Spectral correlation analysis of Hammett substituent constants and biological activities of some (*E*)-1-(4-phenoxyphenyl)-3-phenylprop-2-en-1-ones

N. Kalyanasundaram[1], S. P. Sakthinathan[1], R. Suresh, D. Kamalakkannan[1], S. John Joseph[1], G. Vanangamudi[1,*], G. Thirunarayanan[2]

[1]PG & Research Department of Chemistry, Government Arts College, C-Mutlur, Chidambaram - 608102, India

[2]Department of Chemistry, Annamalai University, Annamalainagar - 608002, India

*E-mail address: drgvsibi@gmail.com

ABSTRACT

A series of aryl chalcones have been synthesized from 4-phenoxyacetophonone with various substituted benzaldehydes. The purity of all chalcones has been checked using their physical constants and spectral data. These spectral data have been correlated with Hammett substituent constants and F and R parameters using single and multi-linear regression analysis. From the results of statistical analysis, the effect of substituents on the above spectral data has been studied. The single parameter correlation with few Hammett constants and F and R parameters gave satisfactory correlation coefficients whereas all multiple correlations gave satisfactory correlation coefficients with Resonance, Field and Swain-Lupton's parameters. The antimicrobial activities of all chalcones have been studied using Bauer-Kirby method.

*Keywords***: substituted styryl 4-phenoxyphenylketones; UV-spectra; IR-spectra; NMR-spectra; Hammett constants; substituent effects; regression analysis and antimicrobial activities

1. INTRODUCTION

The quantitative structure activity relationship and quantitative structure property relationships were used for finding the structure of molecule, quantitative and qualitative analysis. Spectral data of organic compounds are useful for prediction of structure, stereo chemical and physicochemical properties [1]. There is considerable information avail in literature concerning the transmission of electronic effects in molecule undergoing isomer equilibration in ground state. For example enol and enones, α, β-unsaturated ketones [2]. The 2*E* chalcones are α, β-unsaturated ketones possess methylene structural moieties and they belongs to biomolecules. Many alkyl-alkyl, alkyl-aryl and aryl-aryl categories of chalcones were synthesized [3] and extracted from natural plants [4] by organic chemists. Due to C-C

single bond rotation [5] of carbonyl and alkene carbons, they exist as *E s-cis* and *s-trans* and *Z s-cis* and *Z s-trans* conformers. These structural conformers of chalcones have been confirmed by NMR and IR spectroscopy. the aldol condensation is useful for the formation of carbon-carbon bonds in many kinds of carbonyl compounds [6], due to the importance of the methylene structural unit, which is found in many naturally occurring compounds, antibiotics, and the use of cyclic and acyclic ketones as precursors for the synthesis of pyrimidine derivatives [7]. The basic skeleton of chalcones figures widely in natural products which are known to have multi-pronged activity [8]. Many of the chalcones are used as agrochemicals and drugs [9]. The condensation of ketones with aldehydes is of special interest, and the crossed-aldol condensation is an effective pathway for those preparations. Generally chalcones possess various multipronged activities [10] such as anticancer, antimicrobial [11], antioxidant [12] antiviral [13], anti-aids [14], insect antifeedant [10], antimalarial [15], anti-plasmodial [16] agrochemicals and drugs [17]. These potentials are also applied for the study of structure activity relationships [18]. From through literature survey it is observed that there is no report on the effect of substituents- QSAR or QPR study with these compounds, in the past. Therefore the authors take effort to synthesis some substituted styryl 4-Phenoxy phenyl ketones and study the correlation analysis with their UV, IR and NMR data and their antimicrobial activities by using Kirby-Bauer [19] disc diffusion technique.

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 (λmax, nm), of all chalcones in spectral grade solvent. Infrared spectra (KBr, 4000-400 cm^{-1}) were recorded AVATAR-300 Fourier transform spectrophotometer. BRUKER-300 MHz NMR spectrometer was used for recording NMR spectra operating at 300 MHz for ^{1}H spectra and 125.46 MHz for ^{13}C spectra in CDCl$_3$ solvent using TMS as internal standard.

2. 2. Synthesis of chalcones

X = H, 3-Br, 4-Br, 4-Cl, 4-F, 2-OCH$_3$, 4-OCH$_3$, 4-CH$_3$, 3-NO$_2$, 4-NO$_2$
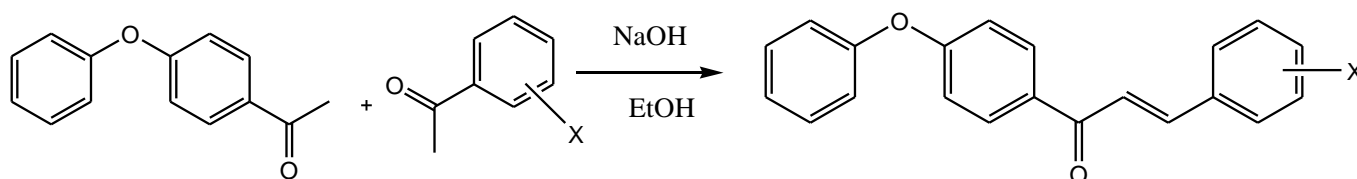
Scheme 1. Synthesis of substituted styryl 4-phenoxyphenyl ketones.

A solution of benzaldehyde (0.01 mol) and 4-phenoxyacetophenone (0.01 mol), sodium hydroxide (0.5 g) and 10 ml of ethanol were shaken occasionally for 1 hour [3]. The completion of the reaction was monitored by TLC. The resulting precipitate was filtered and

washed with cold water. The product appeared as pale yellow solid. Then the products are recrystallized using ethanol to obtain pale yellow glittering solid melting at 88-90 °C. The physical constants are presented in Table 1.

Table 1. Physical constants of substituted styryl 4-phenoxyphenyl ketones.

Entry	X	M. F.	M. W.	Yield (%)	m.p. (°C)
1	H	$C_{21}H_{16}O_2$	300	93	88-90 (85-86) [20]
2	3-Br	$C_{21}H_{15}BrO_2$	379	91	117-119
3	4-Br	$C_{21}H_{15}BrO_2$	379	88	124-126
4	4-Cl	$C_{21}H_{15}ClO_2$	334	89	134-136
5	4-F	$C_{21}H_{15}FO_2$	318	88	110-112
6	2-OCH$_3$	$C_{22}H_{18}O_3$	330	87	105-107
7	4-OCH$_3$	$C_{22}H_{18}O_3$	330	89	108-110 (97) [20]
8	4-CH$_3$	$C_{22}H_{18}O_2$	314	90	125-127
9	3-NO$_2$	$C_{21}H_{15}NO_4$	345	89	128-130
10	4-NO$_2$	$C_{21}H_{15}NO_4$	345	84	132-134

3. RESULTS AND DISCUSSION

In the present study the spectral linearity of chalcones has been studied by evaluating the substituent effects. The assigned group frequencies of all chalcones like carbonyl stretches νCO, the deformation modes of vinyl part CH *out of plane*, *in-plane*, CH=CH and >C=C< *out of planes* (cm^{-1}), the vinyl hydrogen and chemical shifts δ(ppm), of H$_\alpha$, H$_\beta$, C$_\alpha$, C$_\beta$, CO are assigned and these frequencies are correlated with various substituent constants.

3. 1. UV spectral study

The measured absorption maxima (λmax nm) values of the synthesized chalcones have been recorded and presented in Table 2. These data are correlated with Hammett substituent constants and F and R parameters using single and multi-linear regression analysis Hammett equation employed, for the correlation analysis, involving the absorption maxima is as shown below in equation (1).

$$\lambda = \rho\sigma + \lambda o \qquad (1)$$

where λo is the frequency for the parent member of the series.
The results of statistical analysis [21-23] are presented in Table 3. From the Table 3, the results of statistical analysis of these UV absorption maxima (λmax, nm) values with Hammett substituent constants, except that with 4-NO$_2$ substituent have shown satisfactory

correlations with Hammett substituent constant σ (r = 0.973) and $σ^+$ (r = 0.977). The absorption values except those with 4-F and 4-NO$_2$ substituents have shown satisfactory correlations with Hammett substituent constant $σ_R$ (r = 0.966) and R (r = 0.960) parameter. The absorption values except those with H(parent) and 4-CH$_3$ substituents have shown satisfactory correlations with Hammett substituent constant $σ_I$ (r = 0.936) and except those with H (parent) 2-OCH$_3$ and 4-OCH$_3$ substituents have shown satisfactory correlations with *F* (r = 0.903) parameter.

Also, the multi-regression produced satisfactory correlations with Hammett substituent constants and F and R parameters [24]. The multi correlation equations are given in (2) and (3).

$$λmax \text{ (nm)} = 332.507(±6.526) - 12.374(±13.156)σ_I - 28.973(±12.696)σ_R \quad …(2)$$
$$(R = 0.976, n = 10, P > 95 \%)$$

$$λmax \text{ (nm)} = 323.217 (±6.241) - 16.087(±12.158)F - 27.037(±11.324)R \quad …(3)$$
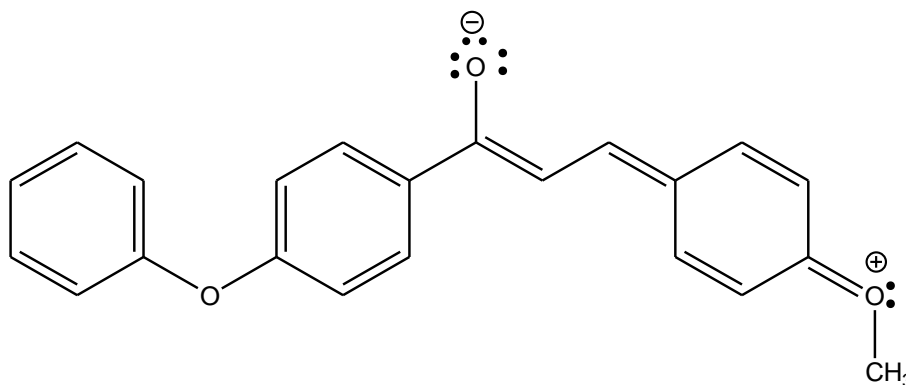$$(R = 0.972, n = 10, P > 95 \%)$$

Fig. 1. The resonance-conjugated structure.

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

Entry	X	$λ_{max}$	CO_{s-cis}	$CO_{s-trans}$	CH_{ip}	CH_{op}	$CH=CH_{op}$	$C=C_{op}$	δHα (ppm)	δHβ (ppm)	δCα (ppm)	δCβ (ppm)	δCO (ppm)
1	H	316	1654.92	1597.06	1247.94	754.17	991.41	499.56	7.092	8.208	121.91	143.62	187.57

No.	Subst.											
2	3-Br	314	1656.85	1598.99	1249.87	783.10	1022.27	491.85	7.057	8.234	119.99	141.82	187.40
3	4-Br	321	1658.76	1598.89	1224.80	746.45	977.91	489.92	7.656	8.205	119.98	142.22	187.45
4	4-Cl	319	1656.85	1597.06	1247.94	748.38	979.84	495.71	7.156	8.212	119.99	142.14	187.44
5	4-F	317	1656.85	1595.13	1240.23	750.31	1001.06	511.14	7.490	8.209	121.78	142.39	187.47
6	2-OCH$_3$	343	1627.92	1593.20	1253.73	759.95	987.55	536.21	7.480	8.185	119.92	143.61	187.42
7	4-OCH$_3$	343	1593.20	1500.62	1253.73	759.65	1029.99	499.56	7.457	8.187	119.93	143.62	187.41
8	4-CH$_3$	327	1653.00	1593.20	1244.09	806.25	1018.41	499.56	7.490	8.199	120.83	143.69	187.52
9	3-NO$_2$	307	1600.92	1529.55	1253.73	808.17	1018.41	513.07	7.278	8.333	120.01	141.07	187.42
10	4-NO$_2$	323	1658.78	1595.13	1240.23	752.24	1018.41	493.78	7.100	8.233	120.03	141.20	187.34

Table 3. Results of statistical analysis of ultraviolet absorption maxima (λmax, nm), infrared absorptions (ν cm^{-1}) and NMR chemical shifts (δ, ppm) of substituted styryl 4-phenoxy 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	0.973	326.438	-21.751	8.545	9	H,3-Br,4-Br,4-Cl,4-F,2-OCH$_3$, 4-OCH$_3$,4-CH$_3$,3-NO$_2$
	σ^{+}	0.977	324.446	-17.95	7.87054	9	H,3-Br,4-Br,4-Cl,4-F,2-OCH$_3$, 4-OCH$_3$,4-CH$_3$,3-NO$_2$
	σ$_I$	0.936	329.653	-17.6478	11.6829	8	3-Br,4-Br,4-Cl,4-F,2-OCH$_3$, 4-OCH$_3$,3-NO$_2$,4-NO2
	σ$_R$	0.966	317.469	-31.071	9.38913	8	H,3-Br,4-Br,4-Cl,2-OCH$_3$, 4-OCH$_3$,4-CH$_3$,3-NO$_2$
	F	0.903	329.671	-16.8886	11.6832	7	3-Br,4-Br,4-Cl,4-F,4-CH$_3$, 3-NO$_2$,4-NO2
	R	0.963	316.768	-27.4512	9.69761	8	H,3-Br,4-Br,4-Cl,2-OCH$_3$, 4-OCH$_3$,4-CH$_3$,3-NO$_2$
CO$_{s\text{-}cis}$	σ	0.817	1640.17	10.30767	26.5224	10	H,3-Br,4-Br,4-Cl,4-F,2-OCH$_3$,4-OCH$_3$,4-CH$_3$,3-NO$_2$,4-NO$_2$
	σ^{+}	0.812	1640.50	16.12202	25.4061	10	H,3-Br,4-Br,4-Cl,4-F,2-OCH$_3$, 4-OCH$_3$,4-CH$_3$,3-NO$_2$,4-NO$_2$
	σ$_I$	0.708	1644.06	-5.98854	26.8321	10	H,3-Br,4-Br,4-Cl,4-F,2-OCH$_3$, 4-OCH$_3$,4-CH$_3$,3-NO$_2$,4-NO$_2$

	σ_R	0.8	1644.62	15.82122	26.5412	10	H,3-Br,4-Br,4-Cl,4-F,2-OCH$_3$, 4-OCH$_3$,4-CH$_3$,3-NO$_2$,4-NO$_2$
	F	0.702	1642.95	-2.91977	26.8651	10	H,3-Br,4-Br,4-Cl,4-F,2-OCH$_3$, 4-OCH$_3$,4-CH$_3$,3-NO$_2$,4-NO$_2$
	R	0.751	1645.50	16.3119	26.4582	10	H,3-Br,4-Br,4-Cl,4-F,2-OCH$_3$, 4-OCH$_3$,4-CH$_3$,3-NO$_2$,4-NO$_2$
CO$_{s\text{-}trans}$	σ	0.804	1579.15	4.616102	36.9488	10	H,3-Br,4-Br,4-Cl,4-F,2-OCH$_3$, 4-OCH$_3$,4-CH$_3$,3-NO$_2$,4-NO$_2$
	σ^+	0.801	1578.42	18.14888	35.6593	10	H,3-Br,4-Br,4-Cl,4-F,2-OCH$_3$, 4-OCH$_3$,4-CH$_3$,3-NO$_2$,4-NO$_2$
	σ_I	0.702	1584.61	-12.5581	36.8578	10	H,3-Br,4-Br,4-Cl,4-F,2-OCH$_3$, 4-OCH$_3$,4-CH$_3$,3-NO$_2$,4-NO$_2$
	σ_R	0.765	1580.68	4.502829	36.9805	10	H,3-Br,4-Br,4-Cl,4-F,2-OCH$_3$, 4-OCH$_3$,4-CH$_3$,3-NO$_2$,4-NO$_2$
	F	0.841	1584.05	-10.5638	36.8902	10	H,3-Br,4-Br,4-Cl,4-F,2-OCH$_3$, 4-OCH$_3$,4-CH$_3$,3-NO$_2$,4-NO$_2$
	R	0.841	1582.98	13.67284	36.7876	10	H,3-Br,4-Br,4-Cl,4-F,2-OCH$_3$, 4-OCH$_3$,4-CH$_3$,3-NO$_2$,4-NO$_2$
CH$_{ip}$	σ	0.920	1246.34	-4.53965	9.29186	6	H,3-Br,4-Cl,4-F,4-CH$_3$,3-NO$_2$
	σ^+	0.903	1246.11	-5.96681	8.91497	7	H,3-Br,4-Cl,4-F,2-OCH$_3$, 4-CH$_3$,3-NO$_2$

	σ_I	0.965	1247.90	-6.02639	9.35878	10	H,3-Br,4-Br,4-Cl,4-F,2-OCH$_3$, 4-OCH$_3$,4-CH$_3$,3-NO$_2$,4-NO$_2$
	σ_R	0.901	1244.71	-5.14126	9.38699	7	H,3-Br,4-Cl,2-OCH$_3$,4-OCH$_3$, 4-CH$_3$,4-NO$_2$
	F	0.901	1248.37	-6.95774	9.29975	7	H,3-Br,4-Cl,2-OCH$_3$,4-OCH$_3$, 4-CH$_3$,3-NO$_2$
	R	0.909	1244.95	-2.97338	9.44806	6	H,3-Br,4-Cl,4-F,4-CH$_3$, 3-NO$_2$
CH$_{op}$	σ	0.8	765.400	9.275061	24.7633	10	H,3-Br,4-Br,4-Cl,4-F,2-OCH$_3$, 4-OCH$_3$,4-CH$_3$,3-NO$_2$,4-NO$_2$
	σ^+	0.8	766.433	5.37808	24.8994	10	H,3-Br,4-Br,4-Cl,4-F,2-OCH$_3$, 4-OCH$_3$,4-CH$_3$,3-NO$_2$,4-NO$_2$
	σ_I	0.812	772.290	-14.3862	24.7940	10	H,3-Br,4-Br,4-Cl,4-F,2-OCH$_3$, 4-OCH$_3$,4-CH$_3$,3-NO$_2$,4-NO$_2$
	σ_R	0.798	772.675	32.63249	23.5016	10	H,3-Br,4-Br,4-Cl,4-F,2-OCH$_3$, 4-OCH$_3$,4-CH$_3$,3-NO$_2$,4-NO$_2$
	F	0.814	772.476	-14.2001	24.7763	10	H,3-Br,4-Br,4-Cl,4-F,2-OCH$_3$, 4-OCH$_3$,4-CH$_3$,3-NO$_2$,4-NO$_2$
	R	0.823	773.18	27.8106	23.7416	10	H,3-Br,4-Br,4-Cl,4-F,2-OCH$_3$, 4-OCH$_3$,4-CH$_3$,3-NO$_2$,4-NO$_2$

CH=CH$_{op}$	σ	0.919	1003.03	9.416676	20.0165	6	H,4-Br,4-Cl,4-F,4-OCH$_3$, 4-CH$_3$
	σ^+	0.902	1004.56	-0.45712	20.4055	6	H,4-Br,4-Cl,4-F,4-OCH$_3$, 4-CH$_3$
	σ_I	0.804	1003.19	3.524465	20.3868	10	H,3-Br,4-Br,4-Cl,4-F,2-OCH$_3$, 4-OCH$_3$,4-CH$_3$,3-NO$_2$,4-NO$_2$
	σ_R	0.792	1007.44	16.41204	19.9291	10	H,3-Br,4-Br,4-Cl,4-F,2-OCH$_3$, 4-OCH$_3$,4-CH$_3$,3-NO$_2$,4-NO$_2$
	F	0.825	1001.99	6.398419	20.3339	10	H,3-Br,4-Br,4-Cl,4-F,2-OCH$_3$, 4-OCH$_3$,4-CH$_3$,3-NO$_2$,4-NO$_2$
	R	0.824	1006.24	7.569515	20.2890	10	H,3-Br,4-Br,4-Cl,4-F,2-OCH$_3$, 4-OCH$_3$,4-CH$_3$,3-NO$_2$,4-NO$_2$
C=C$_{op}$	σ	0.939	505.242	-13.9563	13.5194	8	H,3-Br,4-Br,4-Cl,4-F,4-OCH$_3$, 4-CH$_3$,4-NO$_2$
	σ^+	0.936	503.824	-9.7785	13.7539	7	H,3-Br,4-Br,4-Cl,4-OCH$_3$, 4-CH$_3$,4-NO$_2$
	σ_I	0.702	503.571	-1.4203	14.7417	10	H,3-Br,4-Br,4-Cl,4-F,2-OCH$_3$, 4-OCH$_3$,4-CH$_3$,3-NO$_2$,4-NO$_2$
	σ_R	0.802	497.894	-28.8871	12.5590	10	H,3-Br,4-Br,4-Cl,4-F,2-OCH$_3$, 4-OCH$_3$,4-CH$_3$,3-NO$_2$,4-NO$_2$

		r	I	ρ	s	n	Correlated derivatives
	F	0.812	502.311	1.834035	14.7379	10	H,3-Br,4-Br,4-Cl,4-F,2-OCH$_3$, 4-OCH$_3$,4-CH$_3$,3-NO$_2$,4-NO$_2$
	R	0.811	498.290	-20.9059	13.4459	10	H,3-Br,4-Br,4-Cl,4-F,2-OCH$_3$, 4-OCH$_3$,4-CH$_3$,3-NO$_2$,4-NO$_2$
δH$_\alpha$	σ	0.905	7.36938	-0.27693	0.19485	8	3-Br,4-Cl,4-F,2-OCH$_3$,4-OCH$_3$, 4-CH$_3$,3-NO$_2$,4-NO$_2$
	σ$^+$	0.904	7.34074	-0.18795	0.20290	8	3-Br,4-Cl,4-F,2-OCH$_3$,4-OCH$_3$, 4-CH$_3$,3-NO$_2$,4-NO$_2$
	σ$_I$	0.712	7.36982	-0.11731	0.22517	10	H,3-Br,4-Br,4-Cl,4-F,2-OCH$_3$, 4-OCH$_3$,4-CH$_3$,3-NO$_2$,4-NO$_2$
	σ$_R$	0.905	7.24383	-0.45934	0.19110	8	H,4-Cl,4-F,2-OCH$_3$,4-OCH$_3$, 4-CH$_3$,3-NO$_2$,4-NO$_2$
	F	0.803	7.33565	-0.02546	0.22709	10	H,3-Br,4-Br,4-Cl,4-F,2-OCH$_3$, 4-OCH$_3$,4-CH$_3$,3-NO$_2$,4-NO$_2$
	R	0.905	7.22236	-0.45479	0.18512	8	H,4-Cl,4-F,2-OCH$_3$,4-OCH$_3$, 4-CH$_3$,3-NO$_2$,4-NO$_2$

Chemical shifts	Constants	r	I	ρ	s	n	Correlated derivatives
δ$_{H\beta}$	σ	0.917	8.207	0.08287	0.02885	9	H,3-Br,4-Br,4-Cl,4-F, 2-OCH$_3$,4-OCH$_3$,4-CH$_3$, 4-NO$_2$

	σ^+	0.917	8.215	0.05945	0.03177	9	H,3-Br,4-Br,4-Cl,4-F, 2-OCH$_3$,4-OCH$_3$,4-CH$_3$, 4-NO$_2$
	σ_I	0.925	8.184	0.096313	0.03790	9	H,3-Br,4-Br,4-Cl,4-F, 2-OCH$_3$,4-OCH$_3$,4-CH$_3$, 4-NO$_2$
	σ_R	0.916	8.240	0.11087	0.03428	9	H,3-Br,4-Br,4-Cl,4-F, 2-OCH$_3$,4-OCH$_3$,4-CH$_3$, 4-NO$_2$
	F	0.914	8.187	0.082544	0.03948	9	H,3-Br,4-Br,4-Cl,4-F, 2-OCH$_3$,4-OCH$_3$,4-CH$_3$, 4-NO$_2$
	R	0.906	8.243	0.100915	0.03465	9	H,3-Br,4-Br,4-Cl,4-F, 2-OCH$_3$,4-OCH$_3$,4-CH$_3$, 4-NO$_2$
δC_α	σ	0.814	120.509	-0.45927	0.81457	10	H,3-Br,4-Br,4-Cl,4-F, 2-OCH$_3$,4-OCH$_3$,4-CH$_3$, 3-NO$_2$,4-NO$_2$
	σ^+	0.758	120.458	-0.26364	0.82493	10	H,3-Br,4-Br,4-Cl,4-F, 2-OCH$_3$,4-OCH$_3$,4-CH$_3$, 3-NO$_2$,4-NO$_2$
	σ_I	0.715	120.970	-1.41612	0.75326	10	H,3-Br,4-Br,4-Cl,4-F, 2-OCH$_3$,4-OCH$_3$,4-CH$_3$, 3-NO$_2$,4-NO$_2$
	σ_R	0.704	120.412	-0.13787	0.83649	10	H,3-Br,4-Br,4-Cl,4-F, 2-OCH$_3$,4-OCH$_3$,4-CH$_3$, 3-NO$_2$,4-NO$_2$
	F	0.725	120.732	-0.74882	0.81257	10	H,3-Br,4-Br,4-Cl,4-F, 2-OCH$_3$,4-OCH$_3$,4-CH$_3$, 3-NO$_2$,4-NO$_2$
	R	0.801	120.393	-0.19033	0.83548	10	H,3-Br,4-Br,4-Cl,4-F, 2-OCH$_3$,4-OCH$_3$,4-CH$_3$, 3-NO$_2$,4-NO$_2$

δC_β	σ	0.947	142.926	-2.45457	0.34984	10	H,3-Br,4-Br,4-Cl,4-F, 2-OCH$_3$,4-OCH$_3$,4-CH$_3$, 3-NO$_2$,4-NO$_2$
	σ^+	0.914	142.684	-1.81335	0.47158	10	H,3-Br,4-Br,4-Cl,4-F, 2-OCH$_3$,4-OCH$_3$,4-CH$_3$, 3-NO$_2$,4-NO$_2$
	σ_I	0.992	143.956	-3.76242	0.50149	8	3-Br,4-Br,4-Cl,4-F,2-OCH$_3$, 4-OCH$_3$,3-NO$_2$,4-NO$_2$
	σ_R	0.904	142.122	-2.33418	0.89724	8	3-Br,4-Br,4-Cl,4-F,2-OCH$_3$, 4-OCH$_3$,3-NO$_2$,4-NO$_2$
	F	0.914	143.848	-3.3169	0.62812	9	H,3-Br,4-Br,4-Cl,2-OCH$_3$, 4-OCH$_3$,4-CH$_3$,3-NO$_2$, 4-NO$_2$
	R	0.951	142.069	-2.0656	0.91494	7	3-Br,4-Br,4-Cl,2-OCH$_3$, 4-OCH$_3$,3-NO$_2$,4-NO$_2$
δCO	σ	0.905	187.456	-0.07644	0.06033	8	H,3-Br,4-Br,4-Cl,4-F, 4-CH$_3$,3-NO$_2$,4-NO$_2$
	σ^+	0.903	187.447	-0.04353	0.06418	8	H,3-Br,4-Br,4-Cl,4-F, 4-CH$_3$,3-NO$_2$,4-NO$_2$
	σ_I	0.907	187.520	-0.20307	0.04394	10	H,3-Br,4-Br,4-Cl,4-F, 2-OCH$_3$,4-OCH$_3$, 4-CH$_3$,3-NO$_2$,4-NO$_2$
	σ_R	0.9	187.442	-0.00905	0.06836	8	3-Br,4-Br,4-Cl,4-F,2-OCH$_3$, 4-OCH$_3$,3-NO$_2$,4-NO$_2$
	F	0.916	187.511	-0.16974	0.05083	9	H,3-Br,4-Br,4-Cl,2-OCH$_3$, 4-OCH$_3$,4-CH$_3$,3-NO$_2$,4-NO$_2$

	R	0.902	187.442	-0.00644	0.06838	8	H,3-Br,4-Br,4-Cl,4-F, 2-OCH₃,4-OCH₃,4-CH₃

3. 2. IR spectral study

The carbonyl stretching frequencies (cm^{-1}) of *s-cis* and *s-trans* conformers are shown in Fig. 2. The IR frequency values are presented in Table 2.
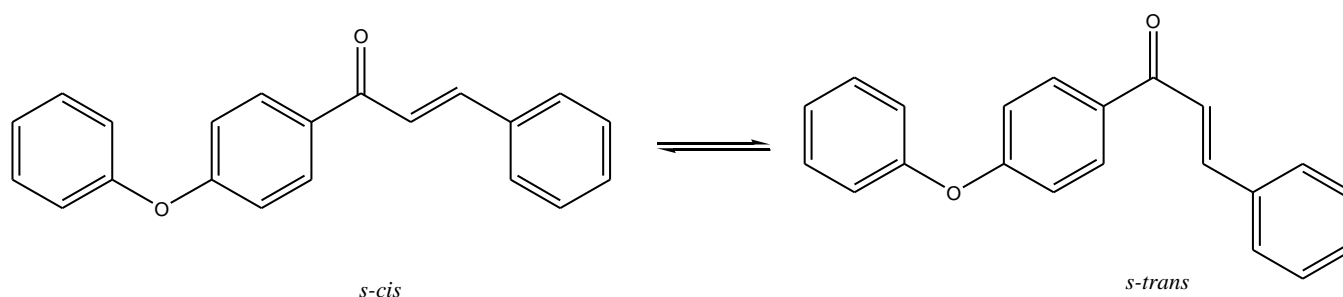
Fig. 2. The *s-cis* and *s-trans* conformers of 4-phenoxy phenyl ketones.

The IR frequency values are correlated with Hammett substituent constants and Swain-Lupton's parameters [24] are presented in Table 3. While seeking Hammett correlation [25-40] involving group frequencies, the form of the Hammett equation employed is

$$\nu = \rho\sigma + \nu_0 \qquad \dots (4)$$

where ν is the carbonyl frequencies of substituted system.

From Table 3, the IR frequency CO*s-cis* and CO*s-trans* values have shown poor correlations (r < 0.900) with Hammett substituent constants and *F* and *R* parameters. This is attributed to weak polar, inductive, field and resonance effects of the substituents for predicting the reactivity on the IR frequency through resonance. This is evident with resonance conjugative structure shown in Fig. 1.

The infrared frequency of CH$_{ip}$, except those with 4-Br, 2-OCH₃, 4-OCH₃ and 4-NO₂ substituents have shown satisfactory correlation with Hammett substituent constant σ (r = 0.920) and R (r = 0.909) parameter, except those with 4 -Br, 4-OCH₃ and 4-NO₂ substituents have shown satisfactory correlation with Hammett substituent constant σ$^+$ (r = 0.903), except those with 4-Br, 4-F and 4-NO₂ substituents have shown satisfactory correlation with Hammett substituent constant σ$_R$ (r = 0.901) and except those with 4-Br, 4-F and 3-NO₂ substituents have shown satisfactory correlation with *F* (r = 0.901) parameter. The remaining Hammett substituent constant σ$_I$ have shown poor correlations (r < 0.900) This is attributed to the weak field and resonance effects of the substituents for predicting the reactivity on the infrared frequency through resonance as per the conjugative structure as shown in Fig. 1.

The infrared frequency of CH_{op} with all Hammett substituent constants and *F* and *R* parameters has shown poor correlation (r < 0.900). The infrared frequency of $CH=CH_{op}$ except those with 3-Br, 2-OCH_3, 3-NO_2 and 4-NO_2 substituents have shown satisfactory correlation with Hammett substituent constant σ (r = 0.919) and $σ^+$ (r = 0.909) and $C=C_{op}$ except those with 2-OCH_3 and 3-NO_2 substituents have shown satisfactory correlation with Hammett substituent constant σ (r = 0.939) and $σ^+$ (r = 0.936). The remaining Hammett substituent constants and F and R parameters have shown poor correlations (r < 0.900) This is attributed to the weak field and resonance effects of the substituent for predicting the reactivity on the infrared frequency through resonance as per the conjugative structure as shown in Fig. 1.

Some of the single regression analyses have shown poor correlation, it is decided to go for multi-regression analyses. The multi-regression produced satisfactory correlations with Hammett substituent constants and *F* and *R* parameters [24]. The multi correlation equations are given in (5) - (16).

$$νCO_{s\text{-}cis} (cm^{-1}) = 1648.347(±19.504) − 9.151(±3.319)σ_I + 17.372(±2.944)σ_R \qquad …(5)$$
$$(R = 0.917, n = 10, P > 90 \text{ %})$$

$$νCO_{s\text{-}cis} (cm^{-1}) = 1646.873(±19.027) − 3.406(±1.066)F + 16.399(±2.522)R \qquad … (6)$$
$$(R = 0.917, n = 10, P > 90 \text{ %})$$

$$νCO_{s\text{-}trans}(cm^{-1}) = 1586.305(±27.157) − 13.803(±1.747)σ_I + 6.843(±1.833)σ_R \qquad …(7)$$
$$(R = 0.910, n = 10, P > 90 \text{ %})$$

$$νCO_{s\text{-}trans}(cm^{-1}) = 1587.387(±26.385) − 10.977(±2.401)F + 13.955(±2.873)R \qquad …(8)$$
$$(R = 0.913, n = 10, P > 90 \text{ %})$$

$$νCH_{ip}(cm^{-1}) = 1246.853(±6.854) − 5.253(±1.818)σ_I − 4.251(±1.335)σ_R \qquad …(9)$$
$$(R = 0.920, n = 10, P > 90 \text{ %})$$

$$νCH_{ip}(cm^{-1}) = 1247.71(±6.666) − 6.875(±1.987)F − 2.797(±1.095)R \qquad …(10)$$
$$(R = 0.921, n = 10, P > 90 \text{ %})$$

$$νCH_{op}(cm^{-1}) = 781.215(±16.885) − 20.973(±2.039)σ_I + 36.188(±3.849)σ_R \qquad …(11)$$
$$(R = 0.940, n = 10, P > 95 \text{ %})$$

$$νCH_{op}(cm^{-1}) = 779.207(±16.832) − 15.036(±2.792)F + 28.197(±3.541)R \qquad …(12)$$
$$(R = 0.935, n = 10, P > 95\text{%})$$

$$νCH=CH_{op}(cm^{-1}) = 1007.222(±14.701) + 0.554(±0.637)σ_I + 16.318(±2.600)σ_R \qquad …(13)$$
$$(R = 0.921, n = 10, P > 90 \text{ %})$$

$$νCH=CH_{op}(cm^{-1}) = 1003.768(±14.550) + 6.179(±1.345)F + 7.411(±2.399)R \qquad …(14)$$
$$(R = 0.913, n = 10, P > 90 \text{ %})$$

$$νC=C_{op}(cm^{-1}) = 496.282(±9.235) + 3.960(±1.617)σ_I − 29.558(±3.966)σ_R \qquad …(15)$$
$$(R = 0.982, n = 10, P > 95 \text{ %})$$

$$\nu C{=}C_{op}(cm^{-1}) = 497.306(\pm 9.663) + 2.455(\pm 1.825)F - 20.969(\pm 2.533)R \qquad \ldots(16)$$
$$(R = 0.941, n = 10, P > 95\ \%)$$

3. 3. NMR Spectral study

3. 3. 1. ^{1}H NMR spectra

The 1H NMR spectra of the chalcones under investigation have been recorded in deuteriated dimethyl sulphoxide employing tetramethylsilane (TMS) as internal standard. The signals of the ethylenic protons have been assigned. They are calculated as AB or AA^0 BB^0 systems respectively. The assigned chemical shifts values are presented in Table 2. In nuclear magnetic resonance spectra, the proton or the ^{13}C 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

$$\delta = \delta_0 + \rho\sigma \qquad \ldots (17)$$

where δ_0 is the chemical shift of unsubstituted system.

The assigned Hα and H$_\beta$ proton chemical shifts (ppm) are correlated with various Hammett sigma constants. The results of statistical analysis [20-23] are presented in Table 3. The Hα chemical shifts (δ, ppm) correlated with Hammett constants and F and R parameters, except those with H (parent) and 4-Br have shown satisfactory correlations with a few Hammett substituent constants σ (r = 0.905) and σ^+ (r = 0.904) and except those with 3-Br and 4-Br substituents have shown satisfactory correlations with Hammett substituent constant σ_R (r = 0.905) and R (r = 0.905) parameter.

The H$_\beta$ chemical shifts (δ, ppm) correlated with Hammett constants and F and R parameters, except that with 3-NO$_2$ substituent have shown satisfactory correlation with Hammett substituent constant σ (r = 0.917), σ+ (r = 0.919), σ_I (r = 0.925), σ_R (0.916), F (0.914) and R (r = 0.906) parameters.

The remaining few Hammett substituent constants and swain-Lupton's parameters [24] have shown poor correlations (r < 0.900). This is attributed to the weak polar and resonance effects of the substituent for predicting the reactivity on the chemical shifts through resonance as per the conjugative structure shown in Fig. 1.

Some of the single regression analyses have shown poor correlations with Hammett substituent constants and swain-Lupton's parameters [24]. It is decided to go for multi-regression, the multi-regression analysis produced satisfactory correlations with the chemical shifts of (δ, ppm) Hα and Hβ. The multi correlation equations are given in (18)-(21).

$$\delta H_\alpha(ppm) = 7.258(\pm 0.141) - 0.035(\pm 0.284)\sigma_I - 0.453(\pm 0.274)\sigma_R \qquad \ldots(18)$$
$$(R = 0.942, n = 10, P > 90\ \%)$$

$$\delta H_\alpha(ppm) = 7.227(\pm 0.133) - 0.012(\pm 0.259)F - 0.454(\pm 0.242)R \qquad \ldots(19)$$
$$(R = 0.957, n = 10, P > 95\ \%)$$

$$\delta H_\beta(ppm) = 8.208(\pm 0.020) + 0.078(\pm 0.41)\sigma_I + 0.097(\pm 0.040)\sigma_R \qquad \ldots(20)$$
$$(R = 0.997, n = 10, P > 95\ \%)$$

$$\delta H_\beta(ppm) = 8.211(\pm 0.019) + 0.080(\pm 0.038)F + 0.099(\pm 0.035)R \qquad \ldots(21)$$
$$(R = 0.997, n = 10, P > 95\ \%)$$

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

From Table 3, the $\delta C\alpha$ chemical shifts values have shown poor correlations (r< 0.900) with Hammett substituent constants and *F* and *R* parameters. This is attributed to weak polar, inductive, field and resonance effects of the substituents for predicting the reactivity on the chemical shift through resonance. This is evident with resonance conjugative structure shown in Fig. 1.

The δC_β chemical shift, with all the substituents have shown satisfactory correlations with Hammett substituent constants namely σ (r = 0.947) and σ^+ (r = 0.914). The δC_β chemical shift values, except those with H (parent) and 4-CH$_3$ substituents have shown satisfactory correlations with Hammett substituent constants σ_I (r = 0.992) and σ_R (r = 0.904), except that with 4-F substituent have shown satisfactory correlations with *F* (r = 0.914) parameter and except those with H (parent), 4-F and 4-CH$_3$ substituents have shown satisfactory correlations with *R* (r = 0.951) parameter.

The δCO chemical shifts, except those with 2-OCH$_3$ and 4-OCH$_3$ substituents have shown satisfactory correlations with Hammett substituent constants namely σ (r = 0.905) and σ^+ (r = 0.903), except that with 4-CH$_3$ substituent have shown satisfactory correlations with Hammett substituent constant namely σ_R (r = 0.907), except that with 4-F substituent have shown satisfactory correlations with *F* (r = 0.914) parameter and except those with 3-NO$_2$ and 4-NO$_2$ substituents have shown satisfactory correlations with *R* parameter. The remaining Hammett substituents have shown poor correlations (r < 0.900). This is due to the weak polar effect of the substituents for predicting the reactivity on the chemical shift through resonance as per the conjugative structure shown in Fig-1

Some of the single parameter correlation was fails in regression, while seeking the multi-regression analysis correlations were satisfactorily obtained within these carbon chemical shifts and the multi-regression equations are given in (22)-(27).

$$\delta CO(ppm) = 187.527(\pm 0.032) - 0.208(\pm 0.064)\sigma I + 0.026(\pm 0.062)\sigma_R \qquad \ldots(22)$$
$$(R = 0.977, \text{n} = 10, \text{P} > 90\ \%)$$

$$\delta CO(ppm) = 187.510(\pm 0.036) - 0.170(\pm 0.071)F - 0.002(\pm 0.066)R \qquad \ldots(23)$$
$$(R = 0.966, \text{n} = 10, \text{P} > 95\ \%)$$

$$\delta C_\alpha(ppm) = 120.997(\pm 0.555) - 1.435(\pm 0.119)\sigma I + 0.105(\pm 1.080)\sigma_R \qquad \ldots(24)$$
$$(R = 0.943, \text{n} = 10, \text{P} > 95\ \%)$$

$$\delta C_\alpha(ppm) = 120.692(\pm 0.584) - 0.744(\pm 0.137)F - 0.171(\pm 1.059)R \qquad \ldots(25)$$
$$(R = 0.924, \text{n} = 10, \text{P} > 95\ \%)$$

$$\delta C_\beta(ppm) = 143.525(\pm 0.146) - 3.444(\pm 0.294)\sigma I - 1.750(\pm 0.283)\sigma_R \qquad \ldots(26)$$
$$(R = 0.998, \text{n} = 10, \text{P} > 95\ \%)$$

$$\delta C_\beta(ppm) = 143.375(\pm 0.184) - 3.258(\pm 0.358)F - 1.982(\pm 0.334)R \qquad \ldots(27)$$
$$(R = 0.997, \text{n} = 10, \text{P} > 95\ \%)$$

3. 4. Antimicrobial activities

3. 4. 1. Antibacterial sensitivity assay

Antibacterial sensitivity assay was performed using Kirby-Bauer [19] 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 foreceps. 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.

3. 4. 2. Antifungal sensitivity assay

Antifungal sensitivity assay was performed using Kirby-Bauer [19] 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 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.

Plate - 1
Fig. 2. Petri-dishes for Anti-bacterial activity of substituted 4-phenoxy phenyl ketones.
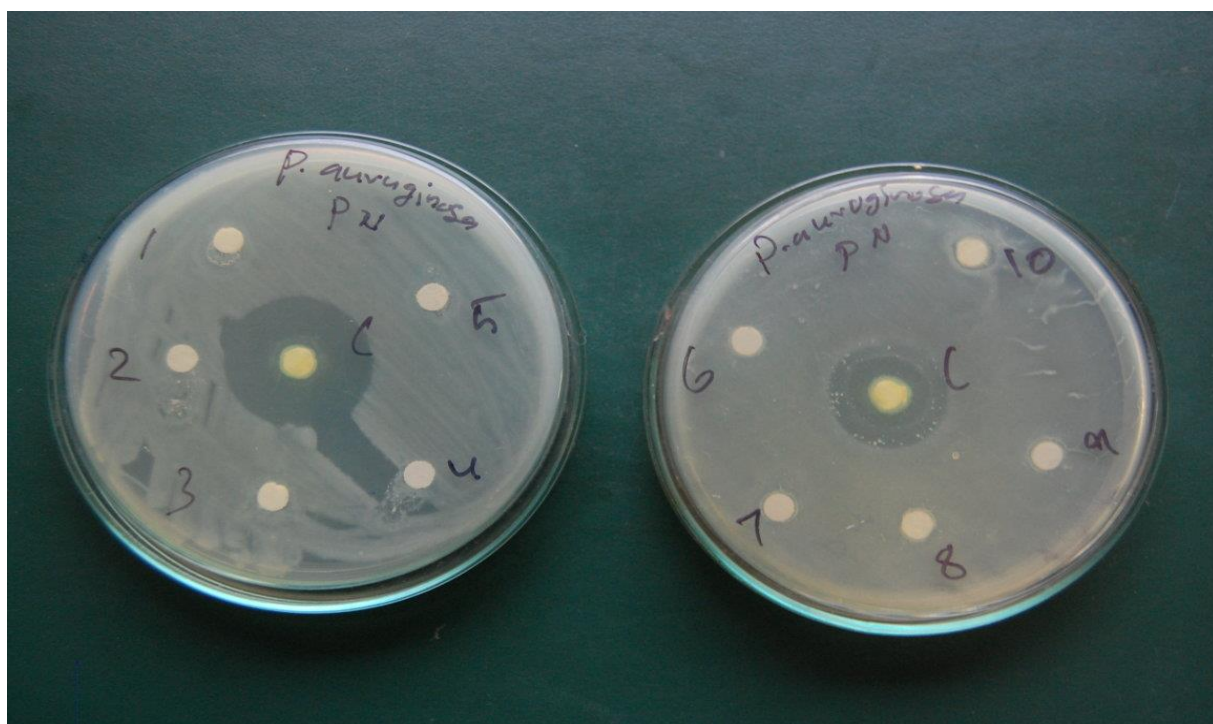
Plate – 2

Plate - 3
Fig. 2(continue). Petri-dishes for Anti-bacterial activity of substituted 4-phenoxy phenyl ketones.
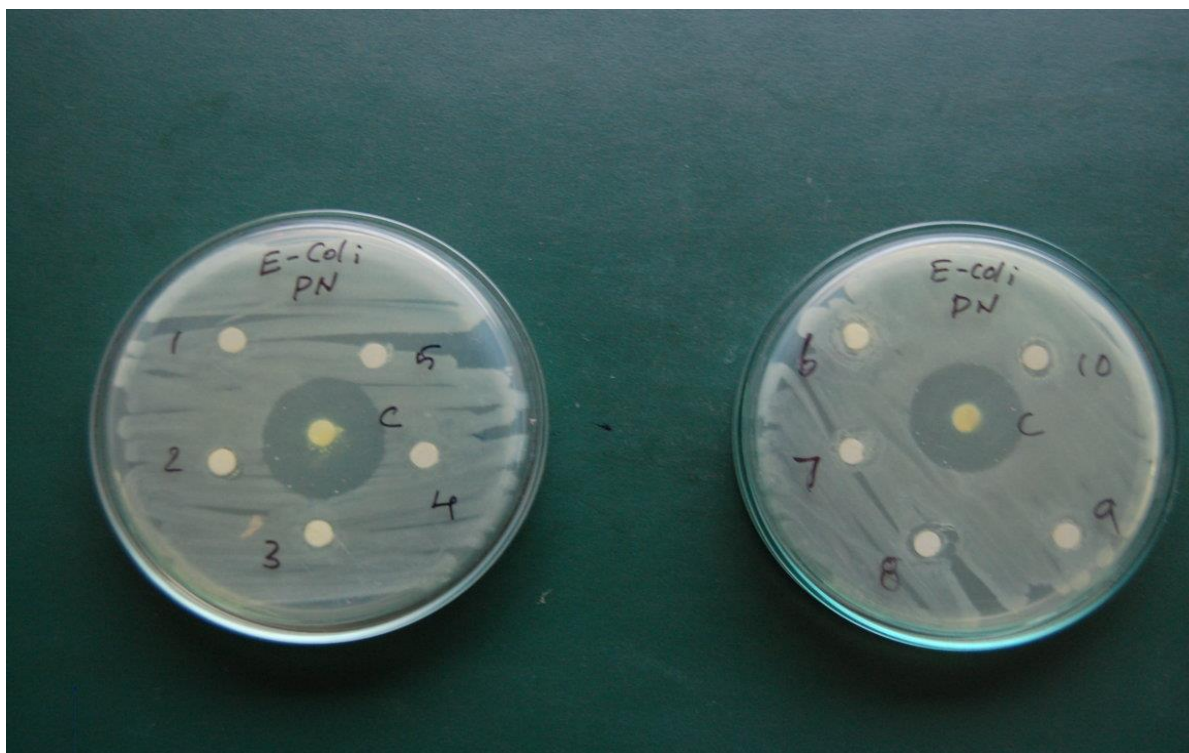
Plate - 4

Plate – 5

Fig. 2(continue). Petri-dishes for Anti-bacterial activity of substituted 4-phenoxy phenyl ketones.

Table 4. Antibacterial activity of substituted styryl 4-phenoxy phenyl ketones.

S. No.	Substituent	Zone of Inhibition (mm)				
		Gram positive Bacteria			Gram negative Bacteria	
		B. subtilis	*M. luteus*	*S. aureus*	*E. coli*	*P. aeruginosa*
1	H	8	-	9	-	7
2	3-Br	7	7	7	8	7
3	4-Br	7	-	9	7	-
4	4-Cl	7	7	10	-	-
5	4-F	-	7	7	-	8
6	2-OCH$_3$	-	-	8	8	-
7	4-OCH$_3$	7	-	8	8	7
8	4-CH$_3$	-	-	-	9	-
9	3-NO$_2$	-	-	8	7	8
10	4-NO$_2$	7	-	-	8	9
Standard	Ampicillin	16	16	21	19	15
Control	DMSO	-	-	-	-	-
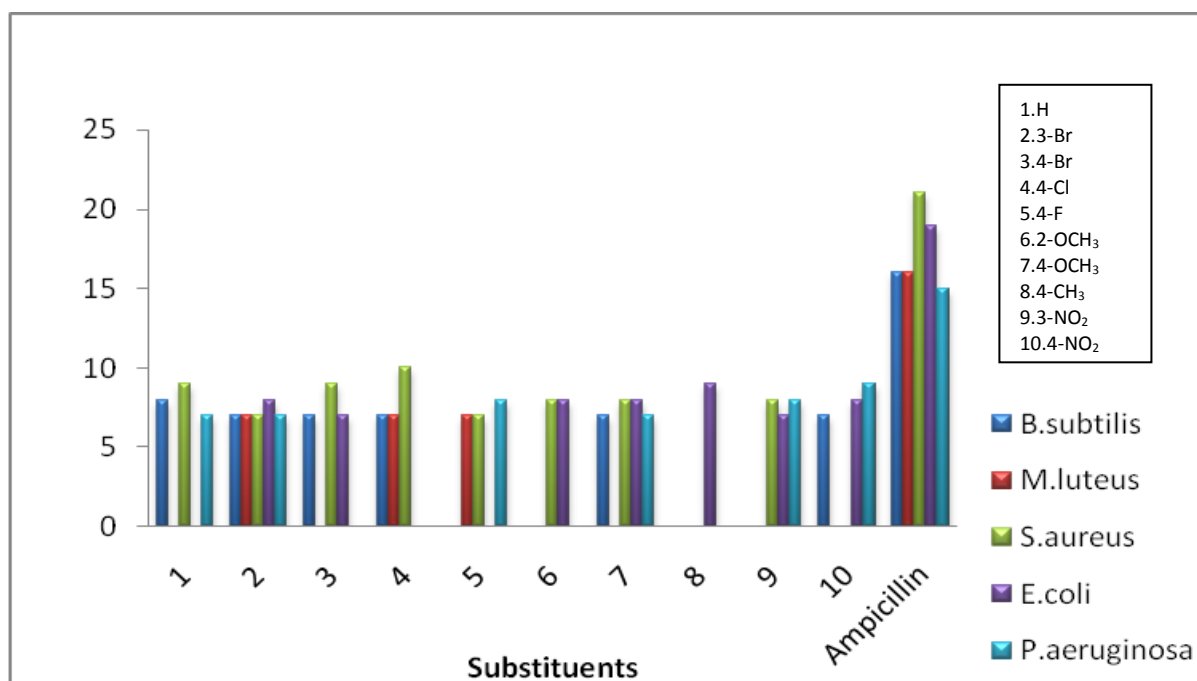
Fig. 3. Chart for Antibacterial activity of substituted styryl 4-phenoxy phenyl ketones.

The antibacterial effect of the styryl 4-phenoxy phenyl chalcones is shown in Fig. 3 for Plates (1)-(5). Analysis of the zone of inhibition values are given in Table-4 and the Clustered column Chart Fig-3. H(parent), 4-Cl and 4-Br substituent has shown markable antibacterial activity against *S. aureus*. All the substituents except 4-Cl have shown moderate antibacterial activity against *E. coli* and *P. aeruginosa*. All the substituents except 4-F, 2-OCH$_3$ and 4-CH$_3$ have shown moderate antibacterial activity against *B. subtilis.*

The antifungal effect of the styryl 4-phenoxy phenyl ketones is shown in Fig. 5 for Plates (11-14). Analysis of the zone of inhibition values is given Table 5 and the Clustered column Chart Fig. 6. Analysis of the Zone of inhibition (mm) values reveals that only four substituent compounds with H (parent), 4-Cl, 3-NO$_2$ and 4-NO$_2$ have shown moderate antifungal activities against *A. niger*. The compounds with 4-CH$_3$, 3-NO$_2$ and 4-NO$_2$ substituents have shown good antifungal activities against *T. viride*. The remaining substituents have shown moderate antifungal activities against *T. viride*.
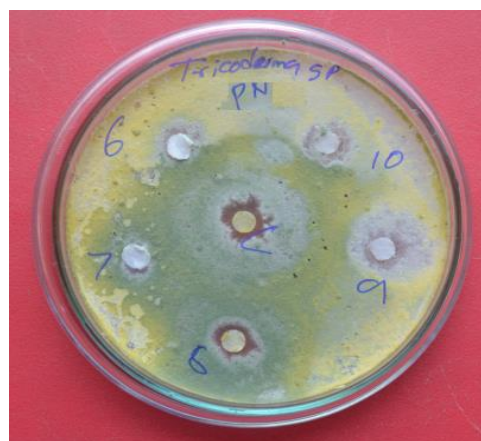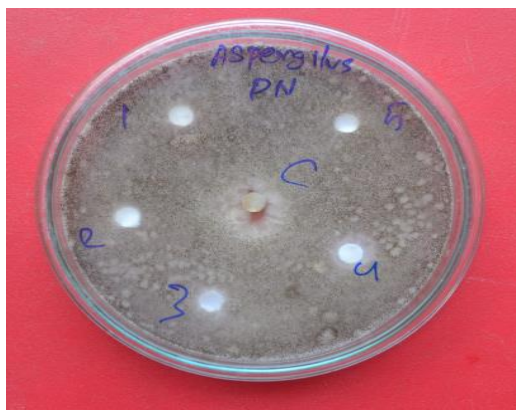

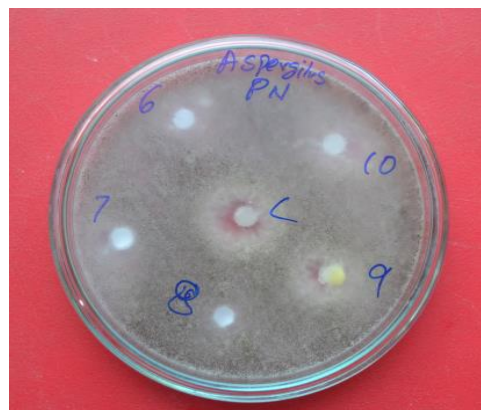Plate - 6

Plate - 7

Plate - 8

Plate - 9

Fig. 4. Antifungal activities substituted styryl 4-phenoxyphenyl ketones.

Table 5. Antifungal activity of substituted styryl 4-phenoxyphenyl ketones.

S. No	Substituents	Zone of Inhibition (mm)	
		A. niger	*T. viride*
1	H	7	9
2	3-Br	-	9
3	4-Br	7	7
4	4-Cl	8	8
5	4-F	7	8
6	2-OMe	-	7
7	4-OMe	7	7
8	4-Me	7	11
9	$3-NO_2$	9	11
10	$4-NO_2$	9	11
Standard	Miconazole	14	13
Control	DMSO	-	-
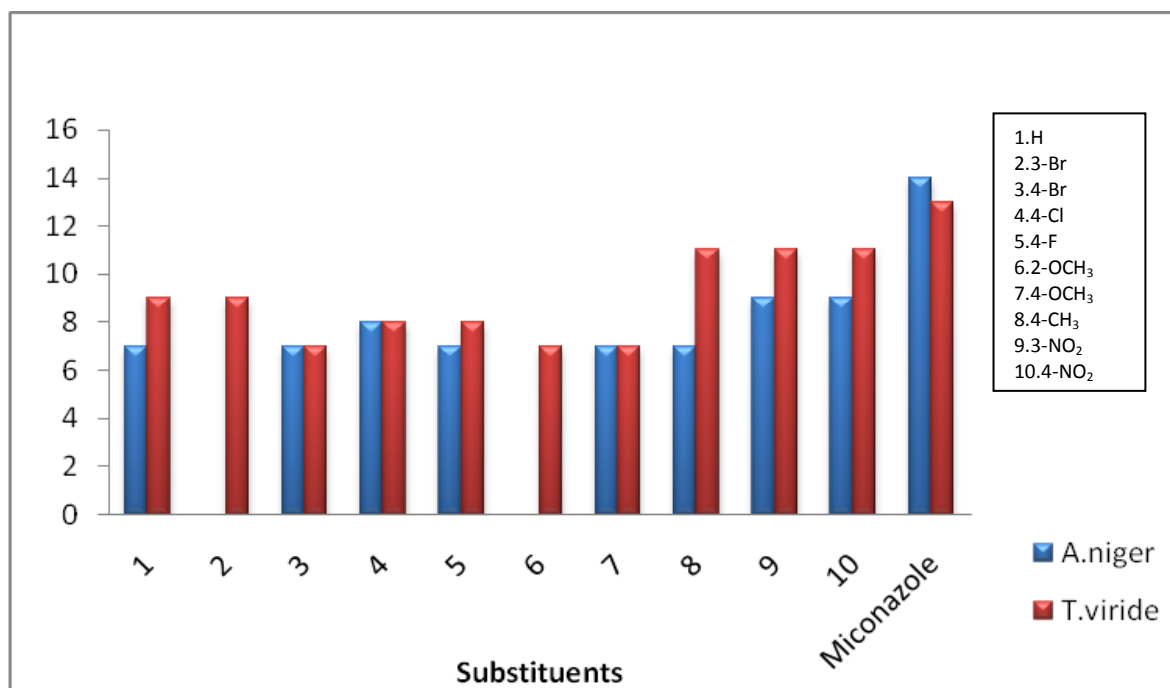
Fig. 6. Chart for antifungal activity of substituted 4-phenoxy phenyl ketones.

4. CONCLUSIONS

Some chalcones have been synthesized by condensation of ketone and benzaldehydes. These chalcones have been characterized by their physical constants, 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 imines have been studied using Bauer-Kirby method.

References

[1] Ranganathan K., Arulkumaran R., Kamalakkannan D., Vanangamudi G., Thirunarayanan G., *IUP J. Chem.* 4(2) (2011) 60-69.

[2] Wang Y. H., Zou J. W., Zhang B., Lu Y. X., Jin H. X., Yu Q. S., *J Mol Struct (Theochem)* 755(31) (2005) 1-2.

[3] Thirunarayanan G., Vanangamudi G., Subramanian M., Umadevi U., Sakthinathan, S. P., Sundararajan R., *Elixir Org. Chem.* 39(2011) 4643-4653.

[4] Yankep E., Fomumand Z. T, Dangne E., *Phytochem.* 46 (1997) 59.

[5] Mulliken R. S., *J. Chem. Phys.* 7 (1939) 121-131.

[6] Smith M. B., March J., *Adv. Org. Chem, Reac, Mech & Stru*, Wiley: New York, 2001, 1218-1224.

[7] Deli J. Lorand, T. Szabo, D. Foldesi, A. *Pharmaz.* 39 (1984) 539.

[8] Winternitz F., Conder G., Vassort P., *Tetrahedron Lett.* 26 (1986) 5981.

[9] Misra S. S., Tewari R. S., *J Ind. Chem. Soc.* 50 (1973) 68.

[10] Thirunarayanan G., *J. Ind. Chem. Soc*. 84 (2008) 447.

[11] Sivakumar M., Phrabusreeneivasan S., Kumar V., Doble M., *Bioorg. Med. Chem. Lett*. 17(10) (2007) 3169.

[12] Weber M. W., Hunsaker L. A., Abcouwer S. F., Decker L. M., Vander Jagat D. L., *Bioorg. Med. Chem*. 13 (2005) 3811.

[13] Parmer V. S., Bishit K. S., Jain R., Singh S., Sharma S. K., Gupta S., Malhotra S., Tyagi O. D., Vardhan A., Pati H. N., Berghe D. V., Vlietinek A. J., *Ind. J. Chem.* 35B (1996) 220.

[14] Deng J., Sanchez T., M. Lalith Q. A., *Bioorg. Med. Chem*. 15(14) (2007) 4985.

[15] Dominguez J. N., Leon C., Rodrigues J., *IL Farmaco*. 60(4) (2005) 307.

[16] Arulkumaran R., Sundararajan R., Vanangamudi G., Subramanian M., Ravi K., Sathiyendidran V., Srinivasan S.Thirunarayanan G., *IUP J. Chem.* 3(1) (2010) 82-98.

[17] Mirinda C. L., Aponso G. L., Stevens J. F, *Cancer Lett.* 149(1-2) (2000) 21.

[18] Sung D. D., Ananthakrishna Nadar P., *Ind. J. Chem.* 39A (2000) 1066.

[19] Bauer A. W., Kirby W. M., Sherris J. C., Truck M., *Am. J. Clin. Pathol.* 45 (1996) 493-498.

[20] Drabu Sushma, *Asian Journal of Chemistry* V19(7) (2007) 5743-5746.

[21] Mala V., Sathiyamoorthy K., Sakthinathan S. P., Kamalakkannan D., Suresh R., Vanangamudi G., Thirunarayanan G., *Q-Science Connect.* 2013.
DOI: http://dx.doi.org/10.5339/connect.2013.

[22] Kamalakkannan D., Vanangamudi G., Arulkumaran R., Thirumurthy K., Mayavel P., Thirunarayanan G., *Elixir Org. Chem.* 46 (2012) 8157-8166.

[23] Sathiyamoorthi K., Mala V., Sakthinathan S. P., Suresh R., Kamalakkannan D., Vanangamudi G., Thirunarayanan G., *Spectrochim. Acta Part* 112A (2013) 245-256.

[24] Swain C. G., Lupton E. C. Jr., *Am. Chem. Soc.* 90 (1968) 4328-4337.

[25] R. Arulkumaran, 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.

[26] S. P. Sakthinathan, R. Suresh, V. Mala, K.Sathiyamoorthi, D. Kamalakkannan, K. Ranganathan, R. Arulkumaran, S. Vijayakumar, R. Sundararajan, G. Vanangamudi, G. Thirunarayanan, *International Letters of Chemistry, Physics and Astronomy* 6 (2013) 77-90.

[27] K. Sathiyamoorthi, V. Mala, R. Suresh, S. P. Sakthinathan, D. Kamalakkannan, K. Ranganathan, R. Arulkumaran, R. Sundararajan, S. Vijayakumar, G. Vanangamudi, G. Thirunarayanan, *International Letters of Chemistry, Physics and Astronomy* 7(2) (2013) 102-119.

[28] G. Thirunarayanan, K. G. Sekar, *International Letters of Chemistry, Physics and Astronomy* 8(2) (2013) 160-174.

[29] K. G. Sekar, G. Thirunarayanan, *International Letters of Chemistry, Physics and Astronomy* 8(3) (2013) 249-258.

[30] S. Vijayakumar, R. Arulkumaran, 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.

[31] G. Thirunarayanan, K. G. Sekar, *International Letters of Chemistry, Physics and Astronomy* 10(1) (2013) 18-34.

[32] R. Sundararajan, R. Arulkumaran, 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.

[33] S. John Joseph, R. Arulkumaran, D. Kamalakkannan, S. P. Sakthinathan, R. Sundararajan, R. Suresh, S. Vijayakumar, K. Ranganathan, N. Kalyanasundaram, G. Vanangamudi, G. Thirunarayanan, *International Letters of Chemistry, Physics and Astronomy* 4 (2014) 48-65.

[34] G. Thirunarayanan, R. Sundararajan, R. Arulkumaran, *International Letters of Chemistry, Physics and Astronomy* 4 (2014) 82-97.

[35] G. Thirunarayanan, *International Letters of Chemistry, Physics and Astronomy* 4 (2014) 109-116.

[36] G. Thirunarayanan, *International Letters of Chemistry, Physics and Astronomy* 5 (2014) 89-98.

[37] S. John Joseph, D. Kamalakkannan, R. Arulkumaran, S. P. Sakthinathan, R. Suresh, R. Sundararajan, S. Vijayakumar, K. Ranganathan, G. Vanangamudi, G. Thirunarayanan, *International Letters of Chemistry, Physics and Astronomy* 5 (2014) 99-123.

[38] G. Thirunarayanan, S. Pazhamalai, K. G. Sekar, *International Letters of Chemistry, Physics and Astronomy* 8 (2014) 38-46.

[39] Ranganathan K., et al., *International Letters of Chemistry, Physics and Astronomy* 4 (2012) 66-75.

[40] Arulkumaran R., et al., *International Letters of Chemistry, Physics and Astronomy* 4 (2012) 17-38.