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Silica-bonded 5-*n*-propyl-octahydro-pyrimido[1,2-*a*]azepinium chloride (SB-DBU)Cl as a highly efficient, heterogeneous and recyclable silica-supported ionic liquid catalyst for the synthesis of benzo[*b*]pyran, bis(benzo[*b*]pyran) and spiro-pyran derivatives

Alireza Hasaninejad[a,*], Nooshin Golzar[a], Maryam Beyrati[a], Abdolkarim Zare[b], Mohammad Mahdi Doroodmand[c]

[a] Department of Chemistry, Faculty of Sciences, Persian Gulf University, Bushehr 75169, Iran
[b] Department of Chemistry, Payame Noor University (PNU), Tehran 19395-4697, Iran
[c] Department of Chemistry, College of Science, Shiraz University, Shiraz 71454, Iran

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Silica-supported catalyst
Malono derivatives

ABSTRACT

The reaction of 3-chloropropyl silica (SilprCl) with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in dry acetone affords silica-bonded 5-*n*-propyl-octahydro-pyrimido[1,2-a]azepinium chloride (SB-DBU)Cl as a new silica-supported ionic liquid catalyst. Afterward, (SB-DBU)Cl is used for the efficient synthesis of 4*H*-benzo[*b*]pyran derivatives *via* the one-pot, three-component reaction of carbonyl compounds (cyclohexane-1,3-dione, 5,5-dimethylcyclohexane-1,3-dione or 3-methyl-1-phenyl-2-pyrazolin-5-one) with aromatic aldehydes and alkylmalonates. Moreover, some novel bis(benzo[*b*]pyran)s and a broad range of structurally diverse spiro-pyrans containing oxindole and/or quinoxaline moiety in their structures are synthesized using (SB-DBU)Cl. The catalyst is recycled and reused fifteen times with unchanged yield.

1. Introduction

The important advantages of solid acids and bases such as operational simplicity, environmental compatibility, non-toxicity, reusability, low cost, and ease of isolation recommend them as suitable catalytic systems in organic synthesis [1]. In fact, simplified recovery and reusability are critical advantages of heterogeneous catalytic systems, which could lead to novel environmentally benign chemical procedures for academia and industry [2]. Metal colloids, mineral clays and supported reagents on silica gel, alumina and other solid supports are various types of heterogeneous and reusable catalytic systems, which have been designed and used in organic synthesis. Between them, silica-supported catalysts have attracted more attention because they are inexpensive, easy to prepare, and insoluble in most of organic solvents, which makes them being recycled from various reactions.

1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) is an amidine base which has been used as catalyst in different organic transformations [3–6]. It is especially useful where side reactions are problem due to the inherent nucleophilicity of basic nitrogen [7–9]. DBU has some unique properties, and is useful catalyst in organic synthesis; nevertheless, its liquid form at room temperature makes the work-up procedure very hard [10–14]. Moreover, DBU cannot be recovered, and eliminated as residue in many reported procedures [10–14]. Recent efforts in order to overcome this problem were led to the preparation of ionic liquids based DBU such as [DBU][Ac], [DBU][Lac] and [DBU][Tfa] [15,16,6]. These types of catalysts are recoverable; however tedious work-up procedures are needed to recover the catalyst from the reaction media [15,16,6]. Thus, search for finding a heterogeneous, recoverable and reusable derivative of DBU is very desirable.

2-Amino-4*H*-benzo[*b*] pyran derivatives are of importance as they have been used in cosmetics and pigments, and also as potentially biodegradable agrochemicals [17]. Moreover, poly-functionalized 4*H*-benzo[*b*]pyrans constitute structural units of many natural products [18] and biologically interesting compounds possessing various pharmacological properties

* Corresponding author. Fax: +98 771 4222319.
E-mail address: a_hasaninejad@yahoo.com (A. Hasaninejad).

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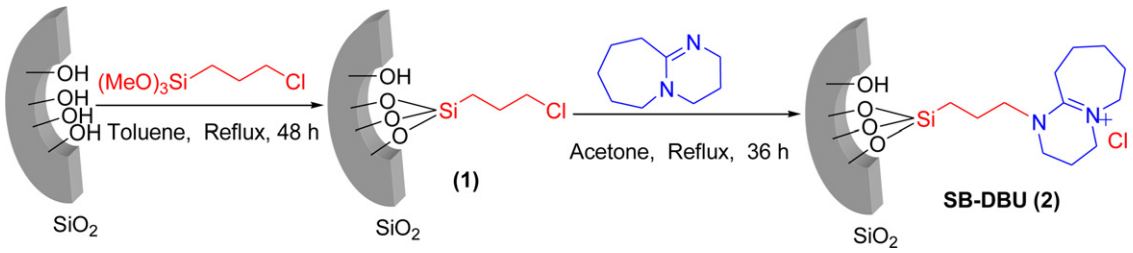


Scheme 1. The preparation of (SB-DBU)Cl.

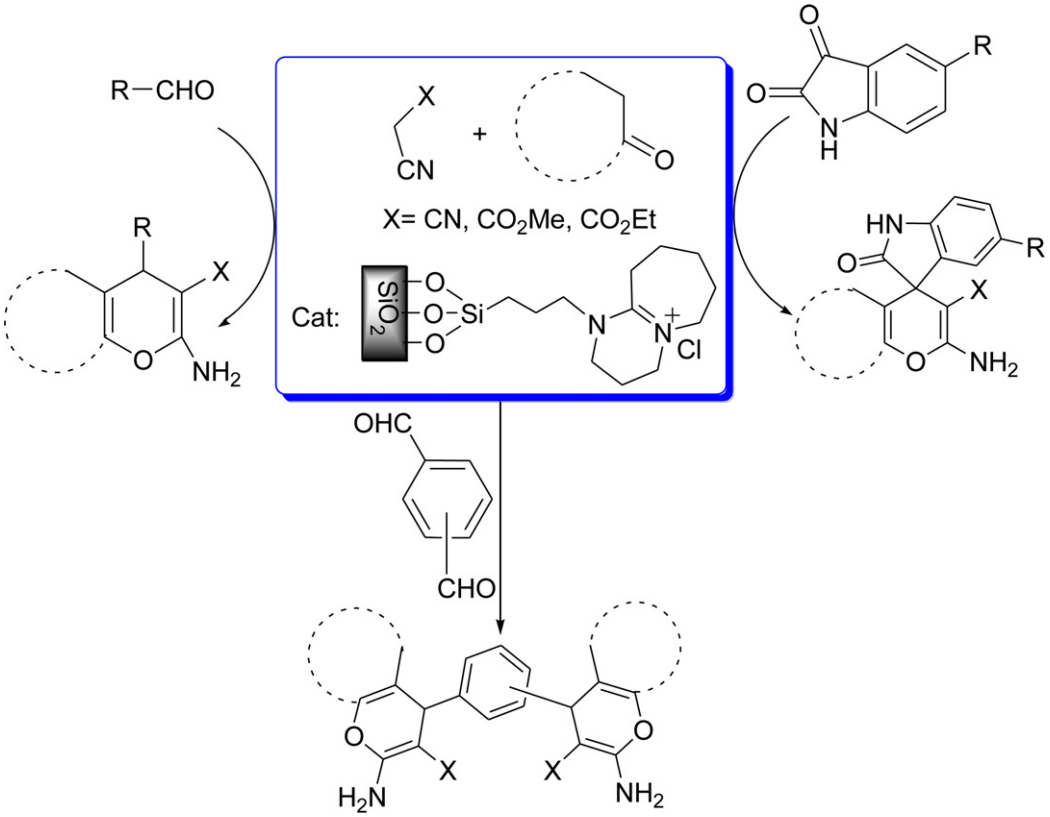
[19], such as antitum or [20], and antibacterial [21–23] activities. 4*H*-benzo[*b*]pyrans are also potential calcium channel antagonists, which are structurally similar to biologically active 1,4-dihydropyridines [24]. Some catalysts such as hexadecyltrimethyl ammonium bromide (HMTAB) [25], triethylbenzylammonium chloride (TEBA) [26], rare earth perfluorooctanoate [$RE(PFO)_3$] [27], and (*S*)-proline [28] have been used for the synthesis of 4*H*-benzo[*b*]pyrans. However, most of these methods suffer from some drawbacks such as low yields, long reaction times, and the use of expensive catalysts, harsh reaction conditions and tedious work-up. Moreover, in most of them, catalyst is not recyclable.

In continuation of our researches on the design and application of heterogeneous and reusable solid catalysts in organic synthesis and multi-component reactions [29–33], recently we prepared SB-DABCO that was used for the synthesis of 4*H*-benzo[*b*]pyrans [33]. However, this paper explained the bonding of DABCO as a solid base to silica. In some cases, DABCO could be separated from the reaction mixture without the need to bond to a bed. In continuation of our work to develop new and eco-friendly synthetic methodologies and studies on basic catalysts, we found that DBU has many unique properties, but its liquid form with low boiling point makes the application of this catalyst and also work-up procedure very hard. However some efforts have been done to prepare ionic liquids based-DBU but tedious work-up to recover the catalyst from the reaction media shows that supporting of DBU on a bed and heterogenization of this catalyst is highly desirable. Herein we wish to describe the preparation of silica-bonded 5-*n*-propyl-octahydro-pyrimido[1,2-*a*]azepinium chloride (SB-DBU)Cl from 3-chloropropyl silica (SilprCl) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (Scheme 1), and its application as a heterogeneous and easy recoverable silica-supported ionic liquid catalyst for the synthesis of benzo[*b*]pyrans, novel bis(benzo[*b*]pyran)s, 2′-aminospiro[indoline-3,4′-pyran]-2-one and spiro[indeno[1,2-*b*]quinoxaline-11,4′-pyran]-2′-amine derivatives (Scheme 2).

2. Experimental

2.1. Chemicals and apparatus

All chemicals were purchased from Merck or Fluka Chemical Companies. The chemicals were used in this study with their purity included: 1,3-cyclohexanedione (≥98%), 3-methyl-1-phenyl-2-pyrazolin-5-one (≥98%), 4-hydroxycoumarin (≥98%), 4-nitrobenzaldehyde (≥98%), thiophen-2-carbaldehyde (≥98%),



Scheme 2. The synthesis of 4*H*-benzo[*b*]pyran, bis(benzo[*b*]pyran) and spiro-pyran derivatives using (SB-DBU)Cl.

4-(trifluoromethyl)-benzaldehyde (≥98%), 4-Chlorobenzaldehyde (≥98%), 2-chlorobenzaldehyde (≥98%), 4-hydroxybenzaldehyde (≥98%), malononitrile (≥98%), ethyl cyanoacetate (≥98%), methyl cyanoacetate (≥98%), 1,8-diazabicyclo[5.4.0]undec-7-ene (≥98%), isophthaldialdehyde (≥98%), terephthalddialdehyde (≥98%), isatin (≥98%), 1,2-diaminobenzene (≥98%), dimedone (99%), benzaldehyde (≥99%), 4-ethoxybenzaldehyde (≥99%), 4-ethoxybenzaldehyde (≥99%), 3-phenoxybenzaldehyde (≥99%), 4-isopropylbenzaldehyde (≥99%), 5-fluoroisatin (≥99%), ninhydrin (≥99%), acetone (≥99.5%), ethanol (≥99.5%), acenaphthenquinone (≥97%), 2-naphthaldehyde (≥97%), phenylglyoxal monohydrate (≥97%), 4-methylbenzaldehyde (≥97%), 4-cyanobenzaldehyde (95%), 5-methylisatin (95%), 5-bromoisatin (90%), 3-chloropropyl silica (230–400 mesh, estent of labeling: 2.5% loading, matrix active group 8% functionalized). All known compounds were identified by comparison of their melting points and ^{1}H NMR data with those reported in the literature. The ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) were run on a Bruker Avance DPX-250, FT-NMR spectrometer. Microanalysis was performed on a Perkin-Elmer 240-B microanalyzer. Measurements of surface area and pore size distribution were made using the Brunauer–Emmet–Teller (BET) method in a Quanta Sorb machine. Melting points were recorded on a Stuart Scientific Apparatus SMP3 (UK) in open capillary tubes. 3-Chloropropyl silica (**1**, SilprCl) was prepared according to the reported procedure [39].

2.2. Preparation of silica-bonded 5-n-propyl-octahydro-pyrimido[1,2-a]azepinium chloride (SB-DBU)Cl

A mixture of 3-chloropropyl silica (1.0 g) and DBU (0.76 g, 5.0 mmol) in dry acetone (30 mL) was added to a 50 mL round-bottomed flask connected to a reflux condenser. The mixture was stirred under reflux conditions for 36 h. The resulting mixture was then filtered, washed with dry acetone (30 mL) and dried at room temperature to give (SB-DBU)Cl as a white powder (1.10 g).

Initially, silica-bonded 5-*n*-propyl-octahydro-pyrimido[1,2-*a*]azepinium chloride (SB-DBU)Cl was prepared by the reaction of 3-chloropropyl silica (SilprCl) (**1**) with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in dry acetone (Scheme 1). The catalyst structure was characterized by infrared (IR) spectroscopy (sp^3 C—H stretching at 2920–2980 cm^{-1}, C=N stretching at 1650 cm^{-1}, CH_2 bending at 1460 cm^{-1}, Si—C stretching at 1220 cm^{-1} and Si—O stretching at 1080–1120 cm^{-1} as a broad bond) (the IR spectra of silica-*n*-propyl chloride and (SB-DBU)Cl are available in Supporting Information (Figs. S[1] and S[2])).

We also determined the loading level of DBU based on the chlorine content by titrimetric analysis according to the reported procedure [34] [primary standard: C_{NaCl} = 0.02 M; titrant (standard solution): C_{AgNO_3} = 0.0204 M; indicator: K_2CrO_4; titrate: SB-DBU (129.2 mg), deionized water (25 mL) and K_2CrO_4 (0.25 mL)]. For further confidence on the results obtained from the precipitate titration, potentiometric titration was also performed. For this purpose, 0.2 g of the sample was added to 5.0 mL of H_2O, and titrated by Ag^+ standard solution using a potentiometer (Model: LT, Lutron, PH-207). Pt disk and Ag/AgCl (3.0 M) electrodes were applied as the indicator and reference probes, respectively. The results showed that the loading level of DBU was ~0.45 mmol g^{-1}.

The adsorption behaviors of nitrogen gas on both SilprCl and (SB-DBU)Cl were studied using the thermogravimetric (TG) analysis instrumentation system in nitrogen atmosphere at 77 K (Fig. S[3], Supporting Information). According to the BET surface area calculated from the adsorption data (Fig. S[3], Supporting Information), the active surface of the silica support increased to ~70 m^2 g^{-1}.

In another study, the total basicity of SilprCl and (SB-DBU)Cl was measured by temperature programmed desorption (TPD) of CO_2 by TG analysis. The desorption temperature and amount of desorbed CO_2 were considered as indexes of base strength and total number of basic sites, respectively. As the desorption temperature strongly depends the amount of oxygen as well as the temperature ramp during the TG analysis, therefore in this experiment, to have more reproducible data during the thermal analysis of the sample, the analysis was operated at trace amount of air as oxidant as well as low temperature ram 2 °C min^{-1}. Consequently the temperature was run up to higher temperature such as 400 °C.

It was observed that only one major weight loss occurred over SiprCl at range of 260–280 °C, whereas two major weight losses occurred over SB-DBU at ranges of 270–290 °C and 300–310 °C, correspondingly. Although it was difficult to calculate exactly the basic 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. The diagram of CO_2-TPD from SiprCl and (SB-DBU)Cl indicated that (SB-DBU)Cl was a basic catalyst according to desorption temperature and intensity of CO_2 absorbed on this catalyst (the CO_2-TPD plots of SiPrCl and (SB-DBU)Cl are available in Supporting Information (Fig. S[4])).

Thermogravimetric (TG) analysis of (SB-DBU)Cl and SiO_2 was also studied. In this study, (SB-DBU)Cl showed almost 10% weight losses; this weight can be related to the organic moiety (DBU) of (SB-DBU)Cl (about 0.45 mmol of DBU per 1.0 g of the catalyst). These results, which were in accordance with the results obtained from the previous mentioned studies, also confirmed the structure of (SB-DBU)Cl (the thermogram of (SB-DBU)Cl and SiO_2 are available in Supporting Information Fig. S[5]).

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

Carbonyl compound (1.0 mmol), malononitrile (1.0 mmol) and aromatic aldehyde (1.0 mmol) were added in a 25.0 mL round-bottomed flask contained (SB-DBU)Cl (0.11 g, 5.0 mol%) and EtOH (5.0 mL). The resulting mixture was stirred at room temperature (method A) [in order of alkyl cyanoacetates, the reaction was carried out in EtOH/H_2O (1:1) under reflux conditions (method B)]. After completion of the reaction, as monitored by TLC, ethanol (5 mL) was added to the reaction mixture and heated at 60 °C for ~5 min to dissolve the product followed by centrifugation for 10 min to separate the (SB-DBU)Cl. The EtOH was evaporated under reduced pressure to give the crude product. The crude product was dissolved in warm EtOH or aqueous EtOH (6.0 mL) and was allowed to stand at room temperature for 3–5 h. The crystalline solids were collected, washed with ethanol and dried. The same procedure was applied for the preparation of spiro-pyran derivatives and complex compounds; however, in the case of the preparation of complex compounds, 2.0 mmol of carbonyl compound, 2.0 mmol of alkylmalonate and 1.0 mmol of dialdehyde were used. The recovered (SB-DBU)Cl was reused for another time without loss of its activity.

Percent yields of the products were calculated as follows:

$$\%\text{yield} = \frac{\text{actual yield (g)}}{\text{theoretical yield (g)}} \times 100$$

3. Some selected spectral data of the products

3.1. 2-Amino-4-(4-ethoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**6c**)

M.p. = 233–235 °C. ^{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. Anal. Calcd. for $C_{20}H_{22}N_2O_3$: C, 70.99; H, 6.55; N, 8.28. Found: C, 70.93; H, 6.56; N, 8.25.

*3.2. 2-Amino-7,7-dimethyl-4-(naphthalen-2-yl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**6e**)*

M.p. = 258–260 °C. ^{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. Anal. Calcd. for $C_{22}H_{20}N_2O_2$: C, 76.72; H, 5.85; N, 8.13. Found: C, 76.75; H, 5.88; N, 8.12.

*3.3. 2-Amino-7,7-dimethyl-5-oxo-4-(3-phenoxyphenyl)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**6f**)*

M.p. = 193–194 °C. ^{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. Anal. Calcd. for $C_{24}H_{22}N_2O_3$: C, 74.59; H, 5.74; N, 7.25. Found: C, 74.62; H, 5.78; N, 7.26.

*3.4. 2-Amino-7,7-dimethyl-5-oxo-4-(thiophen-2-yl)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**6g**)*

M.p. = 220–222 °C. ^{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. Anal. Calcd. for $C_{16}H_{16}N_2O_2S$: C, 63.98; H, 5.37; N, 9.33. Found: C, 63.92; H, 5.41; N, 9.37.

*3.5. 2-Amino-4-benzoyl-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**6h**)*

M.p. = 220–221 °C. ^{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. Anal. Calcd. for $C_{19}H_{18}N_2O_3$: C, 70.79; H, 5.63; N, 8.69. Found: C, 70.83; H, 5.62; N, 8.72.

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

M.p. = 188–190 °C. ^{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. Anal. Calcd. for $C_{24}H_{25}NO_4$: C, 73.64; H, 6.44; N, 3.58. Found: C, 73.67; H, 6.49; N, 3.63.

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

M.p. = 180–182 °C. ^{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. Anal. Calcd. for $C_{20}H_{20}N_2O_4$: C, 68.17; H, 5.72; N, 7.95. Found: C, 68.23; H, 5.71; N, 7.99.

*3.8. 2-Amino-5-oxo-4-p-tolyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**6o**)*

M.p. = 232–233 °C. ^{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. Anal. Calcd. for $C_{17}H_{16}N_2O_2$: C, 72.84; H, 5.75; N, 9.99. Found: C, 72.88; H, 5.73; N, 10.04.

*3.9. 2-Amino-4-(naphthalen-2-yl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**6p**)*

M.p. = 254–255 °C. ^{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. Anal. Calcd. for $C_{20}H_{16}N_2O_2$: C, 75.93; H, 5.10; N, 8.86. Found: C, 75.97; H, 5.16; N, 8.83.

*3.10. Methyl 2-amino-4-(4-ethoxyphenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carboxylate (**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, 4.16.

*3.11. 6-Amino-4-(4-cyanophenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (**6t**)*

M.p. = 217–219 °C. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 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. Anal. Calcd. for $C_{21}H_{15}N_5O$: C, 71.38; H, 4.28; N, 19.82. Found: C, 71.43; H, 4.22; N, 19.86.

*3.12. 6-Amino-3-methyl-1-phenyl-4-(4-(trifluoromethyl) phenyl)-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (**6u**)*

M.p. = 182–184 °C. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 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. Anal. Calcd. for $C_{21}H_{15}F_3N_4O$: C, 63.63; H, 3.81; N, 14.14. Found: C, 63.68; H, 3.88; N, 14.19.

*3.13. 6-Amino-3-methyl-1-phenyl-4-(thiophen-2-yl)-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (**6v**)*

M.p. = 168–169 °C. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 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. Anal. Calcd. for $C_{18}H_{14}N_4OS$: C, 64.65; H, 4.22; N, 16.75. Found: C, 64.66; H, 4.21; N, 16.79.

*3.14. 6-Amino-4-(4-isopropylphenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (**6x**)*

M.p. = 156–180 °C. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 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. Anal. Calcd. for $C_{23}H_{22}N_4O$: C, 74.57; H, 5.99; N, 15.12. Found: C, 74.73; H, 5.63; N, 15.19.

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

M.p. = 226–288 °C. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 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. Anal. Calcd. for $C_{32}H_{36}N_2O_8$: C, 66.65; H, 6.29; N, 4.86. Found: C, 66.71; H, 6.34; N, 4.89.

*3.16. 4,4′-(1,3-Phenylene)bis(2-amino-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile) (**8b**)*

M.p. = 165 °C dec. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 0.94 (s, 6H), 1.05 (s, 6H), 2.04 (d, *J* = 16.0 Hz, 2H), 2.27 (d, *J* = 16.0 Hz, 2H), 2.38 (d, *J* = 17.3, 2H), 2.49–2.60 (m, 4H), 4.10 (s, 2H), 6.79 (s, 1H), 6.90 (s, 4H), 6.99–7.00 (m, 2H), 7.18 (t, *J* = 7.5, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 27.36, 29.70, 32.52, 36.20, 41.32, 113.66, 120.53, 125.54, 126.64, 128.73, 145.89, 159.41, 163.35, 196.27. Anal. Calcd. for $C_{30}H_{30}N_4O_4$: C, 70.57; H, 5.92; N, 10.97; found C, 70.59; H, 5.88; N, 11.01.

*3.17. 4,4′-(1,3-Phenylene)bis(6-amino-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile) (**8c**)*

M.p. = 198 °C (dec.) ^{1}H NMR (DMSO-d_6, 500 MHz): δ 1.78 (s, 6H), 4.7 (s, 2H), 7.14–7.18 (m, 6H), 7.29–7.35 (m, 4H), 7.48 (t, *J* = 8.0 Hz, 4H), 7.76 (d, *J* = 7.5 Hz, 4H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 13.4, 37.5, 58.9, 99.5, 120.7, 120.8, 127.0, 127.4, 128.1, 130.1, 138.4, 144.6, 146.2, 160.3. Anal. Calcd. for $C_{34}H_{26}N_8O_2$: C, 70.58; H, 4.53; N, 19.37; found C, 70.65; H, 4.51; N, 19.39.

*3.18. 4,4′-(1,4-Phenylene)bis(2-amino-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile) (**8d**)*

M.p. = 304 °C (dec.) ^{1}H NMR (DMSO-d_6, 500 MHz): δ 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. Anal. Calcd. for $C_{26}H_{22}N_4O_4$: C, 68.71; H, 4.88; N, 12.33; found C, 68.78; H, 4.92; N, 12.39.

*3.19. 4,4′-(1,4-Phenylene)bis(2-amino-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile) (**8e**)*

Mp. = 270 °C (dec.). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 0.98 (s, 6H), 1.03 (s, 6H), 2.15–2.24 (m, 4H), 2.46–2.55 (m, 4H), 4.13 (s, 2H), 6.94 (s, 4H), 7.03 (s, 4H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 27.8, 28.0, 29.0, 32.7, 35.8, 50.8, 59.2, 113.7, 120.6, 127.8, 143.7, 159.5, 163.4, 196.6. Anal. Calcd. for $C_{30}H_{30}N_4O_4$: C, 70.57; H, 5.92; N, 10.97; found C, 70.58; H, 5.97; N, 11.06.

*3.20. 4,4′-(1,4-phenylene)bis(6-amino-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile) (**8f**)*

M.p. = 296 °C (dec.) ^{1}H NMR (DMSO-d_6, 500 MHz): 2.19 (s, 3H), 4.72 (s, 1H), 7.21–7.22 (m, 2H), 7.37–7.47 (m, 3H), 7.60–7.62 (m, 2H), 7.69–7.79 (m, 2H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 13.4, 37.5, 58.9, 99.5, 120.7, 120.8, 127.0, 127.5, 128.2, 130.2, 138.4, 144.7, 146.2, 160.4. Anal. Calcd. for $C_{34}H_{26}N_8O_2$: C, 70.58; H, 4.53; N, 19.37; found C, 70.64; H, 4.48; N, 19.40.

*3.21. 2-Amino-2′,5-dioxo-5,6,7,8-tetrahydrospiro[chromene-4,3′-indoline]-3-carbonitrile (**12a**)*

M.p. = 297–299 °C (Lit.[35] 298–299 °C). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 1.90–1.93 (m, 2H), 217–249 (m, 2H), 2.51–2.66 (m, 2H), 6.77 (d, *J* = 7.2 Hz, 1H), 6.9 (d, *J* = 7.0 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.18 (s, 2H), 10.37 (s, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 19.4, 20.6, 27.6, 37.2, 47.7, 58.4, 110.0, 112.7, 118.1, 122.4, 124.0, 128.9, 135.4, 142.8, 159.5, 166.8, 178.9, 195.8. Anal. Calcd. for $C_{17}H_{13}N_3O_3$: C, 66.44; H, 4.26; N, 13.67; found C, 66.52; H, 4.33; N, 13.69.

*3.22. 2-Amino-5′-bromo-2′,5-dioxo-5,6,7,8-tetrahydrospiro[chromene-4,3′-indoline]-3-carbonitrile (**12b**)*

M.p. = 289 °C (dec.) (Lit.[35] 290–292 °C). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 1.91–1.96 (m, 2H), 2.23–2.25 (m, 2H), 2.63–2.64 (m, 2H), 6.74 (d, *J* = 8.0 Hz, 1H), 7.18–7.21 (m, 2H), 7.25 (s, 2H), 10.53 (s, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 20.5, 27.6, 37.1, 47.9, 57.7, 111.9, 112.1, 114.2, 118.0, 126.9, 131.7, 137.8, 142.2, 159.5, 167.4, 178.6, 196.0. Anal. Calcd. for $C_{17}H_{12}BrN_3O_3$: C, 52.87; H, 3.13; N, 10.88; found C, 52.88; H, 3.16; N, 10.91.

*3.23. 2-Amino-5′-fluoro-2′,5-dioxo-5,6,7,8-tetrahydrospiro[chromene-4,3′-indoline]-3-carbonitrile (**12c**)*

M.p. = 283–284 °C. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 1.92–1.93 (m, 2H), 2.19–2.23 (m, 2H), 2.60–2.68 (m, 2H), 6.74–6.77 (m, 1H), 6.94–6.98 (m, 2H), 7.26 (s, 2H), 10.40 (s, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 20.5, 27.6, 37.1, 112.0, 112.2, 115.0, 118.0, 137.1, 139.0, 159.5, 167.2, 179.0, 195.9. Anal. Calcd. for $C_{17}H_{12}FN_3O_3$: C, 62.77; H, 3.72; N, 12.92; found C, 62.80; H, 3.73; N, 12.94.

*3.24. 2-Amino-5′-methyl-2′,5-dioxo-5,6,7,8-tetrahydrospiro[chromene-4,3′-indoline]-3-carbonitrile (**12d**)*

M.p. = 282–284 °C. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 1.76–1.78 (m, 2H), 2.18 (s, 3H), 2.21–2.23 (m, 2H), 2.41–2.44 (m, 2H), 6.68 (d, *J* = 7.0 Hz, 1H), 6.76 (s, 1H), 6.96 (d, *J* = 7.75 Hz, 1H), 7.16 (s, 2H), 10.28 (s, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 20.4, 27.8, 37.8, 47.9, 51.0, 76.9, 110.7, 112.9, 114.4, 126.1, 130.7, 139.3, 144.1, 159.8, 165.7, 168.3, 177.4, 195.8. Anal. Calcd. for $C_{18}H_{15}N_3O_3$: C, 67.28; H, 4.71; N, 13.08; found C, 67.33; H, 4.73; N, 13.11.

*3.25. Methyl 2-amino-5′-bromo-2′,5-dioxo-5,6,7,8-tetrahydrospiro[chromene-4,3′-indoline]-3-carboxylate (**12e**)*

M.p. = 274 °C (dec.). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 1.86–1.88 (m, 2H), 2.17–2.21 (m, 2H), 2.62–2.64 (m, 2H), 3.27 (s, 3H), 6.62 (d, *J* = 8.0 Hz, 1H), 7.02 (s, 1H), 7.19 (dd, *J* = 2.0, 8.0 Hz, 1H), 7.87 (s, 1H), 10.29 (s, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 20.4, 27.8, 37.8, 47.9, 51.0, 76.9, 110.7, 112.9, 114.4, 126.1, 130.7, 139.3, 144.1, 159.8, 165.7, 168.3, 180.4, 195.8. Anal. Calcd. for $C_{18}H_{15}BrN_2O_5$: C, 51.57; H, 3.61; N, 6.68; found C, 51.61; H, 3.61; N, 6.67.

*3.26. Ethyl 2-amino-5′-bromo-2′,5-dioxo-5,6,7,8-tetrahydrospiro[chromene-4,3′-indoline]-3-carboxylate (**12f**)*

M.p. = 274–276 °C. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 0.82 (t, *J* = 7.0 Hz, 3H), 1.86–1.89 (m, 2H), 2.17–2.22 (m, 2H), 2.62–2.64 (m, 2H), 3.69–3.75 (m, 2H), 6.62 (d, *J* = 8.0 Hz, 1H), 7.03 (s, 1H), 7.20–7.22 (m, 1H), 7.91 (s, 2H), 10.30 (s, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 14.0, 20.4, 27.8, 37.8, 47.8, 59.8, 76.6, 110.7, 112.9, 114.4, 126.1, 130.6, 139.4, 144.3, 159.9, 165.6, 168.3, 180.3, 195.8. Anal. Calcd. for $C_{19}H_{17}BrN_2O_5$: C, 52.67; H, 3.95; N, 6.47; found C, 52.68; H, 3.98; N, 6.49.

*3.27. 2-Amino-7,7-dimethyl-2′,5-dioxo-5,6,7,8-tetrahydrospiro[chromene-4,3′-indoline]-3-carbonitrile (**12g**)*

M.p. = 289–291 °C (Lit.[35] 290–292 °C). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 1.00 (s, 3H), 1.03 (s, 3H), 2.07–2.18 (m, 2H), 2.55–2.56 (m, 2H), 6.78 (d, *J* = 7.5 Hz, 1H), 6.87–6.90 (m, 1H), 6.97 (d, *J* = 7.0 Hz, 1H), 7.12–7.15 (m, 1H), 7.20 (s, 2H), 10.38 (s, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 19.4, 27.8, 28.4, 32.8, 47.6, 50.8, 58.3, 110.0, 111.6, 118.1, 122.5, 123.8, 129.0, 135.2, 142.9, 159.6, 164.9, 178.8, 195.7. Anal. Calcd. for $C_{19}H_{17}N_3O_3$: C, 68.05; H, 5.11; N, 12.53; found C, 68.11; H, 5.14; N, 12.57.

*3.28. 2-Amino-5′-bromo-7,7-dimethyl-2′,5-dioxo-5,6,7,8-tetrahydrospiro[chromene-4,3′-indoline]-3-carbonitrile (**12h**)*

M.p. = 304–305 °C (Lit.[35] >300 °C). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 1.00 (s, 3H), 1.02 (s, 3H), 2.11–2.19 (m, 2H), 2.56–2.61 (m, 2H), 6.75 (d, *J* = 8.0 Hz, 1H), 7.20 (s, 1H), 7.31–7.32 (m, 3H), 10.54 (s, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 28.0, 28.4, 32.8, 47.9, 50.8, 27.6, 111.0, 112.0, 114.1, 118.0, 126.8, 131.7, 137.6, 142.3, 159.7, 165.4, 178.5, 195.9. Anal. Calcd. for $C_{19}H_{16}BrN_3O_3$: C, 55.09; H, 3.89; N, 10.14; found C, 55.12; H, 3.95; N, 10.19.

*3.29. 2-Amino-5′-fluoro-7,7-dimethyl-2′,5-dioxo-5,6,7,8-tetrahydrospiro[chromene-4,3′-indoline]-3-carbonitrile (**12i**)*

M.p. = 293 °C (dec.). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 0.97 (s, 3H), 0.98 (s, 3H), 2.11–2.18 (m, 2H), 2.54–2.58 (m, 2H), 6.75–6.78 (m, 1H), 6.94–6.98 (m, 2H), 7.27 (s, 2H), 10.40 (s, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 27.3, 27.9, 31.8, 37.9, 51.3, 56.8, 109.1, 111.0, 113.6, 116.3, 116.9, 128.3, 136.3, 154.8, 158.9, 159.4, 171.1, 197.3. Anal. Calcd. for $C_{19}H_{16}FN_3O_3$: C, 64.58; H, 4.56; N, 11.89; found C, 64.59; H, 4.59; N, 11.95.

*3.30. Ethyl 2-amino-7,7-dimethyl-2′,5-dioxo-5,6,7,8-tetrahydrospiro[chromene-4,3′-indoline]-3-carboxylate (**12j**)*

M.p. = 242–244 °C. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 0.79 (t, *J* = 7.0 Hz, 3H), 0.94 (s, 3H), 1.01 (s, 3H), 2.01 (d, *J* = 16.0 Hz, 1H), 2.15 (d, *J* = 16.0 Hz, 1H), 2.54–2.59 (m, 2H), 3.66–3.73 (m, 2H), 6.66 (d, *J* = 7.5 Hz, 1H), 6.75 (t, *J* = 7.2 Hz, 1H), 6.79–6.84 (m, 1H), 7.05 (t, *J* = 7.7 Hz, 1H), 7.84 (s, 2H), 10.12 (s, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 13.9, 26.8, 27.5, 28.6, 32.4, 47.4, 51.5, 59.5, 77.2, 101.7, 108.9, 113.9, 121.3, 123.0, 128.0, 136.8, 144.9, 159.9, 163.2, 168.5, 180.6, 195.5. Anal. Calcd. for $C_{21}H_{22}N_2O_5$: C, 65.96; H, 5.80; N, 7.33; found C, 65.98; H, 5.84; N, 7.39.

*3.31. 2′-Amino-7′,7′-dimethyl-2,5′-dioxo-5′,6′,7′,8′-tetrahydro-2H-spiro[acenaphthylene-1,4′-chromene]-3′-carbonitrile (**12k**)*

M.p. = 262–264 °C (Lit.[36] 260–262 °C). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 1.02 (s, 3H), 1.03 (s, 3H), 2.04–2.12 (m, 2H), 2.58–2.66 (m, 2H), 7.30 (s, 2H), 7.38 (d, *J* = 7.0 Hz, 1H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.82 (t, *J* = 7.5 Hz, 1H), 7.92–7.94 (m, 2H), 8.26 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 26.6, 26.8, 33.2, 36.5, 52.8, 53.6, 56.6, 99.3, 117.8, 119.3, 123.6, 126.4, 127.9, 128.3, 129.1, 130.9, 131.8, 134.1, 134.6, 153.5, 158.3, 195.9, 198.3. Anal. Calcd. for $C_{23}H_{18}N_2O_3$: C, 74.58; H, 4.90; N, 7.56; found C, 74.63; H, 4.93; N, 7.62.

*3.32. Ethyl 2-amino-5′-bromo-7,7-dimethyl-2′,5-dioxo-5,6,7,8-tetrahydrospiro[chromene-4,3′-indoline]-3-carboxylate (**12l**)*

M.p. = 274 °C (dec.). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 0.82 (t, *J* = 7.2 Hz, 3H), 1.04 (s, 3H), 1.05 (s, 3H), 2.05–2.14 (m, 2H), 2.49–2.53 (m, 2H), 3.69–3.75 (m, 2H), 6.63 (d, *J* = 8.0 Hz, 1H), 7.00 (s, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.91 (s, 2H), 10.30 (s, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 14.3, 27.1, 27.3, 33.2, 35.6, 40.1, 43.9, 49.3, 50.4, 54.6, 61.3, 111.3, 120.1, 125.9, 127.3, 130.9, 136.5, 138.4, 151.2, 171.5, 174.5, 199.6. Anal. Calcd. for $C_{21}H_{21}BrN_2O_5$: C, 54.68; H, 4.59; N, 6.07; found C, 54.69; H, 4.62; N, 6.11.

*3.33. 2-Amino-5′,7,7-trimethyl-2′,5-dioxo-5,6,7,8-tetrahydrospiro[chromene-4,3′-indoline]-3-carbonitrile (**12m**)*

M.p. = 277–279 °C (Lit.[37] 279–280 °C). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 1.01 (s, 3H), 1.03 (s, 3H), 2.09–2.17 (m, 2H), 2.19 (s, 3H), 2.55–2.59 (m, 2H), 6.67 (d, *J* = 7.5 Hz, 1H), 6.78 (s, 1H), 6.93 (d, *J* = 7.5 Hz, 1H), 7.18 (s, 2H), 10.27 (s, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 19.4, 21.53, 28.0, 28.3, 47.7, 50.9, 58.6, 109.8, 111.7, 118.2, 124.4, 129.3, 131.3, 135.3, 140.4, 159.5, 164.8, 178.8, 195.7. Anal. Calcd. for $C_{20}H_{19}N_3O_3$: C, 68.75; H, 5.48; N, 12.03; found C, 68.77; H, 5.51; N, 12.04.

*3.34. Methyl 2-amino-5′-bromo-7,7-dimethyl-2′,5-dioxo-5,6,7,8-tetrahydrospiro[chromene-4,3′-indoline]-3-carboxylate (**12n**)*

M.p. = 263–265 °C. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 0.96 (s, 3H), 1.00 (s, 3H), 2.05–2.15 (m, 2H), 2.46–2.53 (m, 2H), 3.27 (s, 3H), 6.65 (d, *J* = 8.0 Hz, 1H), 6.99 (d, *J* = 2.0 Hz, 1H), 7.20 (dd, *J* = 2.0, 8.0 Hz, 1H), 7.85 (s, 2H), 10.30 (s, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 27.9, 28.3, 32.4, 47.8, 51.0, 51.4, 76.8, 110.8, 112.9, 130.8, 139.2, 144.1, 159.9, 163.8, 168.3, 180.3, 195.7. Anal. Calcd. for $C_{20}H_{19}BrN_2O_5$: C, 53.71; H, 4.28; N, 6.26; found C, 53.75; H, 4.29; N, 6.28.

*3.35. 6′-Amino-5-fluoro-3′-methyl-2-oxo-1′-phenyl-1′H-spiro[indoline-3,4′-pyrano[2,3-c]pyrazole]-5′-carbonitrile (**12o**)*

M.p. = 214 °C (dec.). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 1.05 (s, 3H), 6.94–7.17 (m, 3H), 7.35–7.78 (m, 7H), 10.75 (s, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 12.7, 48.6, 57.3, 111.3, 112.9, 115.8, 116.3, 119.3, 122.4, 125.1, 127.4, 127.8, 135.5, 136.3, 145.9, 154.6, 158.3, 168.9, 177.3. Anal. Calcd. for $C_{21}H_{14}FN_5O_2$: C, 65.11; H, 3.64; N, 18.08; found C, 65.14; H, 3.66; N, 18.13.

*3.36. 6′-Amino-5-bromo-3′-methyl-2-oxo-1′-phenyl-1′H-spiro[indoline-3,4′-pyrano[2,3-c]pyrazole]-5′-carbonitrile (**12p**)*

M.p. = 227–229 °C (Lit.[35] 225–226 °C). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 1.57 (s, 3H), 6.85–6.90 (m, 2H), 6.95 (d, *J* = 7.0 Hz, 1H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.52 (t, *J* = 8.2 Hz, 2H), 7.80 (d, *J* = 8.5 Hz, 2H), 8.15 (s, 1H), 10.71 (s, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 12.5, 51.3, 99.1, 109.7, 120.8, 122.6, 124.0, 127.1, 128.6, 130.2, 136.4, 138.2, 142.8, 144.8, 145.0, 162.1, 168.9, 180.0. Anal. Calcd. for $C_{21}H_{14}BrN_5O_2$: C, 56.27; H, 3.15; N, 15.62; found C, 56.31; H, 3.14; N, 15.69.

*3.37. Methyl 6′-amino-5-bromo-3′-methyl-2-oxo-1′-phenyl-1′H-spiro[indoline-3,4′-pyrano[2,3-c]pyrazole]-5′-carboxylate (**12r**)*

M.p. = 225 °C (dec.). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 1.61 (s, 3H), 3.41 (s, 3H), 6.83 (d, *J* = 8.5 Hz, 1H), 7.21 (s, 1H), 7.32–7.35 (m, 2H), 7.51 (t, *J* = 7.7 Hz, 2H), 8.19 (s, 2H), 10.65 (s, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 12.6, 19.4, 48.6, 51.4, 56.9, 75.1, 98.4, 111.6, 114.3, 120.9, 127.0, 127.2, 130.2, 131.4, 138.2, 138.9, 142.1, 144.8, 144.9, 162.2, 168.6, 179.6. Anal. Calcd. for $C_{22}H_{17}BrN_4O_4$: C, 54.90; H, 3.56; N, 11.64; found C, 54.97; H, 3.58; N, 11.69.

*3.38. Ethyl 6′-amino-5-bromo-3′-methyl-2-oxo-1′-phenyl-1′H-spiro[indoline-3,4′-pyrano[2,3-c]pyrazole]-5′-carboxylate (**12s**)*

M.p. = 233–235 °C. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 0.79 (t, *J* = 8.0 Hz, 3H), 1.64 (s, 3H), 3.72–3.82 (m, 2H), 6.82 (d, *J* = 8.5 Hz, 1H), 7.21 (s, 1H), 7.32–7.36 (m, 2H), 7.51 (t, *J* = 7.7 Hz, 2H), 7.81 (d, *J* = 8.0 Hz, 2H), 8.25 (s, 2H), 10.65 (s, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 12.6, 14.0, 48.5, 59.9, 74.9, 98.4, 111.6, 114.3, 120.9, 127.0, 127.2, 130.2, 131.3, 138.2, 139.1, 142.3, 144.8, 144.9, 162.3, 168.5, 179.7. Anal. Calcd. for $C_{23}H_{19}BrN_4O_4$: C, 55.77; H, 3.87; N, 11.31; found C, 55.78; H, 3.90; N, 11.37.

*3.39. 6′-Amino-3′-methyl-2-oxo-1′-phenyl-1′H,2H-spiro[acenaphthylene-1,4′-pyrano[2,3-c]pyrazole]-5′-carbonitrile (**12t**)*

M.p. = 195–196 °C. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 1.06 (s, 3H), 7.35–7.37 (m, 1H), 7.51–7.54 (m, 2H), 7.59–7.64 (m, 3H), 7.78–7.82 (m, 3H), 7.92–7.95 (m, 1H), 8.08–8.11 (m, 2H), 8.42 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 12.9, 53.6, 58.6, 116.5, 118.9, 121.1, 122.5, 124.6, 125.3, 125.6, 126.8, 128.9, 129.7, 129.9, 130.8, 131.4, 132.7, 136.2, 141.9, 152.5, 177.3, 197.8. Anal. Calcd. for $C_{25}H_{16}N_4O_2$: C, 74.25; H, 3.99; N, 13.85; found C, 74.28; H, 4.02; N, 13.88.

*3.40. 2′-Amino-5-bromo-2,5′-dioxo-5′H-spiro[indoline-3,4′-pyrano[2,3-b]chromene]-3′-carbonitrile (**12u**)*

M.p. = 310 °C (dec.) (Lit.[35] >300 °C). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 6.82 (d, *J* = 8.0 Hz, 1H), 7.39 (dd, *J* = 2.0, 8.5 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.72–7.78 (m, 3H), 7.93 (dd, *J* = 1.0, 8.0 Hz, 1H), 10.80 (s, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 48.7, 57.3, 101.6, 112.2, 113.5, 114.6, 117.5, 117.7, 123.6, 125.8, 128.1, 132.5, 134.5, 136.2, 142.4, 152.9, 156.3, 159.3, 159.4, 177.7. Anal. Calcd. for $C_{20}H_{10}BrN_3O_4$: C, 55.07; H, 2.31; N, 9.63; found C, 55.11; H, 2.33; N, 9.67.

*3.41. 2′-Amino-5-fluoro-2,5′-dioxo-5′H-spiro[indoline-3,4′-pyrano[2,3-b]chromene]-3′-carbonitrile (**12v**)*

M.p. = 304 °C (dec.) (Lit.[35] >300 °C). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 6.84–6.86 (m, 1H), 7.02–7.06 (m, 1H), 7.25 (dd, *J* = 2.5, 8.2 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.71 (s, 2H), 7.76 (t, *J* = 8.5 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 10.70 (s, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 44.9, 56.3, 85.3, 111.1, 113.8, 116.3, 116.9, 117.4, 122.9, 123.4, 125.1, 128.9, 135.6, 136.1, 153.8, 157.6, 158.3, 168.9, 177.3, 181.5. Anal. Calcd. for $C_{20}H_{10}FN_3O_4$: C, 64.00; H, 2.69; N, 11.20; found C, 64.04; H, 2.76; N, 11.28.

*3.42. 2′-Amino-2,5′-dioxo-2H,5′H-spiro[acenaphthylene-1,4′-pyrano[2,3-b]chromene]-3′-carbonitrile (**12w**)*

M.p. = 289 °C (dec.). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 7.47 (d, *J* = 7.0 Hz, 1H), 7.56 (m, 1H), 7.63–7.76 (m, 5H), 7.88 (m, 1H), 8.00–8.02 (m, 3H), 8.34 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 58.5, 103.1, 113.4, 117.6, 117.9, 121.9, 123.0, 123.6, 125.9, 126.0, 129.5, 129.9, 130.7, 132.2, 133.0, 134.5, 142.0, 142.6, 152.9, 156.2, 159.3, 159.7, 203.9. Anal. Calcd. for $C_{24}H_{12}N_2O_4$: C, 73.47; H, 3.08; N, 7.14; found C, 73.54; H, 3.11; N, 7.18.

*3.43. Ethyl 2′-amino-2,5′-dioxo-2H,5′H-spiro[acenaphthylene-1,4′-pyrano[2,3-b]chromene]-3′-carboxylate (**12x**)*

M.p. = 242–243 °C. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 1.22 (t, *J* = 7.0 Hz, 3H), 3.32–3.37 (m, 2H), 7.42 (d, *J* = 7.5 Hz, 2H), 7.52–7.57 (m, 2H), 7.72–7.79 (m, 2H), 7.67 (d, *J* = 7.5 Hz, 2H), 8.08 (d, *J* = 7.5 Hz, 1H), 8.17–8.20 (m, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 13.1, 52.1, 59.5, 77.3, 105.8, 113.4, 117.3, 120.8, 120.9, 123.6, 123.7, 125.2, 125.7, 128.8, 129.2, 130.1, 131.1, 134.3, 135.8, 142.2, 144.7, 152.7, 154.9, 159.6, 159.7, 167.8, 205.6. Anal. Calcd. for $C_{26}H_{17}NO_6$: C, 71.07; H, 3.90; N, 3.19; found C, 71.15; H, 3.98; N, 3.26.

*3.44. 2-Amino-5-oxo-5,6,7,8-tetrahydrospiro[chromene-4,11′-indeno[2,1-b]quinoxaline]-3-carbonitrile (**12y**)*

M.p. = 278 °C (dec.). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 1.89–1.94 (m, 2H), 2.07–2.14 (m, 2H), 2.73–2.81 (m, 2H), 7.33 (s, 2H), 7.52–7.61 (m, 2H), 7.75–7.84 (m, 2H), 8.06–8.09 (m, 2H), 8.16 (dd, *J* = 1.0, 8.0 Hz, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 20.6, 27.8, 37.4, 48.0, 59.5, 113.8, 118.4, 122.2, 125.5, 129.66, 129.69, 129.7, 129.9, 130.5, 136.9, 141.7, 142.4, 152.9, 155.0, 159.6, 166.5, 167.5, 195.9. Anal. Calcd. for $C_{24}H_{16}N_4O_2$: C, 73.46; H, 4.11; N, 14.28; found C, 73.54; H, 4.18; N, 14.36.

*3.45. 2-Amino-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydrospiro[chromene-4,11′-indeno[2,1-b]quinoxaline]-3-carbonitrile (**12z**)*

M.p. = 280 °C (dec.). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 1.00 (s, 3H), 1.03 (s, 3H), 1.97–2.08 (m, 2H), 2.61–2.75 (m, 2H), 7.33 (s, 2H), 7.51–7.55 (m, 2H), 7.59–7.60 (m, 1H), 7.75–7.78 (m, 1H), 7.81–7.84 (m, 1H), 8.05 (dd, *J* = 1.5, 8.2 Hz, 1H), 8.08 (d, *J* = 7.5 Hz, 1H), 8.15 (dd, *J* = 1.0, 8.0 Hz, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 27.5, 27.9, 31.9, 37.8, 43.8, 51.2, 56.3, 107.9, 117.9, 121.3, 125.8, 127.6, 127.7, 127.8, 127.9, 128.8, 129.3, 136.1, 136.9, 139.9, 141.6, 154.3, 158.6, 159.3, 198.9. Anal. Calcd. for $C_{26}H_{20}N_4O_2$: C, 74.27; H, 4.79; N, 13.33; found C, 74.31; H, 4.82; N, 13.36.

*3.46. Methyl 2-amino-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydrospiro[chromene-4,11′-indeno[2,1-b]quinoxaline]-3-carboxylate (**12aa**)*

M.p. = 269 °C (dec.). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 0.94 (s, 3H), 0.99 (s, 3H), 1.84–2.01 (m, 2H), 2.55–2.74 (m, 2H), 2.82 (s, 3H), 7.38–7.48 (m, 3H), 7.64–7.74 (m, 2H), 7.88 (s, 2H), 7.92–7.93 (m, 1H), 8.02 (d, *J* = 7.0 Hz, 1H), 8.09–8.11 (m, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 13.7, 19.4, 27.5, 28.7, 32.6, 47.9, 50.7, 51.2, 56.9, 59.2, 78.0, 114.8, 121.6, 124.6, 128.6, 129.0, 129.45, 129.49, 132.2, 138.6, 141.4, 141.7, 153.8, 157.3, 160.1, 164.2, 167.8, 169.4, 195.7. Anal.

Calcd. for $C_{27}H_{23}N_3O_4$: C, 71.51; H, 5.11; N, 9.27; found C, 71.54; H, 5.19; N, 9.36.

3.47. Ethyl 2-amino-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydrospiro[chromene-4,11′-indeno[2,1-b]quinoxaline]-3-carboxylate (**12ab**)

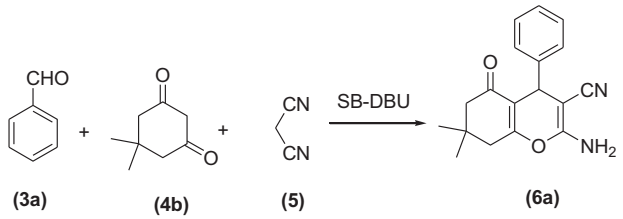
M.p. = 272 °C (dec.). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 0.99 (s, 3H), 1.04 (s, 3H), 1.08 (t, *J* = 7.0 Hz, 3H), 1.85–2.01 (m, 2H), 2.56–2.74 (m, 2H), 3.32–3.45 (m, 2H), 7.39 (d, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 1H), 7.49 (t, *J* = 7.2, 1H), 7.65–7.68 (m, 1H), 7.71–7.74 (m, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.98 (s, 2H), 8.02 (d, *J* = 7.0 Hz, 1H), 8.10 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 13.7, 19.4, 27.5, 28.7, 32.5, 47.8, 51.3, 56.8, 9.2, 77.8, 114.9, 121.5, 124.7, 128.6, 129.0, 129.4, 132.2, 138.8, 141.3, 141.8, 169.4, 195.7. Anal. Calcd. for $C_{28}H_{25}N_3O_4$: C, 71.93; H, 5.39; N, 8.99; found C, 71.99; H, 5.42; N, 9.05.

3.48. 6′-Amino-3′-methyl-1′-phenyl-1′H-spiro[indeno[2,1-b]quinoxaline-11,4′-pyrano[2,3-c]pyrazole]-5′-carbonitrile (**12ac**)

M.p. = 240 °C (dec.) (Lit.[38] 236 °C). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 1.10 (s, 3H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 2H), 7.64–7.71 (m, 5H), 7.81–7.90 (m, 4H), 8.12 (d, *J* = 8.5 Hz, 1H), 8.20 (t, *J* = 8.5 Hz, 2H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 13.8, 43.6, 58.4, 116.9, 118.9, 121.8, 122.7, 125.8, 125.9, 128.8, 128.91, 128.97, 129.0, 129.6, 129.8, 129.9, 135.9, 136.7, 136.9, 139.8, 142.3, 146.1, 154.2, 159.1, 175.9. Anal. Calcd. for $C_{28}H_{18}N_6O$: C, 74.00; H, 3.99; N, 18.49; found C, 74.10; H, 4.09; N, 18.56.

3.49. 2′-Amino-5′-oxo-5′H-spiro[indeno[2,1-b]quinoxaline-11,4′-pyrano[2,3-b]chromene]-3′-carbonitrile (**12ad**)

M.p. = 297 °C (dec.). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 7.44 (d, *J* = 8.0 Hz, 1H), 7.57–7.63 (m, 3H), 7.74–7.81 (m, 5H), 7.84–7.86 (m, 1H), 8.05–8.08 (m, 2H), 8.15–8.20 (m, 1H), 8.19–8.21 (dd, *J* = 1.0, 8.5 Hz, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 113.5, 117.5, 118.0, 122.5, 123.7, 125.9, 126.3, 129.81, 129.88, 130.3, 130.4, 131.0, 133.4, 134.5, 137.3, 141.8, 142.8, 151.5, 153.0, 154.8, 156.5, 159.1, 159.4, 165.4. Anal. Calcd. for $C_{27}H_{14}N_4O_3$: C, 73.30; H, 3.19; N, 12.66; found C, 73.36; H, 3.25; N, 12.69.



Scheme 3. The reaction of benzaldehyde (**3a**) with 5,5-dimethylcyclohexane-1,3-dione (**4b**) and malononitrile (**5**) using (SB-DBU)Cl.

4. Results and discussions

To assess the efficacy and the scope of our new catalyst, initially, the synthesis of 4*H*-benzo[*b*]pyran derivatives *via* the condensation reaction of C—H activated ketones with aromatic aldehydes and alkylmalonates were studied. To optimize the reaction conditions, the condensation of benzaldehyde (**3a**) (1.0 mmol) with 5,5-dimethylcyclohexane-1,3-dione (**4b**) (1 mmol) and malononitrile (**5**) (1.0 mmol) was selected as a model reaction (Scheme 3).

To compare the effect of catalyst loadings, reaction times, and solvents on the reaction, various parametric investigations were examined. The model reaction was examined in the presence of different molar ratios of (SB-DBU)Cl in various solvents 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 5 mol% of the catalyst in ethanol; in these conditions, the corresponding 4*H*-benzo[*b*]pyran **6a** was produced in 94% yield within 35 min (Table 1, entry 8). In this case, average turnover frequency (TOF) value of the catalyst was also higher. Increasing the amount of catalyst to 7 mol% showed no substantial improvement in the yield, whereas the yield was decreased by decreasing the amount of catalyst to 2.5 mol%. Moreover, it was observed that the reaction did not proceed efficiently in the absence of (SB-DBU)Cl after a long time (6 h) (Table 1, entry 10).

The product yields were also measured at different times (Table 1, entries 5–7). As it can be seen in Table 1, the yields of the product in the initial times (5, 10 and 15 min) were low. In these times, the most amounts of the starting materials (benzaldehyde, 5,5-dimethylcyclohexane-1,3-dione and malononitrile) were consumed; however, the product yields were low. This can be

Table 1
The reaction of benzaldehyde (1.0 mmol) with malononitrile (1.0 mmol) and 5,5-dimethylcyclohexane-1,3-dione (1.0 mmol) using (SB-DBU)Cl in different solvents (5 mL) at room temperature.

Entry	Solvent	Catalyst (mol%)	Time (min)	Yield[a] (%)	TON[b]/TOF[c] (min^{-1})
1	EtOH	1.5	35	Trace	–
2	EtOH	1.5	360	40	26.67/0.07
3	EtOH	2.5	35	25	10/0.29
4	EtOH	2.5	180	82	32.8/0.18
5	EtOH	5	5	10	2/0.4
6	EtOH	5	10	23	4.6/0.46
7	EtOH	5	15	40	8/0.53
8	EtOH	5	35	94	18.8/0.54
9	EtOH	7	30	94	13.43/0.45
10	EtOH	-	360	Trace	-
12	$CHCl_3$	5	35	18	3.6/0.1
13	$CHCl_3$	5	360	71	14.2/0.04
14	CH_3CN	5	35	25	5/0.14
15	CH_3CN	5	200	87	17.4/0.09
16	EtOAc	5	35	10	2/0.06
17	EtOAc	5	360	48	9.6/0.03
18	H_2O	5	35	40	8/0.23
19	H_2O	5	120	83	16.6/0.14

[a] Isolated yield.
[b] Average turn over number (mol of product/mol of catalyst).
[c] Average turn over frequency [mol of product/(mol of catalyst × reaction time)].

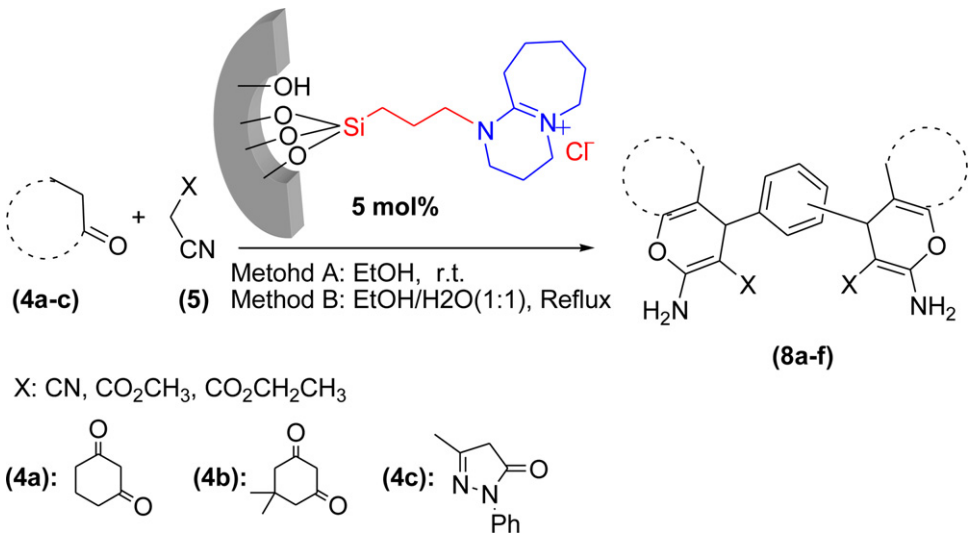
Table 2
The synthesis of 4*H*-benzo[*b*]pyran derivatives from the reaction of C—H activated carbonyl compound (1.0 mmol), aryl aldehyde (1.0 mmol) and malono derivative (1.0 mmol) in the presence of (SB-DBU)Cl (0.05 mmol) in ethanol (5.0 mL) at room temperature.

Entry	Sub.	R	X	Time (min)	Yield[a] (%)	TON[b]/TOF[c] (min^{-1})
6a	**4b**	C_6H_5	CN	35	94	18.8/0.54
6b	**4b**	4-ClC_6H_4	CN	20	93	18.6/0.93
6c	**4b**	4-$OEtC_6H_4$	CN	90	92	18.4/0.20
6d	**4b**	4-$NO_2C_6H_4$	CN	15	95	19/1.27
6e	**4b**	2-Naphthyl	CN	60	97	19.4/0.32
6f	**4b**	3-$PhOC_6H_4$	CN	35	92	18.4/0.53
6g	**4b**	2-Thienyl	CN	35	90	18/0.51
6h	**4b**	C_6H_5-CO	CN	25	95	19/0.76
6i[d]	**4b**	4-$CF_3C_6H_4$	CO_2Et	240	92	18.4/0.08
6j[d]	**4b**	2-Naphthyl	CO_2Et	280	94	18.8/0.07
6k[d]	**4b**	4-CNC_6H_4	CO_2Me	210	91	18.2/0.09
6l[d]	**4b**	4-ClC_6H_4	CO_2Me	180	96	19.2/0.11
6m	**4a**	4-ClC_6H_4	CN	45	92	18.4/0.41
6n	**4a**	4-$NO_2C_6H_4$	CN	20	92	18.4/0.92
6o	**4a**	4-$CH_3C_6H_4$	CN	75	90	18.0/0.24
6p	**4a**	2-Naphthyl	CN	50	94	18.8/0.37
6q	**4a**	2-ClC_6H_4	CN	30	96	19.2/0.64
6r[d]	**4a**	4-ClC_6H_4	CO_2Et	180	93	18.6/0.10
6s[d]	**4a**	4-$EtOC_6H_4$	CO_2Me	360	95	19/0.05
6t	**4c**	4-CNC_6H_4	CN	35	92	18.4/0.53
6u	**4c**	4-$CF_3C_6H_4$	CN	30	94	18.8/0.63
6v	**4c**	2-Thienyl	CN	35	92	18.4/0.53
6w	**4c**	4-HOC_6H_4	CN	70	94	18.8/0.27
6x	**4c**	4-*iso*-Propyl C_6H_4	CN	60	93	18.6/0.31

[a] Isolated yield.
[b] Average turn over number (mol of product/mol of catalyst).
[c] Average turn over frequency [mol of product/(mol of catalyst × reaction time)].
[d] This reaction was carried out in H_2O/EtOH (1/1) under reflux conditions.

attributed to the formation of intermediates during the reaction; according to the results, the time required for the conversion of the starting materials to intermediates, and then to the product was 35 min.

The model reaction was also examined in the presence of (SB-DBU)Cl at room temperature in several solvents including $CHCl_3$, CH_3CN, EtOAc and H_2O (Table 1 entries 12–19). In aprotic solvents ($CHCl_3$, CH_3CN and EtOAc) the yield of product were low, whereas change of solvent from aprotic to protic (EtOH and H_2O) in the same conditions resulted in increasing in the yield of product that this observations can be because of polarity of intermediate and solvation of activated complex. However, as it can be seen in Table 1, ethanol was the best solvent for Knovenagel condensation, Michael addition and finally cyclization reaction of intermediate to form the related product. The condensation of benzaldehyde (**3a**) with 5,5-dimethylcyclohexane-1,3-dione (**4b**) and malononitrile (**5**) was also tested using SiO_2 separately in which the product was obtained in 70% yield within 240 min. Furthermore, the reaction was examined using DBU as catalyst (5.0 mol%) which afforded the product in 78% after 60 min, and DBU could not be recovered. The efficiency of 3-aminopropyl-modified silica gel as a commercially available silica-supported catalyst on the reaction of benzaldehyde with 5,5-dimethylcyclohexane-1,3-dione and malononitrile was also investigated. This catalyst gave the product in 75% within 120 min; this low yield of the product may be related to the reaction of amino group of the catalyst with benzaldehyde. These studies



Scheme 4. The synthesis of complex compounds *via* the condensation of 2.0 equiv. of carbonyl compounds with 2.0 equiv. of alkylmalonates and 1.0 equiv. of dialdehydes.

Table 3
The synthesis of bis-pyranes from the reaction of C—H activated carbonyl compounds (2.0 mmol), alkylmalonates (2.0 mmol) and dialdehydes (1.0 mmol) using (SB-DBU)Cl (0.1 mmol) in ethanol (10 mL) at room temperature.

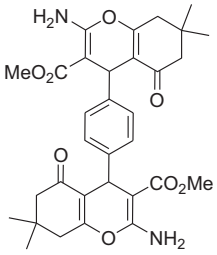
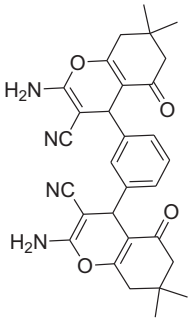
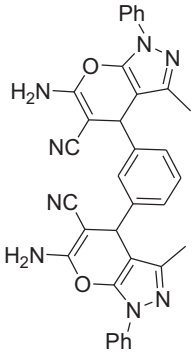
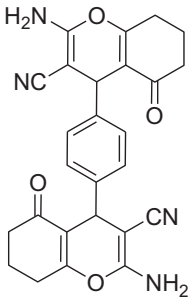
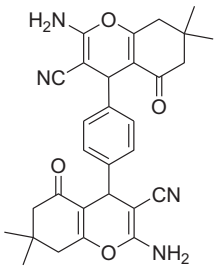
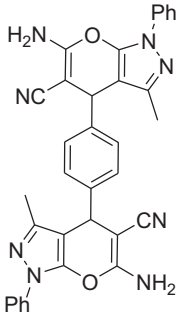
Entry	Subs./X	Product	Time (min)	Yield[a] (%)	TON[b]/TOF[c] (min^{-1})
8a[d]	**4b**/CO_2Me		210	92	18.4/0.09
8b	**4b**/CN		260	90	18/0.07
8c	**4c**/CN		380	95	19/0.05
8d	**4a**/CN		130	91	18.2/0.14
8e	**4b**/CN		140	95	19/0.14

Table 3 (*Continued*)

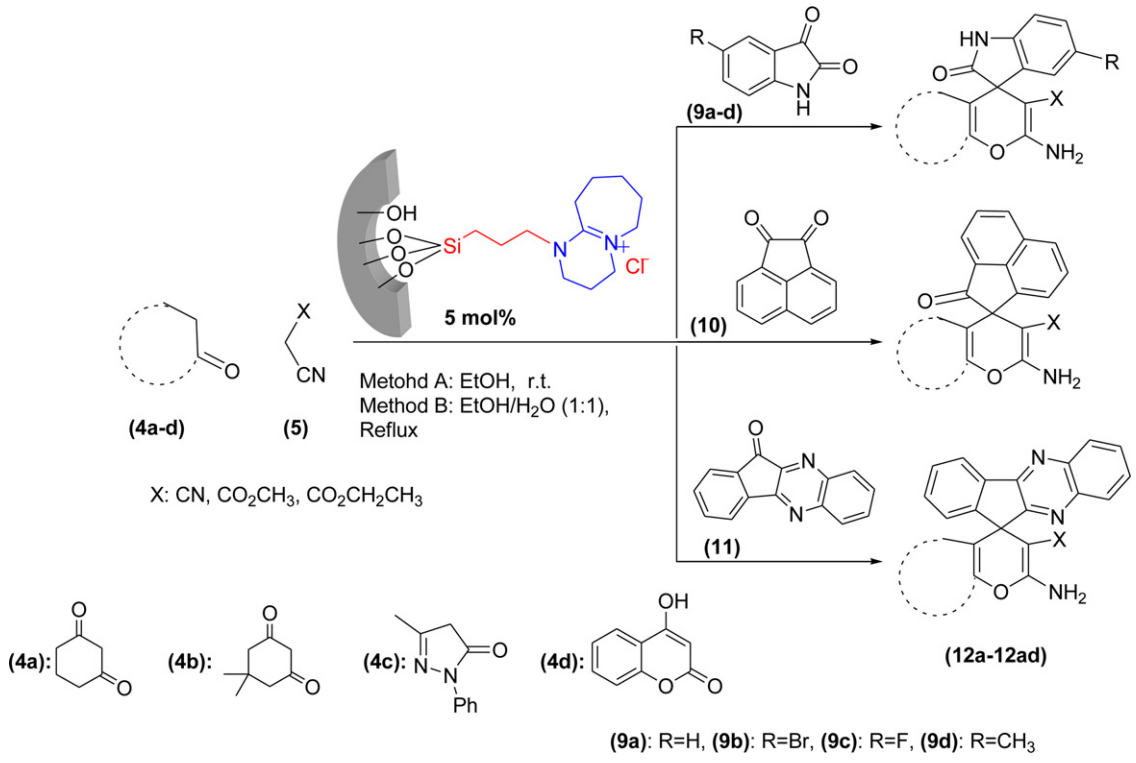
Entry	Subs./X	Product	Time (min)	Yield[a] (%)	TON[b]/TOF[c] (min^{-1})
8f	**4c**/CN		250	93	18.6/0.07

[a] Isolated yield.
[b] Average turn over number (mol of product/mol of catalyst).
[c] Average turn over frequency [mol of product/(mol of catalyst × reaction time)].
[d] Method B was applied for the synthesis of this compound.

confirmed the high efficiency of (SB-DBU)Cl, and its critical role in the reaction.

After optimization of the reaction conditions, a broad range of structurally diverse aldehydes (**3**) were condensed with carbonyl compounds [cyclohexane-1,3-dione (**4a**), 5,5-dimethylcyclohexane-1,3-dione (**4b**) or 3-methyl-1-phenyl-2-pyrazolin-5-one (**4c**)] and alkylmaloates (**5**) in the presence of (SB-DBU)Cl to furnish the corresponding products in high yields and in short reaction times (Table 2). For each reaction, turn over number (TON) and turn over frequency TOF values of (SB-DBU)Cl were also calculated (Table 2).

As it is shown in Table 2, the presence of electron-withdrawing substituents on the aromatic ring of aldehydes accelerated the reaction rate (Table 2, compounds **6d**, **6h**, **6i**, **6k**, **6n**, **6t** and **6u**), whereas electron-releasing substituents decreased the reaction rate (Table 2, compounds **6c**, **6o**, **6s**, **6w** and **6x**). Moreover, the nature of the substituents did not affect on the reaction yields. Aromatic aldehydes bearing sensitive substituents were also successfully applied in the reaction without producing by-products (Table 2, compounds **6k** and **6t**). Furthermore, SB-DBU efficiently catalyzed the reaction when hetero-aromatic aldehydes were applied (Table 2, compounds 6 g and 6 v). In these studies, we found that reflux condition [in H_2O/EtOH (1:1)] was required for the condensation of alkylcyanoacetates with aromatic aldehyde and carbonyl compounds. This can attributed to lower reactivity of alkyl cyanoacetates in comparison with malononitrile.



Scheme 5. The synthesis of spiro-pyrans in the presence of (SB-DBU)Cl.

Table 4
The synthesis of spiro-pyran derivatives from the reaction of C—H activated carbonyl compound (1 mmol), malono derivative (1 mmol) and isatin derivative (1 mmol) in the presence of SB-DBU (0.05 mmol) in ethanol (5 mL) at room temperature.

Entry	Subs./X	Carbonyl compound	Time (min)	Yield[a] (%)	TON[b]/TOF[c] (min^{-1})	M.p. °C (Lit.)
12a	**4a**/CN	**9a**	120	95	19/0.16	297–299 (298–299) [35]
12b	**4a**/CN	**9b**	180	96	19.2/0.11	289 (dec.) (290–292) [35]
12c	**4a**/CN	**9c**	300	96	19.2/0.06	283–284
12d	**4a**/CN	**9d**	210	95	19/0.09	282–284
12e[d]	**4a**/CO_2Me	**9b**	540	96	19.2/0.04	274 (dec.)
12f[d]	**4a**/CO_2Et	**9b**	540	97	19.4/0.04	274–276
12g	**4b**/CN	**9a**	150	97	19.4/0.13	289–291 (290–292) [35]
12h	**4b**/CN	**9b**	150	98	19.6/0.13	304–305 (>300) [35]
12i	**4b**/CN	**9c**	210	98	19.6/0.09	293 (dec.)
12j[d]	**4b**/CO_2Et	**9a**	420	97	19.4/0.05	242–244
12k	**4b**/CN	**10**	60	98	19.6/0.33	262–264 (260–262) [36]
12l[d]	**4b**/CO_2Et	**9b**	420	97	19.4/0.05	274 (dec.)
12m	**4b**/CN	**9d**	180	96	19.2/0.11	277–280 (278–280) [37]
12n[d]	**4b**/CO_2Me	**9b**	360	98	19.6/0.05	263–265
12o	**4c**/CN	**9c**	150	96	19.2/0.13	242 (dec.)
12p	**4c**/CN	**9b**	180	95	19/0.11	227–229 (225–226) [35]
12q[d]	**4c**/CO_2Me	**9a**	420	96	19.2/0.05	227–228
12r[d]	**4c**/CO_2Me	**9b**	540	97	19.4/0.04	225 (dec.)
12s[d]	**4c**/CO_2Et	**9b**	540	97	19.4/0.04	233–235
12t	**4c**/CN	**10**	90	97	19.4/0.22	195–196
12u	**4d**/CN	**9b**	270	97	19.4/0.07	310 (dec.) (>300) [35]
12v	**4d**/CN	**9c**	270	98	19.6/0.07	304 (dec.)
12w	**4d**/CN	**10**	270	98	19.6/0.07	289 (dec.)
12x[d]	**4d**/CO_2Et	**10**	360	97	19.4/0.05	242–243
12y	**4a**/CN	**11**	240	97	19.4/0.08	278 (dec.)
12z	**4b**/CN	**11**	240	98	19.6/0.08	280 (dec.)
12aa[d]	**4b**/CO_2Me	**11**	300	96	19.2/0.06	269 (dec.)
12ab[d]	**4b**/CO_2Et	**11**	390	98	19.6/0.05	272 (dec.)
12ac	**4c**/CN	**11**	390	95	19/0.05	240 (dec.) (236) [38]
12ad	**4d**/CN	**11**	480	98	19.6/0.04	297 (dec.)

[a] Isolated yield.
[b] Average turn over number (mol of product/mol of catalyst).
[c] Average turn over frequency [mol of product/(mol of catalyst × reaction time)].
[d] Method B was applied for the synthesis of this compound.

(SB-DBU)Cl also efficiently catalyzed the synthesis of novel complex compounds **8a**–**8f** *via* the reaction of 2.0 equiv. of carbonyl compounds with 2.0 equiv. of alkylmalonates and 1.0 equiv. of dialdehyde (**7**) (Scheme 4). The respective results are shown in Table 3.

After the successful application of (SB-DBU)Cl for the synthesis of 4*H*-benzo[*b*]pyran and bisbenzo[b]pyran derivatives, we decided to apply this catalyst for the synthesis of spiro-pyran compounds containing oxindole or quinoxaline moiety in their structures. For this purpose, isatin derivatives (**9a**–**9d**), acenaphthenquinone (**10**) or 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**11**) [40] were treated with carbonyl compounds (**4a**–**4d**) and alkylmalonates (**5**) in the presence of (SB-DBU)Cl in EtOH at room temperature or in EtOH/H_2O (1:1) under reflux conditions (Scheme 5). The results are displayed in Table 4. As Table 4 indicates, the procedure worked well when a wide range of substrates were utilized. Four types of substituted isatins and acenaphthenequinone, as well as 11*H*-indeno[1,2-*b*]quinoxalin-11-one were condensed successfully with C—H activated ketones (1,3-cyclohexanediones, 4-hydroxycumarin or 3-methyl-1-phenyl-2-pyrazolin-5-one) and alkylmalonates to afford a broad range of structurally diverse spiro-pyran compounds in excellent yields and in short reaction times.

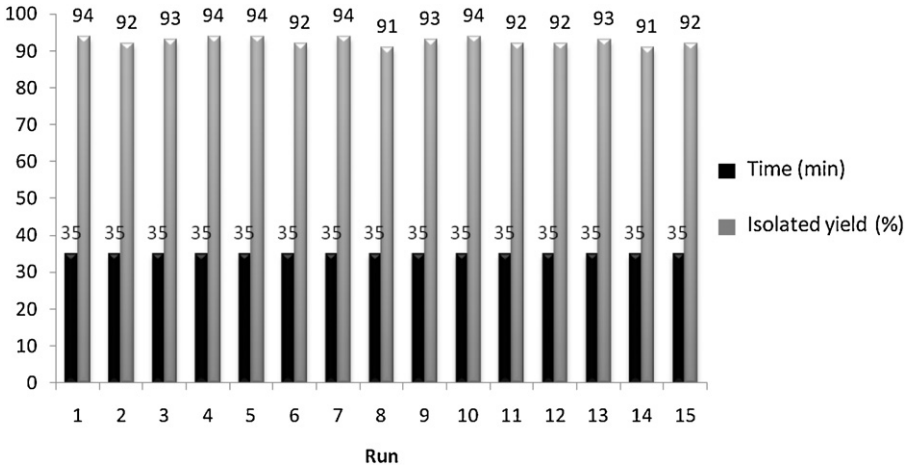
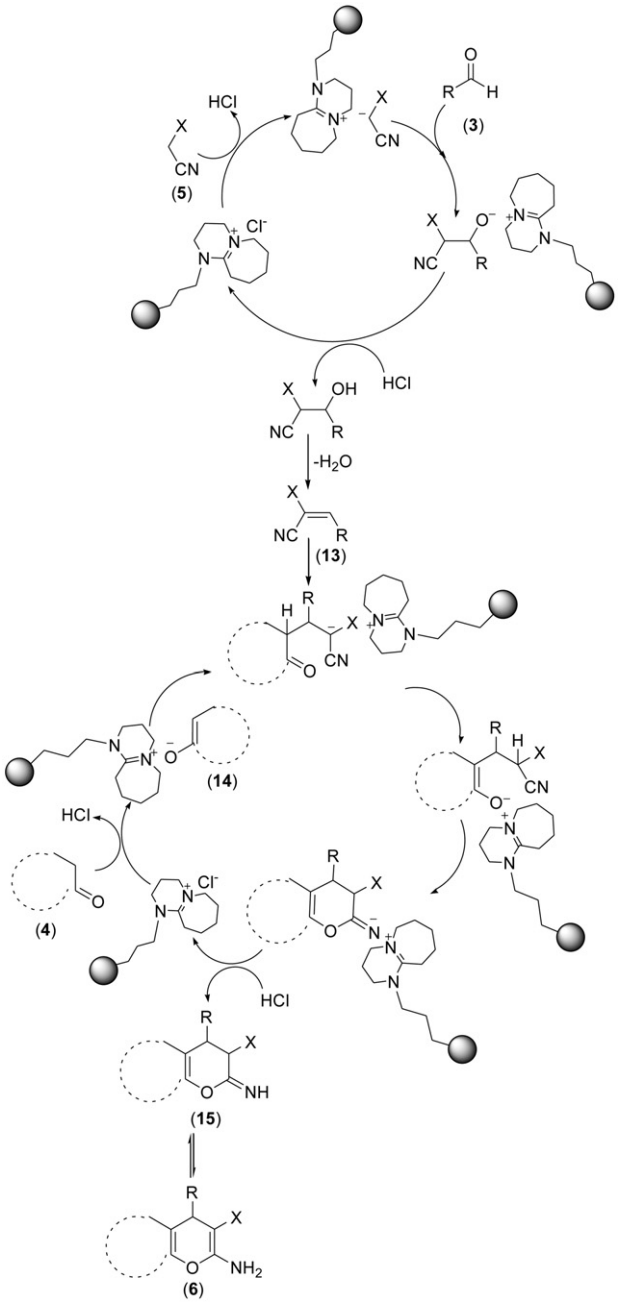


Fig. 1. The reaction of benzaldehyde (1.0 mmol) with malononitrile (1.0 mmol) and 5,5-dimethylcyclohexane-1,3-dione (1.0 mmol) in ethanol (5.0 mL) in the presence of recovered (SB-DBU)Cl at room temperature.



Scheme 6. The proposed mechanism for the synthesis of 4*H*-benzo[*b*]pyrans using (SB-DBU)Cl.

In another study, reusability of the catalyst was studied. For this purpose, the reaction of benzaldehyde (1.0 mmol) with 5,5-dimethylcyclohexane-1,3-dione (1.0 mmol) and malononitrile (1.0 mmol) was performed in the presence (SB-DBU)Cl (0.11 g, 5.0 mol%) in EtOH (5 mL) at room temperature. After completion of the reaction, as monitored by TLC, ethanol (5 mL) was added to the reaction mixture and heated at 60 °C for ~5 min to dissolve the product followed by centrifugation for 10 min to separate the (SB-DBU)Cl and minimize the handling loss of catalyst. After isolation of the product, hot ethanol was added to the recovered (SB-DBU)Cl followed by centrifugation, (SB-DBU)Cl was then dried and successfully used for the next run under identical reaction conditions.

The reusability results are summarized in Fig. 1. As Fig. 1 indicates, (SB-DBU)Cl was successfully recycled and reused for fourteen cycles with unchanged yield. For the reaction, the average TON (mol of product/mol of catalyst) and TOF [mol of product/(mol of catalyst × reaction time)] amounts of the reused (SB-DBU)Cl were 18.55 and 0.53 (min^{-1}), respectively.

A proposed mechanism for the synthesis of benzo[*b*]pyrans is outlined in Scheme 6. Based on this mechanism, (SB-DBU)Cl is an effective catalyst for the formation of olefin 13 which readily prepares *in situ* by Knoevenagel condensation of aryl aldehyde 3 with the active methylene of compound **5**. Afterward, carbonyl compound 4 converts to its corresponding enolate form, **14**, in the presence of (SB-DBU)Cl, which easily reacts with olefin 13 to produce intermediate **15**. Intermediate **15** converts to product **6**, after proton transfer and tautomerization.

5. Conclusions

In summary, we have introduced a novel heterogeneous silica-supported ionic liquid catalyst, silica-bonded 5-*n*-propyl-octahydro-pyrimido[1,2-*a*]azepinium chloride (SB-DBU)Cl, from commercially available and relatively inexpensive starting materials by a simple method. Conversion of a liquid base with low boiling point (DBU) to a heterogeneous catalyst has an improvement in our studies and more advantages than a solid base to become heterogeneous. (SB-DBU)Cl efficiently catalyzed the condensation reactions between C—H activated carbonyl compounds, aromatic aldehydes and alkylmalonates to give 4*H*-benzo[*b*]pyran derivatives in excellent yields. This catalyst was recovered and reused for fourteen reaction cycles with unchanged yield. Moreover, our presented method was highlighted with its efficiency for the synthesis of novel complex compounds, bis(benzo[*b*]pyran)s, *via* the reaction of dialdehydes (1 equiv.) with carbonyl compounds (2 equiv.) and alkylmalonates (2 equiv.). Beside these, a broad range of structurally diverse spiro-pyran derivatives containing oxindole or quinoxaline moiety in their structures were prepared in excellent yields and in short reaction times using (SB-DBU)Cl. Other advantages of our catalyst are its generality and its easy recovery and reusability. In this study we found that, (SB-DBU)Cl works efficiently with 5.0 mol% in comparison with 10 mol% SB-DABCO. For the (SB-DBU)Cl catalyst more than 30 products containing bis(benzo[*b*]pyran)s and spiro-benzo[*b*]pyrans with oxindole or quinoxaline moiety in their structures were prepared, that have not prepared with SB-DABCO.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2013.02.022.

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