

Spectral correlations and antimicrobial activities of some 1-pyrenyl chalcones

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ABSTRACT

A series of 1-pyrenyl chalcones have been synthesized by Crossed-Aldol condensation of 1-acetylpyrene and 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 effect 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 1-pyrenyl 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-ethoxyphenyl 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], antiplosmodial [28], anti-aids [29] and insect antifeedant activities [13, 22]. In the present investigation, the authors have synthesized a series of some substituted styryl 1-pyrenyl ketones, studied the spectral correlations and to evaluate the antimicrobial activities using Bauer-Kirby [30] method.

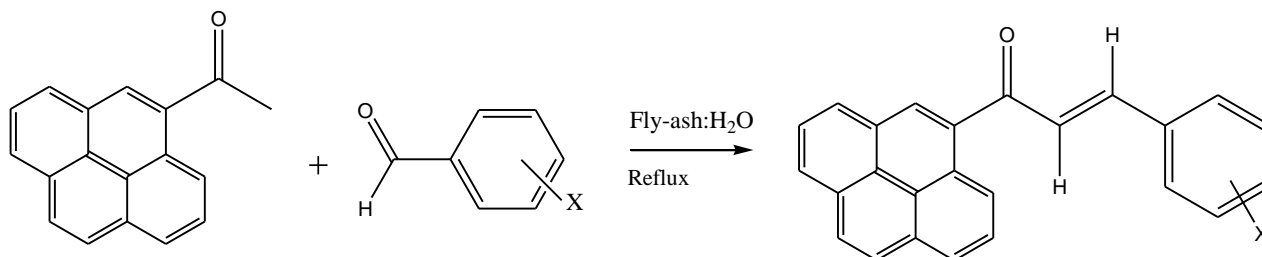
2. EXPERIMENTAL

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 ELICO BL 222 ultraviolet spectrophotometer was utilized for recording the absorption maxima (λ_{max} , nm), of all chalcones in spectral grade methanol. Infrared spectra (KBr, 4000-400 cm⁻¹) were recorded AVATAR-300 Fourier transform spectrophotometer. Bruker AV400 NMR spectrometer was used for recording NMR spectra operating at 400 MHz for ¹H spectra and 125.46 MHz for ¹³C spectra in CDCl₃ 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 styryl-1-pyrenyl chalcones were synthesized by procedure published in literature. An equi-molar quantities of 1-acetylpyrene (2 mmol) and substituted benzaldehydes (2 mmol), Fly-ash(0.5 g) with 20 mL of water [19, 31] (Scheme 1) were refluxed for 4h. and 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, *m*-Br, *p*-Br, *p*-Cl, *p*-F, *o*-CH₃, *p*-CH₃, *m*-NO₂, *p*-NO₂

Scheme 1. Synthesis of substituted styryl 1-pyrenyl ketones.

Table 1. Physical constants and mass spectral data of substituted styryl 1-pyrenyl ketones.

Entry	X	M. F.	M. W.	m.p. (°C)	Mass (m/z)
1	H	C ₂₅ H ₁₆ O	332	122-123 (122-123)[31]	332[M ⁺]
2	<i>m</i> -Br	C ₂₅ H ₁₅ OBr	411	119-120(119-120)[31]	411[M ⁺], 413[M ²⁺]
3	<i>o</i> -Cl	C ₂₅ H ₁₅ OCl	366	119-120(119-120)[31]	366[M ⁺], 368[M ²⁺]
4	<i>m</i> -Cl	C ₂₅ H ₁₅ OCl	366	262-263(262-263)[31]	366[M ⁺], 368[M ²⁺]
5	<i>p</i> -Cl	C ₂₅ H ₁₅ OCl	366	96-97(96-97)[31]	366[M ⁺], 368[M ²⁺]
6	<i>p</i> -F	C ₂₅ H ₁₅ OF	350	108-109(108-109)[31]	350[M ⁺], 352[M ²⁺]
7	<i>p</i> -CH ₃	C ₂₆ H ₁₈ O	346	219-220(219-220)[31]	346[M ⁺]
8	<i>m</i> -NO ₂	C ₂₅ H ₁₅ NO ₃	377	128-129(128-129)[31]	377[M ⁺]
9	<i>p</i> -NO ₂	C ₂₅ H ₁₅ NO ₃	377	136-137(136-137)[31]	377[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 1-pyrenyl 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 1-pyrenyl chalcones were tabulated in Table 2. These values are correlated [1, 2, 6, 10, 19, 21, 23-25, 28, 32] 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 F parameter is satisfactory. The remaining Hammett substituent constants and R parameter were failing in correlation.

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

	9	8	7	6	5	4	3	2	1	Entry
	<i>p</i> -NO ₂	<i>m</i> -NO ₂	<i>p</i> -CH ₃	<i>p</i> -F	<i>p</i> -Cl	<i>m</i> -Cl	<i>o</i> -Cl	<i>m</i> -Br	H	X
	275.50	265.50	274.50	242.00	304.50	282.50	285.50	265.50	276.00	λ_{max}
	1658.30	1662.98	1654.79	1608.09	1655.68	1600.00	1633.17	1676.71	1632.88	CO _(<i>s-cis</i>)
	1594.55	1529.01	1589.31	1552.99	1592.64	1550.68	1590.90	1452.56	1596.71	CO _(<i>s-trans</i>)
	1117.93	1122.05	1161.64	1167.12	1119.07	1123.29	1119.54	1172.60	1106.85	CH _{<i>ip</i>}
	778.08	725.18	866.94	782.09	780.23	761.64	745.10	861.38	763.28	CH _{<i>op</i>}
	1072.71	1074.51	1020.91	1018.52	1075.12	1019.72	1079.45	1068.49	1072.31	CH=CH _{<i>op</i>}
	601.06	559.03	606.86	613.05	602.64	569.86	591.45	583.43	556.41	C=C _{<i>op</i>}
	7.615	7.624	7.418	6.996	7.034	7.477	7.450	8.073	7.470	H _{<i>a</i>}
	8.245	8.132	7.606	7.707	7.686	8.235	8.194	8.407	8.142	H _{<i>β</i>}
	195.50	194.65	196.30	188.51	195.65	195.41	195.54	195.94	196.12	C _{<i>a</i>}
	124.13	122.68	124.12	124.68	124.04	124.12	124.05	121.14	124.12	C _{<i>β</i>}
	142.19	148.75	146.34	142.14	144.44	144.08	141.63	146.56	146.14	CO

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 1-pyrenyl ketones with Hammett σ , σ^+ , σ_I , σ_R and F and R parameters.

Frequency	Constants	r	I	ρ	s	n	Correlated derivatives
UV λ_{max}	σ	0.700	274.53	0.271	18.15	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.707	273.59	3.658	18.09	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.813	278.35	-9.200	17.97	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.823	276.93	19.938	17.65	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.936	284.52	-23.733	16.88	7	3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 3-NO ₂ , 4-NO ₂
	R	0.735	278.70	27.291	16.94	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	$\nu\text{CO}_{s-cis}(\text{cm}^{-1})$	σ	0.823	1634.82	26.691	26.04	9
σ^+		0.726	1637.42	18.291	26.63	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
σ_I		0.510	1640.39	5.195	27.56	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
σ_R		0.905	1651.07	73.370	22.80	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
F		0.848	1644.50	-4.766	27.57	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
R		0.905	1651.33	58.800	23.78	7	H, 2-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
$\nu\text{CO}_{s-trans}(\text{cm}^{-1})$		σ	0.929	1573.48	-43.224	48.57	7
	σ^+	0.825	1570.22	-32.992	49.06	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.820	1586.07	-61.563	47.95	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.770	1563.24	18.929	50.62	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.932	1585.23	-57.920	48.09	8	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.815	1565.90	32.463	50.18	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	$\nu\text{CH}_{ip}(\text{cm}^{-1})$	σ	0.731	1141.58	-24.769	25.43	9
σ^+		0.746	1142.11	-27.509	24.50	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂

	σ_I	0.696	1137.25	-6.887	26.75	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.950	1126.95	-64.242	23.09	8	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.710	1130.38	9.739	26.67	9	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.906	1123.81	-70.923	20.82	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
$\nu\text{CH}_{op}(\text{cm}^{-1})$	σ	0.904	802.65	-61.741	47.33	8	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.849	802.83	-64.510	45.10	8	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.744	819.31	-84.663	46.48	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.718	779.62	-45.019	50.95	9	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.737	813.91	-69.487	48.02	9	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.727	775.77	-60.733	49.78	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
$\nu\text{CH}=\text{CH}_{op}(\text{cm}^{-1})$	σ	0.945	1044.73	38.255	25.93	8	H, 3-Br, 2-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.954	1044.59	40.063	24.33	8	H, 3-Br, 2-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.725	1044.71	27.145	28.11	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.751	1063.98	70.592	24.90	9	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.707	1052.72	7.250	28.98	9	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.858	1066.38	70.903	23.64	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
$\nu\text{C}=\text{C}_{op}(\text{cm}^{-1})$	σ	0.927	592.25	-17.959	21.69	7	3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂
	σ^+	0.935	592.68	-20.090	21.09	7	3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂
	σ_I	0.708	584.21	7.057	22.46	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.950	580.79	-53.970	19.43	7	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 3-NO ₂
	F	0.821	579.73	17.589	22.00	9	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.855	579.21	-52.486	18.76	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
$\delta_{Ha}(\text{ppm})$	σ	0.955	7.333	0.446	0.30	6	H, 2-Cl, 3-Cl, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.957	7.338	0.442	0.29	6	H, 2-Cl, 3-Cl, 4-CH ₃ , 3-NO ₂ , 4-NO ₂

	σ_I	0.718	7.424	0.090	0.34	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.951	7.558	0.829	0.29	7	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 3-NO ₂
	F	0.645	7.494	-0.078	0.34	8	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.989	7.565	0.692	0.30	7	H, 2-Cl, 3-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
$\delta_{H\beta}$(ppm)	σ	0.960	7.880	0.551	0.24	7	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃
	σ^+	0.974	7.875	0.587	0.20	7	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃
	σ_I	0.834	7.877	0.398	0.29	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.740	8.108	0.592	0.28	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.717	7.957	0.195	0.30	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.844	8.125	0.578	0.28	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
δ_{CO}(ppm)	σ	0.991	194.60	0.847	2.57	8	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.919	194.48	1.304	2.53	8	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.934	196.20	-3.330	2.42	8	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.861	195.72	7.518	2.04	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.959	197.12	-5.456	2.08	8	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.865	195.95	7.402	1.89	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
δ_{Ca}(ppm)	σ	0.737	124.04	-1.283	1.07	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.837	123.98	-1.106	1.07	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.952	124.04	-0.914	1.13	7	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-NO ₂ , 4-NO ₂
	σ_R	0.727	123.50	-1.496	1.12	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.718	123.86	-0.447	1.15	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.722	123.51	-1.095	1.13	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
$\delta_{C\beta}$(ppm)	σ	0.906	144.56	0.458	2.59	6	3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 3-NO ₂
	σ^+	0.803	144.76	-0.229	2.59	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-CH ₃ , 3-NO ₂ , 4-NO ₂

	σ_I	0.728	145.80	-2.735	2.49	9	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-NO ₂ , 4-NO ₂
	σ_R	0.949	145.40	6.108	2.25	8	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂
	F	0.839	145.96	-3.046	2.45	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.943	145.41	4.784	2.33	8	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂

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 [33] constants, they gave satisfactory correlations. The multi correlation equations are given in 2 and 3.

$$\lambda_{max} \text{ (nm)} = 280.94(\pm 13.115) - 9.738(\pm 6.290)\sigma_I + 20.359(\pm 13.619)\sigma_R \quad \dots(2)$$

($R=0.927$, $n=9$, $P>90\%$)

$$\lambda_{max} \text{ (nm)} = 286.86(\pm 11.558) - 20.818(\pm 7.369)F + 23.726(\pm 7.587)R \quad \dots(3)$$

($R=0.947$, $n=9$, $P>90\%$)

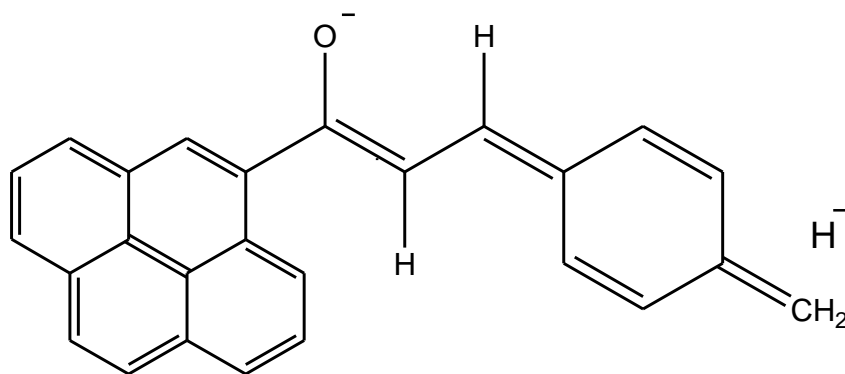


Fig. 1. The resonance – conjugated structure.

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 in Table 2 and the corresponding conformers are shown in Fig. 2.

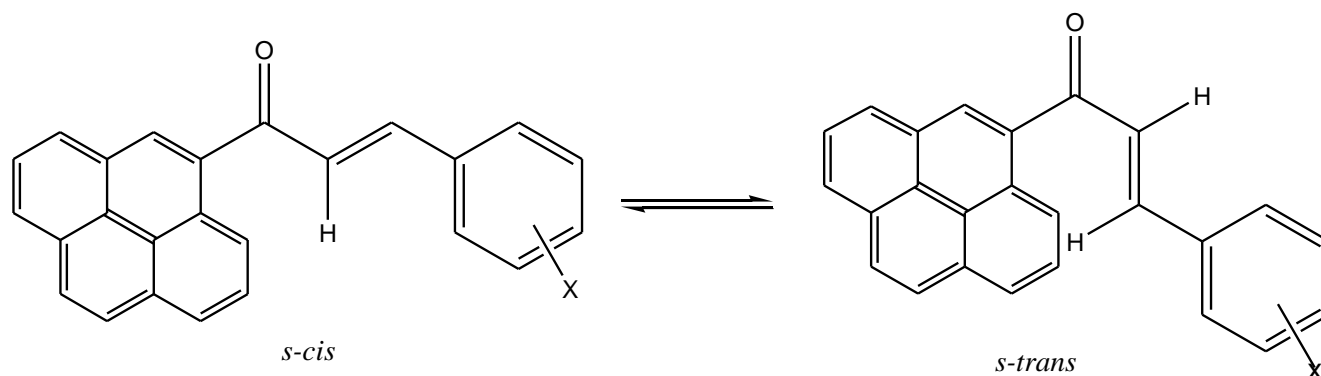


Fig. 2. The *s-cis* and *s-trans* conformers of 1-pyrenyl chalcones.

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 CO *s-cis* and *s-trans* conformers have been correlated with Hammett substituent constants and Swain-Lupton constants [33]. In this correlation the structure parameter Hammett equation employed is as shown in the following equation:

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

Where ν is the carbonyl frequencies of substituted system and ν_0 is the corresponding quantity of unsubstituted system; σ is a Hammett substituent constant, which in principle is characteristics of the substituent and ρ is a reaction constant which is depend upon the nature of the reaction.

The results of statistical analysis [1, 2, 6, 10, 19, 21, 23-25, 28, 32] 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 fail in correlation. The Hammett σ and F parameters gave satisfactory correlation with CO *s-cis* conformers stretches. The remaining Hammett substituent constants and R parameters were fail 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_R and R parameters gave satisfactory correlation. The remaining The remaining Hammett substituent constants and F parameters were fail in correlation. The Hammett 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 $\text{CH}=\text{CH}_{op}$ modes. The inductive, resonance and field components of the substituents are failed in correlation. The Hammett σ , σ^+ and σ_R constants were satisfactorily correlated with $\text{C}=\text{C}_{op}$ modes. The inductive components of the substituents, F and R parameters 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 [33], they gave satisfactory correlations with the infrared red group frequencies. The multi correlation equations are given in 5 - 16.

$$\nu\text{CO}_{s-cis}(\text{cm}^{-1})=1649.72(\pm 17.120)+3.261(\pm 0.319)\sigma_{\text{I}}+73.230(\pm 43.887)\sigma_{\text{R}} \quad \dots(5)$$

$$(R=0.956, n=9, P >95\%)$$

$$\nu\text{CO}_{s-cis}(\text{cm}^{-1})=1650.34(\pm 17.255)+2.509(\pm 0.886)F+59.230(\pm 41.184)R \quad \dots(6)$$

$$(R=0.950, n=9, P >95\%)$$

$$\nu\text{CO}_{s-trans}(\text{cm}^{-1})=1588.82(\pm 35.872)-62.134(\pm 21.906)\sigma_{\text{I}}+21.613(\pm 7.954)\sigma_{\text{R}} \quad \dots(7)$$

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

$$\nu\text{CO}_{s-trans}(\text{cm}^{-1})=1587.50(\pm 34.683)-55.091(\pm 17.120)F+23.032(\pm 8.779)R \quad \dots(8)$$

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

$$\nu\text{CH}_{ip}(\text{cm}^{-1})=1129.09(\pm 17.324)-5.196(\pm 3.727)\sigma_{\text{I}}-64.018(\pm 44.409)\sigma_{\text{R}} \quad \dots(9)$$

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

$$\nu\text{CH}_{ip}(\text{cm}^{-1})=1123.40(\pm 15.112)+1.049(\pm 0.553)F-70.744(\pm 36.069)R \quad \dots(10)$$

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

$$\nu\text{CH}_{op}(\text{cm}^{-1})=814.03(\pm 34.300)-83.570(\pm 68.756)\sigma_{\text{I}}-41.409(\pm 18.926)\sigma_{\text{R}} \quad \dots(11)$$

$$(R=0.947, n=9, P >90\%)$$

$$\nu\text{CH}_{op}(\text{cm}^{-1})=806.58(\pm 32.458)-78.601(\pm 65.622)F-74.189(\pm 37.468)R \quad \dots(12)$$

$$(R=0.956, n=9, P >95\%)$$

$$\nu\text{CH}=\text{CH}_{op}(\text{cm}^{-1})=1053.56(\pm 17.991)+25.309(\pm 6.064)\sigma_{\text{I}}+69.498(\pm 46.119)\sigma_{\text{R}} \quad \dots(13)$$

$$(R=0.956, n=9, P >95\%)$$

$$\nu\text{CH}=\text{CH}_{op}(\text{cm}^{-1})=1059.99(\pm 16.842)+16.302(\pm 4.051)F+73.694(\pm 40.199)R \quad \dots(14)$$

$$(R=0.960, n=9, P >95\%)$$

$$\nu\text{C}=\text{C}_{op}(\text{cm}^{-1})=577.29(\pm 14.497)+8.493(\pm 2.060)\sigma_{\text{I}}-54.337(\pm 37.162)\sigma_{\text{R}} \quad \dots(15)$$

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

$$\nu\text{C}=\text{C}_{op}(\text{cm}^{-1})=574.75(\pm 13.424)+11.380(\pm 7.144)F-50.538(\pm 32.041)R \quad \dots(16)$$

$$(R=0.957, n=9, P >95\%)$$

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, 32] 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. The inductive and Field effects of the substituents were fail in correlations. Hammett σ and σ^+ constants gave satisfactory correlation with H α chemical shifts (δ , ppm). The inductive, field and resonance components of the substituents fail in correlation. The failure in correlation for both chemical

shifts are the reasons stated earlier and associated with the resonance – conjugated structure shown in Fig. 1.

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 [33] 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.

$$\delta H_{\alpha}(\text{ppm})=7.530(\pm 0.221)+0.069(\pm 0.044)\sigma_{\text{I}}+0.826(\pm 0.566)\sigma_{\text{R}} \quad \dots(17)$$

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

$$\delta H_{\alpha}(\text{ppm})=7.562(\pm 0.218)+0.006(\pm 0.004)F+0.693(\pm 0.521)R \quad \dots(18)$$

$$(R=0.948, n=9, P>90\%)$$

$$\delta H_{\beta}(\text{ppm})=7.950(\pm 0.200)+0.382(\pm 0.040)\sigma_{\text{I}}+0.575(\pm 0.051)\sigma_{\text{R}} \quad \dots(19)$$

$$(R=0.952, n=9, P>95\%)$$

$$\delta H_{\beta}(\text{ppm})=8.019(\pm 0.195)+0.271(\pm 0.039)F+0.624(\pm 0.467)R \quad \dots(20)$$

$$(R=0.950, n=9, P>95\%)$$

3. 3. 1. ¹³C NMR spectra

The carbonyl carbon, C α and C β chemical shifts (δ , ppm) of 1-pyrenyl chalcones were assigned and tabulated in Table 2. These chemical shifts are correlated [1, 2, 6, 10, 19, 21, 23-25, 28, 32] 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} constants and F parameters were gave satisfactory correlations with carbonyl carbon chemical shifts of chalcones. The Hammett σ_{I} constants correlated satisfactorily with C α chemical shifts. The C β chemical shifts (δ , ppm) were satisfactorily correlated with the Hammett σ , σ_{R} constants and R parameters. The remaining Hammett substituent constants and F or R parameters were fail 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 1-pyrenyl chalcones were satisfactorily correlated with σ_{I} , σ_{R} and Swain-Luptons'[33] F and R parameters. The multi-regression equation are given in 21-26.

$$\delta \text{CO}(\text{ppm})=197.17(\pm 1.355)-3.533(\pm 2.716)\sigma_{\text{I}}+7.671(\pm 3.474)\sigma_{\text{R}} \quad \dots(21)$$

$$(R=0.971, n=9, P>95\%)$$

$$\delta \text{CO}(\text{ppm})=197.77(\pm 1.009)-4.645(\pm 2.040)F+6.606(\pm 2.408)R \quad \dots(22)$$

$$(R=0.984, n=9, P>95\%)$$

$$\delta C_{\alpha}(\text{ppm})=123.86(\pm 0.823)-0.875(\pm 0.650)\sigma_{\text{I}}-1.458(\pm 0.110)\sigma_{\text{R}} \quad \dots(23)$$

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

$$\delta C_{\alpha}(\text{ppm})=123.74(\pm 0.815)-0.595(\pm 0.064)F-1.197(\pm 0.945)R \quad \dots(24)$$

$$(R=0.926, n=9, P>90\%)$$

$$\delta C_{\beta}(\text{ppm})=146.60(\pm 1.588)-2.900(\pm 1.184)\sigma_{\text{I}}+6.233(\pm 4.072)\sigma_{\text{R}} \quad \dots(25)$$

$$(R=0.958, n=9, P>95\%)$$

$$\delta C_{\beta}(\text{ppm})=146.39(\pm 1.619)-2.511(\pm 0.273)F+4.355(\pm 3.864)R \quad \dots(26)$$

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

3. 4. Antimicrobial activities

Chalcones possess various biological activities such as antibacterial [26, 34], 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, 42]. 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.



Plate-1



Plate-2



Plate-3



Plate-4



Plate-5



Plate-6

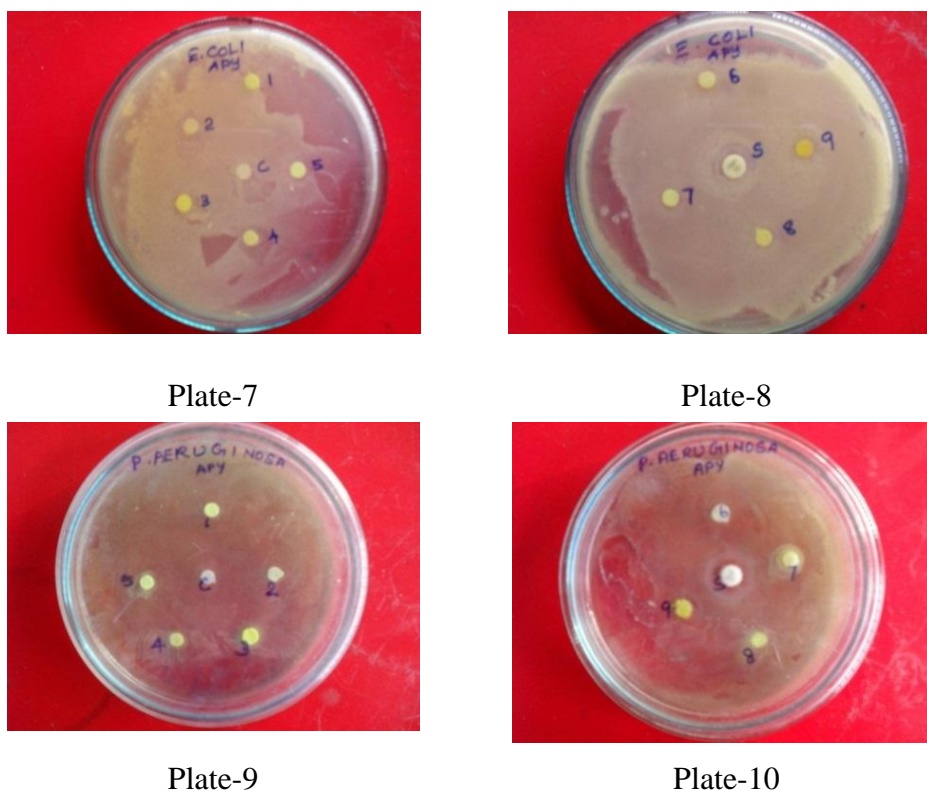


Fig. 3. Antibacterial activities of substituted styryl 1-pyrenyl ketones.

Then the discs with 5mm diameter made up of Whatmann No.1 filter paper, impregnated with the solution of the compound were placed on the medium using sterile forceps. The plates were incubated for 24 hours at 37 °C by keeping the plates upside down to prevent the collection of water droplets over the medium. After 24 hours, the plates were visually examined and the diameter values of the zone of inhibition were measured. Triplicate results were recorded by repeating the same procedure. The antibacterial effect of the styryl 1-pyrenyl 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 3-Br have shown moderate antibacterial activity against all the bacterial species, under investigation. The substituent 3-NO₂ has shown more antibacterial activity than standard (Ampicillin) against *B. subtilis* species. The substituent 2-Cl has shown more antibacterial activity than standard (Ampicillin) against *S. aureus* species. The substituent 4-Cl has shown equal antibacterial activity with standard (Ampicillin) against *M. luteus* species. The parent compound (H) has shown equal activities against all bacteria except *P. aeruginosa*. The compound with 2-Cl, 3-Cl and 4-Cl substituents has shown equal activities against *B. subtilis* bacterial species. The compound with 3-NO₂ and 4-NO₂ substituents has shown equal activities against *M. luteus* and *S. aureus* 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.

Table 4. Antibacterial activity of substituted styryl 1-pyrenyl 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>P. aeruginosa</i>
1	H	7	7	7	7	6
2	3-Br	6	7	6	-	7
3	2-Cl	6	6	9	6	7
4	3-Cl	6	7	6	7	6
5	4-Cl	6	9	6	6	7
6	4-F	7	6	7	6	6
7	4-CH ₃	7	7	8	6	8
8	3-NO ₂	9	6	6	7	6
9	4-NO ₂	6	6	6	8	7
Standard	Ampicillin	8	9	8	9	10
Control	DMSO	-	-	-	-	-

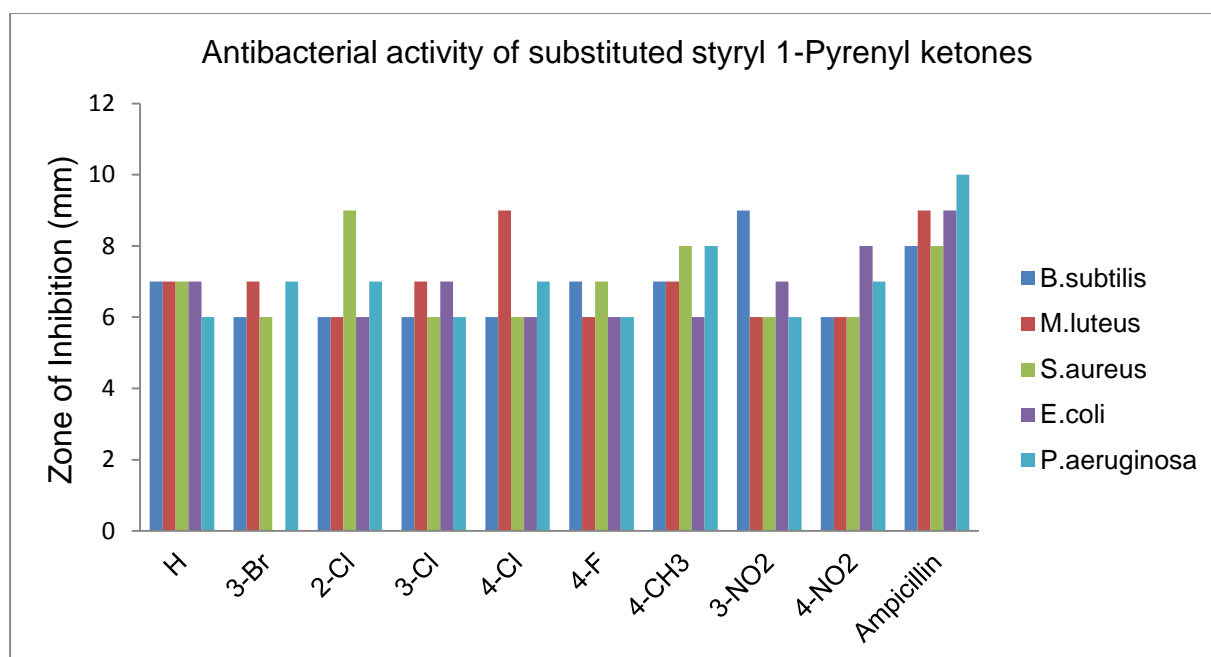


Fig. 4. Antibacterial activity of substituted styryl 1-pyrenyl ketone.

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 1-pyrene ketones is shown in Fig. 5 for Plates (1-6). Analysis of the zone of inhibition as given Table 5 and the Clustered column Chart Fig 6, reveals that all the parent compound, 3-Cl and 3-NO₂ substituents have shown moderate antifungal activities against all the fungal species namely *A. niger*, *P. scup* and *T. viride*, under investigation. The 2-Cl and 4-CH₃ substituents of this have shown inactive for the above three fungal species. The parent compound (H) and 3-Cl substituted compound has shown equal activity against all fungal species namely *A. niger*, *P. scup* and *T. viride*.

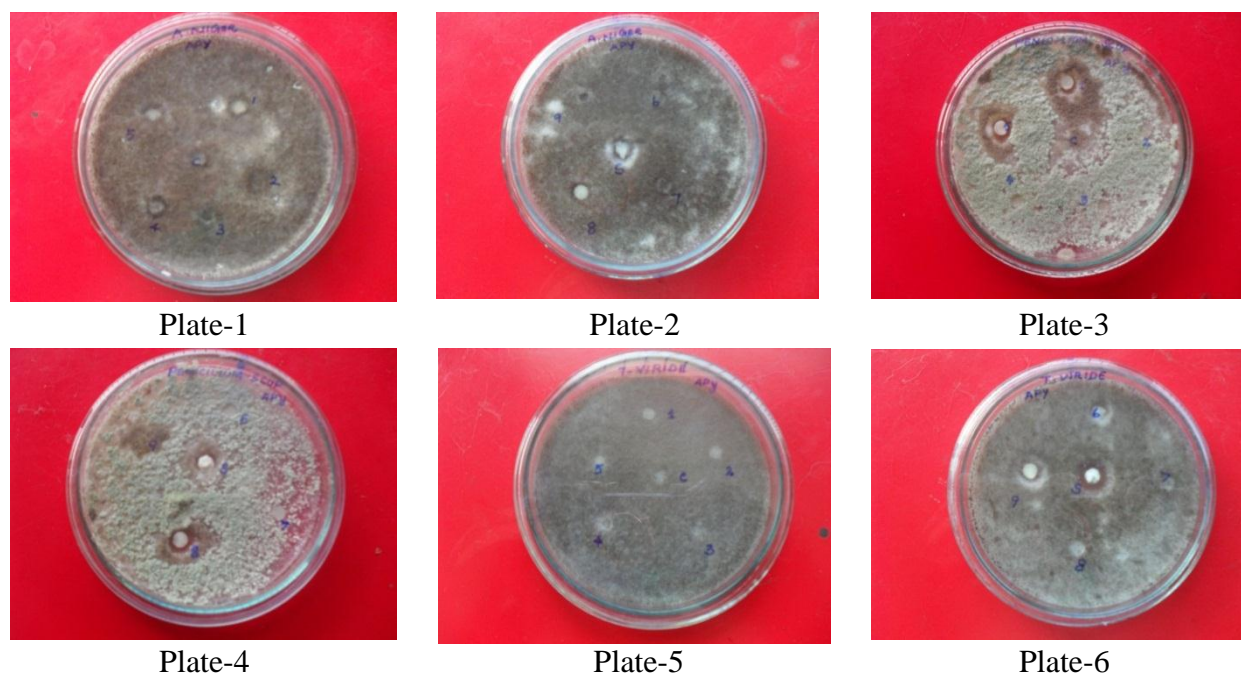


Fig. 5. Antifungal activities substituted styryl 1-pyrenyl ketones.

Table 5. Antifungal activity of substituted styryl 1-pyrenyl ketones

Entry	Substt.	Zone of Inhibition (mm)		
		<i>A. niger</i>	<i>P. spp</i>	<i>T. viride</i>
1	H	6	6	6
2	3-Br	-	-	6
3	2-Cl	-	-	-
4	3-Cl	6	6	6
5	4-Cl	6	7	-
6	4-F	-	6	6
7	4-CH ₃	-	-	-
8	3-NO ₂	6	9	6
9	4-NO ₂	-	-	7
Standard	Miconazole	10	10	10
control	DMSO	-	-	-

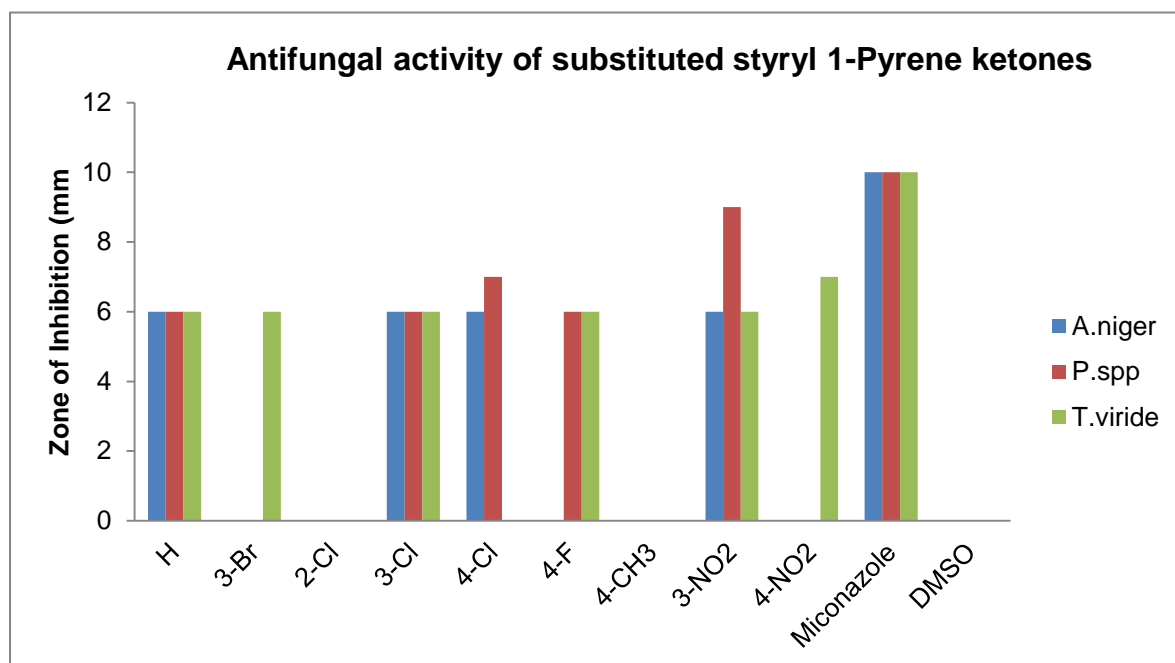


Fig. 6. Antifungal activity of substituted styryl 1-pyrene ketones-clustered column chart.

4. CONCLUSIONS

A series of 1-pyrenyl 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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