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Synthesis Structural and Biological Studies of Substituted Styryl 1,1-Diphenylmethyl Ketones

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Abstract:
A series of 1,1-diphenylmethyl chalcones are synthesized from 1,1-diphenylacetone with various substituted benzaldehydes by crossed aldol condensation. The synthesized chalcones are characterized by their physical constants and spectral data. Antibacterial and anti fungal activities of synthesized chalcones are measured by Kirby-Baury Petri-Disc method. The bacterial strains used are gram positive bacteria Bacillus subtilis, M.luteus and S.aureus gram negative bacteria Escherichia coli, P.aeruginosa and k.pneumonia and anti fungal studies with Aspergillus niger, Tricoderma viride and Mucor species.

Keywords*: Crossed-Aldol condensation; Microwave synthesis ; BF3-Ethylacetate complex ;Styryl 1,1-diphenylmethyl ketones; IR and NMR spectra; Substituent effects; Antimicrobial activities*

1. Introduction

Synthetic organic chemistry plays an important role in medical field especially for synthesis of new drugs for curing particular disease. The main base of new drug discovery was derived from the herbal plants which used in ancient medical treatments. A tremendous changes in medical and bulk drug manufacturing occurs after identification structure of core ingredients of medicinal plants which causing recovery of particular disease. Based on that pattern researchers were directed towards to synthesis that type of core ingredients [1] to meet the medicinal need according to population grouth.Various substituted drugs synthesised at present trends to enhance the drug activity and reducing side effect. Biological activities of synthesised core drug ingredients evaluated [2].
In this series researchers found out that flavonoids family plants contains 1, 3-diaryl propane skeleton is the reason for curing of many diseases. Mmicrowave assisted Aldol and Crossed-Aldol condensation [3-5] were useful for synthesis of 1,3-diaryl propenone compounds. Spectral data were useful for prediction of ground state molecular equilibration such as *E s- cis, s-trans* and *Z s-cis* and *s-trans* conformers [6].
Chalcones are 1, 3 diaryl-2-propenones which available in the flavonoids family contains medicinal effect like anti-microbial[7], anti-inflammatory[8], analgesic[9], anti-ulcerative[10], immune-modulatory[11], anti-malarial[12], anti-cancer[13], anti-viral[14], anti-leishmanial[15], anti-oxidant[16], anti-tubercular[17], anti-hyperglycemic[18] etc. A compound having anti-oxidant activity prevents and counteracts the damage of the human tissue by the normal effects of physiological oxidation [19] etc. Presence of the reactive keto group and the vinylenic group in the chalcone and their analogues possesses the antioxidant activity [20]. Compounds that associated with the antioxidant properties are hydroxyl and phenyl group. Oxidative stress which is caused by the free radical damage is help to deal with the antioxidants [21].
This correlation analysis were applied for studying the transition states of reaction mechanism[22], electrochemical redox behaviour[23], qualitative and quantitative analysis[24,25,26], assessment of substituent effects in oligopeptides[27], enol-enone tautomerism. Recently Subramanian et. al.[28,29] has studied the synthesis and spectral correlations of some heterocyclic chalcones and they observed satisfactory correlations.

Narender and T. Papi Reddy[30] had developed a new methodology to synthesize several substituted aryl styryl ketones by using BF_3-Et_2O. The advantages of this method over the existing methods are high yields, simple work-up, short duration, absence of side reactions and easier separation of the products.
Sathiyamoorthy et al.,[31-32] also studied the same with the some iodo and hydroxy substituted phenyl chalcones. With a view to above, there is no report available for UV, IR and NMR spectral correlation analysis with Hammett substituent constants, *F* and *R* parameters and antimicrobial activities in styryl 1,1-diphenylmethyl ketones. Therefore the authors have taken efforts to study the spectral correlation and antimicrobial activities of the styryl 1,1-diphenylmethyl ketones by synthesis and record their UV, IR and NMR spectra.Based on this reference we were synthesis a series of chalcones using 1,1-diphenylacetone with various substituted benzaldehyde and screening biological activities[33] tabulated in this article.

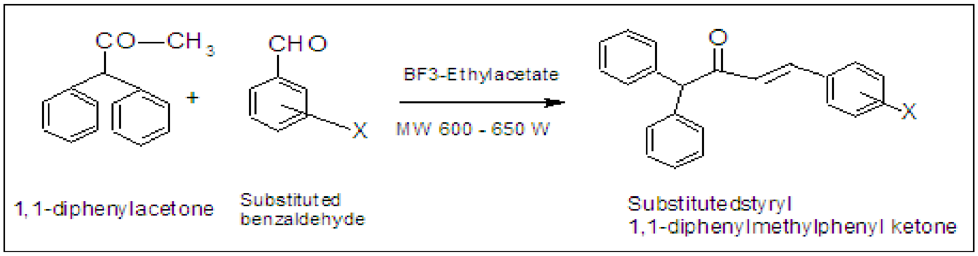
2. Experimental

2.1. Materials and Methods

All chemicals used were purchased from Sigma-Aldrich and E-Merck chemical company. The reaction carried out in *LG-395WA 230 A/C VOLTS 16-800 W* microwave oven. Melting points of all chalcones were determined in open glass capillaries on *V-SCIENTIFIC MP-DS* melting point apparatus and are uncorrected. UV spectra measured from *ELICO BL-222 SPECTROMETER* .Infrared spectra (KBr, 4000-400cm^{-1}) were recorded *SHIMADSU* Fourier transform spectrometer. NMR spectra measured from *INSTRUM AV300* operating at 500MHz 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 substituted styryl 1,1-diphenylmethyl ketones

An appropriate equimolar quantities of each 0.01 mole of 1,1-diphenylacetone and substituted benzaldehyde mixed with 5g BF3-Ethylacetate complex in a sealed boiling tube and stirred for 5 minutes at room temperature. Finally 5 ml water added and irradiated by microwave oven for 5-6 minutes[35] at 650-700 w. The completion of reaction was tested by TLC method. After completion of reaction the mass extracted with 30 ml of dichloromethane. The solution was concentrated and recrystallised with ethanol.



Where X = H, 3 -Br, 4-Br, 2-Cl, 3-Cl, 4 -F, 2-OCH_3, 4-OCH_3, 2-CH_3, 4-CH_3

Sl. No	Substitution	Molecular Formula	Molecular Weight	Yield %	Melting Point ^{0}C
1	H	$C_{22}H_{18}O$	298	74	136
2	3-Br	$C_{22}H_{17}OBr$	377	76	167
3	4-Br	$C_{22}H_{17}OBr$	377	80	169
4	2-Cl	$C_{22}H_{17}OCl$	332.5	75	155
5	3-Cl	$C_{22}H_{17}OCl$	332.5	77	154
6	4-F	$C_{22}H_{17}OF$	316	73	149
7	2-OCH_3	$C_{23}H_{20}O_2$	328	78	141
8	3-CH_3	$C_{23}H_{20}O$	312	73	144
9	2-NO_2	$C_{22}H_{17}NO_3$	343	79	155
10	4-NO_2	$C_{22}H_{17}NO_3$	343	81	159

Table 1: Physical constants and mass spectral data of substituted Styryl 1,1-diphenylmethyl ketones.

3. Result and Discussion

3.1. Spectral linearity

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

3.1.1. UV spectral study

The absorption maxima (λ_{max} nm) of synthesized 1,1-diphenylmethyl phenyl chalcones were measured and presented in Table-2. These absorption maxima (λ_{max} nm) of these chalcones were correlated with Hammett substituent constants and F and R parameters using single and multi-linear regression analysis[1, 4, 28-33,36-41]. Hammett correlation involving the group frequencies and absorption maxima, the form of the Hammett equation employed is

$$\lambda = \rho\sigma + \lambda_O \quad \ldots (1)$$

Where λ_O is the frequency for the parent member of the series.

S. No	Substitution	CO $_{s\text{-}cis}$	CO $_{s\text{-}trans}$	CH$_{ip}$	CH$_{op}$	CH=CH$_{op}$	C=C$_{op}$
1	H	1651.07	1604.77	1159.22	700.16	972.12	596.00
2	3-Br	1633.71	1600.92	1174.65	704.02	1078.21	601.79
3	4-Br	1631.78	1602.85	1174.65	707.88	1080.14	599.86
4	2-Cl	1639.49	1600.92	1172.72	702.09	1078.21	597.93
5	3-Cl	1643.35	1487.12	1170.79	702.09	1070.79	599.86
6	4-F	1683.86	1597.06	1085.92	694.37	999.13	563.21
7	2-OCH_3	1685.79	1593.99	1085.92	696.30	999.13	565.14
8	3-CH_3	1629.85	1600.92	1172.72	698.23	1080.14	601.79
9	2-NO_2	1691.57	1610.56	1082.07	690.52	999.48	569.00
10	4-NO_2	1687.71	1608.63	1082.00	711.73	993.34	565.14

Table 2: Infrared spectral data (ν, cm-1) of substituted Styryl 1,1-diphenylmethyl ketones

S. No	Substitution	δH_α	δ$_{H\beta}$	δCα	δCβ	CO	UV
1	H	7.476	7.671	125.25	138.53	197.35	298.2
2	3-Br	7.492	7.635	124.83	133.40	197.10	303.0
3	4-Br	7.495	7.627	125.66	133.39	197.11	303.0
4	2-Cl	7.456	7.591	125.65	138.32	197.10	308.4
5	3-Cl	7.437	7.627	125.66	134.73	196.03	280.8
6	4-F	7.490	7.658	126.30	138.22	197.06	292.0
7	2-OCH_3	7.477	7.654	127.28	138.23	197.01	291.8
8	3-CH_3	7.434	7.695	124.35	138.67	197.45	310.4
9	2-NO_2	7.515	7.774	124.66	137.93	196.66	270.2
10	4-NO_2	7.551	7.777	124.55	136.26	196.67	270.0

Table 3: ^{1}H NMR ,^{13}C NMR Spectral data of substituted styryl 1,1-diphenylmethyl ketones.

The results of statistical analysis[1, 4, 28-32, 35-40] of these UV absorption maxima (λ_{max}, nm) data with Hammett substituent constants and F and R parameters are presented in Table-3.The Hammett constants σ, σ^+, σ_I, σ_R constants and F and R parameters produced satisfactory correlations for all the substituents excluding 3-Br,4-Br and 2-Cl. If these substituents were included in the correlation, they reduced the correlation significantly.

The failure in correlation is due to the incapable of inductive and resonance effects of substituents on the absorption and is associated with the resonance-conjugative structure shown in Fig-1.

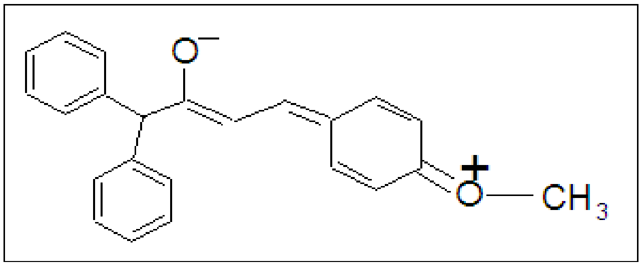


Figure 1: Resonence conjugative structure of substituted styryl 1,1-diphenylmethyl ketone

The multi regression analysis of these frequencies of all ketones with inductive, resonance and Swain–Lupton's[41] constants produce satisfactory correlations as evident in equations (2 and 3).

UV(λ_{max})=311.99 (±4.365) + 15.988(±8.843)σ_I - 21.516(±7.514) σ_R … (2)
(r = 0.967, n = 10, P > 95%)
UV(λ_{max})=312.20 (±4.295) + 13.734(±8.334)F - 18.298(±6.809) R … (3)
(r = 0.973, n = 10, P > 95%)

3.1.2. IR spectral study

The measured carbonyl stretching frequencies (cm^{-1}) of *s-cis* and *s-trans* isomers of present study are presented in Table-2 and the corresponding conformers are shown in Fig-2. The stretching frequencies for carbonyl absorption are assigned based on the assignments made by Hays and Timmons[42] for *s-cis* and *s-trans* conformers at 1690 and 1670 cm^{-1}, respectively. These data have been correlated with Hammett substituent constants and Swain-Lupton's constants [41] and are presented in Table-3. In this correlation the structure parameter Hammett equation employed is as shown in the following equation:

$\upsilon = \rho\sigma + \upsilon_0$ …. (4)

where υ 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 single parameter statistical analysis of carbonyl frequencies of *s-cis* and *s-trans* conformers with all Hammett substituent constants, *F* and *R* parameters were poor correlated. The failure in correlation is due the conjugation between the substituent and the carbonyl group in chalcones and is associated with the resonance conjugative structure shown in Figure 2. Both the conformer gave satisfactory correlation for Hammett substituent constants, *F* and *R* parameters excluding 2-NO_2 substituents. If these substituents were included in the correlation, they reduced the correlation significantly.

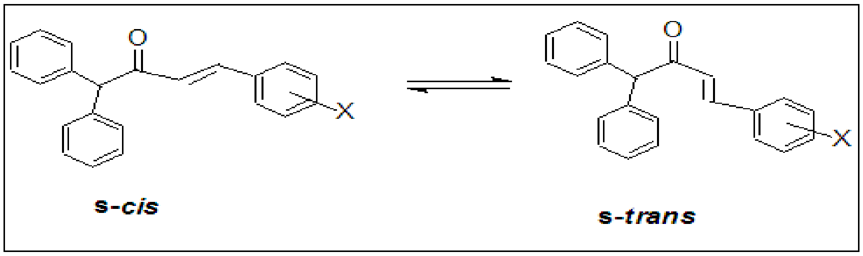


Figure 2: S-cis and s-trans conformers of substituted styryl 1,1diphenylmethyl ketone

In view of the inability of some of the σ constants to produce individually satisfactory correlations, it was thought that worthwhile to seek multiple correlations involving either σ_I and σ_R constants or Swain-Lupton's[41] *F* and *R* parameters. The correlation equations for s-*cis*, s-*trans* and deformation modes are given in equations **5-16**.

$\nu CO_{s\text{-}cis}^{(cm\text{-}1)}$ = 1646.54(±7.554) + 37.568(±15.301)σ_I + 15.734(±13.003) σ_R … (5)
(r = 0.975, n = 10, P > 95%)
$\nu CO_{s\text{-}cis}^{(cm\text{-}1)}$ = 1648.54(±7.917) + 33.385(±15.373)F +18.290(±12.560)R … (6)
(r = 0.971, n = 10, P > 95%)
$\nu CO_{s\text{-}trans}^{(cm\text{-}1)}$ = 1593.01(±3.689) +16.167(±7.473)σ_I - 1.802(±6.351) σ_R … (7)
(r = 0.963, n = 10 P > 95%)
$\nu CO_{s\text{-}trans}^{(cm\text{-}1)}$ = 1592.98(±3.383) + 16.479(±6.569)F + 0.525(±5.367) R … (8)
(r = 0.968, n = 10, P > 95%)
$\nu CH_{ip}^{(cm\text{-}1)}$ = 1214.45(±20.410) - 76.163(±41.343)σI + 22.804(±35.133) σ_R … (9)
(r = 0.9567, n = 10, P > 95%)
$\nu CH_{ip}^{(cm\text{-}1)}$ = 1213.186(±20.117) - 69.389(±39.06)F+ 15.430(±31.911) R … (10)
(r = 0.956, n = 10, P > 95%)

$\nu CH_{op}^{(cm-1)} = 858.867(\pm22.730) - 25.358(\pm46.043)\sigma I - 33.749(\pm39.127)\sigma_R$ … (11)
$(r = 0.939, n = 10, P > 95\%)$
$\nu CH_{op}^{(cm-1)} = 867.270(\pm21.417) - 45.581(\pm41.583)F - 27.896(\pm33.973) R$ … (12)
$(r = 0.947, n = 10, P > 95\%)$
$\nu CH{=}CH_{op}^{(cm-1)} = 1078.457(\pm21.636) - 16.611(\pm43.826)\sigma I + 6.797(\pm37.243)\sigma_R$ … (13)
$(r = 0.914, n = 10, P > 95\%)$
$\nu CH{=}CH_{op}^{(cm-1)} = 1068.56(\pm21.376) + 4.765(\pm41.505)F - 2.407(\pm33.909) R$ … (14)
$(r = 0.904, n = 10, P > 95\%)$
$\nu C{=}C_{op}^{(cm-1)} = 598.258(\pm21.299) - 109.023(\pm43.145)\sigma I - 6.564(\pm36.664)\sigma_R$ … (15)
$(r = 0.970, n = 10, P > 95\%)$
$\nu C{=}C_{op}^{(cm-1)} = 589.74(\pm21.868) - 93.896(\pm42.460)F - 26.752(\pm34.690) R$ … (16)
$(r = 0.967, n = 10, P > 95\%)$

Absoption	Constants	r	I	ρ	s	n	Correlated derivatives
λ_{max}(nm)	σ	0.906	298.26	-25.276	11.54	7	H,3-Cl,4-F,2-OCH$_3$,3-CH$_3$,2-NO$_2$,4-NO$_2$
	σ^+	0.955	295.76	-15.927	13.07	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F,2-OCH$_3$,3-CH$_3$,2-NO$_2$,4-NO$_2$
	σ_I	0.905	310.30	-40.953	13.19	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F,2-OCH$_3$,3-CH$_3$,2-NO$_2$,4-NO$_2$
	σ_R	0.905	286.70	-31.631	13.20	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F,2-OCH$_3$,3-CH$_3$,2-NO$_2$,4-NO$_2$
	F	0.905	307.92	-34.740	13.52	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F,2-OCH$_3$,3-CH$_3$,2-NO$_2$,4-NO$_2$
	R	0.900	283.64	-30.753	12.91	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F,2-OCH$_3$,3-CH$_3$,2-NO$_2$,4-NO$_2$

Frequency	Constant	r	I	ρ	s	n	Correlated derivatives
νCO*s-cis*$^{(cm-1)}$	σ	0.823	1654.01	17.499	26.67	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F,2-OCH$_3$,3-CH$_3$,2-NO$_2$,4-NO$_2$
	σ^+	0.817	1656.12	9.02	27.23	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F,2-OCH$_3$,3-CH$_3$,2-NO$_2$,4-NO$_2$
	σ_I	0.833	1635.99	50.98	25.58	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F,2-OCH$_3$,3-CH$_3$,2-NO$_2$,4-NO$_2$
	σ_R	0.716	1660.17	14.251	27.47	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F,2-OCH$_3$,3-CH$_3$,2-NO$_2$,4-NO$_2$
	F	0.843	1632.44	58.186	24.26	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F,2-OCH$_3$,3-CH$_3$,2-NO$_2$,4-NO$_2$
	R	0.816	1661.51	15.918	27.28	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F,2-OCH$_3$,3-CH$_3$,2-NO$_2$,4-NO$_2$
νCO*s-trans*$^{(cm-1)}$	σ	0.729	1591.21	-2.384	38.96	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F,2-OCH$_3$,3-CH$_3$,2-NO$_2$,4-NO$_2$
	σ^+	0.607	1591.47	-3.735	38.92	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F,2-OCH$_3$,3-CH$_3$,2-NO$_2$,4-NO$_2$
	σ_I	0.673	1591.9	-2.637	38.97	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F,2-OCH$_3$,3-CH$_3$,2-NO$_2$,4-NO$_2$
	σ_R	0.611	1593.88	16.209	38.73	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F,2-OCH$_3$,3-CH$_3$,2-NO$_2$,4-NO$_2$
	F	0.601	1586.89	8.908	38.92	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F,2-OCH$_3$,3-CH$_3$,2-NO$_2$,4-NO$_2$
	R	0.605	1592.89	9.14	38.85	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F,2-OCH$_3$,3-CH$_3$,2-NO$_2$,4-NO$_2$

νCH*ip*$^{(cm-1)}$	σ	0.722	1141.52	-25.174	46.61	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F, 2-OCH_3,3-CH_3,2-NO_2,4-NO_2
	σ^+	0.811	1137.88	-9.683	47.5	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F, 2-OCH_3,3-CH_3,2-NO_2,4-NO_2
	σ_I	0.654	1177.36	-92.493	43.43	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F, 2-OCH_3,3-CH_3,2-NO_2,4-NO_2
	σ_R	0.741	1134.4	-8.643	47.73	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F, 2-OCH_3,3-CH_3,2-NO_2,4-NO_2
	F	0.900	1184.66	-111.47	40.44	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F, 2-OCH_3,3-CH_3,2-NO_2,4-NO_2
	R	0.701	1133.14	-12.57	47.65	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F, 2-OCH_3,3-CH_3,2-NO_2,4-NO_2
νCH*op*$^{(cm-1)}$	σ	0.902	699.77	4.437	6.42	9	H,3-Br,4-Br,2-Cl,3-Cl,4-F, 2-OCH_3,3-CH_3,4-NO_2
	σ^+	0.913	699.87	4.61	6.197	9	H,3-Br,4-Br,2-Cl,3-Cl,4-F, 2-OCH_3,3-CH_3,4-NO_2
	σ_I	0.701	699.22	3.533	6.64	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F, 2-OCH_3,3-CH_3,2-NO_2,4-NO_2
	σ_R	0.913	702.31	8.231	6.313	9	H,3-Br,4-Br,2-Cl,3-Cl,4-F, 2-OCH_3,3-CH_3,4-NO_2
	F	0.813	701.15	-0.961	6.681	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F, 2-OCH_3,3-CH_3,2-NO_2,4-NO_2
	R	0.802	701.45	7.407	6.332	9	H,3-Br,4-Br,2-Cl,3-Cl,4-F, 2-OCH_3,3-CH_3,4-NO_2
νCH=CH*op*$^{(cm-1)}$	σ	0.808	1037.08	-9.306	48.07	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F, 2-OCH_3,3-CH_3,2-NO_2,4-NO_2
	σ^+	0.802	1035.53	-2.468	48.21	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F, 2-OCH_3,3-CH_3,2-NO_2,4-NO_2
	σ_I	0.812	1022.68	28.925	47.86	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F, 2-OCH_3,3-CH_3,2-NO_2,4-NO_2
	σ_R	0.729	1027.49	-39.427	47.07	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F, 2-OCH_3,3-CH_3,2-NO_2,4-NO_2
	F	0.845	1036.51	-3.318	48.23	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F, 2-OCH_3,3-CH_3,2-NO_2,4-NO_2
	R	0.792	1024.75	-44.45	46.49	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F, 2-OCH_3,3-CH_3,2-NO_2,4-NO_2
νC=C*op*$^{(cm-1)}$	σ	0.817	587.63	-7.559	18.44	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F, 2-OCH_3,3-CH_3,2-NO_2,4-NO_2
	σ^+	0.72	586.53	-2.999	18.64	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F, 2-OCH_3,3-CH_3,2-NO_2,4-NO_2
	σ_I	0.814	602.08	-37.642	17.02	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F, 2-OCH_3,3-CH_3,2-NO_2,4-NO_2
	σ_R	0.802	586.29	1.675	18.71	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F, 2-OCH_3,3-CH_3,2-NO_2,4-NO_2
	F	0.9	605.43	-44.649	15.69	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F, 2-OCH_3,3-CH_3,2-NO_2,4-NO_2
	R	0.8	585.84	-0.559	18.72	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F, 2-OCH_3,3-CH_3,2-NO_2,4-NO_2

Chemical shift	constant	r	I	ρ	s	n	Correlated derivatives
$\delta_{H\alpha}$(ppm)	σ	0.916	7.469	0.057	0.028	9	H,3-Br,4-Br,2-Cl,4-F, 2-OCH$_3$,3-CH$_3$,2-NO$_2$,4-NO$_2$
	σ^+	0.925	7.474	0.041	0.03	9	H,3-Br,4-Br,2-Cl,4-F, 2-OCH$_3$,3-CH$_3$,2-NO$_2$,4-NO$_2$
	σ_I	0.915	7.441	0.095	0.031	8	H,3-Br,4-Br,4-F,2-OCH$_3$, 3-CH$_3$,2-NO$_2$,4-NO$_2$
	σ_R	0.9	7.497	0.081	0.03	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F, 2-OCH$_3$,3-CH$_3$,2-NO$_2$,4-NO$_2$
	F	0.9	7.444	0.086	0.031	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F, 2-OCH$_3$,3-CH$_3$,2-NO$_2$,4-NO$_2$
	R	0.91	7.499	0.092	0.031	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F, 2-OCH$_3$,3-CH$_3$,2-NO$_2$,4-NO$_2$
$\delta_{H\beta}$(ppm)	σ	0.904	7.654	0.099	0.057	8	H,3-Br,4-Br,2-Cl,3-Cl,4-F, 2-OCH$_3$,3-CH$_3$,
	σ^+	0.902	7.665	0.027	0.063	8	H,3-Br,4-Br,2-Cl,3-Cl,4-F, 2-OCH$_3$,3-CH$_3$,
	σ_I	0.732	7.626	0.102	0.012	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F, 2-OCH$_3$,3-CH$_3$,2-NO$_2$,4-NO$_2$
	σ_R	0.955	7.698	0.135	0.054	7	H,3-Br,4-Br,2-Cl,3-Cl, 2-NO$_2$,4-NO$_2$
	F	0.833	7.628	0.097	0.061	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F, 2-OCH$_3$,3-CH$_3$,2-NO$_2$,4-NO$_2$
	R	0.849	7.696	0.112	0.057	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F, 2-OCH$_3$,3-CH$_3$,2-NO$_2$,4-NO$_2$
δCO(ppm)	σ	0.905	197.08	-0.591	0.355	9	H,3-Br,4-Br,2-Cl,4-F, 2-OCH$_3$,3-CH$_3$,2-NO$_2$,4-NO$_2$
	σ^+	0.905	197.03	-0.443	0.36	9	H,3-Br,4-Br,2-Cl,4-F, 2-OCH$_3$,3-CH$_3$,2-NO$_2$,4-NO$_2$
	σ_I	0.905	197.43	-1.117	0.367	9	H,3-Br,4-Br,2-Cl,4-F, 2-OCH$_3$,3-CH$_3$,2-NO$_2$,4-NO$_2$
	σ_R	0.831	196.85	-0.515	0.411	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F, 2-OCH$_3$,3-CH$_3$,2-NO$_2$,4-NO$_2$
	F	0.904	197.29	-0.785	0.394	9	H,3-Br,4-Br,2-Cl,4-F, 2-OCH$_3$,3-CH$_3$,2-NO$_2$,4-NO$_2$
	R	0.833	196.82	-0.556	0.402	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F, 2-OCH$_3$,3-CH$_3$,2-NO$_2$,4-NO$_2$
δCα(ppm)	σ	0.914	117.04	-13.468	37.39	9	H,3-Br,4-Br,2-Cl,4-F, 2-OCH$_3$,3-CH$_3$,2-NO$_2$,4-NO$_2$
	σ^+	0.915	116.12	-10.709	37.37	9	H,3-Br,4-Br,2-Cl,4-F, 2-OCH$_3$,3-CH$_3$,2-NO$_2$,4-NO$_2$
	σ_I	0.906	118.96	-11.325	37.75	8	3-Br,4-Br,2-Cl,3-Cl,4-F, 2-OCH$_3$,2-NO$_2$,4-NO$_2$
	σ_R	0.903	113.2	-4.764	37.8	9	H,3-Br,4-Br,2-Cl,4-F, 2-OCH$_3$,3-CH$_3$,2-NO$_2$,4-NO$_2$
	F	0.709	112.37	4.005	37.81	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F, 2-OCH$_3$,3-CH$_3$,2-NO$_2$,4-NO$_2$
	R	0.802	112.37	4.005	37.81	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F, 2-OCH$_3$,3-CH$_3$,2-NO$_2$,4-NO$_2$

$\delta C\beta$(ppm)	σ	0.839	137.23	-2.145	2.103	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F, 2-OCH_3,3-CH_3,2-NO_2,4-NO_2
	σ^+	0.839	137.13	-1.97	2.022	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F, 2-OCH_3,3-CH_3,2-NO_2,4-NO_2
	σ_I	0.854	138.29	-3.559	2.166	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F, 2-OCH_3,3-CH_3,2-NO_2,4-NO_2
	σ_R	0.829	136.34	-2.222	2.099	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F, 2-OCH_3,3-CH_3,2-NO_2,4-NO_2
	F	0.617	137.56	-1.83	2.249	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F, 2-OCH_3,3-CH_3,2-NO_2,4-NO_2
	R	0.721	136.36	-1.728	2.233	10	H,3-Br,4-Br,2-Cl,3-Cl,4-F, 2-OCH_3,3-CH_3,2-NO_2,4-NO_2

Table 4: Results of statistical analysis of UV, IR, ^1H-NMR,and ^{13}C-NMR spectral values of substituted Styryl 1,1-diphenylmethyl ketones with Hammett σ, σ^+, σ_I, σ_R constants and F and R parameters

3.1.3 ^1H NMR Spectral Study

The ^1H NMR spectra of synthesized chalcones have been recorded using deuteriochloroform ($CDCl_3$) as solvent and employing tetramethylsilane (TMS) as internal standard. The ethylenic protons signals of the chalcones were assigned from their spectra. They were calculated as AB or AA' or BB' systems respectively. The lower chemical shifts (ppm) obtained for Hα and higher chemical shifts (ppm) obtained for Hβ in this series of ketones. The vinyl protons give an AB pattern and the β-proton doublets were well separated from the signals of the aromatic protons. The assigned vinyl proton chemical shifts δ(ppm) of all ketones were presented in Table-3.

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

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

where δ_0 is the chemical shift of unsubstituted ketones.

The assigned $H\alpha$ and $H\beta$ proton chemical shifts (ppm) are correlated with various Hammett sigma constants. The results of statistical analysis[1, 4, 28-32, 35-40] are presented in **Table-3**. The obtained correlation is satisfactory for both H_α and H_β with Hammett σ, σ^+, σ_I and σ_R constants also with *F* and *R* parameters excluding 2-Cl, 3-Cl, 2-NO_2 and 4-NO_2 substituents.

While seeking the multi-correlation by the application of Swain-Lupton's[41] treatment to the relative chemical shifts of H_α and H_β with *F* and *R* values is successful with resonance, inductive effect generates the multi regression equations 18-21.

$$\delta H_\alpha(\mathrm{ppm}) = 7.123(\pm 10.082) + 0.1030(\pm 0.1671)\sigma_I + 0.0.1454\pm 0.142)\ \sigma_R \quad \ldots(18)$$
$$(r = 0.969,\ n = 10,\ P > 95\%)$$
$$\delta\ H_\alpha(\mathrm{ppm}) = 7.1211(\pm 0.0792) + 0.122(\pm 0.153)F + 0.149(\pm 0.125)R \quad \ldots(19)$$
$$(r = 0.974,\ n = 10,\ P > 95\%)$$
$$\delta H_\beta(\mathrm{ppm}) = 7.493(\pm 0.0640) + 0.301(\pm 0.439)\sigma_I - 0.175(\pm 0.343)\ \sigma_R \quad \ldots(20)$$
$$(r = 0.957,\ n = 10,\ P > 95\%)$$
$$\delta H_\beta(\mathrm{ppm}) = 7.393(\pm 0.092) + 0.267(\pm 0.180)F - 0.094(\pm 0.147)R \quad \ldots(21)$$
$$(r = 0.958,\ n = 10,\ P > 95\%)$$

3.1.4. ^{13}C NMR Spectral Study

Scientists and physical organic chemists[1, 4, 28-32, 35-40], 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 3. The results of statistical analysis are given in Table-4. Both C_α and C_β chemical shifts (ppm) gave satisfactory correlation with Hammett σ, σ^+, σ_I, σ_R constants and *F* and *R* parameters.

The chemical shifts (ppm) of CO carbons with Hammett substituent constants and *F* and *R* parameters gave poor correlation. The obtained correlation is satisfactory with Hammett σ, σ^+, σ_I and σ_R constants also with *F* and *R* parameters excluding H and 3-CH_3 substituents. This is due to the reason stated earlier and associated with resonance conjugative structure shown in Figure-1.

While seeking the multi-regression analysis through Swain-Lupton's[41] parameter correlations were satisfactorily obtained within these carbon chemical shifts and the regression equations are given in 22-27.

$\delta CO(ppm) = 194.106(\pm 1.206) – 6.198(\pm 2.443)\sigma_I + 1.412(\pm 2.076)\ \sigma_R$ … (22)
(r = 0.950, n = 10, P > 95%)
$\delta CO\ (ppm) = 193.9(\pm 1.230) - 5.515(\pm 2.388)F + 0.700(\pm 1.951)R$ … (23)
(r = 0.953, n = 10, P > 95%)
$\delta C_\alpha\ (ppm) = 118.171\ (\pm 2.347) + 3.479(\pm 4.754)\sigma_I - 1.961(\pm 4.040)\ \sigma_R$ … (24)
(r = 0.960, n = 10, P > 95%)
$\delta C_\alpha\ (ppm) = 119.229\ (\pm 2.382) + 1.489(\pm 4.625)F - 0.159(\pm 3.779)\ R$ … (25)
(r = 0.970, n = 10, P > 95%)
$\delta C_\beta(ppm) = 141.169\ (\pm 2.230) + 0.130(\pm 4.517)\sigma_I - 2.498(\pm 3.838)\ \sigma_R$ … (26)
(r = 0.832, n = 10, P > 95%)
$\delta C_\beta\ (ppm) = 142.091\ (\pm 2.216) - 1.518(\pm 4.302)F - 0.975(\pm 3.515)\ R$ … (27)
(r = 0.809, n = 10, P > 95%)

4. Antimicrobial Activity

4.1. Antibacterial Activity

The newly synthesized chalcones (1-10) were subjected to antimicrobial activity against gram positive bacteria *Bacillus subtilis, M.luteus* and *S.aureus* gram negative bacteria *Escherichia coli, P.aeruginosa* and *k.pneumonias* by using cup and plate method. The agar medium was purchased from *HI MEDIA* Laboratories Ltd, Mumbai, India. The agar medium prepared by dissolving 2.5 g of agar in 100 ml water at boiled condition as per standard procedure. The bubble free medium poured in to Petri dishes and allowed to cool under closed condition for gel formation. After streaking microorganism what man no-40 discs of 6.0 mm in diameter laid on the gel to identify the inhibition zones. The test compounds prepared by dissolving 5 mg each compound in 5 ml of dimethyl sulphoxide. The solution of each compound 0.1 ml were added on what man disc and incubated at 37^0C for 24 Hour. A reference standard drug of gram positive and gram negative bacteria was made by dissolving 5.0 mg of ampicillin in 5.0 ml of distilled water separately. All the experiments were carried out duplicate to avoid error .Simultaneously reference were tested with 0.1 ml of dimethyl sulphoxide which not reveal any zone of inhibition. Diameter of inhibition zone produced by each compound was measured in mm. The results are given in Table-4.

S.No	**Substitution**	**Zone of Inhibition (mm)**					
		Gram positive Bacteria			**Gram negative Bacteria**		
		B.subtilis	***M.luteus***	***S.aureus***	***E.coli***	***P.aeruginosa***	***k.pneumonias***
1	H	10	6	-	-	7	-
2	3-Br	12	8	8	10	8	-
3	4-Br	8	8	-	6	9	7
4	2-Cl	8	9	8	8	10	7
5	3-Cl	7	7	-	6	-	8
6	4-F	7	-	6	-	6	-
7	2-OCH_3	7	7	8	8	8	6
8	3-CH_3	10	8	6	9	8	-
9	2-NO_2	8	6	6	-	8	-
10	4-NO_2	6	7	-	-	6	-
Standard	Ampicillin	9	10	9	13	12	8
Control	DMSO	-	-	-	-	-	-

Table 5: Antibacterial activity of substituted Styryl 1,1-diphenylmethyl ketones
(-) Indicates no zone of inhibition formed

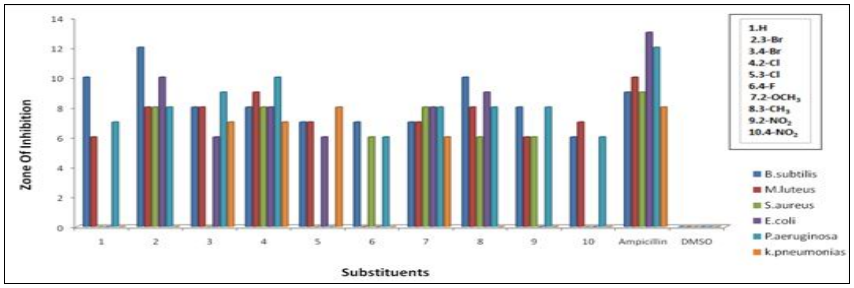


Figure 3: The antibacterial-clustered column chart of substituted Styryl 1,1-diphenylmethyl ketones

.

Plate - 1

Plate - 2

Plate - 3

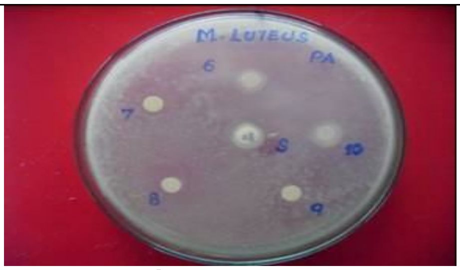


Plate - 4

Plate - 5

Plate - 6

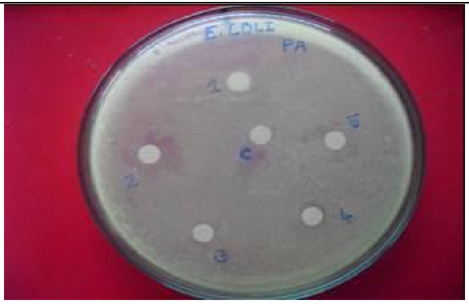


Plate - 7

Plate - 8

Plate - 9

Plate - 10

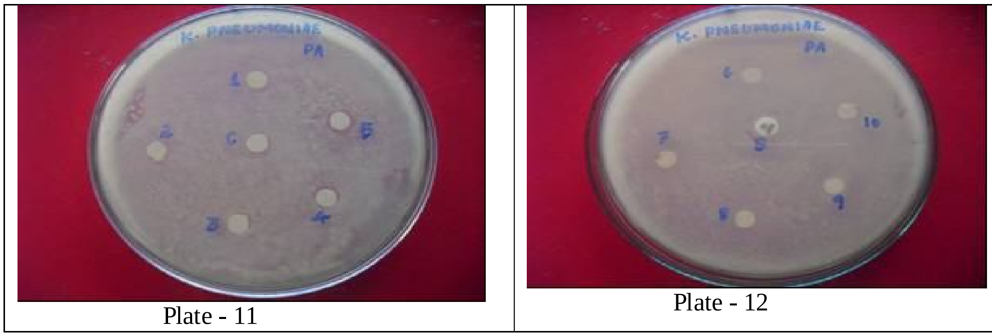


Plate - 11 Plate - 12

Figure 4: The antibacterial images of substituted Styryl 1,1-diphenylmethyl ketones

4.2. Antifungal Activity

All the those compounds screened for antimicrobial activity were also tested for antifungal activity using potato –dextrose-agar (PDA) medium same cup and plate method against *Aspergillus niger*,*Tricoderma viride* and *Mucor species* .Preparation of nutrient broths ,subculture, base layer medium and PDA-medium was done as per the standard procedure. A reference standard drug fluconazole 5mg dissolved in 5ml of water 0.1 ml of solution used as a control which did not reveal any inhibition. The experiments were duplicated to minimize the error. Diameter of inhibition zone produced by each compound was measured in mm and tabulated.

Sl. No	**Substitution**	**Mean zone of inhibition (mm)**		
		A. Niger	***T. Viride***	***M. Species***
1	H	6	6	-
2	3-Br	6	-	-
3	4-Br	-	-	-
4	2-Cl	7	6	-
5	3-Cl	-	-	8
6	4-F	6	6	7
7	2-OCH_3	6	9	7
8	3-CH_3	-	7	8
9	2-NO_2	6	-	8
10	4-NO_2	6	6	6
11	DMF	-	-	-
12	Fluconazole	12	10	9

Table 6: Antifungal activity of substituted Styryl 1,1-diphenylmethyl ketones.
(-) Indicates no zone of inhibition formed

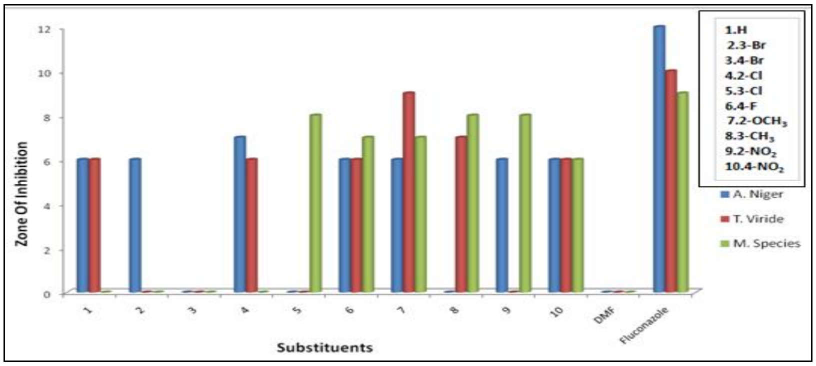


Figure 5: The anti fungal-clustered column chart of substituted Styryl 1,1-diphenylmethyl ketones

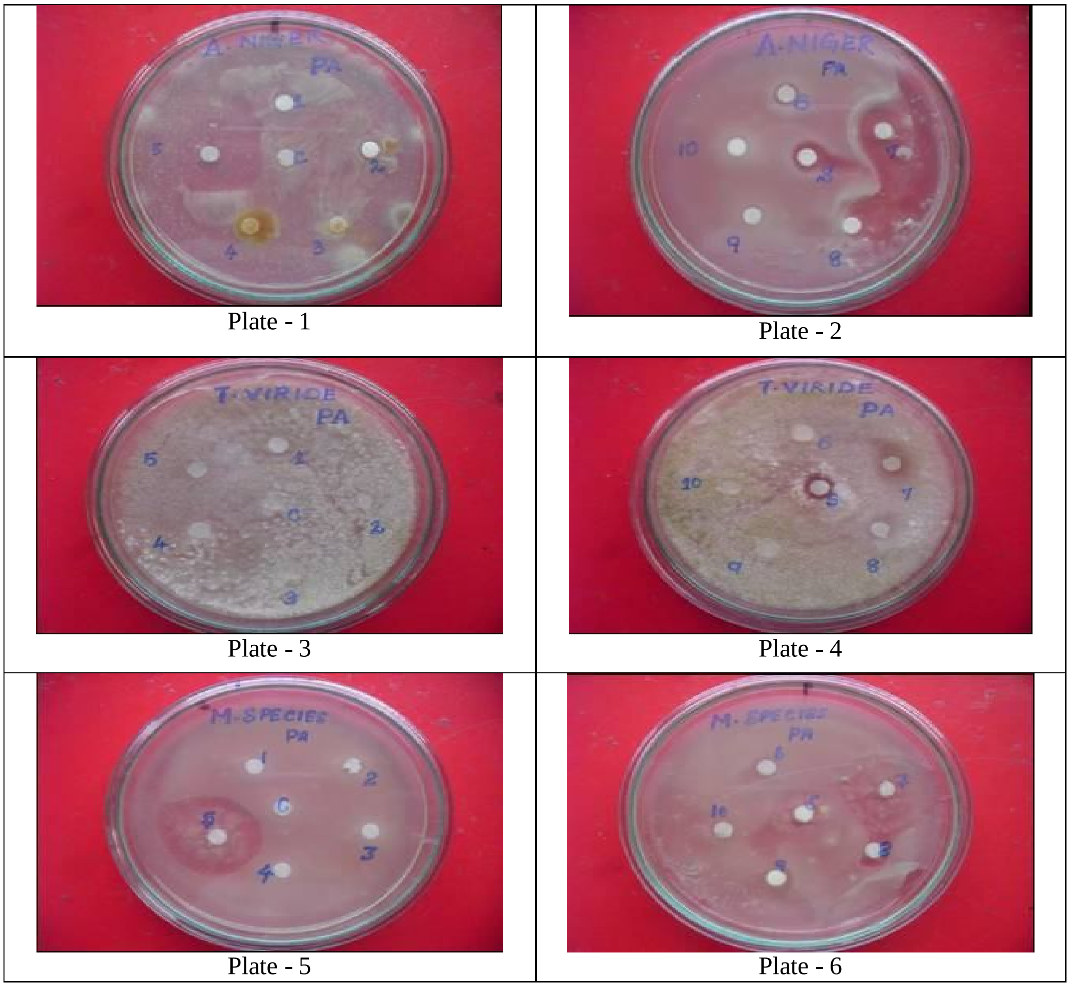


Plate - 1
Plate - 2
Plate - 3
Plate - 4
Plate - 5
Plate - 6

Figure 6: The anti fungal images of substituted Styryl 1,1-diphenylmethyl ketones

5. Conclusion

Some of substituted Styryl 1,1-diphenylmethyl ketones have been synthesized by condensation of 1,1-diphenylacetone and substituted benzaldehydes using microwave irradiation in the presence of Borontrifluoride-ethylacetate catalyst. This reaction protocol offers a simple, easier work-up procedure and good yields. The 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 chalcone have been studied using Bauer-Kirby method. The screening results revealed that compounds containing electron releasing group as substituent showed better antibacterial activity than compound containing electron with drawing group. Compounds containing pharmacopores such as chloro, fluoro and nitro functional group shows more anti fungal activity.

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7. Refrences

1. Arulkumaran.R, Vijayakumar.S, Sakthinathan.S, Kamalakkannan.D, Ranganathan.K, Suresh.R, Sundararajan.R, Vanangamudi.G, Thirunarayanan.G, (2013). J.Chil.Chem. Soc., 58(2), 1553.
2. Yankep.E, Fomumand.Z.T ,Dangne.E (1997), Phytochem., 46, 591.
3. Thirunarayanan.G, Vanangamudi.G, (2007) E-J. Chem., 4(1), 90 .
4. Ranganathan.K, Arulkumaran.R, Kamalakkannan.D, Sundararajan.R, Sakthinathan.S.P, Vijayakumar.S, Suresh.R, Vanangamudi.G, Thirumurthy.K, Mayavel.P, Thirunrayanan.G, (2012). Int.J.Pharm. Med and Bio.Sci., 1(1), 62 .
5. Venkat Reddy.G, aitraie.G,Narsaiah.D, Rambahu.B, Rao.R, (2001). Synth. Commun.31(18), 2881.
6. MullikenR.S**.** (1939). J.Chem.Phys. 7 121 .
7. Hsieh.H.K, Tsao.L.T, Wang.J.P , (2000). J. Pharm. Pharmacol. 52(2), 163.
8. Viana.G.S, Bandeira.M.A, Matos.F, (2003). J.Phytomed. 10, 189

9. Zhao.L.M, Jin.H.S, Sun.L.P,Piao.H.R, Quan.Z.S, (2005), Bioorg.Med.Chem.Lett., 15(22), 5027 .
10. Mukarami.S, Muramatsu.M, Aihara.H, Otomo.S, (1991), Biochem.Pharmacol., 42(7), 1447 .
11. Liu.M, Wilairat.P, Go.L.M, (2001), J.Med.Chem., 44(5), 4443
12. Francesco.E, Salvatore.G, Luigi.M, (2007),Phytochem., 68(7), 939.
13. Onyilagna.J.C, Malhotra.B, Elder.B, Towers.G.H, (1997),Can.J.Plant.Pathol., 19, 133
14. Nielsen.S.F, Chen.M, Theander.T.G, KharazmiA.K, (1997). Bioorg.Med.Chem.Lett., 5, 449.
15. Miranda.C.L, Aponso.G.L.M, (2000), J.Agri.Food.Chem., 48, 3876 **.**
16. SivaKumar.P.M,Geetha Babu.S.K, Mukesh.D, (2007), Chem.Pharm.Bull., 55(1), 44.
17. Satyanarayana.M, Tiwari.P,Tripathi.K, Srivastava.A.K, Pratap.K, (2004). Bioorg.Med.Chem.Lett., 12, 883.
18. Barford.L,Kemp.K, Hansen.M, Kharazmi.A, (2007) ,Int.Immunopharmacol., 2, 545.
19. Maria.J, Moa.G, Mandado.M, (2007). Chem.Phy.Lett.,1 446,
20. Dass.G.K, (2001),Indian J Chem,40, 23 .
21. Ranganathan.K, Suresh.R, Kamalakkannan.D, Arulkumaran.R, Sundararajan.R, Sakthinathan.S.P, Vijayakumar.S, Vanangamudi.G, Thirumurthy.K, Mayavel.P, Thirunarayanan.G, (2012), Int.Lett.Chem.Phy.Astrono., 4, 66 .
22. Griffiths.P.R, Chalmers.J.M, (2002), Handbook of Vibrational Spectroscopy. vol. 4. Chinchester: John-Wiley & Sons; 2576 .
23. Thirunarayanan.G, Surya.S, Srinivasan.S, Vanangamudi.G, Sathyendiran.V, (2010) Spectrochim Acta. 75A, 152 .
24. Vanangamudi.G, Ranganathan.K, Thirunaryanan.G, (2012)World J Chem. 7, 22.
25. Horvath.V, Varga.Z, Kov´acs.A, Mol.J. (2005), Struct,.Theochem, 755(1-3), 247.
26. Anto.R.J, Sukumaran.K, Kuttan.G, Rao.M.A , (1995), Cancer.Lett. 97, 33 .
27. Utpal.B, Sahu.A, Ali.S.S, Kasoju.L, Singh.A, (2008), Food.Res.Inter., 41, 15
28. Subramanian.M, Vanangamudi.G, Thirunarayanan.G, (2013),Spectrochem.Acta, 110A, 116
29. Vanangamudi.G, Subramanian.M, Thirunarayanan.G, (2013), Arab.J.Chem., DOI: 10.1016/j.arabjc.2013.03.006.
30. Narender and Papi Reddy.T, (2007), Tetrahedron. Letts., , 48, 3177**.**
31. Sathiyamoorthi.K, Mala.V, Suresh.R, Sakthinathan.S.P, Kamalakkannan.D, Ranganathan.K, Arulkumaran.R, Sundararajan.R, Vijayakumar.S, Vanangamudi.G, Thirunarayanan.G, (2013), Int.Lett.Chem.Phy.and.Astrono., 7(2), 102
32. Sathiyamoorthi.K, Mala.V, Suresh.R, Sakthinathan.S.P, Kamalakkannan.D.K, Vanangamudi.G, Thirunarayanan.G, (2013), Spectrochim.Acta, DOI:http://dx.doi.org/10.1016/j.saa.2013.04.048.
33. Mala.V, Sathiyamoorthy.K, Sakthinathan.S.P, Kamalakkannan.D, Suresh.R, Vanangamudi.G, Thirunarayanan.G,(2013.) Q-Science Connect. DOI: http://dx.doi.org/10.5339/connect.
34. Bauer.A.W, Kirby.W.M.M, Sherris.J.C, Truck.M, (1966), Am.J.Clin.Pathol., 45, 493 .
35. Dhanaji.H, Jadhav Ramaa.C.S, (2007),Ind.J.Chem., 46, 2064 .
36. Sachin.T, Tabreskhan.P, Rhea.M, Ramaa.C.S, (2010),Int.J.Drug.Desgn.Discov., 1(3), 209
37. Arpita.H More, Jadhav Ramaa.C.S, (2010),Ind.J.Chem., 49B, 364 .
38. Sekar.K.G, Thirunarayanan.G, (2013), Int.Lett.Chem.Phy.Astrono., 8(3), 249 .
39. Arulkumaran.R, Vijayakumar.S, Sundararajan.R, Sakthinathan.S.P, Kamalakkannan.D, Suresh.R, Ranganathan.K, Rajakumar.P.R.R, Vanangamudi.G, Thirunarayanan.G, (2013), Int.Lett.Chem.Phy.Astrono., 5, 21 .
40. Sakthinathan.S.P, Suresh.R, Mala.V, Sathiyamoorthi.K, Kamalakkannan.D, Ranganathan.K, Arulkumaran.R, Vijayakumar.S, Sundararajan.R, Vanangamudi.G, Thirunarnan.G, (2013),Int.Lett.Chem.Phy.Astrono., 6, 77 .
41. Sekar.K.G, Thirunarayanan.G, (2013) , Int.Lett.Chem.Phy.Astrono., 8(2), 160 .
42. Swain.G.C, Lupton.E.C, (1968), Jr., J. Am.Chem.Soc., 90, 4328 .
43. Hays.W.P, Timmons.C.J, (1968), Spectrochim.Acta., 24A, 323