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Introduction of taurine (2-aminoethanesulfonic acid) as a green bio-organic catalyst for the promotion of organic reactions under green conditions†

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Taurine (2-aminoethanesulfonic acid), a semi-essential amino acid that exists in the human body and numerous other living creatures, is used as a green bio-organic catalyst for the promotion of the Knoevenagel reaction between aldehydes and malononitrile. In the same way, tetraketones can also be produced through a Knoevenagel reaction, followed by Michael addition. 2-Amino-3-cyano-4*H*-pyran derivatives are simply prepared *via* a three-component reaction in the presence of taurine as the catalyst. All these reactions are performed in water, a green solvent. The advantages of using of taurine as the catalyst are it is environmentally friendly, low cost, commercially available, easy to separate from the reaction mixture, and has high reusability. Use of this catalyst results in acceptable reaction times, high yields and high purities of the obtained products without utilizing any organic solvents.

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Introduction

The progress of science has been more and more towards environmentally compatible, or "green" processes, with particular focus on catalysts and other materials in organic chemistry. One aspect of these topics is the application of an alternative reaction medium that is free from the problems associated with the numerous traditional volatile solvents. Using this type of media may also increase the chance of separation and reuse of the catalyst. From the viewpoint of green chemistry, it is better to perform the reactions under solvent-free conditions, but when solvent is necessary, water is the best choice.[1] In addition to environmental concerns, chemists prefer to use water as a solvent due to its economic benefits and generally easy separation and work-up conditions. Furthermore, all biological reactions are known to occur in aqueous media. Moreover, numerous organic reactions proceed faster and better in water than in organic solvents.[2]

2-Aminoethane sulfonic acid, or taurine (Fig. 1), is an amino acid that is found in high concentration in the tissues of animals. It is one of the constituent members of bile, which can be found in the large intestine and its amount in the average is one-tenth percent of the total weight of the human body.[3] Taurine appellation refers to its first isolation from ox bile, named *Bos taurus*.[4] The concentration of taurine in mammalian organs is higher in comparison with the other types of the animals; its concentration in insects and arthropods is less than that in mammals, whereas in plants and bacteria, its concentration is negligible.[5] Red algae, although not the brown or green ones, contain high levels of taurine and its *N*-(1-carboxylated) derivatives, but lichens, mushrooms, mosses, and ferns have very low concentrations of this amino acid.[6]

In comparison with other homologue amino acids, taurine is structurally different. It is a β-amino acid with a sulfonic acid group instead of a carboxylic acid group. This difference increases its acidity, *i.e.*, in the range of mineral acids (pK_a = 1.5), compared to carboxylic acid homologues, and unlike those homologues that are not dissociated at biological pH, taurine is in a zwitterionic state at this pH level, which leads to distinct biological properties.[7] According to computational investigations, the neutral conformation of taurine exists in the gas phase, whereas its zwitterionic form exists in water media, which is in agreement with the experimental NMR analysis.[8]

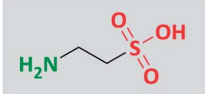

Fig. 1 Taurine.

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Taurine has been used for many years as an ingredient in energy drinks and nutrient supplements and has many biological properties such as osmoregulation, immunomodulation and bile salt formation.[9]

Very recently, silica gel supported taurine was used in the oxidation of sulfides to their corresponding disulfides.[10] Moreover, to the best of our knowledge, there are no other reports of the catalytic activity of this β-amino acid for organic transformations.

In recent decades, performance of standard chemical reactions in aqueous media has been often considered, with particular focus on carbon–carbon bond forming transformations.[11] Several reactions that have been investigated in this capacity are Diels–Alder, Claisen and Aldol condensations, and radical additions.[12]

The Knoevenagel reaction, *i.e.*, treatment of an aldehyde with an active methylene group reported by Emil Knoevenagel in 1894, is one of the most important and notable reactions for C=C bond formation.[13] This reaction is suitable for the preparation of alkenes with electron-withdrawing groups and its products can be used as intermediates for many other types of reactions.[14]

Many conditions have been used to promote the Knoevenagel reaction between aldehydes and malononitrile, including grinding, high pressure, microwaves, and ultrasonics.[15] Different types of catalysts have also been utilized; among the most important are cetyltrimethylammonium bromide (CTMAB),[16] $ReBr(CO)_5$,[17] 1,1,3,3-tetramethylguanidium lactate,[18] $[C_4dabco][BF_4]$,[19] amine-functionalized polyacrylonitrile fiber,[20] Fe_3O_4 MNPs–guanidine,[21] sulfonated carbon/silica composites,[22] MP(DNP),[23] Na_2S/Al_2O_3,[24] silica–L-proline,[25] ZnO,[26] $Ni_xMg_{1-x}Fe_2O_4$,[27] sodium carbonate,[28] hydroxyapatite supported caesium carbonate,[29] *Tamarindus indica* juice,[30] L-proline–IL,[31] and SiO_2–NH_4OAc.[32]

Arylmethylene[bis(3-hydroxy-2-cyclohexene-1-ones)] (tetraketones) firstly were introduced by Merling through the addition of aldehydes with 1,3-diketones *via* a Knoevenagel reaction followed by a Michael addition.[33] These compounds have been extensively used as intermediates for some other important target compounds such as acrilidine diones, thiaxanthenes and xanthene diones.[34] Tetraketones have biological activity as antioxidants, lipoxygenases and tyrosinase inhibitors.[35] Because of the important properties of these products, several methods have been used to achieve them using various catalysts such as $SnCl_2$/HCl,[36] $In(OTf)_3$,[37] $SmCl_3$,[38] $Yb(OTf)_3$–SiO_2 with aniline,[39] Fe_3O_4@SiO_2–SO_3H,[40] PVP-stabilized Ni nanoparticles,[41] choline chloride-based deep eutectic,[42] nano Fe/NaY zeolite,[43] EDDA,[44] and Al/MCM-41.[45]

4*H*-Pyran and its derivatives have attracted much interests because of their important biological activities, such as anticoagulant, spasmolytic, diuretic, anticancer, antianaphylactin,[46] antiallergenic,[47] antiproliferative,[48] antitumor,[49] antibacterial,[50] cytotoxic,[51] mutagenic[52] and sex pheromonal[53] activities. These compounds also are present in the structure of some photoactive materials[54] and natural products[55] and can be used in the synthesis of cosmetics and pigments.[56]

A large number of catalysts were introduced for the synthesis of 2-amino-3-cyano-4*H*-pyran derivatives under various conditions; notable among them are hexadecyldimethyl benzyl ammonium bromide,[57] 1-butyl-3-methyl imidazolium hydroxide,[58] 2,2,2-trifluoroethanol,[59] $Ba(OTf)_2$,[60] tetrabutylammonium chloride,[61] triazine functionalized ordered mesoporous organosilica,[62] tungstic acid functionalized mesoporous SBA-15,[63] *p*-dodecylbenzenesulfonic acid,[64] potassium phthalimide,[65] red sea sand,[66] choline hydroxide,[67] IRMOF-3($Zn_4O(H_2N\text{-}TA)_3$),[68] β-cyclodextrins–glycerine,[69] tris-hydroxymethylaminomethane,[70] squaramide,[71] $Ce(SO_4)_2\cdot 4H_2O$,[72] poly(vinylpyrrolidonium)hydrogen phosphate,[73] L-proline,[74] I_2,[75] and glutamic acid.[76]

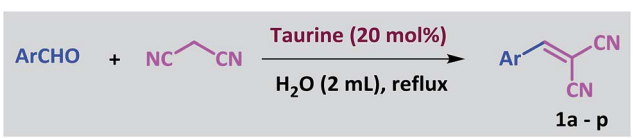
Experimental

All the chemicals for this study were purchased from Merck, Aldrich, and Fluka Chemical Companies and used without further purification. All the products were separated and characterized by their physical properties in comparison with the reported standards. Both the purity determination of the substrates and reaction monitoring were accomplished by thin layer chromatography (TLC) using SIL G/UV 254 silica gel plates. Melting points were determined using a Buchi B-545 apparatus. FT-IR spectra were obtained by a Perkin-Elmer spectrum BX series spectrophotometer (KBr disks). The ^{1}H NMR and ^{13}C NMR spectra were acquired by a Bruker Avance 400 MHz instrument using deuterated solvents.

Table 1 Optimization of the conditions for the Knoevenagel reaction [1g][a]

Entry	Catalyst (mol%)	Solvent	Temp.	Time (min)	Yield[b] (%)
1	—	—	90 °C	90	Trace[c]
2	24	—	90 °C	90	Trace[c]
3	24	$CHCl_3$	Reflux	90	Trace[c]
4	12	EtOH	Reflux	90	Trace[c]
5	24	EtOH	Reflux	90	Trace[c]
6	24	CH_3CN	Reflux	90	Trace[c]
7	12	H_2O	RT	90	Trace[c]
8	24	H_2O	RT	90	87
9	16	H_2O	Reflux	13	91
10	20	H_2O	Reflux	7	98
11	24	H_2O	Reflux	6	95
12	24	H_2O/EtOH (3 : 1)	Reflux	20	86

[a] Reaction conditions: 4-chlorobenzaldehyde (1.0 mmol), malononitrile (1.1 mmol), solvent (2 mL) and required amount of catalyst. [b] The yields are related to the isolated products. [c] The reaction was not completed.



Scheme 1 The Knoevenagel reaction between aldehydes and malononitrile.

Table 2 The Knoevenagel reaction of aldehydes and malononitrile in the presence of taurine as the catalyst in water medium

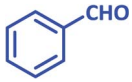
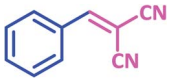
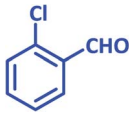
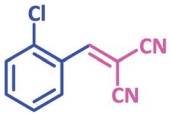
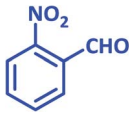
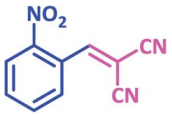
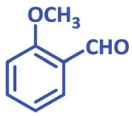
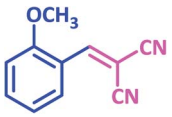
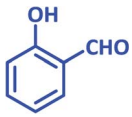
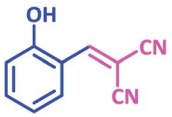
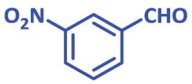
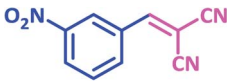
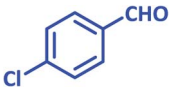
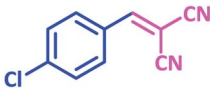
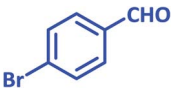
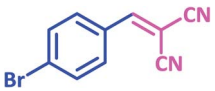
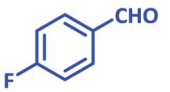
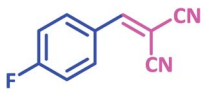
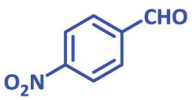
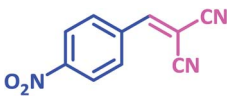
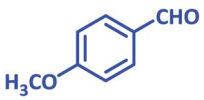
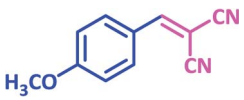
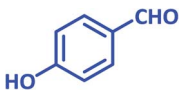
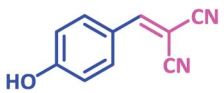
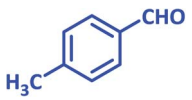
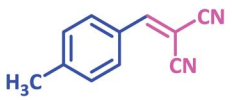
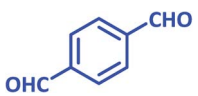
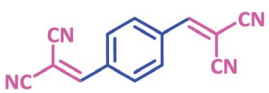
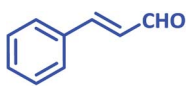
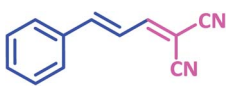
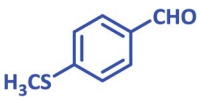
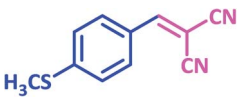
Entry	Aldehyde	Product	Symbol	Time (min)	Yield[a] (%)	Mp (°C) (Obs.)	Mp (°C) (Lit.)
1			**1a**	14	86	82–83	82–84 (ref. 16)
2			**1b**	11	94	92–93	93–94 (ref. 27)
3			**1c**	9	96	138–140	139–140 (ref. 21)
4			**1d**	18	90	81–82	80 (ref. 24)
5			**1e**	15	87	99–101	98–99 (ref. 29)
6			**1f**	10	93	103–105	103–105 (ref. 27)
7			**1g**	7	98	161–163	161–162 (ref. 27)
8			**1h**	9	96	156–158	159–160 (ref. 21)
9			**1i**	12	92	122–124	122–124 (ref. 28)
10			**1j**	15	94	161–163	157–160 (ref. 22)
11			**1k**	20	89	115–117	112–114 (ref. 22)
12			**1l**	14	91	186–188	185–187 (ref. 27)
13			**1m**	10	93	136–137	137–138 (ref. 24)
14			**1n**	8	94	295–297	298–300 (ref. 30)
15			**1o**	10	86	125–127	124–126 (ref. 22)

Table 2 (*Contd.*)

Entry	Aldehyde	Product	Symbol	Time (min)	Yield[a] (%)	Mp (°C) (Obs.)	Mp (°C) (Lit.)
16			**1p**	6	97	155–157	New product

[a] The yields are related to the isolated products.

General procedure for the Knoevenagel condensation of aldehydes and malononitrile

In a 25 mL round-bottomed flask, a mixture of aldehyde (1.0 mmol), malononitrile (1.1 mmol) and taurine (0.025 g, 20 mol%) in water (2 mL) was heated at a reflux temperature for the appropriate time. After the conversion, which was monitored by TLC, 10 mL of water was added and stirred for 3 minutes. During this time, the product was precipitated and subsequently separated by filtration. The separated product was washed several times with water. After drying, the pure product was obtained; there was no need for further purification and addition of organic solvent was not necessary. Furthermore, water was evaporated from the filtrate to re-obtain the taurine catalyst.

General procedure for the synthesis of tetraketones

In a 25 mL round-bottomed flask, a mixture of aldehyde (1.0 mmol), 1,3-cyclodicarbonyl compound (2.0 mmol) and taurine (0.030 g, 24 mol%) in water (2 mL) was heated at reflux for the

Table 3 Optimization of the conditions for the synthesis of tetraketones [2g][a]

Entry	Catalyst (mol%)	Solvent	Temp.	Time (min)	Yield[b] (%)
1	—	—	90 °C	120	Trace[c]
2	24	—	60–90 °C	120	Mixture[c]
3	24	$CHCl_3$	Reflux	120	Trace[c]
4	12	EtOH	Reflux	120	Trace[c]
5	24	EtOH	Reflux	120	30[c]
6	24	CH_3CN	Reflux	120	Trace[c]
7	12	H_2O	RT	120	20[c]
8	24	H_2O	RT	120	35[c]
9	16	H_2O	Reflux	33	91
10	24	H_2O	Reflux	20	96
11	28	H_2O	Reflux	17	92
12	20	H_2O/EtOH (3 : 1)	Reflux	30	83

[a] Reaction conditions: 4-chlorobenzaldehyde (1.0 mmol), dimedone (2.0 mmol), solvent (2 mL) and required amount of the catalyst. [b] The yields are related to the isolated products. [c] The reaction was not completed.

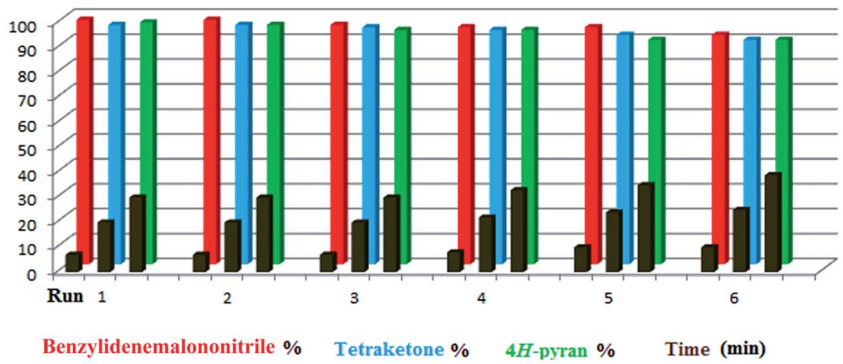
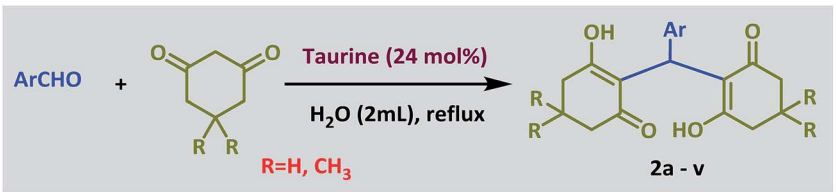


Fig. 2 Reusability of taurine in the model reactions.



Scheme 2 Synthesis of tetraketones.

Table 4 Synthesis of tetraketones in the presence of taurine catalyst in water

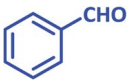
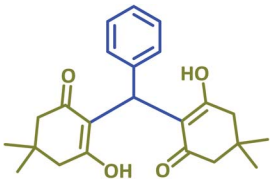
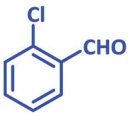
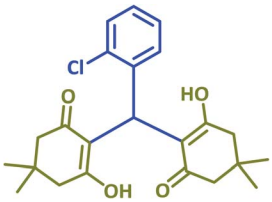
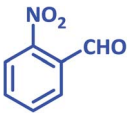
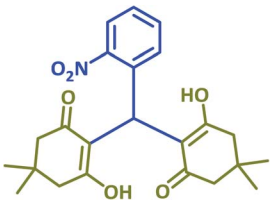
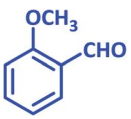
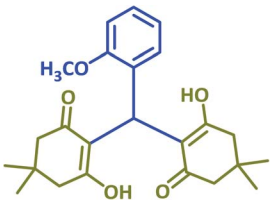
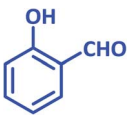
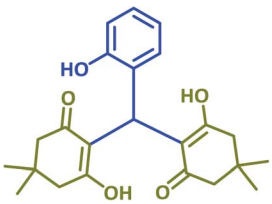
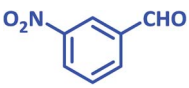
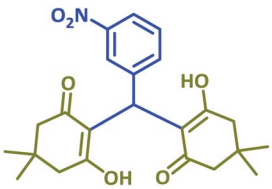
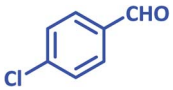
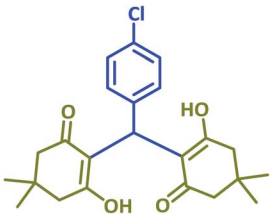
Entry	Aldehyde	Product	Symbol	Time (min)	Yield[a] (%)	Mp (°C) (Obs.)	Mp (°C) (Lit.)
1			**2a**	10	95	181–183	185 (ref. 42)
2			**2b**	15	93	194–196	199–200 (ref. 43)
3			**2c**	10	92	242–243	244–246 (ref. 38)
4			**2d**	25	87	181–183	184–186 (ref. 43)
5			**2e**	20	91	209–211	208–209 (ref. 40)
6			**2f**	25	94	195–197	197–199 (ref. 40)
7			**2g**	20	97	139–141	138–141 (ref. 42)

Table 4 (*Contd.*)

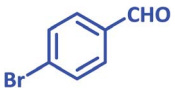
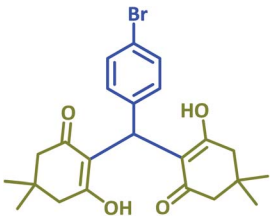
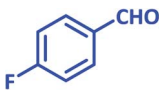
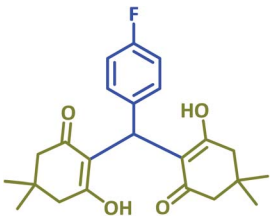
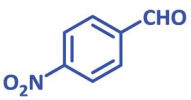
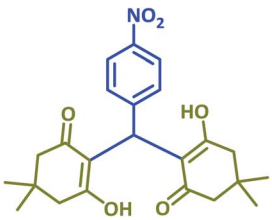
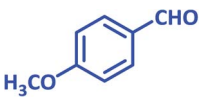
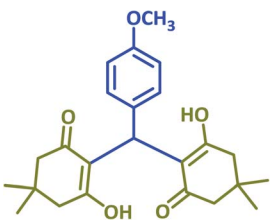
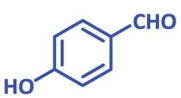
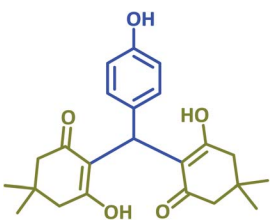
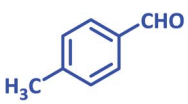
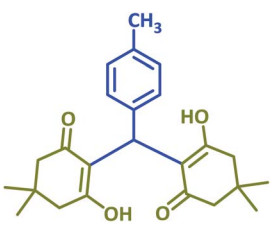
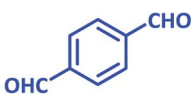
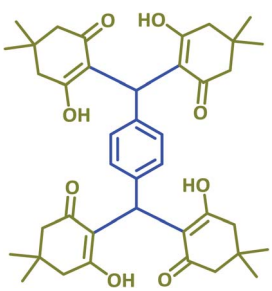
Entry	Aldehyde	Product	Symbol	Time (min)	Yield[a] (%)	Mp (°C) (Obs.)	Mp (°C) (Lit.)
8			**2h**	15	96	159–161	154–156 (ref. 43)
9			**2i**	15	90	183–185	184–186 (ref. 43)
10			**2j**	45	91	185–187	188–190 (ref. 43)
11			**2k**	15	90	142–144	146–148 (ref. 38)
12			**2l**	20	95	182–183	180 (ref. 40)
13			**2m**	25	85	133–135	132 (ref. 41)
14			**2n**	25	85	220–221	225 (ref. 42)

Table 4 (*Contd.*)

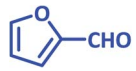
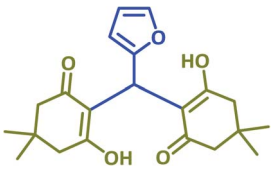
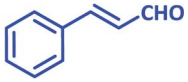
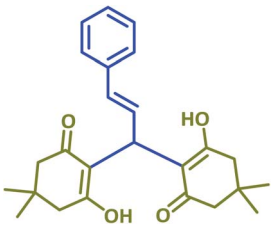
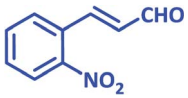
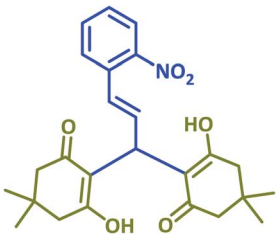
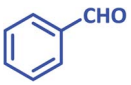
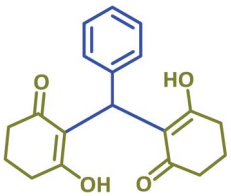
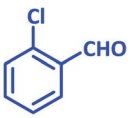
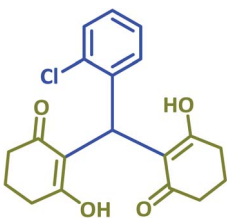
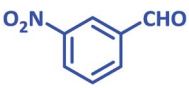
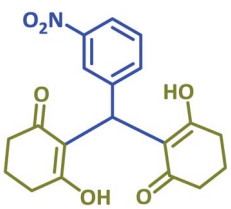
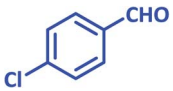
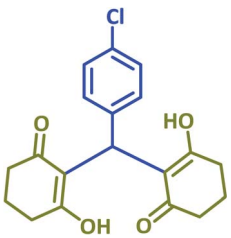
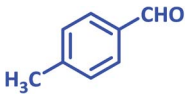
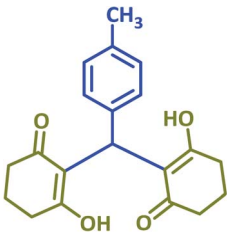
Entry	Aldehyde	Product	Symbol	Time (min)	Yield[a] (%)	Mp (°C) (Obs.)	Mp (°C) (Lit.)
15			**2o**	15	92	151–153	146 (ref. 41)
16			**2p**	30	92	215–218	213–215 (ref. 38)
17			**2q**	45	93	174–176	New product
18			**2r**	15	89	219–220	214–216 (ref. 43)
19			**2s**	20	93	203–205	199–200 (ref. 42)
20			**2t**	30	96	207–209	209–211 (ref. 36)
21			**2u**	25	91	199–200	201–203 (ref. 43)

Table 4 (*Contd.*)

Entry	Aldehyde	Product	Symbol	Time (min)	Yield[a] (%)	Mp (°C) (Obs.)	Mp (°C) (Lit.)
22			**2v**	30	90	189–191	190–191 (ref. 39)

[a] The yields are related to the isolated products.

appropriate time. After completion of the reaction, which was monitored by TLC, 10 mL of water was added and stirred for 3 minutes. During this time, the product was precipitated and subsequently separated by filtration. The separated product was washed several times with water. After drying, the pure product was obtained; there was no need for further purification and addition of organic solvent was not necessary. Furthermore, water was evaporated from the filtrate to re-obtain the taurine catalyst.

Table 5 Optimization of the conditions for the synthesis of 2-amino-3-cyano-4*H*-pyran derivatives [**3i**][a]

Entry	Catalyst (mol%)	Solvent	Temp.	Time (min)	Yield[b] (%)
1	—	—	90 °C	120	Trace[c]
2	24	—	60–90 °C	120	Trace[c]
3	24	$CHCl_3$	Reflux	120	Trace[c]
4	12	EtOH	Reflux	120	Trace[c]
5	24	EtOH	Reflux	120	Trace[c]
6	24	CH_3CN	Reflux	120	Trace[c]
7	12	H_2O	RT	115	90
8	24	H_2O	RT	90	91
9	16	H_2O	Reflux	65	90
10	28	H_2O	Reflux	30	97
11	32	H_2O	Reflux	26	94
12	28	H_2O/EtOH (3 : 1)	Reflux	45	88

[a] Reaction conditions: 4-chlorobenzaldehyde (1.0 mmol), malononitrile (1.1 mmol) and dimedone (1.0 mmol), solvent (2 mL) and required amount of the catalyst. [b] The yields are related to the isolated products. [c] The reaction was not completed.

General procedure for the synthesis of 2-amino-4*H*-chromenes

In a 25 mL round-bottomed flask, a mixture of aldehyde (1.0 mmol), 1,3-cyclodicarbonyl compound (1.0 mmol), malononitrile, (1.1 mmol) and taurine (0.030 g, 28 mol%) in water (2 mL) was heated at reflux for the appropriate time. After the reaction was competed, which was monitored by TLC, 10 mL of water was added and stirred for 3 minutes. During this time, the product was precipitated and subsequently separated by filtration. The separated product was washed several times with water. After drying, the pure product was obtained; there was no need for further purification and addition of organic solvent was not necessary. Furthermore, water was evaporated from the filtrate to re-obtain the taurine catalyst.

Spectroscopic data of the new compounds

2-(4-(Methylthio)benzylidene)malononitrile (1p). IR (KBr, cm^{-1}): 3040, 2217, 1648, 1564, 1094; ^1H NMR (400 MHz, DMSO-d_6): $\delta = 2.58$ (s, 3H), 7.48 (d, $J = 8.4$ Hz, 2H), 7.89 (d, $J = 8.4$ Hz, 2H), 8.42 (s, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): $\delta = 14.30$, 79.10, 114.14, 115.10, 125.87, 127.75, 131.41, 148.92, 160.86 ppm.

2,2′-(3-(2-Nitrophenyl)prop-2-ene-1,1-diyl)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) (2q). IR (KBr, cm^{-1}): 3445, 3070, 2960, 2868, 1600, 1590, 1519, 1380. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.10$ (s, 6H), 1.17 (s, 6H), 2.30–244 (m, 8H), 4.98 (m, 1H), 6.39 (dd, $J = 16.0$, 4.0 Hz, 1H), 6.89 (dd, $J = 16.0$, 2.4 Hz, 1H), 7.35 (dt, $J = 8.0$, 1.6 Hz, 1H), 7.56 (dt, $J = 8.0$, 1.2 Hz, 1H), 7.94 (dd, $J =$

Scheme 3 Synthesis of 2-amino-3-cyano-4*H*-pyran derivatives.

Table 6 Synthesis of 2-amino-3-cyano-4*H*-pyran derivatives in the presence of taurine as the catalyst in water

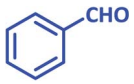
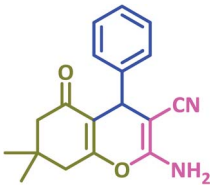
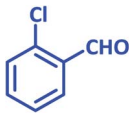
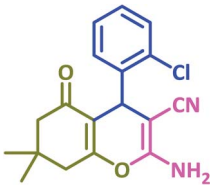
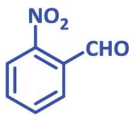
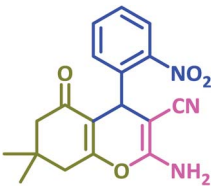
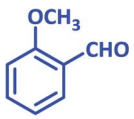
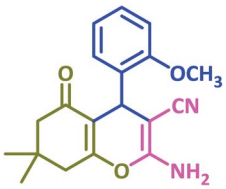
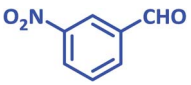
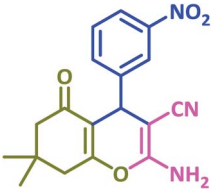
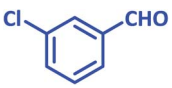
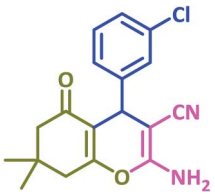
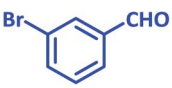
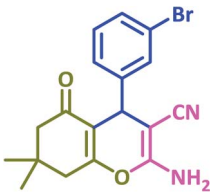
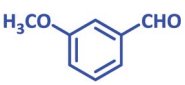
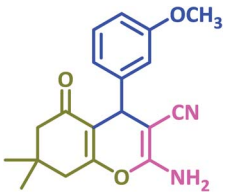
Entry	Aldehyde	Product	Symbol	Time (min)	Yield[a] (%)	Mp (°C) (Obs.)	Mp (°C) (Lit.)
1			**3a**	65	82	231–233	232–234 (ref. 73)
2			**3b**	25	92	209–211	211–213 (ref. 73)
3			**3c**	15	94	222–225	228 (ref. 69)
4			**3d**	70	81	204–206	196–199 (ref. 73)
5			**3e**	45	98	211–213	211–213 (ref. 72)
6			**3f**	30	96	224–226	228–230 (ref. 72)
7			**3g**	25	93	287–289	289–291 (ref. 72)
8			**3h**	35	92	190–192	188–190 (ref. 72)

Table 6 (*Contd.*)

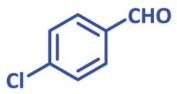
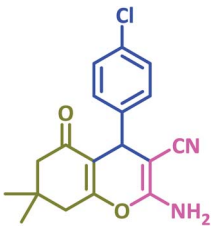
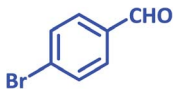
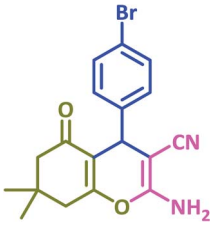
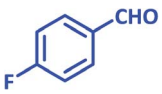
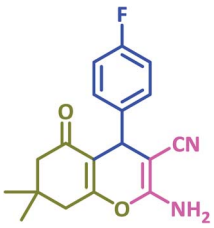
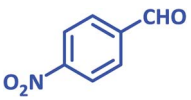
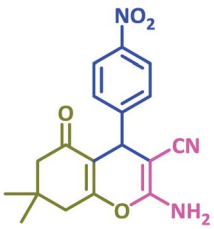
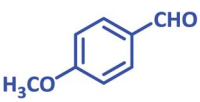
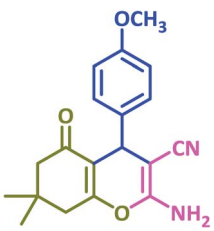
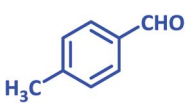
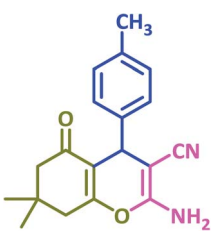
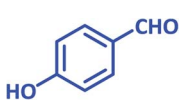
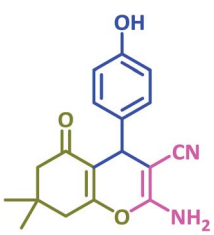
Entry	Aldehyde	Product	Symbol	Time (min)	Yield[a] (%)	Mp (°C) (Obs.)	Mp (°C) (Lit.)
9			**3i**	30	97	208–210	208–210 (ref. 73)
10			**3j**	30	95	203–205	201–203 (ref. 73)
11			**3k**	25	97	210–212	214–215 (ref. 73)
12			**3l**	30	96	180–182	181–183 (ref. 73)
13			**3m**	65	91	193–195	196–198 (ref. 70)
14			**3n**	45	87	217–219	217–219 (ref. 70)
15			**3o**	50	94	220–222	222–224 (ref. 70)

Table 6 (*Contd.*)

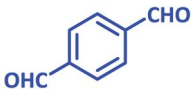
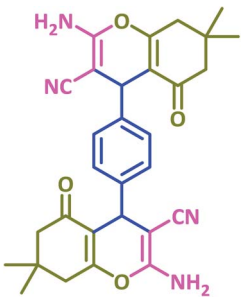
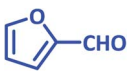
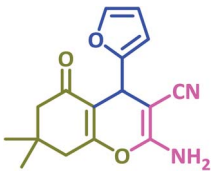
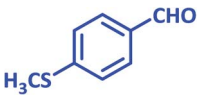
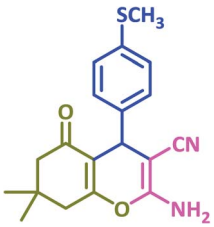
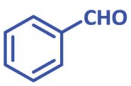
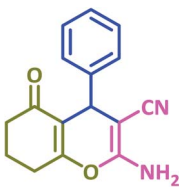
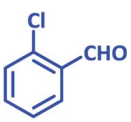
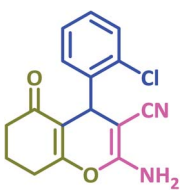
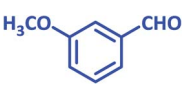
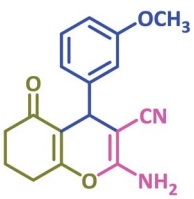
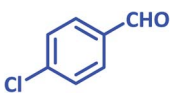
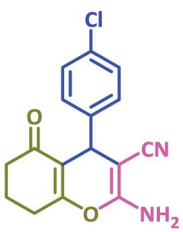
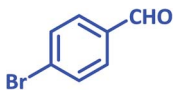
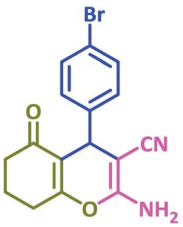
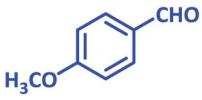
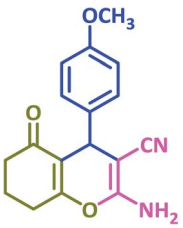
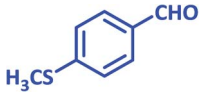
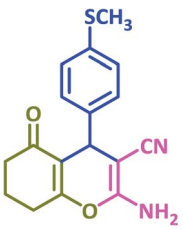
Entry	Aldehyde	Product	Symbol	Time (min)	Yield[a] (%)	Mp (°C) (Obs.)	Mp (°C) (Lit.)
16			**3p**	35	93	266–269	270–275 (ref. 77)
17			**3q**	30	90	223–226	223–225 (ref. 73)
18			**3r**	60	89	211–212	208–209 (ref. 58)
19			**3s**	50	93	212–214	212–213 (ref. 79)
20			**3t**	20	91	209–210	210–212 (ref. 57)
21			**3u**	50	94	202–204	202–204 (ref. 57)
22			**3v**	40	93	221–223	224–226 (ref. 57)

Table 6 (*Contd.*)

Entry	Aldehyde	Product	Symbol	Time (min)	Yield[a] (%)	Mp (°C) (Obs.)	Mp (°C) (Lit.)
23			**3w**	35	98	237–240	234–235 (ref. 63)
24			**3x**	45	85	202–204	206–208 (ref. 63)
25			**3y**	50	92	217–219	New product

[a] The yields are related to the isolated products.

8.0, 1.2 Hz, 1H), 11.27 (br, 1H), 12.12 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.86, 29.73, 31.42, 31.44, 46.20, 46.83, 115.96, 124.53, 125.37, 127.72, 128.80, 133.12, 133.16, 134.64, 147.34, 189.43, 190.05 ppm.

2-Amino-4-(4-(methylthio)phenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (3y). IR (KBr, cm^{-1}): 3318, 3171, 2961, 2913, 2194, 1682, 1647, 1364; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.92–2.00 (m, 2H), 2.24–2.34 (m, 2H), 2.35 (s, 1H), 2.61–2.63 (m, 2H), 4.16 (s, 1H), 7.08 (s, 2H), 7.02 (d, J = 8.4 Hz, 2H), 7.10 (d, J = 8.4 Hz, 2H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 15.29, 20.29, 26.95, 35.46, 36.81, 58.50, 114.17, 120.23, 126.53, 128.31, 136.53, 142.09, 158.88, 158.92, 164.87, 196.35 ppm.

Results and discussion

In recent years, introduction of sulfonic acid based catalysts for the promotion of organic transformations has been an important part of our ongoing research program.[77,78] In continuation of these studies, we were interested in investigating the applicability of taurine, a natural, green and commercially available amino acid containing a sulfonic acid group, in the acceleration of organic reactions. The Knoevenagel reaction was selected as the model reaction. In the optimization study, the reaction was initially carried out in the absence of solvent and catalyst and only a little product was obtained. This result was achieved again even when the catalyst was used under solvent-free conditions. Then, the reaction was tested in chloroform, acetonitrile and ethanol with no significant change in the progress of the reaction. In continue the reaction was studied in water as the solvent. The progress of the reaction at room temperature in water was slow, and became even slower as it proceeded; however, the rate was greatly increased at reflux, so the decision was made to pursue these conditions instead. At the end of this study, the optimal amount of catalyst was determined by systematically altering the amount of taurine (Table 1). The Knoevenagel reaction was then performed with various aromatic aldehydes and malononitrile using the optimized amount of the catalyst (20 mol%, 24 mg) in water and under reflux conditions (Scheme 1). As shown in Table 2, various types of aldehydes containing electron-donating and electron-withdrawing groups were successfully converted to the corresponding nitrile products. No distinct substitution effect was observed for this reaction. The isolated products were extremely pure without the need for any costly purification steps, which can be expensive in terms of time, materials and overall yield.

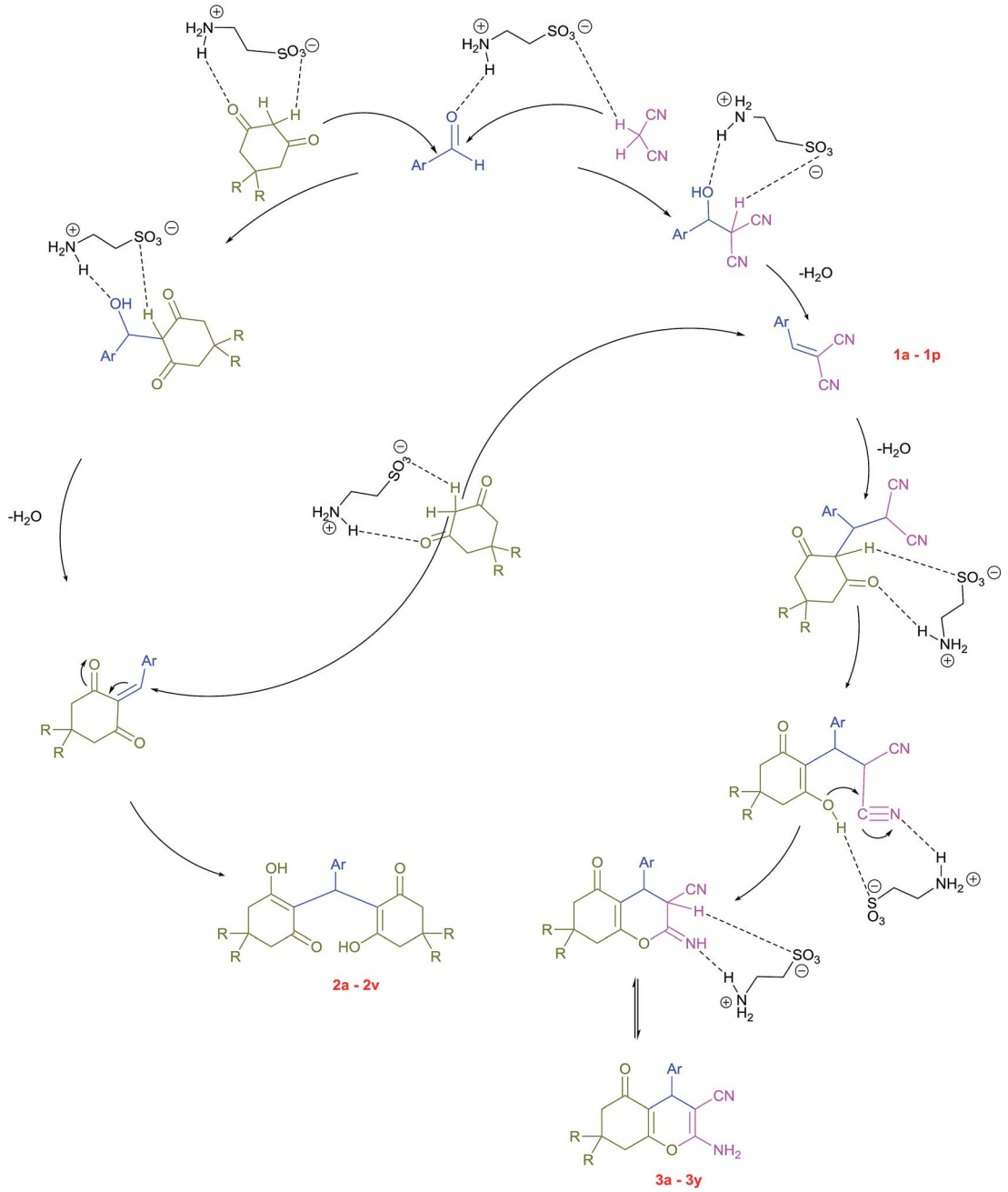
Since taurine is soluble in water, it was easily separated from the products by simple filtration. The filtered solution could be

reused in the same reaction without significant loss of catalytic activity. This procedure was repeated six times for the model reaction; each time, the cycle was completed with no significant change in reaction time or yield. During the recycling studies, the product was separated and its melting point was verified after every run to ensure that the purity remained excellent (Fig. 2). It should be mentioned that since the purity of most of the derivatives was too high, we preferred not to use any organic solvent at all; thus, the melting points in this work are related to the non-recrystallized products.

Next, the efficiency of taurine for promoting the synthesis of tetraketone derivatives was investigated *via* the Knoevenagel reaction, followed by Michael addition of an aldehyde with two equivalents of dimedone or 1,3-cyclohexanedione (Scheme 2).

It should be mentioned that taurine is only suitable to catalyze formation of open chain xanthenes in water and any effort to achieve closed chain xanthenes as single products using this catalyst was not successful.

Only a small amount of product was formed in the absence of a catalyst and solvent at the first step of the optimization of the conditions. When the catalyst was used under solvent-free conditions, a mixture of the products was achieved at different temperatures. As shown in Table 3, the reaction was tested in different solvents and conditions to determine the



Scheme 4 The plausible mechanisms of the studied reactions in the presence of taurine.

optimum conditions (entry 10). Furthermore, various aldehydes were used to prepare diverse tetraketone structures. The aldehydes selected for this purpose produced generally high yields of the desired products with acceptable reaction times and do not require further purification (Table 4). Just like the previous reaction, reusability of the catalyst was studied by selecting a typical reaction and using the catalyst-containing filtrate solution in a new reaction mixture. The process showed good reusability over 6 cycles (Fig. 2).

Ultimately, a one-pot, three-component reaction system was designed containing an aldehyde, either dimedone or 1,3-cyclohexanedione, and malonitrile, to test the ability of taurine to catalyze the formation of 2-amino-3-cyano-4*H*-pyran derivatives.

Optimization of the conditions was performed using a typical reaction of 4-chlorobenzaldehyde, dimedome and malononitrile under a variety of conditions and in the presence of different amounts of taurine as the catalyst. As shown in Table 5, the best results were obtained in refluxing water using 35 mg (28 mol%) catalyst (entry 10).

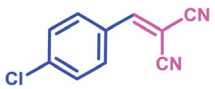
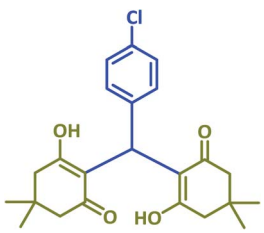
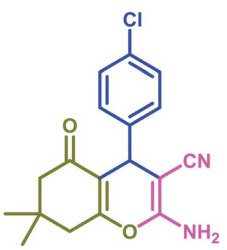
After optimization of the reaction conditions (Scheme 3), different types of aldehydes containing electron-donating and electron-withdrawing groups were subjected to the same reaction. The results showed that all types of aldehydes performed well to give the corresponding products in good to excellent yields.

1,3-Cyclohexanedione was also used in some reactions in place of dimedone and the desired products were obtained (Table 6, entries 20–26). The purity of the isolated products was again such that there was no need for further purification or even recrystallization of the products.

As we have mentioned previously, the reusability of the catalyst was investigated in the model reactions for all three transformations studied (products were **1g**, **2g** and **3i**). In each case, six consecutive runs showed excellent reusability (Fig. 2).

Plausible mechanisms for the abovementioned reactions as catalyzed by taurine are shown in Scheme 4. Taurine acts as a bifunctional donor–acceptor reagent in which the aldehyde carbonyl site is activated by taurine and then attacked by the negatively activated methylene group in malononitrile. Elimination of water in the Knoevenagel reaction results in arylidene malononitriles that can be separated by filtration (compounds **1a–1p**). Moreover, it is believed that the taurine-activated aldehyde can be attacked by a taurine-enolized β-dicarbonyl. Then, after losing water and forming an arylidene dicarbonyl in the Knoevenagel reaction, this species can react with another enolized β-dicarbonyl, leading to a tetraketone (products **2a–2v**). For the three component system, the Knoevenagel product

Table 7 Comparison between existing literature reports and some of the taurine-catalyzed reactions in the current work

Product	Catalyst	Amount	Conditions	Time (min)	Yield (%)
	SiO_2–L-proline[25]	10 mol% (0.100 g)	CH_3CN/80 °C	540	95
	L-Proline–IL[31]	30 mol%	80 °C	1440	96
	MNPs–guanidine[21]	0.39 mol% (0.005 g)	H_2O–PEG/RT	150	96
	SiO_2–NH_4OAc[32]	0.200 g	CH_2Cl_2/reflux	450	90
	HAP–Cs_2CO_3 (ref. 29)	0.200 g	H_2O/80 °C	180	86
	CTMAB[16]	0.50 mmol	H_2O/RT	90	94
	ZnO[26]	0.500 g	H_2O/RT	90	86
	Na_2S/Al_2O_3 (ref. 24)	20 mol% on 0.500 g	CH_2Cl_2/reflux	30	90
	Taurine[a]	**20 mol% (0.025 g)**	**H_2O/reflux**	**7**	**98**
	$SmCl_3$ (ref. 38)	20 mol%	120 °C	20	95
	EDDA[44]	30 mol%	THF/reflux	240	97
	Fe_3O_4@SiO_2–SO_3H[40]	0.010 g	H_2O/RT	80	83
	Al/MCM-41 (ref. 45)	0.100 g	EtOH/reflux	120	88
	ChCl : urea[42]	1 mL	80 °C	120	86
	Fe/NaY[43]	0.025 g	EtOH/reflux	70	98
	Taurine[a]	**24 mol% (0.030 g)**	**H_2O/reflux**	**20**	**97**
	β-Cyclodextrin[69]	0.227 g	Aq glyserin/40 °C	30	90
	IRMOF–Zn complex[68]	4 mol%	60 °C	300	90
	[Ch][OH][67]	10 mol%	H_2O/80 °C	60	86
	Red sea sand[66]	0.500 g	EtOH/reflux	280	85
	Glutamic acid[74]	20 mol%	EtOH/reflux	40	91
	DBSA[64]	20 mol%	H_2O/reflux	240–420	69
	TFE[62]	2 mL	Reflux	300	95
	I_2 (ref. 75)	10 mol%	DMSO/120 °C	210	88
	L-Proline[76]	10 mol%	EtOH/reflux	120	72
	HDMBAB[57]	2.4 mol%	H_2O/80–90 °C	450	90
	TBAC[61]	10 mol%	H_2O/reflux	120	98
	Taurine[a]	**28 mol% (0.035 g)**	**H_2O/reflux**	**30**	**97**

[a] Current work.

is again formed, followed by Michael addition with a β-dicarbonyl. Lastly, enolization occurs, followed by amine–enamine tautomerization in the presence of taurine to produce the 4*H*-pyran derivative (products **3a–3y**).

The results of this study were compared with some existing literature reports in order to better illustrate the utility of taurine in accelerating the reactions under study (Table 7). In each case, the taurine-catalyzed reaction had an advantage wherein it utilized a green catalyst and a nontoxic solvent, featured easy separation of product and catalyst, offered catalyst reusability, and resulted in lower reaction times and higher yields.

Conclusions

The general advantages of taurine as a catalyst in the studied reactions are as follows: it is non-toxic for humans and other living organisms, it offers ease of separation of products and catalyst, it does not require use of organic solvents, it features excellent catalyst recyclability and reusability, it is highly stable and easy to store, and finally, it is commercially available at a low price. All of these points are in full compliance with the requirements of green chemistry.

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