

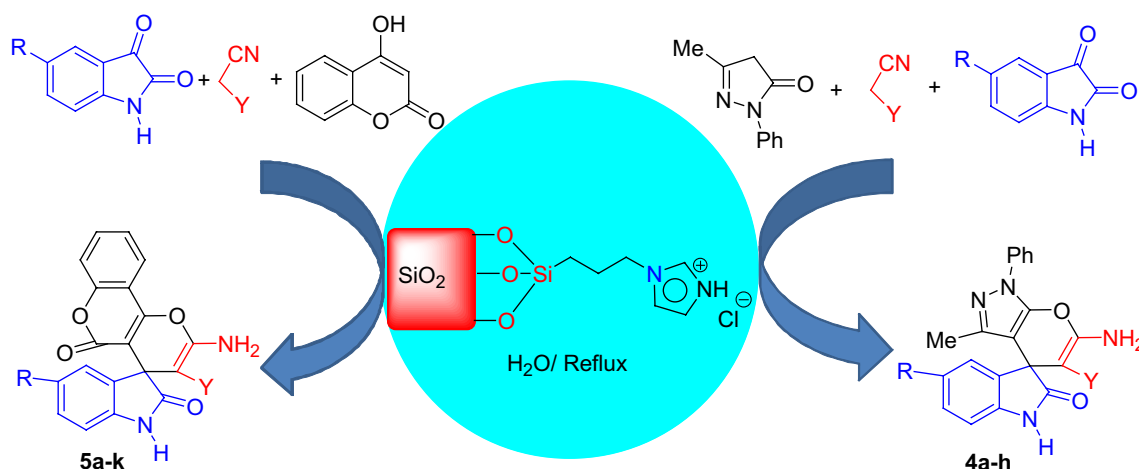
Synthesis of spiro[indoline-3,4'-pyrano[2,3-c]pyrazole] and spiro[indoline-3,4'-pyrano[2,3-c]chromene] derivatives using silica-bonded ionic liquids as a recyclable catalyst in aqueous medium

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Abstract Silica-bonded ionic liquids is employed as a recyclable catalyst for the synthesis of spiro[indoline-3,4'-pyrano[2,3-c]pyrazoles] via one-pot condensation reaction of isatin, activated methylene reagents, and 3-methyl-1-phenyl-5-pyrazolone in refluxing aqueous medium in good to high yields. Also, these silica-bonded ionic liquids were used as catalysts for the synthesis of spiro[indoline-3,4'-pyrano[2,3-c]chromene] derivatives in refluxing aqueous medium in high yields. Catalyst could be recycled for several times without any additional treatment.

Graphical Abstract Silica-bonded ionic liquids is employed as a recyclable catalyst for the synthesis of spiro[indoline-3,4'-pyrano[2,3-c]pyrazoles] and spiro[indoline-3,4'-pyrano[2,3-c]chromene] via one-pot condensation reaction of isatin, activated methylene reagents, and 3-methyl-1-phenyl-5-pyrazolone or 4-hydroxy coumarin respectively in refluxing aqueous medium in good to high yields.



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Keywords Spiro[indoline-3,4'-pyrano[2,3-c]pyrazoles] · Spiro[indoline-3,4'-pyrano[2,3-c]chromenes] · Silica-bonded ionic liquids · Heterogeneous catalyst · Synthesis · Water

Introduction

Spirooxindoles are commonly occurring heterocyclic ring systems and are important structural motifs found in many natural products and pharmaceuticals [1, 2]. The key structural characteristic of these compounds is the spiro ring fused at the C3 position of the oxindole core with varied heterocyclic motifs [3]. Among them, those with an indole moiety exhibit antibacterial and antifungal activities [4, 5]. The significant biological activity and recent synthetic advances of these natural products encouraged the development of biologically promising analogs that would be more efficacious and selective than the original natural products [6]. The privileged spirooxindole skeletons have high potential for the development of some medicinal agents [7]. Two representative examples are NITD609 (**1**) and MI-888 (**2**) in Fig. 1.

The one-pot condensation reaction of isatin, activated methylene reagents, and 1,3-dicarbonyl compounds could

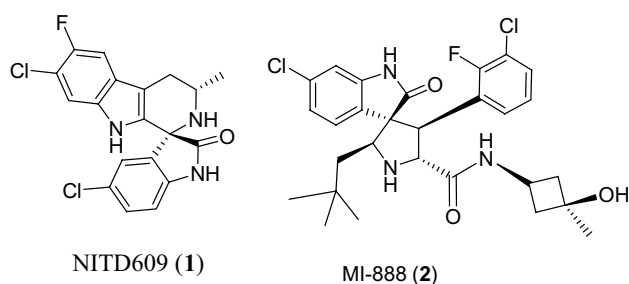


Fig. 1 Two representative examples of spirooxindoles NITD609 and MI-888

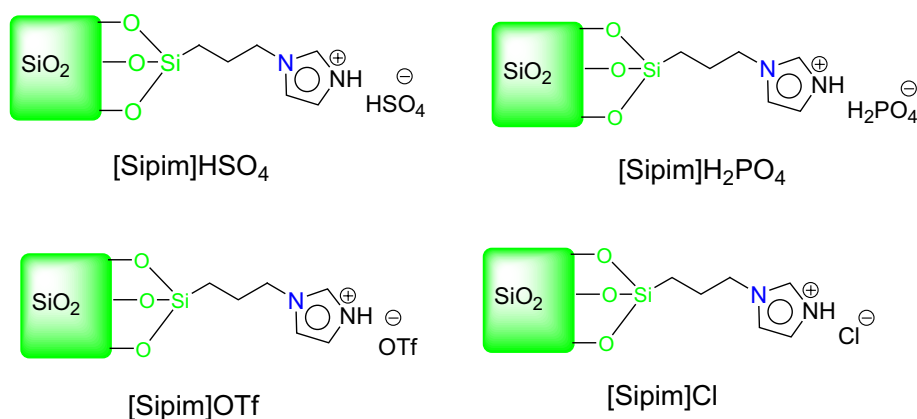
readily afford various spirooxindole structures and has attracted wide attention, and this type of reaction has been achieved by a number of different catalysts and conditions, such as SnCl_4 [8], triethanolamine [9], basic alumina under microwave irradiation [10], surfactant TEBA (triethylbenzylammonium chloride) [11], electrocatalytic multi-component assembling [12], β -cyclodextrin [13], NaCl under sonication [14], ZnS nanoparticles [15], piperidine under ultrasound irradiation [16], CaCl_2 under ultrasonic irradiation [17], 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) [18], ethylenediammonium diformate (EDDF) [19], SBA-Pr- NH_2 [20], sulfated choline based heteropolyanion [21], and L-prolin [22].

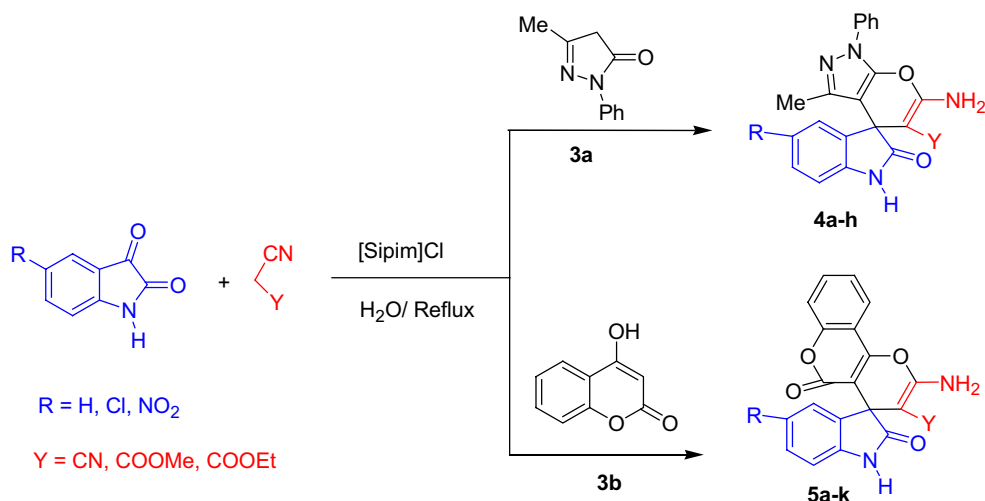
Immobilization of acidic ionic liquids on solid supports has been designed and it can offer important advantages in handling, separation and reuse procedures. Based on economic criteria, it is desirable to minimize the amount of ionic liquid utilized in a potential process. Immobilized acidic ionic liquids have been used as novel solid catalysts, e.g., for esterification, nitration reactions [23], acetal formation [24], Baeyer–Villiger reaction [25], synthesis of α -aminonitriles [26] bis-pyrazolones [27], chromenes [28], 4,4-(arylmethylene)-bis-(3-methyl-1-phenyl-1H-pyrazol-5-ols) [29], 12-aryl-8,9,10,12-tetrahydrobenzo[a]-xanthen-11-ones [30], and 1-(benzothiazolylamino)-phenylmethyl-2-naphthols [31].

In this regard, we introduced a series of silica-bonded ionic liquids such as: silica propyl imidazolium chloride ([Sipim]Cl), silica propyl imidazolium triflate ([Sipim]OTf), *N*-(3-silicapropyl) imidazolium hydrogen sulfate ([Sipim]HSO₄), and *N*-(3-silicapropyl) imidazolium hydrogen phosphate ([Sipim]H₂PO₄) as recyclable catalysts and investigated their catalytic activities in organic transformations [26–28] (Scheme 1).

In continuation of our study on the preparation of solid acids and bases and investigation of their applications in heterocyclic synthesis [32–40], Herein, we describe the synthesis of spirooxindole derivatives via three-component

Scheme 1 The structure of silica-bonded ionic liquids



Scheme 2 Synthesis of spirooxindole derivatives

condensation reaction of isatin, reactive methylene reagents, and 1,3-dicarbonyl compounds using silica-bonded *N*-propylimidazolium chloride ([Sipim]Cl) in aqueous media at reflux conditions (Scheme 2).

Experimental

Chemicals and reagents

Chemicals were purchased from Merck and Aldrich Chemical Companies and use as is. $^1\text{H-NMR}$ spectra we recorded on a Bruker Avance (500 MHz DRX) or Bruker Ultrashield (400 MHz) using DMSO-d_6 as deuterated solvent and with tetramethylsilane (TMS) as internal standard. Melting points were determined in open capillary tubes in a Barnstead Electrothermal 9100 BZ circulating oil melting point apparatus and uncorrected. Reactions were monitored by TLC using silica gel Poly Gram SILG/UV254 plates. All the products were characterized by IR, NMR, Mass spectra and known compounds compared with those reported in literature [11–20]. Solid silica-supported bases such as [Sipim]HSO₄, [Sipim]H₂PO₄, [Sipim]OTf, and [Sipim]Cl were prepared according to our reported procedures [26–28].

Preparation of silica propyl imidazolium chloride [Sipim]Cl

Silicapropyl chloride (10.0 g) was added to a flask containing 100 mL of anhydrous toluene and a large excess of imidazole (10.0 g). The reaction mixture was refluxed with stirring for 24 h. Then, the reaction mixture was cooled to room temperature, transferred to a vacuum glass filter, and washed with toluene, ethanol, and methanol in turn. The silica chemically bonded with imidazolium ([Sipim]Cl) was dried under vacuum at 50 °C for 4 h [26].

General procedure for the synthesis of spirooxindole derivatives

A mixture of isatin (1 mmol), reactive methylene compound (1 mmol) and 1,3-dicarbonyl compound (1 mmol) in the presence of [Sipim]Cl (0.05 g) in water (5 mL) was refluxed with stirring in an oil bath. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was filtered and remaining was washed with warm ethanol (3 × 10 mL) in order to separate [Sipim]Cl catalyst. After cooling the ethanol phase, the precipitates were filtered. The crude products were purified by recrystallization from ethanol (95 %).

6'-Amino-3'-methyl-2-oxo-1'-phenyl-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-5'-carboxylate (4a) (Table 2, entry 1)

mp 235–237 °C, (Ref.: [12] 236–237 °C); $^1\text{H-NMR}$ (400 MHz, DMSO-d_6): δ (ppm) 1.55 (s, 3H, CH₃), 6.91–7.09 (m, 2H, Ar), 7.18 (d, 1H, $J = 6.8$ Hz, Ar), 7.25–7.42 (m, 2H, Ar), 7.48–7.56 (m, 2H, Ar), 7.59 (s, 2H, NH₂), 7.79 (d, 2H, $J = 7.3$ Hz, Ar), 10.75 (s, 1H, NH). $^{13}\text{C-NMR}$ (125 MHz, DMSO-d_6): δ 12.2, 48.2, 56.6, 96.8, 110.3, 118.4, 120.6, 123.1, 125.4, 127.0, 129.8, 129.9, 132.6, 137.7, 142.0, 144.4, 145.4, 161.5, 178.0.

6'-Amino-5-chloro-3'-methyl-2-oxo-1'-phenyl-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-5'-carboxylate (4b) (Table 2, entry 2)

mp 232–233 °C, (Ref.: [14] 232–234 °C); $^1\text{H-NMR}$ (400 MHz, DMSO-d_6): δ (ppm) 1.60 (s, 3H, CH₃), 6.97 (d, 1H, $J = 8.3$ Hz, Ar), 7.32–7.39 (m, 3H, Ar), 7.53 (t, 2H, $J = 8.0$ Hz, Ar), 7.65 (s, 2H, NH₂), 7.79 (d, 2H, $J = 7.8$ Hz, Ar), 10.90 (s, 1H, NH). $^{13}\text{C-NMR}$ (100 MHz, DMSO-d_6):

δ 12.2, 48.5, 56.0, 96.1, 111.8, 118.4, 120.7, 125.7, 127.1, 127.2, 129.7, 129.9, 134.8, 137.7, 140.9, 144.2, 145.5, 161.5, 177.8.

6'-Amino-5-nitro-3'-methyl-2-oxo-1'-phenyl-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-5'-carboxylate (4c) (Table 2, entry 3)

mp 227–229 °C, (Ref.: [14] 226–228 °C); $^1\text{H-NMR}$ (400 MHz, DMSO- d_6): δ (ppm) 1.60 (s, 3H, CH₃), 7.18 (d, 1H, $J = 8.6$ Hz, Ar), 7.37 (t, 1H, $J = 7.3$ Hz, Ar), 7.53 (t, 2H, $J = 7.9$ Hz, Ar), 7.74 (s, 2H, NH₂), 7.80 (d, 2H, $J = 7.8$ Hz, Ar), 8.23 (d, 1H, $J = 1.8$ Hz, Ar), 8.27 (dd, 1H, $J_1 = 8.7$, $J_2 = 2.1$ Hz, Ar), 11.49 (s, 1H, NH). $^{13}\text{C-NMR}$ (100 MHz, DMSO- d_6): δ 11.8, 47.9, 56.0, 94.9, 110.2, 117.8, 120.4, 121.0, 126.5, 126.7, 129.4, 133.3, 137.1, 143.1, 143.6, 145.2, 147.7, 161.2, 178.1.

Methyl-6'-amino-5-chloro-3'-methyl-2-oxo-1'-phenyl-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-5'-carboxylate (4d) (Table 2, entry 4)

mp 224–226 °C; $^1\text{H-NMR}$ (500 MHz, DMSO- d_6): δ (ppm) 1.61 (s, 3H, CH₃), 3.34 (s, 3H, OCH₃), 6.88 (d, 1H, $J = 10.0$ Hz, Ar), 7.11 (d, 1H, $J = 2.5$ Hz, Ar), 7.22 (dd, 1H, $J_1 = 10.0$, $J_2 = 2.5$ Hz, Ar), 7.53 (t, 1H, $J = 10.0$ Hz, Ar), 7.52 (t, 2H, $J = 10.0$ Hz, Ar), 7.82 (d, 2H, $J = 10.0$ Hz, Ar), 8.21 (s, 2H, NH₂), 10.66 (s, 1H, NH). $^{13}\text{C-NMR}$ (125 MHz, DMSO- d_6): δ 12.2, 48.3, 51.0, 74.8, 98.0, 110.7, 120.6, 124.0, 126.2, 126.9, 128.2, 129.9, 137.8, 138.2, 141.3, 144.4, 144.6, 161.8, 168.3, 179.4. Anal calcd for C₂₂H₁₇ClN₄O₄: C, 60.49; H, 3.92; Cl, 8.12; N, 12.83. Found: C, 60.18; H, 3.98; N, 12.71.

Methyl-6'-amino-5-nitro-3'-methyl-2-oxo-1'-phenyl-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-5'-carboxylate (4e) (Table 2, entry 5)

mp 241–243 °C. $^1\text{H-NMR}$ (500 MHz, DMSO- d_6): δ 1.61 (s, 3H, CH₃), 3.33 (s, 3H, OCH₃), 7.09 (d, 1H, $J = 8.8$ Hz, Ar), 7.36 (t, 1H, $J = 7.3$ Hz, Ar), 7.53 (t, 2H, $J = 7.8$ Hz, Ar), 7.83 (d, 2H, $J = 7.8$ Hz, Ar), 7.97 (d, 1H, $J = 2.0$ Hz, Ar), 8.18 (dd, 1H, $J_1 = 8.5$, $J_2 = 2.2$ Hz, Ar), 8.27 (s, 2H, NH₂), 11.27 (s, 1H, NH). $^{13}\text{C-NMR}$ (125 MHz, DMSO- d_6): δ 12.3, 48.2, 51.1, 74.3, 97.3, 109.6, 120.7, 125.9, 127.0, 129.4, 129.8, 137.2, 137.8, 143.0, 144.2, 144.8, 148.9, 161.9, 168.1, 180.2. Anal calcd for C₂₂H₁₇N₅O₆: C, 59.06; H, 3.83; N, 15.65. Found: C, 58.78; H, 3.90; N, 15.51.

Ethyl-6'-amino-3'-methyl-2-oxo-1'-phenyl-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-5'-carboxylate (4f) (Table 2, entry 6)

mp 239–241 °C, (Ref.: [14] 238–240 °C); $^1\text{H-NMR}$ (400 MHz, DMSO- d_6): δ (ppm) 0.75 (t, 3H, $J = 7.2$ Hz, CH₃), 1.59 (s, 3H, CH₃), 3.68–3.81 (m, 2H, OCH₂), 6.84–6.92 (m, 2H, Ar), 6.97 (d, 1H, $J = 7.1$ Hz, Ar), 7.17 (dt, 1H, $J_1 = 7.1$, $J_2 = 1.2$ Hz, Ar), 7.34 (t, 1H, $J = 7.3$ Hz, Ar), 7.52 (t, 2H, $J = 8.1$ Hz, Ar), 7.81 (d, 2H, $J = 7.6$ Hz, Ar), 8.21 (s, 2H, NH₂), 10.52 (s, 1H, NH). $^{13}\text{C-NMR}$ (125 MHz, DMSO- d_6): δ 12.2, 13.6, 47.9, 59.5, 75.0, 98.7, 109.3, 120.4, 122.2, 123.7, 126.8, 128.2, 129.9, 136.2, 137.8, 142.7, 144.4, 144.7, 161.8, 168.3, 179.7.

Ethyl-6'-amino-5-chloro-3'-methyl-2-oxo-1'-phenyl-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-5'-carboxylate (4g) (Table 2, entry 7)

mp 246–247 °C, (Ref.: [15] 246–248 °C); $^1\text{H-NMR}$ (400 MHz, DMSO- d_6): δ (ppm) 0.79 (t, 3H, $J = 7.1$ Hz, CH₃), 1.63 (s, 3H, CH₃), 3.72–3.85 (m, 2H, OCH₂), 6.87 (d, 1H, $J = 8.3$ Hz, Ar), 7.12 (d, 1H, $J = 2.0$ Hz, Ar), 7.23 (dd, 1H, $J_1 = 8.3$, $J_2 = 2.3$ Hz, Ar), 7.35 (t, 1H, $J = 7.4$ Hz, Ar), 7.52 (t, 2H, $J = 7.9$ Hz, Ar), 7.82 (d, 2H, $J = 7.8$ Hz, Ar), 8.27 (s, 2H, NH₂), 10.66 (s, 1H, NH). $^{13}\text{C-NMR}$ (100 MHz, DMSO- d_6): δ 12.2, 13.6, 48.2, 59.6, 74.5, 98.0, 110.7, 120.6, 124.0, 126.2, 126.9, 128.1, 129.9, 137.8, 138.4, 141.6, 144.5, 144.6, 161.9, 168.2, 179.5.

Ethyl-6'-amino-5-nitro-3'-methyl-2-oxo-1'-phenyl-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-5'-carboxylate (4h) (Table 2, entry 8)

mp 267–269 °C, (Ref.: [15] 268–270 °C); $^1\text{H-NMR}$ (400 MHz, DMSO- d_6): δ (ppm) 0.78 (t, 3H, $J = 7.0$ Hz, CH₃), 1.62 (s, 3H, CH₃), 3.71–3.83 (m, 2H, OCH₂), 7.09 (d, 1H, $J = 8.8$ Hz, Ar), 7.36 (t, 1H, $J = 7.4$ Hz, Ar), 7.53 (t, 2H, $J = 8.0$ Hz, Ar), 7.83 (d, 2H, $J = 7.5$ Hz, Ar), 7.98 (d, 1H, $J = 2.3$ Hz, Ar), 8.2 (dd, 1H, $J_1 = 8.9$, $J_2 = 2.3$ Hz, Ar), 8.34 (s, 2H, NH₂), 11.28 (s, 1H, NH). $^{13}\text{C-NMR}$ (100 MHz, DMSO- d_6): δ 12.3, 13.7, 48.0, 59.7, 74.0, 97.3, 109.6, 120.7, 125.9, 127.0, 129.4, 129.9, 137.4, 137.7, 143.0, 144.3, 144.8, 149.1, 162.1, 167.9, 180.3.

6'-Amino-1,3'-dimethyl-2-oxo-1'-phenyl-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-5'-carboxylate (4i) (Table 2, entry 9)

mp 224–226 °C, (Ref.: [12] 226–227 °C); ¹H-NMR (400 MHz, DMSO-d₆): δ (ppm) 1.46 (s, 3H, CH₃), 3.25 (s, 3H, CH₃), 7.10–7.18 (m, 2H, Ar), 7.25 (d, 1H, *J* = 8.3 Hz, Ar), 7.34–7.42 (m, 2H, Ar), 7.52 (t, 2H, *J* = 7.9 Hz, Ar), 7.63 (s, 2H, NH₂), 7.79 (dd, 2H, *J*₁ = 8.7, *J*₂ = 1.0 Hz, Ar). ¹³C-NMR (125 MHz, DMSO-d₆): δ 12.2, 27.0, 47.9, 56.1, 96.6, 109.4, 118.3, 120.6, 123.8, 125.0, 127.1, 129.9, 131.8, 137.7, 143.5, 144.3, 145.4, 161.6, 176.3.

6'-Amino-3',5'-dimethyl-2-oxo-1'-phenyl-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-5'-carboxylate (4j) (Table 2, entry 10)

mp > 270 °C, (Ref.: [12] 288–289 °C); ¹H-NMR (400 MHz, DMSO-d₆): δ (ppm) 1.51 (s, 3H, CH₃), 2.19 (s, 3H, CH₃), 6.78 (d, 1H, *J* = 6.4 Hz, Ar), 6.95 (s, 1H, Ar), 7.01–7.04 (m, 1H, Ar), 7.29–7.32 (m, 1H, Ar), 7.45–7.49 (m, 4H, Ar and NH₂), 7.74 (d, 2H, *J* = 6.4 Hz, Ar), 10.57 (s, 1H, NH). ¹³C-NMR (100 MHz, DMSO-d₆): δ 19.4, 21.4, 48.7, 97.4, 110.4, 118.9, 121.0, 126.2, 127.4, 130.3, 130.4, 132.5, 133.2, 138.1, 140.0, 144.9, 145.8, 161.8, 178.3.

2'-Amino-2,5'-dioxo-5'H-spiro[indoline-3,4'-pyrano[2,3-c]chromene]-3'-carbonitrile (5a) (Table 3, entry 1)

mp > 270 °C, (Ref. [18] 292–294 °C); ¹H-NMR (400 MHz, DMSO-d₆): δ 6.86 (d, 1H, *J* = 8.0 Hz, Ar), 6.94 (t, 1H, *J* = 7.0 Hz, Ar), 7.20–7.25 (m, 2H, Ar), 7.50 (d, 1H, *J* = 8.3 Hz, Ar), 7.55 (t, 1H, *J* = 7.7 Hz, Ar), 7.68 (s, 2H, NH₂), 7.77 (t, 1H, *J* = 7.9 Hz, Ar), 7.95 (dd, 1H, *J*₁ = 8.0, *J*₂ = 1.5 Hz, Ar), 10.69 (s, 1H, NH). ¹³C-NMR (100 MHz, DMSO-d₆): δ 48.1, 57.5, 101.9, 110.0, 112.9, 117.2, 117.5, 122.5, 123.1, 124.6, 125.5, 129.4, 133.5, 134.2, 142.7, 152.5, 155.6, 158.8, 158.9, 177.6.

2'-Amino-5-chloro-2,5'-dioxo-5'H-spiro[indoline-3,4'-pyrano[2,3-c]chromene]-3'-carbonitrile (5b) (Table 3, entry 2)

mp > 270 °C, (Ref. [20] >300 °C); ¹H-NMR (400 MHz, DMSO-d₆): δ 6.87 (d, 1H, *J* = 8.3 Hz, Ar), 7.27 (dd, 1H, *J*₁ = 8.3, *J*₂ = 2.2 Hz, Ar), 7.45 (d, 1H, *J* = 2.3 Hz, Ar), 7.51 (d, 1H, *J* = 8.3 Hz, Ar), 7.56 (dt, 1H, *J*₁ = 7.7, *J*₂ = 0.8 Hz, Ar), 7.75 (s, 2H, NH₂), 7.79 (dt, 1H, *J*₁ = 7.8, *J*₂ = 1.5 Hz, Ar), 7.95 (dd, 1H, *J*₁ = 7.9, *J*₂ = 1.3 Hz, Ar), 10.82 (s, 1H, NH). ¹³C-NMR (100 MHz, DMSO-d₆): δ 48.3, 56.8, 101.2, 111.3, 113.1, 117.2, 117.4, 123.2, 125.1,

125.5, 126.5, 129.3, 134.2, 135.5, 141.6, 152.6, 155.9, 158.9, 159.0, 177.5.

2'-Amino-5-nitro-2,5'-dioxo-5'H-spiro[indoline-3,4'-pyrano[2,3-c]chromene]-3'-carbonitrile (5c) (Table 3, entry 3)

mp > 270 °C; ¹H-NMR (400 MHz, DMSO-d₆): δ 7.09 (d, 1H, *J* = 8.8 Hz, Ar), 7.52 (d, 1H, *J* = 7.8 Hz, Ar), 7.57 (dt, 1H, *J*₁ = 7.7, *J*₂ = 1.0 Hz, Ar), 7.79 (dt, 1H, *J*₁ = 7.4, *J*₂ = 1.5 Hz, Ar), 7.86 (s, 2H, NH₂), 7.96 (dd, 1H, *J*₁ = 8.0, *J*₂ = 1.5 Hz, Ar), 8.22 (dd, 1H, *J*₁ = 8.5, *J*₂ = 2.5 Hz, Ar), 8.37 (d, 1H, *J* = 2.5 Hz, Ar), 11.43 (s, 1H, NH). ¹³C-NMR (100 MHz, DMSO-d₆): δ 48.2, 56.1, 100.7, 110.2, 113.2, 117.2, 117.3, 121.1, 123.3, 125.5, 126.8, 134.3, 134.5, 143.2, 149.1, 152.6, 156.3, 159.2, 159.3, 178.4. Anal calcd for C₂₀H₁₀N₄O₆: C, 59.71; H, 2.51; N, 13.93. Found: C, 59.42; H, 2.57; N, 13.80.

Methyl-2'-amino-2,5'-dioxo-5'H-spiro[indoline-3,4'-pyrano[2,3-c]chromene]-3'-carboxylate (5d) (Table 3, entry 4)

mp > 270 °C, (Ref. [11] 275–277 °C); ¹H-NMR (400 MHz, DMSO-d₆): δ 3.33 (s, 3H, OCH₃), 6.74–6.85 (m, 2H, Ar), 7.02 (d, 1H, *J* = 7.3 Hz, Ar), 7.11 (t, 1H, *J* = 7.5 Hz, Ar), 7.44 (d, 1H, *J* = 8.0 Hz, Ar), 7.51 (t, 1H, *J* = 7.5 Hz, Ar), 7.73 (t, 1H, *J* = 7.4 Hz, Ar), 8.04 (d, 1H, *J* = 7.8 Hz, Ar), 8.09 (s, 2H, NH₂), 10.45 (s, 1H, NH). ¹³C-NMR (100 MHz, DMSO-d₆): δ 47.9, 50.9, 76.3, 104.3, 108.9, 112.9, 116.8, 121.5, 123.3, 123.7, 125.3, 128.5, 133.9, 134.9, 144.4, 152.3, 154.3, 158.2, 158.9, 167.6, 179.4.

Methyl-2'-amino-5-chloro-2,5'-dioxo-5'H-spiro[indoline-3,4'-pyrano[2,3-c]chromene]-3'-carboxylate (5e) (Table 3, entry 5)

mp > 270 °C, (Ref. [20] 279–281 °C); ¹H-NMR (400 MHz, DMSO-d₆): δ 3.35 (s, 3H, OCH₃), 6.76 (d, 1H, *J* = 8.3 Hz, Ar), 7.16 (dd, 1H, *J*₁ = 8.1, *J*₂ = 2.2 Hz, Ar), 7.20 (d, 1H, *J* = 2.2 Hz, Ar), 7.46 (d, 1H, *J* = 8.3 Hz, Ar), 7.53 (t, 1H, *J* = 7.7 Hz, Ar), 7.75 (dt, 1H, *J*₁ = 7.8, *J*₂ = 1.5 Hz, Ar), 8.04 (dd, 1H, *J*₁ = 7.9, *J*₂ = 1.5 Hz, Ar), 8.13 (s, 2H, NH₂), 10.58 (s, 1H, NH). ¹³C-NMR (100 MHz, DMSO-d₆): δ 48.2, 50.9, 75.8, 103.5, 110.1, 113.1, 116.8, 123.5, 124.1, 125.3, 125.4, 128.2, 133.9, 137.0, 143.4, 152.4, 154.7, 158.4, 158.4, 159.0, 167.5, 179.2.

Methyl-2'-amino-5-bromo-2,5'-dioxo-5'H-spiro[indoline-3,4'-pyrano[2,3-c]chromene]-3'-carboxylate (5f) (Table 3, entry 6)

mp > 270 °C, (Ref. [20] 288–290 °C); ¹H-NMR (400 MHz, DMSO-d₆): δ 3.35 (s, 3H, OCH₃), 6.72 (d, 1H, *J* = 8.0 Hz, Ar), 7.26–7.33 (m, 2H, Ar), 7.46 (d, 1H, *J* = 8.3 Hz, Ar),

7.53 (t, 1H, $J = 7.6$ Hz, Ar), 7.75 (t, 1H, $J = 7.9$ Hz, Ar), 8.04 (dd, 1H, $J_1 = 8.0$, $J_2 = 1.2$ Hz, Ar), 8.13 (s, 2H, NH₂), 10.59 (s, 1H, NH). ¹³C-NMR (100 MHz, DMSO-d₆): δ 48.1, 51.0, 75.8, 103.5, 110.7, 113.1, 116.8, 123.5, 125.3, 126.7, 131.1, 133.9, 137.4, 143.8, 152.4, 154.7, 158.4, 159.0, 167.5, 179.1.

Methyl-2'-amino-5-nitro-2,5'-dioxo-5'H-spiro[indoline-3, 4'-pyrano[2,3-c]chromene]-3'-carboxylate (5g) (Table 3, entry 7)

mp > 270 °C; ¹H-NMR (400 MHz, DMSO-d₆): δ 3.36 (s, 3H, OCH₃), 6.95 (d, 1H, $J = 8.5$ Hz, Ar), 7.46 (d, 1H, $J = 8.3$ Hz, Ar), 7.54 (t, 1H, $J = 7.7$ Hz, Ar), 7.76 (t, 1H, $J = 7.9$ Hz, Ar), 8.06 (dd, 1H, $J_1 = 8.0$, $J_2 = 1.5$ Hz, Ar), 8.09 (d, 1H, $J = 2.2$ Hz, Ar), 8.13 (dd, 1H, $J_1 = 8.5$, $J_2 = 2.2$ Hz, Ar), 8.20 (s, 2H, NH₂), 11.21 (s, 1H, NH). ¹³C-NMR (100 MHz, DMSO-d₆): δ 48.0, 51.0, 75.3, 102.9, 108.8, 113.1, 116.9, 119.8, 123.5, 125.3, 126.1, 134.1, 136.0, 142.4, 151.1, 152.4, 155.1, 158.7, 159.1, 167.3, 180.2. Anal calcd for C₂₁H₁₃N₃O₈: C, 57.94; H, 3.01; N, 9.65. Found: C, 57.65; H, 3.07; N, 9.38.

Ethyl-2'-amino-2,5'-dioxo-5'H-spiro[indoline-3,4'-pyrano[2,3-c]chromene]-3'-carboxylate (5h) (Table 3, entry 8)

mp 253–255 °C, (Ref. [18] 252–254 °C); ¹H-NMR (400 MHz, DMSO-d₆): δ 0.83 (t, 3H, $J = 7.2$ Hz, CH₃), 3.71–3.83 (m, 2H, OCH₂), 6.75 (d, 1H, $J = 7.8$ Hz, Ar), 6.81 (dt, 1H, $J_1 = 7.5$, $J_2 = 0.8$ Hz, Ar), 7.02 (d, 1H, $J = 6.8$ Hz, Ar), 7.13 (dt, 1H, $J_1 = 7.7$, $J_2 = 1.2$ Hz, Ar), 7.45 (d, 1H, $J = 8.3$ Hz, Ar), 7.53 (dt, 1H, $J_1 = 7.7$, $J_2 = 1.0$ Hz, Ar), 7.75 (dt, 1H, $J_1 = 7.9$, $J_2 = 1.5$ Hz, Ar), 8.04 (dd, 1H, $J_1 = 8.0$, $J_2 = 1.2$ Hz, Ar), 8.15 (s, 2H, NH₂), 10.43 (s, 1H, NH). ¹³C-NMR (100 MHz, DMSO-d₆): δ 13.6, 47.8, 59.6, 76.0, 104.3, 108.9, 112.9, 116.8, 121.5, 123.3, 123.7, 125.3, 128.4, 133.9, 135.1, 144.6, 152.3, 154.2, 158.2, 159.0, 167.6, 179.3.

Ethyl-2'-amino-5-chloro-2,5'-dioxo-5'H-spiro[indoline-3, 4'-pyrano[2,3-c]chromene]-3'-carboxylate (5i) (Table 3, entry 9)

mp > 270 °C, (Ref. [20] 275–277 °C); ¹H-NMR (400 MHz, DMSO-d₆): δ 0.86 (t, 3H, $J = 7.2$ Hz, CH₃), 3.74–3.86 (m, 2H, OCH₂), 6.75 (d, 1H, $J = 8.0$ Hz, Ar), 7.15–7.22 (m, 2H, Ar), 7.46 (d, 1H, $J = 8.3$ Hz, Ar), 7.53 (t, 1H, $J = 7.7$ Hz, Ar), 7.75 (dt, 1H, $J_1 = 7.8$, $J_2 = 1.3$ Hz, Ar), 8.03 (dd, 1H, $J_1 = 7.8$, $J_2 = 1.3$ Hz, Ar), 8.20 (s, 2H, NH₂), 10.58 (s, 1H, NH). ¹³C-NMR (100 MHz, DMSO-d₆): δ 13.7, 48.1, 59.7, 75.5, 103.6, 110.1, 113.1, 116.8, 123.4, 124.1, 125.3, 125.4, 128.1, 133.9, 137.2, 143.6, 152.4, 154.6, 158.4, 159.1, 167.5, 179.2.

Ethyl-2'-amino-5-bromo-2,5'-dioxo-5'H-spiro[indoline-3, 4'-pyrano[2,3-c]chromene]-3'-carboxylate (5j) (Table 3, entry 10)

mp > 270 °C, (Ref. [20] 280–282 °C); ¹H-NMR (400 MHz, DMSO-d₆): δ 0.87 (t, 3H, $J = 7.2$ Hz, CH₃), 3.74–3.86 (m, 2H, OCH₂), 6.71 (d, 1H, $J = 8.0$ Hz, Ar), 7.27–7.33 (m, 2H, Ar), 7.46 (d, 1H, $J = 8.5$ Hz, Ar), 7.53 (t, 1H, $J = 7.5$ Hz, Ar), 7.75 (dt, 1H, $J_1 = 7.8$, $J_2 = 1.3$ Hz, Ar), 8.03 (d, 1H, $J = 8.0$ Hz, Ar), 8.20 (s, 2H, NH₂), 10.59 (s, 1H, NH). ¹³C-NMR (100 MHz, DMSO-d₆): δ 13.7, 48.0, 59.7, 75.5, 103.6, 110.7, 113.1, 116.8, 123.4, 125.3, 126.8, 131.0, 133.9, 137.6, 144.0, 152.4, 154.6, 158.4, 159.1, 167.5, 179.1.

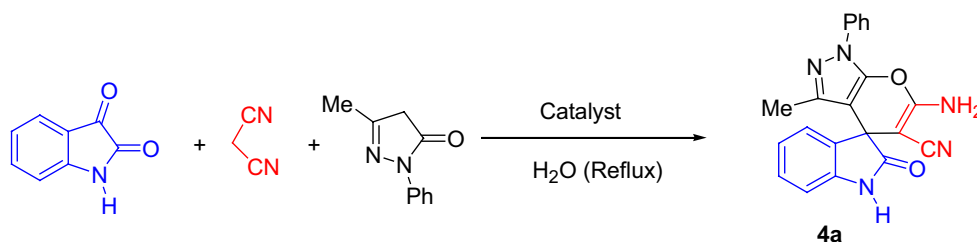
Ethyl-2'-amino-5-nitro-2,5'-dioxo-5'H-spiro[indoline-3, 4'-pyrano[2,3-c]chromene]-3'-carboxylate (5k) (Table 3, entry 11)

mp 267–268 °C; ¹H-NMR (400 MHz, DMSO-d₆): δ 0.85 (t, 3H, $J = 7.1$ Hz, CH₃), 3.80 (q, 2H, $J = 7.1$ Hz, OCH₂), 6.96 (d, 1H, $J = 8.5$ Hz, Ar), 7.46 (d, 1H, $J = 8.3$ Hz, Ar), 7.55 (t, 1H, $J = 7.6$ Hz, Ar), 7.76 (dt, 1H, $J_1 = 7.8$, $J_2 = 1.0$ Hz, Ar), 8.05 (dd, 1H, $J_1 = 7.9$, $J_2 = 1.7$ Hz, Ar), 8.11 (d, 1H, $J = 2.5$ Hz, Ar), 8.15 (dd, 1H, $J_1 = 8.5$, $J_2 = 2.3$ Hz, Ar), 8.28 (s, 2H, NH₂), 11.21 (s, 1H, NH). ¹³C-NMR (100 MHz, DMSO-d₆): δ 13.7, 47.9, 59.8, 74.9, 103.0, 108.9, 113.1, 116.9, 119.9, 123.5, 125.3, 126.1, 134.1, 136.2, 142.4, 151.3, 152.4, 155.1, 158.7, 159.3, 167.2, 180.2. Anal calcd for C₂₂H₁₅N₃O₈: C, 58.80; H, 3.36; N, 9.35. Found: C, 58.49; H, 3.39; N, 9.11.

Results and discussion

The catalytic activity of silica-bonded ionic liquids such as [Sipim]HSO₄, [Sipim]H₂PO₄, [Sipim]OTf, and [Sipim]Cl was investigated as a heterogeneous catalysts in one-pot synthesis of spiro[indoline-3,4'-pyrano[2,3-c]pyrazoles] through three-component reaction of isatin, malononitrile, and 3-methyl-1-phenyl-5-pyrazolone and the results are summarized in Table 1.

For this purpose, the reaction between isatin (1 mmol), malononitrile (1 mmol), and 3-methyl-1-phenyl-5-pyrazolone (1 mmol) was selected as a model reaction in aqueous media in order to establish the feasibility of the strategy and optimize the reaction conditions. All of these silica immobilized propyl imidazolium salts were accomplished this three-component condensation reaction in aqueous media at refluxing conditions. The model reaction was converted into corresponding product (**4a**) in a higher yield using solid [Sipim]Cl (0.05 g) as catalyst (Table 1, entry 5). The lower amounts of [Sipim]Cl (0.03 g) was

Table 1 Condensation reaction of isatin, malononitrile with 3-methyl-1-phenyl-5-pyrazolone in the presence of different amounts of catalysts

Entry	Catalyst	Catalyst loading (g)	Time (min)	Yield ^b %
1		0.05	15	90
2		0.05	15	90
3		0.05	15	85
4		0.03	20	85
5		0.05	15	95
6		0.07	15	95
7 ^c		0.05	60	71
8 ^d		0.05	50	79
9 ^c		0.05	90	70
10		0.20	15	80
11		0.20	15	75
12		0.20	15	75
13		0.20	15	80
14	Without catalyst	-	120	trace

Reaction conditions: isatin (1 mmol), malononitrile (1 mmol), and 3-methyl-1-phenyl-5-pyrazolone (1 mmol) in refluxing water (5 mL)

^a Isolated yield. ^b The reaction was performed at 45 °C.

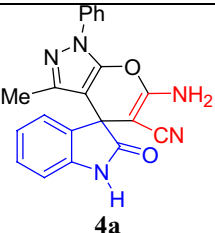
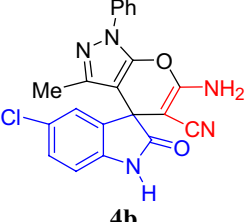
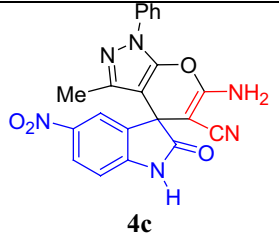
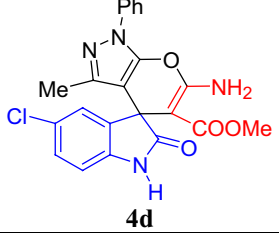
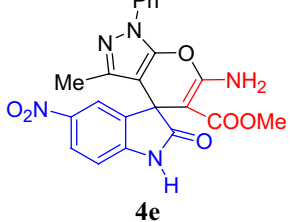
^c The reaction was performed at 80 °C.

^d The reaction was performed at 120 °C under solvent-free conditions

converted the model reaction in longer reaction time and lower yield (Table 1, entry 4) and using higher amounts of the catalyst (0.07 g) did not improve the result to an appreciable extent (Table 1, entry 6). The model reaction was examined at 120 °C and solvent-free conditions (Table 1, entry 9) and lower temperature 45 and 80 °C in water at solvent (Table 1, entries 7 and 8) gave the corresponding product in longer reaction time and lower yields. The model reaction was treated with available

ionic liquids such as imidazolium chloride, imidazolium bromide, imidazolium hydrogen sulfate, and imidazolium hydrogen phosphate and the corresponding product (**4a**) was obtained in the presence of 0.20 mmol of these ionic liquids after 15 min in 75–80 % yields (Table 1, entries 10–13). The optimum conditions was isatin (1 mmol), methylene active compound (1 mmol), 3-methyl-1-phenyl-5-pyrazolone (1 mmol), and [Sipim]Cl (0.05 g) in refluxing aqueous media.

Table 2 Preparation of spiro[indoline-3,4'-pyrano[2,3-c]pyrazole] derivatives catalyzed by [Sipim]Cl in water at reflux conditions

Entry	R	Y	Product	Time (min)	Yield (%) ^b	mp °C	Lit. mp (°C)
1	H	CN	 4a	15	95	235-237	236-237 [12]
2	Cl	CN	 4b	20	85	232-233	232-234 [14]
3	NO ₂	CN	 4c	15	90	227-229	226-228 [14]
4	Cl	COOMe	 4d	75	75	224-226	-
5	NO ₂	COOMe	 4e	60	80	241-243	-

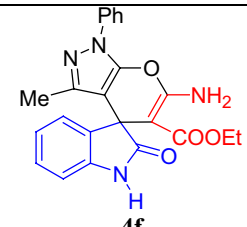
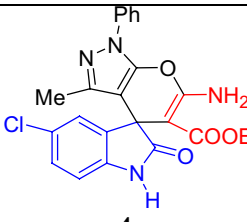
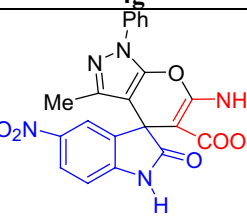
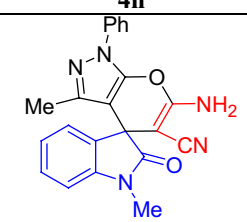
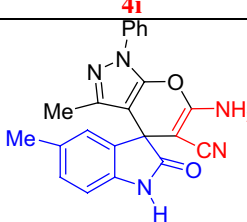
The reaction can tolerate isatin and some of its derivatives carrying both electron-withdrawing group such as NO₂ and halogen such as Cl and the results were reasonable (Table 2). Beside malonitrile, other methylene active compound such as methyl acetoacetate and ethyl acetoacetate reacted under optimized conditions and gave the corresponding products in high yields (Table 2, entries 4–8).

In addition, 4-hydroxy coumarin as 1,3-dicarbonyl compound (enol form) was treated with isatin and methylene active compounds under optimized conditions and the

corresponding spiro[indoline-3,4'-pyrano[2,3-c]chromene derivatives were obtained in high yields (Table 3).

Proposed mechanism for the synthesis of spirooxindole derivatives **4** and **5** was described in Scheme 2 [11, 20]. The process represents a typical cascade reaction in which the isatin **1** first condenses with methylene active compound **2** to afford isatylidene malonitrile derivative **6** in the presence of [Sipim]Cl in water. This step was regarded as a fast Knoevenagel condensation. Then, **6** is attacked via Michael addition of 1,3-dicarbonyl compound **3** to give the intermediate

Table 2 continued

6	H	COOEt	 4f	60	80	239-241	238-240 [14]
7	Cl	COOEt	 4g	90	75	246-247	241-242 [15]
8	NO ₂	COOEt	 4h	75	80	267-269	265-266 [15]
9 ^c	H	CN	 4i	25	91	224-226	226-227 [12]
10	Me	CN	 4j	30	88	>270	288-289 [12]

Reaction conditions: isatin (1 mmol), methylene active compound (1 mmol), 3-methyl-1-phenyl-5-pyrazolone (1 mmol), catalyst (0.05 g), water (5 mL) at refluxing conditions

^a Isolated yield

^b 1-Methyl-isatin was used instead of isatin

7 followed by the cycloaddition of hydroxyl group to the cyano moiety to form the desired product **4** or **5** (Scheme 3).

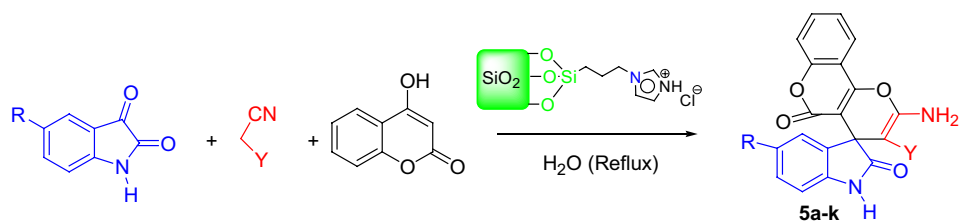
The possibility of recycling the catalyst [Sipim]Cl was examined using the reaction of isatin, malononitrile, and 3-methyl-1-phenyl-5-pyrazolone under the optimized conditions. Upon completion, the reaction mixture was washed with warm ethanol ($3 \times 5 \text{ cm}^3$). The recovered catalyst was dried and reused for subsequent runs. The recycled catalyst was reused four times without any additional treatment. No

observation of any appreciable loss in the catalytic activity of [Sipim]Cl was observed (Fig. 2).

Conclusions

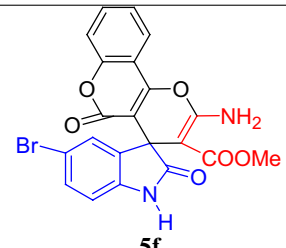
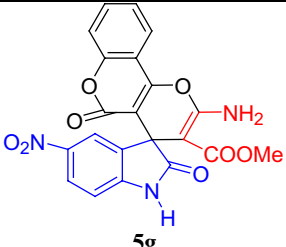
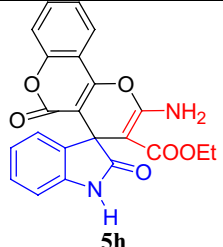
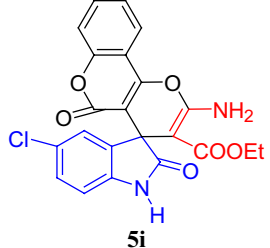
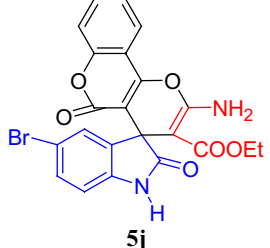
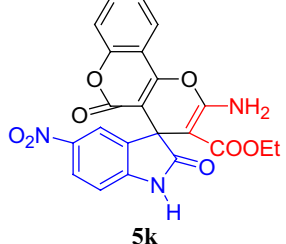
In conclusion, this work shows that [Sipim]Cl which can be prepared by simple operation from commercially available and relative cheap starting materials, efficiently catalyzed the

Table 3 Preparation of spiro[indoline-3,4'-pyrano[2,3-c]chromene] derivatives catalyzed by [Sipim] Cl in water at reflux conditions



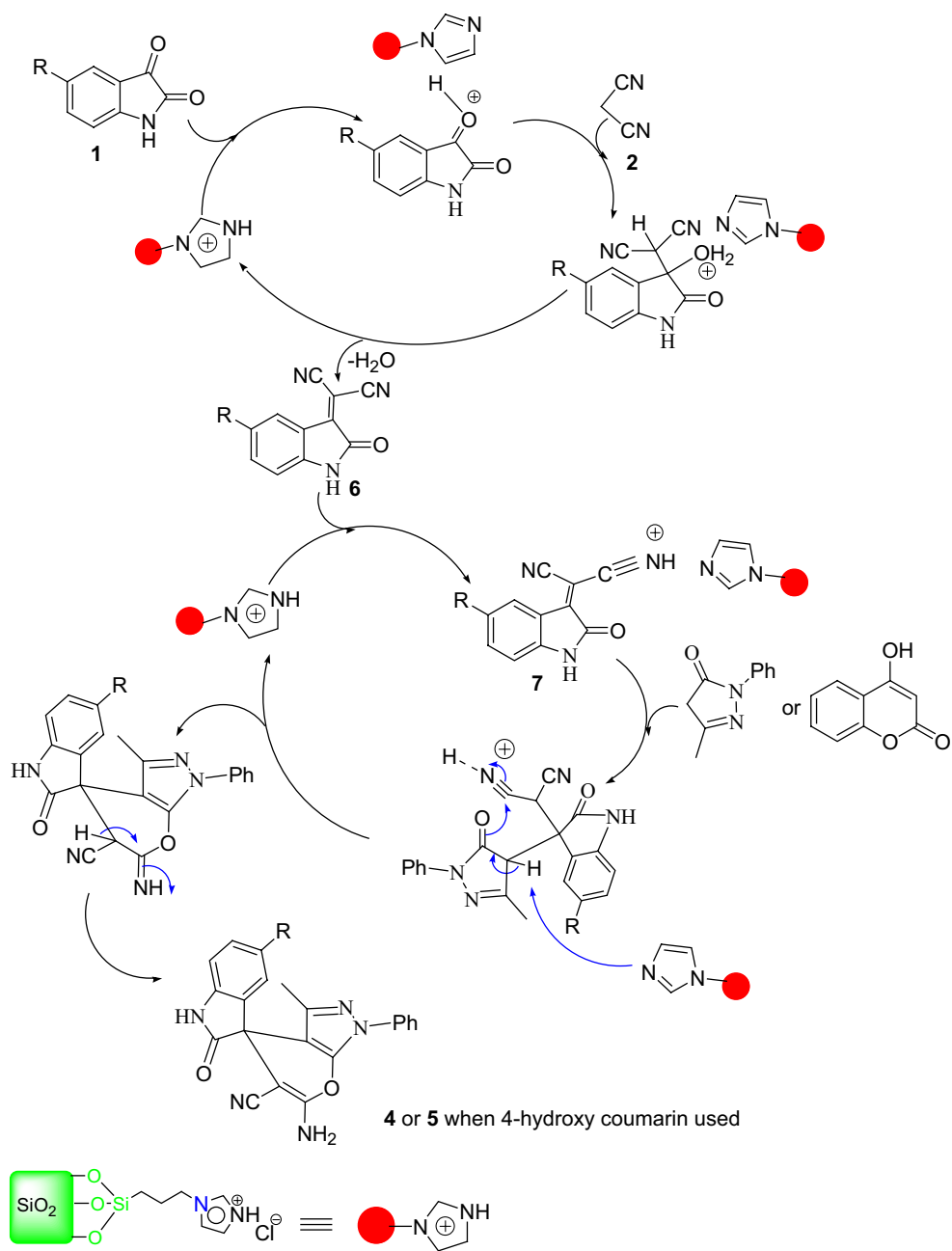
Entry	R	Y	Product	Time (min)	Yield (%) ^b	mp °C	Lit. mp (°C)
1	H	CN		20	90	>270	294-296 [18]
2	Cl	CN		20	85	>270	>300 [20]
3	NO ₂	CN		20	88	>270	-
4	H	COOMe		45	80	>270	275-277 [11]
5	Cl	COOMe		60	75	>270	279-281 [20]

Table 3 continued

6	Br	COOMe	 5f	60	70	>270	288-290 [20]
7	NO ₂	COOMe	 5g	50	80	>270	-
8	H	COOEt	 5h	60	83	253-255	252-254 [18]
9	Cl	COOEt	 5i	90	80	>270	275-277 [20]
10	Br	COOEt	 5j	90	75	>270	280-282 [20]
11	NO ₂	COOEt	 5k	75	80	267-268	-

Reaction conditions: isatin (1 mmol), methylene active compound (1 mmol), 4-hydroxy-coumarin (1 mmol), catalyst (0.05 g), water (5 mL) at refluxing conditions

^a Isolated yield



Scheme 3 Proposed mechanism for the synthesis of spirooxindoles

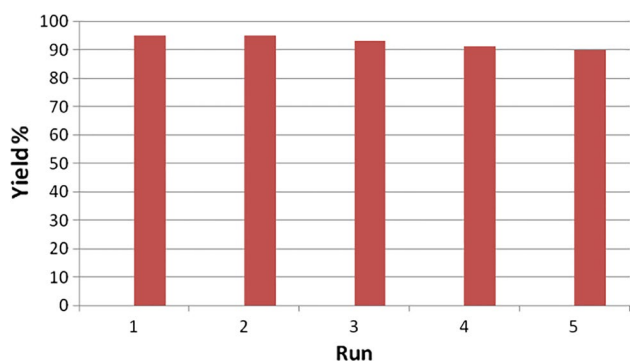


Fig. 2 Recyclability of [Sipim]Cl in the reaction of isatin (1 mmol), malononitrile (1 mmol), 3-methyl-1-phenyl-5-pyrazolone (1 mmol), and [Sipim]Cl (0.05 g) in water (5 mL) under reflux conditions. Reaction time = 15 min

synthesis of spirooxindoles. It could also be recovered and reused for several times without noticeable loss of reactivity.

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