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A Novel Synthesis of Biscoumarin Derivatives Catalyzed by $ZnCl_2$ under Solvent-Free Coditions

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ABSTRACT

Zinc chloride ($ZnCl_2$) is used as an efficient catalyst condensation of 4-hydroxycoumarin and with various aromatic aldehydes leading to the formation of biscoumarin derivatives. Easy isolation of the products, short reaction times, excellent yields and reusability of catalyst was theadvantage of thismethod.

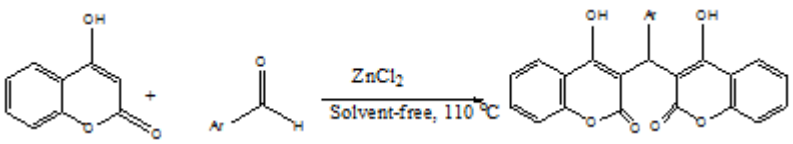
Key words: Bis-coumarins , $ZnCl_2$, Aromatic Aldehydes, Solvent-free Conditions.

INTRODUCTION

Biscoumarin and its derivatives are of considerable interest due to their biological activities such as urease inhibitors[1], HIV inhibitory activity [2], anticoagulant activity [3], treatment of thrombosis [4].

From among various catalyst for synthesis of Biscoumarins, the following catalysts can be referred such as sulfuric acid, phosphorus pentoxide, aluminumchloride, iodine, and trifluoroacetic acid are employed [5-6], molecular iodine [7], [bmim][BF_4] [8], tetrabutylammonium bromide (TBAB) [9], Zn(Proline)$_2$[10], sodium dodecyl sulfate (SDS) [11].Previously, we have synthesized a number of heterocyclic compounds[12-22].

Herein, we report an efficient method for the synthesis of somebiscoumarin derivatives from aromatic aldehydes and 4-hydroxycoumarin catalyzed by Zinc chloride under solvent-free conditions (Scheme 1).



Scheme 1:

EXPERIMENTAL

All chemicals were obtained from Merck or Flukawithout further purification. Silica gel SILG/UV 254 plates were used for TLC. IR spectra were measured on a Shimadzu IR-470 Spectrophotometer. ^{1}H NMR spectra were determined on Bruker400 DRX AVANCE instrument at 400 MHz, respectively.

General procedure for preparation of H1-H4

A mixture of aldehyde (1 mmol), 4-hydroxycoumarin (1 mmol), ammonium acetate (3 mmol) and $ZnCl_2$(15mol %) as a catalyst was stirred at 110 ^{o}C for 35 min. The progress of reaction was monitored by TLC. After finishing, recrystallized from ethanol 95% to give pure products (**H1-H4**)

3,3'-[(3-Nitrophenyl)methylene]bis(4-hydroxy-2*H*-chromen-2-one) (**H1**)

White crystals, Yield: (89%), mp 233-235^{o}C. IR (ν_{max}/cm^{-1}) (VBr): 3120(arom. CH Str.); 1680,1630 (C=O Str.); 1540 , 1340 (NO_2 Str.) ; 1490(C=C Str.).^{1}H-NMR (400.13 MHz $CDCl_3$): δ=6.15(H, s, CH); 7.40-7.61(6H, m, 6CH); 7.69(2H, t,^3J=7.6 Hz, 2CH); 8.03(H, d, ^3J=7.6 Hz, CH); 8.09(H, s, CH); 8.12(H, t, ^3J=7.6 Hz, CH); 8.17(H, d, ^3J=8.0 Hz, CH); 11.40(H, s, OH); 11.60(H, s, OH).

3,3'-[(4-Nitrophenyl)methylene]bis(4-hydroxy-2*H*-chromen-2-one) (H2)

White crystals, Yield: (87%), mp230-232^{o}C.IR (ν_{max}/cm^{-1}) (VBr): 3140(arom. CH Str.); 1670,1610 (C=O Str.); 1580 , 1370 (NO_2 Str.) ; 1480(C=C Str.). ^{1}H-NMR (400.13 MHz $CDCl_3$): δ=6.13(H, s, CH); 7.41-7.47(6H, m, 6CH); 7.69(2H, t,^3J=8.0 Hz, 2CH); 8.02(H, d, ^3J=7.6 Hz, CH); 8.10(H, d, ^3J=7.8 Hz CH); 8.20(2H, d, ^3J=8.8 Hz, 2CH); 11.39(H, s, OH); 11.59(H, s, OH).

3,3'-[(2-Chlorophenyl)methylene]bis(4-hydroxy-2*H*-chromen-2-one) (H3)

White crystals, Yield: (90%), mp225-223 ^{o}C.IR (ν_{max}/cm^{-1}) (VBr): 3120(arom. CH Str.); 1660, 1620 (C=O Str.); 1490(C=CStr.). ^{1}H-NMR (400.13 MHz $CDCl_3$): δ=6.16(H, s, CH); 7.24-7.39(5H, m, 5CH); 7.41(2H, d,^3J=8.0 Hz, 2CH); 7.49(1H, d,^3J=8.0 Hz, CH); 7.64(2H, t, ^3J=7.6 Hz, 2CH); 8.04(2H, m,2CH); 10.95(H, s, OH); 11.67(H, s, OH).

3,3'-[(2-Fluorophenyl)methylene]bis(4-hydroxy-2*H*-chromen-2-one) (H4)

White crystals, Yield: (85%), mp 215-217^{o}C. IR (ν_{max}/cm^{-1}) (VBr): 3130(arom. CH Str.); 1675, 1605 (C=O Str.); 1510(C=C Str.). ^{1}H-NMR (400.13 MHz $CDCl_3$): δ=6.13(H, s, CH); 7.18-7.37(8H, m, 8CH); 7.43(1H, d,^3J=8.2 Hz, CH); 7.65(2H, d,^3J=8.2 Hz, 2CH); 8.03(2H, dd, ^3J=28.0 Hz, ^3J=8.0 Hz, 2CH); 11.33(H, s, OH); 11.56(H, s, OH).

RESULTS AND DISCUSSION

We have been able to introduce an efficient method for the synthesis of biscoumarin derivatives via condensation of 4-hydroxycoumarin with various aromatic aldehydes. Therefore, reported $ZnCl_2$as catalyst which could provide an efficient, cheap, easy separationunder solvent-free condition for the synthesis of biscoumarins with high yield.

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