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MICROWAVE ASSISTED SOLVENT FREE SYNTHESIS OF COUMARINS USING Zn [(L)-Proline]$_2$ CATALYST

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ABSTRACT

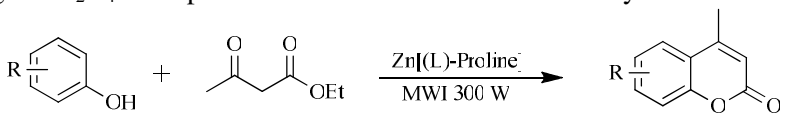
Solvent free synthesis of substituted Coumarins by Von Pechmann condensation of phenols with β-ketoesters catalyzed by Zn [(L)-Proline]$_2$as an organometallic catalyst by microwave irradiation method. Our present protocol is economical and clean comprise of green reagent, solvent and catalyst.

Keywords: Pechmann Condensation, Coumarins, Organometallic Catalyst, MWI, Green Synthesis.

INTRODUCTION

Coumarins[1] and theirs derivatives has attracted considerable attention of medicinal and organic chemist from many years, due to its large number of biological activities like anti-bacterial[2], anti-cancer[3], anti-coagulant, anhelmentic, hypnotic, optical brighteners[4], anti-inflammatory and anti-HIV activities[5].

The representative synthetic routes of Coumarin and its derivatives include Pechmann[6], knoevenagel[7], Perkin[8], Reformatsky[9] and Wittig[10] condensation reactions. Among these, Pechmann condensation is one of the most widely used method for synthesis of Coumarins. Acid catalyst have been used in the Pechmann[6] reaction including use of simple starting materials that is phenol and β-ketoesters in the presence of variety of acidic agents, such as chlorosulfonic acid[11], Sulfuric acid[6], melamine formaldehyde resin supported H^+ ion catalyzed[12], ionic liquid catalyzed[13], oxalic acid catalyzed[14], silica triflate catalyzed, heterogeneous catalyst, zirconia supported catalyst etc. Recently, Pechmann reaction has been carried out by using $CuFe_2O_4$ nano particles[15] and molecular iodine catalyst[16].



Scheme 1.

Zn[(L)-Proline]$_2$ has found very vast applications in reactions such as, Aldol condensation[17], cross coupling reactions[18], rearrangement reaction, condensation reaction, usually acts as strong Lewis acid catalyst and dehydrating agent[19,20].

EXPERIMENTAL

Chemicals and Instruments

All the compounds used in synthesis were of analytical grade; the melting points of the compounds were determined in open head capillary and are uncorrected. The IR spectra of the compounds were recorded in the region of 4000-400 cm^{-1} by using KBr pallet on FT-IR Perkin spectrophotometer. H^1 NMR spectra were recorded on a DRX-300 Bruker FT-NMR spectrophotometer in $CDCl_3$. Satisfactory elemental

analysis was obtained on a Perkin Elmer CHN analyzer. The values of chemical shift are expressed in δ ppm as a unit. All the compounds were checked for purity by thin layer chromatography (TLC).

Synthesis of Zn [(L) proline]$_2$

As reported by Darbre et al[17], the Zinc amino complex was prepared by adding Et_3N (0.6 ml) to the amino acid (4.34 mmol) in MeOH (10 ml), after 10 min, followed by zinc acetate (2.17 mmol). After stirring for 45 min a white precipitate was collected by filtration (95% yields).

Characterization of Zn [(L) proline]$_2$

White solid 1H NMR (300 MHz, $CDCl_3$) d: 1.81 (m, br, 3H); 2.22 (m, br, 1H); 2.98 (s, br, 1H); 3.14 (m, br, 1H); 3.85 (m, br, 1H) (spectrum included) IR (KBr): v (cm^{-1}) 3217 (vs), 2960 (m), 1603 (vs), 1449 (s), 1412 (s), 1329 (m), 848 (m) MS (ESI): m/z 291.21 (M^+)

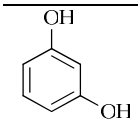
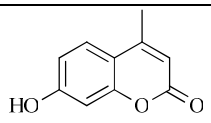
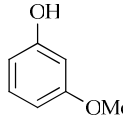
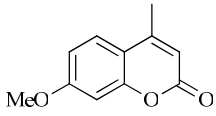
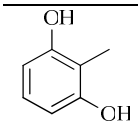
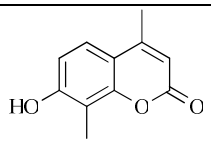
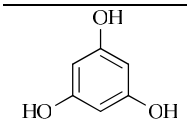
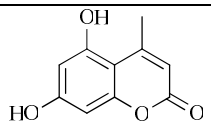
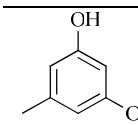
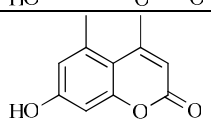
General experimental procedure for synthesis of 7-hydroxy-4-methylcoumarins

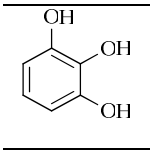
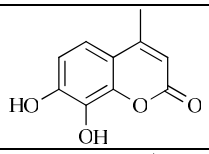
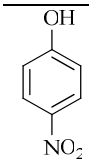
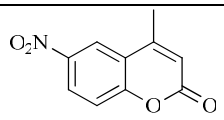
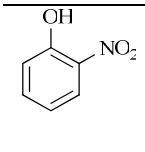
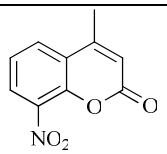
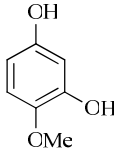
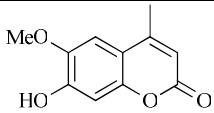
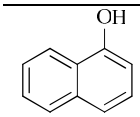
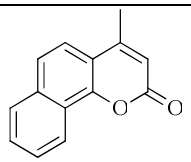
A mixture of resorcinol (10mmol), ethylacetoacetate (10mmol) and Zn [(L)-Proline]$_2$ (20 mol %) were subjected to microwave irradiation at 300W for appropriate time (Table 1). After completion of reaction, as monitor by TLC, the reaction mixture was cooled to room temperature, water was added and stirred for another two minutes, precipitation was filtered off and recrystalised from methanol to afford pure 7-hydroxy-4-methylcoumarins as yellowish prism.

7-hydroxy-4-methylcoumarins

Yield 98 %, mp 184-186 °C. ^{1}H NMR ($CDCl_3$) δ: 2.2 (s, 3H, Me), 6.1 (s, 1H), 6.83 (d, 1H, *J* 2.4 Hz), 6.97 (dd, 1H, *J* 8.7 and 2.4 Hz), 7.5 (d, 1H, *J* 8.7 Hz). IR (KBr, ν/cm^{-1}): 2985, 1740, and 1625. ES/MS, *m/z*: 175 (M-H).

Table-1: Solvent free synthesis of Coumarins via Von Pechmann condensation of substituted phenols with β-ketoesters catalyzed by Zn [(L)-Proline]$_2$by microwave irradiation method (300W)

Substrate	Product	Time in Sec.	M. P. in °C		Yield[a] (%)
			Obs.		
		60	184-86	185[14]	98
		60	158-60	161[14]	95
		60	138-39	138[14]	90
		60	285-86	285[14]	90
		60	257-58	258[14]	92

		80	235-36	237[14]	89
		110	147-49	150[14]	72
		100	183-184	185[14]	79
		90	164-165	165[14]	91
		120	156-158	155[14]	87

[a]Isolated Yield

RESULTS AND DISCUSSION

A mixture of substituted phenols and ethyl acetoacetate was subjected to microwave irradiation of very low power (300W) in presence of Zn $[(L)\text{-Proline}]_2$under solvent free condition (Scheme1).The Progress of reaction was checked by chromatography (TLC). Optimization of reaction condition was achieved by using varying amounts of Zn $[(L)\text{-Proline}]_2$catalyst and best results of yields could be obtained by using 20 mol % of Zn $[(L)\text{-Proline}]_2$catalyst (Table-2).

Table-2: Optimization of reaction condition for synthesis of 7-hydroxy-4-methylcoumarinsunder solvent free condition by microwave irradiation technique at low power (300W) using Zn $[(L)\text{-Proline}]_2$catalyst.

Entry	Catalyst	Mol %	Yield[a]
1	$Zn[(L)\text{-Proline}]_2$	0	--
2	$Zn[(L)\text{-Proline}]_2$	5	stress
3	$Zn[(L)\text{-Proline}]_2$	10	40%
4	$Zn[(L)\text{-Proline}]_2$	15	59%
5	$Zn[(L)\text{-Proline}]_2$	20	98%
6	$Zn[(L)\text{-Proline}]_2$	25	93%
7	$Zn[(L)\text{-Proline}]_2$	30	88%

[a]Isolated Yield

In summary, it can be stated that, the present protocol for synthesis of Coumarins by Pechmann condensation is highly efficient as it avoid use of organic solvents at any stage of reaction, under microwave irradiation technique at very low power (300W) and presence of organometallic biodegradable $Zn[(L)\text{-Proline}]_2$ as a catalyst.

CONCLUSION

Herein, we report the Pechmann condensation reaction of phenols and β-ketoesters using $Zn[(L)\text{-Proline}]_2$as a simple, efficient, eco-friendly, organometallic catalyst under solvent free condition.

(Scheme-1).We carried out a series of substituted phenols with ethylacetoacetate to obtain corresponding Coumarin derivatives in very good yield (Table-1).

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