

Synthesis, Hammett spectral correlation and evaluation of antimicrobial activities of some substituted styryl 4'-piperidinophenyl ketones

K Ranganathan^a, D Kamalakkannan^a, R Suresh^a, S P Sakthinathan^a, R Arulkumaran^a, R Sundararajan^a, V Manikandan^a & G Thirunarayanan^{*b}

^a PG and Research Department of Chemistry, Government Arts College, C-Mutlur 608 102, Chidambaram, India

^b Department of Chemistry, Annamalai University, Annamalainagar 608 002, India

E-mail: drgtnarayanan@gmail.com

Received 27 May 2018; accepted (revised) 7 May 2019

A series containing twelve substituted 4'-piperidinophenyl chalcones have been synthesized from crossed-aldol condensation between 4-piperidionphenyl methyl ketone and substituted benzaldehydes using solid Cu²⁺/Zeolite catalyzed microwave assisted method. The structures of chalcones have been characterized by their physical constants, analytical and spectral data. The observed spectral frequencies have been correlated with Hammett substituents, F and R parameters using both single and multi-regression analyses. All the substituted 4'-piperidinophenyl chalcones have been tested for antimicrobial activities using disc diffusion method.

Keywords: Styryl 4'-piperidinophenyl ketones, Cu²⁺/Zeolite, IR and NMR spectra, Hammett correlation, antimicrobial activities

In recent years, numerous greener and solvent-free^{1,2} synthetic approaches are available for the synthesis of organic compounds. These reactions involving the formation of carbon-carbon bond and carbon-heteroatom bonds are important and interesting in green synthetic route. Based on this the Aldol³, Crossed – Aldol⁴, Knoevenagel⁵, Mannich⁶, Michael⁷, Suzuki⁸, Darzen's⁹ and Wittig¹⁰ reactions have been applied for synthesizing isomeric therapeutically active compounds such as chalcones, alkenes and Mannich bases. Thermal condensation reactions are found to be sluggish and took longer time with poor yields. However in the microwave conditions, shorter reaction time, the rate of reaction is faster, giving appreciable yield involving easier process of isolation of the products. Researchers and scientist have used microwave method for solid phase green synthesis^{5,11,12}. Numerous green catalysts such as Fly-ash: sulphuric acid¹³, ground chemistry catalysts-grinding the reactants with sodium hydroxide¹⁵, anhydrous zinc chloride¹⁴, solid sulphonic acid from aqueous alkali in lower temperature¹⁷, aqueous alkali in lower temperature¹⁶, solid sulphonic acid from bamboo¹⁸, barium hydroxide¹⁹, anhydrous sodium bicarbonate²⁰, microwave assisted synthesis²¹, Fly-ash:water,¹ triphenylphosphite²², alkali earth metals²³, KF/Al₂O₃²⁴, silica-sulphuric acid^{2,25}, and sulfated

titania²¹ have been applied for the synthesis of many number of organic compounds. The diaryl-2-propen-1-ones constitute an important class of natural products belonging to the chalcones and flavonoids family, display interesting biological activities. Chemically they consist of open-chain chalcones and flavonoids in which the two aromatic rings are joined by a three carbon α,β -unsaturated carbonyl system²⁶⁻²⁸. From the chemical studies on the structure of clavacin, it was found that the structural framework, responsible for the antibacterial activity of α,β -unsaturated keto functional group²⁹. The various properties of chalcones have prompted us to synthesize them and study their antimicrobial activity.

The Hammett correlation of spectral data of organic compounds are useful for the prediction of their structure, stereo-chemical and physicochemical properties^{30,31}. The quantitative structure-activity relationship and quantitative property relationship of the organic molecules have been studied from the spectral data associated with their molecular equilibration³². The electronic transition of $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ obtained in 280-350nm in molecules are exhibited by α,β -unsaturated carbonyl compounds. The absorption maxima λ_{max} (nm) of these chalcones are correlated and studied the effects of substituents³³. The vibrational stretching frequency of carbonyl

groups gave two molecular conformers in α,β -unsaturated ketones such as *s-cis* and *s-trans* isomers. The *s-cis* carbonyl group absorption frequencies are higher than those of the *s-trans* carbonyl group absorption frequencies. This structure is based on the molecular equilibration and can be predicted in geometrical isomers, keto-enol tautomerism in unsaturated carbonyl compounds³⁴, alkenes, alkynes, styrenes, nitro-styrenes and naphthyl ketones and their esters^{1,2}. NMR spectroscopy provides the information about the number of protons present in the molecules and their categories either *E* or *Z* in the above molecules. These types of protons can be identified in the organic molecules, based on their coupling constant values. If the molecules contain any substituent in the aromatic ring, corresponding UV absorption maxima λ_{max} (nm), absorption frequencies in IR and NMR chemical shifts vary from chalcones to chalcones depending upon the type of substituents whether they are electron donating or electron withdrawing in nature. From these data the substituent effects can be studied on the particular functional group of the organic compounds by means of correlation analysis³⁵. Now a day's chemists³⁶ have paid more interest for Hammett spectral correlation analysis to explain the substituent effects of organic molecules. Recently, Thirunarayanan *et al.*³⁷ have investigated elaborately the substituent effects on alpha and beta hydrogen and carbons of furyl chalcones. Usha *et al.*³⁸ have studied the ultrasonic method of synthesis and antimicrobial activities of 3-chloro-4-nitrophenyl chalcones. Within the above view there is no information available for spectral correlation of 4'-piperidinophenyl chalcones. Hence the authors have taken efforts to synthesis some 4'-piperidinophenyl chalcones using solvent free solid Cu²⁺/Zeolite catalysed aldol condensation

with microwave irradiation technique and studied the quantitative structure property relationship as well as their antimicrobial activities.

Results and Discussion

Ultra violet spectral study

The measured UV absorption maxima λ_{max} (nm) values of these chalcones are presented in Table I. These UV absorption maxima λ_{max} (nm) values are correlated with Hammett substituent constants and *F* and *R* parameters using single and multi-linear regression analyses¹⁰. Hammett correlation, involving UV absorption maxima values, the form of the Hammett equation employed is as given in equation (1)

$$\lambda = \rho\sigma + \lambda_0 \quad \dots (1)$$

where λ_0 is the frequency for the parent member of the series.

The results of statistical analysis of these values with Hammett substituent constants are presented in Table II. From Table II, the Hammett constant gave satisfactory correlations. All the correlations gave positive ρ values. The remaining Hammett σ^+ , σ_I , σ_R , *F* and *R* parameters produce poor correlations. The poor correlation is due to the inability of the substituents for predicting the reactivity on the absorption through resonance conjugative structure shown in Figure 1.

Some of the single regression analyses have shown poor correlations with few Hammett constants and *F* and *R* parameters. So, it is worthwhile to seek the multi regression analysis. The multi regression analysis of the UV absorption maxima of all ketones with inductive, resonance and Swain – Lupton's³⁵ constants produce satisfactory correlations as evident in equations (2) and (3).

Table I — Ultraviolet λ_{max} (nm) and Infrared spectral data ν (cm⁻¹) of 4'-piperidinophenyl chalcones

Entry	X	UV-Vis λ_{max} (nm)	COs- <i>cis</i>	COs- <i>trans</i>	CH _{ip}	CH _{op}	CH=CH _{op}	>C=C< _{op}
1	H	304.0	1607.00	1592.00	1158.00	769.00	1069.00	567.00
2	3-Br	285.5	1608.00	1588.00	1193.00	754.00	1070.00	577.00
3	4-Br	309.0	1606.00	1584.00	1195.00	748.00	1069.00	593.00
4	4-Cl	309.5	1606.00	1588.00	1196.00	774.00	1093.00	599.00
5	2-F	310.0	1597.00	1563.00	1199.00	745.00	1094.00	567.00
6	4-F	328.5	1608.00	1582.00	1159.00	782.00	1081.00	592.00
7	3-OH	304.0	1603.00	1559.00	1189.00	778.00	1023.00	598.00
8	2-OCH ₃	272.5	1600.00	1558.00	1175.00	755.00	1070.00	553.00
9	4-CH ₃	325.5	1606.00	1587.00	1181.00	762.00	1074.00	592.00
10	3-NO ₂	272.5	1610.00	1588.00	1165.00	751.00	1073.00	579.00
11	4-NO ₂	314.0	1608.00	1597.00	1197.00	759.00	1073.00	595.00
12	3-OC ₆ H ₅	297.5	1610.00	1591.00	1164.00	774.00	1072.00	589.00

Table II — Results of statistical analysis of $Uv\lambda_{max}$ (nm), infrared ν (cm⁻¹) of CO_{s-cis} and CO_{s-trans}, CH_{ip} and op, CH=CHop and >C=C<op modes of 4-piperidinophenyl chalcones with Hammett σ , σ^+ , σ_I , σ_R constants and F and R parameters

Functionality	Constants	r	I	ρ	s	n	Correlated derivatives
λ_{max}	σ	0.910	303.78	-5.564	18.87	11	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	σ^+	0.805	302.86	-2.041	18.94	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	σ_I	0.819	308.71	-15.423	18.63	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	σ_R	0.701	302.39	-1.375	18.97	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	F	0.800	302.67	0.077	18.98	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	R	0.919	301.58	-10.740	22.48	11	H, 3-Br, 2-Cl, 3-Cl, 3-F, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	CO _{s-cis}	σ	0.914	1616.03	-11.372	28.45	11
	σ^+	0.948	1615.80	-26.159	25.17	11	H, 3-Br, 4-Br, 4-Cl, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	σ_I	0.814	1620.93	-18.244	28.42	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	σ_R	0.811	1610.98	-12.649	28.54	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	F	0.701	1621.26	-17.600	28.36	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	R	0.806	1603.50	-39.210	22.35	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
CO _{s-trans}	σ	0.911	1592.55	-6.754	20.20	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	σ^+	0.705	1592.70	-19.259	17.59	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	σ_I	0.820	1598.20	-17.871	19.90	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	σ_R	0.903	1591.83	2.610	20.33	10	H, 3-Br, 4-Br, 4-Cl, 2-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.839	1601.38	-23.989	19.34	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	R	0.806	1606.82	-3.039	20.53	12	H, 3-Br, 2-Cl, 3-Cl, 3-F, 4-F, 3-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
CH _{ip}	σ	0.734	1189.04	10.975	10.54	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	σ^+	0.643	1190.13	13.627	8.60	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	σ_I	0.144	1188.46	6.948	11.12	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	σ_R	0.755	1196.58	24.088	9.22	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅

(Contd.)

Table II — Results of statistical analysis of $UV\lambda_{max}$ (nm), infrared $\nu(\text{cm}^{-1})$ of *COs-cis* and *COs-trans*, CH_{op} and op , $CH=CH_{op}$ and $>C=C<_{op}$ modes of 4-piperidinophenyl chalcones with Hammett σ , σ^+ , σ_I , σ_R constants and F and R parameters (*Contd.*)

Functionality	Constants	r	I	ρ	s	n	Correlated derivatives
CH_{op}	F	0.725	1186.58	10.852	10.87	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	R	0.715	1190.17	-3.750	11.10	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	σ	0.610	794.69	-36.749	16.96	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	σ^+	0.634	788.69	-14.716	19.95	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	σ_I	0.731	798.69	-28.558	20.35	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	σ_R	0.534	777.92	-42.922	18.11	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
$CH=CH_{op}$	F	0.628	796.83	-21.904	20.63	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	R	0.822	784.85	-10.379	20.88	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	σ	0.810	1054.77	-8.756	30.24	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	σ^+	0.804	1052.88	2.663	30.37	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	σ_I	0.710	1047.88	13.344	30.24	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	σ_R	0.367	1043.65	-41.909	28.27	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
$C=C_{op}$	F	0.823	1041.62	27.131	29.55	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	R	0.805	1054.03	3.628	30.35	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	σ	0.830	580.82	13.398	14.68	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	σ^+	0.820	583.47	-0.738	15.43	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	σ_I	0.817	578.83	11.778	15.19	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	σ_R	0.725	586.68	14.542	14.94	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	F	0.711	580.64	6.570	15.34	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅

r = Correlation co-efficient; ρ = Slope; I = Intercept; s = Standard deviation; n = Number of substituents.

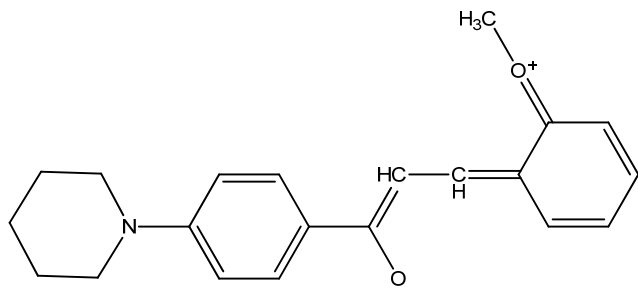


Figure 1 — The resonance-conjugative structure of 2-methoxystyryl-4'-piperidinophenyl ketone

$$\lambda_{(nm)} = 308.66(\pm 13.313) - 15.405(\pm 26.662)\sigma_I - 0.171(\pm 23.393)\sigma_R \quad \dots(2)$$

($R=0.942$, $n=12$, $P>90\%$)

$$\lambda_{(nm)} = 301.35(\pm 12.004) - 0.358(\pm 23.867)F - 5.699(\pm 13.612)R \quad \dots(3)$$

($R=0.963$, $n=12$, $P>90\%$)

Infrared spectral study

The synthesized 4'-piperidinophenyl chalcones exist as *s-cis* and *s-trans* conformers. These *s-cis*

and *s-trans* conformers are confirmed by the carbonyl group doublets obtained in the range of 1600-1700 cm^{-1} . They are given in Figure 2 and the corresponding *s-cis* and *s-trans* carbonyl frequencies (cm^{-1}) of the conformers are presented in Table I. These frequencies are correlated with various Hammett sigma constants and Swain-Lupton's parameters³⁵ by single and multi linear regression analysis^{33, 36, 37, 39}. Hammett correlation employed for the spectral correlations involving group frequencies, the form of the Hammett equation employed is shown in equation (4)

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

where ν_0 is the frequency for the parent member of the series.

The results statistical analysis of single parameter correlations of carbonyl frequencies with substituent constants are presented in Table II. From Table II, the *s-cis* and *s-trans* conformers gave satisfactory correlation with Hammett constants σ , σ^+ , σ_R and R parameters. All correlations gave negative ρ values and the effects of substituents are reversed except σ_R constant. The spectral correlation analysis of CH *in-plane*, CH *out of plane*, CH=CH *out of plane* and C=C *out of plane* modes with Hammett substituent constants and F and R parameters gave poor

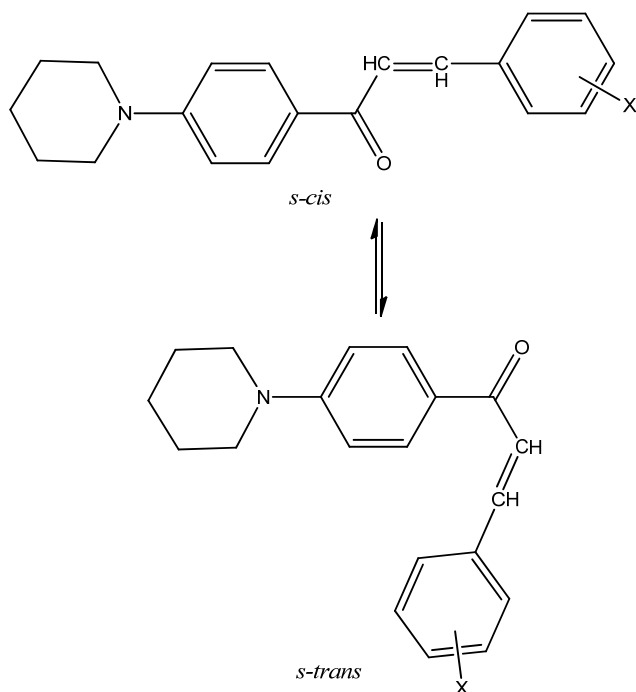


Figure 2 — *s-cis* and *s-trans* conformers of 4'-piperidinophenyl chalcones

correlations. Also this is associated with the resonance-conjugative structure shown in Figure 1.

In this cause some of the σ constants to produce individually satisfactory correlations, it was thought that worthwhile when seeking they are involving the multiple-regression with Hammett σ_I and σ_R constants or Swain-Lupton's³⁵⁻³⁹, F and R parameters. The correlation equations for COs-*cis*, *s-trans* and deformation modes of vinyl parts are given equations (5-16).

$$\begin{aligned} \nu\text{CO}_{s-cis}(\text{cm}^{-1}) &= 1617.94(\pm 20.194) - 17.096(\pm 40.442) \\ &\quad \sigma_I - 11.313(\pm 35.483)\sigma_R \quad \dots(5) \\ (R &= 0.937, n = 12, P > 90\%) \end{aligned}$$

$$\begin{aligned} \nu\text{CO}_{s-cis}(\text{cm}^{-1}) &= 1612.09(\pm 13.849) - \\ & 20.642(\pm 27.535)F \\ & \quad - 39.724(\pm 15.704)R \quad \dots(6) \\ (R &= 0.951, n = 12, P > 95\%) \end{aligned}$$

$$\begin{aligned} \nu\text{CO}_{s-trans}(\text{cm}^{-1}) &= 1599.27(\pm 14.203) - 18.281(\pm 28.443) \\ & \quad \sigma_I + 4.039(\pm 24.955)\sigma_R \quad \dots(7) \\ (R &= 0.960, n = 12, P > 95\%) \end{aligned}$$

$$\begin{aligned} \nu\text{CO}_{s-trans}(\text{cm}^{-1}) &= 1596.72(\pm 10.835) - 25.533(\pm 21.544) \\ & \quad F - 20.159(\pm 12.287)R \quad \dots(8) \\ (R &= 0.940, n = 12, P > 90\%) \end{aligned}$$

$$\begin{aligned} \nu\text{CH}_{ip}(\text{cm}^{-1}) &= 1194.74(\pm 6.548) + 4.538(\pm 13.114) \\ & \quad \sigma_I + 23.734(\pm 11.506)\sigma_R \quad \dots(9) \\ (R &= 0.960, n = 12, P > 95\%) \end{aligned}$$

$$\begin{aligned} \nu\text{CH}_{ip}(\text{cm}^{-1}) &= 1174.86(\pm 10.279) + 9.973(\pm 20.438) \\ & \quad F - 8.876(\pm 11.657)R \quad \dots(10) \\ (R &= 0.950, n = 12, P > 95\%) \end{aligned}$$

$$\begin{aligned} \nu\text{CH}_{op}(\text{cm}^{-1}) &= 787.84(\pm 12.289) - 24.393(\pm 24.610) \\ & \quad \sigma_I - 41.015(\pm 21.592)\sigma_R \quad \dots(11) \\ (R &= 0.931, n = 12, P > 90\%) \end{aligned}$$

$$\begin{aligned} \nu\text{CH}_{op}(\text{cm}^{-1}) &= 794.30(\pm 12.780) - 22.742(\pm 25.410) \\ & \quad F - 10.946(\pm 14.492)R \quad \dots(12) \\ (R &= 0.921, n = 12, P > 90\%) \end{aligned}$$

$$\begin{aligned} \nu\text{CH}=\text{CH}_{op}(\text{cm}^{-1}) &= 1036.43(\pm 19.986) \\ & + 17.740(\pm 40.026) \\ & \quad \sigma_I - 43.296(\pm 35.118)\sigma_R \quad \dots(13) \\ (R &= 0.954, n = 12, P > 95\%) \end{aligned}$$

$$\begin{aligned} \nu\text{CH}=\text{CH}_{op}(\text{cm}^{-1}) &= 1042.61(\pm 18.831) + 27.461(\pm 37.442) \\ & \quad F + 4.312(\pm 21.355)R \quad \dots(14) \\ (R &= 0.937, n = 12, P > 90\%) \end{aligned}$$

$$\nu C=C_{op}(\text{cm}^{-1}) = 582.46(\pm 10.539) + 10.384(\pm 21.106) \sigma_I + 13.730(\pm 18.518) \sigma_R \quad \dots(15)$$

($R = 0.971$, $n = 12$, $P > 95\%$)

$$\nu C=C_{op}(\text{cm}^{-1}) = 580.83(\pm 9.796) + 6.635(\pm 19.477) F + 0.856(\pm 11.108) R \quad \dots(16)$$

($R = 0.900$, $n = 12$, $P > 90\%$)

¹H NMR spectral study

The ¹H NMR spectra of synthesized chalcones were recorded in deuteriochloroform solutions employing tetramethylsilane (TMS) as internal standard. The signals of the ethylenic protons were assigned from their spectra. They are calculated as AB or AA' or BB' systems, respectively. The lower chemical shift values (δ , ppm) have been obtained for H _{α} and higher chemical shifts (δ , ppm) have been obtained for H _{β} in this series of 4'-piperidinophenyl chalcones. The vinyl protons give an AB pattern and the β -proton doublet in most cases is well separated from the signals of the aromatic protons. The characterized vinyl proton chemical shift values (δ , ppm) of all 4-piperidinophenyl chalcones were presented in Table III.

In nuclear magnetic resonance spectra, the ¹H or the ¹³C chemical shifts (δ) depends on the

electronic environment of the nuclei concerned. The assigned chemical shift (δ , ppm) values of vinyl proton have been correlated with reactivity parameters using Hammett equation employed is as given in equation (17)

$$\text{Log } \delta = \text{Log } \delta_0 + \rho\sigma \quad \dots(17)$$

where δ_0 is the chemical shift of unsubstituted ketones.

The assigned H _{α} and H _{β} proton chemical shifts (ppm) are correlated with various Hammett sigma constants. The results of statistical analyses³⁵⁻³⁹ are presented in Table IV. The positive ρ values were obtained in all correlation and are evident for the normal substituent effect operates in all chalcones. A satisfactory correlation obtained for the H _{α} proton chemical shifts (δ , ppm) with Hammett σ , σ^+ , σ_I constants and F parameter. Remaining Hammett σ_R and R parameters were correlated poorly in all synthesized ketones. Similarly, the Hammett σ , σ^+ , σ_I parameters correlated satisfactorily with H _{β} proton chemical shifts (δ , ppm) of all ketones. The polar and resonance effects were failing in correlation. This is due to the reasons stated in earlier and the conjugative structure shown in Figure 1.

Table III — The NMR spectral chemical shift δ (ppm) of 4-piperidinophenyl chalcones

Entry	Substt.	δH_α (1H, <i>d</i>)	δH_β (1H, <i>d</i>)	Ring protons	Substt.	δCO	δC_α	δC_β	Substt.
1	H	7.566	7.783	7.380 - 7.432 (9H, <i>m</i>)	—	187.90	122.21	142.79	—
2	3-Br	7.608	7.997	7.221 - 7.464 (8H, <i>m</i>)	—	186.46	121.21	144.23	—
3	4-Br	7.617	7.954	7.639 - 7.844 (8H, <i>m</i>)	—	186.50	123.62	140.95	—
4	4-Cl	7.637	7.935	6.980 - 7.521 (8H, <i>m</i>)	—	186.51	123.58	140.86	—
5	2-F	7.774	7.964	7.228 - 7.327 (8H, <i>m</i>)	—	186.35	125.35	144.43	—
6	4-F	7.653	7.899	6.929 - 7.309 (8H, <i>m</i>)	—	186.59	122.69	141.11	—
7	3-OH	7.545	7.773	6.824 - 7.231 (8H, <i>m</i>)	3.176 (1H, <i>s</i>)	186.69	122.37	142.78	—
8	2-OCH ₃	7.628	7.773	6.976 - 7.019 (8H, <i>m</i>)	3.823 (3H, <i>s</i>)	186.68	120.27	142.31	55.81 (OCH ₃)
9	4-CH ₃	7.626	7.855	7.740 - 7.792 (8H, <i>m</i>)	2.357 (3H, <i>s</i>)	186.70	121.70	142.41	24.44 (OCH ₃)
10	3-NO ₂	7.758	8.134	8.236 - 8.330 (8H, <i>m</i>)	—	186.38	123.24	139.82	—
11	4-NO ₂	7.731	8.043	8.078 - 8.287 (8H, <i>m</i>)	—	186.24	122.89	139.54	—
12	3-OC ₆ H ₅	7.304	7.935	7.335 - 7.476 (13H, <i>m</i>)	—	186.75	126.60	144.15	—

Table IV — Results of statistical analysis of ^1H NMR of δH_α , δH_β (ppm), ^{13}C NMR of δC_α , δC_β and δCO (ppm) of 4-piperidinophenyl chalcones with Hammett σ , σ^+ , σ_I , σ_R constants and F and R parameters

Functionality	Constants	r	I	ρ	s	n	Correlated derivatives
H_α (ppm)	σ	0.931	7.598	0.113	0.12	11	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.969	7.607	0.167	0.09	11	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.936	7.541	0.202	0.11	11	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.736	7.659	0.173	0.11	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	F	0.947	7.522	0.233	0.11	11	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.819	7.606	-0.054	0.12	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
H_β (ppm)	σ	0.991	7.861	0.301	0.04	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	σ^+	0.920	7.905	0.183	0.06	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	σ_I	0.977	7.768	0.387	0.07	11	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	σ_R	0.852	7.972	0.232	0.09	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	F	0.676	7.791	0.302	0.08	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	R	0.753	7.955	0.136	0.09	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
C_α (ppm)	σ	0.838	122.60	1.943	1.67	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	σ^+	0.914	122.94	0.478	1.79	11	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.833	121.96	2.588	1.70	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	σ_R	0.714	122.76	-0.957	1.79	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	F	0.837	121.89	2.552	1.68	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	R	0.734	123.33	1.347	1.69	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
C_β (ppm)	σ	0.741	142.50	-2.023	1.60	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	σ^+	0.940	142.21	-1.356	1.60	10	H, 4-Br, 4-Cl, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	σ_I	0.939	143.28	-2.995	1.60	9	H, 4-Br, 4-Cl, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 4-NO ₂ , 3-NO ₂
	σ_R	0.756	141.27	-3.731	1.44	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	F	0.827	142.89	-1.855	1.68	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	R	0.819	141.92	-0.738	1.72	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
CO(ppm)	σ	0.944	186.75	-0.568	0.39	11	3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅

(Contd.)

Table IV — Results of statistical analysis of ^1H NMR of δH_α , δH_β (ppm), ^{13}C NMR of δC_α , δC_β and δCO (ppm) of 4-piperidinophenyl chalcones with Hammett σ , σ^+ , σ_I , σ_R constants and F and R parameters (*Contd.*)

Functionality	Constants	r	I	ρ	s	n	Correlated derivatives
	σ^+	0.934	186.67	-0.332	0.41	11	3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	σ_I	0.973	187.19	-1.409	0.30	11	3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	σ_R	0.904	186.66	0.070	0.44	11	3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	F	0.971	187.15	-1.217	0.31	11	3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅
	R	0.808	186.66	0.085	0.44	12	H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OC ₆ H ₅

r = Correlation co-efficient; ρ = Slope; I = Intercept; s = Standard deviation; n = Number of substituents.

Some of the single regression analyses have shown poor correlations with remaining Hammett substituent constants (σ_R & R). It is decided to go for multi-regression, the multi-regression analysis³⁵ produced good correlations with the chemical shifts of (δ , ppm) H_α and H_β . The multi-correlation equations are given in equations (18-22).

$$\delta \text{H}_\alpha(\text{ppm}) = 7.583(\pm 0.079) + 0.186(\pm 0.160) \sigma_I + 0.159(\pm 0.140) \sigma_R \quad \dots(18)$$

($R = 0.953$, $n = 12$, $P > 90\%$)

$$\delta \text{H}_\alpha(\text{ppm}) = 7.510(\pm 0.070) + 0.229(\pm 0.140) \text{F} - 0.048(\pm 0.080) \text{R} \quad \dots(19)$$

($R = 0.961$, $n = 12$, $P > 95\%$)

$$\delta \text{H}_\beta(\text{ppm}) = 7.822(\pm 0.036) + 0.366(\pm 0.073) \sigma_I + 0.204(\pm 0.064) \sigma_R \quad \dots(20)$$

($R = 0.953$, $n = 12$, $P > 95\%$)

$$\delta \text{H}_\beta(\text{ppm}) = 7.825(\pm 0.035) + 0.313(\pm 0.070) \text{F} + 0.144(\pm 0.040) \text{R} \quad \dots(21)$$

($R = 0.542$, $n = 12$, $P > 95\%$)

^{13}C NMR Spectral Study

Spectral analysts and chemists and scientists^{35, 39-41} have made extensive study of ^{13}C NMR spectra for a large number of different ketones and styrenes. The assigned vinyl C_α , C_β and carbonyl carbon chemical shifts are presented in Table III. The results of statistical analysis are given in Table IV. They have been observed a poor correlation linear for the chemical shifts (ppm) of C_α carbon with Hammett substituent constants except σ^+ values. A satisfactory correlation obtained for C_β carbon with polar and inductive effects. Remaining substituent constants fail in correlation. The failure in correlation is due to reasons stated earlier with the resonance-conjugative structure as shown in Figure 1.

The assigned ^{13}C NMR chemical shift values (δ , ppm) of carbonyl carbon have been correlated with Hammett constants using single linear regression analysis and it presented in Table IV. All correlations gave positive ρ values and it is evident for the normal substituent effects operated in all ketones. The correlation of Hammett substituent constants, F and R parameters satisfactorily with $\delta_{\text{C=O}}$ (ppm) values.

The multi-regression³⁵ analysis shows satisfactorily obtained within these carbon chemical shifts and the regression equations are given in (22-27).

$$\delta \text{CO}(\text{ppm}) = 187.24(\pm 0.212) - 1.427(\pm 0.426) \sigma_I + 0.182(\pm 0.374) \sigma_R \quad \dots(22)$$

($R = 0.96$, $n = 12$, $P > 90\%$)

$$\delta \text{CO}(\text{ppm}) = 187.17(\pm 0.198) - 1.213(\pm 0.394) \text{F} + 0.055(\pm 0.255) \text{R} \quad \dots(23)$$

($R = 0.965$, $n = 12$, $P > 95\%$)

$$\delta \text{C}_\alpha(\text{ppm}) = 121.65(\pm 1.197) + 2.707(\pm 2.398) \sigma_I - 1.168(\pm 2.104) \sigma_R \quad \dots(24)$$

($R = 0.911$, $n = 12$, $P > 90\%$)

$$\delta \text{C}_\alpha(\text{ppm}) = 122.22(\pm 0.988) + 2.661(\pm 1.966) \text{F} + 1.414(\pm 1.121) \text{R} \quad \dots(25)$$

($R = 0.951$, $n = 12$, $P > 90\%$)

$$\delta \text{C}_\beta(\text{ppm}) = 142.34(\pm 0.935) - 2.637(\pm 1.873) \sigma_I - 3.525(\pm 1.164) \sigma_R \quad \dots(26)$$

($R = 0.920$, $n = 12$, $P > 90\%$)

$$\delta \text{C}_\beta(\text{ppm}) = 142.71(\pm 1.051) - 1.915(\pm 2.091) \text{F} - 0.786(\pm 1.192) \text{R} \quad \dots(27)$$

($R = 0.942$, $n = 12$, $P > 90\%$)

Microbial activities

Chalcones possess a wide range of therapeutically activities such as antibacterial,⁴² antifungal⁴²,

antiviral⁴³, antifeedant^{3, 28}, anticancer⁴², antimalarial⁴⁴, antituberculosis⁴⁵, anti-AIDS⁴⁶ and antioxidant⁴⁷ activities. These multipronged activities present in different chalcones are examined against respective microbes-bacteria's and fungi.

Antibacterial sensitivity assay

The antibacterial sensitivity assay of all the 4'-piperidinophenyl chalcones was performed using Kirby-Bauer⁴⁸ disc diffusion technique. The antibacterial screening effect of prepared 4'-piperidinophenyl chalcones is shown in Figure 3 (Plates 1-10). The measured zone of inhibition values are given in Table V and the clustered column chart is shown in Figure 4.

All the compounds showed weak to moderate activity against all five microorganisms. All the 4'-piperidinophenylchalcones showed excellent activities on *E. coli* and *M. luteus* species. The substituent H, 3-Br, 3-OCH₃, 4-CH₃ have high activity against *Bacillus subtilis*, *Micrococcus luteus*, *Staphylococcus aureus*, *Escherichia coli* and *Klebsilla pneumoniae*. The substituent 4-CH₃,4-NO₂ has improved antibacterial activity against *E. coli*.

Antifungal sensitivity assay

Antifungal sensitivity assay was performed using Kirby-Bauer⁴⁸ disc diffusion technique. The antifungal screening effect of substituted 4'-piperidinophenyl chalcones in the present study is shown in Figure 5 for Plates (1-6) and the measured zone of inhibition values of the effect is given in Table VI. The clustered column chart is shown in Figure 6. All the 4'-piperidinophenyl chalcones have

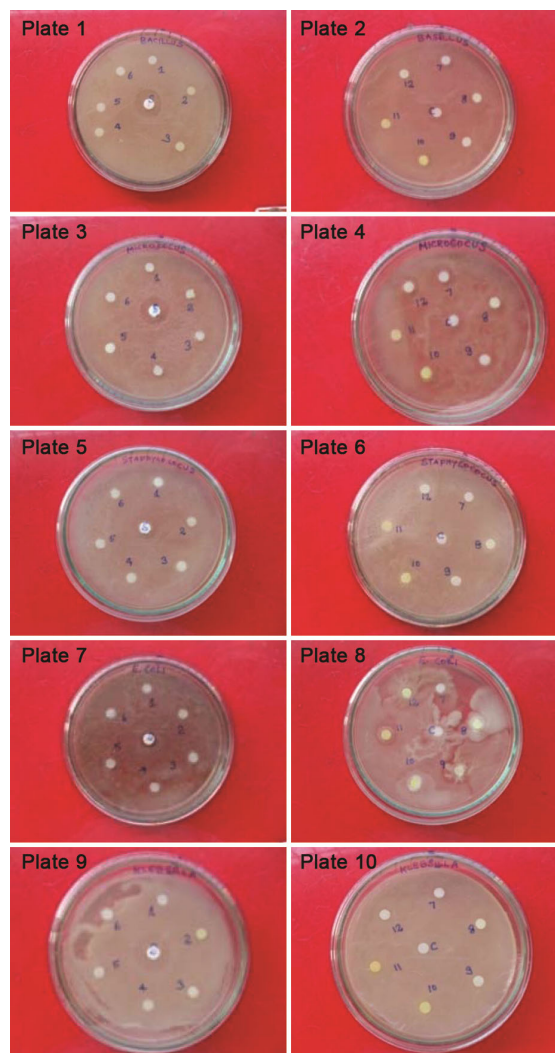


Figure 3 — Antibacterial activities of 4-piperidinophenyl ketones-petri-dishes

Table V — Antibacterial activities of 4-piperidinochalcones

Entry	X	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	8	7	8	7	8
2	3-Br	7	7	8	7	7
3	4-Br	6	6	7	8	7
4	4-Cl	6	8	7	6	—
5	2-F	—	9	—	—	6
6	4-F	7	7	—	7	8
7	3-OH	8	8	7	—	7
8	2-OCH ₃	7	9	7	8	—
9	4-CH ₃	6	7	7	10	—
10	3-NO ₂	6	7	—	8	—
11	4-NO ₂	6	6	—	10	—
12	3-OC ₆ H ₅	8	7	—	8	6
Standard	Ampicillin	22	20	12	10	9
Control	DMSO	—	—	—	—	—

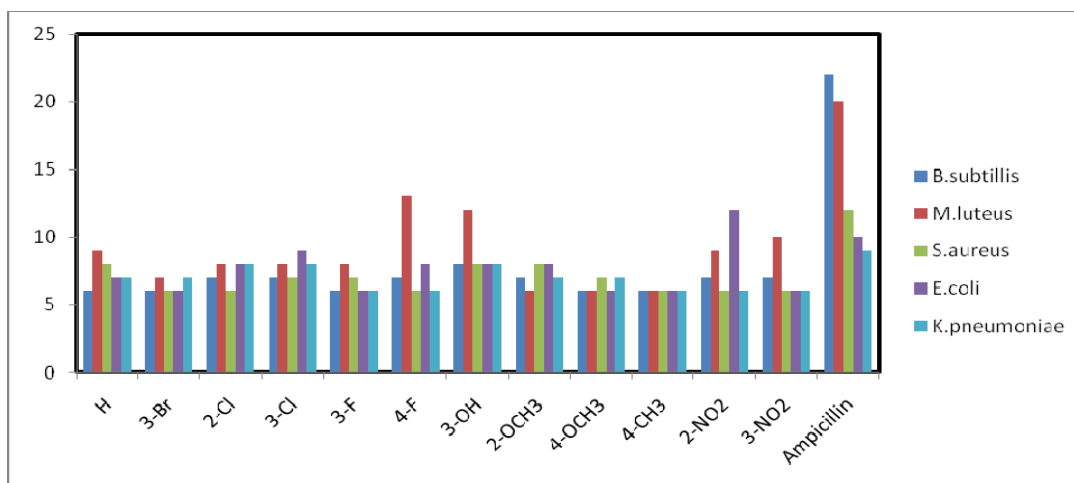


Figure 4 — Antibacterial activities of substituted styryl 4'-piperidino phenyl ketones-zone of inhibition chart

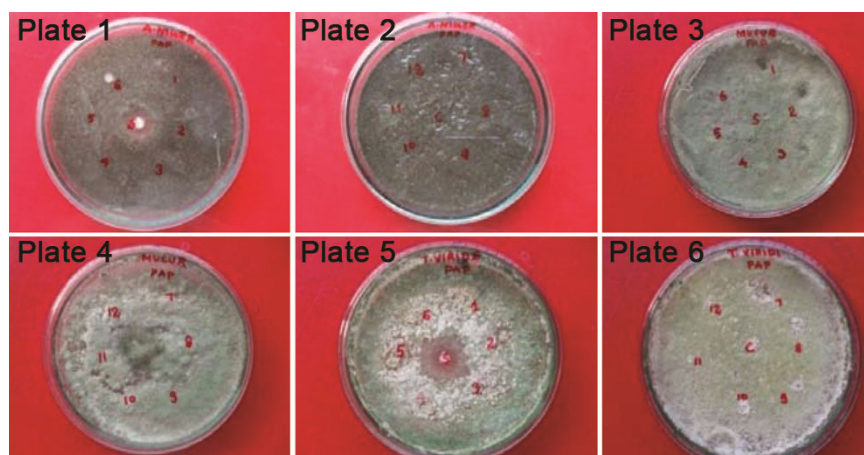


Figure 5 — Antifungal activity of substituted styryl 4'-piperidino phenyl ketones

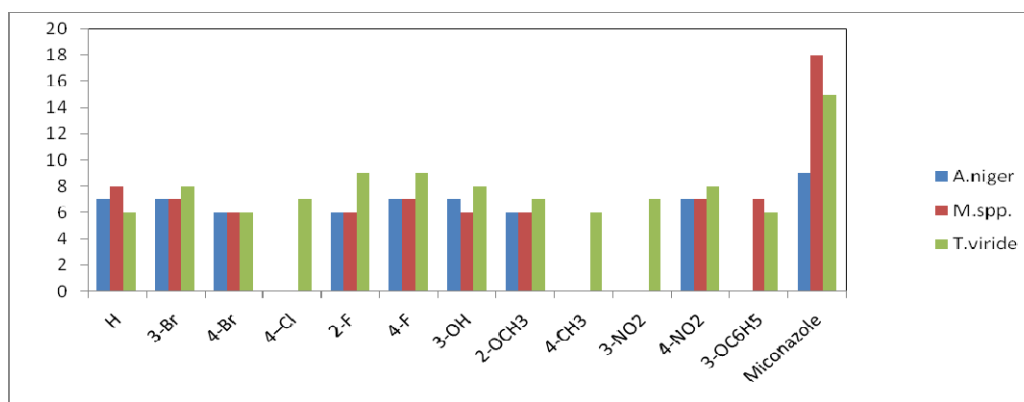


Figure 6 — Antifungal activities of substituted styryl 4'-piperidino phenyl ketones

good antifungal activity against *Trichoderma viride*. The chalcones with 3-Br, 4-F, 4-NO₂ substituents have shown greater antifungal activity against all the three fungal species namely *A. niger*, *M. spp.* and *T. viride* than those with the other substituents present in the series.

Experimental Section

All chemicals were used in this investigation have been procured from E-Merck brand. Mettler FP51 melting point apparatus was used for all the synthesized 4'-piperidinophenyl chalcones are uncorrected. Infrared spectra (KBr, 4000-400cm⁻¹)

Table VI — Antifungal activities of 4-piperidinochalcones

Entry	X	Zone of Inhibition (mm)		
		<i>A. niger</i>	<i>M. spp.</i>	<i>T. viride</i>
1	H	7	8	6
2	3-Br	7	7	8
3	4-Br	6	6	6
4	4-Cl	—	—	7
5	2-F	6	6	9
6	4-F	7	7	9
7	3-OH	7	6	8
8	2-OCH ₃	6	6	7
9	4-CH ₃	—	—	6
10	3-NO ₂	—	—	7
11	4-NO ₂	7	7	8
12	3-OC ₆ H ₅	—	7	6
Standard	Miconazole	9	18	15
Control	DMSO	—	—	—

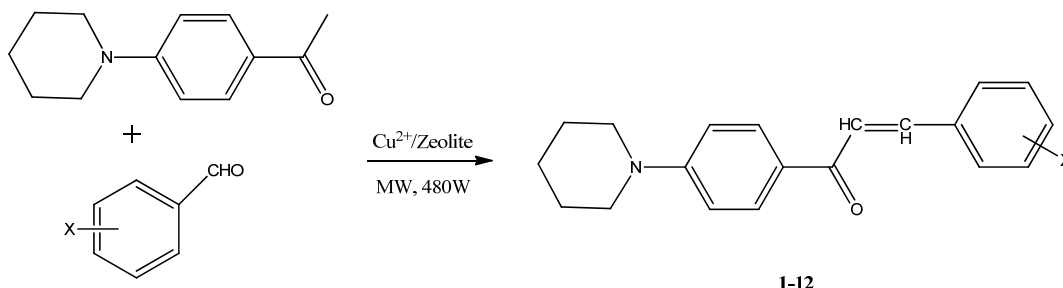
have been recorded on an Avatar-300 Fourier transform spectrophotometer. The NMR spectral all synthesised 4-piperidinophenyl chalcones were recorded in Bruker 400MHz spectrometer. Mass spectra have been recorded on a Shimadzu GC-MS2010 Spectrometer using Electron Impact (EI) techniques.

General procedure for Synthesis of 4-piperidinophenyl chalcones

A mixture containing aryl methyl ketones (2 mmol), aromatic benzaldehydes (2 mmol) and (0.75 mg) of Cu²⁺/Zeolite⁴⁹ were taken in a 50 mL Borosil beaker tube and closed with lid. This mixture was irradiated to microwave oven for 8-10 min (Scheme I) (Samsung, Grill GW73BD Model, 100-750 W, 2450 MHz, 230V AC) at 650 W for 4-5 min and then cooled to room temperature.

Table VII — Physical constants, analytical and mass spectral data of 4'-piperidinophenyl chalcones

Entry	X	Mol. Formula	m.p. (°C)	Mol. Wt.	Time (s)	Yield (%)	MS (<i>m/z</i>)
1	H	C ₂₀ H ₂₁ NO	191-192	291	8	87	291[M ⁺], 263, 214, 207, 188, 160, 131, 103, 84, 77, 55
2	3-Br	C ₂₀ H ₂₀ NOBr	165-166	370	9	85	370[M ⁺], 372[M ²⁺], 295, 214, 208, 188, 180, 160, 155, 84, 79, 77, 55
3	4-Br	C ₂₀ H ₂₀ NOBr	216-217	370	8	86	370[M ⁺], 372[M ²⁺], 295, 214, 208, 188, 180, 160, 155, 84, 79, 77, 55
4	4-Cl	C ₂₀ H ₂₀ NOCl	324-325	325	9	86	325[M ⁺], 327[M ²⁺], 325, 290, 241, 188, 165, 160, 137, 111, 84, 77, 55
5	2-F	C ₂₀ H ₂₀ NOF	262-263	309	8	86	309[M ⁺], 311[M ²⁺], 290, 225, 214, 188, 160, 149, 121, 95, 84, 77, 55
6	4-F	C ₂₀ H ₂₀ NOF	221-222	309	8	85	309[M ⁺], 311[M ²⁺], 290, 225, 214, 188, 160, 149, 121, 95, 84, 77, 55
7	3-OH	C ₂₀ H ₂₁ NO ₂	233-234	307	8	86	307[M ⁺], 290, 223, 214, 188, 160, 147, 131, 119, 93, 84, 77, 55
8	2-OCH ₃	C ₂₁ H ₂₃ NO ₂	111-112	321	8	87	321[M ⁺], 290, 237, 214, 188, 161, 133, 131, 107, 84, 77, 55
9	4-CH ₃	C ₂₁ H ₂₃ NO	229-230	305	9	87	305[M ⁺], 290, 221, 214, 188, 160, 145, 91, 84, 91, 77, 55
10	3-NO ₂	C ₂₀ H ₂₀ N ₂ O ₃	186-187	336	9	87	336[M ⁺], 290, 252, 214, 188, 176, 160, 148, 122, 84, 77, 55
11	4-NO ₂	C ₂₀ H ₂₀ N ₂ O ₃	156-157	336	9	86	336[M ⁺], 290, 252, 214, 188, 176, 160, 148, 122, 84, 77, 55
12	3-OC ₆ H ₅	C ₂₆ H ₂₅ NO ₂	212-213	383	9	86	383[M ⁺], 299, 290, 223, 214, 195, 160, 188, 169, 131, 93, 84, 77, 55



X=H, 3-Br, 4-Br, 4-Cl, 2-F, 4-F, 3-OH, 2-OCH₃, 4-CH₃, 3-NO₂, 4-NO₂, 3-OC₆H₅

Scheme I — Synthesis of substituted styryl-4'-piperidinophenyl ketones

The completion of the reaction was monitored by TLC. After the completion of the reaction 10 mL of dichloromethane was added and the organic layer separated by filtration, yielding solid product on evaporation. The solid, on recrystallization with ethanol, afforded glittering solid. The synthesised 4'-piperidinophenyl chalcones were characterized by their physical constants and spectroscopic data. The physical constants, yield and mass fragments (m/z) values of the 4'-piperidinophenyl chalcones are presented in Table VII.

Conclusions

In conclusion, we have developed an efficient catalytic method for the synthesis of chalcones from aryl methyl ketones and substituted benzaldehydes, by Aldol reaction using Cu^{2+} /Zeolite catalyst under microwave irradiation conditions. This reaction protocol offers a simple, economical, environmentally friendly, non-hazardous, easier work-up procedure with good yields of 4'-piperidinophenyl chalcones. The effects of substituent have been studied between the spectral group frequencies and Hammett substituent constants. The antibacterial and antifungal activities have also been studied.

Acknowledgement

Authors are thankful to SAIF, IIT Madras, for recording NMR spectral data of all 4'-piperidinophenylchalcones.

References

- Thirunarayanan G, Vanangamudi G, Sathiyendiran V & Ravi K, *Indian J Chem*, 50B (2011) 593.
- Thirunarayanan G & Vanangamudi G, *Arkivoc*, 12 (2006) 58.
- Thirunarayanan G, *J Indian Chem Soc*, 85 (2008) 447.
- Thirunarayanan G & Vanangamudi G, *E-J Chem*, 4 (2007) 90.
- Thirunarayanan G, *Indian J Chem*, 46B (2007) 1511.
- Kobayashi S, Kiyohara H & Yamaguchi M, *J Am Chem Soc*, 133 (2011) 708.
- Li W, Wu W, Yang, Liang J X & Ye J, *Synthesis*, 1085 (2011).
- Morris G A & Nguyen S T, *Tetrahedron Lett*, 42 (2001) 2093.
- Wang Z, Xu L, Mu Z, Xia C & Wang H, *J Mol Catal*, 218A (2004) 157.
- Leung S H & Angel S A, *J Chem Educ*, 81 (2004) 1492.
- Thirunarayanan G, *J Korean Chem Soc*, 52(4) (2008) 369.
- Thirunarayanan G & Ananthakrishna Nadar P, *J Indian Chem Soc*, 83(11) (2006) 1107.
- Thirunarayanan G, Mayavel P & Thirumurthy K, *Spectrochim Acta*, 91A (2012) 18.
- Basaif S A, Sobahi T R, Khalil A K & Hassan M A, *Bull Korean Chem Soc*, 26 (11) (2005) 1677.
- Palleros D R, *J Chem Educ*, 81(9) (2004) 1345.
- Kumar P, Kumar S, Husain K & Kumar A, *Chin Chem Lett*, 22(1) (2011) 37.
- Xu Q, Yang Z, Yin D & Zhang F, *Catal Commun*, 9(1) (2008) 1579.
- Zhang Z, Dong Y W & Wang G W, *Chem Lett*, 32(10) (2003) 966.
- Blackwell H E, *Current Opin Chem Biol*, 10(3) (2006) 203.
- Thirunarayanan G, "Proceedings of the 46th Annual Convention of Chemists and International Conference on Recent Research Trends in Chemical Sciences", No. ORG OP5, pp.C13 (2009).
- Krishnakumar B, Velmurugan R & Swaminathan M, *Catal Commun*, 12(5) (2011) 375.
- Johnson B F G, Lewis J, Stephenson G R & Vichi E J S, *J Chem Soc Dalton Trans*, 369 (1978).
- Kiadó A, *J Thermal Anal Calorim*, 76 (2010) 193.
- Xiuying Y & An-Shun P, *J Linyi Teachers Coll*, 23 (2004) O621.3.
- Salehi P, Dabiri M, Zolfigol M A & Fard M A B, *J Braz Chem Soc*, 15(5) (2004) 773.
- Kim B T, Chun J-C & Hwang K-J, *Bull Korean Chem Soc*, 29 (2008) 1125.
- Rao Y K, Fang S-H & Tzeng Y-M, *Bioorg Med Chem*, 12 (2004) 2679.
- Thirunarayanan G, Surya S, Srinivasan S, Vanangamudi G & Sathiyendiran V, *Spectrochim Acta Part A*, 75 (2010) 152.
- Geiger W B & Conn J E, *J Am Chem Soc*, 67 (1945) 112.
- Ranganathan K, Arulkumaran R, Kamalakkannan D, Vanangamudi G & Thirunarayanan G, *IUP J Chem*, 4(2) (2011) 60.
- Mulliken R S, *J Chem Phys*, 7 (1939) 121.
- Thirunarayanan G, *J Korean Chem Soc*, 51(2) (2007) 115.
- Vanangamudi G, Subramanian M, Jayanthi P, Arulkumaran R, Kamalakkannan D & Thirunarayanan G, *Arabian J Chem*, 9 (2016) S717.
- Thirunarayanan G & Ananthakrishna Nadar P, *A J Chem*, 14 (2002) 1518.
- Swain C G & Lupton E C Jr, *J Am Chem Soc*, 90 (1968) 4328.
- (a) Thirunarayanan G, Rajavel R, Vanangamudi G, Kamalakkannan D, Kalyanasundaram N & Rohini S, *IUP J Chem*, 1(2) (2008) 54; (b). Lee S, *Bull Korean Chem Soc*, 29(8) (2008) 1597.
- Thirunarayanan G, Vanangamudi G, Subramanian M, Umadevi U, Sakthinathan S P & Sundararajan R, *Elixir Org Chem*, 39 (2011) 4643.
- Usha V, Thangaraj V & Thirunarayanan G, *Indian J Chem*, 56B (2017) 1094.
- Sung D D & Ananthakrishna Nadar P, *Indian J Chem*, 39A (2000) 1066.
- Thirunarayanan G & Jaishankar P, *Acta Ciencia Indica (C)*, 29 (2003) 183.
- Arulkumaran R, Sundararajan R, Vanangamudi G, Subramanian M, Ravi K, Sathiyendiran V, Srinivasan S & Thirunarayanan G, *IUP J Chem*, 3(1) (2010) 82.
- (a) Sivakumar M, Phrabusreeneivasan S, Kumar V & Doble M, *Bioorg Med Chem Lett*, 17(10) (2007) 3169; (b) Lahtchev K L, Batovska D I, Parushev P V St, Ubiyovck M & Sibirny A A, *Eur J Med Chem*, 43(1) (2008) 1.
- Parmar 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, *Indian J Chem*, 35B (1996) 220.

- 44 Dominguez J N, Leon C & Rodrigues J, *Il Farmaco*, 60(4) (2005) 307.
- 45 Lin Y M, Zhon Y, Flavin M T, Zhon I M, Ne W & Chen F C, *Bioorg Med Chem*, 10(8) (2002) 2795.
- 46 Deng J, Sanchez T & Lalith Q A M, *Bioorg Med Chem*, 15(14) (2007) 4985.
- 47 Weber M W, Hunsaker L A, Abcouwer S F, Decker L M & Vander Jagat D L, *Bioorg Med Chem*, 13 (2005) 3811.
- 48 Bauer A W, Kirby W M M, Sherris J C & Truck M, *Am J Clin Pathol*, 45 (1996) 493.
- 49 Dineshkumar S, Thirunarayanan G, Mayavel P & Muthuvel I, *Ovidius Univ Annals Chem*, 27(1) (2016) 22.