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SiO₂-H₃PO₄ catalyzed solvent free aldol condensation: Synthesis and spectral correlations of some antimicrobial potent aryl *E* 2-propen-1-ones

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ABSTRACT

Some substituted styryl 4-ethylphenyl ketones have been synthesised using solvent free SiO₂-H₃PO₄ catalyzed aldol condensation between 4-ethylphenyl methyl ketone and substituted benzaldehydes under microwave irradiation. The yields of the ketones are more than 85%. The synthesised chalcones were characterized by their analytical, physical and spectroscopic data. The spectral frequencies of these ketones have been correlated with Hammett substituent constants, F and R parameters using single and multi-linear regression analysis. The antimicrobial activities of these ketones have been studied using Bauer-Kirby method.

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KEYWORDS

Styryl 4-ethylphenyl ketones;
SiO₂-H₃PO₄;
Crossed-aldol reaction;
Solvent free synthesis;
Antimicrobial activities.

INTRODUCTION

Many greener and solvent-free^[1,2] synthetic methods available for synthesis of organic compounds. These reactions involving the formation of carbon-carbon bond and carbon-heteroatom bond are important and interesting in green synthesis. Based on this the Aldol^[3], Crossed-aldol^[4], Knoevenagel^[5], Mannich^[6] and Michael^[7] and Wittig^[8] reactions have been applied for synthesising isomeric biologically active compounds such as chalcones, alkenes and Mannich bases. Thermal condensation reactions have been found to be sluggish and time-consuming with poor yields. However in the microwave conditions, the reaction is faster, giving appreciable yield involving easier process of isolation of the products. Scientists and Chemists have used microwave irradiation technique for solid phase green synthesis^[8,9]. Numerous green catalysts such as fly-ash: sulphuric acid¹, silica-sulphuric acid^[10,11] anhydrous zinc

chloride^[12], ground chemistry catalysts-grinding the reactants with sodium hydroxide^[13], aqueous alkali in lower temperature^[14], solid sulphonic acid from bamboo^[15], barium hydroxide^[16] anhydrous sodium bicarbonate^[17], microwave assisted synthesis^[18], Fly-ash: water^[19], triphenylphosphite^[20], alkali earth metals^[21], KF/Al₂O₃^[22] and sulfated titania^[23] and silicotungstic acid^[24] have been reported for the synthesis of many number of organic compounds. Chalcones possess various multipronged activities such as antimicrobial^[25], antidepressants^[26], antiplosmodial^[27], anti-aids^[28] and insect antifeedant activities^[3,29]. Spectral data is useful for prediction of ground state equilibration of organic molecules such as such as *s-cis* and *s-trans* isomers of alkenes, alkynes, benzoyl chlorides, styrenes and α , β -unsaturated ketones^[27,29]. The Quantitative structure activity relationship and quantitative structure property relationships were used for finding the structure of molecule, quantitative and quali-

tative analysis^[27-29]. Their use in structure parameter correlations becomes popular for studying biological activities^[30], normal co-ordinate analysis^[31] and transition states of reaction mechanisms^[32]. Infrared spectroscopy is a powerful tool technique for the qualitative and quantitative study of natural and synthetic molecules^[33]. IR spectroscopy can provide information about the nature, concentration and structure of samples at the molecular level^[34]. A great deal of work has been devoted to the reactivity of α,β -carbonyl compounds particularly, the theoretical study of substituent effects has been studied on long range interactions in the β -sheet structure^[35] of oligopeptides, enone-dienol tautomerism^[36]. Literature study reveals QSAR study of substituted benzo[α] phenazines^[37] cancer agents, Diels-Alder reactions^[38], density functional theory^[39], gas phase reactivity of alkyl allyl sulphides^[40] rotational barriers in selenomides^[41]. Santelli et.al.^[42] have studied the quantitative structural relationships in α,β -unsaturated carbonyl compounds between the half wave reduction potential, the frontier orbital energy and the Hammett σ_p values. Dhimi and Stothers^[43] have extensively studied the ^1H nmr spectra of a large number of acetophenones and styrenes with a view to establish the validity of the additivity of substituent effect in aromatic shielding first observed by Lauterber^[44]. Savin and co-workers^[45] have studied the NMR data of unsaturated ketones of the type $\text{RC}_6\text{H}_4\text{-CH=CH-COMe}$ and sought Hammett correlations for the ethylenic protons. Solcaniova^[46] and co-workers have measured ^1H and ^{13}C NMR spectra of substituted styrenes, styryl phenyls and they obtained good Hammett correlations for the olefinic protons and carbons. At present, scientists^[2,3,5,9,12,27] have paid more interest to correlate the group frequencies of spectral data with Hammett substituent constants to explain the substituent effects of organic compounds. Recently Thirunarayanan co-workers^[2,3,5,9,12,47-49] investigated elaborately the single and multi-regression analysis of substituent effects on alpha and beta hydrogen and carbons of some pyrrolyl, naphthyl and furyl chalcones. However there is no information available in the literature for the synthesis of chalcones using green catalyst $\text{SiO}_2\text{-H}_3\text{PO}_4$ for Crossed-Aldol condensation reaction, correlation study of infrared and NMR spectroscopic data with Hammett equation and antimicrobial activities in the past with sub-

stituted styryl 4-ethoxy phenyl ketones. Therefore the authors have taken efforts to synthesize some substituted styryl 4-ethoxy phenyl ketones by condensation of 4-ethyl phenyl ketones with various substituted benzaldehydes, studied the quantitative structure property relationship from the group frequencies and studied their antimicrobial activities.

EXPERIMENTAL

General

All chemicals used were purchased from Sigma-Aldrich and E-Merck chemical company. Melting points of all chalcones were determined in open glass capillaries on Mettler FP51 melting point apparatus and are uncorrected. Infrared spectra (KBr , $4000\text{-}400\text{cm}^{-1}$) were recorded on AVATAR-300 Fourier transform spectrophotometer. INSTRUM AV300 operating at 500MHz was used for ^1H spectra and 125.46MHz for ^{13}C spectra in DMSO solvent using TMS as internal standard. Mass spectra were recorded on a SIMADZU GC-MS2010 Spectrometer using Electron Impact (EI) techniques.

Preparation of $\text{SiO}_2\text{-H}_3\text{PO}_4$ catalyst

In a 50mL Borosil beaker, 2g of silica (10-20 μ) 2mL of ortho phosphoric acid were taken and mixed thoroughly with glass rod. This mixture was heated on a hot air oven at 85°C for 1h, cooled to room temperature, stored in a borosil bottle and tightly capped. This was characterized by infrared spectra and SEM analysis.

Infrared spectral data of $\text{SiO}_2\text{-H}_3\text{PO}_4$ are $\nu(\text{cm}^{-1})$: 3437(P-OH); 2932, 2849 (P-O-H); 1747, (O=P-OH); 1091(P=O), 800(P-O); 464.

The SEM images of pure SiO_2 and $\text{SiO}_2\text{-H}_3\text{PO}_4$ at two different magnifications are shown in Figures 1(a-d). Figures 1a and 1b depicted that the crystallinity is found to be more in SiO_2 . The spherical shaped particles are clearly seen at both magnifications in Figure 1a and 1b. Figure 1a reveals that the globular structure of pure fly ash (round shaped particle). It also seen from Figure 1c and 1d that some of the particles are slightly corroded by H_3PO_4 (indicated by arrow mark) and this may be due to dissolution of SiO_2 by H_3PO_4 . This will further confirmed by Figure 1d, the well-shaped

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particles of pure SiO₂. Figure 1b is aggregated to Figure 1d due to presence of H₃PO₄.

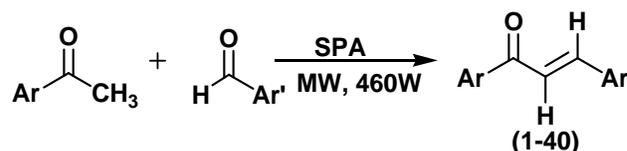
General procedure for synthesis of substituted styryl 4-ethylphenylketones

An appropriate mixture of aryl methyl ketone (2 mmol) and substituted benzaldehydes (2 mmol) and SiO₂-H₃PO₄ (0.5g) taken in 50 ml corning glass tube and tightly capped. The reaction mixture was subjected to microwave irradiation for 8-10 minutes in a microwave oven (Scheme 1) (LG Grill, Intellowave, Microwave Oven, 160-800W) and then cooled to room temperature. Added 10 ml of dichloromethane, the organic layer has been separated which on evaporation yields the solid product. The solid, on recrystallization with benzene-hexane mixture gives glittering pale yellow solid.

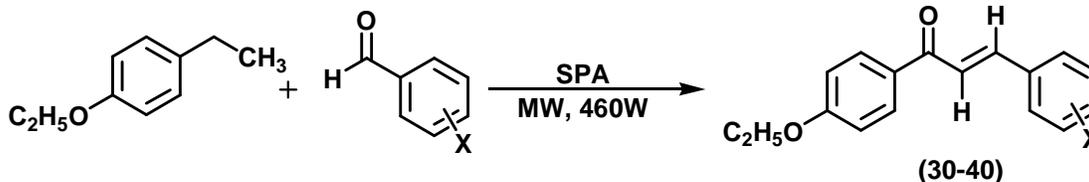
RESULTS AND DISCUSSION

In our organic chemistry research laboratory, we attempts to synthesize aryl chalcone derivatives by crossed-aldol condensation of electron withdrawing as well as electron donating group substituted aryl methyl ketones and benzaldehydes in the presence of vigorous acidic catalyst SiO₂-H₃PO₄ in microwave irradiation. Hence the authors have synthesised the chalcone derivatives by the reaction between 2 mmole of aryl methyl ketones 2 mmole substituted benzaldehydes in microwave irradiation with 0.5 g of SiO₂-H₃PO₄ catalyst (Scheme 1). During the course of this reaction SiO₂-H₃PO₄ catalyses aldol reaction between aryl ketone and aldehydes and elimination of water gave the chalcones. The yields of the chalcones in this reaction

are more than 85%. The proposed general mechanism of this reaction is given in Figure 2. Further we have investigated this reaction with equimolar quantities of the 4-ethoxy acetophenone and benzaldehyde (Scheme 2). In this reaction the obtained yield was 87%. The effect of catalyst on this reaction was studied by varying the catalyst quantity from 0.1 g to 1 g. As the catalyst quantity is increased from 0.1 g to 1 g, the percentage of yield of product is increased from 85 to 87%. Further increase the catalyst amount there is no significant increasing of the percentage of product. This catalytic effect is shown in (Figure 3). The optimum quantity of catalyst loading was found to be 0.2 g. We have carried out this reaction with various substituted ketones and benzaldehydes. The results, analytical and mass spectral data are summarized in TABLE 1. There is no significant effect of substituents on the condensation reaction. This reaction mechanism was proposed based on Rajput and Kaur^[24]. The reusability of this catalyst was studied the aldol reaction of 4-ethyl acetophenone between benzaldehyde and is presented in TABLE 2. From the TABLE 2, first two runs gave 87% product. The third, fourth and fifth runs of reactions gave the yields 86.5%, 86.5% and 86 % of chalcones. There was no appreciable loss in its effect of catalytic activity was observed up to fifth run.



Scheme 1 : Synthesis of aryl chalcones using silica-phosphoric acid catalyzed aldol condensation between aryl ketones and benzaldehydes



X= H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH₃, 4-OCH₃, 2-CH₃, 3-NO₂, 4-NO₂

Scheme 2 : Synthesis of substituted styryl 4-ethoxyphenyl ketones using silica-phosphoric acid catalyzed aldol condensation between aryl ketones and benzaldehydes

Spectral linearity

In the present study the spectral linearity of chalcones has been studied by evaluating the substituent effects^[2,3,5,9,12,27-29, 47-49] on the group frequencies.

The assigned group frequencies of all chalcones line infrared carbonyl stretches ν_{CO} -*cis* and *s-trans*, the deformation modes of vinyl part CH_{out of plane}, *in-plane*, CH=CH and >C=C< *out of planes* (cm⁻¹), NMR chemical shifts δ (ppm) of H _{α} , H _{β} , C _{α} , C _{β} , CO

are assigned and these frequencies are correlated with various substituent constants.

TABLE 1 : Analytical and mass spectral data of chalcones synthesized by $\text{SiO}_2\text{-H}_3\text{PO}_4$ catalyzed aryl methyl ketones and substituted benzaldehydes reaction of the type $\text{Ar-CO-CH}_3 + \text{Ar}'\text{CHO} \rightarrow \text{Ar-CO-CH=CH-Ar}$ under microwave irradiation

Entry	Ar	Ar'	Product	M. W.	Yield (%)	M.p. (°C)	Mass (m/z)
1	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅ COCH =CHC ₆ H ₅	208	86	55-56 (55-58) ^[1]	---
2	C ₆ H ₅	4-ClC ₆ H ₄	C ₆ H ₅ COCH =CHC ₆ H ₄ Cl	242	86	114-115 (112-114) ^[24]	---
3	C ₆ H ₅	C ₁₀ H ₇ (1-Naph)	C ₆ H ₅ COCH =CHC ₁₀ H ₇	273	85	104-105 (104-105) ^[1]	---
4	C ₆ H ₅	4-OHC ₆ H ₄	C ₆ H ₅ COCH =CHC ₆ H ₄ OH	291	84	122-123 (122) ^[1]	---
5	C ₆ H ₅	4-OCH ₃ C ₆ H ₄	C ₆ H ₅ COCH =CHC ₆ H ₄ OCH ₃	291	84	164-165 (164) ^[1]	---
6	4-NH ₂ C ₆ H ₅	C ₄ H ₃ (3-Furyl)	C ₆ H ₅ COCH =CHC ₄ H ₃	213	82	120-121 (119-120) ^[2]	---
7	4-NH ₂ C ₆ H ₄	C ₆ H ₅	4-NH ₂ C ₆ H ₄ COCH =CHC ₆ H ₅	223	82	98-99 (98-99) ^[1]	---
8	4-NH ₂ C ₆ H ₄	4-N (C ₂ H ₅) ₂ C ₆ H ₄	4-NH ₂ C ₆ H ₄ COCH =CHC ₆ H ₄ N(CH ₃) ₂	294	82	90-91 (90-91) ^[1]	---
9	4-NH ₂ C ₆ H ₄	2,6-Cl ₂ C ₆ H ₃	4-NH ₂ C ₆ H ₄ COCH =CHC ₆ H ₃ Cl ₂	291	80	98-99	---
10	4-ClC ₆ H ₄	C ₆ H ₅	4-ClC ₆ H ₄ COCH =CHC ₆ H ₅	242	83	99-100 (98-100) ^[24]	---
11	4-F- C ₆ H ₄	C ₆ H ₅	4-FC ₆ H ₄ COCH =CHC ₆ H ₅	226	83	49-50 (49-50) ^[1]	---
12	2, 4-Cl ₂ C ₆ H ₃	C ₆ H ₅	2,4-Cl ₂ C ₆ H ₃ COCH =CHC ₆ H ₅	276	84	80-82 (80-81) ^[1]	---
13	3, 4-Cl ₂ C ₆ H ₃	C ₆ H ₅	3,4-Cl ₂ C ₆ H ₃ COCH =CHC ₆ H ₅	276	84	100-101 (100-101) ^[1]	---
14	4-(OH) C ₆ H ₄	C ₆ H ₅	2,5-(OH)C ₆ H ₃ COCH=CHC ₆ H ₅	226	84	63-64 (63-64) ^[1]	---
15	C ₁₀ H ₇ (1-Naph)	C ₆ H ₅	C ₁₀ H ₇ COCH: CHC ₆ H ₅	258	84	100-102 (100-102) ^[1]	---
16	4-BrC ₁₀ H ₆ (1-Naph)	C ₆ H ₅	4-BrC ₁₀ H ₆ COCH=CHC ₆ H ₅	396	55	103-104 (103-104) ^[1]	---
17	4-ClC ₁₀ H ₆ (1-Naph)	C ₆ H ₅	4-ClC ₁₀ H ₆ COCH=CHC ₆ H ₅	292	44	122-123 (122-123) ^[1]	---
18	4-OCH ₃ C ₁₀ H ₆ (1-Naph)	C ₆ H ₅	4-OCH ₃ C ₁₀ H ₆ COCH=CHC ₆ H ₅	310	83	113-114 (113-114) ^[1]	---
19	4-CH ₃ C ₁₀ H ₆ (1-Naph)	C ₆ H ₅	4-CH ₃ C ₁₀ H ₆ COCH =CHC ₆ H ₅	284	84	98-99 (98) ^[1]	---
20	C ₁₀ H ₇ (2-Naph)	C ₆ H ₅	C ₁₀ H ₇ COCH: CHC ₆ H ₅	258	84	104-105 (104-105) ^[1]	---
21	6-OCH ₃ C ₁₀ H ₆ (2-Naph)	C ₆ H ₅	6-OCH ₃ C ₁₀ H ₆ COCH=CHC ₆ H ₅	310	85	67-68 (67-68) ^[1]	---
22	6-CH ₃ C ₁₀ H ₆ (2-Naph)	C ₆ H ₅	6-CH ₃ C ₁₀ H ₆ COCH=CHC ₆ H ₅	284	84	123-124 (123-124) ^[1]	---
23	C ₁₃ H ₉ (2-Fluorene)	C ₆ H ₅	C ₁₃ H ₉ COCH =CHC ₆ H ₅	296	80	150-151 (150-151) ^[1]	---
24	C ₁₂ H ₉ (Biphenyl)	C ₆ H ₅	C ₁₂ H ₉ COCH =CHC ₆ H ₅	284	85	153-154 (153-154) ^[1]	---
25	C ₄ H ₃ O (2-Furyl)	C ₆ H ₅	C ₄ H ₃ OCOCH =CHC ₆ H ₅	198	85	80-81 (80-81) ^[1]	---
26	5-CH ₃ C ₄ H ₂ N(2-Pyrrole)	C ₆ H ₅	5-CH ₃ C ₄ H ₂ NCOCH=CHC ₆ H ₅	210	84	137-138 (137-138) ^[1]	---
27	C ₄ H ₃ S (2-Thienyl)	C ₆ H ₅	C ₄ H ₃ SCOCH =CHC ₆ H ₅	204	85	112-113 (112-113) ^[1]	---
28	C ₁₄ H ₁₀ (Anthracene)	C ₆ H ₅	C ₁₄ H ₉ COCH =CHC ₆ H ₅	308	82	124-125 (124-125) ^[1]	---

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Entry	Ar	Ar'	Product	M. W.	Yield (%)	M.p. (°C)	Mass (m/z)
29	5-BrC ₄ H ₂ S (2-Thienyl)	C ₆ H ₅	5-BrC ₄ H ₂ SCoCH =CHC ₆ H ₅	292	86	107-110 (106-107) ⁽¹⁾	---
30	4-C ₂ H ₅ OC ₆ H ₄	C ₆ H ₅	4-C ₂ H ₅ C ₆ H ₄ COCH=CHC ₆ H ₅	236	87	71-72	236[M+], 221, 207, 159, 146, 133, 131, 119, 105, 103, 90, 77, 29, 15
31	4-C ₂ H ₅ OC ₆ H ₄	3-BrC ₆ H ₄	4-C ₂ H ₅ C ₆ H ₄ COCH =CHC ₆ H ₄ Br	314	85	88-89	314[M+], 316[M2+], 284, 208, 180, 167, 159, 155, 146, 133, 118, 90, 77, 15
32	4-C ₂ H ₅ OC ₆ H ₄	4-BrC ₆ H ₄	4-C ₂ H ₅ C ₆ H ₄ COCH =CHC ₆ H ₄ Br	314	86	132-133	314[M+], 316[M2+], 284, 208, 180, 167, 159, 155, 146, 133, 118, 105, 79, 90, 77, 29, 15
33	4-C ₂ H ₅ OC ₆ H ₄	3-ClC ₆ H ₄	4-C ₂ H ₅ C ₆ H ₄ COCH =CHC ₆ H ₄ Cl	270	84	89-90	270[M+], 272[M2+], 265, 255, 235, 165, 159, 133, 124, 118, 105, 79, 90, 77, 29, 15
34	4-C ₂ H ₅ OC ₆ H ₄	4-ClC ₆ H ₄	4-C ₂ H ₅ C ₆ H ₄ COCH =CHC ₆ H ₄ Cl	270	86	126-127	270[M+], 272[M2+], 265, 255, 241, 235, 165, 159, 146, 137, 133, 132, 124, 118, 105, 79, 91, 77, 54, 29, 15
35	4-C ₂ H ₅ OC ₆ H ₄	4-FC ₆ H ₄	4-C ₂ H ₅ C ₆ H ₄ COCH =CHC ₆ H ₄ F	254	86	101-102	254[M+], 256[M2+], 239, 225, 159, 149, 146, 133, 131, 121, 108, 105, 77, 29, 19, 15
36	4-C ₂ H ₅ OC ₆ H ₄	2-OCH ₃ C ₆ H ₄	4-C ₂ H ₅ C ₆ H ₄ COCH =CHC ₆ H ₄ OCH ₃	266	87	98-99	266[M+], 251, 237, 235, 161, 159, 146, 134, 131, 105, 91, 77, 29, 19, 15
37	4-C ₂ H ₅ OC ₆ H ₄	4-OCH ₃ C ₆ H ₄	4-C ₂ H ₅ C ₆ H ₄ COCH =CHC ₆ H ₄ OCH ₃	208	266	91-92	266[M+], 251, 237, 235, 161, 159, 146, 134, 133, 131, 120, 118, 107, 105, 91, 77, 31, 29, 26, 19, 15
38	4-C ₂ H ₅ OC ₆ H ₄	4- CH ₃ C ₆ H ₄	4-C ₂ H ₅ C ₆ H ₄ COCH? CHC ₆ H ₄ CH ₃	250	86	97-98	250[M+], 255, 221, 159, 146, 145, 133, 117, 107, 105, 91, 77, 29, 15
39	4-C ₂ H ₅ OC ₆ H ₄	3- NO ₂ C ₆ H ₄	4-C ₂ H ₅ C ₆ H ₄ COCH =CHC ₆ H ₄ NO ₂	281	85	91-92	281[M+], 266, 252, 176, 159, 148, 122, 105, 77, 27, 26, 15
40	4-C ₂ H ₅ OC ₆ H ₄	3- NO ₂ C ₆ H ₄	4-C ₂ H ₅ C ₆ H ₄ COCH =CHC ₆ H ₄ NO ₂	281	85	118-119	281[M+], 266, 252, 235, 176, 159, 148, 146, 135, 133, 122, 119, 105, 77, 27, 26, 15

TABLE 2 : Reusability of catalyst on condensation of 4-ethoxyacetophenone (2 mmol) and benzaldehydes (2 mmol) under microwave irradiation

Run	1	2	3	4	5
Yield	87	87	86.5	86.5	85

IR spectral study

The synthesized chalcones in the present study are shown in Scheme 2. The carbonyl stretching frequencies (cm⁻¹) of *s-cis* and *s-trans* isomers of present study are presented in TABLE 3 and the corresponding conformers are shown in Figure 4. The stretching frequencies for carbonyl absorption are assigned based on the assignments made by Hays and Timmons^[50] for *s-cis* and *s-trans* conformers at 1690 and 1670 cm⁻¹, respectively.

These data have been correlated with Hammett substituent constants and Swain-Lupton constants^[51]. In this correlation the structure parameter Hammett equation employed is as shown in the following equation:

$$v = \rho\sigma + v_0 \quad (1)$$

Where v is the carbonyl frequencies of substituted system and v_0 is the corresponding quantity of unsubstituted system; σ is a Hammett substituent constant, which in principle is characteristics of the substituent and ρ is a reaction constant which is depend upon the nature of the reaction. Hammett equation is one of the important

tools for studying linear free energy relationships and it has been widely used in structures of the chemical reactivity of substituted aromatic system.

TABLE 3 : The IR spectroscopic data of substituted styryl 4-ethoxyphenyl ketones(entries 30-40)

Entry	Substt	CO <i>s-cis</i>	CO <i>s-trans</i>	CH _{ip}	CH _{op}	CH=CH _{op}	C=C _{op}
30	H	1658.60	1601.13	1049.30	763.19	1189.19	566.45
31	3-Br	1658.76	1610.57	1046.07	795.75	1182.49	577.30
32	4-Br	1656.74	1630.01	1073.18	745.72	1177.39	538.45
33	3-Cl	1659.72	1610.79	1079.82	797.47	1183.06	579.15
34	4-Cl	1664.35	1603.01	1021.05	758.13	1178.08	569.21
35	4-F	1655.47	1598.84	1048.86	744.50	1155.90	532.23
36	2-OCH ₃	1651.99	1601.60	1052.88	795.32	1170.20	526.87
37	4-OCH ₃	1652.94	1608.21	1023.78	754.32	1170.02	551.73
38	2-CH ₃	1653.07	1599.92	1028.36	742.26	1170.34	536.10
39	3-NO ₂	1652.42	1600.93	1036.57	728.37	1175.53	576.57
40	4-NO ₂	1664.95	1600.67	1037.42	712.33	1170.92	539.54

The results of single parameter statistical analysis of carbonyl frequencies with substituent constants are presented in TABLE 4. From TABLE 4, the *s-cis* conformers the correlation of $v_{C=O}$ (cm⁻¹) with Hammett σ , σ^+ and σ_R constants were satisfactory. The remaining Hammett constants and F and R parameters fails in correlation. There is no correlation found for *s-trans* conformers. Some of the correlations gave the negative ρ values obtained for *s-trans* conformers. The positive

ρ values obtained for *s-cis* conformers implies that there is a normal substituent effects operates in all systems. The failure in correlation is due the conjugation between the substituent and the carbonyl group in chalcones as shown in Figure 5.

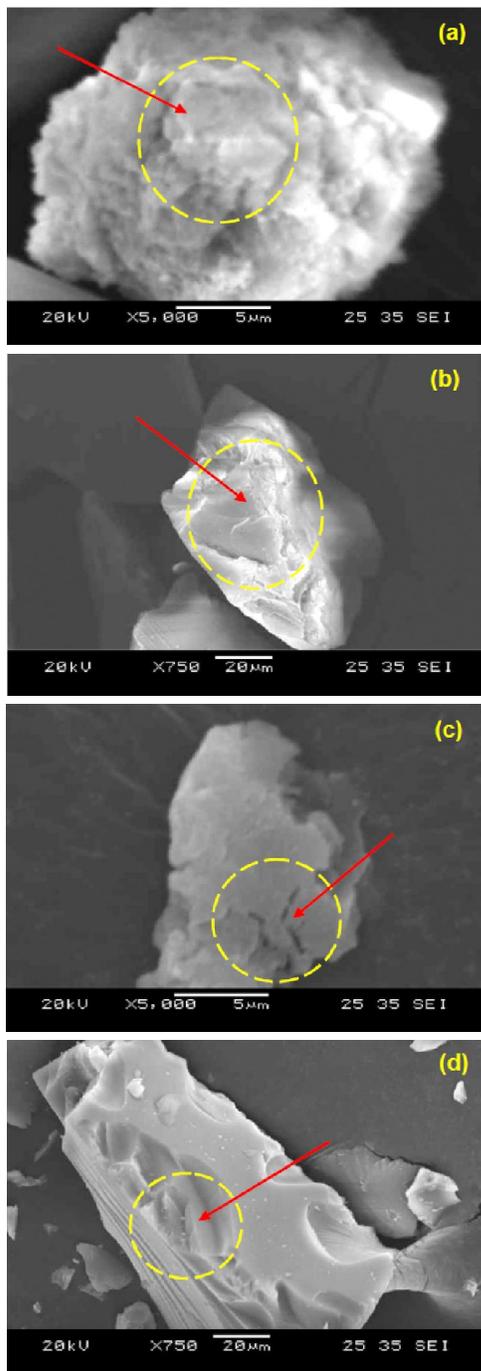


Figure 1 : SEM images of pure SiO₂ and H₃PO₄: (a) Pure SiO₂ (5µm); (b) Pure SiO₂ (20 µm); (c) SiO₂ - H₃PO₄ (5µm) (⇨ - corroded); (d) SiO₂ - H₃PO₄ (20 µm) (⇨ - corroded)

The correlation of CH *in-plane* modes with

Hammett σ constants and R parameters gave poor correlations. The CH *out of plane* modes gave satisfactory correlation with Hammett σ_R constant except 3-Br and 3-Cl substituents. The remaining substituent constants and F and R parameters were fail in the correlation of both the modes for all ketones. A satisfactory correlation obtained for CH=CH *out of plane* with Hammett σ_R and R parameters. The C=C *out of plane* modes with Hammett σ and σ_R gave satisfactory correlations except halogen substituents. All correlation gave positive ρ values and this reveals that there is a normal substituent effects operated in all ketones. The failure in correlation is due the conjugation between the substituent and the carbonyl group in chalcones as shown in Figure 5.

In view of the inability of some of the σ constants to produce individually satisfactory correlations, it was thought that worthwhile to seek multiple correlations involving either σ_I and σ_R constants or Swain-Lupton's^[51], F and R parameters. The correlation equations for *s-cis*, *s-trans* and *deformation modes* are given in equations 2-13.

$$\nu\text{CO}_{s-cis} (\text{cm}^{-1}) = 1656.70(\pm 3.197) + 4.789(\pm 2.167)\sigma_I + 7.553(\pm 0.603)\sigma_R \quad (2)$$

$$(R = 0.950, n = 11, P > 95\%)$$

$$\nu\text{CO}_{s-cis} (\text{cm}^{-1}) = 1657.33(\pm 2.966) + 4.037(\pm 0.157)F + 7.841(\pm 0.542)R \quad (3)$$

$$(R = 0.949, n = 11, P > 90\%)$$

$$\nu\text{CO}_{s-trans} (\text{cm}^{-1}) = 1603.20(\pm 7.203) + 6.382(\pm 1.427)\sigma_I - 1.602(\pm 0.135)\sigma_R \quad (4)$$

$$(R = 0.915, n = 11, P > 90\%)$$

$$\nu\text{CO}_{s-trans} (\text{cm}^{-1}) = 1604.78(\pm 6.729) + 1.766(\pm 1.322)F - 2.184(\pm 1.240)R \quad (5)$$

$$(R = 0.907, n = 11, P > 90\%)$$

$$\nu\text{CH}_{ip} (\text{cm}^{-1}) = 1038.06(\pm 14.882) + 14.321(\pm 2.952)\sigma_I - 8.726(\pm 2.809)\sigma_R \quad (6)$$

$$(R = 0.918, n=11, P>90\%,)$$

$$\nu\text{CH}_{ip} (\text{cm}^{-1}) = 1040.90(\pm 13.905) + 9.078(\pm 2.733)F - 3.100(\pm 2.517)R \quad (7)$$

$$(R = 0.912, n=11, P>90\%,)$$

$$\nu\text{CH}_{op} (\text{cm}^{-1}) = 754.319(\pm 19.405) - 17.068(\pm 3.842)\sigma_I - 55.996(\pm 3.628)\sigma_R \quad (8)$$

$$(R = 0.952, n=11, P>90\%,)$$

$$\nu\text{CH}_{op} (\text{cm}^{-1}) = 761.604(\pm 18.012) - 34.624(\pm 3.594)F - 45.129(\pm 3.259)R \quad (9)$$

$$(R = 0.951, n=11, P>90\%)$$

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TABLE 4 : Results of statistical analysis of infrared $\nu(\text{cm}^{-1})$ CO_{s-cis}, CO_{s-trans}, CH_{ip}, CH_{op}, CH=CH_{op} and C=C_{op} substituted styryl 4-ethoxyphenyl ketones (entries 30-40) with Hammett σ , σ^+ , σ_1 , σ_R constants and F and R parameters

Frequency	Constants	R	I	ρ	S	n	Correlated derivatives
CO _{s-cis}	σ	0.954	1656.03	6.484	4.06	9	H, 3-Br, 4-Br, 3-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 4-NO ₂
	σ^+	0.952	1656.61	4.909	4.11	9	H, 3-Br, 4-Br, 3-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 4-NO ₂
	σ_I	0.732	1654.65	6.532	4.57	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.900	1658.76	8.555	4.30	10	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 4-NO ₂
	F	0.822	1655.48	4.281	4.70	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.844	1658.96	7.956	4.31	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂ , 4-NO ₂
CO _{s-trans}	σ	0.806	1605.96	1.549	9.52	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.817	1603.64	3.180	9.39	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.715	1605.92	6.031	9.43	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.800	1605.29	-0.267	9.54	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.804	1605.49	1.698	9.83	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.806	1609.30	-2.137	9.52	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂ , 4-NO ₂
CH _{ip}	σ	0.817	1044.25	5.831	19.66	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.829	1043.89	11.376	18.91	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.814	1040.43	12.316	19.59	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.707	1044.16	-5.729	19.75	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.811	1041.64	8.981	19.67	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.708	1044.57	-2.835	19.79	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂ , 4-NO ₂
CH _{op}	σ	0.839	763.10	-29.136	27.31	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.829	759.90	-17.188	28.37	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.824	769.55	-29.995	28.86	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.905	747.05	-59.567	25.70	9	H, 4-Br, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.835	772.25	-36.032	28.29	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.800	747.64	-46.065	-46.06	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂ , 4-NO ₂
CH=CH _{op}	σ	0.822	1173.91	5.157	9.12	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.831	1174.18	5.641	8.89	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.824	1178.48	-9.446	9.08	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.949	1178.19	18.493	8.13	8	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-OH, 4-OCH ₃ ,
	F	0.835	1032.52	56.526	34.38	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.801	1054.32	13.132	36.75	9	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃
C=C _{op}	σ	0.974	549.57	24.751	18.78	8	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OCH ₃ , 2-CH ₃ , 3-NO ₂
	σ^+	0.741	552.02	16.891	19.31	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.815	548.49	14.191	20.96	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.947	561.35	40.473	18.64	10	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂
	F	0.825	538.24	17.351	21.22	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.846	526.06	36.205	18.78	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂ , 4-NO ₂

r=Correlation coefficient; ρ = Slope; I=Intercept; s= Standard deviation; n= Number of substituents

$$\nu\text{-CH}=\text{CH}_{op}(\text{cm}^{-1}) = 1184.325(\pm 5.661) - 16.820(\pm 9.127)F + 19.202(\pm 8.491)R \quad (11)$$

$$-14.397(\pm 1.122)\sigma_1 + 21.451(\pm 10.686)\sigma_R \quad (10) \quad (R = 0.971, n=11, P>90\%)$$

 $(R = 0.961, n=11, P>90\%)$

$$\nu\text{-C}=\text{C}_{op}(\text{cm}^{-1}) = 559.19(\pm 14.217) + 5.095(\pm 2.818)\sigma_1 + 39.407(\pm 2.683)\sigma_R \quad (12)$$

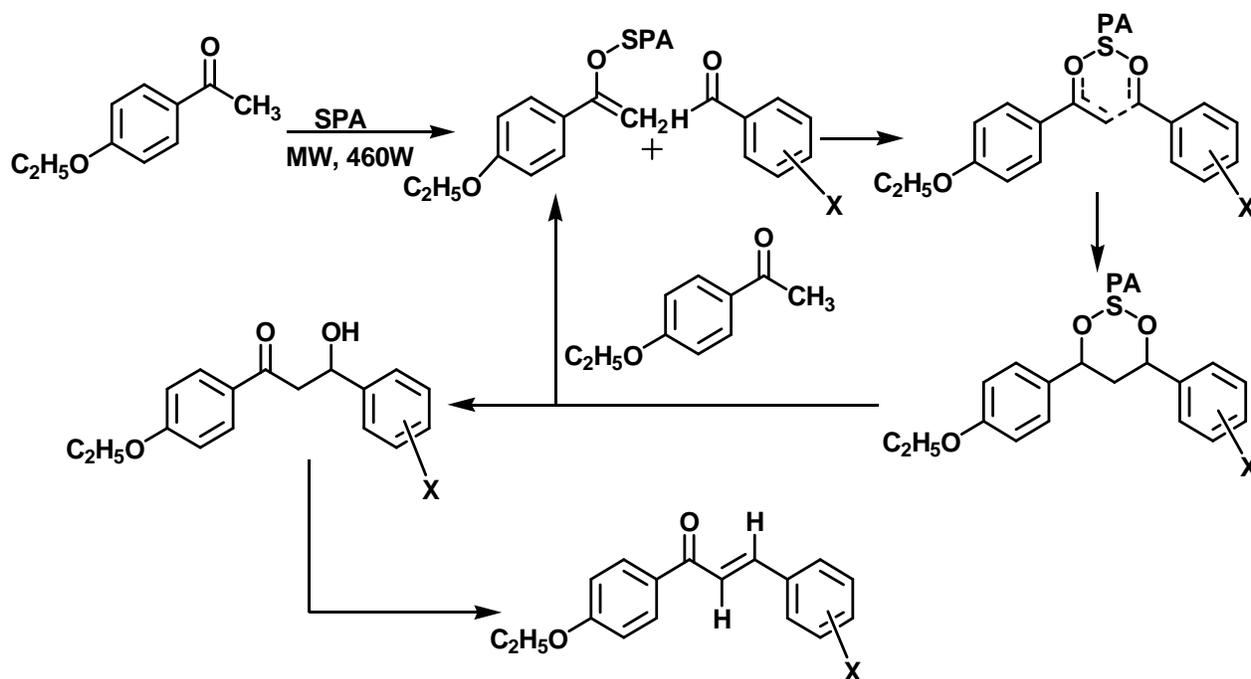


Figure 2 : Proposed mechanism for the synthesis of styryl 4-ethoxyphenyl ketone using silica-phosphoric acid catalyzed aldol condensation between 4-ethoxyacetophenones and benzaldehydes

TABLE 5 : NMR chemical shifts δ (ppm) of substituted styryl 4-ethoxyphenyl ketones (entries 30-40)

Entry	Substituent	δH_{α}	δH_{β}	Substt.	δC_{α}	δC_{β}	δCO	Substt.
30	H	7.557	7.807	---	121.93	143.91	188.76	---
31	3-Br	7.286	7.709	---	123.12	142.05	188.24	---
32	4-Br	7.536	7.727	---	122.44	142.44	188.39	---
33	3-Cl	7.545	7.725	---	123.14	142.15	188.27	---
34	4-Cl	7.523	7.797	---	122.33	142.42	188.44	---
35	4-F	7.485	7.767	---	121.62	142.61	188.51	---
36	2-OCH ₃	7.437	7.785	3.854	119.61	143.76	188.79	63.78
37	4-OCH ₃	7.438	7.781	3.854	119.57	143.77	188.8	63.78
38	2-CH ₃	7.514	7.787	2.393	120.92	144.02	188.87	21.55
39	3-NO ₂	7.674	7.825	---	122.19	140.77	187.82	---
40	4-NO ₂	7.163	7.705	---	123.81	146.6	187.88	---

($R = 0.948$, $n=11$, $P>90\%$)

$$\nu > C = C <_{op} (\text{cm}^{-1}) = 561.783 (\pm 13.287) + 0.685 (\pm 0.026) F + 36.187 (\pm 2.431) R \quad (13)$$

($R = 0.946$, $n=11$, $P>90\%$)

¹H NMR spectral study

The ¹H NMR spectra of synthesized chalcones were recorded in deuteriochloroform solutions employing tetramethylsilane (TMS) as internal standard. The signals of the ethylenic protons were assigned from their spectra. They were calculated as AB or AA' or BB'

systems respectively. The lower chemical shifts (ppm) obtained for H_α and higher chemical shifts (ppm) obtained for H_β in this series of ketones. The vinyl protons give an AB pattern and the β-proton doublets were well separated from the signals of the aromatic protons. The assigned vinyl proton chemical shifts δ (ppm) of all ketones were presented in TABLE 5.

In nuclear magnetic resonance spectra, the proton or the ¹³C chemical shifts (δ) depends on the electronic environment of the nuclei concerned. The assigned vinyl proton chemical shifts (ppm) have been correlated with reactivity parameters using Hammett equation in the form of

$$\text{Log } \delta = \text{Log } \delta_0 + \rho \sigma \quad (14)$$

Where δ_0 is the chemical shift of unsubstituted ketones.

The assigned H_α and H_β proton chemical shifts (ppm) are correlated with various Hammett sigma constants. The results of statistical analysis^[2,3,5,9,12,27-29,47-49] are presented in TABLE 6. The obtained correlations were satisfactory for H_α with Hammett σ , σ^+ , σ_R , constants and R parameters. A fair degree of correlation is obtained for H_β proton chemical shifts (ppm) with Hammett sigma σ , σ^+ constants and R parameters. All correlations gave negative ρ values. The remaining substituent constants were fails in correlation for both the

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proton chemical shifts and is due to the reasons stated in earlier and the conjugative structure shown in Figure 5.

TABLE 6 : Results of statistical analysis of infrared δ (ppm) of ethylenic protons, carbons and carbonyl carbons of substituted styryl 4-ethoxyphenyl ketones (entries 30-40) with Hammett σ , σ^+ , σ_I , σ_R constants and F and R parameters

Frequency	Constants	R	P	I	s	n	Correlated derivatives
δ_{H_a} (ppm)	σ	0.917	-0.068	7.480	0.14	9	H, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂
	σ^+	0.911	-0.033	7.472	0.14	9	H, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂
	σ_I	0.822	-0.135	7.524	0.14	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.901	-0.007	7.467	0.14	9	H, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂
	F	0.820	-0.118	7.515	0.14	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.901	0.007	7.470	0.14	9	H, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂
δ_{H_β} (ppm)	σ	0.936	-0.039	7.772	0.04	8	3-Br, 4-Br, 3-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 4-NO ₂
	σ^+	0.940	-0.033	7.768	0.04	8	3-Br, 4-Br, 3-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 4-NO ₂
	σ_I	0.838	-0.071	7.792	0.04	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.807	-0.013	7.762	0.04	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.833	-0.057	7.787	0.04	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.902	-0.004	7.763	0.04	7	H, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂ ,
δ_{C_a} (ppm)	σ	0.913	2.331	124.39	7.07	10	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 4-NO ₂
	σ^+	0.906	0.938	124.08	7.13	10	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 4-NO ₂
	σ_I	0.848	-14.161	121.63	6.23	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.871	5.051	124.90	7.03	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.845	-12.589	129.08	6.35	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.819	5.164	125.13	7.00	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂ , 4-NO ₂
δ_{C_β} (ppm)	σ	0.927	4.998	140.14	7.02	10	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂
	σ^+	0.921	3.015	140.18	7.03	10	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂
	σ_I	0.953	16.188	134.76	6.079	10	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂
	σ_R	0.801	-0.544	140.93	7.20	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.949	13.947	135.49	6.27	9	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂
	R	0.803	-1.032	140.80	7.20	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂ , 4-NO ₂
δ_{C_O} (ppm)	σ	0.939	2.103	188.76	1.95	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.932	1.350	188.93	2.00	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.926	2.936	188.18	2.05	9	3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.937	3.205	189.67	1.96	9	3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.923	1.997	188.29	2.06	10	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 2-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.937	2.907	189.74	1.97	9	3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 4-OCH ₃ , 3-NO ₂ , 4-NO ₂

r=Correlation coefficient; ρ = Slope; I=Intercept; s= Standard deviation; n= Number of substituents

Application of Swain-Lupton^[51] treatment to the relative chemical shifts of H_a and H_β with F and R values is successful with resonance, inductive and fail with F and R parameter generates the multi regression equations 15-18.

$$\delta H_a (\text{ppm}) = 7.527(\pm 0.109) - 0.140(\pm 0.017)\sigma_I + 0.221(\pm 0.026)\sigma_R \quad (15)$$

(R = 0.922, n = 11, P > 90 %)

$$\delta H_a (\text{ppm}) = 7.518(\pm 0.101) - 0.118(\pm 0.019)F$$

$$+ 0.010(\pm 0.001)R \quad (16)$$

$$(R = 0.920, n = 11, P > 90 \%)$$

$$\delta H_\beta (\text{ppm}) = 7.793(\pm 0.030) - 0.071(\pm 0.061)\sigma_I + 0.051(\pm 0.005)\sigma_R \quad (17)$$

$$(R = 0.938, n = 11, P > 90 \%)$$

$$\delta H_\beta (\text{ppm}) = 7.787(\pm 0.029) - 0.057(\pm 0.005)F - 0.036(\pm 0.001)R \quad (18)$$

$$(R = 0.933, n = 11, P > 90 \%)$$

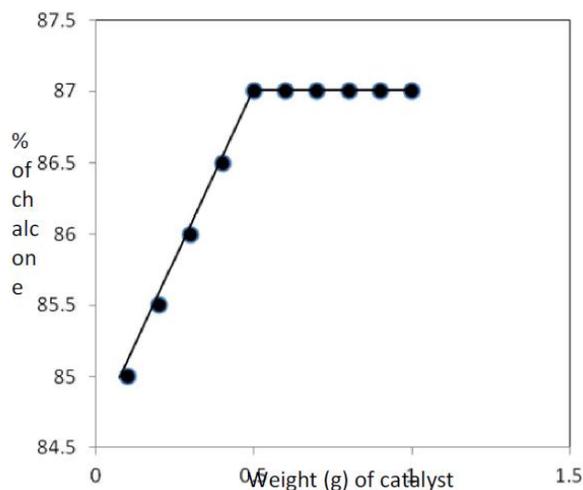


Figure 3 : Effect of catalyst loading

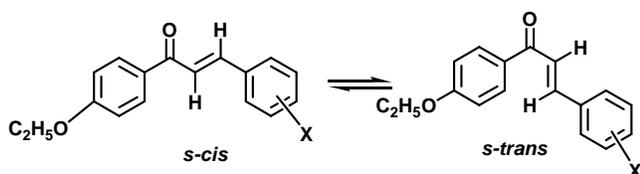


Figure 4 : The *s-cis* and *s-trans* conformers of substituted styryl 4-ethoxyphenyl ketones

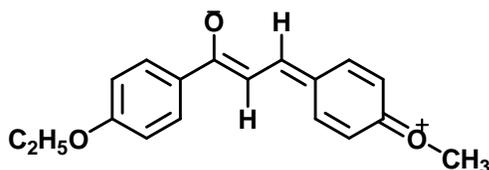


Figure 5 : The resonance – conjugative structure

¹³C NMR spectral study

Spectral analysts, organic chemists and scientists^[2,3,5,9,12,27-29,47-49] have made extensive study of ¹³C NMR spectra for a large number of different ketones and styrenes. The assigned vinyl C_α, C_β and carbonyl carbon chemical shifts are presented in TABLE 5. The results of statistical analysis are given in TABLE 6. The C_α chemical shifts (ppm) gave satisfactory correlation with Hammett substituent constants, F and R parameters along with positive ρ values. The chemical shifts (ppm) of C_β carbon with Hammett σ, σ⁺ constants gave satisfactory correlation. Remaining Hammett σ constants, F and R parameters were fails in correlation. This is due to reasons stated earlier with the resonance conjugative structure shown in Figure 5. The carbonyl carbon chemical shifts (ppm) of all ketones gave satisfactory correlation with Hammett σ, σ⁺, σ₁ constants and F parameters except halogen and nitro substituents.

The Swain Luptons^[51] parameter correlations were satisfactorily obtained within these carbon chemical shifts and the regression equations are given in 29-24.

$$\delta C_{\alpha} (\text{ppm}) = 131.95 (\pm 4.448) - 16.581 (\pm 8.829) \sigma_1 + 8.523 (\pm 0.421) \sigma_R \quad (19)$$

$$(R = 0.956, n = 11, P > 95 \%)$$

$$\delta C_{\alpha} (\text{ppm}) = 130.39 (\pm 4.365) - 13.031 (\pm 8.881) F + 5.515 (\pm 1.671) R \quad (20)$$

$$(R = 0.950, n = 11, P > 95 \%)$$

$$\delta C_{\beta} (\text{ppm}) = 143.643 (\pm 4.358) + 17.141 (\pm 9.087) \sigma_1 - 4.130 (\pm 0.187) \sigma_R \quad (21)$$

$$(R = 0.955, n = 11, P > 95 \%)$$

$$\delta C_{\beta} (\text{ppm}) = 145.162 (\pm 4.428) + 13.990 (\pm 8.703) F - 1.413 (\pm 0.817) R \quad (22)$$

$$(R = 0.950, n = 11, P > 95 \%)$$

$$\delta CO (\text{ppm}) = 188.96 (\pm 1.474) + 1.665 (\pm 0.297) \sigma_1 - 2.851 (\pm 0.278) \sigma_R \quad (23)$$

$$(R = 0.942, n = 11, P > 90 \%)$$

$$\delta CO (\text{ppm}) = 188.97 (\pm 1.352) + 1.909 (\pm 0.265) F + 2.856 (\pm 0.247) R \quad (24)$$

$$(R = 0.943, n = 11, P > 90 \%)$$

Antimicrobial activities

Aryl propenones possess a wide range of multipronged biological activities such as antibacterial, antifungal^[52,53], antiviral^[54], antifeedant^[3,29], anticancer^[55], antimalarial^[56], antituberculosis^[57], antiAIDS^[28] and antioxidant^[58] activities. These multiprolonged activities present in different chalcones are examined against respective microbes-bacteria's and fungi.

Antibacterial sensitivity assay

Measurement of antibacterial sensitivity assay was performed using Kirby-Bauer^[59] disc diffusion technique. In each Petri plate about 0.5 ml of the test bacterial sample was spread uniformly over the solidified Mueller Hinton agar using sterile glass spreader. Then the discs with 5 mm diameter made up of Whatmann No.1 filter paper, impregnated with the solution of the compound were placed on the medium using sterile forceps. The plates were incubated for 24 h at 37°C by keeping the plates upside down to prevent the collection of water droplets over the medium. After 24 h, the plates were visually examined and the diameter values of the zone of inhibition were measured. Triplicate results were recorded by repeating the same procedure.

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TABLE 7 : Antibacterial activities of substituted styryl 4-ethoxyphenyl ketones(entries 30-40)

Entry	X	E. coli	S. aureus	Pseudomonas	Klebsiella	P. vulgaris	Enterococcus faecalis
30	H	+	--	+	±	++	++
31	3-Br	--	++	+	++	+	±
32	4-Br	+	+	++	++	+	++
33	3-Cl	++	±	--	--	+	+
34	4-Cl	++	±	--	--	+	+
35	4-F	+	+	++	+	++	+
36	2-OCH ₃	--	++	+	++	--	++
37	4-OCH ₃	--	++	+	++	--	++
38	4-CH ₃	--	++	+	++	--	++
39	3-NO ₂	+	+	±	--	++	±
40	4-NO ₂	+	++	+	++	+	---

Disc size: 6.35 mm; Duration: 24-45 h; Standard: Ampicillin (30-33 mm) and Streptomycin(20-25 mm); Control: Methanol; —: No activities; ±: Active(8-12 mm); +: Moderately active(13-19 mm); ++: Active(20-24 mm)

TABLE 8 : Antifungal activities of substituted styryl4-ethoxyphenyl ketones(entries 30-40)

Entry	X	Disc diffusion technique(250µg/mL)	Drug dilution method (50µg/mL)	
		<i>Candida albicans</i>	<i>Penicillium</i>	<i>Aspergillus niger</i>
30	H	±	+	+
31	3-Br	---	±	+
32	4-Br	++	+	++
33	4-Cl	+	++	+
34	4-Cl	+	++	+
35	4-F	+	±	±
36	2-OCH ₃	++	---	++
37	4-OCH ₃	++	---	++
38	4-CH ₃	+	+	---
39	3-NO ₂	++	++	+
40	4-NO ₂	+	±	+

Disc size: 6.35 mm; Duration: 24-45 h; Standard: Ampicillin (30-33 mm) and Streptomycin(20-25 mm); Control: Methanol; —: No activities; ±: Active(8-12 mm); +: Moderately active(13-19 mm); ++: Active(20-24 mm)

The antibacterial activities of all prepared epoxides have been studied against two gram positive pathogenic strains *Staphylococcus aureus*, *Enterococcus faecalis* and four gram negative strains *Escherichia coli*, *Klebsiella species*, *Pseudomonas* and *Proteus vulgaris*. The disc diffusion technique was followed using the Kirby-Bauer^[59] method, at a concentration of 250 µg/mL with Ampicillin and Streptomycin used as the standard drugs. The measured antibacterial activities of all

ketones are presented in TABLE 7. Compounds 33 and 34 showed maximum zone of inhibition against *Escherichia coli*, with greater than 20 mm compared to the chalcones 32, 35, 39, and 40 and they are moderately active in 13-19 mm of zone of inhibition. The ketones 31, 36-38 and 40 were found to be effective against *S. aureus* within 20-24 mm of zone of inhibition. Compounds 32, 35, and 39 are moderately active within 13-19 mm of zone of inhibition. The chalcone 39 was active within 8-12 mm of zone of inhibition. The chalcone derivatives 32 and 35 were more active against *Pseudomonas* a showing greater than 20 mm zone of inhibition and the other derivatives showed the zone of inhibitions between 12-19 mm. The ketones 31,32, 36-38 and 40 are effective against *Klebsiella* with 20-24 mm zone of inhibition while the other ketones showed a moderate activity. The chalcones 30, 35 and 39 were active when it is screened against *P. vulgaris* and the other compounds are less effective. The ketones 30, 32, 36-38 showed activities against *E-faecalis* when they are screened with 20-24 mm zone of inhibition.

Antifungal sensitivity assay

Antifungal sensitivity assay was performed using Kirby-Bauer^[59] disc diffusion technique. PDA medium was prepared and sterilized as above. It was poured (ear bearing heating condition) in the Petri-plate which was already filled with 1 ml of the fungal species. The plate was rotated clockwise and counter clock-wise for uniform spreading of the species. The discs were impregnated with the test solution. The test solution was prepared by dissolving 15 mg of the chalcone in 1 ml of DMSO solvent. The medium was allowed to solidify and kept for 24 h. Then the plates were visually examined and the diameter values of zone of inhibition were measured. Triplicate results were recorded by repeating the same procedure.

The study of antifungal activities of all chalcones has been done with *Candida albicans* as the fungal strain using the disc diffusion technique and the other two strains *Penicillium* species and *Aspergillus niger*, the dilution method was adopted. The drug dilution was kept as 50 µg/mL. *Griseofulvin* has been taken as the standard drug. The observed antifungal activities of all chalcones are presented in TABLE 7. The study of an-

tifungal activities of all ketones against *C. albicans*, showed that the three compounds 32, 36, 37 and 39 are effective with 20 mm as the zone of inhibition in 250 µg/ disc while chalcones 33-35, 38 and 40 are active with 13-19 mm zone of inhibition and the compound 31 was the least active with 8-12 mm zone of inhibitions. Compounds 33, 34 and 39 are visible against *Penicillium* species, in the development of the fungal colony and 2-3 colonies are recorded for the compounds 31, 35 and 40. The inhibition of ketones against *A.niger* was less in one compound 38 and the ketones were highly active followed by 32, 36 and 37. Presence of a methoxy, methyl, dimethyl and bromo substituents are responsible for antimicrobial activities of chalcones.

CONCLUSIONS

We have developed an efficient crossed-aldol condensation for synthesis of chalcones using a versatile solid $\text{SiO}_2\text{-H}_3\text{PO}_4$ acid catalyst. The yield of the reaction is more than 85%. The effects of substituent on the group frequencies and the antimicrobial activities of all chalcones have been studied.

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