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## Synthesis and effects of substituent on (*E*)-styryl-3-methyl-2-thienyl chalcones

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### ABSTRACT

Series of eleven substituted of (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-ones compounds by cross-aldol condensation reaction of 3-methylthiophene-2-carbaldehyde with various substituted acetaldehyde in the occurrence of Fly-Ash: H<sub>3</sub>PO<sub>4</sub> catalyst. The effect of catalytic activity of this fly-ash:H<sub>3</sub>PO<sub>4</sub> nanocatalyst was studied with the obtained yield of products under solvent-free conditions. The synthesized substituted (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds was characterized by physical constants, UV, FT-IR, <sup>1</sup>H & <sup>13</sup>C-NMR spectral data. The infrared group frequencies of  $\nu(\text{cm}^{-1})$  of CO<sub>s-cis</sub> & s-trans, CH<sub>ip</sub> and CH<sub>op</sub>, CH=CH<sub>op</sub>, >C=C<<sub>op</sub> modes, Nuclear Magnetic Resonance chemical shifts  $\delta(\text{ppm})$  of H <sub>$\alpha$</sub> , H <sub>$\beta$</sub> , CO, C <sub>$\alpha$</sub>  and C <sub>$\beta$</sub>  of these chalcones were correlated with single and multi-regression analyses of Swain-Lupton's *F* and *R* parameters and Hammett substituent constants.

**Keywords:** (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-ones, Fly-ash:H<sub>3</sub>PO<sub>4</sub> nanocatalyst, solvent-free synthesis, UV, FT-IR & NMR spectra, Hammett correlation analysis, Substituent effects

## 1. INTRODUCTION

Many kinds of chalcones are present various natural higher plants [1]. Chalcones have one or two aromatic benzene rings with carbon-carbon double bonded side chain. The unsaturated side chain contains Carbonyl carbon and carbon-carbon double system [2], which two aromatic rings are linked through the unsaturated carbonyl system, a three carbons of 1, 3-diphenyl-2-propene-1-one chalcones [3, 4]. Various methods have been reported for the preparation of chalcones. Some of them, commonly used for Claisen Schmidt reaction of condensation for equimolar quantities of aryl methyl ketone with aromatic aldehyde in the condition of alkali's like sodium hydroxide, potassium hydroxide, barium hydroxide and lithium hydroxide. The chalcone synthesis using acid catalyst like aluminum trichloride, dry hydrochloride, boron trifluoride, titanium tetrachloride and ruthenium trichloride [5-13] has also reported. To synthesize the chalcone derivative compounds in an approach of green chemistry more beneficiary to avoid pollution, strong acidic or basic condition and use of toxic reagents. Conventionally, condensation of hydroxyl substituted aryl carbonyl is very difficult as side products can be easily formed and unwanted product may be formed in this type of reactions.

When a green chemistry approach was applied for synthesis, it have tremendous features for synthesis for polyhydroxy chalcones with good yield and purity. Different strategies reported for chalcones synthesis include microwave supported synthesis [14-16]. To developing and designing of chemical process, in the term of Green chemistry means eliminate and reduce chemicals hazardous in the generation and use of normal environment. Solvents used in organic synthetic reactions are often toxic, expensive and disposal of such solvents is a serious problem to the environment. Thus, design of solvent free synthesis has received tremendous attention in recent years [17]. The *s*-cis and *s*-trans conformers are possible for chalcone structures. Among which trans chalcone stable in thermodynamically. In plants crude extracts and plants containing some pure chalcones extracts available in liquorice are commercially available due to its pharmacological applications.

A reactive  $\alpha$ ,  $\beta$ -unsaturated carbonyl system is reason for the color of the Chalcone compounds for the open chain flavonoids. Interestingly, reported biologically potential chalcones are responsible for the group of ketoethylene. In the synthesis of five and six membered ring pyrazole and pyrimidine compounds, chalcone is one of important intermediate [18]. Also flavonoids biosynthesis the chalcone compounds can be used as good intermediate [19].

In our research work explain with the synthesis of 3-methylthiophene-2-carbaldehyde with different substituted acetophenones to form aryl chalcone compounds and the structure of all the various synthesized chalcones were consigned on the creation of elemental analysis, UV, FT-IR,  $^1\text{H}$  &  $^{13}\text{C}$  NMR Spectral data.

Literature survey shows that there is not any information available regarding the research work of UV, IR and NMR spectral regression study of substituted (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds. The above spectral data of these (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds have been utilized for studying the relationships of Hammett correlation study through the quantitative structure activity.

## 2. EXPERIMENTAL

### 2. 1. Materials and Methods

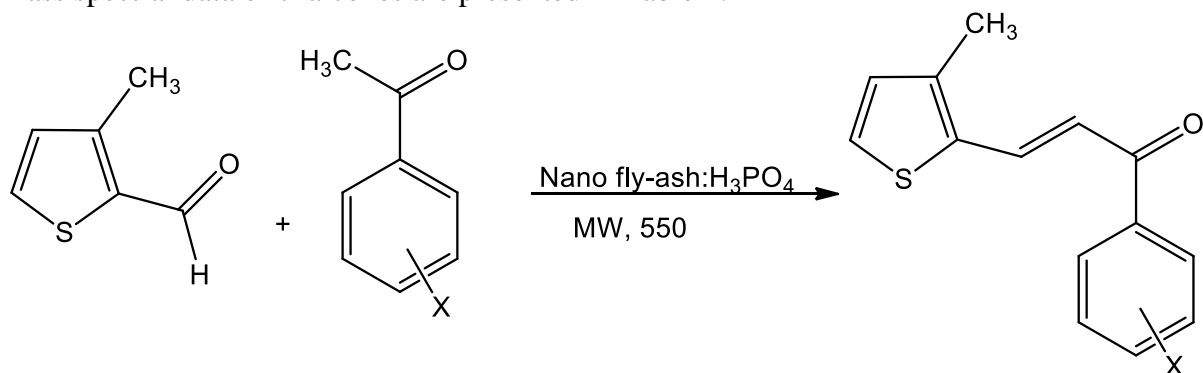
All chemicals purchased from Aldrich chemical company Bangalore. Melting point apparatus of Uncorrected Suntext machine used to detect the melting points of all aryl chalcones with open glass capillaries. Fly-ash was collected from Thermal Power Plant-II, Neyveli Lignite Corporation (NLC), Neyveli, Tamil Nadu. Using double beam (ELICO BL222) Bio-Spectrophotometer for UV spectra of the synthesized chalcones has been noted. IR spectra (KBr, 4000-400  $\text{cm}^{-1}$ ) have been noted on FT-IR AVATAR-300 spectrophotometer. BRUKER-500MHz NMR spectrometers have been used for noted proton and  $^{13}\text{C}$  spectra in  $\text{CDCl}_3$  solvent using internal standard is TMS. The micro analyses of these aryl chalcone compounds were performed in Thermofinnigan analyzer. SEM-EDS analysis of synthesized Fly-ash: $\text{H}_3\text{PO}_4$  nanocatalyst was done using FEI Quanta FEG 200 high-resolution scanning electron microscope. TEM image was recorded using Technai 10 Philips model transmission electron microscope with iTEM software. Particle analysis data for the catalyst was collected using Malvern Mastersizer 2000 particle size analyzer.

### 2.2. Preparation of $\text{H}_3\text{PO}_4$ Catalyst

About 2 g of fly-ash was put in a 100 mL Corning glass conical flask, 2 mL (1.96 g, 2 mmol) of phosphoric acid in 20 mL of isopropanol and 20 mL of double distilled water was added drop-wise and stirred well in a magnetic stirrer for 2 h. Solvent evaporation gave a dirty white fly-ash: $\text{H}_3\text{PO}_4$  catalyst. Further it was dried in a hot air oven for 3 h and stored in a vacuum desiccator [20]. The synthesized solid fly-ash: $\text{H}_3\text{PO}_4$  nanocatalyst was used as catalyst for synthesis of chalcones by condensation of aryl methyl ketones and aldehydes.

### 2. 3. General procedure for preparation of (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds.

Equimolar quantities of 3-methylthiophene-2-carbaldehyde(100mmol) and *meta* and *para* substituted acetophenones (100 mmol) and 0.15 g of fly-ash: $\text{H}_3\text{PO}_4$  nanocatalyst were placed in a Borosil round bottomed flask and mixed thoroughly. Microwave oven was utilized (Scheme 1) at 120  $^\circ\text{C}$  with the regular interval time 30s (Ragatech, RG 31L Scientific Microwave oven, 230 V A/C, 50 Hz, 2450 Hz, 1200 rpm (beam reflector)). After the treatment of the reaction mixture, it gave 95 % of the respective chalcones. The analytical and mass spectral data of chalcones are presented in Table 1.



**Scheme 1.** Synthesis of (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-ones

After complete transformation of the aldehydes as monitored by Thin Layer Chromatography, the mixture was about 20 minutes allowed to stand. The unreacted reagents are removed by filtration. The filtrate was washed with water and recrystallized from absolute ethanol, dried well and keep in a desiccator. The synthesized (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-ones have been confirmed by their physical constants, elemental analysis and spectral data. The physical constants, analytical and micro analysis data of these (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one were showed in Table 1.

The spectral values of synthesized substituted (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-ones are showed in Table 2 and Table-3.

**Table 1.** Physical constants of substituted (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-ones

Entry	X	M. F.	M. W.	Yield (%)	M. P. (°C)	Found (Calcd.)(%)		
						C	H	N
1	H	C <sub>14</sub> H <sub>12</sub> OS	228.31	96	120-121	72.46 (73.65)	5.22 (5.30)	-
2	3-Br	C <sub>14</sub> H <sub>11</sub> BrOS	307.21	92	123-124	53.98 (54.74)	3.58 (3.61)	-
3	4-Br	C <sub>14</sub> H <sub>11</sub> BrOS	307.21	91	130-131	54.36 (54.74)	3.46 (3.61)	-
4	3-Cl	C <sub>14</sub> H <sub>11</sub> ClOS	262.75	97	118-119	63.86 (64.00)	4.16 (4.22)	-
5	4-Cl	C <sub>14</sub> H <sub>11</sub> ClOS	262.75	94	110-111	53.88 (64.00)	4.10 (4.22)	-
6	4-F	C <sub>14</sub> H <sub>11</sub> FOS	246.30	95	124-125	66.98 (68.27)	4.46 (4.50)	-
7	4-I	C <sub>14</sub> H <sub>11</sub> IOS	354.21	93	128-129	47.27 (47.47)	3.01 (3.13)	-
8	4-OCH <sub>3</sub>	C <sub>15</sub> H <sub>14</sub> O <sub>2</sub> S	258.34	90	132-133	69.68 (69.74)	5.42 (5.46)	-
9	4-CH <sub>3</sub>	C <sub>15</sub> H <sub>14</sub> OS	242.34	92	120-121	73.28 (74.34)	5.68 (5.82)	-
10	3-NO <sub>2</sub>	C <sub>14</sub> H <sub>11</sub> NO <sub>3</sub> S	273.31	94	145-146	61.24 (61.52)	3.66 (4.06)	4.84 (5.12)
11	4-NO <sub>2</sub>	C <sub>14</sub> H <sub>11</sub> NO <sub>3</sub> S	273.31	93	142-143	61.48 (61.52)	3.98 (4.06)	4.96 (5.12)

**Table 2.** The UV absorption maxima ( $\lambda_{max}$ , nm), and infrared absorptions ( $\nu$ ,  $\text{cm}^{-1}$ ) frequencies of substituted (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds

Entry	X	UV (nm) $\lambda_{max}$	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>	C=C <sub>op</sub>
1	H	323	1678.17	1592.14	1184.6	755.25	1075.45	689.95
2	3-Br	327	1658.58	1587.43	1200.96	781.54	1042.08	670.84
3	4-Br	341	1644.94	1578.41	1205.51	727.29	1068.93	631.58
4	3-Cl	314	1659.89	1588.74	1205.61	757.98	1044.95	675.23
5	4-Cl	312	1682.82	1586.37	1227.01	708.91	1092.44	631.12
6	4-F	323	1658.04	1596.01	1209.67	803.37	1023.06	677.92
7	4-I	305	1655.43	1590.28	1205.00	791.93	1024.47	671.2
8	4-OCH <sub>3</sub>	323	1648.3	1582.33	1205.91	721.43	1037.94	654.37
9	4-CH <sub>3</sub>	322	1658.23	1601.66	1170.02	793.02	1021.03	683.82
10	3-NO <sub>2</sub>	299	1653.88	1587.22	1207.00	738.28	1085.04	573.57
11	4-NO <sub>2</sub>	310	1654.88	1576.2	1206.41	703.65	1041.92	637.87

**Table 3.** The chemical shifts of <sup>1</sup>H NMR ( $\delta$  ppm) of substituted (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-ones.

Entry	X	<sup>1</sup> H NMR (ppm)		<sup>13</sup> C NMR (ppm)		
		H $\alpha$	H $\beta$	CO	C $\alpha$	C $\beta$
1	H	7.238	7.799	187.75	120.91	135.46
2	3-Br	7.147	7.823	188.04	120.22	135.75
3	4-Br	7.221	8.051	188.58	119.05	136.11
4	3-Cl	7.169	7.471	188.16	120.3	135.03
5	4-Cl	7.024	7.883	196.94	121.87	135.12
6	4-F	7.177	7.816	187.83	120.45	136.44

7	4-I	7.149	7.816	188.7	120.3	136.75
8	4-OCH <sub>3</sub>	7.288	8.032	189.3	119.84	135.19
9	4-CH <sub>3</sub>	7.012	7.55	198.23	121.74	136.88
10	3-NO <sub>2</sub>	7.156	8.028	187.14	117.69	136.37
11	4-NO <sub>2</sub>	7.227	8.098	188.15	118.73	134.19

### 3. RESULTS AND DISCUSSION

#### 3. 1. Spectral linearity

In the current study the spectral linearity of synthesized (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one has been studied by evaluating the substituent effects. The spectral data observed for the (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one, UV  $\lambda_{\max}$  (nm), infrared  $\nu_{\text{C=O}_{\text{S-cis}}}$ ,  $\nu_{\text{C=O}_{\text{S-trans}}}$ ,  $\nu_{\text{CH}_{\text{ip}}}$ ,  $\nu_{\text{CH}_{\text{op}}}$ ,  $\nu_{\text{CH=CH}_{\text{op}}}$ ,  $\nu_{\text{C=C}_{\text{op}}}$ , the <sup>1</sup>H chemical shifts  $\delta$ (ppm) of H $\alpha$ , H $\beta$ , and carbon chemical shifts values of C=O, C $\alpha$  and C $\beta$  are correlation with various substituent constants [19-22].

##### 3. 1. 1. UV spectral study

The measured absorption maxima ( $\lambda_{\max}$  nm) data of the synthesized (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds have been recorded and presented in Table 2. These data are used to correlate the single and multi-linear correlation analysis [23, 24] with Hammett substituent constants  $\sigma$ ,  $\sigma^+$ ,  $\sigma_{\text{I}}$ ,  $\sigma_{\text{R}}$  and *F* and *R* parameters.

For the single and multi-linear correlation analysis employing the Hammett equation containing the absorption maxima is as following equation (1) below.

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

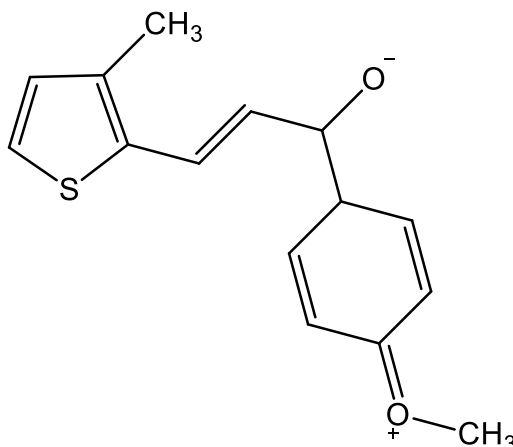
where  $\lambda_0$  is the frequency for the parent participant of the series.

From the Table 4, the Ultra Violet absorption maximum ( $\lambda_{\max}$  nm) values of all substituted (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds of Hammett constants  $\sigma$  ( $r = 0.900$ ),  $\sigma^+$  ( $r = 0.903$ ),  $\sigma_{\text{I}}$  ( $r = 0.903$ ),  $\sigma_{\text{R}}$  ( $r = 0.904$ ) and *R* parameter ( $r = 0.904$ ) have displayed satisfactory correlations. But, Ultra Violet absorption maximum ( $\lambda_{\max}$ nm) values of (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds of *F* parameter have given failed in correlations ( $r < 0.900$ ).

This is reason for weak field effects of substituents for expecting the reactivity on the UV absorption maximum ( $\lambda_{\max}$  nm) through resonance for the following conjugative structure as displayed in Figure 1.

All the correlations have shown negative  $\rho$  values. This indicates the substituent effect reverse in system respect to Ultra Violet absorption maximum ( $\lambda_{\max}$  nm) values in all substituted compounds. Some of the single parameter study correlations of failed for the UV absorption maximum ( $\lambda_{\max}$ nm) values with *F* parameter, it is concluded to go for multi

correlation analysis with Swain-Lupton's [25]. Though multi regression correlation there is satisfactory correlations are observed as presented in the following equations (2) and (3).



**Figure 1.** Resonance-conjugative structure.

$$UV(\lambda_{max}) = 320.39 (\pm 7.6521) - 14.0311 (\pm 15.4391) \sigma_I - 23.1586 (\pm 18.1078) \sigma_R \quad \dots (2)$$

(r = 0.950, n = 11, P > 95%)

$$UV(\lambda_{max}) = 319.89 (\pm 7.6521) - 14.9444 (\pm 14.5519) F - 22.1541 (\pm 14.8144) R \quad \dots (3)$$

(r = 0.953, n = 11, P > 95%)

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

The assigned infrared frequencies ( $\text{cm}^{-1}$ ) of  $\nu\text{CO}_{s-cis}$  and  $s-trans$  conformers,  $\nu\text{C-H}_{ip}$ ,  $\nu\text{C-H}_{op}$ ,  $\nu\text{CH}=\text{CH}_{op}$ ,  $\nu\text{C}=\text{C}_{op}$ , of substituted (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-ones are shown in Table 2.

The measured FT-IR frequency values are correlation analysis [20-24] with Hammett constants and *F* (Field) and *R* (Resonance) parameters using regression of single and multi-linear analysis. The correlation analysis, an absorption maximum of employing Hammett equation is shown below in equation (4).

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

where  $\nu_0$  is the frequency for the parent member of the series.

**Table 4.** The regression analysis results of UV absorption maxima ( $\lambda_{max}$ , nm), FT-IR absorptions ( $\nu$ ,  $cm^{-1}$ ) and NMR chemical shifts ( $\delta$  ppm) of substituted (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds with Hammett  $\sigma$ ,  $\sigma^+$ ,  $\sigma_I$ ,  $\sigma_R$  and *F* & *R* parameters.

Frequency	Constants	r	I	$\rho$	s	n	Correlated derivatives
$\lambda_{max}$	$\sigma$	0.900	321.90	-16.639	10.74	10	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.903	319.43	-8.136	11.58	9	H, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_I$	0.903	324.61	-16.577	11.55	9	H, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_R$	0.904	314.57	-25.281	11.05	9	H, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	<i>F</i>	0.828	323.85	-14.083	11.70	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	<i>R</i>	0.904	313.89	-21.552	11.01	9	H, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
$\nu_{COs-cis}$	$\sigma$	0.808	1660.06	-3.005	11.98	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.804	1659.56	-1.159	12.02	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_I$	0.829	1665.21	-14.835	11.48	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_R$	0.811	1660.28	6.539	11.95	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	<i>F</i>	0.833	1665.95	-16.078	11.33	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	<i>R</i>	0.821	1661.38	10.293	11.76	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
$\nu_{COs-trans}$	$\sigma$	0.948	1590.35	-10.749	6.76	9	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.940	1588.98	-6.591	7.07	10	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_I$	0.905	1595.09	-18.292	6.34	10	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_R$	0.825	1586.55	-9.578	7.49	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	<i>F</i>	0.904	1593.09	-12.718	7.05	10	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>



	<i>R</i>	0.823	1586.43	-7.459	7.52	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
<i>vC-Hip</i>	$\sigma$	0.838	1198.72	16.530	14.13	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.827	1201.07	8.696	14.69	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_I$	0.977	1183.35	48.669	9.67	10	H, 3-Br, 4-Br, 3-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_R$	0.819	1200.50	-14.499	14.98	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	<i>F</i>	0.971	1184.81	43.267	10.72	9	H, 3-Br, 4-Br, 3-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	<i>R</i>	0.815	1200.60	-9.825	15.08	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
		$\sigma$	0.903	761.24	-36.096	35.43	9
<i>vC-Hop</i>	$\sigma^+$	0.922	755.92	-17.862	36.64	9	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_I$	0.830	771.86	-48.003	35.78	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_R$	0.935	744.11	-63.631	35.25	9	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	<i>F</i>	0.814	761.42	-20.673	37.28	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	<i>R</i>	0.938	742.11	-55.771	35.02	9	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
		$\sigma$	0.833	1044.83	25.445	25.44	11
<i>vCH=CHop</i>	$\sigma^+$	0.835	1047.34	20.044	25.18	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_I$	0.817	1043.13	19.116	26.56	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_R$	0.843	1058.56	56.785	24.26	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	<i>F</i>	0.813	1050.12	1.309	26.96	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	<i>R</i>	0.949	1061.15	53.920	23.44	9	H, 3-Br, 4-Br, 3-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
		$\sigma$	0.906	668.44	-61.641	28.49	11
<i>vC=Cop</i>	$\sigma^+$	0.949	660.43	-36.985	31.06	10	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 4-NO <sub>2</sub>
	$\sigma_I$	0.906	690.45	-91.803	28.00	10	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 4-NO <sub>2</sub>

	$\sigma_R$	0.904	643.32	-79.803	31.84	10	H, 3-Br, 4-Br, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$F$	0.905	684.49	-73.772	30.61	9	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 4-NO <sub>2</sub>
	$R$	0.943	642.15	-62.521	32.29	10	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 4-NO <sub>2</sub>
$\delta H_\alpha$	$\sigma$	0.903	7.162	0.008	0.08	8	H, 3-Br, 4-Br, 3-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 3-NO <sub>2</sub>
	$\sigma^+$	0.801	7.164	-0.003	0.08	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_I$	0.816	7.141	0.059	0.08	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_R$	0.807	7.160	-0.031	0.88	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$F$	0.816	7.140	0.058	0.08	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$R$	0.816	7.156	-0.039	0.88	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
$\delta H_\beta$	$\sigma$	0.923	7.806	0.194	0.20	8	H, 3-Br, 4-Cl, 4-F, 4-I, 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.921	7.836	0.093	0.20	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 4-I, 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_I$	0.947	7.687	0.417	0.18	10	H, 3-Br, 4-Br, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_R$	0.820	7.880	0.208	0.20	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$F$	0.844	7.698	0.374	0.19	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$R$	0.814	7.875	0.121	0.21	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
$\delta C=O$	$\sigma$	0.839	190.94	-4.573	3.73	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.862	190.42	-3.228	3.75	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_I$	0.945	192.89	-7.616	3.61	9	3-Br, 4-Br, 3-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_R$	0.808	189.66	-1.664	4.04	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$F$	0.904	192.92	-7.420	3.60	8	3-Br, 4-Br, 3-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$R$	0.806	189.70	-0.986	4.05	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
$\delta C_\alpha$	$\sigma$	0.906	120.66	-2.444	0.99	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>

	$\sigma^+$	0.956	120.35	-1.556	1.08	10	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_I$	0.964	121.47	-3.488	1.00	10	H, 3-Br, 4-Br, 3-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_R$	0.942	119.72	-2.725	1.18	8	3-Br, 4-Br, 3-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$F$	0.959	121.36	-3.094	1.05	9	H, 3-Br, 4-Br, 3-Cl, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$R$	0.936	119.72	-1.942	1.22	8	3-Br, 4-Br, 3-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
$\delta C_\beta$	$\sigma$	0.903	135.94	-0.830	0.83	9	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-OCH <sub>3</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.902	135.81	-0.393	0.86	9	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_I$	0.826	136.12	-0.944	0.85	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_R$	0.813	135.63	-0.845	0.86	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$F$	0.812	135.93	-0.443	0.87	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$R$	0.824	135.58	-0.874	0.85	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-CH <sub>3</sub> , 4-OCH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>

r = Correlation co-efficient;  $\rho$  = slope; I = Intercept; s = Standard deviation; n = Number of substituents;

### 3. 2. 1. 1. IR Spectral Correlation of $\nu CO_{s-cis}$ (cm<sup>-1</sup>)

From the Table 4, the IR frequency  $\nu CO_{s-cis}$  (cm<sup>-1</sup>) values of all substituted (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds with Hammett constants  $\sigma$ ,  $\sigma^+$ ,  $\sigma_I$ ,  $\sigma_R$  and  $F$  and  $R$  parameters are failed correlations ( $r < 0.900$ ). This is the reason of weak field, polar, inductive and resonance effects of substituents for predicting the reactivity on the FT-IR frequency  $\nu CO_{s-cis}$  (cm<sup>-1</sup>) values through resonance as per the conjugative structure as shown in Figure 1.

All the correlations have shown negative  $\rho$  values except  $\sigma_R$  and  $R$  parameter. This indicates the substituent effect for reverse in operation with respect to FT-IR frequency  $\nu CO_{s-cis}$  (cm<sup>-1</sup>) values in all substituted compounds.

### 3. 2. 1. 2. FT-IR Spectral Correlation analysis of $\nu CO_{s-trans}$ (cm<sup>-1</sup>)

From the Table 4, the FT-IR frequency  $\nu CO_{s-trans}$  (cm<sup>-1</sup>) values except 4-Br and 4-OCH<sub>3</sub> substituents of substituted (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds with Hammett substituent constant  $\sigma$  ( $r = 0.948$ ) give satisfactory correlations. Except 4-OCH<sub>3</sub> substituents of the FT-IR frequency  $\nu CO_{s-trans}$  (cm<sup>-1</sup>) values of substituted (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds with Hammett constant  $\sigma^+$  ( $r = 0.940$ ) give satisfactory correlations.

Except 4-F substituent of the FT-IR frequency  $\nu\text{CO}_{s\text{-trans}}$  ( $\text{cm}^{-1}$ ) values of substituted (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds with Hammett constant  $\sigma_I$  ( $r = 0.905$ ) and  $F$  parameter ( $r = 0.904$ ) give satisfactory correlations.

However, IR frequency  $\nu\text{CO}_{s\text{-trans}}$  ( $\text{cm}^{-1}$ ) values of (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds with Hammett constant  $\sigma_R$  and  $R$  parameter are failed in correlations ( $r < 0.900$ ).

This is due to the reason for the weak resonance effect of substituents for expecting the reactivity on the IR frequency  $\nu\text{CO}_{s\text{-trans}}$  ( $\text{cm}^{-1}$ ) values through conjugative resonance structure as displayed in Figure 1.

All the correlations have shown negative  $\rho$  values. This indicates the operation of substituent effect reverse process to FT-IR frequency  $\nu\text{CO}_{s\text{-trans}}$  ( $\text{cm}^{-1}$ ) values in all substituted compounds.

### 3.2.1.3. IR Spectral Correlation of $\nu\text{C-H}_{ip}$ ( $\text{cm}^{-1}$ )

From the Table 4, it is evident that the IR frequency  $\nu\text{C-H}_{ip}$  ( $\text{cm}^{-1}$ ) values except 4-Cl substituent of substituted (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds of Hammett constant  $\sigma_I$  ( $r = 0.977$ ) give satisfactory correlations.

Except 4-Cl and 4-CH<sub>3</sub> substituents of the FT-IR frequency  $\nu\text{C-H}_{ip}$  ( $\text{cm}^{-1}$ ) values of substituted (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds with Hammett constant  $F$  parameter ( $r = 0.971$ ) give satisfactory correlations.

However, IR frequency  $\nu\text{C-H}_{ip}$  ( $\text{cm}^{-1}$ ) values of (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds with Hammett constants  $\sigma$ ,  $\sigma^+$ ,  $\sigma_R$  and  $R$  parameters failed correlations ( $r < 0.900$ ).

This is attributed to the weak resonance and polar effects of substituents for predicting the reactivity on the FT-IR frequency  $\nu\text{C-H}_{ip}$  ( $\text{cm}^{-1}$ ) values through resonance as per the conjugative structure as displayed in Figure 1.

All the correlations have shown positive  $\rho$  values except  $\sigma_R$  and  $R$  parameter. This indicates the operation of normal substituent effect with respect to IR frequency  $\nu\text{C-H}_{ip}$  ( $\text{cm}^{-1}$ ) values in all substituted compounds.

### 3.2.1.4. IR Spectral Correlation study of $\nu\text{C-H}_{op}$ ( $\text{cm}^{-1}$ )

From the Table 4, FT-IR frequency  $\nu\text{C-H}_{op}$  ( $\text{cm}^{-1}$ ) values except 4-Cl and 4-OCH<sub>3</sub> of substituted (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds of Hammett constants  $\sigma$  ( $r = 0.903$ ),  $\sigma^+$  ( $r = 0.922$ )  $\sigma_R$  ( $r = 0.935$ ) give satisfactory correlations.

Except 4-Cl and 4-F substituents of the FT-IR frequency  $\nu\text{C-H}_{op}$  ( $\text{cm}^{-1}$ ) values of substituted (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds with  $R$  parameter ( $r = 0.938$ ) give satisfactory correlations.

However, IR frequency  $\nu\text{C-H}_{op}$  ( $\text{cm}^{-1}$ ) values of (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds with Hammett constant  $\sigma_I$  and  $F$  parameters are failed in correlations ( $r < 0.900$ ).

This is the reason for the weak inductive and field effects of substituents for expecting the reactivity on the FT-IR frequency  $\nu\text{C-H}_{op}$  ( $\text{cm}^{-1}$ ) values through resonance for the conjugative structure as shown in Figure 1. All the correlations give positive  $\rho$  values. This indicates the normal substituent effect of FT-IR frequency  $\nu\text{C-H}_{op}$  ( $\text{cm}^{-1}$ ) values in all substituted (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds.

### 3. 2. 1. 5. IR Spectral study Correlation of $\nu\text{-CH=CH}_{-op}$ ( $\text{cm}^{-1}$ )

From the Table-4, FT-IR frequency  $\nu\text{-CH=CH}_{-op}$  ( $\text{cm}^{-1}$ ) values of except 4-Cl and 4- $\text{CH}_3$  of substituted (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds with *R* parameters ( $r = 0.949$ ) give satisfactory correlations.

However, IR frequency  $\nu\text{-CH=CH}_{-op}$  ( $\text{cm}^{-1}$ ) values of (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds with Hammett constants  $\sigma$ ,  $\sigma^+$ ,  $\sigma_R$ ,  $\sigma_I$  and *F* parameters are failed in correlations ( $r < 0.900$ ).

This is the reason for the weak inductive, polar, resonance and field effects of substituents for predicting the reactivity on the FT-IR frequency  $\nu\text{-CH=CH}_{-op}$  ( $\text{cm}^{-1}$ ) values through resonance for conjugative structure as presented in Figure-1.

All the correlations give positive  $\rho$  values. This indicates the operation of normal substituent effect of FT-IR frequency  $\nu\text{-CH=CH}_{-op}$  ( $\text{cm}^{-1}$ ) values in all substituted (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds.

### 3. 2. 1. 6. IR Spectral study Correlation of $\nu\text{-C=C}_{-op}$ ( $\text{cm}^{-1}$ )

From the Table-4, the FT-IR frequency  $\nu\text{-C=C}_{-op}$  ( $\text{cm}^{-1}$ ) values of all substituted (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds with Hammett constant  $\sigma$  ( $r = 0.906$ ) give satisfactory correlations.

Except 4- $\text{NO}_2$  substituent of the FT-IR frequency  $\nu\text{-C=C}_{-op}$  ( $\text{cm}^{-1}$ ) values of substituted (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds with Hammett constants  $\sigma^+$  ( $r = 0.949$ ),  $\sigma_I$  ( $r = 0.906$ ) and ( $r = 0.943$ ) *R* parameter give satisfactory correlations.

Except 3-Cl substituent of the FT-IR frequency  $\nu\text{-C=C}_{-op}$  ( $\text{cm}^{-1}$ ) values of substituted (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds with Hammett constants  $\sigma_R$  ( $r = 0.904$ ) give satisfactory correlations.

Except 4-F and 3- $\text{NO}_2$  substituents of the FT-IR frequency  $\nu\text{-C=C}_{-op}$  ( $\text{cm}^{-1}$ ) values of substituted (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds with *F* parameter ( $r = 0.905$ ) give satisfactory correlations.

All the correlations give negative  $\rho$  values. This indicates the operation of reverse substituent effect with respect to FT-IR frequency  $\nu\text{-C=C}_{-op}$  ( $\text{cm}^{-1}$ ) values in all substituted (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds.

Some of the single parameter regression poor correlations for the FT-IR frequency  $\nu\text{CO}_{s-cis}$ ,  $\nu\text{CO}_{s-trans}$ ,  $\nu\text{C-H}_{ip}$ ,  $\nu\text{C-H}_{op}$ ,  $\nu\text{CH=CH}_{-op}$ ,  $\nu\text{C=C}_{-op}$  ( $\text{cm}^{-1}$ ) values with Hammett substituent constants and *F* & *R* parameter, it is decided to go for multi correlation analysis with Swain-Lupton's [25] parameters. Whereas looking for the multi correlation analysis there is satisfactory correlations are observed as give in the following equations (5) to (16).

$$\nu\text{CO}_{cis}(\text{cm}^{-1}) = 1666.84(\pm 8.2419) - 15.8173(\pm 16.6290)\sigma_I + 8.9323(\pm 19.5035)\sigma_R \quad \dots(5)$$

( $r = 0.933$ ,  $n = 11$ ,  $P > 90\%$ )

$$\nu\text{CO}_{cis}(\text{cm}^{-1}) = 1667.68(\pm 7.8195) - 15.7030(\pm 15.5795)F + 9.6613(\pm 15.8604)R \quad \dots(6)$$

( $r = 0.955$ ,  $n = 11$ ,  $P > 95\%$ )

$$\nu\text{CO}_{trans}(\text{cm}^{-1}) = 1593.82(\pm 4.4970) - 17.5306(\pm 9.0733)\sigma_I - 6.9264(\pm 10.6417)\sigma_R \quad \dots(7)$$

( $r = 0.960$ ,  $n = 11$ ,  $P > 95\%$ )

$$\nu_{\text{CO}_{\text{trans}}}(\text{cm}^{-1}) = 1591.66(\pm 4.7813) - 13.0282(\pm 9.5262)F - 7.9840(\pm 9.6980)R \quad \dots(8)$$

(r = 0.948, n = 11, P > 90%)

$$\nu_{\text{CH}_{\text{ip}}}(\text{cm}^{-1}) = 1179.3054(\pm 6.2016) + 51.1145(\pm 12.5125)\sigma_{\text{I}} - 22.2311(\pm 14.6754)\sigma_{\text{R}} \dots(9)$$

(r = 0.982 n = 11, P > 95%)

$$\nu_{\text{CH}_{\text{ip}}}(\text{cm}^{-1}) = 1183.3715(\pm 7.4333) + 42.9531(\pm 14.8100)F - 8.0952(\pm 15.0771)R \quad \dots(10)$$

(r = 0.972 n = 11, P > 95%)

$$\nu_{\text{CH}_{\text{op}}}(\text{cm}^{-1}) = 761.40(\pm 24.5701) - 41.6995(\pm 49.5729)\sigma_{\text{I}} - 57.3239(\pm 58.1420)\sigma_{\text{R}} \quad \dots(11)$$

(r = 0.944 n = 11, P > 90%)

$$\nu_{\text{CH}_{\text{op}}}(\text{cm}^{-1}) = 751.29(\pm 24.3795) - 22.8756(\pm 48.5731)F - 56.6926(\pm 49.4490)R \quad \dots(12)$$

(r = 0.939 n = 11, P > 90%)

$$\nu_{\text{CH}=\text{CH}_{\text{op}}}(\text{cm}^{-1}) = 1053.13(\pm 17.4930) + 13.0902(\pm 35.2942)\sigma_{\text{I}} + 54.8050(\pm 41.3951)\sigma_{\text{R}} \dots(13)$$

(r = 0.945 n = 11, P > 90%)

$$\nu_{\text{CH}=\text{CH}_{\text{op}}}(\text{cm}^{-1}) = 1059.78(\pm 16.5316) + 3.4094(\pm 32.9372)F + 54.0574(\pm 33.5312)R \quad (14)$$

(r = 0.945 n = 11, P > 90%)

$$\nu_{\text{C}=\text{C}_{\text{op}}}(\text{cm}^{-1}) = 678.37(\pm 17.7938) - 84.5208(\pm 35.9011)\sigma_{\text{I}} - 66.2244(\pm 42.1068)\sigma_{\text{R}} \dots(15)$$

(r = 0.972 n = 11, P > 95%)

$$\nu_{\text{C}=\text{C}_{\text{op}}}(\text{cm}^{-1}) = 672.77(\pm 18.3289) - 76.3209(\pm 36.5181)F - 65.5962(\pm 37.1767)R \quad \dots(16)$$

(r = 0.966 n = 11, P > 95%)

### 3. 3. The spectral study of NMR

In NMR spectral values, the proton and the <sup>13</sup>C chemical shifts values (δ) depends nuclei present on the electronic environment. The assigned chemical shifts (ppm) have been correlated with reactivity parameters using Hammett equation [20-24] in the form of (17).

$$\delta = \rho\sigma + \delta_0 \quad \dots(17)$$

where δ<sub>0</sub> is the frequency for the parent participant of the series.

#### 3. 3. 1. Spectral <sup>1</sup>H NMR Correlation

##### 3. 3. 1. 1. Spectral <sup>1</sup>H NMR Correlations of H<sub>α</sub>(ppm)

From the Table-4, the assigned H<sub>α</sub> chemical shifts(δ ppm) values of except, 4-Cl, 4-CH<sub>3</sub> and 4-NO<sub>2</sub> substituents of substituted (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds with Hammett constant σ (r = 0.903) give satisfactory correlations.

However, H<sub>α</sub> chemical shifts (δ ppm) values of (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds with Hammett constants σ<sup>+</sup>, σ<sub>I</sub>, σ<sub>R</sub> and *R* and *F* parameters are failed in correlations (r < 0.900).

This is reason for weak inductive, polar, resonance and field effects of substituents for predicting the reactivity on the H $\alpha$  chemical shifts ( $\delta$  ppm) values through resonance for the conjugative structure as shown in Figure-1.

All the correlations give  $\rho$  values for positive values except  $\sigma^+$ ,  $\sigma_R$  and R parameter. It shows the operation of normal effect of substituents with respect to H $\alpha$  chemical shifts ( $\delta$  ppm) values in all substituted (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds.

### 3. 3. 1. 2. Spectral $^1\text{H}$ NMR Correlations of H $\beta$ (ppm)

From the Table 4, the assigned H $\beta$  chemical shifts ( $\delta$  ppm) values of except 4-Br, 3-Cl and 4-OCH $_3$  substituents of the substituted (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds with Hammett constant  $\sigma$  ( $r = 0.923$ ) give satisfactory correlations.

Except 3-Cl and 4-OCH $_3$  substituents of all the substituted (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds with Hammett constant  $\sigma^+$  ( $r = 0.921$ ) give satisfactory correlations.

Except 3-Cl substituent of the substituted (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds with Hammett constant  $\sigma_I$  ( $r = 0.947$ ) give satisfactory correlations.

However, H $\beta$  chemical shifts ( $\delta$  ppm) values of (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds with Hammett constants  $\sigma_R$  and R and F parameters are failed in correlations ( $r < 0.900$ ).

This is reason for the weak resonance and field effects of substituents for predicting the reactivity on the H $\beta$  chemical shifts ( $\delta$  ppm) values through resonance for the following conjugative structure is displayed in Figure 1.

All the correlations give positive  $\rho$  values. This indicates the normal substituent effect for the H $\beta$  chemical shifts ( $\delta$  ppm) values in all substituted (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds.

Few single parameter regressions may fail for the  $^1\text{H}$ NMR Spectral Correlations H $\alpha$  (ppm) and H $\beta$  (ppm) values with Hammett substituent constants and R and F parameter, it is decided to go for multi correlation analysis with Swain-Lupton's [25] parameters. While looking for the multi regression analysis there is satisfactory correlations are observed as give in the following equations (18) to (21).

$$\delta H_{\alpha}(\text{ppm}) = 7.1331(\pm 0.0636) + 0.0636(\pm 0.1284)\sigma_I - 0.0409(\pm 0.1506)\sigma_R \quad \dots(18)$$

( $r = 0.912$ ,  $n = 11$ ,  $P > 90\%$ )

$$\delta H_{\alpha}(\text{ppm}) = 7.1339(\pm 0.0617) + 0.0567(\pm 0.1229)F - 0.0368(\pm 0.1251)R \quad \dots(19)$$

( $r = 0.913$ ,  $n = 11$ ,  $P > 90\%$ )

$$\delta H_{\beta}(\text{ppm}) = 7.7142(\pm 0.1340) + 0.4012(\pm 0.2704)\sigma_I + 0.1482(\pm 0.3172)\sigma_R \quad \dots(20)$$

( $r = 0.949$ ,  $n = 11$ ,  $P > 90\%$ )

$$\delta H_{\beta}(\text{ppm}) = 7.7229(\pm 0.1324) + 0.3794(\pm 0.2638)F + 0.1366(\pm 0.2686)R \quad \dots(21)$$

( $r = 0.947$ ,  $n = 11$ ,  $P > 90\%$ )

### 3. 3. 2. <sup>13</sup>C Nuclear Magnetic Resonance Spectral Correlation

#### 3. 3. 2. 1. <sup>13</sup>C Nuclear Magnetic Resonance Spectral Correlations of C=O (ppm)

From the Table 4, the assigned C=O chemical shifts ( $\delta$  ppm) values of except 4-Cl substituent and parent of substituted (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds with Hammett constants  $\sigma_I$  ( $r = 0.945$ ) give satisfactory correlations.

Except parent, 4-Cl and 4-CH<sub>3</sub> substituent of substituted (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds with *F* parameter ( $r = 0.904$ ) give satisfactory correlations.

However, C=O chemical shifts ( $\delta$  ppm) values of (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds with Hammett constants  $\sigma$ ,  $\sigma^+$ ,  $\sigma_R$  and *R* parameter are failed for the correlations ( $r < 0.900$ ).

This is reason for the weak resonance and polar effects of substituents for expecting the reactivity on the C=O chemical shifts values ( $\delta$  ppm) values through resonance for the following conjugative structure as displayed in Figure 1.

All the correlations give negative  $\rho$  values. This indicates the operation of reverse substituent effect with respect to C=O chemical shifts ( $\delta$  ppm) values in all substituted (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds.

#### 3. 3. 2. 2. <sup>13</sup>C NMR Spectral Correlations of C $\alpha$ (ppm)

From the Table 4, the assigned C $\alpha$  chemical shifts ( $\delta$  ppm) values of substituted (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds with Hammett constants  $\sigma$  ( $r = 0.906$ ) give satisfactory correlations.

Except 4-OCH<sub>3</sub> substituent of substituted (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds with Hammett constant  $\sigma^+$  ( $r = 0.956$ ) give satisfactory correlations.

Except 4-Cl substituent of substituted (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds with Hammett constant  $\sigma_I$  ( $r = 0.964$ ) give satisfactory correlations.

Except parent, 4-Cl and 4-CH<sub>3</sub> substituents of substituted (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds with Hammett constant  $\sigma_R$  ( $r = 0.942$ ) and *R* ( $r = 0.936$ ) parameter give satisfactory correlations.

Except 4-Cl and 4-F substituents of substituted (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds with *F* parameter ( $r = 0.959$ ) give satisfactory correlations. All the correlations give negative  $\rho$  values. This indicates the operation of substituent effect reverse in process with respect to C=O chemical shifts ( $\delta$  ppm) values in all substituted

(*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds.

#### 3. 3. 2. 3. <sup>13</sup>C NMR Spectral Correlations of C $\beta$ (ppm)

From the Table 4, the assigned C $\beta$  chemical shifts ( $\delta$  ppm) values of except 4-OCH<sub>3</sub> and 3-NO<sub>2</sub> substituents of substituted (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds of Hammett constants  $\sigma$  ( $r = 0.903$ ) and  $\sigma^+$  ( $r = 0.902$ ) give satisfactory correlations. However, C $\beta$  chemical shifts ( $\delta$  ppm) values of (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds with Hammett constants  $\sigma_I$ ,  $\sigma_R$  and *R* and *F* parameters are failed in correlations ( $r < 0.900$ ).



This is reason for the weak resonance, field and inductive effects of substituents for expecting the reactivity on the C<sub>β</sub> chemical shifts (δ ppm) values through resonance for the following conjugative structure as shown in Figure 1.

All the correlations give negative ρ values. This indicates the reverse substituent effect for the respect to C<sub>β</sub> chemical shift values (δ ppm) values in all substituted (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds.

Some of the single parameter regression analysis failed for the <sup>13</sup>C Nuclear Magnetic Resonance Spectral Correlations C=O (ppm), C<sub>α</sub> (ppm) and C<sub>β</sub> (ppm) values with Hammett substituent constants and *R* and *F* parameter, it is decided to go for multi correlation analysis with Swain-Lupton's [25] parameters. While looking for the multi correlation analysis there is satisfactory correlations are observed as give in the following equations (22) to (27).

$$\delta\text{CO}(\text{ppm}) = 192.79(\pm 2.6283) - 7.5597(\pm 5.3029)\sigma_I - 0.5209(\pm 6.2196)\sigma_R \dots(22)$$

$$(r = 0.945, n = 11, P > 90\%)$$

$$\delta\text{CO}(\text{ppm}) = 192.69(\pm 2.5361) - 7.4703(\pm 5.0530)F - 1.2872(\pm 5.1441)R \dots(23)$$

$$(r = 0.946, n = 11, P > 90\%)$$

$$\delta\text{C}_\alpha(\text{ppm}) = 121.0656(\pm 0.6494) - 3.2427(\pm 1.3104)\sigma_I - 2.2347(\pm 1.5369)\sigma_R \dots(24)$$

$$(r = 0.973, n = 11, P > 95\%)$$

$$\delta\text{C}_\alpha(\text{ppm}) = 120.9959(\pm 0.6542) - 3.1748(\pm 1.3034)F - 2.0706(\pm 1.3269)R \dots(25)$$

$$(r = 0.907, n = 11, P > 90\%)$$

$$\delta\text{C}_\beta(\text{ppm}) = 135.99(\pm 0.6104) - 0.8663(\pm 1.2316)\sigma_I - 0.7143(\pm 1.4445)\sigma_R \dots(26)$$

$$(r = 0.930, n = 11, P > 90\%)$$

$$\delta\text{C}_\beta(\text{ppm}) = 135.77(\pm 0.5979) - 0.4782(\pm 1.1913)F - 0.8935(\pm 1.2128)R \dots(27)$$

$$(r = 0.928, n = 11, P > 90\%)$$

#### 4. CONCLUSIONS

The series of eleven numbers of substituted (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compound has been synthesized using condensation method of 3-methylthiophene-2-carbaldehyde and substituted acetophenones. These synthesized substituted (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one compounds has been characterized by their phys,ical constants, spectral data. The UV, IR, proton and <sup>13</sup>C NMR spectral value of these (*E*)-3-(3-methylthiophen-2-yl)-1-phenylprop-2-en-1-one has been correlation analysis with the substituent constants of Hammett and *F* and *R* parameters. Substituent effect studied through statistical analyses from the spectral values. UV, IR and <sup>13</sup>C Nuclear Magnetic Resonance spectral correlations produced maximum number of satisfactory correlations. But <sup>1</sup>H spectral values are failed with some Hammett substituents constants and *F* and *R* parameters. But the multi-regression analyses give satisfactory correlations.

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### References

- [1] Star AW, Marby TJ, (1971). *Flavanoid front exudates from two Jamaican ferns*, Pityrogramma tartarea and P. calomelanos, *Phytochem.* 10: 2812-2817.
- [2] Dhar DN, (1981). *The Chemistry of Chalcones and Related Compounds*, Wiley. 213.
- [3] Z. Nowakowska., (2007). A review of anti-infective and anti-inflammatory chalcones, *Eur. J. Med. Chem.* 42: 125-137.
- [4] Maayan S, Ohad N, Soliman K, (2005). Chalcones as potent tyrosinase inhibitors: the importance of a 2,4-substituted resorcinol moiety, *Bio. Org. Med. Chem.* 13(2): 433-441
- [5] Daskiewicz JB, Depeint F, Viornery L, Bayet C, Comte-Sarrazin G, Comte G, Gee MJ, Johnson IT, Ndjoko K, Hostettmann K, Barron D, (2005). Effects of flavonoids on cell proliferation and caspase activation in a human colonic cell line HT29: an SAR study, *J. Med. Chem.* 48: 2790-2804.
- [6] Azad M, Munawar ali M, (2007). Antimicrobial Activity and Synthesis of Quinoline-Based Chalcones, *J. App. Sci.* 7: 2485-2489.
- [7] Prasad Y, Kumar P, Kumar PR, (2008). Synthesis and Antimicrobial Activity of Some New Chalcones of 2-Acetyl Pyridine, *E. J. Chem.* 5: 144-148.
- [8] Iglesias M, Marinas JM, Sinisterra JV, (1987). Ba(OH)<sub>2</sub> as catalyst in organic reactions: Part XVI-Contribution to the study of the michael addition mechanism to chalcone in interfacial solid-liquid conditions, *Tetrahedron* 43: 2335-2342.
- [9] Savanth MD, Chakraborti K, (2006). LiOH·H<sub>2</sub>O as a novel dual activation catalyst for highly efficient and easy synthesis of 1,3-diaryl-2-propenones by Claisen-Schmidt condensation under mild conditions, *J. Mol. Catal.* 244: 20-24.
- [10] Calloway NO, Green LD, (1937). Calloway NO, Green LD. Reactions in the Presence of Metallic Halides. α,β-Unsaturated Ketone Formation as a Side Reaction in Friedel-Crafts Acylations, *J. Am. Chem. Soc.* 59: 809-811.
- [11] Chitra M, Rajendran TV, Duraipandiyam V, Rajan YC, Reuben Jonathan D, (2010). Study on the Synthesis and Bactericidal Activity of Certain Copolyesters Containing Bischalcone Moiety in the Main Chain, *Ind. J. Sci. Technol.* 3: 890-893.
- [12] Narender T, Reddy KP, (2007). A simple and highly efficient method for the synthesis of chalcones by using borontrifluoride-etherate, *Tetrahedron Lett.* 48: 3177-3180.
- [13] Mazza L, Guaram A, (1980). An Improved Synthesis of 1,3-Diphenyl-2-buten-1-ones (β-Methylchalcones), *Synthesis* 1: 41-43.
- [14] [Jayapal MR, (2010). Synthesis and characterization of 2, 6-Dihydroxy substituted chalcones using PEG-400 as a recyclable solvent, *J. Pharm. Sci and Res.*, 1: 125-137.

- [15] Kazi A, Deshmukh S, Aalam KP, (2013). Microwave - assisted synthesis of 2-hydroxy chalcones and their comparative study with conventional method, *Indo. Amer. J. Pharm. Res.* 3(5): 3496-3502.
- [16] Vaidya SS, Mahajan SS, (2011). Microwave assisted synthesis and biological evaluation of substituted chalcones, *Int. J. Res. Pham. Biomed. Sci.* 2(4): 1553-1561.
- [17] Tao J, Kazlauskas R, Hoboken NJ, (2011). Microbial bioprocesses for industrial-scale chemical production. In: *Biocatalysis for Green Chemistry and Chemical Process Development*, John Wiley and Sons, 429-467.
- [18] Kaur N, Kishore D, (2013). Application of Chalcones in Heterocycles Synthesis: Synthesis of 2-(isoxazolo, pyrazolo and pyrimido) Substituted Analogues of 1,4-benzodiazepin-5-carboxamides Linked Through an Oxyphenyl Bridge, *J. Chem. Sci.* 125: 555-560.
- [19] Ávila HP, Smânia EDFA, Monache FD, Smânia Júnior A, (2008). Structure Activity Relationship of Antibacterial Chalcones, *Bioorg. Med. Chem.* 16: 9790-9794.
- [20] John Joseph S, Ranganathan K, Suresh R, Arulkumaran R, Sundararajan R, Kamalakkannan D, Sakthinathan SP, Vanangamudi G, Dineshkumar S, Thirumurthy K, Muthuvel I, Thirunarayanan G, Viveksarathi K, (2017). Synthesis, Characterization and Synthetic Applications of Fly-ash:H<sub>3</sub>PO<sub>4</sub> Nanocatalyst, *Mat. Sci. App. Chem.* 34: 12-20.
- [21] Sakthinathan SP, Suresh R, Kamalakkannan D, Mala V, Sathiyamoorthi K, Thirunarayanan G, (2018). Microwave assisted synthesis, spectral correlation and antimicrobial evaluation of some aryl imines, *J. Chil. Chem. Soc.* 63(2), 3918-3923.
- [22] Manikandan V, Balaji S, Senbagam R, Vijayakumar R, Rajarajan M, Vanangamudi G, Arulkumaran R, Sundararajan R, Thirunarayanan G, (2018). Synthesis and spectral correlation studies of some (E)-N'-1-(substituted benzylidene) benzohydrazides, *World Sci. News* 111, 26-39.
- [23] Jaffee HH, (1953). A reexamination of the Hammett equation. *Chemical Reviews*, 53: 191-261.
- [24] Stewart R, Yates K, (1960). The position of protonation of the carboxyl group, *J. Am. Chem. Soc.* 80: 4059-4061.
- [25] Swain CG, Lupton EC, (1968). Field and resonance components of substituent effects, *J. Am. Chem. Soc.* 90: 4328-4337.