Journal of Molecular Structure 1230 (2021) 129890

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstr

Bis [hydrazinium (1+)] hexafluoridosilicate:$(N_2H_5)_2SiF_6$ novel hybrid crystal as an efficient, reusable and environmentally friendly heterogeneous catalyst for Knoevenagel condensation and synthesis of biscoumarin derivatives

Fatima El hajri[a], Zakaria Benzekri[a,*], Sarra Sibous[a], Ali Ouasri[b,c], Said Boukhris[a], Amina Hassikou[a], Ali Rhandour[b], Abdelaziz Souizi[a]

[a] Laboratory of Organic Chemistry, Catalysis and Environment, Department of Chemistry, Faculty of Sciences, Ibn Tofail University, PB 133-14000, Kenitra, Morocco
[b] Laboratory of Applied Solid Chemistry. Faculty of Sciences, Ibn Tofaïl University, BO 133, 14000 Kenitra, Morocco
[c] Regional Center of Education and Training of the Trades, Madinat Al Irfane, Souissi, BP 6210, Rabat, Morocco

ARTICLE INFO

Article history:
Received 7 April 2020
Revised 14 December 2020
Accepted 31 December 2020
Available online 9 January 2021

Keywords:
Bis [hydrazinium (1+)] hexafluoridosilicate
$(N_2H_5)_2SiF_6$
Knoevenagel
Biscoumarin
Hybrid catalyst
Green chemistry

ABSTRACT

A simple, effective, green and nontoxic protocol was used for the Knoevenagel condensation and the biscoumarin derivatives synthesis. It have demonstrated that the use of a new hybrid crystal as a heterogeneous catalyst makes it possible to obtain several advantages such as: a short reaction time and exceptional catalytic activity. Furthermore, $(N_2H_5)_2SiF_6$ was examined for five successive cycles without significant loss of catalytic activity.

1. Introduction

According to the principles of green chemistry, sustainable synthesis routes are highly sought after, not necessarily to maximize conversions and yields, but rather to minimize energy consumption and waste production [1–2]. In this context, the integration of catalytic processes played an important role in the chemical and pharmaceutical industries [3–4]. This interest is due to the catalyzed reactions simplicity, the energy and solvents reduction and the increase in the product yield.

Generally, the Knoevenagel condensation [5] and the coumarin synthesis are reactions still frequently applied, in the synthesis of certain new drugs like: atorvastatin [6], pioglitazone [7] and MDL 103371 [8]. Moreover, the biscoumarin and their derivatives are known for their anticancer [9,10], antifungal, anti-thrombotic [11], anticoagulant [12],anti-HIV[13] antimicrobial and antioxidant [14] properties. They also used as fluorescent brighteners, effective laser dyes and additives in food and cosmetics [15–17].

According to the interesting chemical and physical properties of biscoumarin derivatives and the Knoevenagel condensation, they are therefore highly desirable to develop simple, ecological and cost-effective procedures for the Knoevenagel condensation [18–26] and the biscoumarin derivatives synthesis [27–35]. Recently, we continued our interest in using excellent heterogeneous catalysts [36–42] which, we evaluated the catalytic activity of new hybrid material in the Knoevenagel condensation and the biscoumarin derivatives synthesis.

2. Experimental section

2.1. Experimental details

Large-purity chemicals were purchased from Sigma-Aldrich, Merck, Fluka and Panreac. All materials were of commercial reagent grade. All reactions were monitored by thin-layer chromatography (TLC) on silica gel plates (Fluka Kieselgel 60 F254). Melting points were taken on a KOFLER hot stage apparatus without any correction. The ^{13}C NMR and ^{1}H NMR spectra were

* Corresponding author.
E-mail address: zakariachimist2014@hotmail.com (Z. Benzekri).

https://doi.org/10.1016/j.molstruc.2021.129890
0022-2860/

recorded on a 300 MHz and 75 MHz Brucker spectrometer in DMSO-d_6.

2.2. General procedure for the preparation of catalyst

Hydrazinium (1+) hexafluorosilicate $(N_2H_5)_2SiF_6$ crystal has been recently synthesized by slow evaporation at room temperature of aqueous solution containing stoichiometric (2:1) amounts of hydrazine NH_2NH_2 and H_2SiF_6 acid [43]. The synthesis method consists to add the H_2SiF_6 acid (Percentage = 34 % in weight) to the pure NH_2NH_2 (Percentage = 100 %) dissolved in the minimal distilled water. The obtained solution was taken under ambient temperature for evaporation; after few weeks, colorless single crystals suitable to X-ray structure determination were obtained [43]. The reaction equation mechanisms adopted for this synthesis may be described as the following:

Firstly: $NH_2NH_{2\,(aq)} + H_2O \rightarrow [OH^-_{\,(aq)} +, {}^+NH_3NH_{2\,(aq)}]$

Secondly: $2\,[OH^-_{(aq),}\,{}^+NH_3NH_{2\,(aq)}] + H_2SiF_6 \rightarrow (N_2H_5)_2SiF_6 + 2H_2O$

2.3. General operating mode of Knoevenagel condensation

A mixture of aromatic aldehyde **1** (**1 mmol**), the active methylene compound **2** (malononitrile, ethyl cyanoacetate or methyl cyanoacetate) (**1 mmol**) and $(N_2H_5)_2SiF_6$ (**0.1 mol %**) were stirred in **2 ml** of ethanol at room temperature. The Progress of the reaction was monitored by TLC using n-hexane / EtOAc (5:1) as an eluent. After completion of reaction, the dichloromethane was added to the reaction mixture, the catalyst was recovered by simple filtration and the filtrate was cooled. The obtained solid was filtered and recrystallized in hot ethanol.

2.4. General operating mode of synthesis of biscoumarin derivatives

A mixture of aromatic aldehyde **1** (**1 mmol**) and 4-hydroxycoumarine **4** (**2 mmol**) in a 50 ml round-bottomed flask, $(N_2H_5)_2SiF_6$ (**0.2 mol %**) was added to 2 ml of ethanol. The reaction mixture was heated at reflux for appropriate time (Table 9). After completion of the reaction as monitored by TLC. The crude reaction mixture was dissolved in CH_2Cl_2 and the catalyst was separated out by a simple filtration. The obtained solid was filtered and recrystallized from hot ethanol.

All the synthesized products **3a-1** [22] and **5a-f** [30,44] are acknowledged and were absolutely characterized by ^{1}H and ^{13}C NMR and confirmed by comparison of their melting points and their spectral data with those reported in the literature.

2.5. Spectroscopic characterization data for the selected products

2.5.1. 2-(4-chlorophenylmethylene) malononitrile (3a)

Colorless solid, yield: 96%, mp 160–162 °C (lit. [22] 159–160 °C); **^{1}H NMR** (300 MHz, DMSO-d_6) δ: 7.67 (d, 2H, J = 8.7 Hz), 7.92 (d, 2H, J = 8.7 Hz), 8.49 (s, 1H, C=CH). **^{13}C NMR** (75 MHz, DMSO-d_6) δ: 160.5, 139.5, 132.5, 131.6, 130.1, 114.4, 113.4, 82.7.

2.5.2. Methyl-3-(4-chlorophenyl)-2-cyanoacrylate (3b)

White solid, yield: 84%, mp 120–121 °C (lit. [22] 120–121 °C); **^{1}H NMR** (300 MHz, DMSO-d_6) δ: 3.84 (t, 3H, OCH_3), 7.65 (d, 2H, J = 8.4 Hz, ArH), 8.04 (d, 2H, J = 8.4 Hz, ArH), 8.38 (s, 1H, C=CH). **^{13}C NMR** (75 MHz, DMSO-d_6) δ: 162.5, 154.2, 138.5, 132.5, 130.6, 129.9, 115.8, 103.4, 53.8.

2.5.3. Ethyl-3-(4-chlorophenyl)-2-cyanoacrylate (3c)

Colorless solid, yield: 73%, mp 89–90 °C (lit. [22] 89–90 °C); **^{1}H NMR** (300 MHz, DMSO-d_6) δ: 1.28 (t, 3H, J = 7.2 Hz, CH_3), 4.29 (q, 2H, J = 7.2 Hz, CH_2), 7.61 (d, 2H, J = 8.7 Hz, ArH), 8.00 (d, 2H, J = 8.7 Hz, ArH), 8.33 (s, 1H, C=CH). **^{13}C NMR** (75 MHz, DMSO-d_6) δ: 162.0, 154.0, 138.5, 132.8, 130.5, 129.8, 115.7, 103.5, 62.9, 14.3.

2.5.4. 2-(phenylmethylene) malononitrile (3d)

Colorless solid, yield: 80%, mp 80–81 °C (lit. [22] 80–81 °C); ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.57–7.70 (m, 3H, ArH), 7.59 (d, 2H, J = 7.2 Hz, ArH), 8.50 (s, 1H, C=CH). **^{13}C NMR** (75 MHz, DMSO-d_6) δ: 155.7, 134.8, 131.7, 131.6, 130.9, 129.9, 114.6, 113.5, 82.0.

2.5.5. Methyl-2-cyano-3-phenylacrylate (3e)

White solid, yield: 67%, mp 84–85 °C (lit. [22] 84–85 °C); **^{1}H NMR** (300 MHz, DMSO-d_6) δ: 3.84 (t, 3H, CH_3), 7.54–7.65 (m, 3H, ArH), 8.03 (d, 2H, J = 8.4 Hz, ArH), 8.38 (s, 1H, C=CH). **^{13}C NMR** (75 MHz, DMSO-d_6) δ: 162.8, 155.6, 133.9, 131.7, 131.6, 129.8, 115.0, 102.8, 53.8.

2.5.6. 2-(p-tolylmethylene) malononitrile (3f)

White solid, yield: 82%, mp 118–119 °C (lit. [22] 118–119 °C); ^{1}H NMR (300 MHz, DMSO-d_6) δ: 2.37 (s, 3H), 7.38 (d, J = 8.4 Hz, 2H), 7.82 (d, J = 8.4 Hz, 2H), 8.39 (s, 1H, C=CH). ^{13}C NMR (75 MHz, DMSO-d_6) δ: 161.6, 146.1, 131.1, 130.5, 129.1, 114.8, 113.8, 80.3, 21.5.

2.5.7. Ethyl-2-cyano-3-p-tolylacrylate (3g)

White solid, yield: 54%, mp 91–92 °C (lit. [22] 91–92 °C); **^{1}H NMR** (300 MHz, DMSO-d_6) δ: 1.31 (t, J = 7.2 Hz, 3H), 2.37 (s, 3H), 4.34 (q, J = 7.4 Hz, 2H), 7.79 (d, J = 7.7 Hz, 2H), 7.90 (d, J = 7.2 Hz, 2H), 8.05 (s, 1H). **^{13}C NMR** (75 MHz, DMSO-d_6) δ: 163.0, 155.5, 144.9, 131.4, 130.4, 129.1, 116.2, 101.2, 63.1, 14.3, 21.3.

2.5.8. 2-(4-nitrophenylmethylene) malononitrile (3h)

Yellow solid, yield: 98%, mp 161–162 °C (lit. [22] 160–161 °C); **^{1}H NMR** (300 MHz, DMSO-d_6) δ: 8.11 (d, J = 8.7 Hz, 2H), 8.29 (d, J = 8.7 Hz, 2H), 8.67 (s, 1H, C=CH). **^{13}C NMR** (75 MHz, DMSO-d_6) δ: 159.7, 150.1, 137.1, 131.9, 124.8, 114.0, 112.9, 82.4.

2.5.9. Methyl-2-cyano-3-(4-nitrophenyl) acrylate (3i)

Yellow solid, yield: 87%, mp 172–173 °C (lit. [22] 172–173 °C); **^{1}H NMR** (300 MHz, DMSO-d_6) δ: 3.88 (s, 3H, CH_3), 8.19 (d, 2H, J = 7.1 Hz, ArH), 8.34 (d, 2H, J = 7.1 Hz, ArH), 8.48 (s, 1H, C=CH). **^{13}C NMR** (75 MHz, DMSO-d_6) δ: 162.1, 153.1, 149.8, 137.6, 132.1, 131.0, 124.4, 115.1, 107.0, 53.9.

2.5.10. Ethyl-2-cyano-3-(4-nitrophenyl) acrylate (3j)

Yellow solid, yield: 83%, mp 168–169 °C (lit. [22] 168–169 °C); **^{1}H NMR** (300 MHz, DMSO-d_6) δ: 1.28 (t, 3H, J = 7.2 Hz, CH_3), 4.29 (q, 2H, J = 7.2 Hz, CH_2), 7.62 (d, 2H, J = 8.4 Hz, ArH), 8.02 (d, 2H, J = 8.4 Hz, ArH), 8.30 (s, 1H, C=CH). **^{13}C NMR** (75 MHz, DMSO-d_6) δ: 162.0, 154.0, 138.4, 132.8, 130.6, 129.9, 115.8, 103.6, 62.9, 14.4.

2.6. 3,3′-(phenylmethylene)bis(4-hydroxy-2H-chromen-2-one) (5a)

White solid. yield: 95%, mp 233–234 °C (lit. [30] 228–230 °C); **^{1}H NMR** (300 MHz, DMSO-d_6) δppm: 7.93 (1H, s, OH), 7.91−7.16 (13H, m, aromatic H), 6.38 (1H, s, CH), 5.63 (1H, br s, OH). **^{13}C NMR** (75 MHz, DMSO-d_6) δppm: 35.95, 104.06, 115.91, 117.99, 123.68, 123.89, 125.51, 126.67, 128.02, 131.83, 140, 152.20, 164.8, 165.39.

2.7. 3,3′-(4-Chlorophenylmethylene)bis-(4-hydroxy-2H-chromen-2-one) (5b)

White solid. yield: 92%, mp 258–260 °C (lit. [30] 254–256 °C); **^{1}H NMR** (300 MHz, DMSO-d_6) δppm: 7.86 (1H, s, OH), 7.83−7.11 (12H, m, aromatic H), 6.27 (1H, s, CH), 5.61 (1H, br s, OH). **^{13}C NMR** (75 MHz, DMSO-d_6) δppm: 35.72, 103.34, 115.61, 119.20, 123.15, 124.03, 127.68, 128.58, 129.56, 131.28, 140.77, 152.41, 164.46, 166.96.

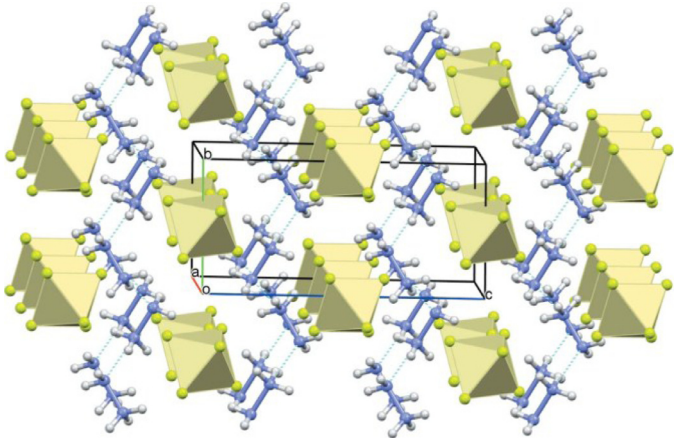


Fig. 1. The crystal structure view of $(N_2H_5)_2SiF_6$ with the anions shown as polyhedral.

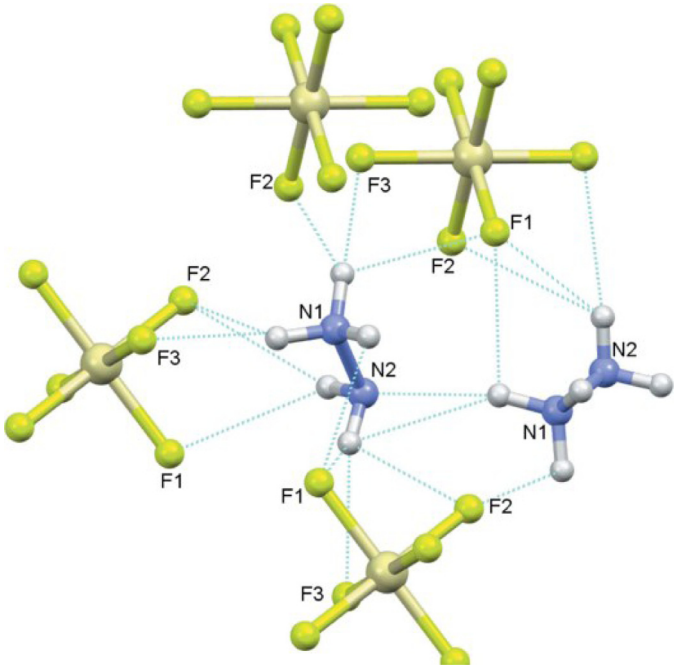
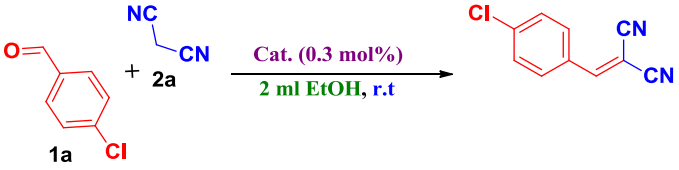


Fig. 2. Illustration of hydrogen bonds between the hydrazinium (1+) cations and $(SiF_6)^{2-}$ anions in the catalyst.

3. Results and discussion

3.1. Structural and vibrational characterization of the catalyst

The crystal structure of the catalyst, $(N_2H_5)_2SiF_6$, is formed by the organic $(N_2H_5)_2{}^{2+}$ cations and the mineral $(SiF_6)^{2-}$ anions, which are linked together through ionic and hydrogen bonds. In the present structure, the slightly distorted $(SiF_6)^{2-}$ octahedra (Si–F distances varying from 1.6777 (4) Å to 1.7100 (4) Å) are arranged in wire parallel to the [1 0 0] direction; The hydrazinium (1+) cations linked together by strong hydrogen bonds N–H···N, form zigzag chains propagating along the [0 1 0] direction (Fig. 1). Each fluorine atom of the $(SiF_6)^{2-}$ is linked to two nitrogen atoms of $(N_2H_5)^+$ cations through bifurcated or trifurcated N—H···F hydrogen bonds giving rise to three-dimensional network structural (Fig. 2).



Scheme 1. Model reaction Condensation of p-chlorobenzaldehyde **1a** and malononitrile **2a**.

3.2. Utilization of hybrid crystal $(N_2H_5)_2SiF_6$ catalyst in the Knoevenagel condensation

Initially, we tested the catalytic capacity of the three hybrid crystals $[NH_3(CH_2)_4NH_3SiF_6 \equiv (C_4Si)$ or $NH_3(CH_2)_6NH_3SiF_6 \equiv (C_6Si)$ or $(N_2H_5)_2SiF_6 \equiv C_0Si]$ in the Knoevenagel condensation. Therefore, we carried out the transformation of parachlorobenzaldehyde **1a** with malononitrile **2a** in 2 ml of ethanol at room temperature as a model reaction (Scheme 1). The results obtained are presented in Table 1.

This table showed that the desired product **3a** is obtained with an excellent yield by carrying out the model reaction in 2 ml of ethanol at room temperature in the presence of 0.3 mol% of the various catalysts that we tested (C_4Si or C_6Si or C_0Si). It should be noted that under similar conditions, but in the absence of a catalyst, only 54 % of the product **3a** is recovered (Table 1, Entry 1), which showed the essential role played by our catalysts. Therefore, the C_0Si was the best catalyst with a 90 % yield (Table 1, Entry 2). After determined the right catalyst (Table 1, Entry 2), we then compared the catalytic activity of our catalytic support with calcium carbonate as a conventional base under the same conditions, we found that our catalyst has a very interesting catalytic activity (Table 1, Entry 2) compared to $CaCO_3$ (Table 1, Entry 5). Afterward, $(N_2H_5)_2SiF_6 \equiv C_0Si$ is recovered by filtration and the filtrate is used as a reaction medium for the model reaction for 3 hours under ambient conditions (Scheme 1). Afterward, the desired product **3a** is recovered with the same yield obtained in the absence of the catalyst (Table 1, Entries 1–6). This result showed that our catalytic support is a heterogeneous catalyst. Then, we studied the effect of the solvent by carrying out the model reaction in the presence of 0.3 mol% of catalyst $(N_2H_5)_2SiF_6$ in 2 ml of various organic solvents under ambient conditions. The obtained results are collated in Table 2. The obtained results showed that this transformation led only to traces of product 3a in the absence

Table 1
Catalytic test on the model reaction.

Entry	Catalyst	Time (min)[b]	Yield (%)[a]
1	–	180	54
2	$(N_2H_5)_2SiF_6 \equiv C_0Si$	30	90
3	$NH_3(CH_2)_4NH_3SiF_6 \equiv (C_4Si)$	30	88
4	$NH_3(CH_2)_6NH_3SiF_6 \equiv (C_6Si)$	30	83
5	$CaCO_3$	60	76
6	recovered solvent	180	54

[a] Isolated yields.
[b] Time reported in min monitored by TLC.

Table 2
Study of the solvent effect on the model reaction.

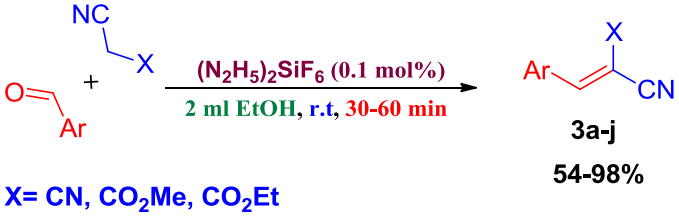
Entry	Solvent (2 ml)	Yield (%)[a]
1	EtOH	90
2	MeOH	67
3	CH_3CN	13
4	THF	88
5	Solvent-free	Trace

[a] Isolated yields.

Table 3
Mass effect of the catalyst in the model reaction.

Entry	$(N_2H_5)_2SiF_6$ (mol%)	$(N_2H_5)_2SiF_6$(mg)	Yield (%)[a]
1	0.05	0.1	81
2	0.1	0.2	96
3	0.2	0.41	94
4	0.3	0.63	90
5	0.4	0.83	84
6	0.5	1.04	82
7	0.6	1.24	78

[a] Isolated yields.



Scheme 2. Synthesis of alkenes catalyzed by $(N_2H_5)_2SiF_6$.

of the solvent (Table 2, Entry 5) and a low yield in the presence of acetonitrile (Table 2, Entry 3). In addition, we have found that the reaction is carried out in the presence of methanol and THF gives good yields (Table 2, Entry 3). Finally, the best result is obtained when the reaction is carried out in ethanol (Table 2, Entry 1).To estimate the optimal quantity of our catalyst required to condense 4-chlorobenzaldehyde with malononitrile in 2 ml of ethanol at room temperature; we varied the catalyst mass between 0.05 to 0.6 mol%. The obtained results are presented in Table 3. The table indicated that the mass 0.1 mol% is the optimal mass for this transformation (Table 3, Entry 2). Then, we have distinguished that more the mass of our catalytic support increased, the yield of the reaction decreased (Table 3, Entries 3–7). Furthermore, we proved that $(N_2H_5)_2SiF_6$ is an excellent catalytic support for the formation of our product **3a** and we will study the range and the versatility of the process of the optimal conditions found, by the use of the various aromatic aldehydes, the malononitrile, ethyl cyanoacetate and methyl cyanoacetate (Scheme 2). The Table 4 showed that the compounds **3a-j** are obtained with a good to excellent yields when the condensations are carried out at ambient temperature. Apparently, Knoevenagel condensation is not significantly affected by the nature of the substituent linked to the aryl group of the aldehyde. To assess the long-term stability of the C_0Si catalyst, it is recovered by simple filtration, washed with ethanol (2 × 10 mL) and dried in the oven. The catalyst is reused directly in the next cycle without further treatment. The efficiency of the recovered catalyst is measured by carrying out the same model reaction. As observed

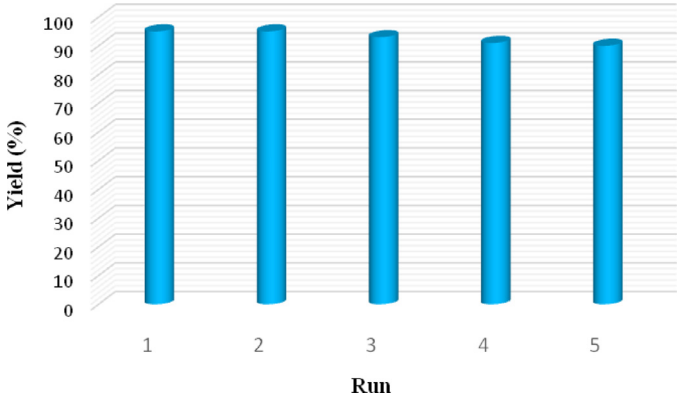
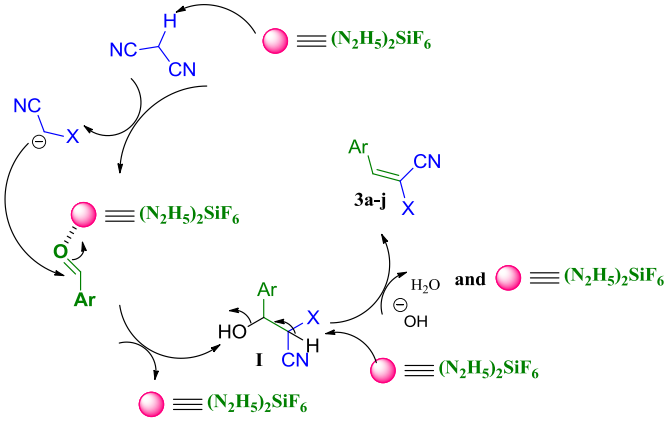


Fig. 3. Reusability of $(N_2H_5)_2SiF_6$ in synthesis of product ***3a***.



Scheme 3. Mechanism suggested for the Knoevenagel condensation in the presence of hybrid crystal $(N_2H_5)_2SiF_6$.

in Fig. 3, it was clear that our catalyst $(N_2H_5)_2SiF_6$ was recycled for five successive cycles without any significant loss of its catalytic power.

Many methods have been successfully developed for carrying out the Knoevenagel condensation reaction. The efficiency of our catalyst was compared with other catalysts cited in the literature. The results are presented in Table 5. These results demonstrated that the catalytic capacity of our catalyst is greater than those reported in the literature (short reaction time, excellent yield, mild reaction conditions). Therefore, we believe that this simple, quick and efficient method is an improvement over other procedures.

The proposed mechanism of Knoevenagel condensation has been illustrated in Scheme 3. Firstly, the deprotonation of mal-

Table 4
Knoevenagel condensation in using $(N_2H_5)_2SiF_6$ catalyst.

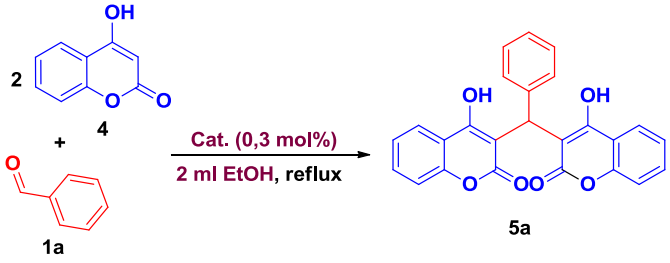
Entry	Product	Ar	X	Time (min)[b]	Yield (%)[a]	M.p(°C)/Lit. m.p (°C) [Refs]
1	**3a**	*p*-ClC_6H_4	CN	30	96	160–162/158–159 [22]
2	**3b**		CO_2Me	30	84	120–121/120–121 [22]
3	**3c**		CO_2Et	30	73	89–90/89–90 [22]
4	**3d**	C_6H_5	CN	30	80	80–81/80–81 [22]
5	**3e**		CO_2Me	60	67	84–85/84–85 [22]
6	**3f**	*p*-MeC_6H_4	CN	30	82	118–119/118–119 [22]
7	**3g**		CO_2Et	60	54	91–92/91–92 [22]
8	**3h**	*p*-$NO_2C_6H_4$	CN	30	98	161–162/160–161 [22]
9	**3i**		CO_2Me	30	87	172–173/172–173 [22]
10	**3j**		CO_2Et	60	83	168–169/168–169 [22]

[a] Isolated yields.
[b] Time reported in min monitored by TLC.

Table 5
Comparison of $(N_2H_5)_2SiF_6$ with other catalysts cited in the literature for the Knoevenagel condensation.

Entry	Catalyst	Conditions	Yield (%)[a]
1	$CaPO_4,2H_2O$	0.01 g, 3 mL EtOH, r.t, 10min	80–96 [22]
2	(MAP,DAP, TSP)	0.01 g, 0.01 g et 0.02 g,3 mL EtOH, r.t, 25–60min	51–97 [23]
3	PMO-IL-NH_2	0.5mol%, solvent free, r.t, 90–180min	88–97 [18]
4	$Na_2Ca(HPO_4)_2$	0.006 g, 3 mL EtOH, t.a, 10–65min	82–99 [24]
5	RhPt@GONPs	0.07 mmol, H_2O:MeOH,(1,2),r.t, 8–35min	85–90 [19]
6	ZrKP-MePh	2mol%, solvent free, r.t, 1h	94–96 [20]
7	Fe_3O_4 MNPs-OSO_3H	10 mg, 3 ml H_2O, reflux, 10–145 min	80–97 [45]
8	Clay A, PC-A	100 mg, 3 ml EtOH/ H_2O, 40 °C, 5–120 min	21–98 [46]
9	[MML-PDO][OAc]	10 mol%, 1 ml H_2O, r.t, 7–600 min	95–99 [47]
10	$(N_2H_5)_2SiF_6$	0.1 mol%, 2 ml EtOH, r.t, 30–60 min	54–98 (Present work)

[a] Isolated yields.



Scheme 4. Model reaction Condensation of benzaldehyde 1a and 4-hydroxycoumarin 4.

Table 6
Studies of the catalytic activity of our catalysts on the synthesis of product 5a.

Entry	Catalyst	Time (min)[b]	Yield (%)[a]
1	–	60	62
2	$(N_2H_5)_2SiF_6$≡ C_0Si	5	90
3	$NH_3(CH_2)_4NH_3SiF_6$≡(C_4Si)	5	73
4	$NH_3(CH_2)_6NH_3SiF_6$≡(C_6Si)	10	65

[a] Isolated yields.
[b] Time reported in min monitored by TLC.

ononitrile by our catalyst. Next, the activation of the aldehyde carbonyl group also the ease of formation of the C-C bond. After, the intermediate (**I**) then undergoes a proton exchange, deprotonation and dehydration, allowing the condensation of the products **3a-j** and regeneration of our catalyst.

3.3. Utilization of hybrid crystal $(N_2H_5)_2SiF_6$ catalyst in the synthesis of biscoumarin derivatives

To study and improve the catalytic activity of our catalysts in the synthesis of biscoumarin derivatives, we chose the condensation of benzaldehyde **1a** and 4-hydroxycoumarins **4** in 2 mL of ethanol at reflux. This reaction is considered as a model reaction (Scheme 4). The obtained results are collated in Table 6. According to the obtained results, we find that in the absence of catalyst, gave a small amount of product in a slow time (Table 6, Entry 1). On the other hand, the same reaction was carried out in the presence of our catalysts (C_0Si, C_4Si, C_6Si) leads to the desired product **5a** with yields of 90 %, 73 % and 65 % respectively (Table 6, Entries 2–4). Then, the suitable catalyst for this reaction was $(N_2H_5)_2SiF_6$ (Table 6, Entry 2). After determining the right catalyst for this reaction, we carried out the model reaction in 2 mL of different solvents such as polar protic solvents (Ethanol, Methanol and Water), polar aprotic solvents (Acetonitrile) and without solvent in the presence of 0.3 mol% of $(N_2H_5)_2SiF_6$ at reflux. The Table 7 showed that the desired product **5a** is obtained with moderate yields when

Table 7
Effect of solvent on the synthesis of product 5a.

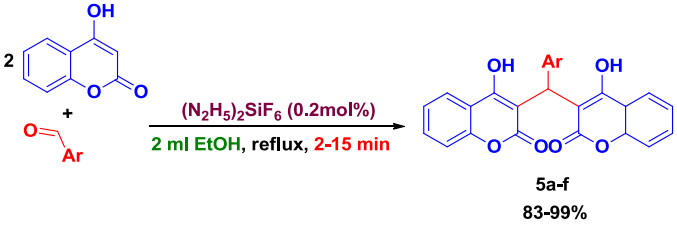
Entry	Solvent (2 ml)	Time (min)[b]	Yield (%)[a]
1	EtOH	5	90
2	MeOH	5	80
3	CH_3CN	6	Trace
4	H_2O	15	60
5	Solvent-free	20	50

[a] Isolated yields.
[b] Time reported in min monitored by TLC.

Table 8
Mass effect on the formation of product 5a.

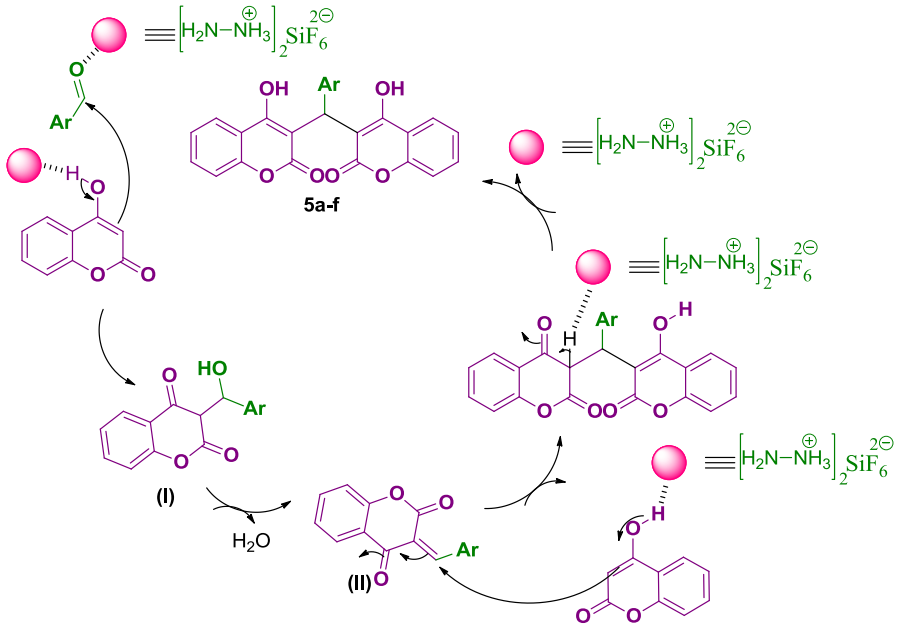
Entry	$(N_2H_5)_2SiF_6$(mol%)	$(N_2H_5)_2SiF_6$(mg)	Time (min)[b]	Yield (%)[a]
1	0.1	0.2	3	84
2	0.2	0.41	3	95
3	0.3	0.63	5	90
4	0.4	0.83	5	88
5	0.5	1.04	5	80
6	0.6	1.24	7	75

[a] Isolated yields.
[b] Time reported in min monitored by TLC.



Scheme 5. Synthesis of the biscoumarin derivatives catalyzed by $(N_2H_5)_2SiF_6$.

the reaction is carried out in polar aprotic solvents (Table 7, Entries 1–2). However, the same transformation carried out in acetonitrile leads to traces of product **5a** (Table 7, Entry 3). Therefore, we find that the optimal solvent for this synthesis is ethanol (Table 7, Entry 1). To predict the ideal mass for this transformation, we studied the evolution of the model reaction yield as a function of the catalyst mass by varying the mass from 0.1 to 0.6 mol%. The reactions are carried out in 2 ml of ethanol at reflux. The present results in Table 8 showed that the quantity of product increased with the increase in the catalysis mass and became maximum for a mass of 0.2 mol% (Table 8, Entries 2–6), beyond this value, considered as a limit, the conversion rate of the reactants decreased. Ultimately, we retained 0.2 mol% of the maximum mass of the catalyst to be used, since this mass corresponds to the optimal yield of the reaction (Table 8, Entry 2). Encouraged by the remarkable results obtained and to justify the catalytic activity of our catalyst, we have studied the generalization of this method by the use of different aromatic aldehydes (Scheme 5). Therefore, a series of substituted



Scheme 6. A plausible Mechanism for the synthesis of biscoumarin derivatives catalyzed by $(N_2H_5)SiF_6$.

Table 9
Synthesis of the biscoumarin derivatives catalyst by $(N_2H_5)_2SiF_6$ below reflux conditions.

Entry	Product	Ar	Time (min)[b]	Yield (%)[a]	M.p (°C)/Lit.m.p (°C) [Refs]
1	5a	C_6H_5	3	95	233–234/228–230 [30]
2	5b	*p*-ClC_6H_4	2	92	258–260/254–256 [30]
3	5c	*p*-MeC_6H_4	8	96	241–244/242–244 [30]
4	5d	*p*-$NO_2C_6H_4$	15	93	238–240/232–234 [30]
5	5e	*p*-$N(Me)_2C_6H_4$	2	99	222–224/216–218 [44]
6	5f	Furfural	5	83	202–204/198–200 [30]

[a] Isolated yields.
[b] Time reported in min monitored by TLC.

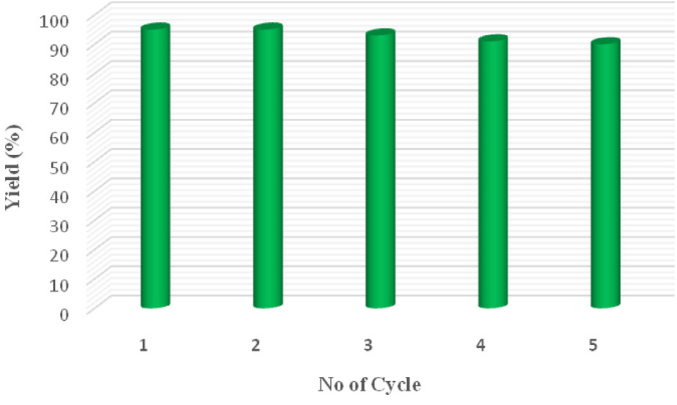


Fig. 4. Recyclability of the catalyst forthe synthesis of 5a.

biscoumarins has been produced with a good to excellent yields and the results are collated in Table 9. After the first reaction, the catalyst was completely recovered, washed with dichloromethane, dried at 70 °C. This catalyst was reused in a new catalytic cycle under the same model reaction conditions. The results are collated in Fig. 4. Analysis of these results, allows us to conclude that our catalyst can be recycled and reused up to 5th time without any significant loss of its catalytic activity. Indeed, the obtained yields

Table 10
Comparison of $(N_2H_5)_2SiF_6$ with other catalyst reported in the literature for the synthesis of biscoumarin derivatives.

Entry	Catalyst	Conditions	Yield (%)[a]
1	MISA	15mol%, H_2O, 80 °C, 12–46min	77–95 [27]
2	P_4VP-CuO	20 mg,5 mL H_2O, reflux, 15–60min	80–93 [28]
3	OBS	50mol%, H_2O:EtOH 2/0.1 mL, reflux, 20–50min	74–91 [29]
4	$Zn(OAc)_2$	0.1 mmol, H_2O, 100 °C, 15–30min	93–98 [30]
5	APVPB	7 mg,sans solvent,70 °C ,10–20 min	86–94 [33]
6	$Zn_3(PO_4)_2{\cdot}4H_2O$	6 mg, 2 ml H_2O, 70 °C, 15–32min	81–84 [35]
7	**$(N_2H_5)_2SiF_6$**	**0.2mol%, 2 mL EtOH, reflux, 2–15 min**	**83–99 (Present work)**

[a] Isolated yields.

from this transformation were quantitative and remain almost unchanged depending on the number of reuse cycles. To show the merit of our work compared to those reported in the literature, we compared the results obtained by the hybrid single crystal with other catalysts in the synthesis of biscoumarin derivatives. From the results of Table 10, it can be seen that among all the examples of the catalysts, we find that our catalytic system was the most efficient from the point of view of short time and high efficiency. Moreover, our catalyst was easy to handle, very available, low cost and nontoxic. The offered mechanism for the formation of biscoumarin derivatives in the presence of $(N_2H_5)_2SiF_6$ as a catalyst is illustrated in Scheme 6. This proposition has already been mentioned in the literature [35,48–50]. Initially, our catalytic support $(N_2H_5)_2SiF_6$ is activated the carbonyl group of substituted aromatic aldehyde which then reacts with 4-hydroxycoumarin to form the intermediate (**I**) by eliminating the molecule from the water obtained, the intermediary (**II**). Subsequently, the catalyst-activated 4-hydroxycoumarin $(N_2H_5)_2SiF_6$ unplanned an addition transformation of the Michael variety vis-à-vis the intermediate (**II**). Finally, the formation of biscoumarin derivatives (**5a-f**).

4. Conclusion

In this work we have developed an efficient, very simple and environmentally friendly protocol for the synthesis of alkenes and

the synthesis of biscoumarin derivatives in the presence of our catalytic support $(N_2H_5)_2SiF_6$ under green conditions. The present method has several advantages such as operational simplicity, easy treatment, reuse of the catalyst repeatedly without significant loss of reactivity as well as the formation of the desired products pure with good to excellent yields and very short reaction times.

Declaration of Competing Interest

The authors of this manuscript report that there are no conflicts of interest relevant to this research work.

Acknowledgments

Authors particularly appreciated the kindness, the availability and the professionalism of the staff of the UTARS-CNRST Center Rabat.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2021.129890.

References

[1] P. Anastas, N. Eghbali, Green chemistry: principles and practice, Chem. Soc. Rev. 39 (1) (2009) 301–312.
[2] R.A. Sheldon, I.W.C.E Arends, U. Hanefeld, GreenChemistry and Catalysis, 2007.
[3] J. Govan, Y.K. Gun'ko, Recent advances in the application of magnetic nanoparticles as a support for homogeneous catalysts, Nanomaterials 4 (2) (2014) 222–241.
[4] Y. Rangraz, F. Nemati, A. Elhampour, Organoselenium–palladium (II) complex immobilized on functionalized magnetic nanoparticles as a promising retrievable nanocatalyst for the "phosphine-free" Heck–Mizoroki coupling reaction, New J. Chem. 42 (18) (2018) 15361–15371.
[5] E. Knoevenagel, Uebereinedarstellungsweise der glutarsäure, Ber. DtschChemGes 27 (2) (1894) 2345–2346.
[6] A. Graul, J. Castaner, Atorvastatin calcium, Drugs Future 22 (1997) 956–968.
[7] L.R. Madivada, R.R. Anumala, G. Gilla, S. Alla, K. Charagondla, M. Kagga, A. Bhattacharya, R. Bandichhor, An improved process for pioglitazone and its pharmaceutically acceptable salt, Org. Process Res. Dev. 13 (6) (2009) 1190–1194.
[8] T.J. Watson, S.W. Horgan, R.S. Shah, R.A. Farr, R.A. Schnettler, C.R. Nevill, R.K. Mishra, B.L. Harrison, P.L. Nyce, C.L. Rand, C.T. Goralski, Chemical development of MDL 103371: An N-methyl-D-aspartate-type glycine receptor antagonist for the treatment of stroke, Org. Process. Res. Dev. 4 (6) (2000) 477–487.
[9] N. Kandaswamy, N. Raveendiran, Synthesis, characterization, in vitro antimicrobial and anticancer evaluation of random copolyesters bearing biscoumarin units in the main chains, Res. Chem. Intermediat. 41 (10) (2015) 7189–7206.
[10] H. Perumalsamy, K. Sankarapandian, K. Veerappan, S. Natarajan, N. Kandaswamy, L. Thangavelu, S.R Balusamy, In silico and In vitro analysis of coumarin derivative induced anticancer effects by undergoing intrinsic pathway mediated apoptosis in human stomach cancer, Phytomedicine 46 (2018) 119–130.
[11] Z.H. Chohan, A.U. Shaikh, A. Rauf, C.T. Supuran, Antibacterial, antifungal and cytotoxic properties of novel N-substituted sulfonamides from 4-hydroxycoumarin, J. Enzyme Inhib. Med. Chem. 21 (6) (2006) 741–748.
[12] I. Manolov, C. Maichle-Moessmer, I. Nicolova, N. Danchev, Synthesis and anticoagulant activities of substituted 2, 4-Diketochromans, biscoumarins, and chromanocoumarins, Arch. Pharm. 339 (6) (2006) 319–326.
[13] C.X. Su, J.F. Mouscadet, C.C. Chiang, H.J. Tsai, L.Y. Hsu, HIV-1 integrase inhibition of biscoumarin analogues, Chem. Pharm. Bull. 54 (5) (2006) 682–686.
[14] I. Kostova, G. Momekov, M. Zaharieva, M. Karaivanova, Cytotoxic activity of new lanthanum (III) complexes of bis-coumarins, Eur. J. Med. Chem. 40 (6) (2005) 542–551.
[15] F. Bigi, L. Chesini, R. Maggi, G. Sartori, Montmorillonite KSF as an inorganic, water stable, and reusable catalyst for the Knoevenagel synthesis of coumarin-3-carboxylic acids, J. Org. Chem. 64 (3) (1999) 1033–1035.
[16] D. Cooke, B. Fitzpatrick, R. O'Kennedy, T. McCormack, D. Egan, in: Coumarins–Multifaceted Molecules with Many Analytical and Other Applications. Coumarins: Biology, Applications and Mode of Action, John Wiley & Sons, Chichester, 1997, pp. 303–332.
[17] M.K. Potdar, S.S. Mohile, M.M. Salunkhe, Coumarin syntheses via Pechmann condensation in Lewis acidic chloroaluminate ionic liquid, *Tetrahedron Lett*, 42 (52) (2001) 9285–9287.
[18] D. Elhamifar, S. Kazempoor, B. Karimi, Amine-functionalized ionic liquid-based mesoporous organosilica as a highly efficient nanocatalyst for the Knoevenagel condensation, Catal. Sci. Technol. 6 (12) (2016) 43184326.
[19] B. Şen, E.H. Akdere, A. Şavk, E. Gültekin, Ö. Paralı, H. Göksu, F. Şen, A novel thiocarbamide functionalized graphene oxide supported bimetallic monodisperse Rh-Pt nanoparticles (RhPt/TC@ GO NPs) for Knoevenagel condensation of aryl aldehydes together with malononitrile, Appl. Catal. B Environ. 225 (2018) 148–153.
[20] O. Rosati, D. Lanari, R. Scavo, D. Persia, F. Marmottini, M. Nocchetti, O. Piermatti, Zirconium potassium phosphate methyl and/or phenyl phosphonates as heterogeneous catalysts for Knoevenagel condensation under solvent free conditions, Micropor. Mesopor. Mat. 268 (2018) 251–259.
[21] P. Kaliyan, S. Matam, S.P. Muthu, Water extract of onion catalyzed Knoevenagel condensation reaction: an efficient green procedure for synthesis of α-cyanoacrylonitriles and α-cyanoacrylates, Asian J. *Green Chem.* 3 (2) (2018) 125–287.
[22] Z. Benzekri, K. El Mejdoubi, S. Boukhris, B. Sallek, B. Lakhrissi, A. Souizi, Dicalcium phosphate dehydrate DCPD as a highly efficient and reusable catalyst for Knoevenagel condensation, Synth. Commun. 46 (5) (2018) 442–451.
[23] I. Bahammou, A. Esaady, S. Boukhris, R. Ghailane, N. Habbadi, A. Hassikou, A. Souizi, Direct use of mineral fertilizers MAP, DAP, and TSP as heterogeneous catalysts in organic reactions, Mediterr.J.Chem. 5 (6) (2016) 615–623.
[24] S. Chehab, Y. Merroun, T. Ghailane, N. Habbadi, S. Boukhris, A. Hassikou, A. Souizi, A new process for $Na_2Ca(HPO_4)_2$ synthesis and its application as a heterogeneous catalyst in Knoevenagel condensation, Mediterr. J. Chem. 7 (1) (2018) 56–67.
[25] A. Samui, N. Kesharwani, C. Haldar, S.K. Sahu, Fabrication of nanoscale covalent porous organic polymer: An efficacious catalyst for Knoevenagel condensation, Microporous Mesoporous Mater. (2020) 110112.
[26] M. Yousefian, Z. Rafiee, Cu-metal-organic framework supported on chitosan for efficient condensation of aromatic aldehydes and malononitrile, Carbohydrpolym 228 (2020) 115393.
[27] N. Iravani, M. Keshavarz, M. Mousavi, M Baghernejad, Melamine trisulfonic acid: An efficient and recyclable solid acid catalyst for the green synthesis of Biscoumarin derivatives, Iran. J. Catal. 5 (1) (2015) 65–71.
[28] F. Shirini, A. Fallah-Shojaei, L. Samavi, M. Abedini, A clean synthesis of bis (indolyl) methane and biscoumarin derivatives using P 4 VPy–CuO nanoparticles as a new, efficient and heterogeneous polymeric catalyst, RSC Adv. 6 (54) (2016) 48469–48478.
[29] B. Maleki, Green synthesis of bis-Coumarin and Dihydropyrano [3, 2-c] chromene derivatives catalyzed by o-Benzenedisulfonimide, Org. Prep. Proced. Int. 48 (3) (2016) 303–318.
[30] V.D. Patil, K.P. Patil, N.R. Sutar, P.V. Gidh, Efficient synthesis of biscoumarins using zinc acetate as a catalyst in aqueous media, Chem. Int. 3 (3) (2017) 240–243.
[31] M. Zarei, M.A. Zolfigol, A.R. Moosavi-Zare, Noroozizadeh, Trityl bromide versus nano-magnetic catalyst in the synthesis of henna-based xanthenes and bis–coumarins, J. Iran. Chem. Soc. 14 (10) (2017) 2187–2198.
[32] A. Zare, Sanjideh, Phthalimide-N-sulfonic acid and Isatin-N-sulfonic acid as highly efficient catalysts for the synthesis of bis-coumarins, J. Iran. Chem. Soc. 6 (2018) 1–12.
[33] E. Noroozizadeh, A.R. Moosavi-Zare, M.A. Zolfigol, M. Zarei, R. Karamian, M. Asadbegy, S.H.M Farida, Synthesis of bis-coumarins over acetic acid functionalized poly (4-vinylpyridinum) bromide (APVPB) as a green and efficient catalyst under solvent-free conditions and their biological activity, J. Iran. Chem. Soc. 15 (2) (2018) 471–481.
[34] B. Zeynizadeh, M. Sadeghbari, N.N. Pesyan, Fabrication and characterization of the immobilized Cu (II) and Ni (II) species on silica-coated copper ferrite: as novel magnetically reusable nanocatalysts toward synthesis of biscoumarins, J. Iran. Chem. Soc. 17 (1) (2020) 73–88.
[35] A.E. Hallaoui, S. Chehab, T. Ghailane, B. Malek, O. Zimou, S. Boukhriss, R. Ghailane, Application of phosphate fertilizer modified by Zinc as a Reusable efficient heterogeneous catalyst for the synthesis of biscoumarins and dihydropyrano [3, 2-c] Chromene-3-carbonitriles under green conditions, Polycycl. Aromat. Compd. (2020) 1–20.
[36] Z. Benzekri, R. Benhdidou, S. Hamia, H. Serrar, S. Boukhris, B. Sallek, A. Hassikou, A. Souizi, A green and simple protocol one-pot Biginelli condensation using dicalcium phosphate as reusable catalyst, J. Mex. Chem. Soc. 61 (3) (2017) 217–221.
[37] Z. Benzekri, H. Serrar, S. Sibous, S. Boukhris, A. Ouasri, A. Rhandour, A. Souizi, Hybrid crystal $NH_3(CH_2)_4NH_3SiF_6$ as an efficient catalyst for the synthesis of benzoxazoles, benzimidazoles and benzothiazoles under solvent-free conditions, Green Chem. Lett. Rev. 9 (4) (2016) 223–228.
[38] Z. Benzekri, S. Sibous, H. Serrar, A. Ouasri, S. Boukhris, A. Rhandour, A. Souizi, $NH_3(CH_2)_5NH_3BiCl_5$: an efficient and recyclable catalyst for the synthesis of benzoxazole, benzimidazole and benzothiazole heterocycles, J. Iran. Chem. Soc. 15 (12) (2018) 2781–2787.
[39] Z. Benzekri, S. Sibous, H. Serrar, S. Boukhris, A. Hassikou, R. Ghailane, A. Souizi, Efficient synthesis of 1, 4-Dihydropyrano [2, 3-c] pyrazoles using snail shell as a biodegradable and reusable catalyst, Org. Prep. ProcedInt. 51 (6) (2019) 566–575.
[40] Z. Benzekri, S. Sibous, H. Serrar, A. Ouasri, S. Boukhris, R. Ghailane, A. Rhandour, A. Souizi, $NH_3(CH_2)_5NH_3BiCl_5$as a new hybrid and efficient catalyst for the synthesis of 1-(benzothiazolylamino) methyl-2-naphthol derivatives under solvent-free conditions, J. Mol. Struct. 1202 (2020) 127308.
[41] H. El Aadad, Z. Benzekri, S. Boukhris, A. Chahine, Synthesis, characterization of polystyrene-phosphate films and their application as heterogeneous catalyst for Knoevenagel condensation in solvent-free conditions, J. Chem. Sci. 132 (1) (2020) 1–13.

[42] Z. Benzekri, H. El Aadad, S. Sibous, H. Serrar, S. Boukhris, A. Chahine, A. Souizi, Improvement of the catalytic performance of hybrid nanocomposite based on phosphate-benzimidazole in Knoevenagel condensation, Heliyon 6 (11) (2020) e05293.
[43] A. Ouasri, F. Lambarki, A. Rhandour, M. Saadi, L. El Ammari, Crystal structure and Hirshfeld surface analysis of bis [hydrazinium (1+)] hexafluoridosilicate:$(N_2H_5)_2SiF_6$, Acta Cryst. 75 (10) (2019) 1507–1510.
[44] M. Faisal, F.A. Larik, A. Saeed, A highly promising approach for the one-pot synthesis of biscoumarins using HY zeolite as recyclable and green catalyst, J. Porous. Mat. (2018) 1–12, doi:10.1007/s10934-018-0625-0.
[45] L. Shiri, S. Zarei, M. Kazemi, D. Sheikh, Sulfuric acid heterogenized on magnetic Fe_3O_4 nanoparticles: A new and efficient magnetically reusable catalyst for condensation reactions, Appl. Organomet. Chem. 32 (2018) e3938.
[46] H. Ouaddari, D. Beqqour, J. Bennazha, I.E. El Amrani, A. Albizane, A. Solhy, R.S. Varma, Natural Moroccan clays: Comparative study of their application as recyclable catalysts in Knoevenagel condensation, Sustain. Chem. Pharm. 10 (2018) 1–8.
[47] H. Xu, L. Pan, X. Fang, B. Liu, W. Zhang, M. Lu, T.Ding Y.Xu, H. Chang, Knoevenagel condensation catalyzed by novel Nmm-based ionic liquids in water, Tetrahedron Lett. 58 (2017) (2017) 2360–2365.
[48] J. Albadi, A. Mansournezhad, S. Salehnasab, Green synthesis of biscoumarin derivatives catalyzed by recyclable $CuO–CeO_2$ nanocomposite catalyst in water, Res. Chem. Intermediat. 41 (8) (2015) 5713–5721.
[49] R. Teimuri-Mofrad, S. Tahmasebi, E. Payami, Fe_3O_4@ SiO_2@ Im-bisethylFc $[HC_2O_4]$ as a novel recyclable heterogeneous nanocatalyst for synthesis of bis–coumarin derivatives, Appl. Organomet. Chem. 33 (6) (2019) e4773.
[50] B. Akhlaghinia, P. Sanati, A. Mohammadinezhad, Z. Zarei, The magnetic nanostructured natural hydroxyapatite (HAP/Fe_3O_4NPs): an efficient, green and recyclable nanocatalyst for the synthesis of biscoumarin derivatives under solvent-free conditions, Res. Chem. Intermediat. 45 (5) (2019) 3215–3235.