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ORIGINAL ARTICLE

# Solvent free synthesis, spectral correlation and antimicrobial activities of some 2*E* 4′-nitrochalcones

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**Abstract** A series containing twelve substituted styryl 4′-nitrophenyl ketones have been synthesized using solvent free $SiO_2$–$H_2SO_4$ catalysed aldol reaction under microwave condition. The yield of chalcones is found to be more than 80%. These synthesized ketones have been characterized by their physical constants and spectral data. The spectral frequencies of these chalcones have been correlated with Hammett substituent constants, *F* and *R* parameters. From the results of statistical analyses the effect of substituents on the frequencies has been predicted. The antimicrobial activities of all ketones have also been studied with the help of Bauer–Kirby method.


## 1. Introduction

Chalcone is 1,3-diphenyl-2-propene-1-one, in which two aromatic rings are linked by a three carbon α,β-unsaturated carbonyl system. Chalcones possess conjugation and a completely delocalized π-electron system on both benzene rings. Chalcones have been isolated from several plants, and are precursors of flavone compounds. Chalcones are well known intermediates for synthesizing various heterocyclic compounds. The compounds with the backbone of chalcones have been reported to possess various properties by which they find many applications in different fields. Many chalcones have been used as agro chemicals and drugs (Mirinda et al., 2000; Monostory et al., 2003; Nowakowska, 2007; Majinda et al., 2001; Sitaram Kumar et al., 2007). A variety of methods are available for the synthesis of chalcones, the most convenient method is the one that involves the Crossed-Aldol condensation of equimolar quantities of acetylated aliphatic or aromatic

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compounds with substituted benzaldehydes in the presence of aqueous alcoholic alkali (Thirunarayanan and Ananthakrishna Nadar, 2002). Claisen–Schmidt and aldol condensation of equimolar quantities of aryl methyl ketone with substituted benzaldehydes in the presence of alcoholic alkali (Venkat Reddy et al., 2001; Thirunarayanan and Ananthakrishna Nadar, 2006a,b; Thirunarayanan 2007a,b) also yield chalcones in appreciable quantities. Nowadays numerous reagents have been used for the synthesis of chalcones such as anhydrous zinc chloride (Thirunarayanan and Ananthakrishna Nadar, 2006a,b), Clay (Ballini et al., 2001), ground chemistry catalysts-grinding the reactants with sodium hydroxide (Thirunarayanan, 2008a), aqueous alkali in lower temperatures (Basaif et al., 2005), solid sulphonic acid from bamboo (Xu et al., 2008), barium hydroxide (Blackwell, 2006), anhydrous sodium bicarbonate (Zhang et al., 2003), Fly-ash:water, microwave irradiation (Thirunarayanan 2007a,b, 2012) and sulphated titania (Krish-akumar et al., 2011). In recent years, correlation analysis has been applied by chemists for solving the molecular equilibration in ground state through spectral data. On the basis of spectral data, *s-cis* and *s-trans* isomers of alkenes, α,β-unsaturated ketones, aldehydes etc., have been investigated using ground state molecular conformational equlibria (Thirunarayanan and Ananthakrishna Nadar, 2006a,b; Thirunarayanan, 2008b). Recently Ranganathan et al., (Ranganathan et al., 2012) have applied the single and multi-regression analysis for investigating the effect of substituents on α and β hydrogens and carbons of furyl and thienyl chalcones. Literature survey shows that there is little information regarding the study of solvent free synthesis, infrared and NMR spectral study and antimicrobial activities of substituted styryl nitro phenyl ketones. Hence the authors have taken efforts for synthesizing the ketones and studying the effect of substituents through the spectral data and their antimicrobial activities.

## 2. Experimental

### 2.1. General

All chemicals used have been purchased from Sigma–Aldrich and E-Merck chemical companies. Melting points of all chalcones have been determined in open glass capillaries on a Mettler FP51 melting point apparatus and are uncorrected. The UV spectra of all synthesized chalcones have been recorded on a SHIMADZU-1650 SPECTROMETER in spectral grade methanol. Infrared spectra (KBr, 4000–400 $cm^{-1}$) have been recorded on a AVATAR-300 Fourier transform spectrophotometer. The NMR spectra of all ketones were recorded in BRUKER 400 spectrometer operating at 500 MHzfor $^{1}H$ NMR spectra and 125.46 MHz for $^{13}C$ NMR spectra in DMSO solvent using TMS as internal standard. Mass spectra have been recorded on a SHIMADZU GC-MS2010 Spectrometer using Electron Impact (EI) techniques.

### 2.2. Preparation of catalyst

The $SiO_2$–$H_2SO_4$ catalyst has been prepared as per the procedure published in the literature (Thirunarayanan et al., 2012). In a 50 mL Borosil beaker, 1 g of silica and 0.8 mL (0.5 mol) of sulphuric acid have been taken and mixed thoroughly with a glass rod. This mixture has been heated on a hot air oven at 85 °C for 1 h, cooled to room temperature, stored in a borosil bottle and tightly capped. This catalyst was characterized by infrared spectra and SEM analysis.

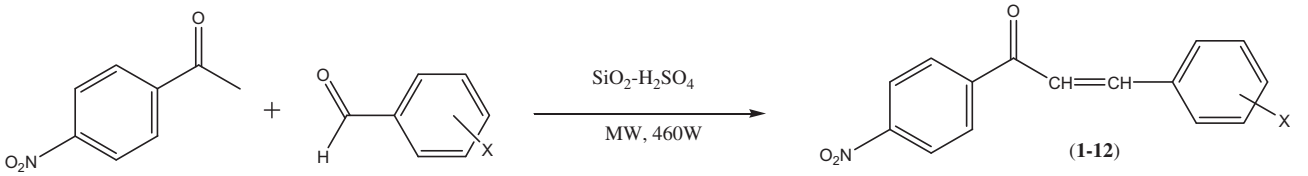
### 2.3. Synthesis of 4′-nitrochalcones

An appropriate mixture of 4-nitroacetophenone (2 mmol), substituted benzaldehydes (2 mmol) and 0.5 g of $SiO_2$–$H_2SO_4$ has been taken in a borosil tube and tightly capped. The mixture has been placed in a microwave oven and treated under microwave condition for 8–10 min (Scheme 1) (LG Grill, Intellowave, Microwave Oven, 160–800 W) and then cooled to room temperature. The reaction mixture was mixed with 10 mL of dichloromethane and stirred well, kept aside for 10 min. The catalyst was separated by filtration. The organic layer with dichloromethane was washed with distilled water and separated though separating funnel, evaporation of organic layer afforded the solid chalcone. The solid, on recrystallization with benzene–hexane mixture yields glittering solid. The insoluble catalyst has been recycled by washing the solid reagent on the filter by ethyl acetate (8 mL) followed by drying in an oven at 100 °C for 1 h. This catalyst is made reusable for further reactions. The analytical, yield and mass spectral data of these chalcones are presented in Table 1.

## 3. Results and discussion

### 3.1. Spectral correlations

In the present investigation UV absorption maxima from UV spectra and the spectral linearity of chalcones have been studied by evaluating the effect of substituents. The assigned group frequencies of all chalcones like carbonyl stretches νCO, the




| Entry | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| X | H | 3-Br | 4-Br | 3-Cl | 4-Cl | 4-F | 2-$OCH_3$ | 4-$OCH_3$ | 4-$CH_3$ | 2-$NO_2$ | 3-$NO_2$ | 4-$NO_2$ |

**Scheme 1** Synthesis of 4′-nitrochalcones by $SiO_2$–$H_2SO_4$ catalysed aldol condensation under solvent free conditions.