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Silica bonded *n*-propyl-4-aza-1-azoniabicyclo[2.2.2]octane chloride (SB-DABCO): A highly efficient, reusable and new heterogeneous catalyst for the synthesis of 4*H*-benzo[*b*]pyran derivatives

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ABSTRACT

The reaction of 3-chloropropyl silica with diazabicyclo[2.2.2]octane in dry acetone affords silica bonded *n*-propyl-4-aza-1-azoniabicyclo[2.2.2]octane chloride (SB-DABCO) as a new basic catalyst. The catalyst is used for the efficient synthesis of 4*H*-benzo[*b*]pyran derivatives *via* one-pot three-component reaction of cyclic ketones/1,3-diketones with aromatic aldehydes and alkylmalonates.

1. Introduction

Base-catalyzed condensation and addition reactions are industrially important in the production of drugs, fragrances and chemical intermediates [1]. One of the most important classes of these reactions is C–C coupling reactions, such as Aldol and Knoevenagel condensations as well as Michael reactions [2–4]. Conventionally, almost stoichiometric amounts of homogeneous bases are used for such purposes [5,6,1]. In such systems, several difficult issues arise, of which we may address to the isolation of the products, the corrosive nature of the reaction mixture and formation of large amounts of waste materials. Therefore, improved synthesis routes in terms of product purity, yield, and minimal waste formation are highly desirable. Moreover, replacement of liquid acids and bases with the corresponding cleaner solid alternatives, possessing desirable characteristics such as being non-stoichiometric, non-corrosive and reusable, is necessary in view of environmentally benign. Solid acid catalysts have been extensively studied and applied in numerous reactions so far [7]; however, solid base catalysts have not been extensively studied [8]. The potential use of microporous and mesoporous base catalysts in fine chemical production is enormous [9]. These heterogeneous catalysts are known to suppress side reactions, which include self-condensation and oligomerization, resulting in better selectivity and product yield. This means cost and energy savings for the downstream separation and purification of the product. It also avoids the complex neutralization and separation steps needed to recover the homogeneous base catalysts from the reaction mixture. The recovered solid catalysts can be readily regenerated for further use.

1,4-Diazabicyclo[2.2.2]octane (DABCO), a cage-like compound, is a small diazabicyclic molecule with weak alkalescency and medium-hindrance [10]. DABCO has been applied as an inexpensive, eco-friendly, high reactive and non-toxic base catalyst for various organic transformations, including ring opening of aziridines with amines or thiols [11], oxidative deprotection of (tetrahydropyranyl) ethers and silyl ethers [12], conversion of tetrahydropyranyl ethers into acetates [13], regioselective nucleophilic aromatic substitution reaction [14], synthesis of isoxazolines [15], synthesis of *N*-arylphthalimides [16], synthesis of industrially important polyurethane foams [17], and Baylis–Hillman reactions [18]. Nevertheless, in many of these cases, DABCO has not been recovered, and eliminated as a residue.

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Because of the diversity in pharmacological activities, the synthesis of compounds having benzopyran rings has attracted great interest since many years [19]. The pyran pharmacophore is an important core structure of many natural products showing antibacterial, antitumor, antiallergic, antibiotic, hypolipidemic, and immunomodulating activities [20]. Substituted 2-amino-4*H*-pyrans have a special importance among the 6-membered oxygen-containing heterocycles as they have been used as anticancer and antimicrobial agents [21], and photoactive materials [22]. 2-Amino-4*H*-pyran derivatives have been also utilized in synthesis of blood anticoagulant warfarin [23] and tacrine analogs (cholinesterase inhibitors) [24]. Some catalysts such as hexadecyltrimethyl ammonium bromide (HMTAB) [25], triethylbenzylammonium chloride (TEBA) [26], rare earth perfluorooctanoate ($RE(PFO)_3$) [27], (*S*)-proline [28], and amino functionalized ionic liquids [29] have been used for the synthesis of 4*H*-benzo[*b*]pyrans so far. However, most of these methods suffer from some drawbacks such as low yields, long reaction times, harsh reaction conditions, tedious work-up procedures and application of expensive catalysts. Moreover, in most of the reported methods, catalysts are not recyclable. Therefore, development of an efficient, one-pot, chemoselective procedure for the synthesis of benzo[*b*]pyrranes is of considerable interest.

As part of our research program to develop selective, efficient and green methods and catalysts in organic synthesis [30], we report here the preparation of silica bonded *n*-propyl-4-aza-1-azoniabicyclo[2.2.2]octane chloride (SB-DABCO), as a novel heterogeneous and recyclable catalyst, from the reaction of 3-chloropropyl silica (SilprCl) with DABCO (Scheme 1), and its successful application in the synthesis of 4*H*-benzo[*b*]pyran derivatives *via* the one-pot three-component condensation of cyclic ketones/1,3-diketones with aromatic aldehydes and alkylmalonates (Scheme 2).

2. Experimental

2.1. Chemicals and apparatus

All known compounds were identified by comparison of their melting points and ^{1}H NMR data with those reported in the literature. FT-IR spectra were recorded with a Jasco FT-IR, model 460 at 4 cm^{-1} resolution. Self-supported disks of the materials were prepared having a diameter of 2.5 cm, weighing *ca.* 100 mg, with a disk thickness sufficiently thin to allow the measurements by the transmission technique. The ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) were run on a Bruker Avance DPX-250, FT-NMR spectrometer. Microanalyzis was performed on a Perkin-Elmer 240-B microanalyzer. Melting points were recorded on a Stuart Scientific Apparatus SMP3 (UK) in open capillary tubes. All chemicals were purchased from Merck or Fluka Chemical Companies. The chemicals purity include silica gel: 60 (0.040–0.063 mm); toluene: 99.9%; 3-chloropropyltrimethoxysilane: 98%; triethylamine: 99%; ethanol: 99.5%; 1,4-diazabicyclo[2.2.2]octane: 98%; ethyl acetate: 99.8%; dimedone: 99%; benzaldehyde: 99%; 4-chlorobenzaldehyde: 98%; 2-chlorobenzaldehyde: 99%; 4-ethoxybenzaldehyde: 99%; 4-nitrobenzaldehyde: 98%; 4-*iso*-propylbenzaldehyde: 98%; 2-naphthylaldehyde: 97%; 4-methylbenzaldehyde: 97%; 3-phenoxybenzaldehyde: 99%; 2-oxo-2-phenylacetaldehyde: 98%; 2-thienylcarbaldehyde: 98%; 4-cyanobenzaldehyde: 99%; 4-hydroxybenzaldehyde: 98%; 4-(trifluoromethyl)benzaldehyde: 98%; Malononitrile: 98%; ethyl 2-cyanoacetate: 99%; methyl 2-cyanoacetate: 99%; cyclohexane-1,3-dione: 98% and 3-methyl-1-phenyl-1H-pyrazol-5(4H)-one: 98%.

2.2. Basicity measurements

The basicity measurements of silica bonded *n*-propyl chloride (SiPrCl) and silica bonded *n*-propyl-4-aza-1-azoniabicyclo[2.2.2]octane chloride (SB-DABCO) were analyzed by temperature programmed desorption (TPD) of CO_2 with TGA method. About 0.5 g of the sample was packed in a quartz tube and the initial flushing was carried out with dry nitrogen for 3 h. Afterward, CO_2 was passed over the catalyst bed; by this process, CO_2 was adsorbed by the catalyst. After adsorption, the system was evacuated to remove the physisorbed CO_2, and again CO_2 was passed through the system. The adsorption and evacuation processes were repeated five times for saturating the samples. The extent of CO_2 adsorbed over each sample was measured by TGA in a homemade system. Nitrogen, as purge gas, was passed during desorption of CO_2. The TGA study was conducted at a heating rate of 10 °C min^{-1} up to 400 °C.

2.3. Preparation of silica bonded n-propyl chloride

Silica (25.0 g) was first immersed in hydrochloric acid for 24 h, and washed with deionized water, and dried under vacuum at 120 °C for 8 h. The activated silica (25.0 g) was suspended in dry toluene (300 mL), and then an excess amount of 3-chloropropyltrimethoxysilane (25.0 mL), and triethylamine (as a catalyst, 2.5 mL) was added. The suspension was mechanically stirred and refluxed for 48 h. Afterward, the reaction mixture was cooled to room temperature, transferred to a vacuum glass filter, and washed with toluene, ethanol–water mixture, deionized water in turn and finally with methanol. The resulting solid was dried under vacuum at 60 °C for 4 h to give silica bonded *n*-propyl chloride [38].

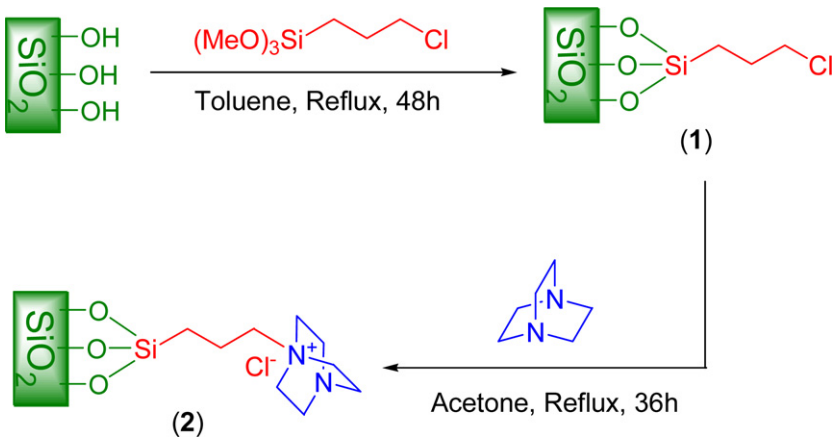
2.4. Preparation of silica bonded n-propyl-4-aza-1-azoniabicyclo[2.2.2]octane chloride (SB-DABCO)

3-Chloropropyl silica (1 g) and DABCO (0.56 g, 5 mmol) were added in a 50 mL round-bottomed flask contained dry acetone (30 mL) connected to a reflux condenser, and refluxed for 36 h. Afterward, the reaction mixture was cooled to room temperature, transferred to a vacuum glass filter, and washed with acetone, ethanol, and methanol in turn. The resulting solid was dried under vacuum at 50 °C for 4 h to give SB-DABCO as a white powder (1.127 g).

2.5. General procedure for the preparation of 4H-benzo[b]pyran derivatives

Ketone (1 mmol), malononirile (1 mmol) and aldehyde (1 mmol) were added in a 25 mL round-bottomed flask contained SB-DABCO (0.06 g, 6 mol%) and ethanol (5 mL), and the resulting mixture was stirred at room temperature (method A). After completion of the reaction (as monitored by TLC), the ethanol was evaporated. EtOAc (15 mL) was added to the mixture, stirred for 5 min and filtered to separate the catalyst. Then, the solvent of the filtrate was evaporated and the crude product was purified by recrystallization from hot ethanol. The recycled catalyst was washed by EtOAc and acetone, dried and reused.

Note: When alkylcyanoacetates were applied instead of malononirile, the reactions were carried out in EtOH/H_2O (1/1) under reflux conditions (method B).



Scheme 1. The preparation of silica bonded *n*-propyl-4-aza-1-azoniabicyclo[2.2.2]octane chloride (SB-DABCO).

2.6. Selected spectral data of the products

2.6.1. 2-Amino-4-(phenyl)-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4H-chromene-3-carbonitrile (compound 6a)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.96 (s, 3H), 1.03 (s, 3H), 2.12–2.15 (m, 2H), 2.39 (m, 2H), 4.29 (s, 1H), 5.15 (s, 2H), 7.11 (t, J = 9.0 Hz, 1H), 7.14 (d, J = 3.5 Hz, 2H), 7.19 (t, J = 9.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 27.9, 29.2, 32.5, 36.0, 51.0, 62.3, 114.3, 119.6, 127.3, 127.8, 128.8, 144.0, 158.4, 162.1, 196.3.

2.6.2. 2-Amino-4-(4-chlorophenyl)-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4H-chromene-3-carbonitrile (compound 6b)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.98 (s, 3H), 1.07 (s, 3H), 2.13-2.22 (m, 2H), 2.40 (m, 2H), 4.32 (s, 1H), 5.20 (s, 2H), 7.13 (d, J = 4.25 Hz, 1H), 7.20 (d, J = 3.5 Hz, 2H).^{13}C NMR ($CDCl_3$, 125 MHz): δ 27.9, 29.2, 32.5, 35.6, 51.0, 62.1, 114.0, 119.3, 129.0, 129.4, 133.0, 142.5, 158.4, 162.2, 196.2.

2.6.3. 2-Amino-4-(4-ethoxyphenyl)-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4H-chromene-3-carbonitrile (compound 6c)

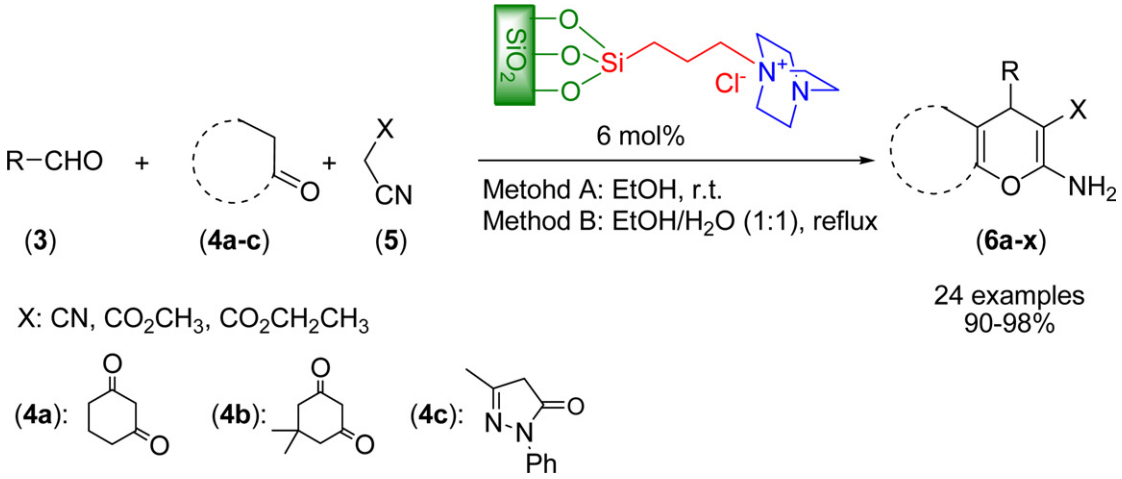
^{1}H NMR (DMSO-d_6, 500 MHz): δ 0.94 (s, 3H), 1.02 (s, 3H), 1.29 (t, J = 6.75 Hz, 3H), 2.09 (d, J = 16.0 Hz, 1H), 2.23 (d, J =16.0 Hz, 1H), 2.45-2.53 (m, 2H), 3.96-3.97 (m, 2H), 4.11 (s, 1H), 6.81(d, J = 8.5 Hz, 2H), 6.93 (s, 2H), 7.03 (d, J = 8.5 Hz, 2H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 15.5, 27.9, 29.2, 32.9, 35.6, 50.8, 59.4, 63.7, 113.9, 114.9, 120.6, 129.0, 137.5, 158.0, 159.3, 162.9, 196.5.

2.6.4. 2-Amino-4-(4-nitrophenyl)-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4H-chromene-3-carbonitrile (compound 6d)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.99 (s, 3H), 1.08 (s, 3H), 2.16–2.20 (m, 2H), 2.44 (m, 2H), 4.32 (s, 1H), 5.32 (s, 2H), 7.38 (d, J = 4.25 Hz, 2H), 7.11 (d, J = 4.15 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 27.9, 29.2, 32.5, 36.2, 50.9, 62.1, 113.3, 119.0, 124.2, 129.0, 147.3, 151.3, 158.7, 162.8, 196.2.

2.6.5. 2-Amino-5,6,7,8-tetrahydro-7,7-dimethyl-4-(naphthalen-7-yl)-5-oxo-4H-chromene-3-carbonitrile (compound 6e)

^{1}H NMR (DMSO-d_6, 500 MHz): δ 0.92 (s, 3H), 1.01 (s, 3H), 1.87-1.92 (m, 1H), 1.94–1.97 (m, 1H), 2.61-2.69 (m, 2H), 4.39 (s, 1H), 7.06 (s, 2H), 7.32–7.34 (d, J = 10 Hz, 1H), 7.44–7.50 (m, 2H), 7.69 (s, 1H), 7.83–7.86 (m, 2H), 7.89 (d, J = 8.0 Hz, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 20.6, 21.4, 23.3, 27.4, 36.6, 37.2, 58.9, 114.4, 120.6, 126.4, 126.5, 126.5, 126.9, 128.2, 128.5, 128.9, 132.8, 133.7, 143.0, 159.3, 165.4, 196.7.



Scheme 2. The synthesis of 4*H*-benzo[*b*]pyran derivatives in the presence of SB-DABCO.

2.6.6. 2-Amino-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4-(3-phenoxyphenyl)-4H-chromene-3-carbonitrile (compound 6f)

^{1}H NMR (DMSO-d_6, 500 MHz): δ 0.91 (s, 3H), 1.02 (s, 3H), 2.10 (d, J = 16.0 Hz, 1H), 2.26 (d, J = 16.0 Hz, 1H), 2.41–2.53 (m, 2H), 4.17 (s, 1H), 6.75 (s, 1H), 6.80 (d, J = 8.0 Hz, 1H), 6.92 (d, J = 8.0 Hz, 1H), 6.92–7.01 (m, 4H), 7.13 (t, J = 7.2 Hz, 1H), 7.29 (t, J = 7.7 Hz, 1H), 7.37 (t, J = 8.0 Hz, 2H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 27.5, 29.3, 32.5, 36.2, 50.8, 58.8, 113.2, 117.4, 118.0, 119.4, 120.4, 123.0, 124.3, 130.8, 130.8, 147.8, 157.2, 157.5, 159.3, 163.5, 196.4.

2.6.7. 2-Amino-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4-(thiophen-2-yl)-4H-chromene-3-carbonitrile (compound 6g)

^{1}H NMR (DMSO-d_6, 500 MHz): δ 0.97 (s, 3H), 1.06 (s, 3H), 2.14 (d, J = 16.0 Hz, 1H), 2.29 (d, J = 16.0 Hz, 1H), 2.42 (d, J = 16.0 Hz, 1H), 2.52 (d, J = 16.0 Hz, 1H), 4.53 (s, 1H), 6.85 (d, J = 3.5 Hz, 1H), 6.89–6.91 (m, 1H), 7.10 (s, 2H), 7.30-7.31 (m, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 27.3, 29.5, 31.2, 32.6, 50.7, 58.9, 113.8, 120.4, 124.8, 125.2, 127.6, 150.1, 159.7, 163.3, 196.3.

2.6.8. 2-Amino-4-benzoyl-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (compound 6h)

^{1}H NMR (DMSO-d_6, 500 MHz): δ 1.05 (s, 3H), 1.07 (s, 3H), 2.12 (d, J = 16.0 Hz, 1H), 2.34 (d, J = 16.0 Hz, 1H), 2.41 (d, J = 17.5 Hz, 1H), 2.61 (d, J =17.5 Hz, 1H), 4.98 (s, 1H), 7.23 (s, 2H), 7.55 (t, J = 7.75 Hz, 2H), 7.68 (t, J = 7.5 Hz, 1H), 8.05 (d, J = 7.5 Hz, 2H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 27.2, 29.5, 33.2, 36.7, 50.4, 53.0, 111.5, 119.9, 129.5, 129.7, 134.4, 136.6, 160.9, 164.8, 196.8, 199.4.

2.6.9. Ethyl 2-amino-4-(4-trifluoromethylphenyl)-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4H-chromene-3-carboxylate (compound 6i)

^{1}H NMR (DMSO-d_6, 500 MHz): δ 0.88 (s, 3H), 1.03 (s, 3H), 1.06 (t, J = 7.0 Hz, 3H), 2.06 (d, J = 8.0 Hz, 1H), 2.26 (d, J = 8.0 Hz, 1H), 2.47 (d, J = 8.8 Hz, 1H), 2.56 (d, J = 8.75 Hz, 1H), 3.91–3.95 (m, 2H), 4.56 (s, 1H), 7.35 (d, J = 4.0 Hz, 2H), 7.57 (d, J = 4.0 Hz, 2H), 7.63 (s, 2H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 15.0, 27.4, 29.4, 32.7, 34.5, 50.7, 59.7, 77.8, 115.6, 125.5, 129.5, 151.9, 160.0, 163.4, 168.6, 196.7.

2.6.10. Ethyl 2-amino-5,6,7,8-tetrahydro-7,7-dimethyl-4-(naphthalen-7-yl)-5-oxo-4H-chromene-3-carboxylate (compound 6j)

^{1}H NMR (DMSO-d_6, 500 MHz): δ 0.88 (s, 3H), 1.03 (s, 3H), 1.07 (t, J = 7.5 Hz, 3H), 2.03 (d, J = 16.0 Hz, 1H), 2.26 (d, J = 16.0 Hz, 1H), 2.50 (d, J = 14.5 Hz, 1H), 2.57 (d, J = 17.5 Hz, 1H), 3.87-3.98 (m, 2H), 4.67 (s, 1H), 7.30 (d, J = 8.5 Hz, 1H), 7.39–7.45 (m, 2H), 7.59 (s, 2H), 7.63 (s, 1H), 7.75 (d, J = 8.5 Hz, 1H), 7.78–7.83 (m, 2H). ^{13}C NMR (DMSO-d_6,125 MHz): δ 15.0, 27.2, 29.5, 32.7, 34.4, 50.8, 59.6, 78.5, 116.1, 126.1, 126.7, 126.9, 127.3, 128.1, 128.1, 128.3, 132.5, 133.5, 144.5, 159.9, 163.1, 168.8, 196.7.

2.6.11. Methyl 2-amino-4-(4-cyanophenyl)-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4H-chromene-3-carboxylate (compound 6k)

^{1}H NMR (DMSO-d_6, 500 MHz): δ 0.86 (s, 3H), 1.02 (s, 3H), 2.06 (d, J = 16.0 Hz, 1H), 2.26 (d, J = 16.0 Hz, 1H), 2.45–2.57 (m, 2H), 3.48 (s, 3H), 4.55 (s, 1H), 7.32 (d, J = 8.0 Hz, 2H), 7.66-7.68 (m, 4H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 27.3, 29.4, 32.7, 34.7, 50.7, 51.4, 77.3, 109.5, 115.4, 119.7, 129.5, 132.7, 152.7, 160.1, 163.5, 168.8, 196.6.

2.6.12. Methyl 2-amino-4-(4-chlorophenyl)-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4H-chromene-3-carboxylate (compound 6l)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.98 (s, 3H), 1.12 (s, 3H), 2.18 (d, J = 8.1 Hz, 1H), 2.26 (d, J = 8.1 Hz, 1H), 2.40–2.48 (m, 2H), 3.62 (s, 3H), 4.70 (s, 1H), 6.23 (s, 2H), 7.19–7.23 (m,4H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 27.7, 29.5, 32.6, 33.6, 41.1, 51.1, 51.4, 80.5, 116.9, 128.4, 129.8, 132.1, 144.7, 158.9, 161.9,169.7, 196.6.

2.6.13. 2-Amino-5,6,7,8-tetrahydro-5-oxo-4(4-chlorophenyl)-4H-chromene-3-carbonitrile (compound 6m)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.84–1.88 (m, 1H), 1.92–1.97 (m, 1H), 2.21–2.29 (m, 5H) 2.57-2.61 (m, 2H), 4.15 (s, 1H), 6.95 (s, 2H), 7.04 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H). ^{13}C NMR (DMSO/$CDCl_3$, 125 MHz): δ 20.5, 27.3, 33.8, 37.1, 60.3, 114.1, 119.4, 127.4, 128.5, 130.3, 130.5, 133.5, 140.9, 158.6, 164.6,196.2.

2.6.14. 2-Amino-5,6,7,8-tetrahydro-5-oxo-4(4-nitrophenyl)-4H-chromene-3-carbonitrile (compound 6n)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.21–2.26 (m, 1H), 2.27–2.32 (m, 1H), 2.41–2.52 (m, 2H), 2.61–2.69 (m, 2H), 4.57 (s, 1H), 4.69 (s, 2H), 7.46 (d, J = 4.4 Hz, 2H), 8.19(d, J = 4.4 Hz, 2H).

2.6.15. 2-Amino-5,6,7,8-tetrahydro-5-oxo-4-p-tolyl-4H-chromene-3-carbonitrile (compound 6o)

^{1}H NMR (DMSO-d_6, 500 MHz): δ 1.84–1.88 (m, 1H), 1.92–1.97 (m, 1H), 2.21–2.29 (m, 5H) 2.57–2.61 (m, 2H), 4.15 (s, 1H), 6.95 (s, 2H), 7.04 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 20.6, 21.4, 27.3, 35.9, 37.2, 59.2, 114.8, 120.6, 127.9, 129.7, 136.4, 142.7, 159.3, 165.1, 196.6.

2.6.16. 2-Amino-5,6,7,8-tetrahydro-4-(naphthalen-7-yl)-5-oxo-4H-chromene-3-carbonitrile (compound 6p)

^{1}H NMR (DMSO-d_6, 500 MHz): δ 1.87–1.92 (m, 1H), 1.94–1.97 (m, 1H), 2.21–2.26 (m, 1H), 2.27–2.32 (m, 1H), 2.61–2.69 (m, 2H), 4.39 (s, 1H), 7.06 (s, 2H), 7.32–7.34 (d, J = 8.5 Hz, 1H), 7.44–7.50 (m, 2H), 7.69 (s, 1H), 7.83–7.86 (m, 2H), 7.89 (d, J = 8.0 Hz, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 20.6, 27.4, 36.6, 37.2, 58.9, 114.4, 120.6, 126.4, 126.5, 126.5, 126.9, 128.2, 128.5, 128.9, 132.8, 133.7, 143.0, 159.3, 165.4, 196.7.

2.6.17. 2-Amino-5,6,7,8-tetrahydro-4-(2-chlorophenyl)-5-oxo-4H-chromene-3-carbonitrile (compound 6q)

^{1}H NMR (DMSO-d_6, 500 MHz): 1.89–1.98 (m, 2H), 2.19–2.49 (m, 2H), 2.59–2.62 (m, 2H), 4.70 (s, 1H), 6.99 (s, 2H), 7.19 (t, J = 7.5 Hz, 2H), 7.25(t, J = 7.15 Hz, 1H), 7.35(d, J = 7.7 Hz, 1H). ^{13}C NMR (DMSO/$CDCl_3$, 125 MHz): δ 20.5, 27.3, 33.8, 37.1, 60.3, 114.1, 119.4, 127.4, 128.5, 130.3, 130.5, 133.5, 140.9, 158.6, 164.6,196.2.

2.6.18. methyl 2-amino-4-(4-ethoxyphenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carboxylate (compound 6s)

M.P. = 149–150 °C. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 1.27 (m, 3H), 1.79 (m, 1H), 1.92 (m, 1H), 2.23–2.25 (m, 2H), 2.49–2.58 (m, 2H), 3.49 (s, 3H), 3.92 (m, 2H), 4.49 (s, 1H), 6.73 (m, 2H), 7.02 (m, 2H), 7.50 (s, 2H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 15.5, 20.7, 27.1, 32.9, 37.2, 51.3, 63.6, 78.7, 114.5, 118.0, 129.2, 139.3, 157.5, 160.1, 164.5, 169.2, 196.8. Anal. Calcd for $C_{19}H_{21}NO_5$: C, 66.46; H, 6.16; N, 4.08. Found: C, 66.51; H, 6.23; N, 4.1

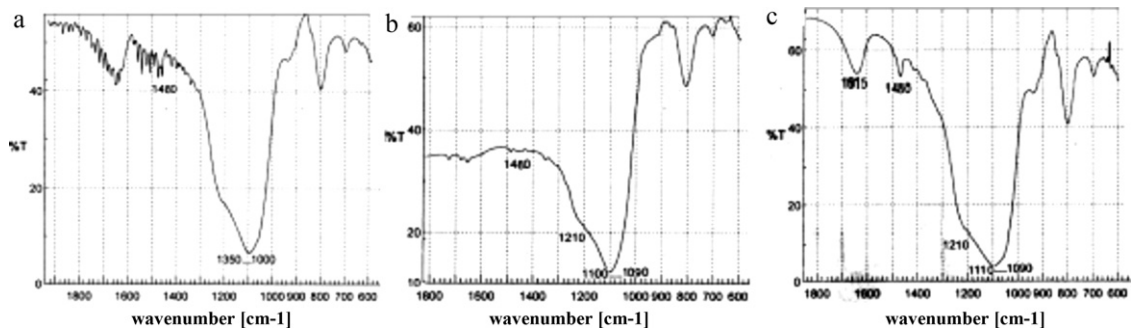


Fig. 1. IR spectra of DABCO (a), silica bonded *n*-propylchloride (b) and silica bonded *n*-propyl-4-aza-1-azoniabicyclo[2.2.2]octane chloride (SB-DABCO) (c).

2.6.19. 6-Amino-4-(4-cyanophenyl)-1,4-dihydro-3-methyl-1-phenylpyrano[2,3-c]pyrazole-5-carbonitrile (compound 6t)

^{1}H NMR (DMSO-d_6, 500 MHz): 1.77 (s, 3H), 4.83 (s, 1H), 7.30–7.33 (m, 3H), 7.47–7.50 (m, 4H), 7.78 (d, J = 8.5 Hz, 2H), 7.82 (d, J = 8.0 Hz, 2H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 13.4, 37.5, 57.9, 98.5, 110.8, 119.6, 120.6, 120.9, 127.1, 129.8, 130.1, 133.5, 138.3, 144.9, 145.9, 150.0, 160.5.

2.6.20. 6-Amino-4-(4-(trifluoromethyl)phenyl)-1,4-dihydro-3-methyl-1-phenylpyrano[2,3-c]pyrazole-5-carbonitrile (compound 6u)

^{1}H NMR (DMSO-d_6, 500 MHz): 1.78 (s, 3H), 4.84 (s, 1H), 7.31–7.34 (m, 3H), 7.48–7.51 (m, 4H), 7.72 (d, J = 7.5 Hz, 2H), 7.78 (d, J = 7.5 Hz, 2H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 13.4, 37.3, 58.2, 98.7, 120.6, 120.9, 126.4, 127.1, 129.5, 130.2, 138.3, 144.8, 146.0, 149.1, 160.5.

2.6.21. 6-Amino-1,4-dihydro-3-methyl-1-phenyl-4-(thiophen-2-yl)pyrano[2,3-c]pyrazole-5-carbonitrile (compound 6v)

^{1}H NMR (DMSO-d_6, 500 MHz): 1.92 (s, 3H), 5.08 (s, 1H), 6.97 (m, 1H), 7.07 (d, J = 3.0 Hz, 1H), 7.27 (s, 2H), 7.32 (t, J = 7.5 Hz, 1H), 7.43 (d, J = 5.0 Hz, 1H), 7.49 (t, J = 8.0 Hz, 2H), 7.77 (d, J = 8.0 Hz, 2H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 13.3, 32.8, 59.4, 99.5, 120.6, 120.8, 125.8, 126.3, 127.1, 127.5, 130.2, 138.2, 144.3, 146.2, 149.6, 160.0.

2.6.22. 6-Amino-4-(4-(hydroxy)phenyl)-1,4-dihydro-3-methyl-1-phenylpyrano[2,3-c]pyrazole-5-carbonitrile (compound 6w)

^{1}H NMR ($CDCl_3$, 500 MHz): 1.78 (s, 3H), 4.55 (s, 1H), 6.71 (d, J = 4.0 Hz, 2H), 7.03 (d, J = 4.0 Hz, 2H), 7.11 (s, 2H), 7.30 (t, J = 7.0 Hz, 1H),7.48 (t, J = 7.4 Hz, 2H). 7.77 (d, J = 4.0 Hz, 2H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 13.4, 36.9, 59.7, 99.9, 116.1, 120.8, 120.9, 126.9, 129.6, 130.2, 134.8, 138.5, 144.6, 146.2, 157.2, 160.1.

2.6.23. 6-Amino-1,4-dihydro-4-(4-isopropylphenyl)-3-methyl-1-phenylpyrano[2,3-c]pyrazole-5-carbonitrile (compound 6x)

^{1}H NMR (DMSO-d_6, 500 MHz): 1.19 (d, J = 8.3 Hz, 6H), 1.79 (s, 3H), 2.86 (m, 1H), 4.63 (s, 1H), 7.16–7.71 (m, 11H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 13.3, 32.8, 59.4, 99.5, 120.6, 120.8, 125.8, 126.3, 127.1, 127.5, 130.2, 138.2, 144.3, 146.2, 149.6, 160.0.

2.6.24. Dimethyl 4,4′-(1,4-phenylene)bis(2-amino-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carboxylate) (compound 8a)

M.p. = 226–288 °C. ^{1}H NMR (DMSO-d_6, 500 MHz): 0.81 (s, 6H), 1.00 (s, 6H), 2.05 (d, J = 16.0 Hz, 2H), 2.22 (d, J = 16.5 Hz, 2H), 2.4–2.5 (m, 4H), 3.47 (s, 6H), 4.45 (s, 2H), 6.93 (s, 4H), 7.5 (s, 4H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 27.0, 29.5, 32.7, 33.2, 50.7, 51.3, 78.5, 116.8, 127.6, 144.5, 160.3, 163.0, 169.1, 196.6.

2.6.25. 4,4′-(1,4-phenylene)bis(2-amino-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile) (compound 8b)

M.p. = 304 °C (dec.) ^{1}H NMR (DMSO-d_6, 500 MHz): 1.94 (m, 4H), 2.28 (m, 4H), 2.60 (m, 4H), 4.14 (s, 2H), 6.95 (s, 4H), 7.05 (s, 4H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 20.5, 27.3, 35.7, 37.1, 59.0, 59.1, 114.7, 120.7, 127.9, 143.7, 159.4, 159.5, 165.4, 165.5, 196.8.

2.6.26. 4,4′-(1,4-phenylene)bis(6-amino-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile) (compound 8c)

M.p. = 296 °C (dec.) ^{1}H NMR (DMSO-d_6, 500 MHz): 2.19 (s, 6H), 4.72 (s, 2H), 7.21–7.22 (m, 4H), 7.37–7.47 (m, 6H), 7.60–7.62 (m, 4H), 7.69–7.79 (m, 4H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 12.7, 22.4, 58.3, 118.8, 119.7, 120.1, 127.1, 128.3, 129.0, 129.4, 132.3, 138.1, 148.6, 177.1.

3. Results and discussions

At first, SB-DABCO was prepared form the reaction of 3-chloropropyl silica and DABCO as shown in Scheme 1. The catalyst structure was demonstrated with IR spectroscopy. The FT-IR spectra of the DABCO (a), silica bonded *n*-propylchloride (b), and silica bonded *n*-propyl-4-aza-1-azoniabicyclo[2.2.2]octane chloride (c) samples are presented in Fig. 1. The pure DABCO shows a characteristic broad absorbance at 1000–1100 cm^{-1} (C–N stretching), and at 1480 cm^{-1} for CH_2 bending. In the spectrum of silica bonded *n*-propyl chloride, absorbances at 1460 and 1210 cm^{-1} were observed which indicate the presence of CH_2 bending and Si–C stretching, respectively. There are four characteristic peaks in the spectrum of SB-DABCO. The C–N^+ stretching at 1615 cm^{-1}, CH_2 bending at 1480 cm^{-1}, Si–C stretching at 1210 cm^{-1}, and Si–O stretching at 1110–1090 cm^{-1} as a broad bond. Compared with the spectrum of silica bonded *n*-propyl chloride, SB-DABCO exhibits the characteristic band at 1615 cm^{-1} due to the fact that C–N^+ group appeared after the reaction of silica bonded *n*-propyl chloride with DABCO. These results prove that the DABCO was successfully linked to silica bonded *n*-propyl chloride to give SB-DABCO.

For more investigation about the structure of the catalyst, the amount of carbon dioxide, produced by the oxidation of the catalyst during the thermogravimetric (TG) analysis, was determined using a carbon dioxide sensor. The spectroscopic results are shown in Fig. 2.

As it can be seen in Fig. 2, the ratio of carbon atoms presented in silica bonded *n*-propyl chloride structure (B) relative to that exist in silica bonded *n*-propyl-4-aza-1-azoniabicyclo[2.2.2]octane chloride structure (A) was evaluated to one third. This ratio is partially

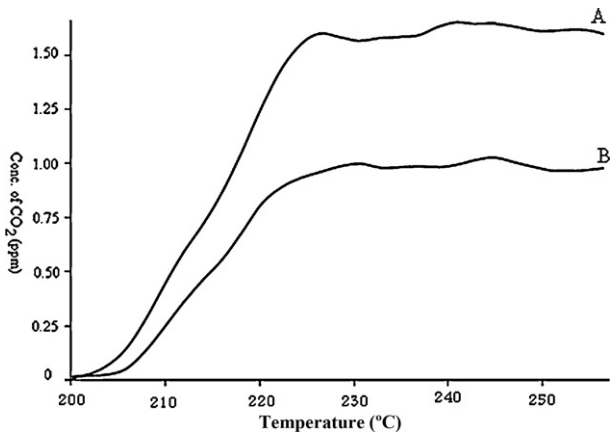


Fig. 2. Diagram of produced CO_2 versus temperature for silica bonded *n*-propyl-4-aza-1-azoniabicyclo[2.2.2]octane chloride (A) and silica bonded *n*-propyl chloride (B).

the same as the results obtained based on the spectroscopic data shown in Fig. 2.

We also determined the loading level of DABCO (1.014 mmol/g) based on the chlorine content by titrimetric analysis, with employing a recent procedure [31], which is shown to be in good agreement with the results obtained from TGA and conventional elemental analysis. Nitrogen content of the silica bonded *n*-propyl-4-aza-1-azoniabicyclo[2.2.2]octane chloride was 2.85% by conventional elemental analysis. The thermal stability of SB-DABCO was also investigated using a self-made TG analysis instrument, and the results are shown in Fig. 3. Fig. 3 shows the thermogram of the sample at an air flow of 3 mL min^{-1} and temperature ramp of 2 °C min^{-1}. The weight lost at around 90 °C can be related to the desorption of water vapor and other volatile organic compounds which have been adsorbed on the catalyst. Following the thermogram, the decrease observed in the slope of the diagram, starting at around 220 °C can be related to the loss of the covalently bound organic group.

The adsorption behavior of nitrogen gas on each silica bonded *n*-propyl chloride and silica bonded *n*-propyl-4-aza-1-azoniabicyclo[2.2.2]octane chloride have also been studied using the TG analysis instrumentation system and nitrogen atmosphere (Fig. 4). The results reveal that a significant increase to ~160 m^2 kg^{-1} was observed in the active surface area of the silica support when modified with DABCO catalyst.

The total basicity of silica bonded *n*-propyl chloride (SiPrCl) and silica bonded *n*-propyl-4-aza-1-azoniabicyclo[2.2.2]octane chloride (SB-DABCO) was measured by temperature programmed desorption (TPD) of CO_2 by TGA method. The desorption temperature and amount of CO_2 desorbed are considered as indexes of base strength and total number of base sites, respectively. It is observed that only one major weight losses occurred over SiPrCl at range of 230–250 °C. Moreover, it is observed that two major weight losses occurred over SB-DABCO. The first and second weight losses occurred between 250–270 °C and 310–330 °C, respectively. Although it was difficult to exactly express the strength on a definite scale and to count the number of basic sites quantitatively, TPD could be used to evaluate the relative strength of basic sites. Fig. 5 shows the spectra of CO_2-TPD from samples SiPrCl and SB-DABCO, which indicate that the SB-DABCO is a basic catalyst according to desorption temperature and intensity of CO_2 absorbed on this catalyst.

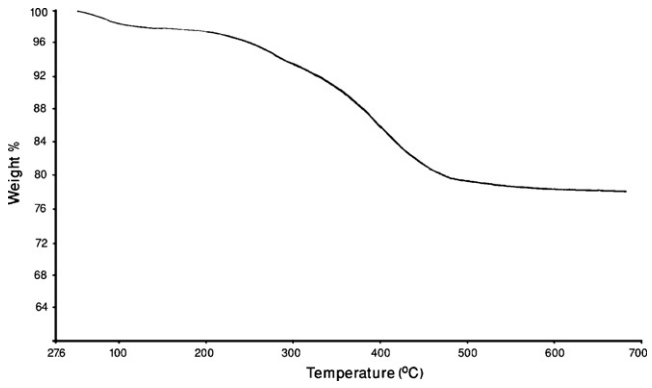
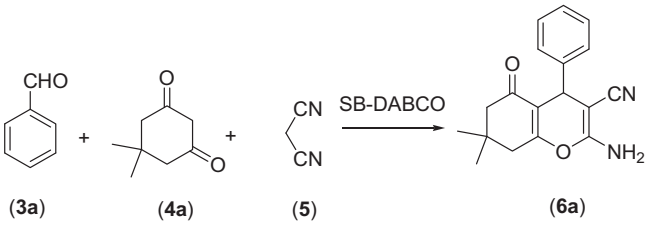


Fig. 3. The thermogravimeric analysis diagram of silica bonded *n*-propyl-4-aza-1-azoniabicyclo[2.2.2]octane chloride.



Scheme 3. The reaction of benzaldehyde (3a) with 5,5-dimethylcyclohexane-1,3-dione (4a) and malononitrile (5) leading to compound 6a using SB-DABCO.

To further evaluate the efficacy of our new catalyst, the condensation reaction of C–H activated ketones with aromatic aldehydes and alkylmalonates for the synthesis of 4*H*-benzo[*b*]pyran derivatives was studied. To obtain the optimal reaction conditions, the condensation of benzaldehyde (3a) (1 mmol) with 5,5-dimethylcyclohexane-1,3-dione (4a) (1 mmol) and malononitrile (5) (1 mmol) in the presence of SB-DABCO was selected as a model reaction to produce compound 6a (Scheme 3).

The reaction was examined in the presence of different molar ratios of SB-DABCO in ethanol at room temperature. The results are summarized in Table 1. As Table 1 indicates, higher yield and shorter reaction time were obtained when the reaction was carried out in the presence of 6 mol% of the catalyst in ethanol; in these conditions, the corresponding 4*H*-benzo[*b*]pyran (6a) was obtained in 96% yield within 35 min (Table 1 entry 3). The model reaction was also examined in the presence of SB-DABCO at room temperature in several solvents including $CHCl_3$, CH_2Cl_2, CH_3CN, EtOAc and H_2O, (Table 1 entries 7–12). As it can be seen in Table 1, ethanol was the best solvent for this reaction.

The reaction of benzaldehyde (3a) with 5,5-dimethylcyclohexane-1,3-dione (4a) and malononitrile (5) was also checked in the presence of SiO_2 in which a substantial increase in the reaction time (240 min) and decrease in the yield (70%) were observed.

Table 1
The reaction of benzaldehyde (1 mmol) with malononitrile (1 mmol), and 5,5-dimethylcyclohexane-1,3-dione (1 mmol) in the presence of SB-DABCO at room temperature.

Entry	Solvent (5 ml)	Catalyst (mol %)	Time (min)	Yield[a] (%)
1	EtOH	1.5	300	47
2	EtOH	3	150	85
3	EtOH	6	35	96
4	EtOH	9	30	95
6	EtOH	-	300	Trace
7	$CHCl_3$	6	300	60
8	CH_2Cl_2	6	300	68
10	CH_3CN	6	180	85
11	EtOAc	6	300	52
12	H_2O	6	90	87

[a] Isolated yield.

Table 2
The synthesis of 4*H*-benzo[*b*]pyran derivatives in the presence of SB-DABCO.

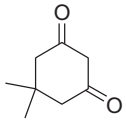
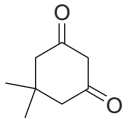
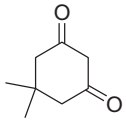
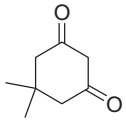
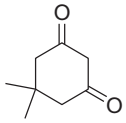
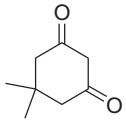
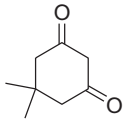
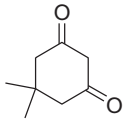
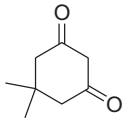
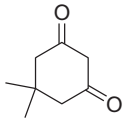
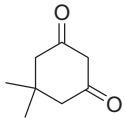
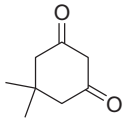
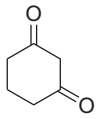
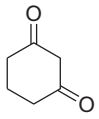
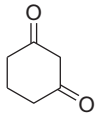
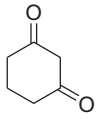
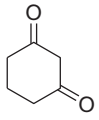
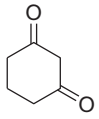
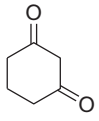
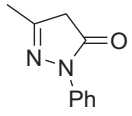
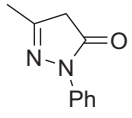
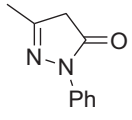
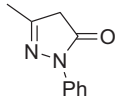
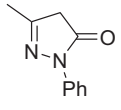
Entry	Substrate	R	X	Method	Time (min)	Yield[a] (%)	M.p. (°C)	
							Found	Reported
6a		C_6H_5	CN	A	35	96	227–229	226–228 [32]
6b		4-ClC_6H_4	CN	A	25	95	237–239	239–241 [33]
6c		4-$EtOC_6H_4$	CN	A	55	91	233–235	–
6d		4-$NO_2C_6H_4$	CN	A	20	90	173–174	176–178 [33]
6e		2-naphthyl	CN	A	40	96	258–260	–
6f		3-$phOC_6H_4$	CN	A	25	96	193–194	-
6g		2-thienyl	CN	A	50	92	220–222	–
6h		C_6H_5-CO	CN	A	30	93	220–221	–
6i		4-$CF_3C_6H_4$	CO_2Et	B	300	90	155–156	–
6j		2-naphthyl	CO_2Et	B	180	97	188–190	–
6k		4-CNC_6H_4	CO_2Me	B	140	95	180–182	–
6l		4-ClC_6H_4	CO_2Me	B	180	95	166–168	167–168 [34]

Table 2 (*Continued*)

Entry	Substrate	R	X	Method	Time (min)	Yield[a] (%)	M.p. (°C)	
							Found	Reported
6m		4-ClC_6H_4	CN	A	40	95	225–227	224–226 [35]
6n		4-$NO_2C_6H_4$	CN	A	25	94	236–237	234–236 [35]
6o		4-$CH_3C_6H_4$	CN	A	40	92	232–233	–
6p		2-naphthyl	CN	A	30	97	254–255	–
6q		2-ClC_6H_4	CN	A	30	95	209–211	210–212 [35]
6r		4-ClC_6H_4	CO_2Et	B	120	98	183–184	–
6s		4-$EtOC_6H_4$	CO_2Me	B	250	97	149–150	–
6t		4-CNC_6H_4	CN	A	25	96	217–219	–
6u		4-$CF_3C_6H_4$	CN	A	30	97	182–184	–
6v		2-thienyl	CN	A	40	96	168–169	–
6w		4-OHC_6H_4	CN	A	60	93	206–208	210–212 [36]
6x		4-isopropyl-C_6H_4	CN	A	60	93	158–160	–

[a] Isolated yield.

To probe the efficiency and the scope of our method, a broad range of structurally diverse aldehydes (3) were condensed with cyclohexane-1,3-dione (4a)/5,5-dimethylcyclohexane-1,3-dione (4b)/3-methyl-1-phenyl-2-pyrazolin-5-one (4c) and alkyl nitriles (5) to furnish the corresponding 4*H*-benzo[*b*]pyrans in high yields and in relatively short reaction times (Scheme 2). The results are displayed in Table 2.

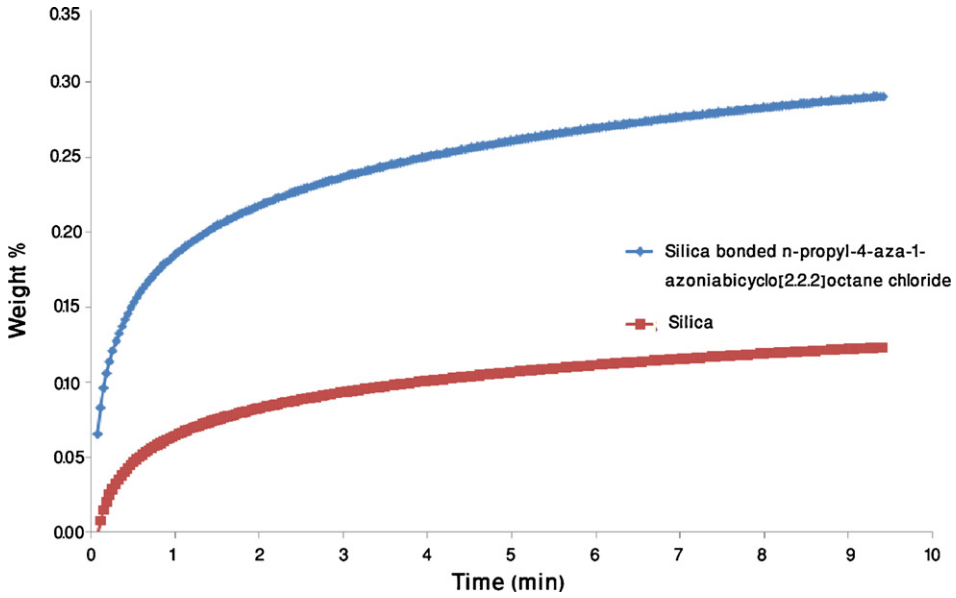


Fig. 4. The nitrogen adsorption isotherm of silica (red), and silica bonded *n*-propyl-4-aza-1-azoniabicyclo[2.2.2]octane chloride (blue).

In this study, we found that higher temperature (reflux conditions) was required for the condensation of alkylcyanoacetates with aromatic aldehyde and cyclohexane-1,3-dione/5,5-dimethylcyclohexane-1,3-dione/3-methyl-1-phenyl-2-pyrazolin-5-one in H_2O/EtOH (1/1) in the presence of SB-DABCO (method B, Table 2). This can be attributed to the lower reactivity of alkylcyanoacetates compared to malononitrile. Furthermore, as it is shown in Table 2, the presence of electron-withdrawing substituents on the aromatic ring of aryl aldehydes accelerated the reaction rate (Table 2, entries 6d, 6h, 6i, 6k, 6n, 6t and 6u), whereas electron-releasing substituents reduced the reaction rate (Table 2, entries 6c, 6o, 6s, 6w and 6x). The nature of substituents did not affect the reaction yields. Moreover, aromatic aldehydes bearing sensitive substituent as well as hetero-aromatic aldehyde (such as thiophene2-carbaldehyde) were applied successfully in the reaction to provide the corresponding benzo[*b*]pyrans without by-products (Table 2, entries (6k, 6t, 6g and 6v).

In addition, the complex structures of 8a, 8b and 8c were synthesized *via* the condensation of cyclohexane-1,3-dione/5,5-dimethylcyclohexane-1,3-dione/3-methyl-1-phenyl-2-pyrazolin-5-one (2 equivalents) with alkylnitriles (2 equivalents) and terephthalaldehyde (7) (1 equivalents) for the first time (Scheme 4).

On the other hand, it is known that the reaction of carbonyl compounds with derivatives of cyaoacetic acid gives 3-cyanopyridine-2(1*H*)-ones 9 and 2,6-dicyanoanilines 10 as by-products [37]. Meanwhile, the hydrolysis of the nitrile or ester groups leads to the formation of by-products 11 or 12 (Scheme 5). A distinct characterization of the present method, illustrated in this

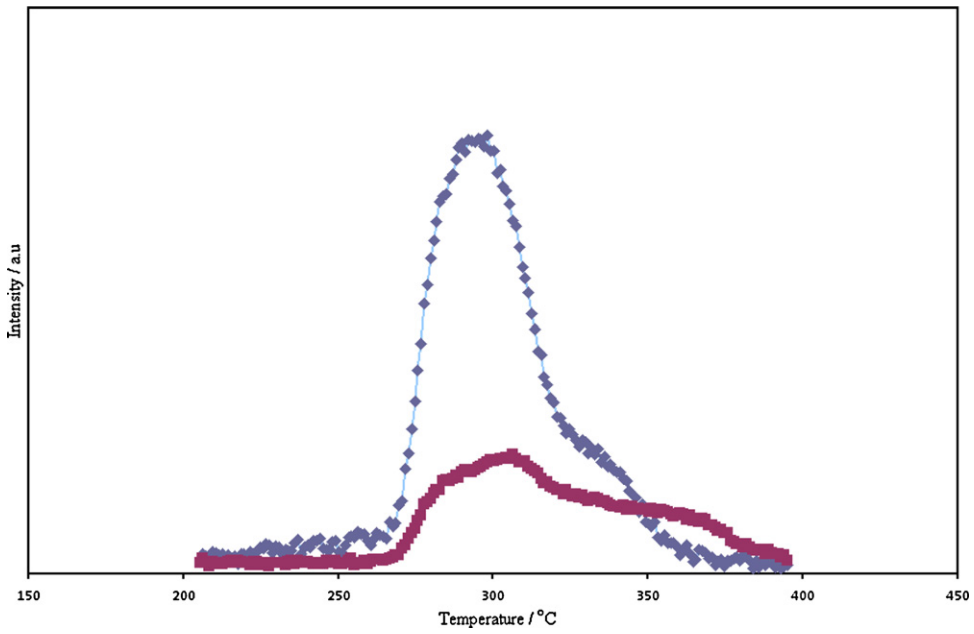
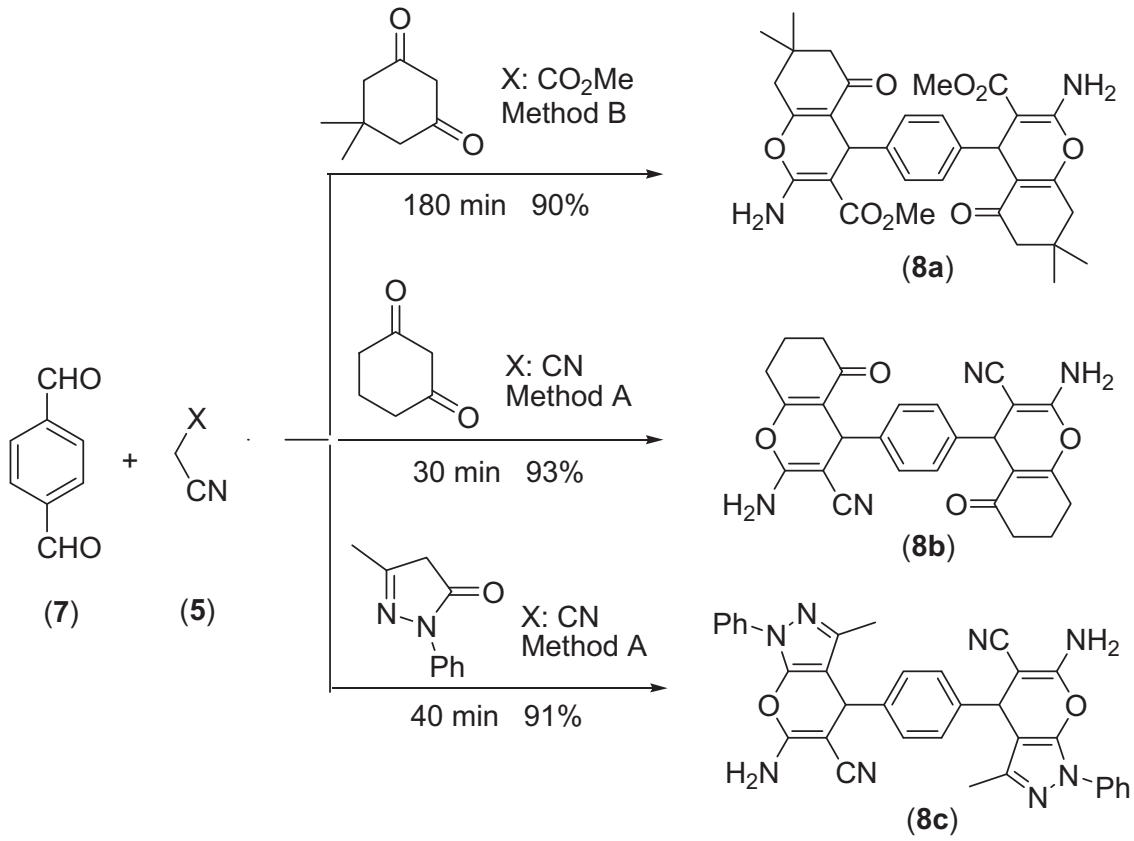
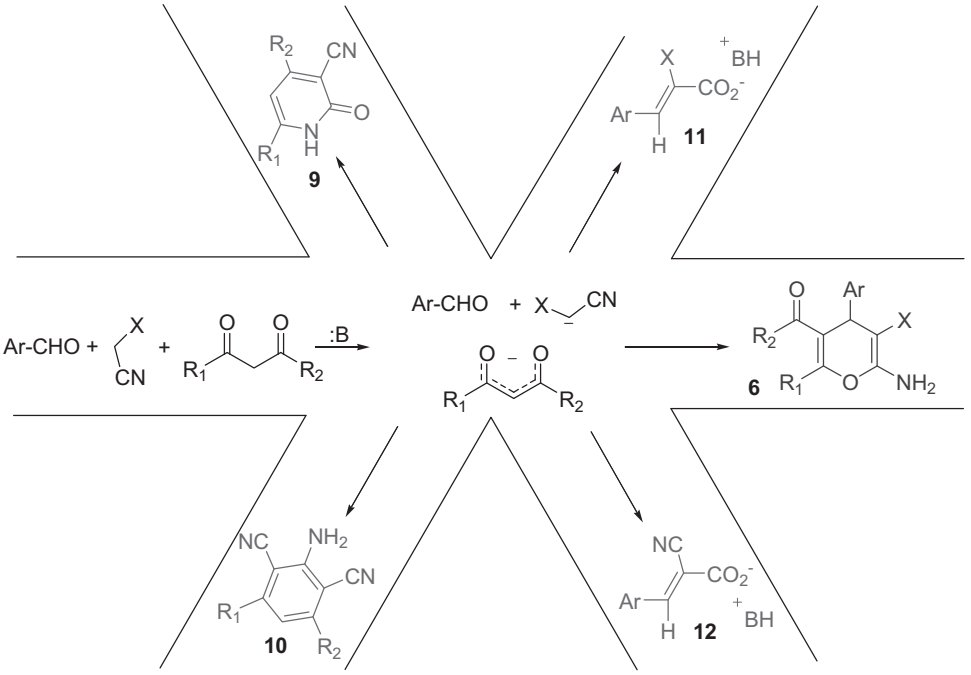


Fig. 5. The CO_2-TPD plots of SiPrCl (red) and SB-DABCO (blue).



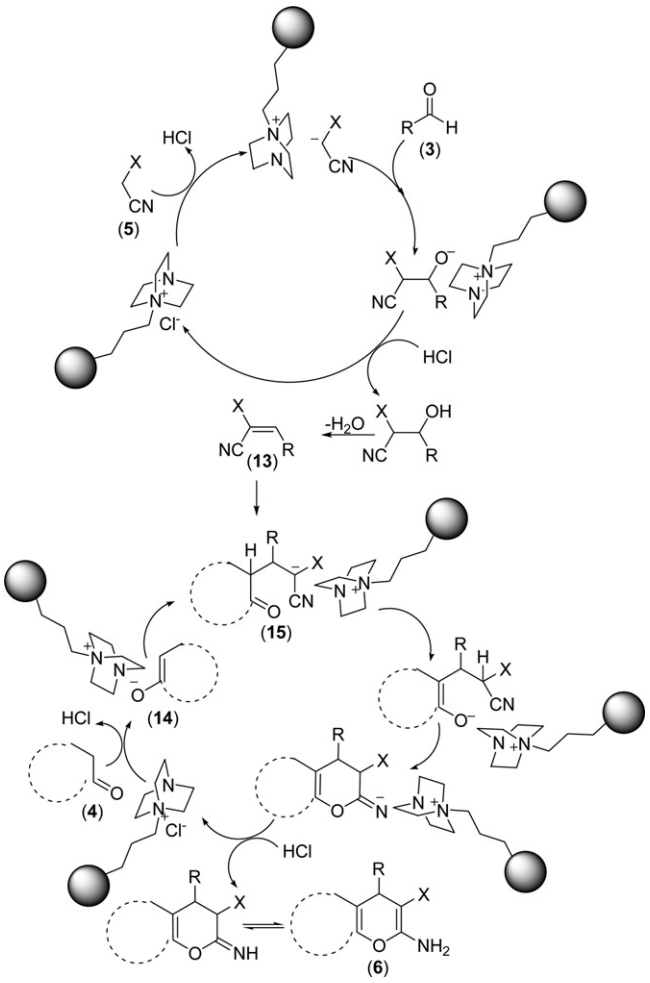
Scheme 4. The reaction of cyclohexane-1,3-dione, 5,5-dimethylcyclohexane-1,3-dione or 3-methyl-1-phenyl-2-pyrazolin-5-one (2 eq) with alkyl nitriles (2 eq) and terephthalaldehyde (1 eq).



Scheme 5. The three-component synthesis of 2-amino-benzo[*b*]pyran (blue) and theoretically possible by-products (red).

work, is the formation of benzo[*b*]pyrans 6 without by-product. Using this method, twenty seven compounds were obtained in good yield (purity not less than 90%) without additional purification.

The selectivity in the synthesis of 4*H*-benzo[*b*]pyrans 6 in the presence of SB-DABCO can be explained by the strict sequence of the reactions shown in Scheme 6. Based on this mechanism, SB-DABCO is effective catalyst for the formation of olefin 13, which readily prepares *in situ* from Knoevenagel condensation of aldehyde 3 with highly active CH-acidic cyanoacetic ester derivative 5. We consider this to be so, because unsaturated nitriles 13 are

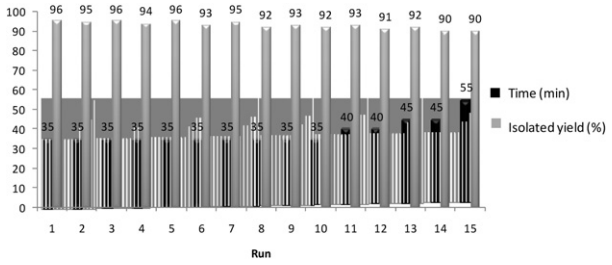


Scheme 6. The proposed mechanism for the synthesis of 4*H*-benzo[*b*]pyrans in the presence of SB-DABCO.

formed very easily in the absence of compound 4. Then, carbonyl compound 4, in the presence of SB-DABCO, subsequently converts to its corresponding enolate form 14, and adds to the unsaturated nitrile 13 by Michael reaction to produce intermediate 15, and enolate oxygen attacks nucleophilically nitrile group (Thorpe-Ziegler type reaction). Finally, after the tautomeric proton shift, 2-amino-4*H* benzo[*b*]pyran 6 is formed.

Table 3
Comparative the condensation of malononitrile with benzaldehyde and 5,5-dimethy-cyclohexane-1,3-dione using the reported catalysts versus SB-DABCO.

Entry	Reagents and conditions	Time (min)	Yield (%)	Ref.
4	Na_2SeO_4, 0.1 g, EtOH/H_2O, reflux	60	97	[33]
1	Hexadecyldimethyl benzyl ammonium bromide (HDMBAB), 12 mol%, H_2O, 90 °C	360	92	[35]
2	Tetra-methyl ammonium hydroxide (TMAH), 10 mol%, H_2O, r.t.	120	81	[34]
3	Rare earth perfluorooctanoate ($RE(PFO)_3$), 5 mol%, EtOH, 60 °C	300	90	[27]
1	NaOCl, 10 mol%, Grinding, r.t.	15	80	[39]
5	SB-DABCO, 6 mol%, EtOH, r.t.	35	96	Our catalyst



Graph 1. The reaction of benzaldehyde (1 mmol) with malononitrile (1 mmol) and 5,5-dimethylcyclohexane-1,3-dione (1 mmol) in ethanol (5 ml) using recovered SB-DABCO at room temperature.

In order to compare the capability and efficiency of our catalyst with respect to the previously reported catalysts for the preparation of 4*H*-benzo[*b*]pyrans, the results for the synthesis of compound 6a, employing these catalysts, are tabulated in Table 3. As it is clear from Table 3, SB-DABCO is more efficient than the others.

In another study, the condensation of benzaldehyde (3a) with 5,5-dimethylcyclohexane-1,3-dione (4a) and malononitrile (5) was tested in the presence of recovered silica bonded *n*-propyl-4-aza-1-azoniabicyclo[2.2.2]octane chloride to establish the reusability of the catalyst (Graph 1). As it is shown in Graph 1, no loss of the catalytic activity was observed even after fifteen cycles of the reaction.

4. Conclusions

We have introduced a highly efficient, heterogeneous, and reusable novel catalyst for the one-pot, three-component condensation of cyclic ketones/1,3-diketones with aromatic aldehydes and alkyl nitriles. The promising points for the presented methodology are the high efficiencies, generality, short reaction times, mild reaction conditions, clean reaction profiles, and simplicity which makes it a desirable and useful method for the synthesis of 4*H*-benzo[*b*]pyrans as biologically interesting compounds.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcata.2011.04.012.

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