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# Solvent free synthesis, spectral linearity, antimicrobial, antioxidant and insect antifeedant activities of some 1-methyl-2-pyrrolyl chalcones

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# ABSTRACT

Some 2*E* N-methyl-2-pyrrolyl chalcones have been synthesized using greener catalyst fly-ash:sulphuric acid assisted solvent free environmentally benign Crossed-Aldol reaction. The yields of chalcones are more than 90%. The synthesized chalcones are characterized by their physical constants and spectral data. The spectral group frequencies have been correlated with various Hammett substituent constants using single and multi-linear regression analyses. The antimicrobial, antioxidant and insect antifeedant activities of all chalcones have been studied.

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### **INTRODUCTION**

There are various green chemistry synthetic methods such as stereospecific<sup>[1]</sup>, stereo selective<sup>[2]</sup>, enantiomeric excess (ee, SS/SR/RS/RR)<sup>[3]</sup>, available for organic synthesis of stereo chemical compounds, cis- and trans- or E and Z isomers of alkenes<sup>[4]</sup>, alkynes<sup>[5]</sup>, scis and s-trans (cc/ct/tt) conformers of α,β-unsaturated aldehydes<sup>[6]</sup>, ketones<sup>[7]</sup>, acids<sup>[8]</sup>, acid chlorides<sup>[9]</sup> and esters<sup>[10]</sup>, (ccc/ctc/cct/ttc/ttt) conformers of conjugated polyenes<sup>[11]</sup>, ee ( $\alpha S$ ,  $\beta R$ ) oxiranes and ketooxiranes<sup>[12]</sup>. Many green catalysts have been used for synthesizing chalcones such as silica-sulphuric acid<sup>[13]</sup>, anhydrous zinc chloride<sup>[14]</sup>, Clay<sup>[15]</sup>, ground chemistry catalysts-grinding the reactants with sodium hydroxide<sup>[16]</sup>, aqueous alkali in lower temperature<sup>[17]</sup>, solid sulphonic acid from bamboo<sup>[18]</sup>, barium hydroxide<sup>[19]</sup> anhydrous sodium bicarbonate<sup>[20]</sup>, microwave assisted

# KEYWORDS

Fly-ash:sulphuric acid; Greener synthesis; Crossed-aldol reaction; Spectral linearity; Biological activities.

synthesis<sup>[21]</sup>, Fly-ash:water<sup>[22]</sup>, nano titanium and magnesium oxides<sup>[23]</sup>. These catalysts are used in Aldol, Crossed-Aldol, Claisen-Schmidt, Friedel-Crafts cinnamoylation and Knovenegal reactions for synthesizing chalcones and it derivatives. These catalysts do have the advantages that they are non-toxic, leading to pollution free environment, involving lesser reaction time, giving better yield, and using lesser quantity of solvent and handling simple and easy procedures. Chalcones possess various multipronged activities such as antimicrobial<sup>[24]</sup>, antioxidant<sup>[25]</sup>, anticancer<sup>[26]</sup>, antiviral<sup>[27]</sup>, antitumor<sup>[28]</sup>, antimalarial<sup>[29]</sup>, antifertile<sup>[30]</sup>, cardiovascular<sup>[31]</sup>, antidepressants<sup>[32]</sup>, antiplasmodial<sup>[33]</sup>, anti-aids<sup>[34]</sup> and insect antifeedant activities<sup>[35,36]</sup>. Chalcones undergo conformational equilibration in the ground state such as s-cis and s-trans conformers as evidenced and confirmed by infrared spectral studies. This physicochemical property of chalcone is associated with spectral lin-

earity<sup>[7,33,37]</sup>. This spectral linearity has been studied by Hammett equation using single and multi-linear regression analyses. In the present investigation, the authors wish to report a new catalyst Fly-ash:sulphuric acid for synthesizing chalcones by Crossed-Aldol condensation reaction. The yields of chalcones are more than 90%. The synthesized chalcones are characterized by their physical constants, Mass, IR and NMR spectral data as they are unknown compounds so far. The purities of the synthesized chalcones have been checked by their physical constants and their spectral data. Therefore the authors have taken efforts to synthesize some aryl chalcones by solvent free method and to study the spectral linearity, antimicrobial and insect antifeedant activities of chalcones.

#### EXPERIMENTAL

#### Materials and methods

All chemicals are procured from E-Merck brand. Fly ash was collected from Thermal Power Plant-II, Neyveli Lignite Corporation (NLC), Neyveli, Tamil Nadu, India. Melting points of all chalcones were determined in open glass capillaries on Mettler FP51 melting point apparatus and are uncorrected. Infrared spectra (KBr, 4000-400cm<sup>-1</sup>) were recorded on Avatar-300 Fourier transform spectrophotometer. The NMR spectra of all compounds are recorded in Instrum AV300 spectrometer operating at 500 MHz for <sup>1</sup>H NMR spectra and 125.46 MHz for <sup>13</sup>C NMR spectra in CDCl<sub>3</sub> solvent using TMS as internal standard. Electron impact (EI, 70 eV) and chemical ionization mode FAB<sup>+</sup> mass spectra were recorded with a Varian 500 spectrometer.

### **Preparation of catalyst**

In a 50mL Borosil beaker, 1g of fly-ash and 0.8mL (0.5mol) of *p*-toluenesulphonic acid are taken and mixed thoroughly with glass rod. This mixture is heated on a hot air oven at 85°C for 1h, cooled to room temperature, stored in a borosil bottle and tightly capped. This is characterized by infrared spectral data. Infrared spectral data of fly-ash: sulphuric acid is v(cm<sup>-1</sup>): 3456(OH); 3010 (C-H); 1495, 1390(C-S); 1336, 1154(S=O); 1136, 1090, 976, 890, 850, 820, 667, 658, 620, 580, 498, 425.

TABLE 1 : Analytical and mass spectral data of 1-methyl-2-pyrrolyl chalcones

Entry	R	М. F.	F. W.	Yield (%)	М.р. (°С)	Mass (m/z)
1	Н	C <sub>14</sub> H <sub>13</sub> NO	212	94	209-210 (209) <sup>[39]</sup>	212[M <sup>+</sup> ], 196, 134, 131, 108, 103, 97, 80, 77, 66, 65, 27, 15.
2	3-Br	C <sub>14</sub> H <sub>12</sub> BrNO	290	92	166-167	290[M <sup>+</sup> ], 292[M <sup>+2</sup> ], 273, 208, 154, 108, 81, 77,15
3	4-Br	C <sub>14</sub> H <sub>12</sub> BrNO	290	93	161-162	290[M <sup>+</sup> ], 292[M <sup>+2</sup> ], 273, 210, 208, 180, 154, 108, 81, 77, 15
4	3-Cl	C <sub>14</sub> H <sub>12</sub> ClNO	246	90	220-221	246[M <sup>+</sup> ], 248,[M <sup>+2</sup> ], 230, 165, 108, 111, 77, 15
5	4-Cl	C <sub>14</sub> H <sub>12</sub> ClNO	246	93	250-221	246[M <sup>+</sup> ], 248,[M <sup>+2</sup> ], 230, 210, 165, 108, 137, 134, 123, 111, 77, 65, 35, 15
6	4-F	$C_{14}H_{12}FNO$	230	90	231-232	230[M <sup>+</sup> ], 232[M <sup>+2</sup> ], 214, 210, 149, 134, 123, 121, 108, 95, 93, 77, 65, 15
7	2-OH	$C_{14}H_{13}NO_2$	228	90	246-247	228[M <sup>+</sup> ], 212, 147, 119, 108, 17, 15,
8	3-OH	$C_{14}H_{13}NO_2$	228	90	252-253	228[M <sup>+</sup> ], 212, 147, 119, 108, 106, 134, 93, 77, 17, 15,
9	4-OH	$C_{14}H_{13}NO_2$	228	93	212-213	228[M <sup>+</sup> ], 212, 147, 134, 121, 119, 108, 106, 134, 93, 80, 77, 65, 17, 15,
10	$3-OCH_3$	$C_{15}H_{15}NO_2$	242	92	122-123	242[M <sup>+</sup> ], 226, 210, 161, 133, 108, 107, 91, 80, 77, 15,
11	$4-CH_3$	C <sub>15</sub> H <sub>15</sub> NO	226	94	128-129	226[M <sup>+</sup> ], 210, 161, 134, 133, 108, 107, 91, 80, 77, 66, 31, 15,
12	3-NO <sub>2</sub>	$C_{14}H_{12}N_2O_3$	256	91	149-150	256[M <sup>+</sup> ], 241, 176, 148, 108, 80, 77, 45,15,
13	$4-NO_2$	$C_{14}H_{12}N_2O_3$	256	94	184-185	256[M <sup>+</sup> ], 241, 176, 148, 134, 122, 108, 80, 77, 55, 45, 15,

#### Synthesis of 1-methyl-2-pyrrole chalcones

An appropriate equimolar quantities of 1-methyl-2-acetylpyrrole (2 mmol), substituted benzaldehydes (2 mmol) and fly-ash:sulphuric acid (0.5 g) are taken in ACE tube and tightly capped. The mixture is subjected to microwave heating for 2-4 minutes in a microwave oven (Scheme 1) (LG Grill, Intellowave, Microwave Oven, 160-800W) and then cooled to room temperature<sup>[38]</sup>. The reaction mixture is treated with ethanol and the separated solid is filtered, washed with n-hexane and dried. The solid, on recrystallization with benzene-hexane mixture gives glittering pale yellow solid. The catalyst is recycled by washing the solid reagent remained on the filter by ethyl acetate (10 mL) followed by drying in an oven at 100°C for 2h and it is made

Orqanic CHEMISTRY An Indian Journal reusable for further reactions.

The analytical and mass spectral data of unknown chalcones are presented in (TABLE 1). The Infrared

spectral data of chalcones are given in (TABLE 2). The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectral data are given in (TABLE 3).

Entry	R	CO <sub>(s-cis)</sub>	CO <sub>(s-trans)</sub>	CH ip	CH op	CH=CH op	C=C <sub>op</sub>	Substituent styryl part
1	Н	1642.45	1584.32	1208.26	744.98	1068.69	690.60	
2	3-Br	1648.24	1593.52	1101.38	783.91	1066.29	667.35	
3	4-Br	1648.57	1592.40	1208.90	748.00	1067.02	693.42	
4	3-C1	1693.15	1649.24	1178.08	777.31	1020.62	657.53	
5	4-C1	1650.94	1595.79	1092.06	779.93	1067.08	652.95	
6	4-F	1608.49	1553.20	1158.49	782.72	1080.71	685.71	
7	2-OH	1679.43	1601.31	1121.55	767.87	1019.53	647.27	3508.71
8	3-OH	1643.27	1587.07	1166.81	746.39	1074.00	646.32	3465.89
9	4-OH	1652.36	1625.95	1152.69	756.32	1029.25	685.36	3486.23
10	3-OCH <sub>3</sub>	1697.18	1638.36	1194.52	789.04	1030.14	652.48	1276.34
11	4-CH <sub>3</sub>	1687.67	1632.76	1185.57	714.32	1019.54	652.05	
12	3-NO <sub>2</sub>	1650.08	1594.86	1185.33	738.86	1068.38	667.79	
13	4-NO <sub>2</sub>	1650.81	1598.90	1107.00	750.35	1067.51	673.36	

TABLE 2 : Infrared spectral data v(cm<sup>-1</sup>) of substituted styryl 1-methyl-2-pyrrolyl ketones

TABLE 3 : The <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts  $\delta$ (ppm) of substituted styryl 1-methyl-2-pyrrolyl ketones

Entry	R	Η <sub>α</sub> (1H,d)	Η <sub>β</sub> ) (1H,d)	Phenyl proto	ring ns	Subst.	Pyr P	rolering rotons	P	CH <sub>3</sub> - in yrrolering	СО	Ca	C <sub>β</sub>	C <sub>1</sub>	<b>C</b> <sub>2</sub>
1	Н	7.409	7.745	7.213-7.34	l(5H,m)		6.381-6	5.753 (3H,	m)	3.852	181.73	123.56	141.37	135.24	126.34
2	3-Br	7.381	7.641	7.007-7.307	(4H, m)		6.148-6	.934 (3H,	m)	4.035	179.14	125.07	139.57	137.52	130.26
3	4-Br	7.379	7.654	7.099-7.544	(4H, m)		6.192-6	.891 (3H,	m)	4.028	178.98	123.86	139.68	133.87	129.21
4	3-Cl	6.652	8.201	7.082-8.951	(4H, m)		5.984-6	.934 (3H,	m)	4.038	183.67	124.26	139.03	135.96	126.34
5	4-Cl	7.399	7.655	7.129-7.582	(4H, m)		6.199-6	5.220 (3H,	m)	4.029	178.76	123.75	139.33	133.30	128.61
6	4-F	6.706	6.915	6.876-7.380	(4H, m)		6.094-6	.747 (3H,	m)	4.988	193.41	124.42	145.02	131.97	127.45
7	2-OH	6.786	7.697	6.987-7.582	(4H, m)		6.031-6	5.04 (3H, 1	n)	4.881	182.30	123.08	139.36	115.32	159.65
8	3-OH	7.376	7.617	7.102-7.546	(4H, m)		6.191-6	.930 (3H, 1	m)	4.023	184.00	123.93	145.91	136.31	112.76
9	4-OH	7.731	8.869	7.032-8.563	(4H, m)		6.196-6	5.790 (3H,	m)	4.173	181.23	122.06	141.29	126.23	127.59
10	3-OCH <sub>3</sub>	7.269	7.528	7.303-7.428	(4H, m)	3.732 (3H, s)	6.368-6	5.854 (3H,	m)	3.987	180.36	124.81	142.38	136.28	109.82
11	4-CH <sub>3</sub>	7.365	7.429	7.311-7.401	(4H, m)	2.654 (3H, s)	6.112-6	5.254 (3H,	m)	4.058	181.92	123.05	139.50	133.20	127.52
12	3-NO <sub>2</sub>	7.504	7.751	7.1657.871	(4H, m)		6.230-6	.938 (3H,	m)	4.048	182.36	124.08	138.32	136.85	122.45
13	$4-NO_2$	7.821	7.896	7.191-7.579	(4H, m)		6.251-6	.954 (3H,	m)	4.051	183.84	124.95	140.36	141.38	127.50
Enti	y I	۲.	<b>C</b> <sub>3</sub>	C <sub>4</sub>	<b>C</b> <sub>5</sub>	С	6 S	ubstt.	C <sub>2</sub> ,	C C	3'	C <sub>4'</sub>	C <sub>5</sub> ,	Μ	ethyl
1	H	ł	128.65	127.95	128.65	126	.34		136.2	21 124	.25 1	18.65	131.5	8 3	6.65
2	3-	Br	126.58	130.55	131.85	125	.07		137.5	52 125	.07 1	19.37	132.5	4 3	7.63
3	4-	Br	131.57	123.86	131.57	129	.21		135.9	95 123	.86 1	19.08	131.7	2 3	7.84
4	3-	Cl	134.85	129.65	131.26	124	.58		137.0	02 125	.02 1	19.32	130.9	8 3	6.98
5	4-	Cl	128.91	133.30	128.91	128	.61		135.1	11 124	.53 1	19.10	131.3	5 3	7.28
6	4-	·F	112.57	161.35	112.57	127	.45		136.0	02 124	.42 1	19.19	132.0	8 3	6.89
7	2-0	ЭH	114.98	130.58	122.59	128	.53		137.2	25 125	.32 1	20.56	131.2	7 3	6.25
8	3-0	ΟH	162.17	119.20	134.21	119	.25		136.3	31 123	.93 1	21.92	134.2	1 3	7.28
9	4-0	DH	115.87	158.36	115.87	127	.59		137.6	58 124	.67 1	22.89	134.7	4 3	6.98



(1)

	r algr	90 ~									
Entry	R	C <sub>3</sub>	<b>C</b> <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>	Substt.	C <sub>2</sub> ,	C <sub>3'</sub>	C <sub>4'</sub>	C <sub>5</sub> ,	Methyl
10	3-OCH <sub>3</sub>	165.37	114.29	114.32	119.82	59.68(OCH <sub>3</sub> )	138.24	125.38	124.77	131.25	36.91
11	$4-CH_3$	130.05	137.65	130.05	127.52	27.89(CH <sub>3</sub> )	136.52	124.87	123.87	132.47	36.57
12	3-NO <sub>2</sub>	149.52	121.37	130.57	133.52		137.21	125.71	124.58	131.25	37.04
13	4-NO <sub>2</sub>	124.08	147.58	124.08	127.50		138.32	124.08	123.58	132.43	37.81
					сно			,0			



R= H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 3-OH, 4OH, 3-OCH<sub>3</sub>, 4-CH<sub>3</sub>, 3-NO<sub>2</sub>, 4-NO<sub>2</sub>

Scheme 1 : Synthesis of substituted styryl1-methyl2-pyrrolyl chalcones

v =

#### **RESULTS AND DISCUSSION**

Fly ash is a waste air-pollutant and it has many chemical species<sup>[10,40]</sup> SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO, MgO and insoluble residues. The waste fly-ash is converted into useful catalyst fly-ash:sulphuric acid by mixing fly-ash and sulphuric acid. The sulphonic acid group and chemical species present in the fly-ash have enhanced the catalytic activity. During the course of the reactions these species are responsible for the promoting effects on condensation between the heterocyclic ketone and aryl aldehydic groups leading to the formation of unsaturated ketone. In these experiments the products are isolated and the catalyst is washed with ethyl acetate, heated to 100°C then made reusable for further reactions without any appreciable change in the catalytic activity. In this protocol the reaction gives better yields of the chalcones during the condensation without any environmental discharge.

#### **Spectral linearity**

In the present study the spectral linearity of chalcones has been studied by evaluating the substituent effects. The assigned group frequencies of all chalcones like carbonyl stretches vCO, the deformation modes of vinyl part CH *out of plane*, *in-plane*, CH=CH and >C=C< *out of planes* (cm<sup>-1</sup>), the vinyl hydrogen and chemical shifts  $\delta$ (ppm), of H<sub>a</sub>, H<sub>b</sub>, C<sub>a</sub>, C<sub>b</sub>, CO are assigned and these frequencies are correlated with various substituent constants.

#### **IR** spectral study

The effect of substituents on the infrared carbonyl



frequencies has been reported previously in several studies<sup>[37]</sup>. The carbonyl group stretching frequency can be assumed to be "mass insensitive". The carbonyl group frequency has been successfully correlated with Hammett  $\sigma$  constants in acetophenones<sup>[41]</sup> benzophenones<sup>[42]</sup> and benzoyl chlorides<sup>[43]</sup>, naphthacyl bromides and esters<sup>[10]</sup>.

While seeking Hammett correlation involving group frequencies, the form of the Hammett equation employed is

$$\rho\sigma + v_{o}$$

where  $v_0$  is the frequency for the parent member of the series.



Figure 1 : The *s*-*cis* and *s*-*trans* conformers of 1-methyl-2pyrrolyl chalcones

The series of chalcones chosen in the present study possess  $\alpha$ ,  $\beta$ - unsaturated carbonyl system. They are expected to exist in *s*-*cis* and *s*-*trans* conformations are shown in (Figure 1). The carbonyl stretching fre-

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quencies (cm<sup>-1</sup>) of *s-cis* and *s-trans* isomers in the present study are presented in (TABLE 2). The lowest carbonyl frequency is observed in both the conformers when strongest electron withdrawing groups is present in phenyl ring while highest frequency is noted when strongest electron attracting group is present in phenyl ring. The same trend is observed in the present investigation also. These frequencies are separately analyzed through various Hammett sigma constants using single and multi-regression analyses.

The results of the statistical analysis are presented in (TABLE 4). From (TABLE 4), vCO *s*-*cis* conformers (cm<sup>-1</sup>) have been satisfactorily correlated for all substituents, with Hammett  $\sigma_1$  constant and F parameters, ex-

cluding H, 3-Cl and 3-NO<sub>2</sub> substituents. The polar and F parameters give positive  $\rho$  values and the other constants show negative  $\rho$  values. This means that the inductive and field effects of substituents operate normal substituent effects<sup>106</sup> on the *s*-*cis* conformers and the other constants reverse the substituent effects. Field effects of the substituents only give the satisfactory correlation with vCO *s*-*trans* conformers except for H and 3-OH substituents. Polar and inductive effects of substituents are found to fail in correlation. This is due to the incapability of transmitting the effects of substituents from the phenyl ring as per the conjugative structure shown in (Figure 2). All correlations produce negative  $\rho$  values. The degree of transmission of the substituent effects is higher in vCO

TABLE 4 : Results of statistical analysis of infrared infrared v (cm<sup>-1</sup>) CO<sub>s-cis</sub>, CO<sub>s-trans</sub>, CH<sub>ip</sub>, CH<sub>op</sub>, CH=CH<sub>op</sub> and C=C<sub>op</sub> substituted styryl 1-methyl-2 pyrrolyl ketones with Hammett  $\sigma$ ,  $\sigma_{+}$ ,  $\sigma_{1}$ ,  $\sigma_{R}$  constants and F and R parameters

	Constant						Completed design
Frequency	Constants	r	ρ	1	<u>s</u>	<u>n</u>	Correlated derivatives
	σ	0.813	1659.52	-9.675	25.68	13	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 3-OH,
	+	0 700	1 ( 5 5 0 0	0.067	25.02	10	4-OH, 3-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	σ	0.700	1657.89	0.067	25.93	13	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 3-OH,
		0.007	1671 60	26.25	04.05	10	4-OH, 3-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_{\mathrm{I}}$	0.927	16/1.69	-36.25	24.35	10	3-Br, 4-Br, 4-F, 2-OH, 3-OH, 4-OH, 3-OCH <sub>3</sub> ,
$CO_{s-cis}$		0.702	1652.00	20.70	25.20	12	$4-0CH_3$ , $3-NO_2$ , $4-NO_2$
	$\sigma_{R}$	0.702	1652.82	-20.79	25.39	13	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 3-OH,
	F	0.029	1677.01	10 022	22.07	10	$4-OH, 5-OCH_3, 4-CH_3, 5-NO_2, 4-NO_2$
	Г	0.938	10/7.91	48.925	25.97	12	$3-D\Gamma, 4-D\Gamma, 5-C\Gamma, 4-C\Gamma, 4-\Gamma, 2-O\Gamma, 5-O\Gamma, 4-OL -2 OCL -4 CL -2 NO -4 NO$
	D	0.804	1656 96	2 7 2 0	25.01	12	$4-OH, 5-OCH_3, 4-CH_3, 5-NO_2, 4-NO_2$
	ĸ	0.804	1030.80	-2.750	23.91	15	H, 5-DI, 4-DI, 5-CI, 4-CI, 4-F, 2-OH, 5-OH, 4-OH - 2-OCH - 4-CH - 2-NO - 4-NO
		0.014	1605 27	10.264	27.06	12	$4-OH, 5-OCH_3, 4-CH_3, 5-NO_2, 4-NO_2$
	0	0.814	1003.27	-10.304	27.00	15	H, 5-DI, 4-DI, 5-CI, 4-CI, 4-F, 2-OH, 5-OH, 4-OH - 2-OCH - 4-CH - 2-NO - 4-NO
	<b>~</b> <sup>+</sup>	0 780	1602 76	2 002	77 77	12	$4-OH, 5-OCH_3, 4-CH_3, 5-NO_2, 4-NO_2$
	0	0.789	1005.70	-5.002	21.21	15	$A \cap H = 2 \cap C H = 4 \cap C H = 2 \cap A \cap A \cap A$
	<i>c</i> .	0.810	1614 30	27 021	2674	12	4-011, 5-00113, 4-0113, 5-1002, 4-1002
	0I	0.819	1014.30	-27.931	20.74	15	A OH 3 OCH. A CH. 3 NO. A NO.
$CO_{s-trans}$	<b>G</b> P	0.812	1600 30	-13 779	27 10	13	$H_{3-Br} 4-Br_{3-C1} 4-C1 4-F_{2-OH} 3-OH$
	OR	0.012	1000.50	13.777	27.10	15	4-OH 3-OCH <sub>2</sub> 4-CH <sub>2</sub> 3-NO <sub>2</sub> 4-NO <sub>2</sub>
	F	0.932	1621 77	-44 251	25.82	11	3-Br 4-Br 3-Cl 4-Cl 4-F 2-OH 4-OH
	-	0.752	1021.77	11.201	23.02		$3-OCH_2$ , $4-CH_2$ , $3-NO_2$ , $4-NO_2$
	R	0.800	1603.08	-1.532	27.32	13	H. 3-Br. 4-Br. 3-Cl. 4-Cl. 4-F. 2-OH. 3-OH.
						-	4-OH, 3-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	σ	0.818	1161.86	-21.548	41.82	13	H. 3-Br. 4-Br. 3-Cl. 4-Cl. 4-F. 2-OH. 3-OH.
							4-OH, 3-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma^{\scriptscriptstyle +}$	0.704	1158.62	-3.433	21.29	13	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 3-OH,
							4-OH, 3-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_{\rm I}$	0.932	1187.33	-75.69	39.94	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 3-OH,
СЦ							4-OH, 3-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
$C\Pi_{ip}$	$\sigma_{R}$	0.803	1160.02	6.226	42.55	13	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 3-OH,
							4-OH, 3-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	F	0.833	1187.78	-71.506	40.05	13	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 3-OH,
							4-OH, 3-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	R	0.904	1156.97	-4.590	42.54	10	H, 4-Br, 3-Cl, 4-F, 2-OH, 3-OH, 4-OH,
							3-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3NO <sub>2</sub>

Frequency	Constants	r	ρ	Ι	s	n	Correlated derivatives
	σ	0.912	758.76	7.926	22.94	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 3-OH,
							4-OH, 3-OCH <sub>3</sub> , 4-CH <sub>3</sub>
СН	$\sigma^+$	0.931	759.59	12.190	21.29	13	H, 3-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 3-OH, 4-OH,
							3-OCH <sub>3</sub> , 4-CH <sub>3</sub>
	$\sigma_{\rm I}$	0.811	754.69	13.929	22.96	13	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 3-OH,
							4-OH, 3-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3NO <sub>2</sub> , 4-NO <sub>2</sub>
CHOp	$\sigma_R$	0.825	754.36	-23.099	22.37	13	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 3-OH,
							4-OH, 3-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3NO <sub>2</sub> , 4-NO <sub>2</sub>
	F	0.819	750.64	22.866	22.66	13	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 3-OH,
							4-OH, 3-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3NO <sub>2</sub> , 4-NO <sub>2</sub>
	R	0.803	759.19	-21.111	23.11	13	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 3-OH,
							4-OH, 3-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 3NO <sub>2</sub> , 4-NO <sub>2</sub>
	σ	0.846	1047.33	31.402	22.08	13	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 3-OH,
							4-OH, 3-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 3NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma^{+}$	0.833	1051.74	13.992	23.46	13	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 3-OH,
							4-OH, 3-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 3NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_{\rm I}$	0.835	1034.71	45.988	23.26	13	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 3-OH,
CH=CH <sub>on</sub>							4-OH, 3-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3NO <sub>2</sub> , 4-NO <sub>2</sub>
000 000 p	$\sigma_R$	0.849	1064.00	48.381	21.12	13	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 3-OH,
	_						4-OH, 3-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3NO <sub>2</sub> , 4-NO <sub>2</sub>
	F	0.835	1034.16	44.091	23.29	13	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 3-OH,
	-						4-OH, 3-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3NO <sub>2</sub> , 4-NO <sub>2</sub>
	R	0.823	1057.54	14.057	24.25	13	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 3-OH,
							4-OH, 3-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3NO <sub>2</sub> , 4-NO <sub>2</sub>
	σ	0.909	666.37	4.606	17.81	9	3-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 3-OCH <sub>3</sub> ,
	+	0.015		- 000	1.7	0	4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	σ	0.917	666.92	5.080	17.62	9	3-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 3-OCH <sub>3</sub> ,
		0.000	664 OF	<b>7</b> 011	1202	10	4-CH <sub>3</sub> , $3$ -NO <sub>2</sub> , $4$ NO <sub>2</sub>
	$\sigma_{\rm I}$	0.808	664.07	7.911	1782	13	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 3-OH,
$C=C_{on}$		0.004	<b>(22)</b> 0 6		1 6 0 0	0	4-OH, 3-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
0p	$\sigma_{R}$	0.934	672.96	24.074	16.82	9	3-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 3-OCH <sub>3</sub> ,
		0.010	(20 5 (	11.065	17.75	0	$4-CH_3$ , $3-NO_2$ , $4-NO_2$
	F	0.912	638.56	11.065	17.75	9	3-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 3-OCH <sub>3</sub> ,
	р	0.020	(72 (1	17 000	16.40	0	$4-CH_3$ , $5-NO_2$ , $4-NO_2$
	K	0.839	0/3.61	17.202	16.43	9	3-Br, 3-UI, 4-UI, 2-UH, 3-UH, 3-UCH <sub>3</sub> ,
							$4-CH_3$ , $3-NO_2$ , $4NO_2$

r=Correlation coefficient; p= Slope; I=Intercept; s= Standard deviation; n= Number of substituents

*s-cis* than in vCO*s-trans* conformers.

Shorter<sup>[45]</sup> and Thirunarayanan and Jaishankar<sup>[44]</sup>.

The substituent effects on the deformation modes of CHop/ip, CH=CH and C=Cop of vinyl parts of substituted styryl 1-methyl-2-pyrrolyl ketones have been studied, based on the work of Thirunarayanan and Jaishankar<sup>[44]</sup>. The larger value of deformation mode frequency for the system is due to the low mobility of electrons between the >C = C< and the -CH= CHframe work. The observed -CH out of plane, -CH inplane and - CH = CH- out of plane frequencies in the present study are given in (TABLE 2). All the deformation modes of stretching frequencies of substituted styryl 1-methyl-2-pyrrolyl ketones have been correlated with different substituent constants according to John From (TABLE 4), the regression analysis of CH*ip* modes with Hammett  $\sigma_1$  constant and R parameters produce satisfactory correlation along with negative  $\rho$  values for all substituents, excluding 3-Br, 4-Br, 4-Cl, 3-NO<sub>2</sub> and 4-NO<sub>2</sub> substituents. The Polar and Field effects of the substituents fail in the correlation. All correlations produce negative  $\rho$  values and reverse the substituent effects on the CH*ip* modes. A satisfactory correlation is found for CH*op* modes with Hammett  $\sigma$  and  $\sigma^+$  constants excluding 4-Br, 4-Cl, 3-NO<sub>2</sub> and 4-NO<sub>2</sub> substituents. When these constants are included in the regression the correlation decreases considerably. Inductive, Field and Resonance effects of the substituents

(R

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fail in the correlation. This is due to the reason stated earlier with the conjugative structure shown in (Figure 2). The ability of transmission of electronic effects of the substituents is equal in both CH<sub>an</sub> and CH<sub>in</sub> modes.



Figure 2 : Resonanace conjugative structure

The assigned CH=CHop and C=Cop deformation modes of substituted styryl 1-methyl-2-pyrrolyl ketones are presented in (TABLE 2) and they are correlated with Hammett sigma constants and F and R parameters. The results of regression analysis are presented in (TABLE 4). From (TABLE 4), it is evident that CH=CHop deformation modes fail to correlate with Hammett sigma constants and F and R parameters. This is due to the incapability of transmittance of effects of substituents on the above vinyl portion in all ketones along with the conjugated structure shown in (Figure 2). All correlations produce positive  $\rho$  values and it shows that the normal substituent effects operate in all ketones.

Hammett  $\sigma$  constants and F parameter give satisfactory correlation with C=Cop deformation modes of substituted styryl 1-methyl-2-pyrrolyl ketones. Inductive and resonance effects of the substituents fail in the correlation in these deformation modes along with positive p values. This shows that the effects of substituents normally operate in all ketones.

Some of the single regression analysis produce poor correlation with vCO stretches, CHip, op, CH=CHop and C=Cop modes. The results of multi regression analysis show a satisfactory correlation for these frequencies with Swain-Lupton and F and R parameters[46] in all infrared group frequencies. The correlation equations are given in (2-13).

$\nu CO_{s-cis}^{(cm-1)} = 1666.83(\pm 23.246) -$	
$30.235(\pm 4.481)\sigma_{I} - 10.557(\pm 3.453)\sigma_{R}$	(2)
(R = 0.928, n = 13, P > 90%)	
$vCO_{s-cis}^{(cm-1)} = 1679.85(\pm 20.139)$	
-50.577(±3.862)F +3.327(±1.204)R	(3)
(R = 0.938, n = 13, P > 90%)	
$vCO_{s-trans}^{(cm-1)} = 1611.83(\pm 25.041)$	

$$-24.849(\pm 4.827)\sigma_{I} - 5.356(\pm 0.375) \sigma_{R}$$
(4)  

$$(R = 0.920, n = 13, P > 90\%)$$

$$vCO_{s-trans}^{(cm-1)} = 1624.11(\pm 21.685)$$

$$-46.240(\pm 4.159)F + 4.005(\pm 2.000)R$$
(5)  

$$(R = 0.933, n = 13, P > 90\%)$$

$$vCH_{ip}^{(cm-1)} = 1205.51(\pm 36.424)$$

$$-98.1821(\pm 7.021)\sigma_{I} + 39.455(\pm 5.411) \sigma_{R}$$
(6)  

$$(R = 0.940, n = 13, P > 90\%)$$

$$vCH_{ip}^{(cm-1)} = 1190.23(\pm 33.66)$$

$$-73.603(\pm 6.457)F + 4.224(\pm 0317)R$$
(7)  

$$(R = 0.934, n = 13, P > 90\%)$$

$$+33.566(\pm 3.895)\sigma_{\rm I} - 34.459(\pm 3.002)\sigma_{\rm R}$$
(8)

$$(\Lambda = 0.933, \Pi = 13, \Gamma > 90\%$$

$$+25.426(\pm 3.641)$$
F -5.156( $\pm 1.788$ )R

$$(R = 0.921, n = 13, P > 90\%)$$

$$+22.782(\pm 3.853)\sigma_{1}+40.670(\pm 2.938)\sigma_{R}$$
(10)

$$(R = 0.951, n = 13, P > 95\%)$$
  
 $(CH-CH (cm-1) = 1039 60(+19 339) + 39 463$ 

$$\pm 3.709)F + 9.331(\pm 1.821)R$$
(11)

+2.682(±0.235)F+16.881(±1.301)R (13)  
(
$$R = 0.939$$
,  $n = 13$ ,  $P > 90\%$ )

# <sup>1</sup>H spectral study

The <sup>1</sup>H NMR spectra of nine chalcones under investigation are recorded in deuterated chloroform employing tetramethylsilane (TMS) as internal standard. The signals of the ethylenic protons were assigned. They are calculated as AB or AA'BB' systems respectively[47-<sup>49]</sup>. The chemical shifts of  $H_{a}$  are at higher field than those of H<sub>B</sub> in this series of ketones. The ethylenic protons give an AB pattern and the  $\beta$ -proton doublet in most cases which is well separated from the signals of the aromatic protons. The assigned chemical shifts of the ethylenic protons are presented in (TABLE 3).

In nuclear magnetic resonance spectra, the proton chemical shifts  $\delta(ppm)$  depends on the electronic environment of the nuclei concerned. These shifts can be correlated with reactivity parameters. Thus the Hammett

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equation may be used in the form as

 $\operatorname{Log} \delta = \operatorname{Log} \delta_0 + \rho \sigma$ 

where  $\delta_0$  is the chemical shift in the corresponding parent compound.

The assigned <sup>1</sup>H NMR chemical shifts (ppm) of  $\delta H_{\alpha}$  and  $\delta H_{\beta}$  of substituted styryl 1-methyl-2-pyrrolyl ketones are presented in (TABLE 3). These chemical shifts are correlated with Hammett substituent constants and F and R parameters. The results of statistical analysis these chemical shifts (ppm) are shown in (TABLE 5).

From TABLE 5, it is evident that Hammett  $\sigma$ ,  $\sigma$ +,  $\sigma_{I}$  and F and R parameters have been correlated satisfactorily with H<sub>a</sub> chemical shifts excluding 3-Cl, 4-F, 2-OH and 4-OH substituents. All correlations give positive  $\rho$  values. This shows that the normal substituent effects operate in all ketones. The resonance effects fail in correlation. This is due to the incapability of substituents for predicting the reactivity through the substituent effects on the vinyl H<sub>a</sub> proton chemical shifts and is associated with the conjugative structure shown in (Figure 2).

TABLE 5 : Results of statistical analysis of NMR chemical shifts (ppm) of  $\delta H_{\alpha} \delta H_{\beta}$ ,  $\delta CO$ ,  $\delta C_{\alpha}$  and  $\delta C_{\beta}$  of substituted styryl 1-methyl-2-pyrrolyl ketones with Hammett  $\sigma$ ,  $\sigma^{+}$ ,  $\sigma_{I} \sigma_{R}$  constants and F and R parameters

Frequency	Constants	r	ρ	Ι	S	n	Correlated derivatives
-	σ	0.920	0.205	7.258	0.37	10	H, 3-Br, 4-Br, 4-Cl, 2-OH, 3-OH, 3-OCH <sub>3</sub> ,
							4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma^{+}$	0.904	0.261	7.289	0.37	13	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 3-OH,
							4-OH, 3-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
δ <sub>Hα</sub> (ppm)	$\sigma_{\rm I}$	0.905	0.098	7.253	0.37	10	H, 3-Br, 4-Br, 4-Cl, 3-OH, 4-OH, 3-OCH <sub>3</sub> ,
§ (nnm)							4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
$O_{H\alpha}(PPIII)$	$\sigma_{R}$	0.843	0.738	7.470	0.32	13	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 3-OH,
							4-OH, 3-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	F	0.908	-0.159	7.355	0.37	13	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 3-OH,
							4-OH, 3-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	R	0.924	0.224	7.375	0.36	13	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 3-OH,
							4-OH, 3-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	σ	0.908	-0.101	7.754	0.46	12	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 3-OH,
							3-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma^{\scriptscriptstyle +}$	0.916	-0.125	7.742	0.45	13	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 3-OH,
							4-OH, 3-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_{\rm I}$	0.811	-0.265	7.839	0.46	13	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 3-OH,
δ <sub>HB</sub> (ppm)							4-OH, 3-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
o <sup>Hb</sup> (bbm)	$\sigma_{R}$	0.913	0.251	7.791	0.49	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 3-OCH <sub>3</sub> ,
							4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	F	0.824	-0.552	7.964	0.45	13	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 3-OH,
							4-OH, 3-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	R	0.907	0.088	7.717	0.46	13	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 3-OH,
							4-OH, 3-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	σ	0.802	-0.273	182.48	3.92	13	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 3-OH,
							4-OH, 3-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma^{+}$	0.911	-0.724	182.46	3.89	13	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 3-OH,
							4-OH, 3-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_{\rm I}$	0.924	4.824	180.59	3.80	9	Н, 3-С1,2-ОН, 3-ОН,4-ОН, 3-ОСН <sub>3</sub> , 4-ОСН <sub>3</sub> ,
δCO							3-NO <sub>2</sub> , 4-NO <sub>2</sub>
(ppm)	$\sigma_{R}$	0.921	-3.311	181.63	3.83	12	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH,
							3-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	F	0.947	9.314	181.62	3.44	9	H, 3-Cl, 2-OH, 3-OH,4-OH, 3-OCH <sub>3</sub> , 4-CH <sub>3</sub> ,
	-						3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	R	0.904	-2.152	181.62	42.54	10	H, 4-Br, 3-Cl, 4-F, 2-OH, 3-OH, 4-OH, 3-OCH <sub>3</sub> ,
							4-CH <sub>3</sub> , 3NO <sub>2</sub>
	σ	0.974	1.786	123.64	0.58	12	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 3-OH,
$\delta C_{\alpha}(ppm)$	+	0.0-0		100.00	0		3-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
u ( <b>r r</b> )	$\sigma_{\perp}$	0.978	1.145	123.88	0.55	13	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 3-OH,
							4-OH, 3-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>

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Frequency	Constants	r	ρ	l	S	n	Correlated derivatives
	$\sigma_{\rm I}$	0.847	2.149	123.10	0.77	13	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 3-OH, 4-
							OH, 3-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_{R}$	0.841	1.408	124.26	0.81	13	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 3-OH, 4-
							OH, 3-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	F	0.843	1.909	123.13	0.79	13	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 3-OH, 4-
							OH, 3-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	R	0.936	0.759	124.20	0.82	10	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-OH, 4-OH, 4-CH <sub>3</sub> , 3-
							$NO_2, 4-NO_2$
	σ	0.932	-2.116	141.18	2.30	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 2-OH, 4-OH, 3-OCH <sub>3</sub> ,
							4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma^{\scriptscriptstyle +}$	0.937	-1.527	140.90	2.25	9	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 2-OH, 4-OH, 4-CH <sub>3</sub> , 3-
							$NO_2$
	$\sigma_{\rm I}$	0.924	-3.040	142.01	2.35	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 2-OH, 4-OH, 3-OCH <sub>3</sub> ,
$\delta C_{2}(nnm)$							4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
oc <sub>β</sub> (ppm)	$\sigma_{R}$	0.839	-3.795	139.93	2.23	13	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 3-OH, 4-
							OH, 3-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	F	0.803	-0.417	141.02	2.43	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 2-OH, 4-OH, 3-OCH <sub>3</sub> ,
							4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	R	0.906	-3.964	139.38	1.08	13	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 3-OH, 4-
							OH, 3-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>

r=Correlation coefficient; p= Slope; I=Intercept; s= Standard deviation; n= Number of substituents

The  $H_{\beta}$  chemical shifts of these ketones produce satisfactory correlations with the Hammett  $\sigma$ ,  $\sigma^+$ ,  $\sigma_1$  and R parameters along with negative  $\rho$  values. This shows that the reversed substituent effects operate in all ketones. Here the Inductive and Polar effects are of less effective leading to poor correlation.

Single parameter correlations of  $H_{\alpha}$  and  $H_{\beta}$  chemical shifts from <sup>1</sup>H NMR are found to fail with the Hammett sigma constants and F and R parameters. While seeking the multi-regression analysis of these chemical shifts there is satisfactory correlations with Swain-Lupton and F and R parameters<sup>[46]</sup>. The correlated multi regression equations are given in (15-18).

$\delta H_{a}(ppm) = 7.655(\pm 0.301)$	
$-0.399(\pm 0.058)\sigma_{I} + 0.874(\pm 0.044)\sigma_{R}$	(15)
(R = 0.952, n = 13, P > 90%)	
$\delta H_{a}(ppm) = 7.506(\pm 0.302)$	
-0.288(±0.056)F +0.288(±0.021)R	(16)
(R = 0.928, n = 13, P > 90%)	
$\delta H_{\rm g}(\rm ppm) = 8.033(\pm 3.257)$	
$-0.505(\pm 0.081)\sigma_{I} + 0.422(\pm 0.061)\sigma_{R}$	(17)
(R = 0.923, n = 13, P > 90%)	
$\delta H_{B}(ppm) = 8.060(\pm 0.375)$	
- 0.634(±0.072)F +0.164(±0.035)R	(18)
(R = 0.927, n = 13, P > 90%)	

#### <sup>13</sup>C NMR spectral study

The assigned carbonyl carbon chemical shifts (ppm)

of  $\delta CO$ ,  $\delta C_{\alpha}$  and  $\delta C_{\beta}$  of substituted styryl 1-methyl-2pyrrolyl ketones are presented in TABLE 4 and these chemical shifts are correlated with Hammett sigma constants and F and R parameters. The results of statistical analysis is shown in (TABLE 5). From the TABLE 5, it is evident that the chemical shifts (ppm) of CO carbon, have been correlated satisfactorily with Hammett  $\sigma^+$ ,  $\sigma_{I}$ ,  $\sigma_{R}$  constants and F parameter excluding 3-Br, 4-Br, 4-Cl and 4-F substituents. Some of the correlations give positive  $\rho$  values while the others give negative  $\rho$ values. Hamett  $\sigma$  and R parameters are found to fail in correaltion. This is due to the reason stated earlier as per the conjugtive structure given in (Figure 2).

The assigned chemical shifts(ppm) of  $C_{\alpha}$  and  $C_{\beta}$  vinyl carbons in substituted styryl 1-methyl-2-pyrrolyl ketones have been correlated with Hammett sigma constants and F and R parameters. The correlation of  $C_{\alpha}$  chemical shifts with Hammett  $\sigma$ ,  $\sigma$ + constants and R parameter is satisfactory excluding 3-Cl, 3-OH, 4-OH and 3-OCH<sub>3</sub> giving positive  $\rho$  values. This shows that the normal substituent effects operate in all ketones. The inductive, resonance and field effects of the substituents fail in correlation. This is due to the reason stated earlier and is associated with the conjugated structure shown in (Figure 2).

The  $C_{\beta}$  chemical shifts(ppm) of substituted styryl 1methyl-2-pyrrolyl ketones produce satisfactory corre-



(22)

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lations with Hammett sigma constants and R parameter excluding 4-F, 3-OH, 3-OCH<sub>3</sub> and 4-NO<sub>2</sub> substituents, giving negative  $\rho$  values. Resonance and filed effects of the substituents are found to fail in correlation. This is due to the reason stated earlier along with the conjugated structure in (Figure 2).

Single parameter correlations of the <sup>13</sup>C NMR chemical shifts(ppm) of CO,  $C_{\alpha}$  and  $C_{\beta}$  carbons fail with Hammett sigma constants and F and R parameters. While seeking the multi regression analysis of these chemical shifts, there is satisfactorily correlations with Swain-Lupton and F and R parameters<sup>[46]</sup>. The correlated multi regression equations are given in (19-24).

$\delta CO(ppm) = 183.76(\pm 3.314)$	
$+8.345(\pm0.638)\sigma_{I}$ -6.135 $(\pm0.492)\sigma_{R}$	(19)
(R = 0.942, n = 13, P > 90%)	
δCO (ppm) = 181.32(±2.649)	
+11.040(±5.080)F -3.475(±0.249)R	(20)

$$(R = 0.959, n = 13, P > 95\%)$$

$$\delta C_{\alpha} (ppm) = 123.48 (\pm 0.791) + 1.668(\pm 0.316)\sigma_{I} + 0.843(\pm 0.105)\sigma_{R}$$
(21)  
(R = 0.952, n = 13, P > 95%)

$$\delta C_{\alpha}(\text{ppm}) = 123.466 \ (\pm 0.642)$$

+ 
$$1.628(\pm 0.123)$$
F +  $0.564(\pm 0.060)$ R  
( $R = 0.950$ ,  $n = 13$ , P >  $95\%$ )

$$\delta C_{\rm g}(\rm ppm) = 140.437 \, (\pm 0.208)$$

$$-1.086(\pm 0.4017)\sigma_{\rm I} - 3.427(\pm 0.309)\sigma_{\rm R}$$
(23)  
(R = 0.940, n = 13, P > 90%)

$$\delta C_{\beta} (ppm) = 138.60 (\pm 1.493)$$
  
+1.649(\pm 2.864)F - 4.161(\pm 1.406) R (24)

$$(R = 0.968, n = 13, P > 95\%)$$

# **Microbial activities**

Chalcones possess a wide range of biological activities<sup>[24-36]</sup>. These multipronged activities are associated with different unsaturated ketones. Hence, it is intended to examine their activities against respective microbes-bacteria's, fungi and insect anti-feedants.

# Antibacterial sensitivity assay

Antibacterial sensitivity assay is performed using Kirby-Bauer<sup>[50]</sup> disc diffusion technique. In each Petri plate about 0.5 ml of the test bacterial sample is spread uniformly over the solidified Mueller Hinton agar using sterile glass spreader. Then the discs with 5mm diameter made up of Whatman No.1 filter paper, impreg-



nated with the solution of the compound are placed on the medium using sterile forceps. The plates are 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 are visually examined and the diameter values of the zone of inhibition have been measured. Triplicate results are recorded by repeating the same procedure.

The antibacterial screening effect of synthesized chalcones is shown in (Figure 3; Plates 1-12). The zone of inhibition is compared using (TABLE 6) and the Clustered column Chart is shown in (Figure 4). From the chart, it is inferred that the chalcone with -OH substituent at 3<sup>rd</sup> position shows excellent activity against all microorganisms except for *S.aureus*. This series shows excellent activity against *P.aeruginosa*.

TABLE 6 : Antibacterial activities of substituted styryl 1	-
methyl-2-pyrrolyl ketones	

			Zone of Inhibition (mm)							
			Gra B	m pos acteri	itive ia	Gram negative Bacteria				
S. No.	Compound	R	<b>B.subtilis</b>	M.luteus	S.aureus	E.coli	K.pneumoniae	P.aeruginosa		
1	E-1	Н	8	8	8	6	6	7		
2	E-2	3-Br	8	8	7	7	8	6		
3	E-3	4-Br	10	6	6	7	7	7		
4	E-4	3-Cl	6	6	7	6	6	6		
5	E-5	4-Cl	7	8	7	6	6	8		
6	E-6	4-F	8	7	7	7	6	7		
7	E-7	2-OH	7	6	7	7	7	8		
8	E-8	3-OH	7	6	6	8	7	7		
9	E-9	4-OH	77		7	8	7	7		
10	E-10	3-OCH <sub>3</sub>	6	7	6	8	8	7		
11	E-11	4-CH <sub>3</sub>	6	6	6	7	6	6		
12	E-12	3-NO <sub>2</sub>	6	7	6	6	6	6		
13	E-13	4-NO <sub>2</sub>	6	8	6	6	7	7		
	Standard	Ampicillin	25	20	-	8	20	8		
	Control	DMSO	-	-	-	-	-	-		

### Antifungal sensitivity assay

Antifungal sensitivity assay is performed using Kirby-Bauer<sup>[50]</sup>disc diffusion technique. PDA medium is prepared and sterilized as above. It is poured (ear

bearing heating condition) in the Petri-plate which is already filled with 1 ml of the fungal species. The plate is rotated clockwise and counter clock-wise for uniform spreading of the species. The discs are impregnated with the test solution. The test solution is prepared by dissolving 15mg of the chalcone in 1ml of DMSO solvent. The medium is allowed to solidify and kept for 24 hours. Then the plates are visually examined and the diameter values of zone of inhibition have been measured. Triplicate results are recorded by repeating the same procedure. The antifungal activity of substituted chalcones synthesized in the present study is shown in (Figure 5; Plates 1-6) and the zone of inhibition values of the effect is given in (TABLE 7) and the clustered column chart, is shown in (Figure 6). Analysis of the clustered column chart, indicates that the fluoro substituted chalcones have very good activity on all the three fungal species. The substituents like 4-Cl, 4-F, 3-OCH<sub>3</sub> and 4-NO<sub>2</sub>, shows greater antifungal effect on M.spp. The fluoro substituted Chalcone shows excellent activity on *T.viride* species.



Plate 1



Plate 4



Plate 7



Plate 10



Plate 2



Plate 5



Plate 8



Figure 3: Antibacterial activities of 1-methyl-2-pyrrolyl chalcones-petri dishes

Plate 3

Plate 6



Plate 9



Plate 12

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Figure 4 : Antibacterial activities of 1-methyl-2-pyrrolyl chalcones: Clustered column chart

 

 TABLE 7 : Antifungal activities of substituted styryl1-methyl-2-pyrrolyl ketones

S.	Commonwal	р	Zone of Inhibition (mm				
No.	Compound	ĸ	A.niger	M.spp	T.viride		
1	E-1	Н	6	8	-		
2	E-2	3-Br	-	7	7		
3	E-3	4-Br	5	7	6		
4	E-4	3-C1	5	5	6		
5	E-5	4-Cl	5	6	6		
6	E-6	4-F	6	5	7		
7	E-7	2-OH	6	5	6		
8	E-8	3-OH	5	6	6		
9	E-9	4-OH	-	6	8		
10	E-10	3-OCH <sub>3</sub>	5	-	5		
11	E-11	4-CH <sub>3</sub>	-	-	5		
12	E-12	3-NO <sub>2</sub>	5	5	6		
13	E-13	4-NO <sub>2</sub>	6	6	6		
	Standard	Miconazole	8	9	15		

### Antioxidant activity

All synthesized 1-methyl-2-pyrrolyl ketones possess significant biological activities. The basic skeleton of enone, present widely in natural products are known to have multi-pronged activity<sup>[15-18]</sup>. Presence of polar functional groups, hydrophobic moiety and absence of steric hindrance near the aryl ring are the important factors for the presence of biological activities of oxiranes and their derivatives. In this present study it is observed that only two of the synthesized chalcones have fair antioxidant activity.

# Measurement of antioxidant activity of 1-methyl-2-pyrrolyl chalcones

Antioxidant activities of all synthesized1-methyl-2pyrrolyl chalcones have been evaluated by the DPPH radical scavenging effect<sup>[25]</sup>. The 0.1 M acetate is prepared by dissolving 1.64 g of sodium acetate in 15 mL of water and 150 µL of acetic acid. The final volume is adjusted to 20 mL by adding water. The 0.2 mmole of DPPH solution is prepared by dissolving 3.9 g of DPPH in 50 mL of ethanol.  $\infty$ -Tocoferol (1 mg in 10 mL of ethanol) solution is prepared. A series of test tubes are arranged with 1.0 mL of buffer solution mixed with 0.5 mL of DPPH solution. A series of various concentrations of synthesized chalcones and  $\infty$ -Tocoferol (1 µg in 1 mL of ethanol) are added to each tube and mixed well. After 30 min at RT the absorbance of each solution is measured by UV-Vis spectrophotometer at 517 nm. A mixture of buffer solution and ethanol are used as the reference for the spectrophotometer. A graph is plotted with the weight of the compound vs absorptions and  $IC_{50}$ values. The antioxidant activity is expressed in terms of  $IC_{50}$  (µg/mL, concentration required to inhibit DPPH radical formation by 50%). ∞-Tocoferol is used as a positive control. From this experiment the chalcones (6-9) were found to have a satisfactory antioxidant activity.

#### Insect antifeedant activity

The multipronged activities are present in different chalcones and in the present study, it is intended to examine their insect antifeedant activities against castor

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*semilooper.* The larvae of *Achoea Janata* L are reared as described on the leaves of caster *Riclnus communls* in the laboratory at the temperature range of  $26^{\circ}C \pm 1^{\circ}C$  and a relative humidity of 75-85%. The leaf - disc bio-

assay method<sup>[35,36,51]</sup> is used against the  $4^{th}$  instar larvae to measure the antifeedant activity. The  $4^{th}$  instar larvae is selected for testing because the larvae at this stage feed very voraciously.



Plate-5

Plate-6

Figure 5 : Antifungal activities of 1-methyl-2-pyrrolyl chalcones: Petri-dishes

# Measurement of insect antifeedant activity of 1methyl-2-pyrrolyl chalcones

Leaf discs of a diameter of 1.85 cm are punched from castor leaves with the petioles intact. All chalcones are dissolved in acetone at a concentration of 200 ppm and dipped for 5 minutes. The leaf discs have been airdried and placed in one litre beaker containing little water in order to facilitate translocation of water. Therefore the leaf discs remain fresh throughout the duration of the rest, 4<sup>th</sup> instar larvae of the test insect, which has been preserved on the leaf discs of all chalcones and allowed to feed on them for 24 hours. The area of the leaf discs consumed has been measured by Dethlers<sup>[52]</sup> method. The observed antifeedant activity of chalcones was presented in (TABLE 8).

From (TABLE 8) reveals that the compounds (2-



5) are found to reflect remarkable antifeedant among all other chalcones. This test is performed with the insects which took only two-leaf disc soaked under the solution of this compound. Compounds (3-5) also show enough antifeedant activity but their activities are lesser than (2). Further, compound (2) is subjected to measure the antifeedant activity at different 50, 100, 150 ppm concentrations and the observation reveals that as the concentration decreases, the activity also decreases. From the results in (TABLE 9), it is observed that the chalcone (2) shows an appreciable antifeedant activity at 200 ppm concentration.



Figure 6 : Antifungal activities of 1-methyl-2-pyrrolyl chalcones: Clustered column chart

Entry	Subst.	4-6	6-8	8-10	10-12	12-6	6-8	8am-	12Nn- 2nm	2-4	Total leaf disc
······		pm	рш	pm	pm	am	am	14111	2pm	pm	consumed in 24 ms
1	Н	1	1	0.5	0.5	0.5	1	1	1	1	8
2	3-Br	0.5	0.5	0.25	0	0.5	0.5	0.25	0.25	0.25	2.5
3	4-Br	0.5	0.5	0.25	0	0.5	0.5	0.25	0.25	0.25	2.5
4	3-Cl	0.5	0.5	0.25	0	0	0.5	0.25	0.25	0.25	2
5	4-Cl	0.0	0.25	0.25		0	0.25	0	0.25	0	1
6	4-F	0.5	1	0	0	0	0	0	0	1	2.5
7	2-OH	0.5	0	0	0.5	0	0.25	0	0.25	0.5	2
8	3-OH	1	0	0	1	1	1	0	0	0	4
9	4-OH	0.5	1	0	1.5	2	0	0	0	0	4
10	3-OCH <sub>3</sub> 1	0.5	0.5	1	1	0	1	1	1	9	
11	4-CH <sub>3</sub>	0.5	1	0.5	2	2	0.5	0.5	1	1	7
12	3-NO <sub>2</sub>	1	0.5	0.5	2	1	1	1	0	0	7
13	$4-NO_2$	0.5	0.5	1	1	1	1	0	0	0	5

TABLE 8 : Insect antifeedant activities of substituted styryl 1-methyl-2-pyrrolyl ketones

TABLE 9 : The Insect antifeedant activities of substituted styryl-1-methyl-2-pyrrolyl ketones (6) in the concentration of 50,100 and 150 ppm concentration.

ррт	4-6 pm	6-8 pm	8-10 pm	10-12 pm	12am- 6am	6-8 am	8am- 12Nn	12Nn- 2pm	2-4 pm	Total leaf disc consumed in 24 hrs
50	0.5	0.5	0	0	0	0	0	0	0	0.1
100	0	0.2	0.2	0.1	0	0	0	0	0	0.5
150	0	0.0	0.25	0	0	0	0	0	0	0.25

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## CONCLUSIONS

The authors have synthesized a series of some substituted styryl 1-methyl-2-pyrrolyl ketones using solid fly-ash:sulphuric acid catalyzed greener crossed-aldol reaction in microwave irradiation. The spectral linearity of these chalcones have been studied using hammett correlation of spectral group frequencies with Hammett substituent constants, F, R and Swain-Lupton's parameters through single and multi-regression analysis. The biological activities of all synthesized chalcones have been studied.

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