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## Synthesis, effect of substituents and antimicrobial activities of some 4-bromophenyl chalcones

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### ABSTRACT

Elven (*E*)-1-(4-bromophenyl)-3-(substituted phenyl)-2-propen-1-ones are formed using sodium hydroxide catalyzed Aldol condensation between 4-bromoacetophenone and substituted benzaldehyde. The production of these chalcone compounds are above 90%. These  $\alpha$ ,  $\beta$  unsaturated ketones were specified by their physical constants and spectral data (UV, IR, <sup>1</sup>H and <sup>13</sup>C-NMR). Hammett substituted constants ( $\sigma$ ,  $\sigma^+$ ,  $\sigma_I$  &  $\sigma_R$  and F and R parameters have been used for correlating the spectral values of these  $\alpha$ ,  $\beta$  unsaturated ketones by using single and multi-linear regression analysis. The impacts of substituents on the spectral data have been known on statistical analysis. By using Bauer-Kirby method the anti-microbial activities of these (*E*)-1-(4-bromophenyl)-3-(substituted phenyl)-2-propen-1-ones compounds are estimated.

**Keywords:** (*E*)-1-(4-bromophenyl)-3-(substituted phenyl)-2-propen-1-ones; UV spectra; IR spectra; NMR spectra; Substituent effects; Antimicrobial activities

### 1. INTRODUCTION

Chalcones are  $\alpha$ ,  $\beta$  unsaturated ketones, possess methylene structural moieties and they belongs to biomolecules.  $\alpha$ ,  $\beta$  unsaturated ketones of the categories alkyl-alkyl, alkyl-aryl and

aryl-aryl have been synthesized [1] and extracted from natural plants [2] by organic chemists. For synthesizing chalcones various methods are available such as Aldol, Crossed-Aldol, Claisen-Schmidt, Knoevenagel reactions, Greener methods-Grinding of reactants, solvent free and oxides of nanoparticles with microwave irradiation. Solvent free Aldol condensation and Crossed-Aldol condensation [3-5] assisted by microwave were useful for synthesis of carbonyl compounds.

Many catalyst were used for proceedings the chalcones synthesis reactions namely, Ethanol-NaOH [6], Methanol-KOH [7], EtOH-potassium hydroxide [8], Magnesium chloride [5], silica-H<sub>2</sub>SO<sub>4</sub> [9], anhydrous ZnCl<sub>2</sub> [10], clay [11], Hydrotalcite [12], ground chemistry catalysts-grinding the reactants with NaOH [13], aqueous alkali in lower temperature [14], solid sulphonic acid from bamboo [15], Ba(OH)<sub>2</sub> [16], anhydrous Na<sub>2</sub>CO<sub>3</sub> [17], microwave irradiation preparation [18], fly-ash: H<sub>2</sub>O [19], fly-ash: H<sub>2</sub>SO<sub>4</sub> [20], fly-ash: PTS [21], NaOH-CTABr [22], SiO<sub>2</sub>-H<sub>3</sub>PO<sub>4</sub> [23], SOCl<sub>2</sub> [24] and sulfated titania [25]. For prediction of ground state equilibration such *s-cis* and *s-trans* conformers the spectral data of these E-chalcones were used. The effects of substituent of the UV absorption maximum ( $\lambda_{\max}$ , nm), IR group frequencies ( $\nu$ , cm<sup>-1</sup>) and NMR chemical shift ( $\delta$ , ppm) values of  $\alpha$ ,  $\beta$ -proton and carbons of 4-ethoxyphenyl chalcones compounds and benzimidazole chalcones compounds have been studied detail by Janaki et al., [23]. In their studies, spectral data were observed satisfactory and correlated well with Hammett substituent constants ( $\sigma$ ,  $\sigma^+$ ,  $\sigma_I$  &  $\sigma_R$ ) and F and R parameters.

The  $\alpha$ ,  $\beta$  unsaturated carbonyl compounds, possess various multipronged activities such as antimicrobial [26], antidepressants [27], antiplosmoidal [28], anti-aids [29] and insect antifeedant activities [13,22]. A list of elven (*E*)-1-(4-bromophenyl)-3-(substituted phenyl)-2-propen-1-ones synthesized, studied the spectral correlations and evaluate to the antimicrobial activities against micro species using Bauer-Kirby [30] method.

## 2. EXPERIMENTAL

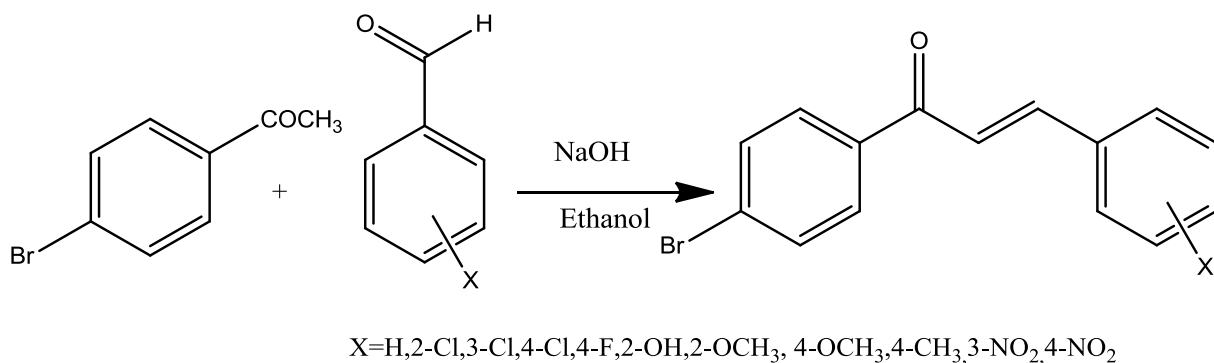
### 2. 1. General

All used chemicals were purchased from Sigma-Aldrich and E-Merck chemical companies. Melting points of all  $\alpha$ ,  $\beta$  unsaturated ketone compounds were determined in open glass capillaries on Mettler FP51 melting point apparatus. The ELICO BL 222 ultraviolet spectrophotometer was utilized for recording the absorption maxima ( $\lambda_{\max}$ , nm), of all  $\alpha$ ,  $\beta$  unsaturated ketone compounds in spectral grade methyl alcohol. Infrared spectra (KBr, 4000-400 cm<sup>-1</sup>) were recorded AVATAR-300 Fourier transform spectrophotometer. Bruker AV400 NMR spectrometer was used for recording NMR spectra operating at 500 MHz for <sup>1</sup>H spectra and 125.46 MHz for <sup>13</sup>C spectra in CDCl<sub>3</sub> solvent using TMS as internal standard.

### 2. 3. Synthesis of (*E*)-1-(4-bromophenyl)-3-(substituted phenyl)-2-propen-1-ones

Eqimolar quantities of 4-bromoacetophenone (1mmol) and benzaldehyde (1mmol) were taken in a 250 ml conical flask and mixed with sodium hydroxide (0.5 g) in 10 mL of absolute ethanol for 1 hr [31] and it is shown in (**Scheme 1**). The resultant mixture was cooled at room temperature. Final product obtained was a pale yellow solid. This crude product was recrystallization by ethanol. Which result in glittering pale yellow. The physical constant values and analytical data of all (*E*)-1-(4-bromophenyl)-3-(substituted phenyl)-2-propen-1-

ones were presented in Table 1. The ultraviolet, infrared and NMR spectroscopic data of synthesized (*E*)-1-(4-bromophenyl)-3-(substituted phenyl)-2-propen-1-ones were tabulated in Table 2.



**Scheme 1.** Synthesis of (*E*)-1-(4-bromophenyl)-3-(substituted phenyl)-2-propen-1-ones.

**Table 1.** The physical constant values and analytical data of (*E*)-1-(4-bromophenyl)-3-(substituted phenyl)-2-propen-1-ones.

Entry	X	M.F.	M.W.	Yield (%)	m.p. (°C)
1	H	C <sub>15</sub> H <sub>11</sub> BrO	287	85	155 (155-157) [31]
2	2-Cl	C <sub>15</sub> H <sub>10</sub> BrOCl	321	84	218
3	3-Cl	C <sub>15</sub> H <sub>10</sub> BrOCl	321	86	120
4	4-Cl	C <sub>15</sub> H <sub>10</sub> BrOCl	321	86	115
5	4-F	C <sub>15</sub> H <sub>10</sub> BrOF	305	83	141
6	2-OH	C <sub>15</sub> H <sub>11</sub> BrO <sub>2</sub>	303	80	108
7	2-OCH <sub>3</sub>	C <sub>16</sub> H <sub>13</sub> BrO <sub>2</sub>	321	84	141
8	4-OCH <sub>3</sub>	C <sub>16</sub> H <sub>13</sub> BrO <sub>2</sub>	321	85	197
9	4-CH <sub>3</sub>	C <sub>16</sub> H <sub>13</sub> BrO	305	86	148
10	3-NO <sub>2</sub>	C <sub>15</sub> H <sub>10</sub> BrO <sub>3</sub> N	332	82	128
11	4-NO <sub>2</sub>	C <sub>15</sub> H <sub>10</sub> BrO <sub>3</sub> N	332	80	136

**Table 2.** The ultraviolet absorption maxima ( $\lambda_{\max}$ , nm), infrared absorptions ( $\nu$ ,  $\text{cm}^{-1}$ ) and NMR chemical shifts ( $\delta$ , ppm) of substituted (*E*)-1-(4-bromophenyl)-3-(substituted phenyl)-2-propen-1-ones.

Entry	X	UV ( $\lambda_{\max}$ , nm)	IR ( $\nu$ , $\text{cm}^{-1}$ )				
			CO( <i>s-cis</i> )	CO( <i>s-trans</i> )	CH <sub>ip</sub>	CH <sub>op</sub>	CH=CH <sub>op</sub>
1	H	314.0	1656.85	1593.13	1178.51	761.88	1029.99
2	2-Cl	264.0	1658.78	1593.13	1209.37	771.53	1072.42
3	3-Cl	304.0	1658.78	1589.34	1207.44	771.53	1076.28
4	4-Cl	316.0	1685.79	1579.70	1178.54	713.66	1066.64
5	4-F	314.0	1675.79	1589.70	1176.54	715.66	1063.64
6	2-OH	264.0	1655.85	1583.20	1113.00	716.88	1078.56
7	2-OCH <sub>3</sub>	347.0	1653.00	1589.34	1159.22	738.74	1070.49
8	4-OCH <sub>3</sub>	347.0	1656.85	1593.20	1111.00	761.88	1068.56
9	4-CH <sub>3</sub>	325.0	1654.92	1589.34	1170.79	738.74	1068.56
10	3-NO <sub>2</sub>	259.0	1678.07	1583.56	1176.58	736.81	1072.42
11	4-NO <sub>2</sub>	259.0	1683.86	1585.49	1118.71	763.81	1062.78
Entry	X	IR ( $\nu$ , $\text{cm}^{-1}$ )	<sup>1</sup> H NMR ( $\delta$ , ppm)		<sup>13</sup> C NMR ( $\delta$ , ppm)		
		C=C <sub>op</sub>	H <sub><math>\alpha</math></sub>	H <sub><math>\beta</math></sub>	C <sub><math>\alpha</math></sub>	C <sub><math>\beta</math></sub>	CO
1	H	572.86	7.500	7.841	121.48	145.43	189.39
2	2-Cl	574.79	7.723	8.208	124.28	141.22	197.34
3	3-Cl	574.79	7.490	7.758	122.62	143.60	188.90
4	4-Cl	547.78	7.245	7.617	128.50	141.90	197.14
5	4-F	567.78	7.416	7.792	121.15	144.05	189.19
6	2-OH	566.72	7.670	8.140	121.06	141.22	197.15
7	2-OCH <sub>3</sub>	536.21	7.376	7.813	119.16	145.28	189.88
8	4-OCH <sub>3</sub>	576.72	7.376	7.813	119.16	145.28	189.40
9	4-CH <sub>3</sub>	534.28	7.455	7.821	120.48	145.53	189.47
10	3-NO <sub>2</sub>	570.93	7.486	8.081	122.01	145.73	196.59
11	4-NO <sub>2</sub>	547.78	7.494	8.174	123.97	146.81	196.50

### 3. RESULTS AND DISCUSSION

#### 3. 1. Spectral linearity

In this study the Hammett spectral linearity of these synthesized (*E*)-1-(4-bromophenyl)-3-(substituted phenyl)-2-propen-1-ones has been analyzed by evaluating the substituent effects on the group frequencies. The assigned spectroscopic data of all (*E*)-1-(4-bromophenyl)-3-(substituted phenyl)-2-propen-1-ones such as absorption maximum  $\lambda_{max}$  (nm) of carbonyl groups, infrared carbonyl stretches of  $\nu_{CO_{s-cis}}$  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 shift  $\delta$ (ppm) values of  $H_{\alpha}$ ,  $H_{\beta}$ ,  $C_{\alpha}$ ,  $C_{\beta}$ , CO are assigned and these data are correlated with various substituent constants ( $\sigma$ ,  $\sigma^+$ ,  $\sigma_I$  &  $\sigma_R$ ) and F and R parameters.

#### 3. 1. 1. UV spectral correlations

The obtained UV absorption maximum values ( $\lambda_{max}$ , nm) of synthesized (*E*)-1-(4-bromophenyl)-3-(substituted phenyl)-2-propen-1-one compounds were tabulated in Table 2. The absorption maximum ( $\lambda_{max}$  nm) values of these (*E*)-1-(4-bromophenyl)-3-(substituted phenyl)-2-propen-1-one compounds are correlated with Hammett substituent constants ( $\sigma$ ,  $\sigma^+$ ,  $\sigma_I$  &  $\sigma_R$ ) and F and R parameters using single and multi-linear regression analysis. Hammett correlation involving the group frequencies and absorption maximum are expressed the form of Hammett equation as shown in equation (1).

$$\lambda_{max} = \rho\sigma + \lambda_0 \quad \dots(1)$$

where  $\lambda_0$  is the frequency for the parent member of the series.

The results of statistical analysis of these UV absorption maxima ( $\lambda_{max}$ , nm) data with Hammett substituent constants ( $\sigma$ ,  $\sigma^+$ ,  $\sigma_I$  &  $\sigma_R$ ) and F and R parameters are listed in Table 3.

**Table 3.** Results of statistical analysis of infrared  $\nu$  ( $cm^{-1}$ )  $CO_{s-cis}$ ,  $CO_{s-trans}$ ,  $CH_{ip}$ ,  $CH_{op}$ ,  $CH=CH_{op}$  and  $C=C_{op}$  substituted (*E*)-1-(4-bromophenyl)-3-(substituted phenyl)-2-propen-1-ones with Hammett  $\sigma$ ,  $\sigma^+$ ,  $\sigma_I$ ,  $\sigma_R$  constants and F and R parameters.

Freq.	Constt.	r	I	$\rho$	s	n	Correlated derivatives
$\lambda_{max}$ (nm)	$\sigma$	0.906	308.38	-60.511	25.85	9	H,3-Cl, 4-Cl, 4-F, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.907	303.24	-49.762	24.06	10	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_I$	0.805	328.40	-74.850	30.86	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_R$	0.941	289.23	-51.941	32.73	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>

	F	0.747	326.98	-67.264	31.65	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	R	0.657	288.02	-49.048	32.54	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
<b>CO<sub>s-cis</sub></b>	$\sigma$	0.732	1662.50	23.661	9.14	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.666	1664.69	15.112	10.64	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_I$	0.722	1651.07	39.177	9.26	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_R$	0.841	1670.48	22.434	11.73	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	F	0.716	1650.82	37.796	9.33	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	R	0.905	1670.45	19.139	11.98	7	H, 2-Cl, 3-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> , 3-NO <sub>2</sub>
<b>CO<sub>s-trans</sub></b>	$\sigma$	0.781	1588.62	-4.364	4.42	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.722	1588.20	-2.575	4.57	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_I$	0.395	1590.88	-7.661	4.39	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_R$	0.436	1587.55	-2.391	4.73	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	F	0.732	1590.83	7.129	4.42	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	R	0.801	1587.48	-2.304	4.72	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
<b>CH<sub>ip</sub></b>	$\sigma$	0.325	1161.30	19.369	35.95	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.904	1162.43	28.276	33.55	7	2-Cl, 3-Cl, 4-Cl, 4-F, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>

	$\sigma_I$	0.808	1159.09	12.426	36.70	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_R$	0.643	1170.51	30.007	35.81	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	F	0.765	1163.90	-0.764	36.83	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	R	0.765	1173.52	36.990	34.97	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
<b>CH<sub>op</sub></b>	$\sigma$	0.675	743.03	13.511	23.16	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.653	744.12	12.662	22.83	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_I$	0.346	745.37	-1.991	23.82	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_R$	0.763	752.37	32.008	21.98	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	F	0.876	751.56	-18.032	23.38	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	R	0.632	753.08	31.48	21.70	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
<b>CH=CH<sub>op</sub></b>	$\sigma$	0.564	1066.31	0.680	13.70	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.706	1066.40	-0.237	13.70	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_I$	0.654	1058.29	22.285	12.55	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_R$	0.754	1062.44	-17.191	12.78	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	F	0.675	1058.34	20.974	12.62	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>

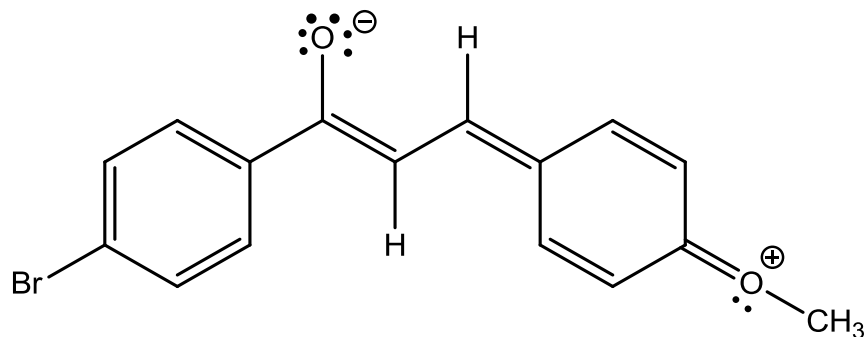
	R	0.761	1062.19	-15.679	12.80	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
<b>C=C<sub>op</sub></b>	$\sigma$	0.767	560.13	6.995	16.82	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.791	560.77	4.676	16.88	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_I$	0.608	555.89	13.946	16.72	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_R$	0.809	560.97	0.048	17.07	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	F	0.806	555.65	13.857	16.70	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	R	0.642	560.35	-2.265	17.05	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
<b><math>\delta H_a</math> (ppm)</b>	$\sigma$	0.812	7.471	0.032	0.13	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.624	7.472	0.066	0.13	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_I$	0.457	7.479	-0.010	0.14	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_R$	0.732	7.473	-0.010	0.14	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	F	0.624	0.479	-0.010	0.14	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	R	0.623	0.747	0.003	0.14	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
<b><math>\delta H_b</math> (ppm)</b>	$\sigma$	0.635	7.819	0.187	0.19	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.823	7.907	0.169	0.18	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>



	$\sigma_I$	0.635	7.821	0.256	0.19	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_R$	0.761	7.946	0.139	0.20	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	F	0.678	7.825	0.231	0.20	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	R	0.856	7.951	0.136	0.20	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
<b><math>\delta C O</math> (ppm)</b>	$\sigma$	0.941	196.22	4.926	3.65	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.784	192.64	3.951	3.60	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_I$	0.657	189.77	8.360	3.63	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_R$	0.549	193.58	3.365	4.06	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	F	0.632	190.30	6.552	3.87	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	R	0.864	193.77	3.585	4.03	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
<b><math>\delta C_a</math> (ppm)</b>	$\sigma$	0.905	121.72	3.754	2.35	9	H, 3-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.905	122.04	3.052	2.29	10	H, 2-Cl, 3-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_I$	0.900	120.37	4.945	2.54	10	H, 2-Cl, 3-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_R$	0.832	123.06	3.911	2.58	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	F	0.783	120.90	3.303	2.69	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> ,4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>

	R	0.844	123.24	3.993	2.53	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
$\delta C_{\beta}$ (ppm)	$\sigma$	0.823	144.06	1.020	2.01	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.807	144.17	0.291	2.05	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_I$	0.841	144.33	-0.406	2.05	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_R$	0.904	144.97	3.418	1.81	8	H, 3-Cl, 4-F, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	F	0.603	144.30	-0.303	2.05	11	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	R	0.904	144.93	2.804	1.86	8	H, 3-Cl, 4-F, 2-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
r = correlation coefficient, I = intercept, $\rho$ = slope, s = standard deviation, n = number of correlated derivatives							

From the Table 3, the UV absorption maxima ( $\lambda_{max}$ , nm) values satisfactorily correlated with Hammett substituent constants  $\sigma$  ( $r = 0.906$ ),  $\sigma^+$  ( $r = 0.907$ ) and  $\sigma_R$  ( $r = 0.941$ ) only. The remaining Hammett substituent constant  $\sigma_I$  and F & R ( $r < 0.900$ ) parameters failed in correlation. This is due to the weak inductive and field effects of substituents for predicting the reactivity on the absorption. This is attributed to the resonance conjugative structure shown in Fig. 1. All the correlations with Hammett constants and F and R parameters have shown negative  $\rho$  values. This indicates the reverse substituent effect with respect to UV absorption maximum  $\lambda_{max}$  (nm) values of all aryl  $\alpha$ ,  $\beta$ -unsaturated ketone compounds. The single parameter correlation did not obey the Hammett substituents constants in the regression.



**Fig. 1.** The resonance – conjugated structure.

when the UV absorption maximum values of all  $\alpha$ ,  $\beta$ -unsaturated ketone compounds were subjected to multi-regression analysis with inductive, resonance and Swain-Lupton's [32] constants, they correlations were satisfactory as shown in equations (2 and 3).

$$\lambda_{\max} (\text{nm}) = 315.57 (\pm 21.101) - 64.817 (\pm 42.208) \sigma_I - 39.891 (\pm 36.286) \sigma_R \quad \dots(2)$$

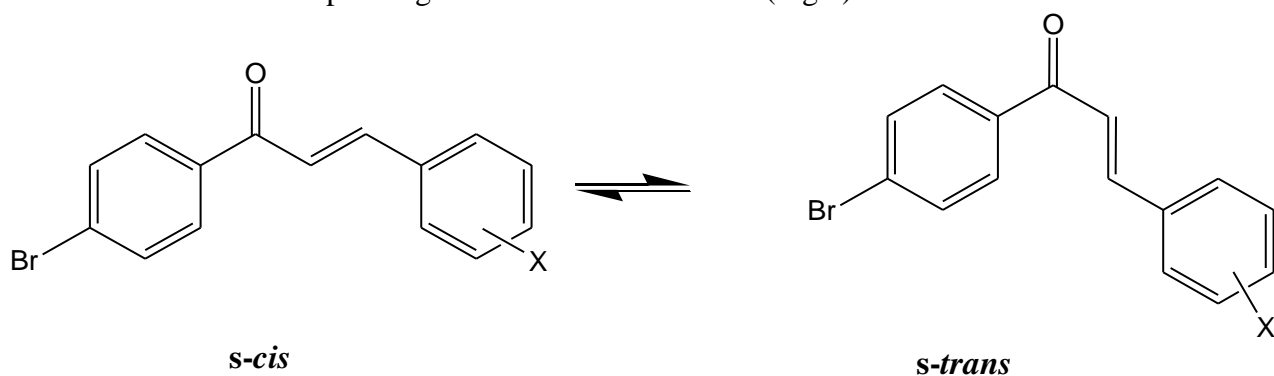
(R = 0.960, n = 11, P > 95%)

$$(\lambda_{\max} (\text{nm}) = 313.36 (\pm 19.986) - 63.866 (\pm 39.399) F - 45.924 (\pm 32.036) R \quad \dots(3)$$

(R = 0.961, n = 11, P > 95%)

### 3. 1. 2. IR spectral study

The synthesized  $\alpha$ ,  $\beta$  unsaturated ketones in the present study are shown in Scheme 1. The carbonyl stretching frequencies ( $\text{cm}^{-1}$ ) of *s-cis* and *s-trans* of isomers are tabulated in Table 2 and the corresponding conformers are shown in (Fig 2).



**Fig. 2.** The *s-cis* and *s-trans* conformers of 4-bromophenyl chalcones.

The assigned carbonyl stretching frequencies ( $\text{cm}^{-1}$ ) of *s-cis* and *s-trans* conformers have been correlated with Hammett substituent constants and Swain-Lupton constants [32]. 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  $\nu$  is the carbonyl frequencies of substituted system and  $\nu_0$  is the corresponding quantity of unsubstituted system;  $\sigma$  is a Hammett substituent constant, which in principle is characteristics of the substituent only and independent of the nature of reaction.  $\rho$  is a reaction constant is depends upon the nature of the reaction (temperature, solvent, catalyst and pressure).

The results of statistical analysis were shown in Table 3. From table 3, the resonance component R ( $r = 0.905$ ) only correlated satisfactorily with  $\text{CO}_{s-cis}$  conformers. The Hammett substituent constants and F parameters were failing ( $r < 0.900$ ) in correlation. All the Hammett substituent constants and F & R parameters gave poor correlation ( $r < 0.900$ ) with  $\nu\text{CO}_{s-trans}$  conformers. This is because of the reasons stated in earlier and associated with the resonance conjugative structure shown in (Fig 1).

The correlation of  $\text{CH}_{ip}$  modes with Hammett constant  $\sigma^+$  ( $r = 0.904$ ) only gave satisfactory correlation. The remaining Hammett substituent constants and  $F$  &  $R$  parameters were failing ( $r < 0.900$ ) in correlation.  $\text{CH}_{op}$  modes of all  $\alpha$ ,  $\beta$  unsaturated ketone compounds poorly correlated ( $r < 0.900$ ) with Hammett substituent constants ( $\sigma$ ,  $\sigma^+$ ,  $\sigma_I$  &  $\sigma_R$ ) and  $F$  &  $R$  parameters. This failure in correlation is due to the weak polar, inductive, field and resonance effects of the substituents and associated with the resonance conjugative structure as shown in (Fig 1).

All Hammett substituent constants ( $\sigma$ ,  $\sigma^+$ ,  $\sigma_I$  &  $\sigma_R$ ) and  $F$  &  $R$  parameters gave poor ( $r < 0.900$ ) correlation with  $\text{CH}=\text{CH}_{op}$  modes. The polar, inductive, field and resonance components of the substituents are failed in correlation. All the Hammett substituent constants ( $\sigma$ ,  $\sigma^+$ ,  $\sigma_I$  &  $\sigma_R$ ) and  $F$  &  $R$  parameters gave poor ( $r < 0.900$ ) correlation with  $\text{C}=\text{C}_{op}$  modes. The polar, inductive, field and resonance components of the substituents are failed in correlation. This is due to the reasons stated earlier and associated with the resonance conjugative structure as shown in (Fig 1).

Most of the correlations with Hammett constants and  $F$  and  $R$  parameters have shown positive  $\rho$  values. This indicates the operation of normal substituent effect with respect to infrared frequency values of all aryl  $\alpha$ ,  $\beta$ -unsaturated ketone compounds.

The single parameter correlation did not obey the Hammett substituents constants in the regression. When the infrared group frequencies of all  $\alpha$ ,  $\beta$ -unsaturated ketone compounds were subjected to multi-regression analysis with inductive, resonance and Swain-Lupton's [32] constants, they correlations were satisfactory as shown in equations (5-16).

$$\nu\text{CO}_{s-cis} (\text{cm}^{-1}) = 1655.71(\pm 4.317) + 11.041(\pm 9.525)\sigma_I - 6.212(\pm 9.498)\sigma_R \quad \dots(5)$$

( $R = 0.901$ ,  $n = 12$ ,  $P > 90\%$ )

$$\nu\text{CO}_{s-cis} (\text{cm}^{-1}) = 1656.37(\pm 3.960) + 11.041(\pm 9.251)F - 1.361(\pm 6.487)R \quad \dots(6)$$

( $R = 0.934$ ,  $n = 12$ ,  $P > 90\%$ )

$$\nu\text{CO}_{s-trans} (\text{cm}^{-1}) = 1596.31(\pm 19.795) - 22.022(\pm 43.671)\sigma_I + 31.278(\pm 43.548)\sigma_R \quad \dots(7)$$

( $R = 0.928$ ,  $n = 12$ ,  $P > 95\%$ )

$$\nu\text{CO}_{s-trans} (\text{cm}^{-1}) = 1601.9(\pm 16.091) - 29.158(\pm 37.588)F + 41.695(\pm 26.359)R \quad \dots(8)$$

( $R = 0.952$ ,  $n = 12$ ,  $P > 95\%$ )

$$\nu\text{CH}_{ip} (\text{cm}^{-1}) = 838.43(\pm 200.21) + 650.994(\pm 441.690)\sigma_I - 152.515(\pm 440.450)\sigma_R \quad \dots(9)$$

( $R = 0.945$ ,  $n = 12$ ,  $P > 90\%$ )

$$\nu\text{CH}_{ip} (\text{cm}^{-1}) = 861.04(\pm 185.277) + 607.587(\pm 432.806)F - 50.738(\pm 303.506)R \quad \dots(10)$$

( $R = 0.943$ ,  $n = 12$ ,  $P > 90\%$ )

$$\nu\text{CH}_{op} (\text{cm}^{-1}) = 761.842(\pm 22.766) - 18.811(\pm 50.226)\sigma_I + 9.372(\pm 50.085)\sigma_R \quad \dots(11)$$

( $R = 0.913$ ,  $n = 12$ ,  $P > 90\%$ )

$$\nu\text{CH}_{op} (\text{cm}^{-1}) = 750.432(\pm 20.130) - 12.707(\pm 47.024)F - 29.773(\pm 32.975)R \quad \dots(12)$$

( $R = 0.929$ ,  $n = 12$ ,  $P > 90\%$ )

$$\nu_{\text{CH}=\text{CH}_{op}}(\text{cm}^{-1}) = 1077.76(\pm 12.100) + 24.303(\pm 26.695)\sigma_1 + 39.129(\pm 26.620)\sigma_R \quad \dots(13)$$

(R = 0.949, n = 12, P > 90%)

$$\nu_{\text{CH}=\text{CH}_{op}}(\text{cm}^{-1}) = 1077.12(\pm 10.141) + 21.968(\pm 23.690)F + 36.332(\pm 16.613)R \quad \dots(14)$$

(R = 0.960, n = 12, P > 95%)

$$\nu_{\text{C}=\text{C}_{op}}(\text{cm}^{-1}) = 553.123(\pm 17.200) + 31.288(\pm 37.946)\sigma_1 + 53.956(\pm 37.839)\sigma_R \quad \dots(15)$$

(R = 0.947, n = 12, P > 90%)

$$\nu_{\text{C}=\text{C}_{op}}(\text{cm}^{-1}) = 547.991(\pm 17.307) + 18.686(\pm 40.430)F + 20.442(\pm 28.351)R \quad \dots(16)$$

(R = 0.926, n = 12, P > 90%)

### 3. 2. NMR spectral study

#### 3. 2. 1. <sup>1</sup>H NMR spectra

From the <sup>1</sup>H NMR spectra of α, β unsaturated ketone compounds chemical shift (δ, ppm) values of H<sub>α</sub> and H<sub>β</sub> are assigned and tabulated in Table 2. These chemical shift values were correlated with Hammett substituent constants and F and R parameters.

The statistical analysis of these chemical shifts is presented in Table 3. From Table 3, all the Hammett substituent constants (σ, σ<sup>+</sup>, σ<sub>I</sub> & σ<sub>R</sub>) and F & R parameters gave poor (r < 0.900) correlation with H<sub>α</sub> chemical shift (δ, ppm) values of all α, β unsaturated ketone compounds. The polar, inductive, Field and resonance components of the substituents fail in correlation. All the correlations have shown positive ρ values with a few Hammett constants σ, σ<sup>+</sup> and R parameter. This indicates the operation of normal substituent effect with respect to δH<sub>α</sub> chemical shift (ppm) values of all aryl α, β-unsaturated ketone compounds.

All the Hammett substituent constants (σ, σ<sup>+</sup>, σ<sub>I</sub> & σ<sub>R</sub>) and F & R parameters gave poor correlation (r < 0.900) with H<sub>β</sub> chemical shifts (δ, ppm) values of all chalcones compound. The polar, 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).

All the correlations have shown positive ρ values with all Hammett constants and F and R parameters. This indicates the operation of normal substituent effect with respect to δH<sub>β</sub> chemical shift (ppm) values of all aryl α, β-unsaturated ketone compounds.

The single parameter correlation did not obey the Hammett substituents constants in the regression. When the <sup>1</sup>H NMR chemical shift (δ, ppm) values of all α, β-unsaturated ketone compounds were subjected to multi-regression analysis with inductive, resonance and Swain-Lupton's [32] constants, they correlations were satisfactory as shown in equations (17-20).

$$\delta H_{\alpha}(\text{ppm}) = 7.476(\pm 0.102) - 0.008(\pm 0.205)\sigma_1 - 0.009(\pm 0.176)\sigma_R \quad \dots(17)$$

(R = 0.902, n = 11, P > 90%)

$$\delta H_{\alpha}(\text{ppm}) = 7.480(\pm 0.099) - 0.010(\pm 0.195)F + 0.003(\pm 0.159)R \quad \dots(18)$$

(R = 0.901, n = 11, P > 90%)

$$\delta H_{\beta}(\text{ppm}) = 7.852(\pm 0.145) + 0.231(\pm 0.290)\sigma_1 + 0.096(\pm 0.249)\sigma_R \quad \dots(19)$$

(R = 0.943, n = 11, P > 90%)

$$\delta H_{\beta} (\text{ppm}) = 7.863(\pm 0.139) + 0.221(\pm 0.275)F + 0.125(\pm 0.223)R \quad \dots(20)$$

$$(R = 0.933, n = 12, P > 90\%)$$

### 3. 2. 2. $^{13}\text{C}$ NMR spectra

The carbonyl carbon,  $C_{\alpha}$  and  $C_{\beta}$  chemical shift ( $\delta$ , ppm) values of 4-bromophenyl chalcone compounds were assigned and tabulated in Table 2. These chemical shift values were correlated with Hammett substituent constants and F and R parameters. The results of statistical analysis are shown in Table 3.

From Table 3,  $\delta\text{CO}$  chemical shift (ppm) values of all aryl  $\alpha, \beta$ -unsaturated ketone compounds have shown satisfactory correlation with the Hammett substituent constant  $\sigma$  ( $r = 0.941$ ) only. The remaining Hammett constants ( $\sigma^+$ ,  $\sigma_I$  &  $\sigma_R$ ) and F & R parameters were gave poor correlations ( $r < 0.900$ ) with carbonyl carbon chemical shift values of all chalcones compounds. The Hammett constants  $\sigma$  ( $r = 0.905$ ),  $\sigma^+$  ( $r = 0.905$ ) and  $\sigma_I$  ( $r = 0.900$ ) were correlated satisfactorily with  $C_{\alpha}$  chemical shifts. The remaining Hammett substituent constant and F and R parameters were failing ( $r < 0.900$ ) in correlations.

The  $C_{\beta}$  chemical shifts ( $\delta$ , ppm) were satisfactorily correlated with the Hammett constant  $\sigma_R$  ( $r = 0.904$ ) and R ( $r = 0.904$ ) parameter. The remaining Hammett substituent constants ( $\sigma$ ,  $\sigma^+$  &  $\sigma_I$ ) and F parameter were failing ( $r < 0.900$ ) in correlations. This is due to the reasons stated in earlier and associated with the resonance conjugative structure shown in (Fig 1).

Most of the correlations have shown positive  $\rho$  values with all Hammett constants and F and R parameters. This indicates the operation of normal substituent effect with respect to  $\delta\text{CO}$  chemical shift (ppm) values of all the aryl  $\alpha, \beta$ -unsaturated ketone compounds.

The single parameter correlation did not obey the Hammett substituents constants in the regression. When the  $^{13}\text{C}$  chemical shift (ppm) values of all  $\alpha, \beta$ -unsaturated ketone compounds were subjected to multi-regression analysis with inductive, resonance and Swain-Lupton's [32] constants, they correlations were satisfactory as shown in equations (5-16).

$$\delta C_{\alpha} (\text{ppm}) = 121.38(\pm 1.751) + 4.155(\pm 3.504)\sigma_I + 3.139(\pm 3.012)\sigma_R \quad \dots(21)$$

$$(R = 0.951, n = 11, P > 95\%)$$

$$\delta C_{\alpha} (\text{ppm}) = 122.04 (\pm 1.708) + 3.018(\pm 3.368)F + 3.846(\pm 2.738)R \quad \dots(22)$$

$$(R = 0.951, n = 11, P > 95\%)$$

$$\delta C_{\beta} (\text{ppm}) = 145.51 (\pm 1.307) - 1.328(\pm 2.615)\sigma_I + 3.665(\pm 2.248)\sigma_R \quad \dots(23)$$

$$(R = 0.950, n = 11, P > 95\%)$$

$$\delta C_{\beta} (\text{ppm}) = 145.14 (\pm 1.316) - 0.512(\pm 2.595)F + 2.830(\pm 2.110)R \quad \dots(24)$$

$$(R = 0.942, n = 1, P > 90\%)$$

$$\delta\text{CO} (\text{ppm}) = 190.38(\pm 2.639) + 7.883(\pm 5.280)\sigma_I + 1.900(\pm 4.539)\sigma_R \quad \dots(25)$$

$$(R = 0.950, n = 11, P > 95\%)$$

$$\delta\text{CO} (\text{ppm}) = 191.27(\pm 2.618) + 6.309(\pm 5.161)F + 3.276(\pm 4.539)R \quad \dots(26)$$

$$(R = 0.941, n = 11, P > 90\%)$$

### 3. 3. Microbial activities

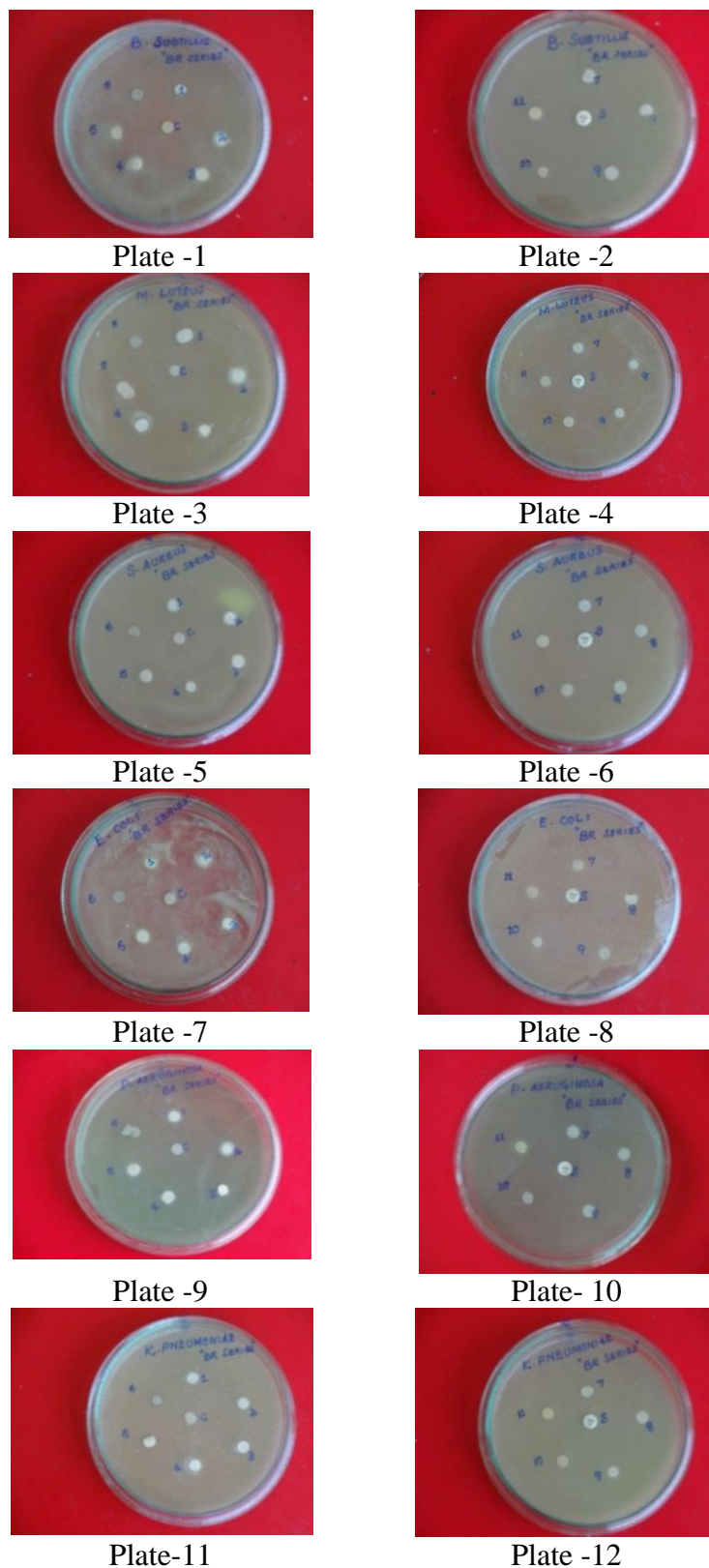
#### 3. 3. 1. Antibacterial sensitivity assay

Kirby-Bauer [34] disc diffusion technique was used for performing Antibacterial sensitivity assay test. In each Petri plate about 0.5 ml of the tested bacterial sample was spread uniformly over the Solidified Mueller Hinton agar using sterile glass spreader. Whatmann No.1 filter paper disc of 5mm diameter impregnated with the solution of the chalcone compounds using sterile forceps. These discs were upside down for incubated at 37 °C for 1 day. After 1day, visual examination diameter values of the zone of inhibition were measured. Same method was repeated and triplicate results were observed.

The antibacterial activity of the 4-bromophenyl chalcone compounds is shown in (Fig. 3) for Plates (1)-(12). Analysis of the zone of inhibition as given Table 4 and the Clustered column Chart (Fig 4) reveals that all the substituents have shown moderate antibacterial activity against *B. subtilis* species, under investigation. Only four compounds with 4-Cl, 4-F, 2-OCH<sub>3</sub> and 3-NO<sub>2</sub> substituents have shown excellent antibacterial activity than standard Ampicillin against *Micrococcus luteus*. All the substituents except 4-Cl and 2-OCH<sub>3</sub> have shown moderate antibacterial activity against *S.aureus*.

**Table 4.** Antibacterial activity of (*E*)-1-(4-bromophenyl)-3-(substituted phenyl)-2-propen-1-ones.

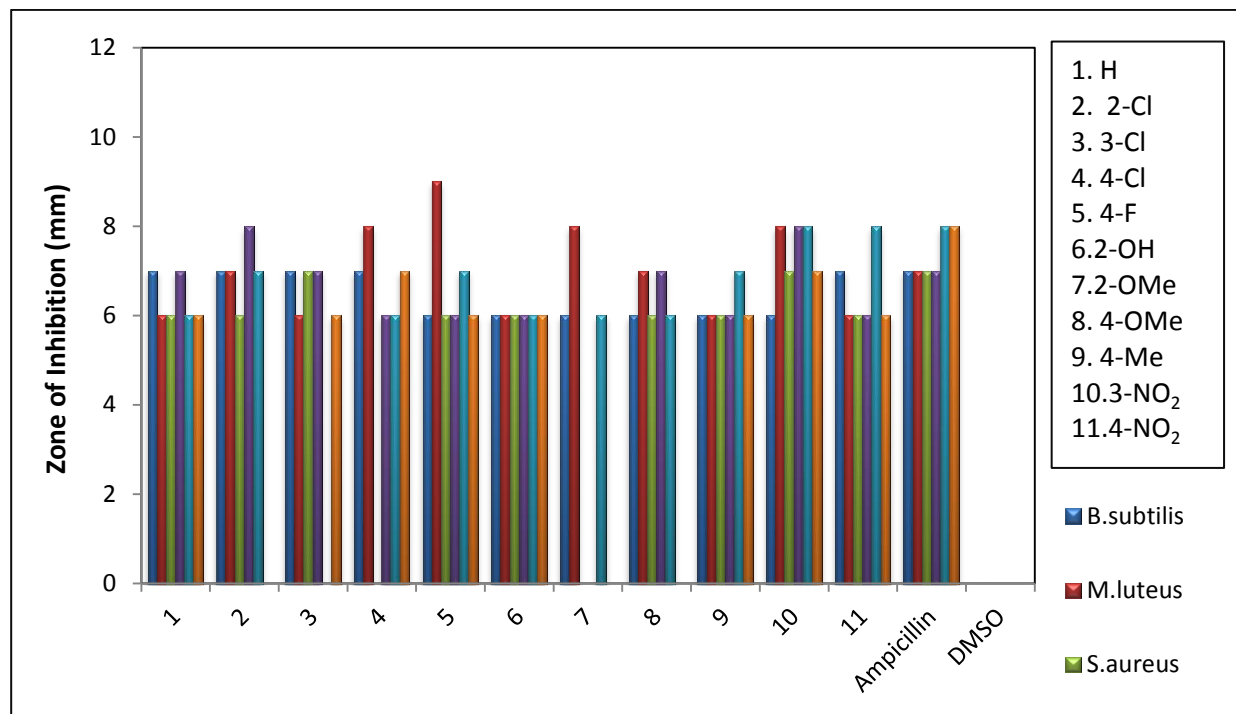
S. No	X	Zone of Inhibition (mm)					
		Gram positive Bacteria			Gram negative Bacteria		
		<i>B. subtilis</i>	<i>M. luteus</i>	<i>S. aureus</i>	<i>E. Coli</i>	<i>P. aeruginosa</i>	<i>K. pneumoniae</i>
1	H	7	6	6	7	6	6
2	2-Cl	7	7	6	8	7	-
3	3-Cl	7	6	7	7	-	6
4	4-Cl	7	8	-	6	6	7
5	4-F	6	9	6	6	7	6
6	2-OH	6	6	6	6	6	6
7	2-OCH <sub>3</sub>	6	8	-	-	6	-
8	4-OCH <sub>3</sub>	6	7	6	7	6	-
9	4-CH <sub>3</sub>	6	6	6	6	7	6
10	3-NO <sub>2</sub>	6	8	7	8	8	7
11	4-NO <sub>2</sub>	7	6	6	6	8	6
Standard Ampicillin		7	7	7	7	8	8
Control DMSO		-	-	-	-	-	-



**Fig. 3.** Antibacterial activities of 4-bromophenyl chalcone compounds-petri dish plates.



Two compounds with 2-Cl and 3-NO<sub>2</sub> substituents have shown excellent antibacterial activity than standard Ampicillin against *Escherichia coli*. Only two compounds with 3-NO<sub>2</sub> and 4-NO<sub>2</sub> substituents have shown good antibacterial activity equal to standard Ampicillin against *Pseudomonas aeruginosa*. All the substituents except 2-Cl, 2-OCH<sub>3</sub> and 4-OCH<sub>3</sub> have shown moderate antibacterial activity against *Klebsiella pneumonia*.



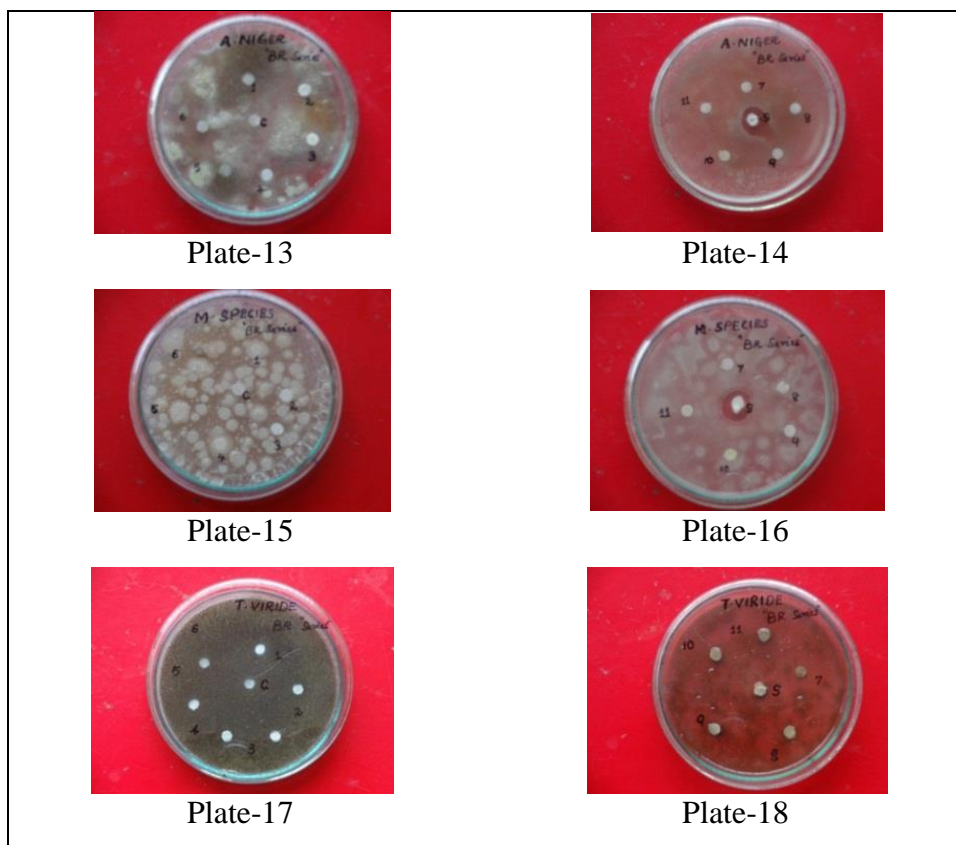
**Fig. 4.** Clustered column Chart of Antibacterial activity of substituted styryl -4-bromophenyl chalcone compounds

### 3. 3. 2. Antifungal sensitivity assay

Kirby-Bauer [34] disc diffusion technique was used for antifungal sensitivity assay. Potassium dextrose Agar 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 tested fungal species. The plate was rotated clockwise and counter clock-wise for uniform spreading of the species. The discs were impregnated with the test solution. The test solution was prepared by dissolving 15 mg of the chalcone compounds in 1mL of DMSO solvent. The medium was allowed to solidify and kept for 1 day.

After 1day, visual examination diameter values of the zone of inhibition were measured. Same method was repeated and triplicate results were observed. The antifungal effect of the styryl 4-bromophenyl chalcone compounds is shown in (Fig. 5) for Plates (13-18). Analysis of the zone of inhibition as given Table 5 and the Clustered column Chart (Fig. 6) reveals that only two compounds with 3-Cl and 4-Cl substituents have shown moderate antifungal activity against *Aspergillus niger*. Only four aryl  $\alpha$ ,  $\beta$ -unsaturated ketone compounds with H (parent), 4-Cl, 2-OCH<sub>3</sub> and 4-OCH<sub>3</sub> substituents have shown moderate antifungal activity against

*Mucor species*. Only six compounds with H (parent), 2-Cl, 2-OH, 4-OCH<sub>3</sub>, 3-NO<sub>2</sub> and 4-NO<sub>2</sub> substituents have shown moderate antifungal activity against *Trichoderma viride*.

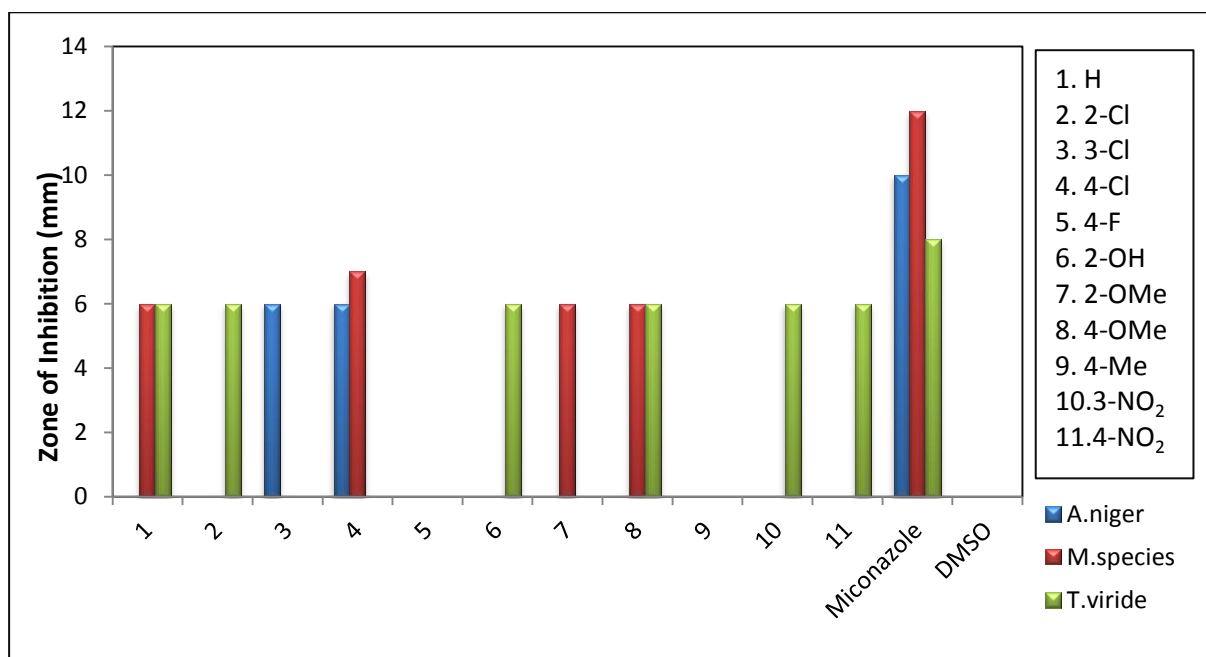


**Fig. 5.** Antifungal activities of 4-bromophenyl chalcone compounds-petri dish plates.

**Table 5.** Antifungal activity of substituted styryl- 4-bromophenyl chalcone compounds.

S. No.	Compounds	Zone of Inhibition (mm)		
		<i>A. niger</i>	<i>M. species</i>	<i>T. viride</i>
1	H	-	6	6
2	2-Cl	-	-	6
3	3-Cl	6	-	-
4	4-Cl	6	7	-
5	4-F	-	-	-
6	2-OH	-	-	6

7	2-OCH <sub>3</sub>	-	6	
8	4-OCH <sub>3</sub>	-	6	6
9	4-CH <sub>3</sub>	-	-	-
10	3-NO <sub>2</sub>	-	-	6
11	4-NO <sub>2</sub>	-	-	6
Standard	Miconazole	10	12	8
Control	DMSO	-	-	-



**Fig. 6.** Clustered column chart of antifungal activity of substituted styryl-4-bromophenyl chalcone compounds.

#### 4. CONCLUSIONS

Some (*E*)-1-(4-bromophenyl)-3-(substituted phenyl)-2-propen-1-ones compounds are formed using sodium hydroxide catalyzed Aldol condensation between 4-bromoacetophenone and substituted benzaldehyde. This reaction protocol offers a simple, easier work-up procedure and good yields. The production of these (*E*)-1-(4-bromophenyl)-3-(substituted phenyl)-2-propen-1-ones compounds are above 90 %. These (*E*)-1-(4-bromophenyl)-3-(substituted phenyl)-2-propen-1-ones were specified by their physical constants and spectral data (UV, IR, <sup>1</sup>H and <sup>13</sup>C-NMR). Hammett substituted constants  $\sigma$ ,  $\sigma^+$ ,  $\sigma_I$  and  $\sigma_R$  and F and R parameters have been used for correlating the spectral values of these chalcones ketones by

using single and multi-linear regression analysis. The impacts of substituents on the spectral data have been known on statistical analysis. By using Bauer-Kirby method the anti-microbial activities of these (*E*)-1-(4-bromophenyl)-3-(substituted phenyl)-2-propen-1-ones compounds are estimated.

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