J. Chem. Sci. Vol. 124, No. 5, September 2012, pp. 1097–1105.

A practical one pot synthesis of novel 2-hydroxy-4-chromanone derivatives from 3-formylchromone

ZEBA N SIDDIQUI* and FARHEEN FAROOQ
Department of Chemistry, Aligarh Muslim University, Aligarh 202 002, India
e-mail: siddiqui_zeba@yahoo.co.in

MS received 30 August 2011; revised 19 March 2012; accepted 19 April 2012

Abstract. A one pot synthesis of 4-chromanone derivatives (**5a–j**) is described using Zn[(L)(proline)]$_2$ as catalyst in aqueous media. The compounds have been characterized on the basis of elemental and spectral data (IR, ^{1}H NMR and mass). The advantages of this protocol include high yields, mild reaction conditions, environmentally benign and simple operational procedure. The use of water as solvent and Zn[(L)proline]$_2$ as recyclable, non-toxic catalyst make such synthesis a truly green process.

Keywords. 3-Formylchromone; Zn[(L)proline]$_2$; 4-chromanone; water; green synthesis.

1. Introduction

Chromone moiety forms an important component of pharmacophores of a number of biologically active molecules of synthetic as well as natural origin.[1] Chromone and their derivatives are found in nature as pigments in plant leaves and flowers. They are important for the synthesis of various oxygen heterocycles including xanthones and transition metal chelates.[2] They are widely present in nature and exhibit low toxicity along with a wide variety of useful properties.[3] They are reported to exhibit significant biological activities including antiinflammatory,[4] antiallergic,[5] antibacterial,[6] neuroprotective,[7] anti HIV,[8] antioxidant,[9] antifungal,[10] etc. They also display spasmolytic, cardiotonic, antiarrhythmic[11] and anticancer properties.[12]

3-Formylchromone (4-oxo-4H-1-benzopyran-3-carboxaldehyde) has been frequently used for the synthesis of various heterocyclic derivatives ever since its convenient synthesis was reported by Nohara *et al.*[13] Derivatives of 3-formyl chromone are useful synthetic building blocks in both organic and medicinal chemistry.[14] 3-Formylchromone has been chosen for the present study due to the reason that it carries three electron deficient centres viz. α,β-unsaturated keto function, a carbonyl group in the form of formyl group at position 3 and a very reactive electrophilic centre at C-2. In the present paper, the products (chromanones) of reaction of 3-formylchromone with primary aromatic/heteroaromatic amines under green reaction conditions have been investigated. It is pertinent to mention that chromanones represent an important group of compounds which display a remarkable domain of biochemical and pharmacological actions. They have been examined for antioxidant,[15] antibacterial,[16] antimalarial,[17] anticancer,[18] antifungal,[19] topoisomerase I inhibitor,[20] psychoanaleptic, antiamoebic and antidepressant properties.[21] Some chromanone derivatives have been evaluated for *in vitro* antiviral activities against human immunodeficiency virus (HIV) and Simian immunodeficiency virus (SIV).[22,23] They have also been claimed to be active in photosynthesis[24] and have hereditary bleaching effect (similar to antibiotics) on the plastid system of *Euglena gracilis.*[25] Other 4-chromanone derivatives have also been found useful in the treatment of bronchial asthma.[21]

As a result, for the synthesis of 4-chromanone derivatives different methods have been developed.[26,27] These methods have certain drawbacks such as prolonged reaction time, use of toxic and volatile organic solvents and varied yields. The replacement of these hazardous solvents with the environmentally benign solvents is one of the key areas of green chemistry.[28] Among various green solvents, water is the most popular as it is inexpensive, thermally stable, recoverable, biologically compatible, and non-toxic. In recent years, water-mediated organic synthesis has become one of the most important aspects in organic chemistry in order to meet the environmental demands.[29] This strategy becomes one of the most powerful green chemical technologies if such reactions could be carried out using homogeneous or

*For correspondence

heterogeneous recyclable Lewis acid catalyst. Lewis acids have been found to catalyse conjugate addition reactions effectively under mild reaction conditions avoiding undesirable side reaction products. Therefore, in spite of the reported methods for this transformation, there is a need to develop more efficient, simple and milder protocol which can fulfill both these requirements. For the coordination of Zn, proline is a suitable amino acid, as its secondary amino group and carboxylate function being ideally suited for Zn^{2+} in low coordination number and makes Zn complex, a moderately soft Lewis acid. Zn[(L)proline]$_2$ has attracted much attention in the recent years in various organic transformations (Aldol,[30] nitroaldol,[31] Hantzsch reaction,[32] Knoevenagel condensation,[33] etc.) due to its inherent properties like reusability, greater selectivity, operational simplicity, non-corrosiveness, inexpensive, and ease of isolation. In continuation of our efforts in developing selective, efficient, mild and ecofriendly synthetic methodologies for the preparation of biologically relevant heterocyclic derivatives[34–36] here, we describe a simple and convenient method for the synthesis of 4-chromanone derivatives (**5a–j**) by the reaction of 3-formylchromone **1** with different primary aromatic and heteroaromatic amines (**2a–j**) using Zn[(L)proline]$_2$ complex as a water-tolerant Lewis acid catalyst in water. To the best of our knowledge, the synthesis of 4-chromanone derivatives using Zn[(L)proline]$_2$ in aqueous media has not been reported so far.

2. Experimental

2.1 *Material and methods*

Melting points were taken in Reichert Thermover instrument and are uncorrected. The IR spectra were recorded on FT-IR spectrometer in KBr, ^{1}H-NMR spectra on a Bruker DRX-300 using tetra methyl silane (TMS) as an internal standard. Chemical shifts are reported in ppm downfield from TMS, coupling constants J are given in Hz. Mass spectra were obtained on a DART-MS recorded on a JEOL-Accu TOF JMS-T100LC mass spectrometer having a *DART* source. The micro analytical data were collected on Elementar vario EL III elemental analyzer. 3-Formylchromone[13] and Zn[(L)proline]$_2$[44] were synthesized by reported procedures. Other chemicals were of commercial grade and used without further purification. The purity of all compounds was checked on silica gel (E-Merck G_{254}) plates using iodine vapours as visualizing agents.

2.2 *General procedure for the synthesis of 2-hydroxychromanones* (**5a–j**)

A mixture of 3-formylchromone **1** (1.00 mmol), amines **2a–j** (1.00 mmol), Zn [(L)proline]$_2$ (10 mol%) and water (10 ml) was refluxed in a heating mantle at reflux temperature for an appropriate time (table 1). After completion of reaction, as monitored by TLC, reaction mixture was cooled to room temperature. The crude product was extracted with dichloromethane, washed with water, dried over anhydrous sodium sulphate and concentrated to furnish (**5a–j**). The pure compounds were obtained by recrystallization from methanol–chloroform mixture (8:2). The catalyst was recovered by simple separation of aqueous and organic phases. The catalyst present in the aqueous layer was recovered by precipitating the aqueous layer by the addition of acetone and used for the subsequent cycle.

2.3 *Spectral data of the products*

2.3a *3-(Pyridylaminomethylene)-2-hydroxy-chroman-4-one* (**5a**): Light yellow solid; m.p. 121–124°C; IR (KBr): 3355, 3280, 1650, 1376 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.53 (s, 1H, OH), 5.71 (s, 1H, H-2), 6.84–7.66 (m, 7H, ArH), 7.99 (d, J = 7.8 Hz, 1H, C-5), 8.33 (d, J = 11.4 Hz, H-9), 12.09 (d, J = 11.4 Hz, 1H, NH, D_2O exchangeable); MS (ESI-MS): m/z 268.15 (M^+). Anal. Calcd. for $C_{15}H_{12}N_2O_3$: C 67.22 H 4.51 N 10.45. Found: C 67.02 H 4.28 N 10.66.

2.3b *3-(Benzothiazolylaminomethylene)-2-hydroxy-chroman-4-ones* (**5b**): Light yellow solid; m.p. 142–145°C; IR (KBr): 3209, 3078, 1648, 1373 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.53 (s, 1H, OH), 5.72 (s, 1H, H-2), 7.05 (d, J = 11.4 Hz, 1H, H-9), 7.10–7.99 (m, 7H, ArH), 8.06 (d, J = 7.8 Hz, C-5), 12.31 (d, J = 11.4 Hz, 1H, NH, D_2O exchangeable); MS (ESI-MS): m/z 324.15 (M^+). Anal. Calcd. for $C_{17}H_{12}N_2O_3S$: C 63.02 H 3.73 N 8.64. Found: C 62.80 H 3.95 N 8.41.

2.3c *3-(p-Tolylaminomethylene)-2-hydroxy-chroman-4-one* (**5c**): Light yellow solid; m.p. 150–155°C; IR (KBr): 3320, 3200, 1653, 1365 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.51(s, 3H, CH_3), 3.18 (s, 1H, OH), 5.91 (s, 1H, H-2), 6.80–7.73 (m, 7H, ArH), 7.89 (d, J = 7.8 Hz, C-5), 8.33 (d, J = 12.3 Hz, 1H, H-9), 12.19 (d, J = 12.3 Hz, 1H, NH, D_2O exchangeable); MS (ESI-MS): m/z 281.14 (M^+). Anal. Calcd. for $C_{17}H_{15}NO_3$: C 72.66 H 5.380 N 4.98. Found: C 72.89 H 5.61 N 4.72.

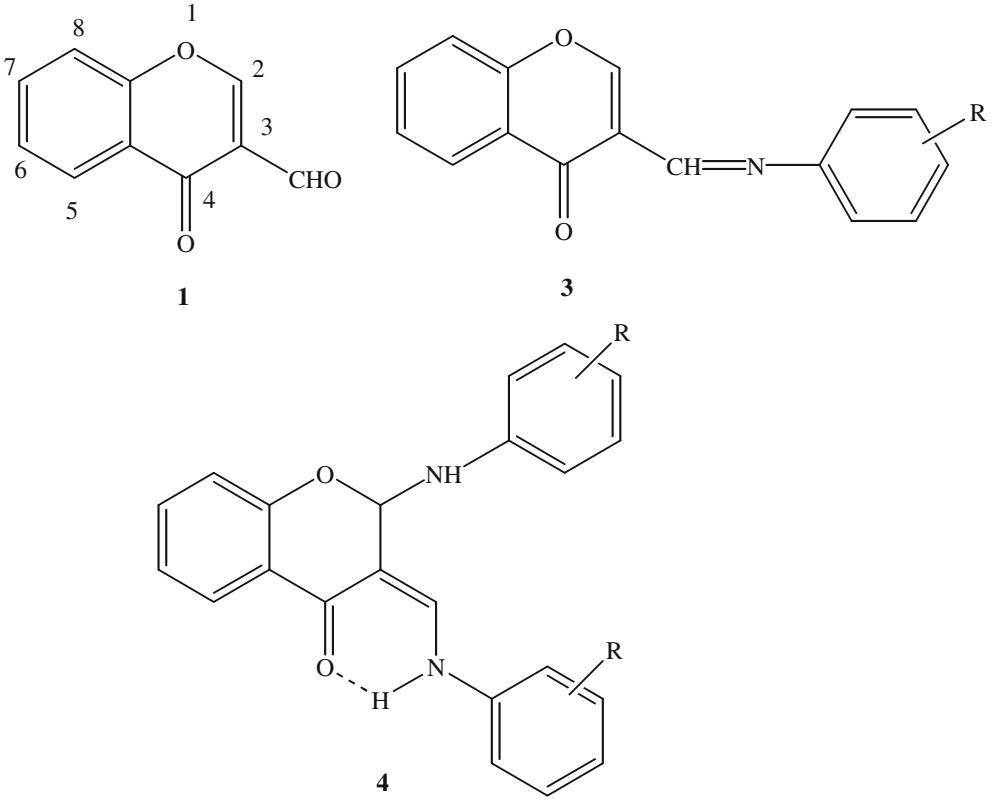
2.3d *3-(p-Methoxyphenylaminomethylene)-2-hydroxychroman-4-one* **(5d)**: Yellow crystals; m.p. 120–123°C; IR (KBr): 3376, 3078, 1672, 1378 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$,): δ 3.64 (s, 3H, OCH_3), 6.51 (s, 1H, OH), 6.57 (s, 1H, H-2), 7.09–8.34 (m, 7H, ArH), 7.91 (d, J = 10.5 Hz, 1H, H-9), 8.41 (d, J = 7.8 Hz, C-5), 12.28 (d, J = 10.50 Hz, 1H, NH, D_2O exchangeable); MS (ESI-MS): m/z 297.14 (M^+). Anal. Calcd. for $C_{17}H_{15}NO_4$: C 68.74 H 5.09 N 4.71. Found: C 68.50 H 4.85 N 4.90.

2.3e *3-(p-Nitrophenylaminomethylene)-2-hydroxychroman-4-one* **(5e)**: Light yellow crystals; m.p. 170–173°C; IR (KBr): 3184, 1656, 1369 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$,): δ 5.81 (s, 1H, OH), 6.16 (s, 1H, H-2), 6.64 (d, J = 12.0 Hz, 1H, H-9), 6.92–8.27 (m, 7 H, ArH), 8.32 (d, J = 8.1 Hz, C-5), 12.21 (d, J = 11.7 Hz, 1H, NH, D_2O exchangeable); MS (ESI-MS): m/z 312.13 (M^+). Anal. Calcd. for $C_{16}H_{12}N_2O_5$: C 61.54 H 3.87 N 8.97. Found: C 61.34 H 4.10 N 9.20.

2.3f *3-(m-Nitrophenylaminomethylene)-2-hydroxychroman-4-one* **(5f)**: Yellow solid; m.p. 168–172°C; IR (KBr): 3410, 3263, 1665, 1343 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.80 (s, 1H, OH), 6.17 (s, 1H, H-2), 6.97 (d, J = 13.5 Hz, 1H, H-9), 7.00–8.36 (m, 7 H, ArH), 8.89 (d, J = 9.6 Hz, C-5); MS (ESI-MS): m/z 312.15 (M^+). Anal. Calcd. for $C_{16}H_{12}N_2O_5$: C 85.70 H 6.55 N 8.27. Found: C 85.24 H 6.56 N 8.15.

2.3g *3-(α-Naphthylaminomethylene)-2-hydroxychroman-4-one* **(5g)**: Yellow solid; m.p. 150–153°C; IR (KBr): 3245, 3099, 1678, 1337 cm^{-1}; ^1H NMR (300 MHz $CDCl_3$): δ 3.55 (s, 1H, OH), 6.52 (s, 1H, H-2), 7.10–8.35 (m, 10 H, ArH), 7.93 (d, J = 10.8 Hz, 1H, H-9), 8.41 (d, J = 8.1 Hz, C-5), 13.75 (d, J = 11.1 H, NH, D_2O exchangeable); MS (ESI-MS): m/z 317.06 (M^+). Anal. Calcd. for $C_{20}H_{15}NO_3$: C 75.77 H 4.73 N 4.41. Found: C 75.98 H 4.93 N 4.62.

2.3h *3-(p-Hydroxyphenylaminomethylene)-2-hydroxychroman-4-one* **(5h)**: Yellow solid; m.p. 160–162°C; IR (KBr): 3340, 3220, 3284, 1645, 1362 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 5.57 (s, 1H, OH), 6.66–7.76 (m, 7H, ArH), 6.58 (s, 1H, H-2), 8.39 (d, J = 8.1 Hz, C-5), 8.84 (d, J = 12.9 Hz, 1H, H-9), 11.52(s, 1H, OH), 12.84 (d, J = 12.9, 1H, NH, D_2O exchangeable); MS (ESI-MS): m/z 283.11 (M^+). Anal. Calcd. for $C_{16}H_{13}NO_4$: C 67.92 H 4.63 N 4.94. Found: C 68.11 H 4.83 N 4.68.



Scheme 1. Structure of **1, 3**, and **4**.

Table 1. Zn [(L)proline]$_2$ catalysed reaction of 3-formylchromone (1mmol) with amines (1mmol) in water.

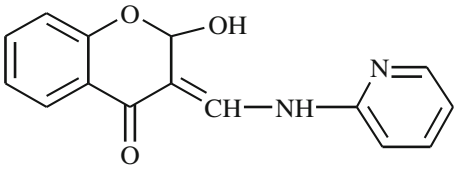
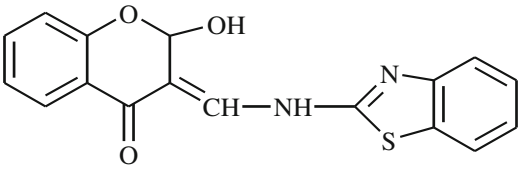
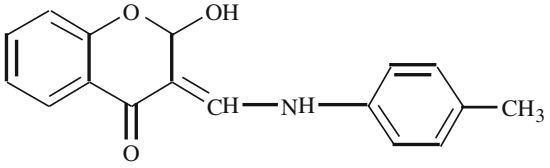
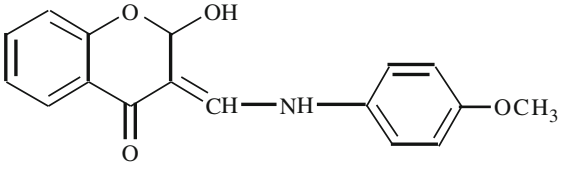
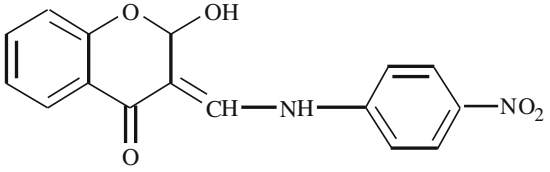
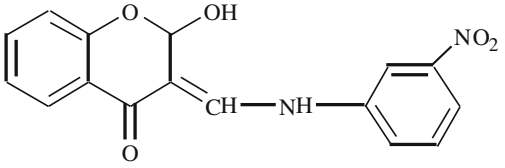
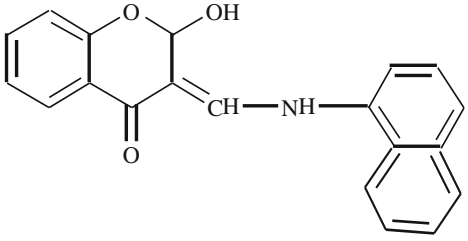
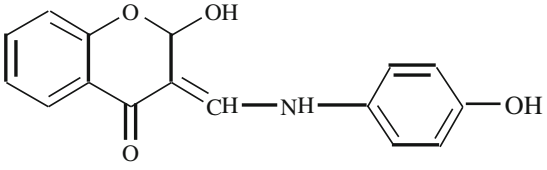
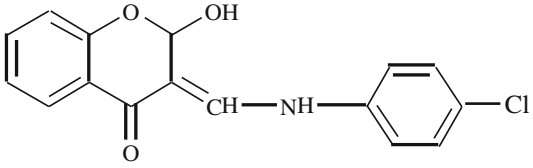
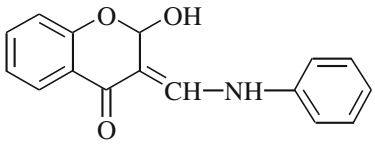
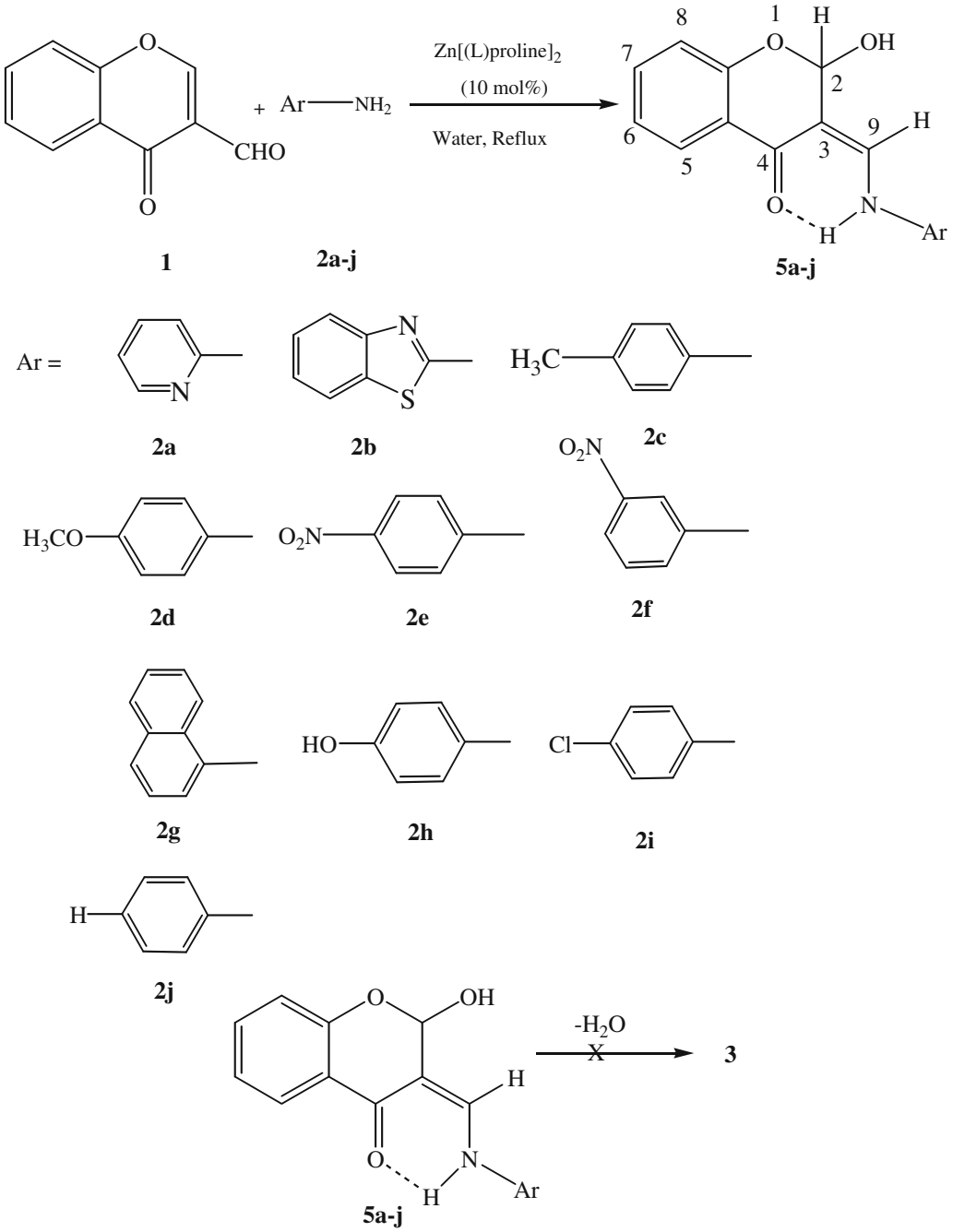
Entry	Reactant	Product	Time[a] (min)	Yield[b] (%)
1	**2a**		10	93
2	**2b**		10	92
3	**2c**		12	89
4	**2d**		15	89
5	**2e**		10	90
6	**2f**		15	88
7	**2g**		10	90
8	**2h**		12	87
9	**2i**		15	87

Table 1. *continued.*

Entry	Reactant	Product	Time[a] (min)	Yield[b] (%)
10	**2j**		12	92

[a]Reaction progress monitored by TLC. [b]Isolated yield



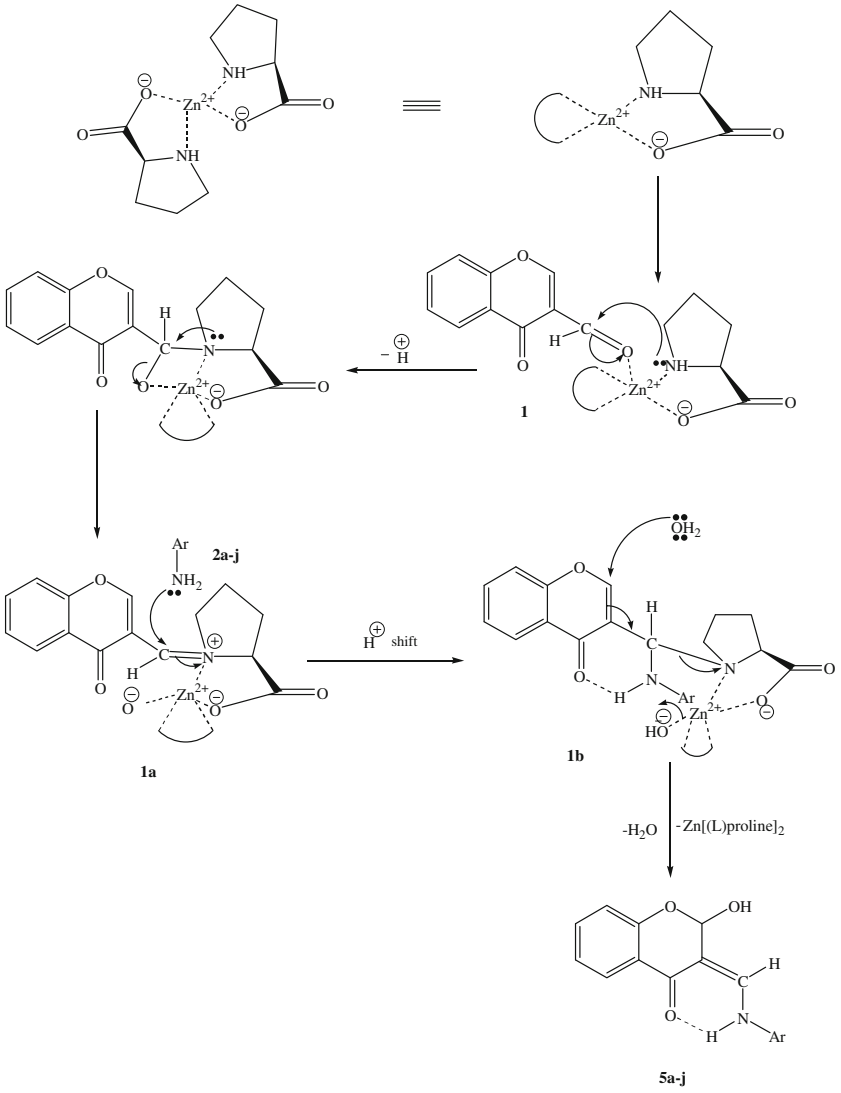
Scheme 2. Zn [(L)proline]$_2$ catalysed synthesis of 4-chromanone derivatives **(5a–j)**.

2.3i *3-(p-Chlorophenylaminomethylene)-2-hydroxy-chroman-4-one* **(5i)**: Light yellow solid; m.p. 142–145°C; IR (KBr): 3441, 3267, 1669, 1380 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$,): δ 4.99 (s, 1H, OH), 5.27 (s, 1H, H-2), 7.19–8.12 (m, 7H, ArH), 8.06 (d, J = 13.8 Hz, 1H, H-9), 8.17 (d, J = 8.1 Hz, C-5), 10.33 (d, J = 13.8, 1H, NH, D_2O exchangeable); MS (ESI-MS): m/z 301.12 (M^+). Anal. Calcd. for $C_{16}H_{12}NO_3Cl$: C 63.73 H 3.98 N 4.64. Found: C 63.50 H 4.19 N 4.38.

2.3j *3-(Phenylaminomethylene)-2-hydroxy-chroman-4-one* **(5j)**: Yellow solid; m.p. 135–138°C; IR (KBr): 3184, 1653, 1317 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.92 (s, 1H, OH), 5.65 (s, 1H, H-2), 6.84–7.66 (m, 7H, ArH), 7.89 (d, J = 7.8 Hz, C-5), 8.34 (d, J = 10.8 Hz, 1H, H-9), 11.59 (d, J = 10.5 Hz, 1H, NH, D_2O exchangeable); MS (ESI-MS): m/z 267.10 (M^+). Anal. Calcd. for $C_{16}H_{13}NO_3$: C 71.97 H 4.90 N 5.04. Found C 71.75 H 5.13 N 5.04.

3. Results and discussion

Chromones usually undergo ring opening reactions via nucleophilic attack at the C-2 position.[37] The reaction between equimolar quantities of **1** and aromatic amines (**2a–j**) affords a mixture of **3** and **4** which are difficult to separate[38] (scheme 1). The Schiff base **3,** however, has been obtained when a mixture of **1** and aromatic amines is refluxed for two to several hours in organic solvents (benzene/toluene,[39,40] ethanol[41] in the presence of *p*-toluene-sulphonic acid (PTS) in varied yield (low to good)). In order to achieve the synthesis of (**3**) under green environment, a mixture of (**1**) and different aromatic/heteroaromatic amines (**2a–j**) was refluxed in



Scheme 3. Proposed mechanism for the Zn[(L)proline]$_2$ complex catalysed synthesis of chromanone derivatives (**5a–j**).

water in the presence of Zn[(L)proline]$_2$. All the reactions were found to be completed within 10–15 min and afforded unexpected chromanone derivatives (**5a–j**) in excellent yields (87–93%) instead of Schiff base (**3**) (table 1, scheme 2). The newly synthesized compounds were characterized using elemental and spectroscopic data. Thus, the infrared (IR) spectrum of (**5a**) displayed an absorption band at 3355 cm^{-1} and 3280 cm^{-1} due to the presence of OH and NH groups, respectively. The absorption bands at 1650 and 1376 cm^{-1} indicated the presence of C=O and C–N groups, respectively. The proton magnetic resonance spectrum (^{1}H NMR) of the compound showed the singlet of H-2 proton at δ 5.71. (The diagnostic singlet for H-2 proton in chromone appears at δ 7.88.[42] A downfield doublet integrating for one proton at δ 8.33 (J = 11.4 Hz) was assigned to H-9 proton. The doublet of H-5 proton appeared at δ 7.99 (J = 7.8 Hz). Another downfield doublet discernible at δ 12.09 (J = 11.4 Hz) was assigned to NH proton. The relatively higher downfield effect on NH proton was due to intramolecular H-bonding in its Z-configuration. The remaining three protons of chromanone and four protons of pyridine moieties were present in the form of multiplets at δ 6.84–7.66. Further confirmation for the structure was provided by mass spectrum, which showed M$^+$ at m/z 268.15.

The plausible mechanism for the synthesis of (**5a–j**) in the presence of Zn [(L)proline]$_2$ has been depicted in scheme 3. Zn is capable of binding with the carbonyl oxygen increasing the reactivity of parent carbonyl group in **1**. Subsequently, formation of imine (**1a**) with proline takes place. This is followed by nucleophilic attack of amines (**2a–j**) to the imine (**1a**) to form hydrogen bonded adduct (**1b**). Finally, water as nucleophile attacks on electrophilic C-2 centre with the expulsion of Zn[(L)proline]$_2$ to give the desired 2-hydroxy chromanones (**5a–j**). Further, attempts were made to get (**3**) via dehydration of (**5a**) under different conditions such as heating in the presence of PTS, Al_2O_3, H_2SO_4, P_2O_5 etc. The dehydration of (**5a–j**) did not succeed probably due to the formation of stable hydrogen bonded keto-amine system[43] (scheme 2).

Then we studied the efficacy of the catalyst. We investigated the reaction of **1** with 2-aminopyridine **2a** as model reaction using different Lewis acid catalysts, different molar ratios of catalyst and different temperatures. Then, we optimized the reaction conditions by increasing/decreasing the catalyst loading and temperature. After systematic screening, we observed that the best results were obtained when the reactions were carried out with 10 mol% of Zn[(L)proline]$_2$ in water at reflux temperature. With amount less than 10 mol% of the catalyst the reaction either did not complete or took several hours to complete, whereas increasing the amount of catalyst more than 10 mol% did not either increase the product yield or the reaction rate. At room temperature in the presence of Zn[(L)proline]$_2$/H_2O and in the absence of Zn[(L)proline]$_2$/H_2O at reflux temperature reaction times were prolonged and yield of the product was very low (table 2, entries 2 and 3). Further, we also scrutinized the reaction by employing various other Lewis acids such as $CuSO_4$, $CuCl_2$, $ZnCl_2$, $AlCl_3$, $Zn(OAc)_2$, L-proline, $FeCl_3$. Data showed that by using L-proline alone product **5a** was obtained within short reaction time but in very low yields (table 2, entry 4). In the presence of $Zn(OAc)_2$, the reaction was not successful, to give any desirable product (table 2, entry 5). When $CuSO_4$, $CuCl_2$ (table 2, entries 6 and 7) were used to promote the reaction, a mixture of products was obtained in low yield. Further, the catalysts with high Lewis acidity such as $ZnCl_2$, $AlCl_3$ and $FeCl_3$ failed to catalyse the reaction efficiently and resulted in poor yields of the corresponding products (table 2, entries 8, 9, 10). These results confirmed the high catalytic activity of Zn[(L)proline]$_2$ in the current synthesis.

Table 2. Reaction of 3-formylchromone (1 mmol) with 2-aminopyridine (1 mmol) in the presence of various catalysts in water.

Entry	Catalyst	Temperature	Time[a]	Yield[b] (%)
1	Zn[(L)proline]$_2$	reflux	10 min	93
2	Zn[(L)proline]$_2$	r.t	6 h	46
3	-	reflux	10 h	42
4	L-proline	reflux	50 min	42
5	$Zn(OAc)_2$	reflux	8 h	15
6	$CuSO_4$	reflux	7 h	40
7	$CuCl_2$	reflux	5 h	40
8	$ZnCl_2$	reflux	6 h	34
9	$AlCl_3$	reflux	6 h	35
10	$FeCl_3$	reflux	45 min	25

[a]Reaction progress monitored by TLC. [b]Isolated yield

Table 3. Recycling study of the Zn [(L)proline]$_2$ (10 mol%) for the model reaction.[a]

Catalyst recycle	Time (min)[b]	Yield[c] (%)
I	10	93
II	10	93
III	10	93
IV	10	90
V	10	87

[a]Reaction of 3-formylchromone (1 mmol) with 2-aminopyridine (1 mmol) in water.
[b]Reaction progress monitored by TLC. [c]Isolated yield

3.1 *Recycling study*

One of the special properties of Zn[(L)proline]$_2$ is its insolubility in organic solvents and solubility in water which allows simple and quantitative recovery of the catalyst. The reaction of 3-formylchromone (**1**) with 2-aminopyridine (**2a**) in the presence of Zn[(L)proline]$_2$ in water was taken as model reaction for recycling studies. After completion of reaction in specified time, by cooling the reaction mixture to room temperature, the crude product was extracted with dichloromethane and the catalyst was recovered by separation of aqueous and organic phases. The catalyst was recovered by precipitating the aqueous layer by simple addition of acetone and drying at 80°C for 2.5 h. To rule out the possibility of catalyst leaching, the recovered catalyst was recycled to promote the model reaction affording the corresponding products (table 3). The results revealed that catalyst exhibited excellent catalytic activity up to three cycles.

4. Conclusion

In conclusion, Zn[(L)proline]$_2$ is an efficient catalyst for the preparation of 4-chromanone derivatives by the condensation of 3-formylchromone with different aromatic and heteroaromotic amines. The catalyst showed a unique class of catalysis in comparison with other catalysts. The reactions using Zn[(L)proline]$_2$ in water prevented uncontrolled by-products and were easy to handle. The notable advantages of this green methodology are mild reaction conditions, use of water as solvent, cleaner reaction profiles, simplicity in operation, excellent yields of the products, faster reaction rates, recyclability of the catalyst with no loss in its activity and zero discharge to the environment.

Acknowledgements

Financial assistance in the form of major research project [F.No. 37-15/2009 (SR)] and Special Assiatance Programme scheme (Departmental Research Support Phase I) from the University Grants Commission, New Delhi, is gratefully acknowledged. The authors would also like to thank Sophisticated Analytical Instruments Facility, Central Drug Research Institute, Lucknow for spectral data.

References

1. (a) Dewick P M and Harborne J B (eds) 1994 *The flavonoids: Advances in research since 1986* (New York: Chapmann & Hall) p 23; (b) Gill, M, Thomson R H (eds) 1993 *The Chemistry of Natural Products*, 2nd ed, (Surrey: Blackie) p 60
2. Arjunan V, Subramanian S and Mohan S 2004 *Spectrochim. Acta* **A60** 995
3. Sasnovskikh V Y and Irgashev R A 2007 *Tetrahedron Lett.* **48** 7436
4. Hutter J A, Salman M, Stavinoha W B, Satsangi N, Williams R F, Streeper R T and Weintranb S T 1996 *J. Nat. Prod.* **59** 541
5. Fitzmaerice C and Wragg A H 1966 *Chem. Abstr.* **65** 3444
6. Deng Y, Lee J P, Ramamonjy M T, Snyder J K, Etages S A, Kanada D, Snyder M P and Turner C J 2000 *J. Nat. Prod.* **63** 1082
7. Larget R, Lockhart B, Renard P and Largeron M 2000 *Biorg. Med. Chem. Lett.* **10** 835
8. Groweiss A, Cardellins J H and Boyd M R 2000 *J. Nat. Prod.* **63** 1537
9. Kuroda M, Uchida S, Watanabe K and Mimaki Y 2009 *Phytochemistry* **70** 288
10. Prakash O, Kumar R and Prakash V 2008 *Eur. J. Med. Chem.* **43** 435
11. Gabor M 1988 *The pharmacology of benzopyrone derivatives and related compounds* (Budapest: Akademiai Kiado) p 91
12. Loa J, Chow P and Zhang K 2009 *Cancer Chem. Pharmacol.* **63** 1007
13. Nohara A, Umetani T and Sanno Y 1974 *Tetrahedron* **30** 3553
14. Sosnovskikh V Y, Moshkin V S and Kodess M I 2008 *Tetrahedron Lett.* **49** 6856
15. Lee H, Lee K, Jung J K, Cho J E and Theodorakis E A 2005 *Bioorg. Med. Chem. Lett.* **15** 2745
16. Cottiglia F, Dhanapal B, Sticher O and Heilmann J 2004 *J. Nat. Prod.* **67** 537
17. Rukachaisirikul V, Tansakul C, Saithong S, Pakawatchai C, Isaka M and Suvannakad R 2005 *J. Nat. Prod.* **68** 1674
18. Morrison E, Rundberget T, Kosiak B, Aastveit A H and Bernhoft A 2002 *Mycopathologia* **153** 49
19. Yang G, Jiang X and Yang H 2002 *Pest Manag. Sci.* **58** 1063
20. Boege F, Straub T, Kehr A, Boesenberg C, Christiansen K, Andersen A, Jakob F and Köhrle J 1996 *J. Bio. Chem.* **271** 2262
21. Ellis G P 1977 *Chromenes, chromanones and chromones*, Canada, New York, USA: John Wiley and Sons, pp 345
22. Xu Z Q, Buckheit R W, Stup T L, Flavin M T, Khilevich A, Rizzo J D, Lin L and Zembower D E 1998 *Bioorg. Med. Chem. Lett.* **8** 2179
23. Kostova I, Raleva S, Genova P and Argirova R 2006 *Bioinorg. Chem. Appl.* **2006** 1
24. Kralova K, Lacova M and Stankovicova H 1996 *Biol. Plant* **38** 397
25. El-Shaaer H M, Foltinova El-P, Lacova M, Chovancova J and Stankovicova H II 1998 *Farmaco* **53** 224
26. Stankovicova H, Lacova M, Gaplovsky A, Chavanova J and Paranayova N 2001 *Tetrahedron* **57** 3455
27. Kułaczkowska A D and Mazur L 2011 *J. Mol. Struct.* **985** 233
28. Li C-J 2005 *Chem. Rev.* **105** 3095

29. Lindstrom U M 2002 *Chem. Rev.* **102** 2751
30. Kofoed J, Darbre T and Reymond J L 2006 *Chem. Commun.* **14** 1482
31. Reddy K R, Rajasekhar C V and Krishna G G 2007 *Synth. Commun.* **37** 1971
32. Sivamurugan V R, Kumar S, Palanichamy M and Murugesan V 2005 *J. Heterocyclic Chem.* **42** 969
33. Siddiqui Z N, Musthafa T N M, Praveen S and Farooq F 2011 *Med. Chem. Res.* **20** 1438
34. Musthafa T N M, Siddiqui Z N, Husain F M and Ahmad I 2011 *Med. Chem. Res.* **20** 1473
35. Siddiqui Z N, Praveen S and Farooq F 2010 *Chemical Papers* **64** 818
36. (a) Siddiqui Z N, Farooq F, Musthafa T N M 2011 *Green Chem. Lett. Rev.* **4** 63; (b) Siddiqui Z N, Farooq F, 2011 *Catal. Sci. Technol.* **1** 810; (c) Siddiqui Z N Musthafa, T N M 2011 *Tetrahedron lett.* **52** 4008
37. Kostka K, 1966 *Roczniki Chem.* **40** 1683
38. Fitton A O, Frost J R, Houghton P G and Suschitzky H 1979 *J. Chem. Soc. Perkin Trans.* **2** 1691
39. Gadwal S and Sandhu J S 2000 *J. Chem. Soc. Perkin Trans.* **1** 2827
40. Fitton A O, Frost J R, Houghton P G and Suschitzky H 1977 *J. Chem. Soc. Perkin Trans.* **1** 1450
41. Khan K M, Ambreen N, Hussain S, Parveen S and Choudhary M I 2009 *Bioorg. Med. Chem.* **17** 2983
42. Ellis G P 1977 *Chromenes, chromanones and chromones*, chapter 9. Canada, (New York, USA: John Wiley and Sons) p 563
43. Dudek G O 1963 *J. Am. Chem. Soc.* **85** 694
44. Sivamurugan V, Deepa K, Palanichamy M and Murugesan V 2004 *Synth. Commun.* **34** 3833