

Spectral correlation analysis and antimicrobial activities of some 2,4-dimethoxy phenyl chalcones

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ABSTRACT

A series of 2,4-dimethoxy phenyl chalcones have been synthesized by Crossed-Aldol condensation of 2,4-dimethoxy phenyl and various substituted benzaldehydes. The purities of these chalcones have been checked by their physical constants, UV, IR, NMR and MASS spectral data. The spectral data of these chalcones have been correlated with Hammett sigma constants, F and R parameters using single and multi-linear regression analysis. From the results of statistical analysis, the effects of substituents on the spectral group frequencies have been discussed. The anti-microbial activities of these chalcones have been evaluated using Bauer-Kirby method.

Keywords: substituted styryl 2,4-dimethoxy phenyl ketones; UV spectra; IR spectra; NMR spectra; substituent effects; antimicrobial activities

1. INTRODUCTION

The σ,β unsaturated ketones are called as enones. They possess carbonyl moiety and it was bonded with aryl or alkyl groups in both sides. They are very important molecules for synthesising heterocycles and possess multipronged activities [1]. Various solvent assisted and green synthetic methodologies have been reported for the synthesis of aryl enones. The Crossed-Aldol [2], Claisen Schmidt [3], Knoevenagel [4] and Wittig [5] reactions are important for the synthesis of enones. Many catalyst were used for proceedings the above said reactions namely, EtOH-NaOH [6], MeOH-KOH [7], EtOH-KOH [8], MgCl₂ [5], silica-sulphuric acid [9], anhydrous zinc chloride [10], clay [11], Hydrotalcite [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], fly-ash:H₂SO₄ [20], fly-ash:PTS [21], NaOH-CTABr [22], SiO₂-H₃PO₄ [23], SOCl₂ [24] and

sulfated titania [25]. The spectral data of these E- chalcones were useful for prediction of ground state equilibration like *s-cis* and *s-trans* conformers. Recently, Janaki et al., [23] have elaborately studied the effects of substituent on the ultraviolet absorption (λ_{max} , nm), infrared group frequencies (ν , cm^{-1}) and NMR chemical shifts (δ , ppm) of σ , β - proton and carbons of 4-ethoxy phenyl chalcones and benzimidazole chalcones. In their studies, they observed satisfactory and good correlations for each spectral data with Hammett substituent constants, F and R parameters. Chalcones possess various multipronged activities such as antimicrobial [26], antidepressants [27], antiplosmoidal [28], anti-aids [29] and insect antifeedant activities [13, 22]. In the present investigation, the authors have synthesized a series of some substituted styryl 2,4-dimethoxy phenyl ketones, studied the spectral correlations and to evaluate the antimicrobial activities using Bauer-Kirby [30] method.

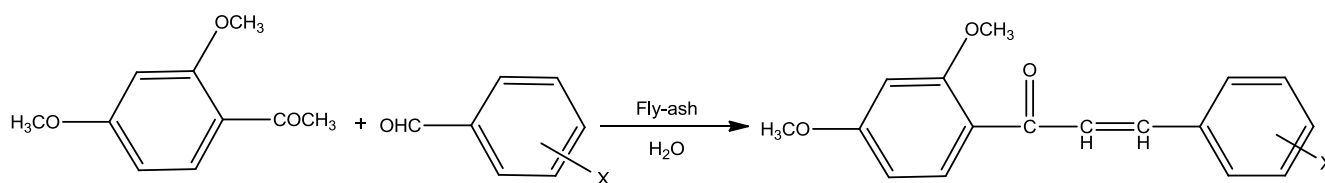
2. EXPERIMENTAL

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 ultraviolet spectrophotometer was utilized for recording the absorption maxima (λ_{max} , nm), of all chalcones in spectral grade solvent. Infrared spectra (KBr, $4000\text{-}400\text{cm}^{-1}$) were recorded AVATAR-300 Fourier transform spectrophotometer. BRUKER AVANCE III-500MHz NMR spectrometer was used for recording NMR spectra operating at 500MHz for ^1H spectra and 125.46 MHz for ^{13}C spectra in CDCl_3 solvent using TMS as internal standard. Mass spectra of all chalcones were recorded on SHIMADZU spectrometer using chemical ionization technique.

2. 2. Synthesis of Chalcones

All substituted 2,4-dimethoxy phenyl chalcones were synthesized by procedure published in literature [19,31]. An equi-molar quantities of 2,4-dimethoxy acetophenone (2 mmol) substituted benzaldehydes (2 mmol), Fly-ash (0.5 g) and 20 mL of water (Scheme 1) were refluxed for 4h. The completion of the reaction was monitored by thin layer chromatography. After completion of the reaction, the solid product was separated by filtration. Further the product was purified by column chromatography using dichloromethane and ethyl acetate mixture as eluent. The physical constants, analytical and mass fragments were presented in Table 1.



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

Scheme 1. Synthesis of substituted styryl 2, 4-dimethoxy phenyl ketones.

Table 1. Physical constants and mass spectral data of substituted styryl 2,4-dimethoxy phenyl ketones.

Entry	X	M. F.	M. W.	Yield (%)	m.p. (°C)	Mass (m/z)
1	H	C ₁₇ H ₁₆ O ₃	268	95	78-80 (80.5-81) [32]	268 [M+]
2	4-Br	C ₁₇ H ₁₅ BrO ₃	347	90	133-135	347[M+], 349[M2+]
3	2-Cl	C ₁₇ H ₁₅ ClO ₃	302	89	118-120 (119-120) [33]	302[M+], 304[M2+]
4	3-Cl	C ₁₇ H ₁₅ ClO ₃	302	88	115-116	302[M+], 304[M2+]
5	4-Cl	C ₁₇ H ₁₅ ClO ₃	302	88	117-119 (118-120) [33]	302[M+], 304[M2+]
6	4-F	C ₁₇ H ₁₅ FO ₃	286	87	96-98 (98) [34]	286[M+], 288[M2+]
7	2-OCH ₃	C ₁₈ H ₁₈ O ₄	298	92	105-106 (106-107) [35]	298[M+]
8	3-NO ₂	C ₁₇ H ₁₅ NO ₅	313	86	185-187	313[M+]
9	4-NO ₂	C ₁₇ H ₁₅ NO ₅	313	85	190-191 (191) [36]	313[M+]

3. RESULTS AND DISCUSSION

In the present study the authors have studied the effects of substituents on the spectral data such as ultraviolet absorption maxima (λ_{\max} , nm), infrared spectral carbonyl and deformation modes (ν , cm⁻¹), the chemical shifts (δ , ppm) of α , β protons, and carbonyl carbons of synthesized 2,4-dimethoxy phenyl chalcones with Hammett substituent constants, F and R parameters using single and multi-linear regression analysis for predicting the reactivity on the group frequencies.

3. 1. UV spectral study

The measured ultraviolet absorption maxima (λ_{\max} , nm) of all 2,4-dimethoxy phenyl chalcones were tabulated in Table 2. These values are correlated [1,2,6,10,19,21,23-25,28,37] 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.

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

The results of statistical analysis are presented in Table 3. From the Table 3, the correlation of absorption maxima (λ_{\max} , nm) with σ and σ^+ parameter is satisfactory. The remaining Hammett substituent constants, F and R parameter were failing in correlation. This

is due to the inductive 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. In single parameter correlation, the Hammett substituents constants not obeyed in the regression. While seeking these parameters in multi-regression, with F and R Swain-Lupton's [37] constants, they gave satisfactory correlations. The multi correlation equations are given in (2) and (3).

$$\lambda_{max} \text{ (nm)} = 310.89(\pm 12.776) - 16.935(\pm 24.427)\sigma_I - 34.183(\pm 19.1018)\sigma_R \quad \dots(2)$$

(R = 0.965, n = 9, P > 95 %)

$$\lambda_{max} \text{ (nm)} = 312.72(\pm 11.184) - 21.889(\pm 21.648)F - 32.685(\pm 18.371)R \quad \dots(3)$$

(R = 0.963, n = 9, P > 95 %)

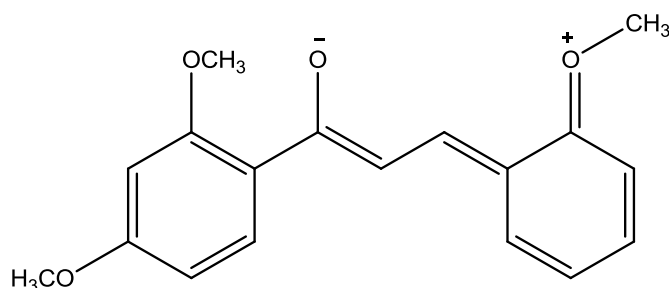


Fig. 1. The resonance- conjugated structure.

Table 2. The ultraviolet absorption maxima (λ_{max} , nm), infrared absorptions (ν , cm^{-1}) and NMR chemical shifts (δ , ppm) of substituted styryl 2,4-dimethoxy phenyl ketones.

Entry	X	λ_{max}	CO_{s-cis}	$\text{CO}_{s-trans}$	CH_{ip}	CH_{op}	$\text{CH}=\text{CH}_{op}$	$\text{C}=\text{C}_{op}$	$\delta\text{H}\alpha$ (ppm)	$\delta\text{H}\beta$ (ppm)	$\delta\text{C}\alpha$ (ppm)	$\delta\text{C}\beta$ (ppm)	δCO (ppm)
1	H	307.80	1608.63	1585.49	1132.21	825.53	1024.20	557.43	7.543	7.703	122.25	135.52	190.51
2	4-Br	309.40	1660.71	1596.85	1128.36	821.68	1022.27	543.93	7.533	7.627	122.04	134.49	190.09
3	2-Cl	301.40	1600.99	1511.63	1111.00	823.60	1016.49	563.21	7.512	8.067	121.96	133.83	190.22

9	4-NO ₂	314.60	1662.64	1516.05	1139.93	831.32	1026.13	538.14	7.712	7.814	121.54	141.95	189.28
8	3-NO ₂	287.00	1602.85	1527.62	1107.14	815.89	1014.57	542.01	7.592	7.707	122.23	138.46	189.35
7	2-OCH ₃	343.60	1604.77	1506.41	1165.00	825.54	1024.20	526.57	7.410	7.669	125.05	142.08	190.68
6	4-F	308.00	1606.70	1554.63	1130.29	825.53	1022.27	478.35	7.449	7.641	122.14	131.76	190.25
5	4-Cl	311.00	1658.78	1593.85	1132.22	817.52	1020.34	542.00	7.519	7.645	122.06	135.73	190.11
4	3-Cl	299.80	1600.92	1556.28	1109.07	819.75	1014.56	534.28	7.336	7.618	121.94	137.44	189.95

Table 3. Results of statistical analysis of ultraviolet absorption maxima (λ_{max} , nm), infrared absorptions (ν , cm^{-1}) and NMR chemical shifts (δ , ppm) of substituted styryl 2,4-dimethoxy phenyl ketones with Hammett σ , σ^+ , σ_I , σ_R and F and R parameters.

Frequency	Constants	r	I	ρ	s	n	Correlated derivatives
λ_{max}	σ	0.906	316.19	-28.59	11.97	8	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 3-NO ₂ , 4-NO ₂
	σ^+	0.907	316.11	-26.66	11.49	8	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂
	σ_I	0.802	320.82	-26.21	15.33	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.861	302.88	-36.99	12.86	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.820	318.40	-20.56	15.55	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂

	R	0.855	303.01	-32.04	13.61	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
CO _{s-cis}	σ	0.703	1616.74	25.48	28.72	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.792	1617.69	20.40	29.05	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.823	1605.88	38.50	29.25	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.908	1629.25	36.79	28.68	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.714	1612.99	22.29	29.90	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.906	1628.84	30.42	29.15	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
CO _{s-trans}	σ	0.819	1552.33	-10.03	38.46	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.711	1552.52	-10.23	38.40	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.905	1577.65	-62.50	36.32	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.711	1552.64	16.33	38.40	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.903	1571.77	-48.80	36.88	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.745	1550.94	5.606	38.63	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
CH _{ip}	σ	0.905	1135.45	-28.88	15.85	8	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ ,
	σ^+	0.906	1136.05	-29.59	14.54	8	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ ,
	σ_I	0.825	1141.79	-30.22	18.31	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.845	1122.76	-32.88	17.23	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.845	1137.43	-20.21	18.79	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.842	1122.74	-29.19	17.59	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
CH _{op}	σ	0.902	823.40	-1.811	5.001	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.905	823.36	-1.553	5.004	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.815	824.59	-3.665	4.989	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.810	822.62	-1.995	5.020	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.803	823.34	-0.847	5.045	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.811	822.57	-1.995	5.018	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
CH=CH _{op}	σ	0.903	1021.49	-3.793	4.420	8	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ ,
	σ^+	0.903	1021.62	-4.085	4.307	8	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ ,

	σ_I	0.832	1023.70	-7.085	4.409	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.813	1020.17	-2.245	4.017	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.819	1022.26	-3.798	4.569	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.815	1020.07	-2.515	4.604	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
C=C _{op}	σ	0.812	532.98	13.14	25.56	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.832	530.38	22.42	24.17	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.828	551.83	-35.15	24.97	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.905	544.83	50.70	22.15	8	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.905	563.68	-61.19	21.63	8	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.906	547.60	59.23	20.10	7	H, 4-Br, 3-Cl, 4-Cl, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
$\delta H\alpha$	σ	0.906	7.466	0.184	0.09	8	H, 4-Br, 2-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.905	7.470	0.158	0.09	8	H, 4-Br, 2-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.829	7.440	0.160	0.11	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.907	7.564	0.310	0.07	8	H, 4-Br, 2-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.822	7.460	0.114	0.11	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.904	7.567	0.288	0.08	8	H, 4-Br, 2-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
$\delta H\beta$	σ	0.812	7.704	0.067	0.15	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.924	7.689	0.122	0.14	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.812	7.681	0.088	0.15	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.814	7.734	0.080	0.15	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.801	7.716	0.010	0.15	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.821	7.743	0.114	0.14	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
δCO	σ	0.997	190.36	-1.271	0.110	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.995	190.32	-1.042	0.223	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.907	190.86	-1.835	0.321	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.908	189.80	-1.424	0.325	8	4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.906	190.67	-1.394	0.380	7	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-NO ₂ , 4-NO ₂

	R	0.907	189.80	-1.285	0.353	8	4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
$\delta C\alpha$	σ	0.907	122.86	-2.073	0.757	8	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 3-NO ₂ , 4-NO ₂
	σ^+	0.907	122.84	-1.903	0.731	8	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 3-NO ₂ , 4-NO ₂
	σ_I	0.824	123.18	-1.863	1.030	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.906	121.90	-2.635	0.841	8	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 3-NO ₂ , 4-NO ₂
	F	0.821	123.03	-1.519	1.042	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.854	121.93	-2.198	0.915	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
$\delta C\beta$	σ	0.901	136.38	1.698	3.719	8	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 3-NO ₂ , 4-NO ₂
	σ^+	0.901	136.61	0.745	3.763	8	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 3-NO ₂ , 4-NO ₂
	σ_I	0.801	135.97	1.863	3.756	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.821	137.30	2.923	3.693	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.804	137.10	-0.670	3.774	9	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.903	137.59	4.076	3.601	8	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 3-NO ₂ , 4-NO ₂

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.

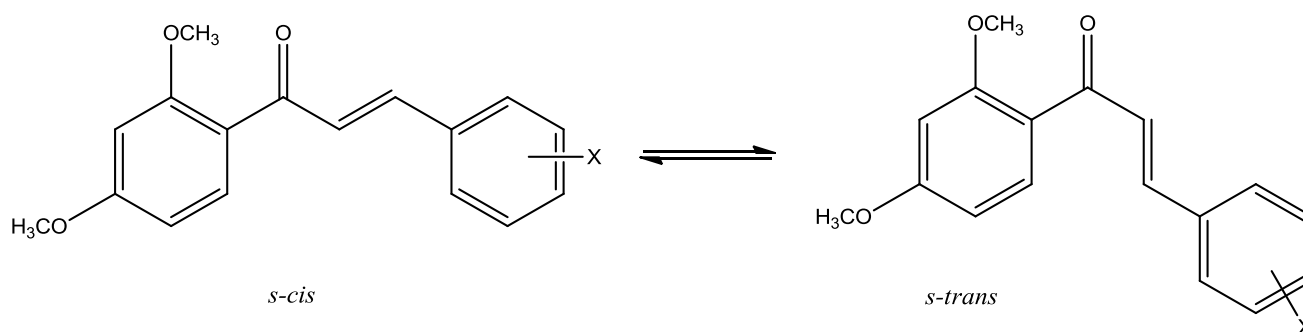


Fig. 2. The *s-cis* and *s-trans* conformers of 2,4-dimethoxy phenyl chalcones.

The stretching frequencies for carbonyl absorption are assigned based on the assignments made by Hays and Timmons [2] for *s-cis* and *s-trans* conformers at 1690 and 1670 cm^{-1} , respectively. The assigned infrared COs-*cis* and *s-trans* conformers have been correlated with Hammett substituent constants and Swain-Lupton constants [37]. In this

correlation the structure parameter Hammett equation employed is as shown in the following equation:

$$v = \rho\sigma + v_0 \quad \dots (4)$$

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.

The results of statistical analysis [1,2,6,10,19,21,23-25,28,37] were shown in Table 3, From Table 3, The resonance component only correlated satisfactorily with CO *s-cis* conformers stretches. The remaining Hammett substituent constants and F parameters were failing in correlation. The Hammett σ_I and F parameters gave satisfactory correlation with CO *s-trans* conformers stretches. The remaining Hammett substituent constants and R parameters were failing in correlation. This is due to the reasons stated in earlier and associated with the resonance conjugative structure shown in Fig. 1.

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

The Hammett σ and σ^+ constants gave satisfactory correlation with $CH=CH_{op}$ modes. The remaining Hammett substituent constants and F and R parameter failed in correlation due to the inductive, resonance and field components of the substituents. The Hammett σ_R constants, F and R were satisfactorily correlated with $C=C_{op}$ modes. The inductive components of the substituents σ , σ^+ and σ_I constants failed in correlation. This is due to the reasons stated earlier and associated with the resonance conjugative structure as shown in Fig. 1. 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 [37], they gave satisfactory correlations with the infrared red group frequencies. The multi correlation equations are given in (5-16).

$$vCO_{s-cis}(\text{cm}^{-1}) = 1615.14(\pm 28.913) + 29.85(\pm 55.27)\sigma_I + 31.83(\pm 43.226)\sigma_R \quad \dots(5)$$

($R = 0.938$, $n = 9$, $P > 90\%$)

$$vCO_{s-cis}(\text{cm}^{-1}) = 1618.40(\pm 25.419) + 23.55(\pm 49.20)F + 31.11(\pm 41.755)R \quad \dots(6)$$

($R = 0.933$, $n = 9$, $P > 90\%$)

$$vCO_{s-trans}(\text{cm}^{-1}) = 1585.78(\pm 36.70) - 70.10(\pm 70.17)\sigma_I + 27.97(\pm 54.873)\sigma_R \quad \dots(7)$$

($R = 0.939$, $n = 9$, $P > 90\%$)

$$vCO_{s-trans}(\text{cm}^{-1}) = 1572.50(\pm 32.75) - 48.63(\pm 63.40)F + 4.185(\pm 53.804)R \quad \dots(8)$$

($R = 0.930$, $n = 9$, $P > 90\%$)

$$vCH_{ip}(\text{cm}^{-1}) = 1133.31(\pm 17.133) - 22.305(\pm 32.757)\sigma_I - 29.183(\pm 25.615)\sigma_R \quad \dots(9)$$

($R = 0.951$, $n = 9$, $P > 95\%$)

$$\nu\text{CH}_{ip}(\text{cm}^{-1}) = 1132.24(\pm 14.962) - 21.422(\pm 28.962)F - 29.822(\pm 24.577)R \quad \dots(10)$$

$$(R = 0.949, n = 9, P > 90 \%)$$

$$\nu\text{CH}_{op}(\text{cm}^{-1}) = 824.16(\pm 5.1344) - 3.2715(\pm 9.8163)\sigma_I - 1.452(\pm 7.6762)\sigma_R \quad \dots(11)$$

$$(R = 0.917, n = 9, P > 90 \%)$$

$$\nu\text{CH}_{op}(\text{cm}^{-1}) = 822.99(\pm 4.4550) - 0.9296(\pm 8.6235)F - 2.0228(\pm 7.3179)R \quad \dots(12)$$

$$(R = 0.911, n = 9, P > 90 \%)$$

$$\nu\text{CH}=\text{CH}_{op}(\text{cm}^{-1}) = 1023.38(\pm 4.540) - 6.781(\pm 8.680)\sigma_I - 1.119(\pm 6.7882)\sigma_R \quad \dots(13)$$

$$(R = 0.932, n = 9, P > 90 \%)$$

$$\nu\text{CH}=\text{CH}_{op}(\text{cm}^{-1}) = 1021.80(\pm 4.007) - 3.904(\pm 7.756)F - 2.629(\pm 6.5823)R \quad \dots(14)$$

$$(R = 0.924, n = 9, P > 90 \%)$$

$$\nu\text{C}=\text{C}_{op}(\text{cm}^{-1}) = 569.04(\pm 20.073) - 51.226(\pm 38.378)\sigma_I + 59.210(\pm 30.011)\sigma_R \quad \dots(15)$$

$$(R = 0.966, n = 9, P > 95 \%)$$

$$\nu\text{C}=\text{C}_{op}(\text{cm}^{-1}) = 573.69(\pm 12.846) - 58.862(\pm 24.867)F + 57.517(\pm 21.102)R \quad \dots(16)$$

$$(R = 0.983, n = 9, P > 95 \%)$$

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 [1,2,6,10,19,21,23-25,28,37] of these chemical shifts is presented in Table 3. From Table 3, the H α chemical shifts (δ , ppm) correlated with Hammett σ , σ^+ , σ_R constants and R parameters were gave satisfactory correlations with H α chemical shifts of chalcones.

The remaining Hammett substituent constant σ_I and F parameter were failing in correlations due to the inductive and field effects of the substituents. Hammett σ^+ constant only one gave satisfactory correlation with H β chemical shifts (δ , ppm). The remaining Hammett substituent constants and parameter failure in correlation for both chemical shifts are the reasons stated earlier and associated with the resonance – conjugated structure shown in Fig. 1.

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 [37] 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).

$$\delta\text{H}_\alpha(\text{ppm}) = 7.526(\pm 0.079) + 0.079(\pm 0.152)\sigma_I + 0.2969(\pm 0.119)\sigma_R \quad \dots(17)$$

$$(R = 0.974, n = 9, P > 95 \%)$$

$$\delta\text{H}_\alpha(\text{ppm}) = 7.511(\pm 0.068) + 0.126(\pm 0.131)F + 0.292(\pm 0.111)R \quad \dots(18)$$

$$(R = 0.974, n = 9, P > 95 \%)$$

$$\delta H_{\beta}(\text{ppm}) = 7.701(\pm 0.155) + 0.070(\pm 0.297)\sigma_I + 0.068(\pm 0.232)\sigma_R \quad \dots(19)$$

$$(R = 0.901, n = 9, P > 90 \%)$$

$$\delta H_{\beta}(\text{ppm}) = 7.736(\pm 0.132) + 0.015(\pm 0.256)F + 0.115(\pm 0.217)R \quad \dots(20)$$

$$(R = 0.902, n = 9, P > 90 \%)$$

3. 3. 2. ^{13}C NMR spectra

The carbonyl carbon, C_{α} and C_{β} chemical shifts (δ , ppm) of 2,4-dimethoxy phenyl chalcones were assigned and tabulated in Table 2. These chemical shifts are correlated [1,2,6,10,19,21,23-25,28,37] with Hammett substituent constants, F and R parameters. The results of statistical analysis are shown in Table 3. From Table 3, the Hammett σ , σ^+ , σ_I , σ_R constants, F and R parameters were gave satisfactory correlations with carbonyl carbon chemical shifts of chalcones. The Hammett σ , σ^+ and σ_R constants correlated satisfactorily with C_{α} chemical shifts. The C_{β} chemical shifts (δ , ppm) were satisfactorily correlated with the Hammett σ , σ^+ and σ_R constants. The remaining Hammett substituent constant σ_I , F and R parameters were failing in correlations. This is due to the reasons stated in earlier and associated with the resonance conjugative structure shown in Fig. 1.

The multi regression analysis of carbonyl carbon, C_{α} and C_{β} chemical shifts (δ , ppm) of 2,4-dimethoxy phenyl chalcones were satisfactorily correlated with σ_I , σ_R and Swain-Luptons' [37] F and R parameters. The multi-regression equation is given in (21-26).

$$\delta \text{CO}(\text{ppm}) = 190.52(\pm 0.087) - 1.517(\pm 0.167)\sigma_I - 1.172(\pm 0.130)\sigma_R \quad \dots(21)$$

$$(R = 0.998, n = 9, P > 95 \%)$$

$$\delta \text{CO}(\text{ppm}) = 190.44(\pm 0.072) - 1.448(\pm 0.140)F - 1.328(\pm 0.119)R \quad \dots(22)$$

$$(R = 0.998, n = 9, P > 95 \%)$$

$$\delta C_{\alpha}(\text{ppm}) = 122.47(\pm 0.829) - 1.201(\pm 1.585)\sigma_I - 2.435(\pm 1.240)\sigma_R \quad \dots(23)$$

$$(R = 0.968, n = 9, P > 95 \%)$$

$$\delta C_{\alpha}(\text{ppm}) = 122.64(\pm 0.739) - 1.610(\pm 1.430)F - 2.245(\pm 1.214)R \quad \dots(24)$$

$$(R = 0.965, n = 9, P > 95 \%)$$

$$\delta C_{\beta}(\text{ppm}) = 136.77(\pm 3.804) + 1.120(\pm 7.273)\sigma_I + 2.737(\pm 5.687)\sigma_R \quad \dots(25)$$

$$(R = 0.921, n = 9, P > 90 \%)$$

$$\delta C_{\beta}(\text{ppm}) = 137.81(\pm 3.197) - 0.505(\pm 6.189)F + 4.061(\pm 5.252)R \quad \dots(26)$$

$$(R = 0.933, n = 9, P > 90 \%)$$

3. 4. Antimicrobial activities

Chalcones possess various biological activities such as antibacterial [26,38], antifungal [26], antioxidant [8], antiviral [9], antimalarial [10], antiplasmodial [28], antituberculosis [12], antiproliferative [13], antileishmanial [14], anti-inflammatory [15], antianalgesic and sedative [16], insect antifeedants [13,22]. Halogenated chalcones possess insect antifeedant activities [13,22,39-44]. The presence of a reactive α , β -unsaturated keto function in chalcones was found to be responsible for their antimicrobial activity. At present, scientists have paid more

interest to correlate the group frequencies of spectral data with Hammett substituent constants to explain the substituent effects of organic compounds.

3. 4. 1. Antibacterial sensitivity assay

Antibacterial sensitivity assay was performed using Kirby-Bauer [30] 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 5mm diameter made up of Whatmann No.1 filter paper, impregnated with the solution of the compound was placed on the medium using sterile forceps.



Plate-1



Plate-2

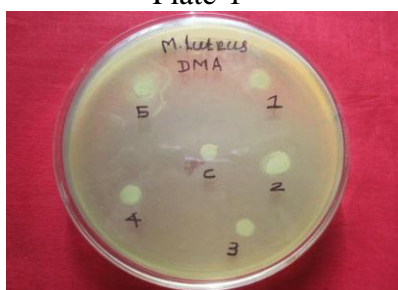


Plate-3



Plate-4

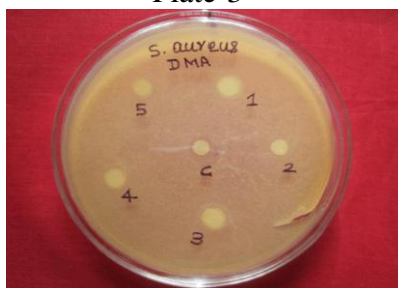


Plate-5



Plate-6

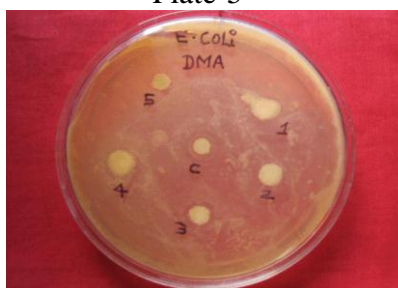


Plate-7

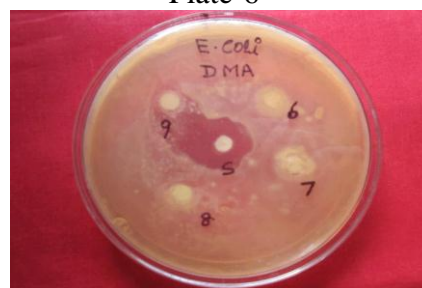


Plate-8

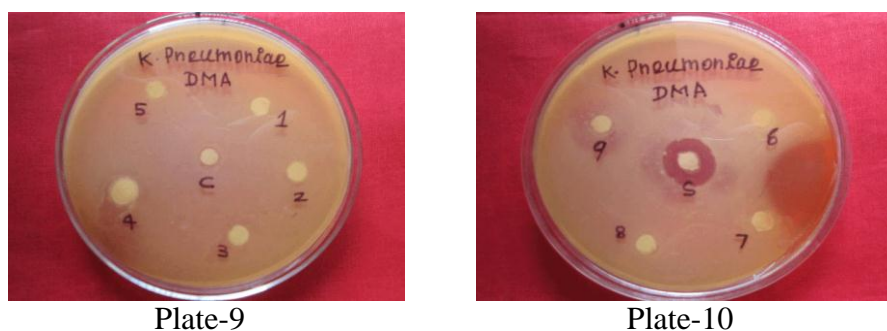


Fig. 3. Antibacterial activities of substituted 2,4-dimethoxy phenyl ketones.

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.

The antibacterial effect of the styryl 2,4-dimethoxy phenyl ketones is shown in Fig. 3 for Plates (1)-(10). Analysis of the zone of inhibition as given Table 4 and the Clustered column Chart Fig. 4, reveals that all the substituents except 4-NO₂ and 2-Cl have shown moderate antibacterial activity against all the bacterial species, under investigation.

Table 4. Antibacterial activity of substituted styryl 2,4-dimethoxy phenyl ketones.

Entry	Substt.	Zone of Inhibition (mm)				
		Gram positive Bacteria			Gram negative Bacteria	
		<i>B. subtilis</i>	<i>M. luteus</i>	<i>S. aureus</i>	<i>E. coli</i>	<i>K. pneumoniae</i>
1	H	-	6	6	7	-
2	4-Br	8	7	-	6	6
3	2-Cl	9	-	7	8	6
4	3-Cl	8	-	6	7	7
5	4-Cl	-	9	-	6	-
6	4-F	7	6	-	6	-
7	2- OCH ₃	8	-	9	6	6
8	3-NO ₂	8	7	8	7	7
9	4-NO ₂	7	6	9	9	7
Standard	Ampicillin	14	12	14	13	12
Control	DMSO	-	-	-	-	-

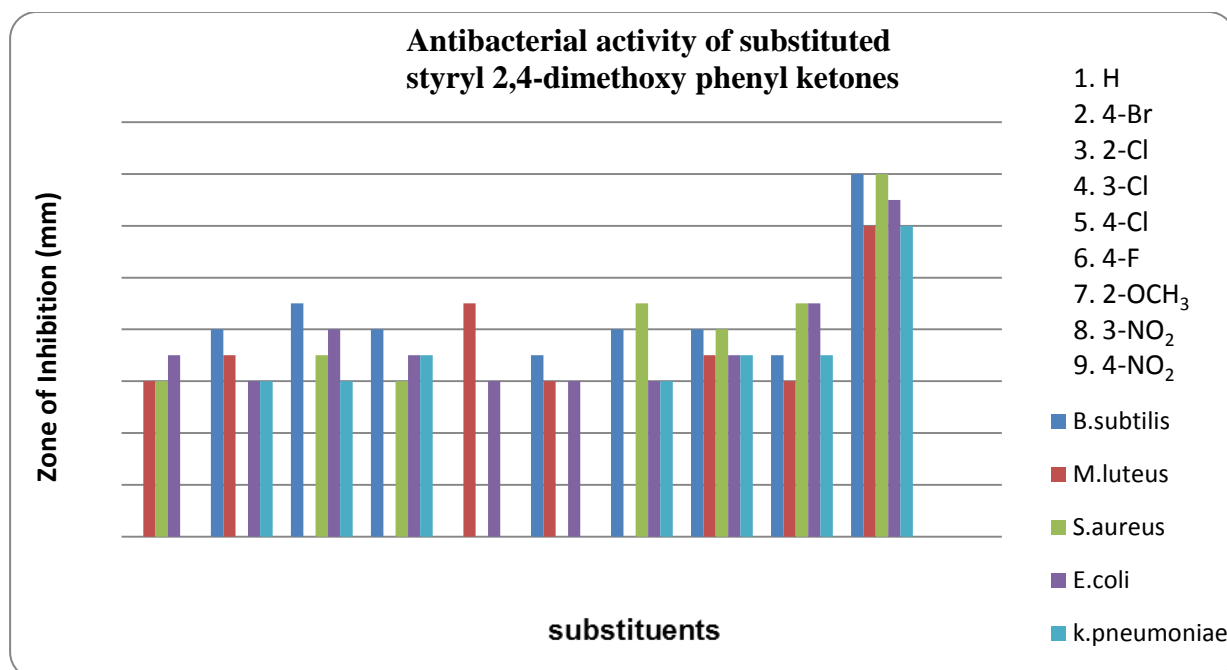


Fig. 4. Antibacterial activity of substituted styryl 2,4-dimethoxy phenyl ketone.

The substituent 4-NO₂ has shown more antibacterial activity against *S. aureus* and *E. coli* species. The parent (H) compound has shown moderate antibacterial activity than standard (Ampicillin) against *M. luteus* and *S. aureus* species. The substituent 4-Cl has shown poor activity *M. luteus* and *E. coli* species. The substituent 3-NO₂ has shown equal activities against all bacteria except *B. subtilis* and *S. aureus*. The compound with 4-Br, 3-Cl, 2-OCH₃ and 3-NO₂ substituents has shown equal activities against *B. subtilis* bacterial species. The compound with 2-OCH₃ and 3-NO₂ substituents has shown equal activities against *E. coli* and *K. pneumoniae* bacterial species.

3. 4. 2. Antifungal sensitivity assay

Antifungal sensitivity assay was performed using Kirby-Bauer [30] 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 2,4-dimethoxy phenyl ketones is shown in Fig. 5 for Plates (1-4). Analysis of the zone of inhibition as given Table 5 and the Clustered column Chart Fig 6. The substituent 2-Cl and 3-NO₂ has shown more antifungal activities against all the fungal species namely *A. niger* and *T. viride*. The parent (H) compound and 4-Br substituents have shown moderate antifungal activities against all the fungal species namely *A. niger* and *T. viride*, under investigation. The 4-Cl, 4-F and 2-OCH₃ substituents of this

have shown inactive for the above two fungal species. The parent compound (H), 2-Cl, 4-Cl and 4-F substituted compound has shown equal activity against fungal species *T. viride*.

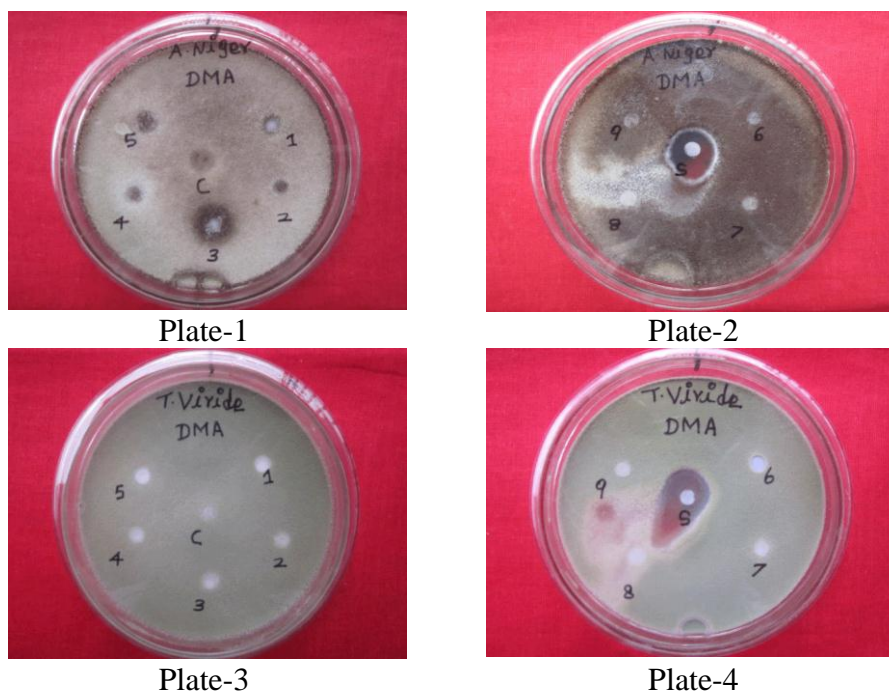


Fig. 5. Antifungal activities substituted styryl 2,4-dimethoxy phenyl ketones.

Table 5. Antifungal activity of substituted styryl 2,4-dimethoxy phenyl ketones.

Entry	Substt.	Zone of Inhibition (mm)	
		<i>A. niger</i>	<i>T. viride</i>
1	H	7	6
2	4-Br	6	-
3	2-Cl	9	6
4	3-Cl	6	-
5	4-Cl	-	6
6	4-F	-	6
7	2-OCH ₃	-	-
8	3-NO ₂	7	8
9	4-NO ₂	6	-
Standard	Miconazole	12	13
control	DMSO	-	-

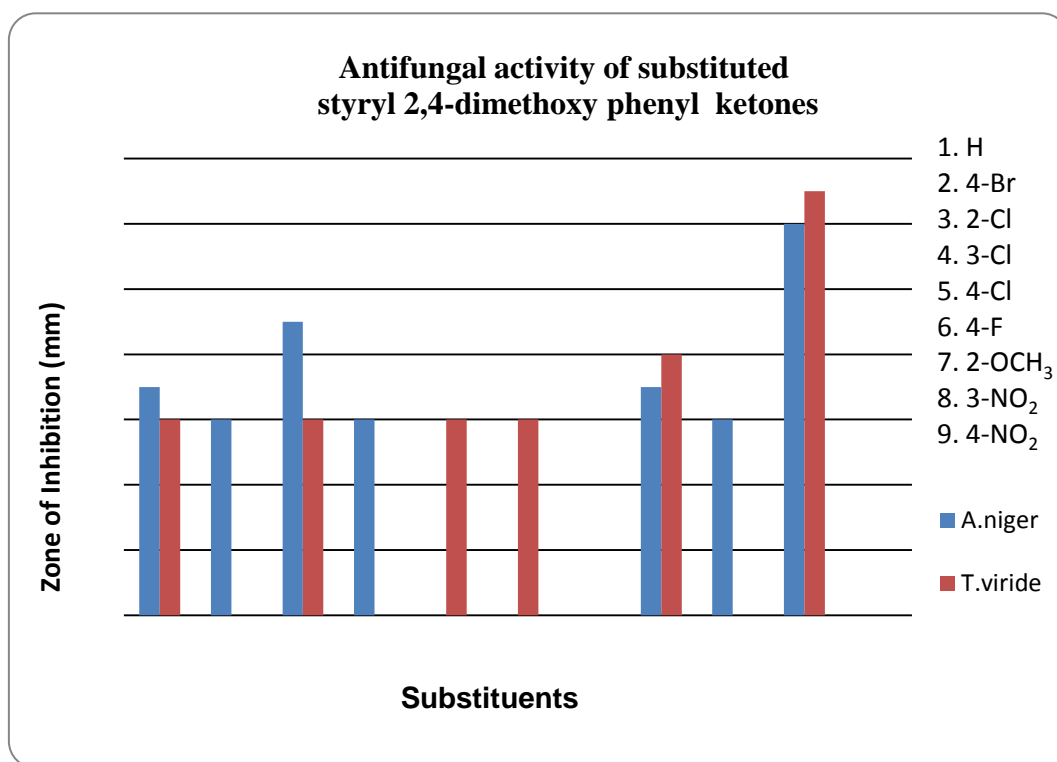


Fig. 6. Antifungal activity of substituted styryl 2,4-dimethoxy phenyl ketones-clustered column chart.

4. CONCLUSIONS

A series of 2,4-dimethoxy phenyl chalcones have been synthesized by Crossed-Aldol condensation. The spectral data of these chalcones have been correlated with Hammett sigma constants, F and R parameters using single and multi-linear regression analysis. From the results of statistical analysis, the effects of substituents on the spectral group frequencies have been discussed. The anti-microbial activities of these chalcones have been studied.

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References

- [1] Thirunarayanan G., Vanangamudi G., Subramanian M., *Organic Chem: An Indian J.* 9(1) (2013) 1-16.
- [2] Janaki P., Sekar K. G., Thirunarayanan G., *J. Saudi Chem. Soc.* 2013, Accepted and in press. DOI: org/10.1016/j.jscs.2012.11.013.
- [3] Holla B. S., Akberali P. M., Shivananda M. K., *IL Farmaco* 55 (2000) 256-261.
- [4] Venkat Reddy G., Maitraie D., Narsaiah B., Rambabu Y., ShanthanRao P., *Synth. Commun* 31(18) (2004) 2882-2884.
- [5] Orsini F., Sello G., Fumagalli T., *Synlett.* (2006), 1717-1718.

- [6] Vanangamudi G., Subramanian S., Jayanthi P., Arulkumaran R., Kamalakkannan D., Thirunarayanan G., *Arab. J. Chem.*, 201, DOI: 10.1016/j.arabjc.2010.07.019.
- [7] Tran T. D., Park H., Ecker G. F., Thai K. M., *2,3'-Hydroxychalcone Analogues: Synthesis and Structure-PGE2 Inhibitory Activity Relationship*, 12th International Electronic Conference on Synthetic Organic Chemistry (ECSOC-12) 1-30 November 2008; <http://www.usc.es/congresos/ecsoc/12/ECSOC12.htm> & <http://www.mdpi.org/ecsoc-12> No. C0011, pp 1-7.
- [8] Mohan S. B., Behera T. P., Ravi Kumar B. V. V., *Int. J. ChemTech. Res.* 2(3) 2010 1634-1637.
- [9] Thirunarayanan G., Vanangamudi G., *Arkivoc.* 12 (2006) 58-64.
- [10] Thirunarayanan G., Ananthakrishna Nadar P., *J. Indian Chem. Soc.* 83(11) (2006) 1107-1112.
- [11] Ballini R., Bosica G., Maggi R., Ricciutelli M., Righi P., Sartori G., Sartorio R., *Green Chem.* 3 (2001) 178-180.
- [12] Solhy A., Tahir R., Sebti S. Skouta R., Bousmina M., Zahouily M., Larzek M., *Appl. Catal. A: General.* 374 (2010) 189-193.
- [13] Thirunarayanan G., *J. Indian Chem. Soc.* 84 (2008) 447-451.
- [14] Basaif S. A., Sobahi T. R., Khalil A. K., Hassan M. A., *Bulletin of the Korean Chem. Soc.* 26(11) (2005) 1677-1681.
- [15] Xu Q., Yang Z., Yin D., Zhang F., *Catal. Commun.* 9(1) (2008) 1579-1582.
- [16] Kumar P., Kumar S., Husain K., Kumar A., *Bioorg. Med. Chem.* 18(14) (2010) 4965-4974.
- [17] Zhang Z., Dong Y., W., Wang G. W., *Chem. Lett.* 32(10) (2003) 966-967.
- [18] Thirunarayanan G., *IUP. J. Chem.* 3(4) (2010) 35-54.
- [19] Thirunarayanan G., et al., *Elixir Org. Chem.* 45 (2012) 7898-7905.
- [20] Thirunarayanan G., Mayavel P., Thirumurthy K., *Spectrochimica Acta.* 91A (2012) 18-22.
- [21] Sundararajan R., et al., *Int. J. Pharm. Chem. Sci.* 1(4) (2012) 1657-1677.
- [22] Thirunarayanan G., Surya S., Srinivasan S., Vanangamudi G., Sathiyendiran V., *Spectrochim. Acta.* 75A (2010) 152-156.
- [23] Janaki P., Sekar K. G., Thirunarayanan G., *Org. Chem: An Indian J.* 9(2) (2013) 68-80.
- [24] Arulkumaran R., Vijayakumar S., Sundararajan R., Sakthinathan S. P., Kamalakkannan D., Suresh R., Ranganathan K., Vanangamudi G., Thirunarayanan G., *International Letters of Chemistry, Physics and Astronomy 4* (2012) 17-38.
- [25] Kamalakkannan D, Vanangamudi G, Arulkumaran R, Thirumurthy K, Mayavel P, Thirunarayanan G, *Elixir Org. Chem.*, 46, 2012, 8157-8166.
- [26] Sivakumar M., PhrabuSreeneivasan S., Kumar V., Doble M., *Bioorg. Med Chem. Lett.* 17(10) (2007) 3169-3172.

- [27] Liu X., Go M. L., *Bioorg. Med.Chem.* 14(1) (2006) 153-163.
- [28] Arulkumar R, et al., *IUP J. Chem.* 3(1) (2010) 82-98.
- [29] Deng J., Sanchez T., Lalith Q. A. M., *Bioorg. Med. Chem.* 15(14) (2007) 4985-5002.
- [30] Bauer A. W., Kirby W. M. M., Sherris J. C., Truck M., *Am. J. Clin. Pathol.* 45 (1966) 493-496.
- [31] Thirunarayanan G., "Fly-ash: H₂O Assisted Aldol Condensation: Effect of Solvents on the Synthesis of Some Aryl (*E*) 2-propen-1-ones" Accepted article in *Annales, UMCS Chem. J.*, 2013.
- [32] Marquardt F. H., *Helv. Chim. Acta.* 48 (7) (1965) 1476-1485.
- [33] Liu Xiaoling, *Bioorg. Med. Chem.* 14(1) (2006) 153-163.
- [34] Buu-Hoi Ng. Ph., *J. Org. Chem.* 22 (1957) 193-7.
- [35] Vandrewala H. P., *J. Univ. Bom Sci: Phys Sci, Math, Biol. Sci. Med.* 16 (1948) 43-5.
- [36] Kauffmann Hugo, *Ber. Dtsch. Chem. Ges.* 54B (1921) 795-802.
- [37] Swain C. G., Lupton Jr. E. C., *J. Am. Chem. Soc.* 90(16) (1968) 4328-4337.
- [38] Deiva C. M., Pappano N. B., Debattisata N. B., *Rev. Microbiol.* 29(4) (1998) 307-310.
- [39] Thirunarayanan G., *J. Saudi Chem. Soc.*, 2011. DOI:10.1016/j.jscs.2011.12.003.
- [40] K. Ranganathan, R. Suresh, D. Kamalakkannan, R. Arulkumar, R. Sundararajan, S. P. Sakthinathan, S. Vijayakumar, G. Vanangamudi, K. Thirumurthy, P. Mayavel, G. Thirunarayanan, *International Letters of Chemistry, Physics and Astronomy* 4 (2012) 66-75.
- [41] R. Arulkumar, S. Vijayakumar, R. Sundararajan, S. P. Sakthinathan, D. Kamalakkannan, R. Suresh, K. Ranganathan, P. R. Rajakumar, G. Vanangamudi, G. Thirunarayanan, *International Letters of Chemistry, Physics and Astronomy* 5 (2013) 21-38.
- [42] S. Vijayakumar, R. Arulkumar, R. Sundararajan, S. P. Sakthinathan, R. Suresh, D. Kamalakkannan, K. Ranganathan, K. Sathiyamoorthy, V. Mala, G. Vanangamudi, G. Thirunarayanan, *International Letters of Chemistry, Physics and Astronomy* 9(1) (2013) 68-86.
- [43] Thirunarayanan G., Sekar K. G., *International Letters of Chemistry, Physics and Astronomy* 10 (2013) 18-34.
- [44] R. Sundararajan, R. Arulkumar, S. Vijayakumar, D. Kamalakkannan, R. Suresh, S. John Joseph, K. Ranganathan, S. P. Sakthinathan, G. Vanangamudi, G. Thirunarayanan, *International Letters of Chemistry, Physics and Astronomy* 1 (2014) 67-73.

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