

Preheated Fly-Ash as Catalyst for the Synthesis of Chalcones under Microwave Irradiation, Correlation Studies and Anti-Microbial Activities

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Abstract: A series of 2, 6-dimethoxyphenyl chalcones have been synthesized by Crossed-Aldol condensation of 2, 6-dimethoxyacetophenone and substituted benzaldehydes. The purities of these chalcones have been checked by their physical constants, UV, IR, and NMR spectral data. The spectral data of these chalcones have been correlated with Hammett substituents constants, F and R parameters using single and multi-linear regression analysis. From the results of statistical analysis, the effect of substituents on the spectral group frequencies has been discussed. The anti-microbial activities of these chalcones have been evaluated using Bauer-Kirby disc diffusion method.

Keywords: Substituted styryl 2, 6-dimethoxyphenyl ketones; UV spectra, IR spectra, NMR spectra, Substituent effects, Antimicrobial activities.

1 Introduction

Enones or chalcones are 1, 3-diphenyl-2-propene-1-ones, in which two aromatic rings are linked by a three carbon α , β -unsaturated carbonyl system. Chalcones possess conjugated double bonds and a completely delocalized π -electron system on both the benzene rings. Chalcones can be isolated from several plants, and are precursors of flavone compounds. The name "Chalcone" was given by Kostanecki and Tambor [1]. Chalcones are well known intermediates for synthesizing various heterocyclic compounds. The compounds with the backbone of chalcones have been reported to possess various properties. Many of the chalcones are used as agro chemicals and also as drugs [2]. A variety of methods are available for the synthesis of chalcones and the most convenient method is the Crossed-Aldol condensation or Claisen-Schmidt condensation method.

Both the methods involve appropriate quantities of acetylated aliphatic or aromatic compounds, substituted aromatic aldehydes and aqueous alcoholic alkali or greener catalysts [3, 4]. Numerous catalysts, such as fly-ash: sulphuric acid [5], silica-sulphuric acid [6,7] anhydrous zinc chloride [8], ground chemistry catalysts-grinding the reactants with sodium hydroxide [9], aqueous alkali in lower temperatures [10], solid sulphonic acid from bamboo [11], barium hydroxide [12], anhydrous sodium bicarbonate [13], microwave [14], fly-ash:water [15], triphenylphosphite [16] alkali earth metals [17], KF/Al₂O₃

[18], sulfated titania [19], silicotungstic acid [20] SOCl₂ [21], preheated fly-ash [22], SiO₂-H₃PO₄ [23] and hydroxy apatite [24] have been utilized for the synthesis of chalcones, in solvent-assisted or solvent-free conditions. Chalcones possess various multipronged activities such as, antimicrobial [25], anti-viral [26], anti-cancers [27], anti-malarial [28], anti-AIDS [29], anti-plasmodial [30] and insect antifeedant activities [31]. In recent years, correlation analysis is applied by chemists to solve spectral problems. Conformational equilibrium [32] in the ground state of organic molecules has been investigated for *s-cis* and *s-trans* isomers of alkenes, α , β -unsaturated ketones, aldehydes, acyl halides and their esters, on the basis of spectral data. The present investigation is aimed at studying the effect of substituents and antimicrobial activities of some aryl styryl ketones. Recently, Thirunarayanan et al [33] have investigated the single and multi-substituent effects on alpha and beta hydrogens and carbons of furyl chalcones. Arulkumaran et al [34, 35] have studied the effect of substituents and antimicrobial activities of some substituted styryl 4'-nitrophenyl and 3-thienyl ketones. Similarly, Subramanian et al [36, 37] have investigated the synthesis, effects of substituents and antimicrobial activities of some substituted styryl 3-thienyl and furyl chalcones. Literature reviews reveal that there are no reports available for the solvent-free synthesis, study of substituent effects and antimicrobial activities with 2, 6-dimethoxyphenyl chalcones. Therefore, the authors have taken efforts to synthesize and to study the effect of substituents from spectral data of 2, 6-dimethoxyphenyl

chalcones. The antimicrobial activities of these chalcones have also been studied using Bauer-Kirby [38] disc diffusion method.

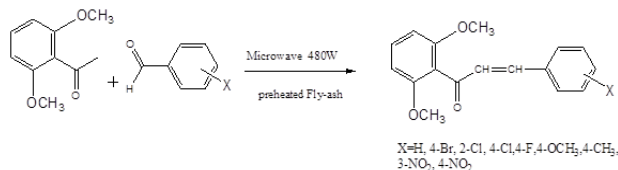
2 Experimental

2.1 General

All chemicals used were purchased from Sigma-Aldrich and E-Merck chemical companies. Melting points of all chalcones were determined in open glass capillaries on Mettler FP51 melting point apparatus and are uncorrected. The ELICO BL 222 ultraviolet spectrophotometer was utilized for recording the absorption maxima (λ_{\max} , nm), of all chalcones in spectral grade methanol. Infrared spectra (KBr, 4000-400 cm^{-1}) were recorded AVATAR-300 Fourier transform spectrophotometer. Bruker AV400 NMR spectrometer was used for recording NMR spectra operating at 400 MHz for ^1H spectra and 125.46 MHz for ^{13}C spectra in CDCl_3 solvent using TMS as internal standard.

2.2 Synthesis of Chalcones

Appropriate quantities of 2, 6-dimethoxyacetophenone (0.01mol) with benzaldehyde (0.01mol) and preheated fly-ash [39] (0.5g) were taken in 50ml corning glass tube and tightly capped. The reaction mixture was subjected to microwave irradiation for 8-10 minutes in a microwave oven (IFB Microwave Oven, 480W)(Scheme 1) 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 have been recrystallization with benzene-hexane yields glittering solid with melting point 70-72°C.



Scheme 1

Table 1: The physical constants and analytical data of styryl-2, 6-dimethoxy-phenyl ketones.

Entry	X	M.F.	M.W.	Yield (%)	m.p.(°C)
1	H	C ₁₇ H ₁₆ O ₃	268	90	70-72
2	4-Br	C ₁₇ H ₁₅ O ₃ Br	347	93	80-81
3	2-Cl	C ₁₇ H ₁₅ O ₃ Cl	302	94	74-75
4	4-Cl	C ₁₇ H ₁₅ O ₃ Cl	302	92	138-139
5	4-F	C ₁₇ H ₁₅ O ₃ F	286	90	84-85
6	4-OCH ₃	C ₁₈ H ₁₈ O ₄	298	92	110-111
7	4-CH ₃	C ₁₈ H ₁₈ O ₃	282	91	112-113
8	3-NO ₂	C ₁₇ H ₁₅ O ₅ N	313	91	144-145
9	4-NO ₂	C ₁₇ H ₁₅ O ₅ N	313	92	133-134

3. Results and discussion

3.1 Spectral linearity

In the present study the Hammett spectral linearity of these synthesized chalcones has been studied by evaluating the substituent effects on the group frequencies. The assigned spectroscopic data of all chalcones such as absorption maximum λ_{\max} (nm) of carbonyl groups, infrared carbonyl stretches of νCO_{s-cis} and $s-trans$, the deformation modes of vinyl part CH_{out} of *plane*, *in-plane*, $\text{CH}=\text{CH}$ and $>\text{C}=\text{C}<$ of *planes* (cm^{-1}), NMR chemical shifts δ (ppm) of H_α , H_β , C_α , C_β , CO are assigned and these data are correlated with various substituent constants.

3.1.1 UV spectral correlations

The measured ultraviolet absorption maxima (λ_{\max} , nm) of all 2, 6-methoxyphenyl chalcones were tabulated in Table 2. These values are correlated with Hammett substituent constants, F and R parameters using single and multi-linear regression analysis. While seeking Hammett correlation, involving UV absorption maximum values, the form of the Hammett equation employed is as given in equation.

$$\lambda_{\max} = \rho\sigma + \lambda_0 \quad (1)$$

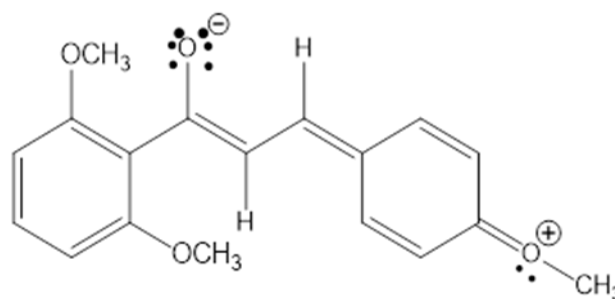


Fig 1: The resonance – conjugated structure.

Table 2: The ultraviolet absorption maxima (λ_{max} , nm), infrared absorptions (ν , cm^{-1}) and NMR chemical shifts (δ , ppm) of substituted Styryl-2, 6-dimethoxyphenyl ketones

Entry	X	λ_{max}	CO(<i>s-cis</i>)	CO(<i>s-trans</i>)	CH _{ip}	CH _{op}	CH=CH _{op}	C=C _{op}	H _a	H _β	C _a	C _β	CO
1	H	312.8	1648.21	1601.65	1195.60	753.35	1014.56	568.89	7.571	7.823	121.74	143.95	188.59
2	4-Br	310.4	1657.88	1602.09	1187.58	723.82	1025.93	540.99	7.439	7.599	119.46	141.58	192.00
3	2-Cl	297.4	1663.57	1600.00	1167.29	727.26	1037.05	546.82	7.420	8.057	120.11	138.93	192.17
4	4-Cl	310.6	1659.26	1603.71	1170.72	726.66	1022.00	563.77	7.423	7.614	119.42	141.54	192.02
5	4-F	329.4	1652.54	1596.27	1184.47	762.44	1025.89	543.76	7.491	7.783	121.34	142.72	188.41
6	4-OCH ₃	333.4	1660.57	1587.48	1170.75	716.57	1026.36	546.18	7.300	7.622	118.74	143.45	192.60
7	4-CH ₃	316.0	1661.23	1589.90	1174.06	717.82	1024.58	531.28	7.536	8.001	122.56	138.95	190.16
8	3-NO ₂	275.2	1664.63	1604.16	1163.51	729.92	1042.54	561.67	7.418	7.695	120.31	139.48	191.31
9	4-NO ₂	308.2	1660.27	1604.87	1177.89	860.27	1024.44	569.86	7.606	7.696	121.27	141.59	198.26

Table 3: Results of statistical analysis of UV λ_{max} , infrared $\nu(cm^{-1})$ CO_{s-cis}, CO_{s-trans}, CH_{ip}, CH_{op}, CH=CH_{op} and C=C_{op} substituted styryl-2,6-dimethoxyphenyl ketones with Hammett σ , σ^+ , σ_I , σ_R constants and F and R parameters.

Frequency	Constants	r	I	ρ	s	n	Correlated derivatives
λ_{max}	σ	0.907	317.15	-34.245	12.53	7	H, 4-Br, 2-Cl, 4-Cl, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	σ^+	0.907	314.27	-26.458	11.37	8	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 4-NO ₂
	σ_I	0.831	320.63	-26.593	16.76	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.900	302.48	-55.047	12.75	7	H, 4-Br, 2-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 4-NO ₂
	F	0.810	316.64	-15.527	17.74	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.900	300.88	49.656	11.87	7	H, 4-Br, 2-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 4-NO ₂
	CO _{s-cis}	σ	0.833	1657.71	4.902	5.27	9
σ^+		0.822	1658.27	2.780	5.40	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
σ_I		0.838	1655.63	7.913	5.17	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
σ_R		0.738	1657.71	4.902	5.27	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
F		0.782	1656.65	5.021	5.41	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
R		0.764	1659.41	3.820	5.50	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
CO _{s-trans}		σ	0.908	1596.07	14.313	3.91	7
	σ^+	0.900	1597.27	11.097	3.19	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.854	1593.50	14.000	5.61	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.862	1601.47	17.957	5.29	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.843	1594.74	10.311	6.13	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.845	1602.10	16.755	4.92	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	CH _{ip}	σ	0.823	1178.00	-6.728	10.88	9
σ^+		0.812	1177.19	-2.190	11.13	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
σ_I		0.732	1182.56	-14.755	10.44	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
σ_R		0.743	1176.61	-1.811	11.18	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
F		0.823	1181.13	-10.568	10.78	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
R		0.805	1176.45	-2.202	11.18	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
CH _{op}		σ	0.959	731.74	74.383	39.03	9
	σ^+	0.842	740.07	43.379	42.52	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.783	719.97	68.680	44.77	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.743	758.88	86.730	43.97	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.754	718.37	69.613	44.34	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.745	759.73	69.470	45.51	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	CH=CH _{op}	σ	0.843	1025.08	9.876	7.87	9
σ^+		0.754	1026.02	6.896	7.92	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
σ_I		0.756	1020.04	18.129	7.21	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
σ_R		0.811	1027.62	4.069	8.70	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
F		0.845	1020.71	15.676	7.53	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
R		0.812	1027.76	3.807	8.69	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
C=C _{op}		σ	0.843	548.12	22.527	11.80	9

	σ^+	0.815	550.68	12.899	12.93	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.730	546.36	16.130	14.01	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.705	557.78	36.286	11.89	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.819	548.59	9.876	14.42	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.610	558.81	32.610	11.52	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
$\delta_{H\alpha}$ (ppm)	σ	0.831	7.451	0.080	0.09	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.735	7.456	0.070	0.09	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.815	7.490	-0.061	0.09	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.854	7.499	0.223	0.13	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.811	7.483	-0.039	0.09	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.852	7.503	0.189	0.08	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
$\delta_{H\beta}$ (ppm)	σ	0.824	7.787	-0.112	0.17	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.803	7.767	-0.010	0.17	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.849	7.868	-0.267	0.16	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.805	7.759	-0.039	0.17	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.804	7.860	-0.235	0.16	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.822	7.768	0.014	0.17	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
δ_{CO} (ppm)	σ	0.854	190.80	4.638	0.58	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.844	191.34	2.558	2.77	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.844	189.55	5.630	2.68	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.840	192.48	5.319	2.83	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.783	190.16	3.876	2.89	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.838	192.54	4.298	2.85	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
$\delta_{C\alpha}$ (ppm)	σ	0.800	120.54	0.012	1.34	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.705	120.52	0.173	1.33	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.753	121.33	-2.037	1.21	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.735	120.80	1.782	1.27	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.828	121.09	-1.341	1.28	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.830	120.82	1.447	1.27	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
$\delta_{C\beta}$ (ppm)	σ	0.831	141.66	-1.584	1.91	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.741	141.58	-1.537	1.83	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.815	141.80	-1.173	1.98	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.792	141.00	-2.468	1.36	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.853	141.57	-0.551	1.58	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.832	140.90	-2.371	1.35	9	H, 4-Br, 2-Cl, 4-Cl, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂

The results of statistical analysis are presented in Table 3. From the Table 3, the UV absorption maxima (λ_{max} , nm) have been satisfactory correlation with Hammett substituent constants σ , σ^+ , σ_R and R parameter. The remaining Hammett substituent constants and F parameter were failing in correlation. This is due to the inductive, field and resonance effects of substituents incapable for predicting the reactivity on the absorption and is associated with the resonance conjugated structure as shown in Fig. 1.

$$\lambda_{max}(nm)=311.11(\pm 8.486)-21.306(\pm 17.022)\sigma_I + 52.178(\pm 19.620)\sigma_R \quad (2)$$

(R = 0.978, n = 9, P > 95%)

$$\lambda_{max}(nm)=307.76(7.861)-17.375(\pm 15.487)F- 50.317(\pm 15.760)R \quad (3)$$

(R = 0.980, n = 9, P > 95%)

In single parameter correlation, the Hammett substituents constants not obeyed in the regression. All the correlations with Hammett constants and F and R parameters have shown negative ρ values. This indicates the operation of reverse substituent effect in all aryl α,β -unsaturated ketone

compounds.

While seeking these parameters in multi-regression, with F and R Swain-Lupton's [40] constants, they gave satisfactory correlations. The multi correlation equations are given in 2 and 3.

3.2 IR spectral study

The synthesized chalcones in the present study are shown in Scheme 1. The carbonyl stretching frequencies (cm^{-1}) of *s-cis* and *s-trans* of isomers are tabulated in Table 2 and the corresponding conformers are shown in Fig. 2.

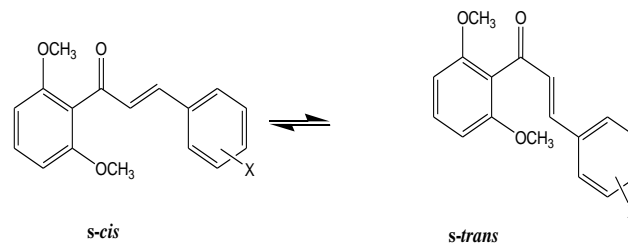


Fig 2: The *s-cis* and *s-trans* conformers of 2, 6-dimethoxyphenyl chalcones.

The assigned infrared CO *s-cis* and *s-trans* conformers have been correlated with Hammett substituent constants and Swain-Lupton constants [40]. In this correlation the structure parameter Hammett equation employed is as shown in the following equation:

$$\nu = \rho\sigma + \nu_0 \quad (4)$$

Where ν is the carbonyl frequencies of substituted system and ν_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.

The results of statistical analysis were shown in Table 3, from table 3, all the Hammett substituent constants and F and R parameters gave poor correlation with CO *s-cis* conformers stretches. The Hammett substituent constant σ and σ^+ satisfactory correlation with $\nu\text{CO}_{s-trans}$ conformers stretches .The remaining Hammett substituent constants and F & R parameters gave poor correlation with $\nu\text{CO}_{s-trans}$ conformers stretches. This is due to the reasons stated in earlier and associated with the resonance conjugative structure shown in Fig. 1.

All the Hammett substituent constants and F and R parameters gave poor correlation with CH_{ip} modes of all chalcones. The Hammett substituent constant σ only gave satisfactory correlation with CH_{op} modes of all chalcones. The remaining Hammett substituent constants and F & R parameters were failing in correlation. This failure in correlation is due to the incapability of resonance effects of the substituents and associated with the resonance conjugative structure as shown in Fig. 1.

The all Hammett substituent constants and F & R parameters gave poor correlation with $\text{CH}=\text{CH}_{op}$ modes. The all Hammett substituent constants and F & R parameters gave poor correlation with $\text{C}=\text{C}_{op}$ modes. This is due to the reasons stated earlier and associated with the resonance conjugative structure as shown in Fig. 1.

All the correlations with Hammett constants and F and R parameters have shown positive ρ values. This indicates the operation of normal substituent effect with respect to all the infrared frequency values except $\nu\text{CH}_{ip}(\text{cm}^{-1})$ of all aryl α,β -unsaturated ketone compounds.

Some of the single parameter correlations with Hammett substituent constants were not obeyed in the regression. While seeking these parameters in multi-regression with F and R Swain-Lupton's constants [40] they gave satisfactory correlations with the infrared red group frequencies. The multi correlation equations are given in 5 - 16.

$$\begin{aligned} \nu\text{CO}_{s-cis}(\text{cm}^{-1}) &= 1656.27(\pm 3.813) - 7.555(\pm 7.649)\sigma_I - \\ & 3.530(\pm 8.816)\sigma_R \quad (5) \\ (R = 0.941, n = 9, P > 90\%) \end{aligned}$$

$$\begin{aligned} \nu\text{CO}_{s-cis}(\text{cm}^{-1}) &= 1657.36(\pm 3.862) + 5.169(\pm 7.609)F + \\ & 4.017(\pm 7.743)R \quad (6) \\ (R = 0.932, n = 9, P > 90\%) \end{aligned}$$

$$\begin{aligned} \nu\text{CO}_{s-trans}(\text{cm}^{-1}) &= 1596.47(\pm 3.050) + 12.349(\pm 6.118)\sigma_I + \\ & 16.294(\pm 7.052)\sigma_R \quad (7) \\ (R = 0.982, n = 9, P > 95\%) \end{aligned}$$

$$\begin{aligned} \nu\text{CO}_{s-trans}(\text{cm}^{-1}) &= 1597.77(\pm 2.776) + 10.942(\pm 5.469)F + \\ & 17.171(\pm 5.566)R \quad (8) \\ (R = 0.982, n = 9, P > 95\%) \end{aligned}$$

$$\begin{aligned} \nu\text{CH}_{ip}(\text{cm}^{-1}) &= 1182.529(\pm 7.800) - 14.772(\pm 15.647)\sigma_I + \\ & 0.176(\pm 18.035)\sigma_R \quad (9) \\ (R = 0.934, n = 9, P > 90\%) \end{aligned}$$

$$\begin{aligned} \nu\text{CH}_{ip}(\text{cm}^{-1}) &= 1180.67(\pm 7.833) + 10.664(\pm 15.433)F - \\ & 2.607(\pm 15.705)R \quad (10) \\ (R = 0.927, n = 9, P > 90\%) \end{aligned}$$

$$\begin{aligned} \nu\text{CH}_{op}(\text{cm}^{-1}) &= 734.30(\pm 30.439) + 60.719(\pm 61.058)\sigma_I + \\ & 78.555(\pm 70.376)\sigma_R \quad (11) \\ (R = 0.958, n = 9, P > 95\%) \end{aligned}$$

$$\begin{aligned} \nu\text{CH}_{op}(\text{cm}^{-1}) &= 731.111(\pm 28.735) + 72.266(\pm 56.611)F + \\ & 72.219(\pm 57.609)R \quad (12) \\ (R = 0.958, n = 9, P > 95\%) \end{aligned}$$

$$\begin{aligned} \nu\text{CH}=\text{CH}_{op}(\text{cm}^{-1}) &= 1020.35(\pm 5.382) + 17.961(\pm 10.796)\sigma_I + \\ & 1.650(\pm 12.444)\sigma_R \quad (13) \\ (R = 0.956, n = 9, P > 90\%) \end{aligned}$$

$$\begin{aligned} \nu\text{CH}=\text{CH}_{op}(\text{cm}^{-1}) &= 1021.49(\pm 5.414) + 15.838(\pm 10.666)F + \\ & 4.409(\pm 10.854)R \quad (14) \\ (R = 0.952, n = 9, P > 95\%) \end{aligned}$$

$$\begin{aligned} \nu\text{C}=\text{C}_{op}(\text{cm}^{-1}) &= 552.669(\pm 8.507) + 12.625(\pm 17.065)\sigma_I + \\ & 34.587(\pm 19.669)\sigma_R \quad (15) \\ (R = 0.965, n = 9, P > 95\%) \end{aligned}$$

$$\begin{aligned} \nu\text{C}=\text{C}_{op}(\text{cm}^{-1}) &= 554.42(\pm 8.066) + 11.089(\pm 15.890)F + \\ & 33.032(\pm 16.170)R \quad (16) \\ (R = 0.965, n = 9, P > 95\%) \end{aligned}$$

3. 3 NMR Spectral study

3. 3. 1 ¹H NMR spectra

From the ¹H NMR spectra of chalcones the chemical shifts (δ , ppm) H_α and H_β are assigned and tabulated in Table 2.

These chemical shifts were correlated with Hammett substituent constants, F and R parameters.

The statistical analysis of these chemical shifts is presented in Table 3. From Table 3, the all Hammett substituent constants and F & R parameters gave poor correlation with H α chemical shifts (δ , ppm) values of all chalcone compounds.

All the correlations have shown positive ρ values with a few Hammett constants and R parameter. This indicates the operation of normal substituent effect with all aryl α , β -unsaturated ketone compounds.

The all Hammett substituent constant and F and R parameters gave poor correlation with H β chemical shifts (δ , ppm) values of all chalcone compounds. The polar, inductive Field and resonance components of the substituents fail in correlation. The failure in correlation for both chemical shifts are the reasons stated earlier and associated with the resonance – conjugated structure shown in Fig. 1.

All the correlations have shown negative ρ values with Hammett constants and F parameter except R parameter. This indicates the operation of reverse substituent effect with respect to for δ H β chemical shift (ppm) values of all the ketone compounds

Some of the single parameter correlations with Hammett substituent constants were not obeyed in the regression. While seeking these parameters in multi-regression, with F and R Swain-Lupton's [40] constants, they gave satisfactory correlations with the chemical shifts of (δ , ppm) H α and H β . The multi correlation equations are given in 17-20.

$$\begin{aligned} \delta H_{\alpha}(\text{ppm}) = & 7.533(\pm 0.061) - 0.085(\pm 0.123)\sigma_1 + \\ & 0.234(\pm 0.141)\sigma_R \end{aligned} \quad (17)$$

(R = 0.953, n = 9, P > 95%)

$$\begin{aligned} \delta H_{\alpha}(\text{ppm}) = & 7.516(\pm 0.061) - 0.033(\pm 0.121)F + \\ & 0.188(\pm 0.123)R \end{aligned} \quad (18)$$

(R = 0.953, n = 9, P > 95%)

$$\begin{aligned} \delta H_{\beta}(\text{ppm}) = & 7.868(\pm 0.122) - 0.267(\pm 0.245)\sigma_1 - \\ & 0.003(\pm 0.282)\sigma_R \end{aligned} \quad (19)$$

(R = 0.940, n = 9, P > 90%)

$$\begin{aligned} \delta H_{\beta}(\text{ppm}) = & 7.861(\pm 0.121) - 0.235(\pm 0.238)F + \\ & + 0.005(\pm 0.242)R \end{aligned} \quad (20)$$

(R = 0.937, n = 9, P > 90%)

3. 3. 2 ¹³C NMR spectra

The carbonyl carbon, C α and C β chemical shifts (δ , ppm) of 2, 6-dimethoxyphenyl chalcones were assigned and tabulated in Table 2. These chemical shifts are correlated

with Hammett substituent constants, F and R parameters.

The results of statistical analysis are shown in Table 3. From Table 3, the all Hammett constants and F & R parameters were gave poor correlations with carbonyl carbon chemical shifts of chalcones.

All the correlations have shown positive ρ values with all Hammett constants F and R parameters. This indicates the operation of normal substituent effect with respect to δ C α chemical shift (ppm) values of all aryl α , β -unsaturated ketone compounds.

The all Hammett substituent constants and F & R parameters were gave satisfactory correlation with C α chemical shifts.

All the correlations have shown positive ρ values with a few Hammett constants R parameter. This indicates the operation of normal substituent effect with respect to δ C α chemical shift (ppm) values of all aryl α , β -unsaturated ketone compounds.

The C β chemical shifts (δ , ppm) were poor correlated with all the Hammett substituent constants and F & R parameters. This is due to the reasons stated in earlier and associated with the resonance conjugative structure shown in Fig. 1.

All the correlations have shown negative ρ values with all Hammett constants and F and R parameters. This indicates the reverse substituent effect with respect to δ C β chemical shift (ppm) values of all aryl α , β -unsaturated ketone compounds.

The multi regression analysis of carbonyl carbon, C α and C β chemical shifts (δ , ppm) of 2, 6-dimethoxyphenyl chalcones were satisfactorily correlated with σ_1 , σ_R and Swain-Luptons' [40] F and R parameters. The multi-regression equations are given in 21-26.

$$\begin{aligned} \delta C_{\alpha}(\text{ppm}) = & 121.71(\pm 0.833) - 2.249(\pm 1.671)\sigma_1 + \\ & 2.085(\pm 1.926)\sigma_R \end{aligned} \quad (21)$$

(R = 0.955, n = 9, P > 95%)

$$\begin{aligned} \delta C_{\alpha}(\text{ppm}) = & 121.33 (\pm 0.891) - 1.289(\pm 1.756)F + \\ & 1.397(\pm 1.787)R \end{aligned} \quad (22)$$

(R = 0.940, n = 9, P > 90%)

$$\begin{aligned} \delta C_{\beta}(\text{ppm}) = & 141.37(\pm 1.425) - 0.935(\pm 2.859)\sigma_1 - \\ & 2.342(\pm 3.295)\sigma_R \end{aligned} \quad (23)$$

(R = 0.934, n = 9, P > 90%)

$$\begin{aligned} \delta C_{\beta}(\text{ppm}) = & 141.15 (\pm 1.376) - 0.639(\pm 2.712)F - \\ & 2.396(\pm 2.760)R \end{aligned} \quad (24)$$

(R = 0.934, n = 9, P > 90%)

$$\delta \text{CO}(\text{ppm}) = 190.39(\pm 1.835) + 5.161(\pm 3.681)\sigma_1 +$$

$$4.624(\pm 4.243)\sigma_R \quad (25)$$

$$(R = 0.953, n = 9, P > 95\%)$$

$$\delta CO(\text{ppm}) = 190.94(\pm 1.904) + 4.039(\pm 3.751)F + 4.452(\pm 3.817)R \quad (26)$$

$$(R = 0.953, n = 9, P > 95\%)$$

4 Microbial activities

4.1 Antibacterial sensitivity assay

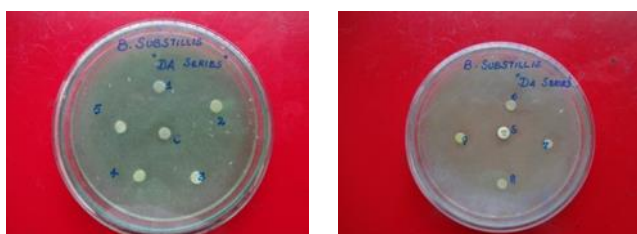


Plate-1



Plate-2

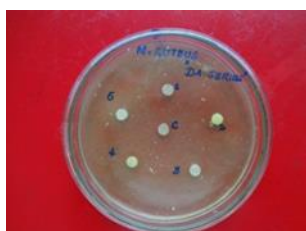


Plate-3



Plate-4



Plate-5



Plate-6

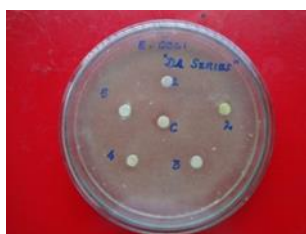


Plate-7



Plate-8



Plate-9



Plate-10



Plate-11



Plate-12

Fig 3: Antibacterial activities of styryl-2, 6-dimethoxyphenyl ketones-petri dish plate.

Antibacterial sensitivity assay was performed using Kirby-Bauer [38] disc diffusion technique. In each Petri plate about 0.5ml of the test bacterial sample was spread uniformly over the Solidified Mueller Hinton agar using sterile glass spreader. Then the discs with 5mm 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 hours at 37°C by keeping the plates upside down to prevent the collection of water droplets over the medium. After 24 hours, 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.

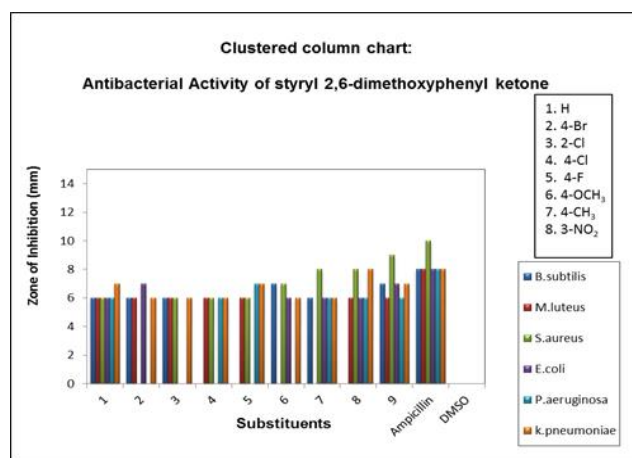


Fig 4: Clustered column Chart of Antibacterial activity of substituted styryl-2,6-dimethoxyphenyl ketone

The antibacterial effect of the styryl-2,6-dimethoxyphenyl ketone is shown in Fig. 3 for Plates (1)-(12). Analysis of the zone of inhibition as given Table-4 and the Clustered

column Chart Fig 4 reveals that only three aryl α,β -unsaturated ketone compounds with 4-CH₃, 3-NO₂ and 4-NO₂ substituents have shown good antibacterial activity against *S.aureus*. Only one aryl α,β -unsaturated ketone compound with 3-NO₂ substituent has shown good antibacterial activity against *k.pneumoniae*.

Only two aryl α,β -unsaturated ketone compounds with H(parent) and 4-NO₂ substituents have shown moderate antibacterial activity against all the six bacterial species. All the nine compounds have shown antibacterial against *k.pneumoniae*.

4.2 Antifungal sensitivity assay

Table 4: Antifungal activity of substituted styryl-2,6-dimethoxyphenyl ketone compounds

S.No	Compounds	Zone of Inhibition (mm)		
		<i>A.niger</i>	<i>M.species</i>	<i>T.viride</i>
1	H	-	6	-
2	4-Br	-	7	-
3	2-Cl	-	6	-
4	4-Cl	7	6	-
5	4-F	-	-	6
6	4-OCH ₃	-	-	6
7	4-CH ₃	7	6	6
8	3-NO ₂	-	8	6
9	4-NO ₂	-	7	6
Standard	Miconazole	10	12	8
control	DMSO	-	-	-

Antifungal sensitivity assay was performed using Kirby-Bauer [38] 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 1mL of DMSO solvent. The medium was allowed to solidify and kept for 24 hours. 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 antifungal effect of the styryl-2,6-dimethoxyphenyl ketone is shown in Fig. 5 for Plates (13-18). Analysis of the zone of inhibition as given Table 4 and the Clustered column Chart Fig 6 reveals that only one aryl α,β -unsaturated ketone compound with 3-NO₂ substituent has shown good antifungal activity against *M.species*.

Only two aryl α,β -unsaturated ketone compounds with 4-Cl and 4-CH₃ substituents have shown moderate antifungal activity against *A.niger*. Six aryl α,β -unsaturated ketone compounds with H (parent), 4-Br, 2-Cl, 4-Cl, 4-CH₃ and 4-

NO₂ substituents have shown moderate antifungal activity *M.species*.

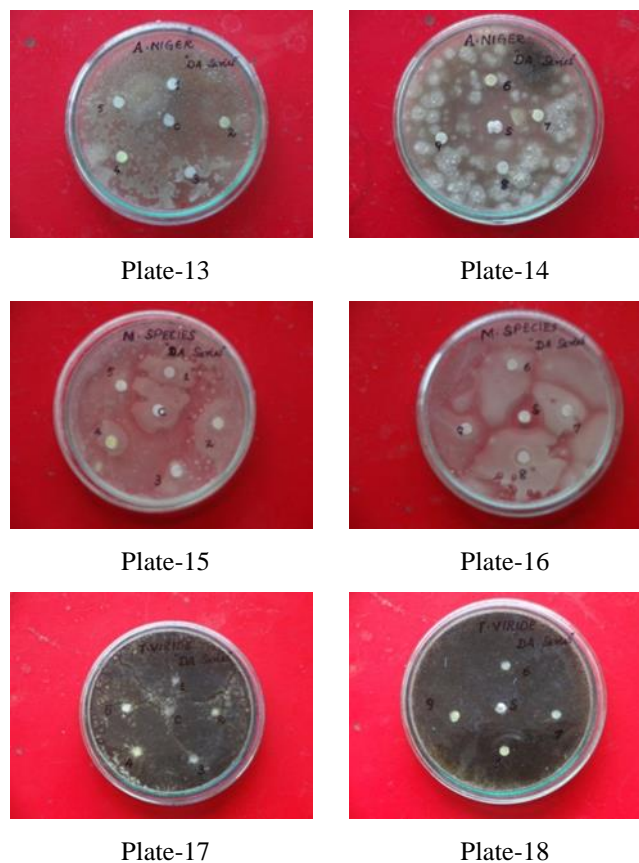


Fig 5: Antifungal activities of styryl-2,6-dimethoxyphenyl ketone-petri dish plates.

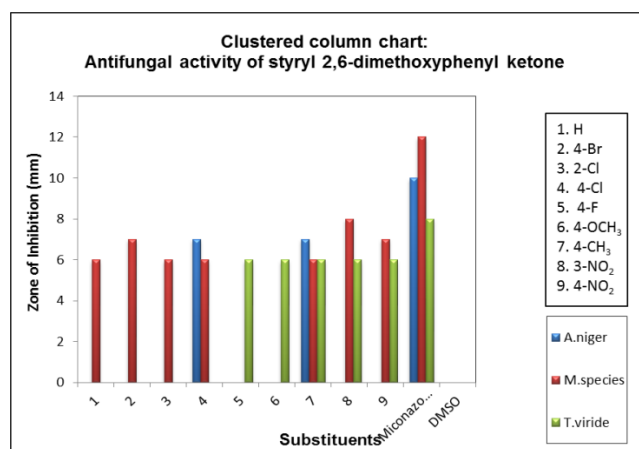


Fig 6: Clustered column Chart of Antifungal activity of substituted Styryl-2, 6-dimethoxyphenyl ketone.

Analysis of the Zone of inhibition (mm) values reveals that only five aryl α,β -unsaturated ketone compounds with 4-F, 4-OCH₃, 4-CH₃, 3-NO₂ and 4-NO₂ substituents have shown

moderate antifungal activity activity *T.viride*. Only one compound CH₃ has shown moderate antifungal activity against all the three species.

5 Conclusions

We have developed an efficient crossed-aldol condensation for synthesis of chalcones using preheated fly-ash catalyst. The yield of the reaction is more than 90%. The purities of these synthesized chalcones are checked by their physical constants, analytical and spectral data. The UV, IR, NMR spectral data of these chalcones has been correlated with Hammett substituent constants, F and R parameters. From the results of statistical analyses the effects of substituent on the spectral data have been studied. The antimicrobial activities of all synthesized chalcone have been studied using Bauer-Kirby method.

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