiyani and Ghorbani, 2014), and ionic liquids (Kai et al., 2009; Balalaie et al., 2008). However, many of these methodologies are associated with one or more disadvantages such as expensive reagents, drastic reaction conditions, low yields, tedious work-up procedures, and co-occurrence of several side reactions. Therefore, a more effective and environmentally friendly process is needed.

In continuation of our interest in environment friendly protocols for synthesizing different moiety of heterocyclic derivatives in good yields (Maddila and Jonnalagadda, 2013a; Maddila et al., 2013b, 2013c, 2015d, 2015e, 2015f), we herein report a one-pot reaction of aldehydes, β-naphthol and malononitrile in ethanol as solvent in the presence of V-CaHAp as a heterogeneous catalyst by the condensation for the synthesis of benzochromenes derivatives in excellent yields.

2. Materials and methods

2.1. Preparation of catalyst

Hydroxyapatite (HAp) was synthesized using a co-precipitation method (Dasireddy et al., 2012, 2013). A solution of $(NH_4)_2HPO_4$ (2.3 g), (1 mmol) (Aldrich, 98.5%) was diluted with 200 mL double distilled water and brought to basic (pH 11) using dilute ammonia solution. Similarly, a calcium nitrate tetrahydrate, $Ca(NO_3)_2$š$4H_2O$ (11.9 g), (0.175 mmol) (Aldrich, 99%) solution was prepared and adjusted to a pH 11. This solution was diluted to 200 mL using double distilled water. The $(NH_4)_2HPO_4$ solution was then added dropwise to the $Ca(NO_3)_2$š$4H_2O$ solution with constant stirring at room temperature (R.T.) over a period of 30 min. The reaction mixture was maintained at pH 11 by using dilute ammonia. The resultant white gelatinous precipitate was heated to and maintained at 90 °C for 1 h and then allowed to cool to room temperature. Thereafter, the precipitate was filtered and washed repeatedly with water until the filtrate was neutral, thus having ensured the removal of excess dilute ammonia. The HAp was then dried in an oven overnight at 100 °C and thereafter, calcined at 550 °C. V_2O_5 was synthesized by the thermal decomposition of NH_4VO_3 at 450 °C for 5 h in air. The loading of 1, 2.5 and 5 wt% vanadia on the Ca-HAp supports was performed by wet impregnation method. The preferred amounts of V_2O_5 were deferred in 30 mL of distilled water and added to the Ca-HAp support. Water was removed by evaporation with constant stirring at 90–100 °C. The solid was dried overnight at 110 °C and later calcinated at 550 °C at 550 °C for 5 h.

2.2. Characterization of catalysts

The different metal oxide phases in the catalysts were observed using powder X-ray diffraction (XRD) performed on a Bruker D8 Advance instrument, equipped with an Anton Paar XRK 900 reaction chamber, a TCU 750 temperature control unit and a Cu Kα radiation source with a wavelength of 1.5406 nm at 40 kV and 40 mA. Diffractograms were recorded over the range 15–90° with a step size of 0.5 per second. The Brunauer–Emmett–Teller (BET) surface area, total pore volume and average pore size were measured using a Micrometrics Tristar II surface area and porosity analyzer. Prior to the analysis, the powdered samples (~0.180 g) were degassed under N_2 for 12 h at 200 °C using a Micrometrics Flow Prep 060 instrument. Textural properties of catalyst samples were measured by N_2 adsorption–desorption isotherms obtained at −196 °C. The SEM measurements were carried out using a JEOL JSM-6100 microscope equipped with an energy-dispersive X-ray analyzer (EDX). The images were taken with an emission current of 100 μA by a Tungsten (W) filament and an accelerator voltage of 12 kV. The catalysts were secured onto brass stubs with carbon conductive tape, sputter coated with gold and viewed in JEOL JSM-6100 microscope. The TEM images were viewed on a Jeol JEM-1010 electron microscope. The images were captured and analyzed by using iTEM software. The particle sizes obtained were the average particle size of 40–60 particles and the standard deviation is done in order to determine the range of the particle sizes.

2.3. Materials, methods and instruments

All the chemicals and reagents (Aldrich) required for the reaction were of analytical grade and were used without any further purification. Bruker AMX 400 MHz NMR spectrometer was used to record the ^1H NMR, ^{13}C NMR and ^{15}N NMR spectral values. The DMSO-d_6 solution was utilized for this while TMS served as the internal standard for reporting all the chemical shifts in δ (ppm). HRMS was obtained on a Bruker 7-tesla FT-ICR MS equipped with an ESI source.

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The FT-IR spectrum for the samples was recorded using a Perkin Elmer Perkin Elmer Precisely 100 FT-IR spectrometer at the 400–4000 cm^{-1} area. Purity of all the reaction products was confirmed by TLC using aluminum plates coated with silica gel (Merck Kieselgel 60 F254).

2.4. General procedure for the synthesis of benzochromene

A mixture of β-naphthol (1 mmol), benzaldehyde (1 mmol), and malononitrile (1 mmol) was dissolved in ethanol (10 ml), VCaHAp (30 mg) catalyst was added at room temperature and the reaction mixture was stirred continuously for 20 min. TLC was performed to observe the complete consumption of starting material in the reaction mixture (Scheme 1). A crude product was obtained upon filtering the reaction mass and subsequent evaporation under reduced pressure. Further, this crude was recrystallized by ethanol to obtain pure product (**4a–k**). The filtered catalyst was washed with ethanol and dried. The recovered catalyst was reused for six successive runs.

2.5. Physical data

2.5.1. 3-Amino-1-(2-methoxyphenyl)-1H-benzo[f]chromene-2-carbonitrile (4a)

^{1}H NMR (400 MHz, DMSO-d_6) δ = 3.88 (s, 3H, OCH_3), 5.59 (s, 1H, CH), 6.77 (t, J = 7.3 Hz, 1H, ArH), 6.84 (d, J = 6.6 Hz, 1H, ArH), 6.87 (s, 2H, NH_2), 7.02 (d, J = 8.2 Hz, 1H, ArH), 7.14 (t, J = 1.4 Hz, 1H, ArH), 7.31 (d, J = 8.9 Hz, 1H, ArH), 7.37–7.45 (m, 2H, ArH) 7.73 (d, J = 8.1 Hz, 1H, ArH), 7.90 (d, J = 9.0 Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): 160.1 (C–NH_2), 155.6, 147.1, 133.6, 130.6, 130.3, 129.2, 128.5, 128.4, 127.9, 127.1, 124.8, 122.9, 121.0, 120.4, 116.7, 115.8, 111.7, 56.9 (C–CN), 55.9 (MeO), 31.5 (CH); ^{15}N NMR (40.55 MHz, DMSO-d_6) δ 6.87 (s, 2H, NH_2); FT-IR (KBr, cm^{-1}): 3434, 3343, 2962, 2188, 1645, 1509, 1459, 1397; HRMS of $[C_{21}H_{16}N_2O_2-H]^+$ (m/z): 327.1133; Calcd.: 327.1134.

2.5.2. 3-Amino-1-(4-methoxyphenyl)-1H-benzo[f]chromene-2-carbonitrile (4b)

^{1}H NMR (400 MHz, DMSO-d_6) δ = 3.65 (s, 3H, OCH_3), 5.22 (s, 1H, CH), 6.80 (d, J = 8.6 Hz, 2H, ArH), 6.91 (s, 2H, NH_2), 7.10 (t, J = 9.9 Hz, 4H, ArH), 7.31 (t, J = 6.7 Hz, 2H, ArH), 7.40–7.43 (m, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): 159.5 (C–NH_2), 157.9, 146.6, 137.8, 131.7, 129.3, 128.4, 127.9, 126.9, 124.8, 123.6, 120.5, 116.7, 115.8, 114.4, 113.9, 58.1 (C–CN), 54.9 (MeO), 37.2 (CH); ^{15}N NMR (40.55 MHz, DMSO-d_6) δ 6.91 (s, 2H, NH_2); FT-IR (KBr, cm^{-1}): 3316, 2186, 1692, 1591, 1406, 1343; HRMS of $[C_{21}H_{16}N_2O_2-H]^+$ (m/z): 327.1123; Calcd.: 327.1124.

2.5.3. 3-Amino-1-(4-bromophenyl)-1H-benzo[f]chromene-2-carbonitrile (4c)

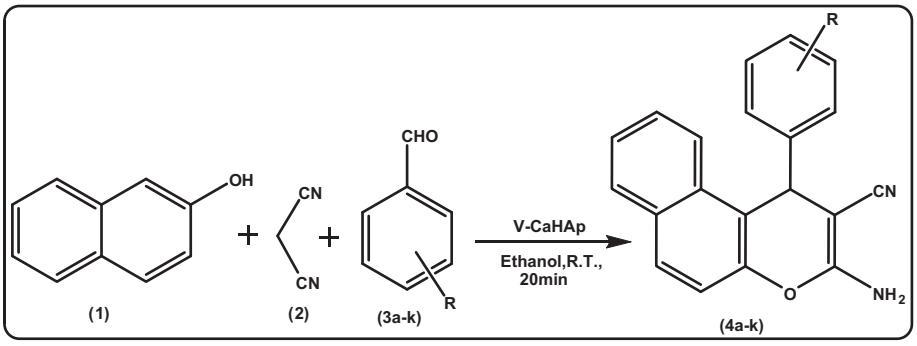
^{1}H NMR (400 MHz, DMSO-d_6) δ = 5.33 (s, 1H, CH), 7.02 (s, 2H, NH_2), 7.14 (d, J = 8.4 Hz, 2H, ArH), 7.33(d, J = 9.0 Hz, 1H, ArH), 7.43 (t, J = 8.4 Hz, 3H, ArH), 7.73–7.76 (m, 1H, ArH), 7.80 (d, J = 7.7 Hz, 1H, ArH) 7.90–7.95 (m, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): 159.6 (C–NH_2), 155.2, 146.7, 145.0, 131.5, 130.7, 129.1, 124.9, 123.4, 122.5, 119.6, 116.7, 115.0, 108.6, 57.3 (C–CN), 37.3 (CH); ^{15}N NMR (40.55 MHz, DMSO-d_6) δ 7.02 (s, 2H, NH_2); FT-IR (KBr, cm^{-1}): 3324, 2189, 1649, 1584, 1403, 1231; HRMS of $[C_{20}H_{13}BrN_2O-2H]^+$ (m/z): 374.1139; Calcd.: 374.1144.

2.5.4. 3-Amino-1-(2,5-dimethoxyphenyl)-1H-benzo[f]chromene-2-carbonitrile (4d)

^{1}H NMR (400 MHz, DMSO-d_6) δ = 3.53 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 5.55 (s, 1H, CH), 6.36 (s, 1H, ArH), 6.70 (d, J = 6.4 Hz, 1H, ArH), 6.90 (s, 2H, NH_2), 6.95 (d, J = 8.6 Hz, 1H, ArH), 7.31 (d, J = 8.5 Hz, 1H, ArH), 7.40–7.45 (m, 2H, ArH), 7.76 (d, J = 7.3 Hz, 1H, ArH), 7.88 (s, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): 160.1 (C–NH_2), 153.3, 149.9, 147.0, 134.8, 130.6, 130.2, 129.1, 128.4, 127.1, 124.8, 122.9, 120.3, 116.6, 115.7, 115.0, 112.9, 111.5, 56.8 (C–CN), 56.6 (MeO), 55.0 (MeO), 31.7 (CH); ^{15}N NMR (40.55 MHz, DMSO-d_6) δ 6.90 (s, 2H, NH_2); FT-IR (KBr, cm^{-1}): 3444, 3331, 2832, 2188, 1666, 1590, 1406, 1218; HRMS of $[C_{22}H_{18}N_2O_3-H]^+$ (m/z): 357.1169; Calcd.: 357.1168.

2.5.5. 3-Amino-1-(2,3-dimethoxyphenyl)-1H-benzo[f]chromene-2-carbonitrile (4e)

^{1}H NMR (400 MHz, DMSO-d_6) δ = 3.75 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 5.48 (s, 1H, CH), 6.60 (d, J = 7.4 Hz 1H, ArH), 6.81 (d, J = 7.3 Hz, 1H, ArH), 6.89 (t, J = 7.9 Hz, 1H, ArH), 6.97 (s, 2H, NH_2), 7.31 (d, J = 8.9 Hz, 1H, ArH), 7.37–7.46 (m, 2H, ArH), 7.86–7.90 (m, 3H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): 160.1 (C–NH_2), 152.1, 146.7, 145.0, 138.4, 130.5, 130.3, 129.1, 128.3, 127.0, 124.8, 124.2, 123.0, 120.8, 120.6, 116.7, 116.1, 111.0, 60.7 (C–CN), 57.0 (MeO),



Scheme 1 Synthesis of benzochromene derivatives.

55.4 (MeO), 32.5 (CH); ^{15}N NMR (40.55 MHz, DMSO-d_6) δ 6.97 (s, 2H, NH_2); FT-IR (KBr, cm^{-1}): 3463, 3183, 2939, 2200, 1668, 1586, 1409, 1234. HRMS of $[C_{22}H_{18}N_2O_3-H]^+$ (m/z): 357.1046; Calcd.: 357.1042.

2.5.6. 3-Amino-1-(2,4-dimethoxyphenyl)-1H-benzo[f] chromene-2-carbonitrile (4f)

^{1}H NMR (400 MHz, DMSO-d_6) δ = 3.65 (s, 3H, OCH_3), 3.66 (s, 3H, OCH_3), 5.23 (s, 1H, CH), 6.58 (dd, J = 8.3 Hz, 7.6 Hz, 1H, CH), 6.78 (d, J = 8.3 Hz, 1H, ArH), 6.88 (d, J = 1.9 Hz, 1H, ArH), 6.93 (s, 2H, NH_2), 7.09 (d, J = 8.5 Hz, 1H, ArH), 7.40–7.45 (m, 2H, ArH), 7.76–7.89 (m, 3H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): 159.5 (C–NH_2), 155.2, 148.5, 147.4, 146.6, 138.3, 134.5, 130.7, 130.2, 126.0, 125.9, 124.8, 116.7, 115.7, 112.0, 111.0, 108.5, 58.0 (C–CN), 55.4 (MeO), 55.3 (MeO), 37.5 (CH); ^{15}N NMR (40.55 MHz, DMSO-d_6) δ 6.93 (s, 2H, NH_2); FT-IR (KBr, cm^{-1}): 3331, 2938, 2186, 1650, 1509, 1403, 1231; HRMS of $[C_{22}H_{18}N_2O_3-H]^+$ (m/z): 357.1154; Calcd.: 357.1162. HRMS of $[C_{22}H_{18}N_2O_3-H]^+$ (m/z): 357.1441; Calcd.: 357.1438.

2.5.7. 3-Amino-1-(3-hydroxyphenyl)-1H-benzo[f]chromene-2-carbonitrile (4g)

^{1}H NMR (400 MHz, DMSO-d_6) δ = 5.23 (s, 1H, CH), 6.54 (t, J = 14.1 Hz, 2H, ArH), 6.67 (d, J = 7.4 Hz, 1H, ArH), 6.96 (s, 2H, NH_2), 7.05 (t, J = 15.4 Hz, 1H, ArH), 7.33 (d, J = 8.9 Hz, 1H, ArH), 7.39–746 (m, 2H, ArH), 7.83 (d, J = 7.9 Hz, 1H, ArH), 7.91 (t, J = 8.7 Hz, 2H, ArH), 9.33 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): 159.6 (C–NH_2), 157.5, 147.0, 146.7, 130.7, 130.2, 129.5, 129.3, 128.3, 127.0, 124.8, 123.5, 120.5, 116.7, 115.7, 113.7, 113.6, 57.9 (C–CN), 38.0 (CH); ^{15}N NMR (40.55 MHz, DMSO-d_6) δ 6.96 (s, 2H, NH_2); FT-IR (KBr, cm^{-1}): 3449, 3353, 2169, 1638, 1584, 1409, 1231; HRMS of $[C_{20}H_{14}N_2O_2-H]^+$ (m/z): 313.0880; Calcd.: 313.0885.

2.5.8. 3-Amino-1-(2-chlorophenyl)-1H-benzo[f]chromene-2-carbonitrile (4h)

^{1}H NMR (400 MHz, DMSO-d_6) δ = 5.70 (s, 1H, CH), 6.98 (s, 1H, ArH), 7.05 (s, 2H, NH_2), 7.17 (t, J = 3.1 Hz, 2H, ArH), 7.34 (d, J = 8.8 Hz, 1H, ArH), 7.39–7.48 (m, 3H, ArH) 7.62 (d, J = 8.1 Hz, 1H, ArH) 7.91–7.96 (m, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): 159.8 (C–NH_2), 147.1, 142.5, 131.0, 130.0, 129.8, 129.5, 128.4, 128.1, 127.4, 125.0, 122.6, 119.8, 116.7, 114.7, 56.1 (C–CN), 35.0 (CH); ^{15}N NMR (40.55 MHz, DMSO-d_6) δ 7.05 (s, 2H, NH_2); FT-IR (KBr, cm^{-1}): 3457, 33,238, 2178, 1655, 1590, 1408, 1219; HRMS of $[C_{20}H_{13}ClN_2O-H]^+$ (m/z): 331.1089; Calcd.: 331.1093.

2.5.9. 3-Amino-1-(4-chlorophenyl)-1H-benzo[f]chromene-2-carbonitrile (4i)

^{1}H NMR (400 MHz, DMSO-d_6) δ = 5.32 (s, 1H, CH), 7.02 (s, 2H, NH_2), 7.19 (d, J = 8.4 Hz, 2H, ArH), 7.28–7.35 (m, 3H, ArH), 7.38–7.43 (m, 2H, ArH), 7.78 (d, J = 7.8 Hz, 1H, ArH), 7.88–7.93 (m, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): 159.6 (C–NH_2), 146.7, 144.5, 131.1, 130.7, 129.9, 129.6, 128.7, 128.6, 128.4, 127.1, 124.9, 123.4, 120.3, 118.2, 116.7, 57.4 (C–CN), 37.3 (CH); ^{15}N NMR (40.55 MHz, DMSO-d_6) δ 7.02 (s, 2H, NH_2); FT-IR (KBr, cm^{-1}): 3408, 3323, 2193, 1641, 1590, 1402, 1232. HRMS of $[C_{20}H_{13}ClN_2O-H]^+$ (m/z): 331.1210; Calcd.: 331.1208.

2.5.10. 3-Amino-1-(2-fluorophenyl)-1H-benzo[f]chromene-2-carbonitrile (4j)

^{1}H NMR (400 MHz, DMSO-d_6) δ = 5.52 (s, 1H, CH), 7.05–7.09 (m, 3H, ArH & NH_2), 7.13–7.20 (m, 3H, ArH), 7.32 (d, J = 8.9 Hz, 1H, ArH), 7.39–7.48 (m, 2H, ArH), 7.74 (d, J = 8.3 Hz, 1H, ArH), 7.92 (t, J = 9.2 Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): 160.0 (C–NH_2), 158.1, 147.0, 131.9, 131.8, 130.6, 129.9, 129.7, 129.6, 128.9, 128.8, 127.2, 124.9, 122,6, 120.2, 117.8, 115.5, 114.2, 55.9 (C–CN), 32.4 (CH); ^{15}N NMR (40.55 MHz, DMSO-d_6) δ 7.05 (s, 2H, NH_2); FT-IR (KBr, cm^{-1}): 3438, 3341, 2181, 1637, 1588, 1412, 1236; HRMS of $[C_{20}H_{13}FN_2O-H]^+$ (m/z): 315.0952; Calcd.: 315.0957.

2.5.11. 3-Amino-1-(4-ethylphenyl)-1H-benzo[f]chromene-2-carbonitrile (4k)

^{1}H NMR (400 MHz, DMSO-d_6) δ = 1.09 (t, J = 7.3 Hz, 3H, CH_3), 2.47 (t, J = 7.2 Hz, 2H, CH_2), 5.24 (s, 1H, CH), 6.93 (s, 2H, NH_2), 7.08 (s, 4H, ArH), 7.33 (d, J = 8.8 Hz, 1H, ArH), 7.41 (t, J = 6.2 Hz, 2H, ArH); 7.84 (d, J = 7.7 Hz, 1H, ArH), 7.90 (t, J = 8.6 Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): 159.6 (C–NH_2), 146.2, 143.0, 141.9, 130.7, 130.1, 129.3, 128.0, 127.4, 127.0, 126.8, 126.0, 125.9, 124.8, 123.5, 122.5, 120.5, 116.7, 115.8, 58.0 (C–CN), 37.6 (CH), 27.6 (CH_2), 15.3 (CH_3); ^{15}N NMR (40.55 MHz, DMSO-d_6) δ 6.93 (s, 2H, NH_2); FT-IR (KBr, cm^{-1}): 3423, 3321, 2189, 1649, 1491, 1403, 1232; HRMS of $[C_{22}H_{18}N_2O-H]^+$ (m/z): 325.0929; Calcd.: 325.0932.

2.5.12. 3-Amino-4-(2-methoxyphenyl)-4H-benzo[h]chromene-2-carbonitrile (5a)

^{1}H NMR (400 MHz, DMSO-d_6) δ = 3.78 (s, 3H, OMe), 5.24 (s, 1H, CH), 6.87 (d, 1H, J = 7.1 Hz, ArH), 6.99 (s, 2H, NH_2), 7.01–7.20 (m, 4H, ArH), 7.53–7.60 (m, 3H, ArH), 7.84 (d, J = 7.8 Hz, 1H, ArH), 8.24 (d, J = 8.0 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): 160.8 (C–NH_2), 156.3, 142.9, 133.1, 132.5, 128.9, 128.2, 126.5, 125.7, 123.7, 120.6, 118.0, 111.5, 55.6 (C–CN), 55.3 (MeO), 34.3 (CH); ^{15}N NMR (40.55 MHz, DMSO-d_6) δ 6.99 (s, 2H, NH_2); FT-IR (KBr, cm^{-1}): 3420, 3314, 2192, 1644, 1494, 1400, 1235; HRMS of $[C_{21}H_{16}N_2O_2-H]^+$ (m/z): 327.1400; Calcd.: 327.1402.

2.5.13. 2-Amino-4-(4-bromophenyl)-7-hydroxy-4H-chromene-3-carbonitrile (6a)

^{1}H NMR (400 MHz, DMSO-d_6) δ = 4.64 (s, 1H, CH), 6.40 (d, 1H, J = 2.3 Hz, ArH), 6.49 (dd, 1H, J = 2.3 Hz, 8.3 Hz, ArH), 6.77 (d, 1H, J = 8.4 Hz, ArH), 6.89 (s, 2H, NH_2), 7.12 (d, 2H, J = 8.3 Hz, ArH), 7.49 (d, 2H, J = 8.3 Hz, ArH), 9.74 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): 160.2 (C–NH_2), 157.1, 148.7, 145.7, 131.4, 129.6, 120.4, 119.7, 113.6, 112.4, 102.2, 55.7 (C–CN), 36.9 (CH); ^{15}N NMR (40.55 MHz, DMSO-d_6) δ 6.89 (s, 2H, NH_2); FT-IR (KBr, cm^{-1}): 3470, 3307, 2189, 1635, 1505, 1397, 1151; HRMS of $[C_{16}H_{11}BrN_2O_2-2H]^+$ (m/z): 340.0512; Calcd.: 340.0515.

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2.5.14. 2-Amino-4-(4-hydroxyphenyl)-7-hydroxy-4H-chromene-3-carbonitrile (6b)

^{1}H NMR (400 MHz, DMSO-d$_6$) δ = 4.48 (s, 1H, CH), 6.37 (d, 1H, J = 2.0 Hz, ArH), 6.47 (dd, 1H, J = 2.1 Hz, 8.40 Hz, ArH), 6.65–6.75 (m, 5H, ArH & NH_2), 6.94 (d, 2H, J = 8.3 Hz, ArH), 9.27 (s, 1H, OH), 9.65 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): 160.0 (C–NH_2), 156.8, 155.9, 148.7, 136.7, 129.8, 128.3, 120.7, 115.1, 114.2, 112.2, 102.0, 56.7 (C–CN), 38.0 (CH); ^{15}N NMR (40.55 MHz, DMSO-d$_6$) δ 6.75 (s, 2H, NH_2); FT-IR (KBr, cm^{-1}): 3478, 3348, 2191, 1647, 1505, 1403, 1149; HRMS of $[C_{16}H_{12}N_2O_3-H]^+$ (m/z): 279.0058; Calcd.: 279.0055.

2.5.15. 3-Amino-4-(4-bromophenyl)-4H-pyrano[3,2-h] quinoline-2-carbonitrile (7a)

^{1}H NMR (400 MHz, DMSO-d$_6$) δ = 4.99 (s, 1H, CH), 7.18–7.24 (m, 5H, ArH & NH_2), 7.51–7.65 (m, 4H, ArH), 8.35 (dd, 1H, J = 8.3, 1.4 Hz, ArH), 8.94 (dd, 1H, J = 8.3, 1.4 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): 160.2 (C–NH_2), 150.2, 144.9, 142.9, 137.4, 136.0, 131.6, 129.9, 127.7, 126.7, 123.7, 122.2, 121.3, 120.2, 120.1, 55.5 (C–CN), 39.5 (CH); ^{15}N NMR (40.55 MHz, DMSO-d$_6$) δ 7.21 (s, 2H, NH_2); FT-IR (KBr, cm^{-1}): 3299, 3173, 2193, 1655, 1485, 1401, 1113; HRMS of $[C_{19}H_{12}BrN_3O-2H]^+$ (m/z): 375.1108; Calcd.: 375.1106.

2.5.16. 3-Amino-4-(4-hydroxyphenyl)-4H-pyrano[3,2-h] quinoline-2-carbonitrile (7b)

^{1}H NMR (400 MHz, DMSO-d$_6$) δ = 4.82 (s, 1H, CH), 6.69 (d, 2H, J = 8.3 Hz, ArH), 7.02–7.21 (m, 5H, ArH & NH_2), 7.57–7.62 (m, 2H, ArH), 8.32 (d, 1H, J = 8.1 Hz, ArH), 8.92 (d, 1H, J = 3.2 Hz, ArH), 9.35 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): 161.1 (C–NH_2), 160.0, 156.3, 150.1, 142.7, 137.4, 130.1, 135.9, 129.9, 128.6, 127.5, 127.0, 123.4, 122.4, 122.0, 120.5, 115.3, 56.4 (C–CN), 40.3 (CH); ^{15}N NMR (40.55 MHz, DMSO-d$_6$) δ 7.20 (s, 2H, NH_2); FT-IR (KBr, cm^{-1}): 3331, 3210, 2199, 1666, 1512, 1408, 1138; HRMS of $[C_{19}H_{13}N_3O_2-H]^+$ (m/z): 315.2146; Calcd.: 315.2149.

2.5.17. Ethyl-2-amino-7-hydroxy-4-(2-methoxyphenyl)-4H-chromene-3-carboxylate (8a)

^{1}H NMR (400 MHz, DMSO-d$_6$) δ = 0.93 (t, 3H, J = 7.0 Hz, CH_3), 3.77 (s, 3H, OMe), 3.81–3.86 (m, 2H, CH_2), 5.20 (s, 1H, CH), 6.18 (d, 1H, J = 6.5 Hz, ArH), 6.37–6.42 (m, 2H, ArH), 6.80 (t, 1H, J = 6.6 Hz, ArH), 6.89 (d, 1H, J = 7.8 Hz, ArH), 6.97 (d, 2H, J = 8.6 Hz, ArH), 7.52 (s, 2H, NH_2), 9.25 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): 160.9 (C–NH_2), 156.7, 156.2, 149.1, 133.9, 129.1, 128.4, 127.9, 120.7, 120.7, 113.9, 112.1, 111.5, 102.0, 55.2 (C–CN), 59.2 (CH_2), 33.5 (CH), 15.9 (CH_3); ^{15}N NMR (40.55 MHz, DMSO-d$_6$) δ 7.52 (s, 2H, NH_2); FT-IR (KBr, cm^{-1}): 3345, 3117, 2195, 1649, 1530, 1410, 1145; HRMS of $[C_{19}H_{19}NO_5-H]^+$ (m/z): 340.1143; Calcd.: 340.1140.

3. Results and discussion

3.1. Chemistry

In the preliminary experiments, various solvents were screened for the synthesis of benzochromenes in the presence of VCaHAp catalyst. As a model reaction, the reaction of β-naphthol (1 mmol), malononitrile (1 mmol) and benzaldehyde (1 mmol) in the presence of VCaHAp in different solvents was investigated, and the results are summarized in Table 1. It was found that polar protic solvents such as CH_3OH, C_2H_5OH and water were much better than non-polar and polar aprotic solvents (hexane, toluene, DMF). Trace amounts of product were observed when H_2O was used as solvent, presumably due to the aggregation of the hydrophobic catalyst. Although CH_3OH was effective, low yield was obtained when the catalyst was reused. Similarly, the combination of ethanol–H_2O (1:1 v/v) yielded 73% of the product. Hence, ethanol proved most suitable solvent for this condensation in terms of yield (98%) and reaction time.

Table 1 Optimization of various solvents for the synthesis of **5a** by 2.5% VCaHAps.

Entry	Catalyst	Time (min)	Solvent	Yield (%)
1	V-CaHAp	75	Toluene	13
2	V-CaHAp	100	*n*-Hexane	10
3	V-CaHAp	80	DMF	19
4	V-CaHAp	20	Ethanol	98
5	V-CaHAp	20	Methanol	54
6	V-CaHAp	30	H_2O	31
7	V-CaHAp	60	EtOH:H_2O	73

Further, to optimize the reaction conditions and catalyst loading, a model reaction of β-naphthol (1 mmol), malononitrile (1 mmol) and benzaldehyde (1 mmol) was carried out. The results show that in the absence of catalyst, there was no reaction for 12 h (Table 2, entry 1). Moreover, the reaction was unaffected with the various types of organic or inorganic acidic catalysts such as acetic acid, CeO_2, Fe_2O_3, SiO_2 and PTSA at room temperature for 12 h (Table 2, entries 2–6). A trace amount of the anticipated product was achieved using L-proline, $BmimBF_4$ ionic liquids as a catalyst at room temperature (Table 2, entries 7 & 8). Later, the reaction was performed with various basic catalysts such as NaOH, K_2CO_3, TEA, pyridine and Mg-V/CO_3 HTlc. Low yield of product was obtained even after 4 h in the presence of ethanol as solvent (Table 2, entries 9–13). Further, the reaction was conducted at room temperature for screening with different hydroxyapatites such as CaHAp, BaHAp, SrHAp catalysts. The results showed that moderate yield (54–69%) could be obtained after a reaction time of 1 h (Table 2, entries 14–16). The impact of V loading on hydroxyapatite in modifying its catalytic efficiency was further investigated. To find the ideal loading of VCaHAp on catalyst activity, reactions with 1%, 2.5% and 5% V doped CaHAp were carried out under otherwise comparable conditions. The percentage of V loading was found to have an influence on the reaction yield as well as reaction time (Table 2, entries 17–19). The efficacy of this catalytic system was further tested by comparing it with two other V supported HAps under similar conditions. The use of V-BaHAp and V-SrHAp gave lower product yields (Table 2, entry 20 & 21). An optimum reaction condition was found to be 2.5% VCaHAp at 20 min which resulted in 98% product yield.

We also studied the effect of the amount of V-CaHAp on the model reaction. As shown in Table 3, the best results were

Table 2 Optimal condition for the synthesis of **5a** by 2.5% VCaHAp catalyst.[a]

Entry	Catalyst	Solvent	Condition	Time (h)	Yield (%)[b]
1	–	–	RT	12	–
2	CH_3COOH	EtOH	RT	12	–
3	CeO_2	EtOH	RT	12	–
4	Fe_2O_3	EtOH	RT	12	–
5	SiO_2	EtOH	RT	12	–
6	PTSA	EtOH	RT	12	–
7	L-proline	EtOH	RT	6.0	18
8	$(Bmim)BF_4$	EtOH	RT	6.0	14
9	NaOH	EtOH	RT	4.0	23
10	K_2CO_3	EtOH	RT	4.0	27
11	TEA	EtOH	RT	4.0	25
12	Pyridine	EtOH	RT	4.0	28
13	Mg-V/Tlc	EtOH	RT	3.5	32
14	CaHAp	EtOH	RT	1.0	69
15	BaHAp	EtOH	RT	1.0	65
16	SrHAp	EtOH	RT	1.5	54
17	1% V-CaHAp	EtOH	RT	0.83	92
18	2.5% V-CaHAp	EtOH	RT	0.33	98
19	5.0% V-CaHAp	EtOH	RT	0.33	98
18	V-BaHAp	EtOH	RT	0.33	94
19	V-SrHAp	EtOH	RT	0.33	91

–: No reaction.
[a] All products were characterized by IR, ^{1}H NMR, ^{13}C NMR, ^{15}N NMR and HRMS spectral analysis.
[b] Isolated yields.

Table 3 Optimization of the amount of 2.5% V-CaHAp as catalyst in the synthesis of **5a**.

Entry	Catalyst (mg)	Time (min)	Yield (%)
1	V-CaHAp (10 mg)	40	85
2	V-CaHAp (20 mg)	35	88
3	V-CaHAp (30 mg)	20	98
4	V-CaHAp (40 mg)	20	96
5	V-CaHAp (50 mg)	20	98

achieved with 30 mg V-CaHAp (Table 3, entry 3); on further increasing the amount of V-CaHAps (40 mg, 50 mg) the yield of the reaction was almost unaffected (Table 3, entries 4 & 5). The yield decreased when the amount of catalyst was reduced to 20 mg and 10 mg, and prolonging the reaction time did not improve the yield (Table 3, entries 1 & 2).

The scope of the catalyzed MCR was further explored. Choosing the conditions optimal for the synthesis of benzochromenes, i.e. 30 mg of V-CaHAp at RT and ethanol as solvent (Scheme 1), we employed various structurally different aldehydes (**3a–k**) for the MCR. To our delight, most of the reactions afforded desired benzochromene derivatives (**4a–k**) in good to excellent yields (89–98%) with good selectivity and with no by-products. The results are depicted in Table 4. The benzaldehydes with substrates bearing electron donating or electron-withdrawing groups on the aromatic ring proceeded smoothly and formed the corresponding substituted benzochromenes in good to excellent yields under the chosen conditions. Structure of the solid substituted benzochromenes **(4a–k)** was established and confirmed on the basis of spectral data (^{1}H NMR, ^{13}C NMR, ^{15}N NMR (GHSQC) and HRMS). Table 5 compares the present method with previous reports.

We propose a plausible mechanism for this reaction (Scheme 2). The reaction mechanism reveals the sequence of base-catalyzed reactions proposed to explain formation of the benzochromenes. In the first step, 2-arylidenemalononitrile **(3)** is made by a fast Knoevenagel condensation of malononitrile (1) with arylaldehyde (2) catalyzed by the V-CaHAp. Further, 2-arylidenemalononitrile (3) consequently reacts with β-naphthol (4) to obtain intermediate 5. In the further step, a Michael reaction of 5–7 in the presence of the mild basic catalyst produces the intermediate. Intramolecular cyclization and subsequently tautomerization afford the desired benzochromenes.

The scope and the overview of the present process were then additionally proved by the reaction of resorcinol or 8-hydroxyquinoline or α-naphthol with various aromatic aldehydes and malononitrile or ethylcyanoacetate to afford good yields in reasonable reaction times (Scheme 3).

3.2. BET surface area and elemental analysis

Fig. 1 displays the N_2 adsorption–desorption isotherms and the BJH pore size distribution of VCaHAp catalyst. The N_2 sorption isotherm possessed by the sample is typical for type IV with H2 hysteresis, which indicates that the sample reserves the tubular mesopores. The Barrett–Joyner–Halenda (BJH) pore size distribution shows that the catalyst has a narrow pore diameter range. Results from the textural studies showed that, the specific surface area, pore volume and pore diameter were calculated at 20.251 $m^2\,g^{-1}$, 6.883 nm and 0.055 $cm^3\,g^{-1}$, respectively. The relative-pressure (P/P_0) range of 0.3–0.7 of the hysteresis loops indicates the fairly small pore size and good homogeneity of the catalyst. The ICP analysis results showed the presence of a nominal amount of V in the catalyst (2.48 wt%).

3.3. X-ray diffraction

The XRD patterns of the synthesized vanadium supported calcium hydroxyapatite (VCaHAp) are shown in Fig. 2. All the crystalline phases observed from the XRD patterns were coordinated with the Joint Committee on Powder Diffraction Standards (JCPDS) files. The sample shows vanadium pentoxide diffractograms diffraction peaks of *d*-spacing values at 2.76, 2.88 and 3.43 Å corresponding to the 2θ angles between 30° and 35° referenced in JCPDS File No. 9-387 and the hydroxyapatite phases with d-spacing values of 2.63, 2.72 and 2.79 2.63 Å for 2θ angles between 30° and 35° correlating with JCPDS File No. 9-390. The peaks detected in the diffractogram show the polycrystalline nature of the material. The average crystallite size of this sample was obtained to be 5.9 nm using the Scherrer equation based on the highest intensity diffraction peaks of V-CaHAp.

3.4. Scanning electron microscopy & TEM

Fig. 3 shows the representative SEM surface morphology of the as-prepared and calcined VCaHAp sample. From the SEM image, hydroxyapatite appeared puffy in shape with particle size around 30–40 nm. The catalyst also appears as bulky

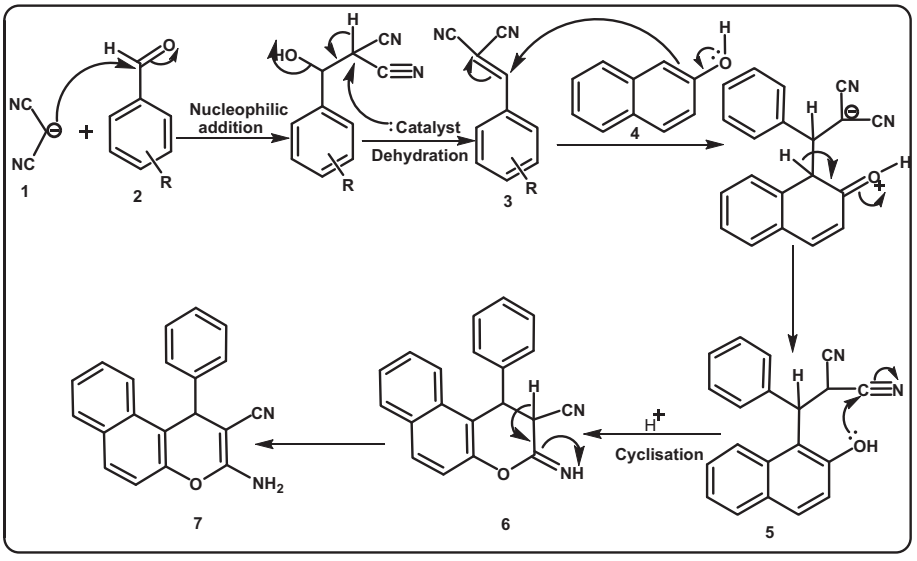
Table 4 Synthesis of benzochromene derivatives catalyzed by 2.5% V-CaHAp catalyst.

Entry	*R*	Product	Time (min)	Yield (%)	Mp (°C)	Lit Mp (°C)
1	2-MeO	4a	15	98	186–187	–
2	4-OMe	4b	18	96	190–192	190–191 Kiyani and Ghorbani (2014)
3	4-Br	4c	20	89	241–242	242–244 Kiyani and Ghorbani (2014)
4	2,5-$(OMe)_2$	4d	20	95	221–223	–
5	2,3-$(OMe)_2$	4e	16	92	201–203	–
6	2,4-$(OMe)_2$	4f	19	89	253–255	–
7	3-OH	4g	15	90	230–231	–
8	2-Cl	4h	20	93	270–271	270–272 Kai et al. (2008)
9	4-Cl	4i	18	91	210–212	210–211 Meng et al. (2011)
10	2-F	4j	18	97	204–206	–
11	4-C_2H_5	4k	16	98	225–227	–
12	2-MeO	5a	15	92	204–206	203–205 Maalej et al. (2012)
13	4-Br	6a	20	90	227–228	227–229 Baghbanian et al. (2013)
14	4-OH	6b	18	89	250–252	252–254 Dekamin et al. (2013)
15	4-Br	7a	16	90	230–232	–
16	4-OH	7b	20	92	241–243	–
17	2-MeO	8a	20	94	218–219	–

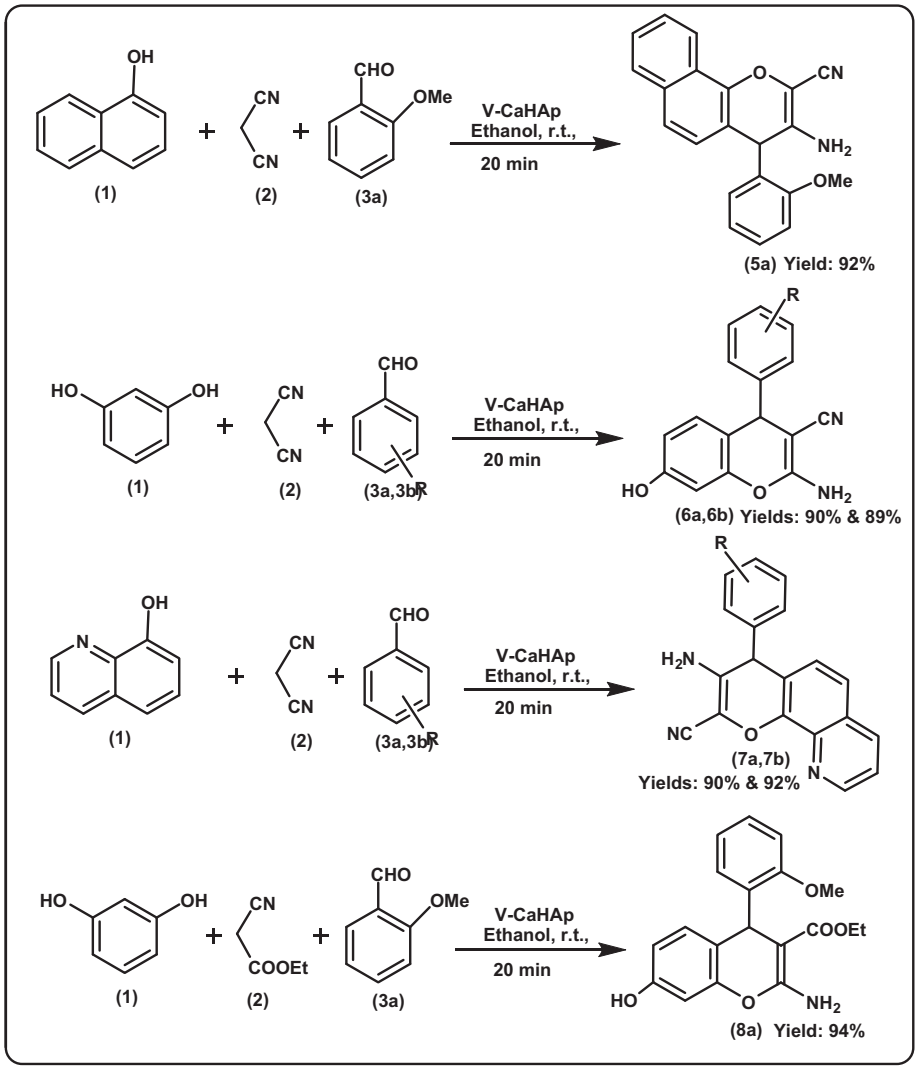
–: New compounds/no literature available.

Table 5 Comparison of synthesis of **5a** reaction method with previous reports.

Catalyst	Time (h)	Yield (%)	Reusable	Temperature	References
[bmim]OH	0.33	90	0	Reflux/100 °C	Kai et al. (2008)
CAN	0.50	92	0	Reflux/120 °C	Kumar et al. (2010)
Na_2HPO_4	1.0	94	0	Δ/120 °C	Meng et al. (2011)
$N_2H_4CSO_2$	8.0	<89	6 runs	Δ/50 °C	Verma and Jain (2012)
$H_{14}[NaP_5W_{30}O_{110})$	4.5	91	3 runs	Reflux/100 °C	Heravi et al. (2007)
$[Cu(bpdo)_2ṡ2H_2O]^{2+}$/SBA-15	0.84	<92	2 runs	Reflux/150 °C	Malakooti et al. (2013)
PVPy	0.75	<93	6 runs	Δ/80 °C	Albadi et al. (2013)
STA	4.0	<90	4 runs	Δ/120 °C	Farahi et al. (2014)
Nanozeolite CP	0.50	<94	4 runs	Reflux/120 °C	Baghbanian et al. (2013)
PPI	1.05	<90	0	Reflux/110 °C	Kiyani and Ghorbani (2014)
VCaHAp	<0.33	98	6 runs	r.t	This study



Scheme 2 Plausible mechanism for the synthesis of benzochromenes.



Scheme 3 Generality of the other possible reactions.

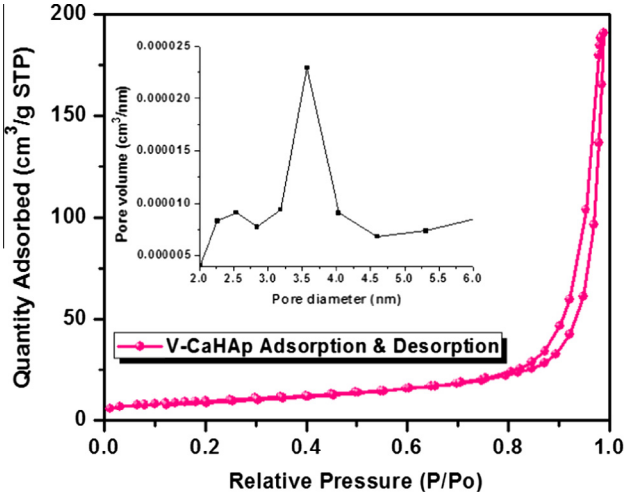


Figure 1 N_2 adsorption and desorption spectra of 2.5% V-CaHAp catalysts.

sticks with irregular shapes to correspond to the vanadium pentoxide. SEM–EDX analysis was performed to get information about the presence of the surface composition Fig. 4. EDX analysis showed successful dispersion of vanadia on the surface of hydroxyapatite sample. The result revealed that vanadia was homogenously dispersed on the surface of hydroxyapatite and the EDX analysis results are in agreement with the ICP analysis results. The morphologies of the prepared vanadium loaded hydroxyapatite were investigated by TEM and are shown in Fig. 5. It indicates that the catalyst has the shape of an irregular rod into uneven morphology with a diameter range from 54 to 68 nm.

3.5. Reusability of VCaHAps

The reusability of the heterogeneous catalyst was investigated. After completion of reaction, the catalyst was recovered by filtration, washed with ethanol and dried under vacuum. The recovered catalyst was reused for at least 6 run times with a slight loss in catalytic activity (Fig. 6). The activity decrease observed with the regenerated catalyst on reusing could be

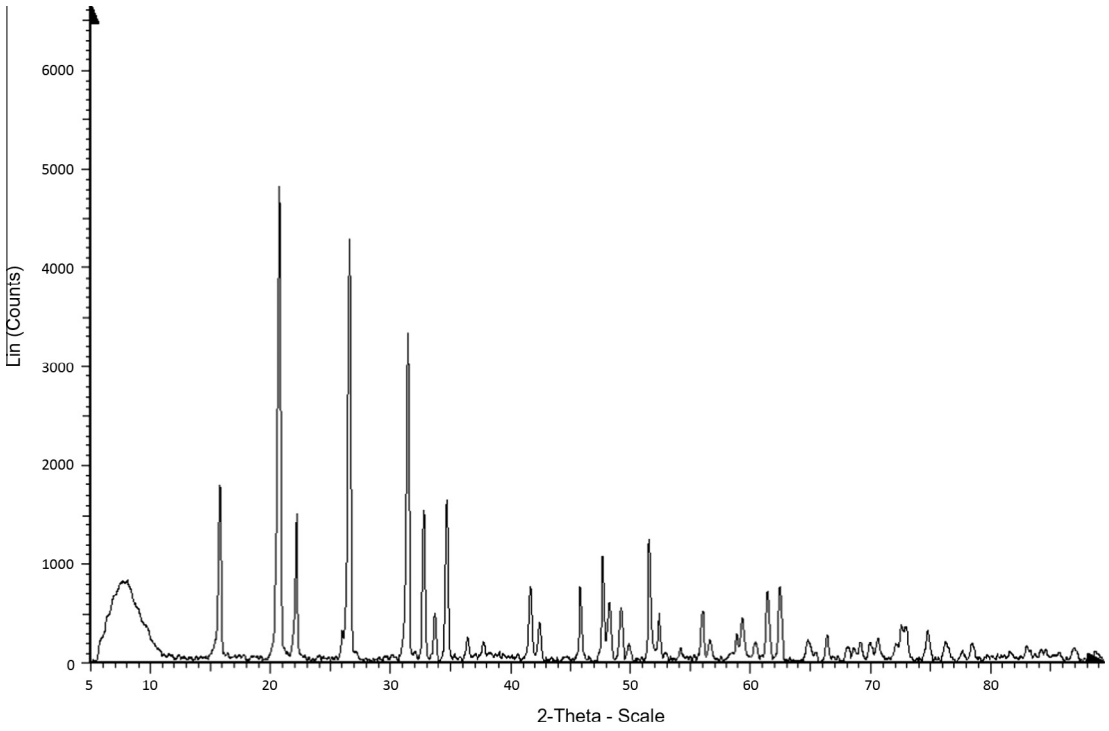


Figure 2 XRD spectrum of 2.5% V-CaHAp catalyst.

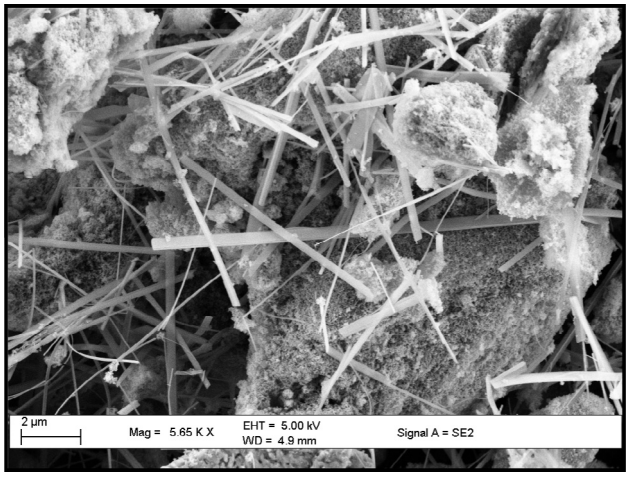


Figure 3 SEM micrograph of 2.5% VCaHAp catalyst.

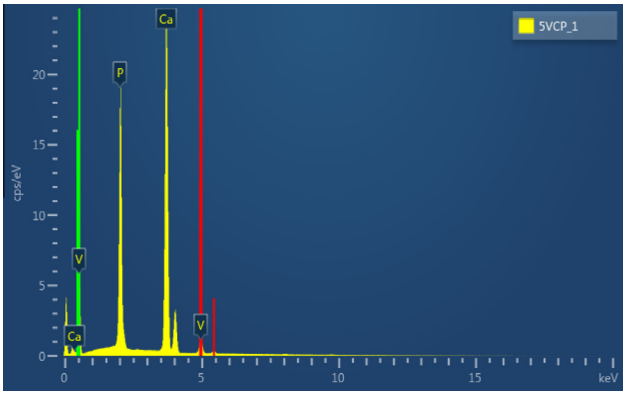


Figure 4 SEM–EDX micrograph of 2.5% VCaHAp catalyst.

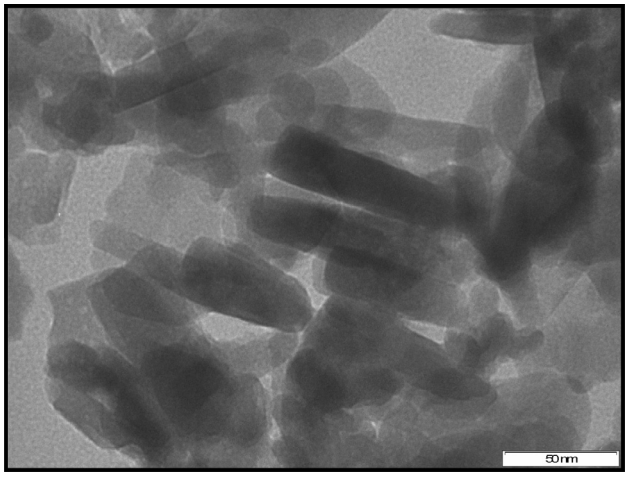


Figure 5 TEM micrograph of 2.5% VCaHAp catalyst.

due to partial loss of basic sites or surface area of the catalyst during reaction/regeneration. The filtrate after reaction was analyzed for leached metal content by ICP–OES. No trace of metal was detected, confirming no leaching (Figs. 7a and 7b).

4. Conclusion

In conclusion, we report an environmentally benign, an expedient and an efficient one-pot multicomponent green synthesis of benzochromene derivatives using VCaHAp as an heterogeneous catalyst in green solvent media and with good atom efficiency. This simple and recyclable heterogeneous catalyst, VCaHAp demonstrates high catalytic activity for this multicomponent reaction. The present procedure brings about a number of benefits such as readily available start-

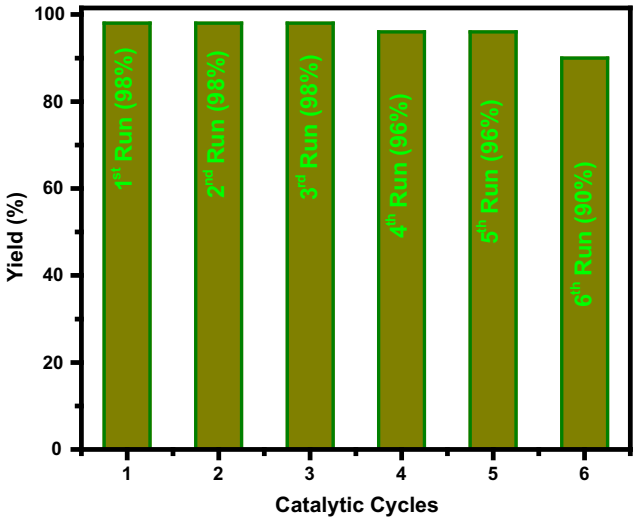


Figure 6 Recyclability of 2.5% VCaHAp catalyst.

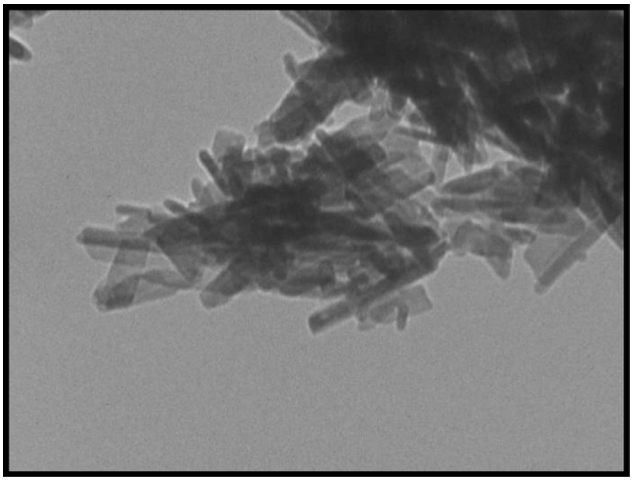


Figure 7a TEM micrograph of recycled 2.5% VCaHAp catalyst.

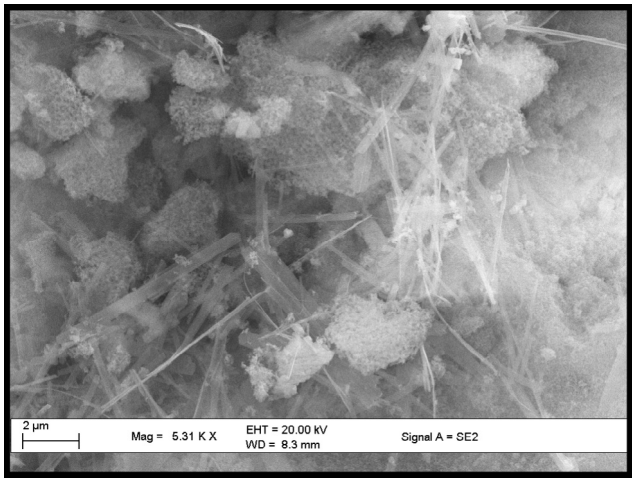


Figure 7b SEM micrograph of recycled 2.5% VCaHAp catalyst.

ing materials, short reaction time, excellent yields, purity of products, cost-effectiveness, use of small amount of inexpensive catalyst and environmentally benign green solvent. High proficiency and easy operation make this new eco-friendly strategy attractive for hypothetical research and prospective applications.

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