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Synthesis and spectral Hammett correlation analysis of some (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds

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ABSTRACT

A series of substituted of (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds by cross-aldol condensation reaction of 5-bromothiophene-2-carbaldehyde with various substituted acetaldehyde in the presence sodium hydroxide (base). The synthesized substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds was characterized by physical constants, UV, FT-IR, ^{1}H & ^{13}C-NMR spectral data. The group frequencies of infrared $\upsilon(cm^{-1})$ of CO *s-cis* and *s-trans*, CH in-plane and out of plane, CH=CH out of plane, >C=C< out of plane modes, NMR chemical shifts δ (ppm) of H_{α}, H_{β}, CO, C_{α} and C_{β} of these chalcones were correlated with Hammett substituent constants, *F* and *R* parameters using single and multi-regression analyses.

Keywords**:** (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-ones, UV, FT-IR and NMR spectra, Substituent constants, Hammett correlation analysis, Substituent effects

1. INTRODUCTION

Chalcones are one of the major classes of natural products with widespread distribution in fruits, vegetables, spices, tea and soy based foodstuff have been recently subjects of great interest for their interesting pharmacological activities [1]. Many alkyl-alkyl, alkyl-aryl and aryl-aryl categories of chalcones have been synthesized and extracted from natural plants by organic chemists. The general method for the synthesis of the aryl chalcones is the reaction of aromatic ketones and various substituted aromatic aldehydes in solvents like ethanol [2,3], and also aromatic aldehydes and various substituted aromatic ketones in solvents like ethanol. The basic skeleton of chalcones widely in natural products and which are known to have multi-pronged activity [4]. Many of the chalcones are used as agrochemicals and drugs [5,6]. Chalcones are used for well-known intermediate compounds for synthesizing various pyrimidines and pyrazoles [7].

The vibrational stretches of carbonyl groups gave two molecular conformers in unsaturated ketones such as s-cis and s-trans isomers. The s-cis carbonyl group stretches are higher than those of the s-trans carbonyl group. Based on this, the structure of molecular equilibration can be predicted in geometrical isomers, keto-enol tautomers in unsaturated carbonyl compounds [8,9], alkenes, alkynes, styrenes, nitro-styrenes and naphthyl ketones and their esters [10]. Moraleda et. al. [11] have studied to found good correlation of α,β-unsaturated carbonyl compounds with half-wave potential, LUMO-HOMO energies with Hammett σ*p* constants. Correlation analysis have been applied for studying the transition states of reaction mechanism [12], enol-enone tautomerism, assessment of substituent effects in oligopeptides [13], qualitative and quantitative analysis [14-16], electrochemical redox behaviour [17].

In present research work the authors have explain with the reaction of 5-bromothiophene-2-carbaldeyde with different substituted acetophenones to form (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds and the structure of all the synthesized chalcones were consigned on the creation of elemental analysis, UV, FT-IR, ^{1}H and ^{13}C NMR Spectral data. Literature survey shows that there is no information available regarding the study of UV, IR and NMR spectral correlation of substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds. The above spectral data of these (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds have been utilized for studying the quantitative structure activity relationships through Hammett correlations.

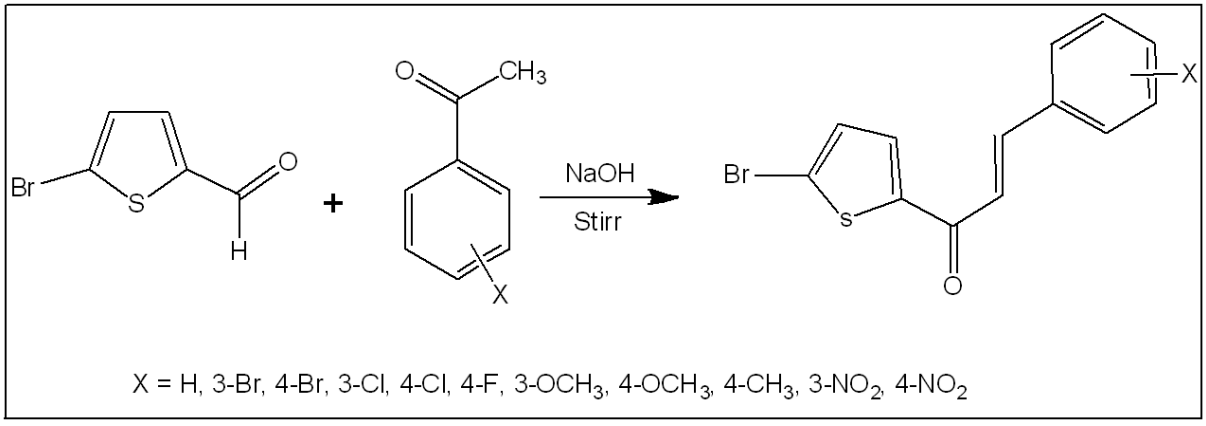
2. EXPERIMENTAL

2. 1. Methods and Materials

All chemicals procured from Aldrich chemical company Bangalore. Uncorrected Suntex melting point apparatus are detect the melting points of all aryl chalcones used by the open glass capillaries. The UV spectra of the chalcones synthesized have been noted using double beam-ELICO BL222 Bio-Spectrophotometer. Infrared spectra (KBr, 4000-400 cm^{-1}) have been recorded on FT-IR AVATAR-300 spectrophotometer. BRUKER-500MHz Nuclear Magnetic Resonance spectrometers have been used for noted proton and ^{13}C spectra in $CDCl_3$ solvent using internal standard is TMS. The micro analyses of these aryl chalcone compounds were performed in Thermofinnigan analyzer.

2. 2. General procedure for synthesis of (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds

All (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds have been synthesized and their purities were examined by the data reported in the literature [18]. An appropriate mixture of 5-bromothiophene-2-carbaldehyde (100 mmol) and *ortho*, *meta* and *para* substituted acetophenones (100 mmol) and aqueous sodium hydroxide (200 ml 0.5 M) in presence of absolute ethyl alcohol (**Scheme 1**) are taken in the conical flask. The above reactants are vigorously stirred for 30 minutes at room temperature. After complete conversion of the aldehydes as examined by TLC method, the mixture was permitted to stand 20 minutes. Remove the reagents using filtration method. The distilled water is used to wash the filtrate. After the washing process the filtrate was recrystallized using absolute ethyl alcohol and the products are well dried and keep in a desiccator.



Scheme 1. Synthesis of (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds.

3. RESULTS AND DISCUSSION

In the current study the spectral linearity of synthesized (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one has been studied by evaluating the substituent effects. The spectral observed data such as UV λmax (nm), infrared νC=O*s-cis* and *s-trans*, CH in-plane and out of plane, CH=CH out of plane, >C=C< out of plane modes, NMR chemical shifts δ(ppm) of H_α, H_β, CO, C_α and C_β of these (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-ones are presented in **Tables 1 and 2**. These spectroscopic data were correlated with various substituent constants [19-22].

3. 1. UV spectral study

The measured absorption maxima (λ_{max} nm) data of the synthesized (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds have been noted and presented in **Table 2.** These data are used to correlate the single and multi-linear regression analysis [20-23] with Hammett substituent constants and *F* and *R* parameters. The results of statistical analysis are presented in **Table 3**.

For the correlation analysis employing the Hammett equation containing the absorption maxima equation (1) is as shown below

.

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

where: λo is the frequency for the parent participant of the series.

From the **Table 3**, it is evident that the Ultra violet absorption maximum (λ_{max}nm) values of all substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds of Hammett substituent constants σ_R (r = 0.905), F parameter (r = 0.905) and R parameter (r = 0.905) have shown satisfactory correlations.

However, UV absorption maximum (λ_{max} nm) values of (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds of Hammett substituent constants σ, σ^+ and σ_I have shown poor correlations (r < 0.900). The conjugative structure of resonance is predicting the reactivity on UV absorption is attributed for weak polar and inductive effects of substituents as shown in **Figure 1.**

Table 1. The ultraviolet absorption maxima ($\lambda_{max,}$ nm), and infrared absoptions (υ, cm^{-1}) spectral values of substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds

Entry	X	UV (λ_{max}, nm)	IR ν (cm^{-1})					
			CO *s-cis*	CO *s-trans*	CH*ip*	CH*op*	CH=CH*op*	C=C*op*
1	H	265.0	1658.78	1587.42	1197.79	781.17	1039.63	522.71
2	3-Br	328.0	1654.92	1577.77	1199.72	790.81	1041.56	530.42
3	4-Br	322.0	1654.92	1589.34	1111.00	794.64	1068.56	524.64
4	3-Cl	323.0	1653.00	1583.56	1199.72	798.53	1016.49	538.14
5	4-Cl	322.0	1656.85	1591.27	1176.58	790.81	1016.49	532.35
6	4-F	348.0	1666.50	1595.13	1663.08	798.53	1045.42	576.07
7	3-OCH_3	333.0	1658.78	1579.70	1193.94	719.45	1022.27	582.50
8	4-OCH_3	313.0	1656.85	1597.06	1166.93	790.81	1020.34	596.00
9	4-CH_3	316.0	1658.78	1577.77	1188.15	790.81	1024.20	567.07
10	3-NO_2	310.0	1656.85	1597.06	1166.93	790.81	1020.34	582.50
11	4-NO_2	315.0	1654.92	1581.63	1107.14	798.53	1028.06	555.50

Table 2. The chemical shifts of NMR (δ ppm) spectral values of substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds.

Entry	X	^{1}H NMR (ppm)		^{13}C NMR (ppm)		
		Hα	Hβ	CO	Cα	Cβ
1	H	7.220	7.804	188.68	128.11	136.62
2	3-Br	7.141	7.816	188.05	126.88	132.82
3	4-Br	7.162	7.820	188.41	128.11	136.79
4	3-Cl	7.152	7.824	188.16	126.45	137.01
5	4-Cl	7.171	7.817	188.20	120.32	132.69
6	4-F	7.085	7.817	187.80	120.38	134.22
7	3-OCH_3	7.200	7.806	189.19	119.45	136.23
8	4-OCH_3	7.240	7.800	187.76	115.15	135.50
9	4-CH_3	7.220	7.793	188.94	120.99	132.17
10	3-NO_2	7.241	7.895	187.11	127.17	133.98
11	4-NO_2	7.165	7.860	187.97	123.92	137.99

Table 3. The statistical analysis results of ultraviolet absorption maxima ($\lambda_{max,}$ nm), infrared absoptions (υ, cm^{-1}) and Nuclear Magnetic Resonance chemical shifts (δ, ppm) of substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds with Hammett σ, σ^{+}, $\sigma_{I,}$ σ_R and *F* and *R* parameters.

Frequency	Constants	r	I	ρ	s	n	Correlated derivatives
λ_{max}	σ	0.701	316.65	4.774	21.51	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	σ^{+}	0.704	316.82	4.594	21.46	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	σ_I	0.747	302.01	41.536	18.95	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2

	σ_R	0.905	309.13	-52.827	17.98	10	3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	F	0.905	297.81	50.121	17.41	10	3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	R	0.905	307.70	-44.820	17.76	10	3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
*v*CO*s-cis*	σ	0.943	1658.36	-4.420	3.42	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	σ^+	0.903	1657.93	-2.827	3.49	10	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	σ_I	0.901	1658.36	-2.618	3.70	10	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	σ_R	0.904	1656.05	-8.126	3.28	10	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	F	0.900	1656.82	1.385	3.74	10	H, 3-Br, 4-Br, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	R	0.904	1655.85	-6.829	3.26	10	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
*v*CO*s-trans*	σ	0.908	1587.48	-1.868	7.83	8	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3
	σ^+	0.902	1587.94	-4.484	7.55	9	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-NO_2
	σ_I	0.903	1583.17	10.292	7.43	8	3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-CH_3, 3-NO_2
	σ_R	0.901	1586.23	-5.106	7.77	9	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2
	F	0.903	1582.47	11.645	7.29	8	3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-CH_3, 3-NO_2
	R	0.901	1586.18	-3.920	7.29	8	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 3-OCH_3, 4-CH_3, 3-NO_2
*v*C-H*ip*	σ	0.721	1240.10	-109.778	55.53	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	σ^+	0.752	1231.37	-81.007	55.28	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	σ_I	0.811	1187.75	73.475	59.25	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	σ_R	0.702	1152.43	-387.891	34.25	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2

	F	0.584	1126.01	225.366	49.68	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	R	0.457	1146.41	-309.096	36.22	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
*v*C-H*op*	σ	0.818	783.14	12.308	23.43	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	σ^+	0.841	787.05	-5.899	23.65	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	σ_I	0.834	773.27	33.379	22.34	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	σ_R	0.834	791.81	36.333	22.37	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	F	0.830	774.67	28.250	22.72	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	R	0.837	793.20	32.644	22.10	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
*v*CH=CH*op*	σ	0.804	1031.70	-2.197	16.92	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	σ^+	0.809	1030.59	3.152	16.87	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	σ_I	0.807	1029.37	4.871	16.89	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	σ_R	0.804	1030.61	-3.661	16.92	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	F	0.801	1028.03	16.826	8.011	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	R	0.806	1030.25	16.909	4.28	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
*v*C=C*op*	σ	0.822	559.31	-17.863	27.52	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	σ^+	0.833	559.08	-19.249	26.61	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	σ_I	0.810	559.98	-12.323	28.07	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	σ_R	0.901	551.27	-24.899	27.67	8	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH

	F	0.805	552.98	-5.888	28.19	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	R	0.902	549.15	-27.211	27.21	8	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3
H_α	σ	0.901	7.187	-0.026	0.04	8	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 3-OCH_3, 4-OCH_3, 4-CH_3
	σ^+	0.902	7.185	-0.022	0.04	9	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 3-OCH_3, 4-OCH_3, 4-CH_3, 4-NO_2
	σ_I	0.846	7.217	-0.094	0.04	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	σ_R	0.831	7.193	0.070	0.04	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	F	0.905	7.225	-0.111	0.04	9	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3
	R	0.902	7.192	0.051	0.04	9	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-CH_3, 3-NO_2, 4-NO_2
H_β	σ	0.987	7.805	0.077	0.01	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	σ^+	0.974	7.814	0.044	0.02	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	σ_I	0.974	7.787	0.093	0.02	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	σ_R	0.965	7.837	0.090	0.02	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	F	0.967	7.789	0.082	0.02	9	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 3-OCH_3, 4-OCH_3, 4-CH_3, 4-NO_2
	R	0.901	7.839	0.072	0.02	8	3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-NO_2
δC=O	σ	0.845	188.39	-0.824	0.54	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	σ^+	0.813	188.24	-0.173	0.61	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	σ_I	0.907	188.89	-1.819	0.41	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	σ_R	0.825	188.09	-0.673	0.59	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	F	0.907	188.89	-1.724	0.43	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2

	R	0.824	188.08	-0.539	0.59	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
C_α	σ	0.854	121.71	7.327	3.77	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	σ^+	0.864	122.18	5.993	3.50	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	σ_I	0.825	121.90	3.834	4.47	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	σ_R	0.908	125.55	13.475	3.41	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	F	0.808	122.77	11.461	4.55	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	R	0.906	125.93	11.505	3.32	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
δC_β	σ	0.825	134.76	1.144	2.05	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	σ^+	0.831	134.82	1.352	2.00	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	σ_I	0.847	134.62	1.229	2.09	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	σ_R	0.812	135.28	1.161	2.09	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	F	0.809	134.77	0.806	2.10	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	R	0.812	135.30	0.945	2.09	11	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2

r = Correlation co-efficient; ρ = slope; I = Intercept; s = Standard deviation; n = Number of substituents.

Positive ρ values are shown all the correlations except σ_R and R parameter. This indicates the operation of normal substituent effect with respect to UV absorption maximum (λ_{max} nm) values in all substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds. Some of the correlations of single parameter failed for the Ultra Violet absorption maximum (λ_{max} nm) values with Hammett constants, it is concluded to drive for regression of multi analysis with Swain-Lupton's [24]. While seeking the multi regression analysis there is satisfactory correlations are observed as presented in the following equations (2) and (3).

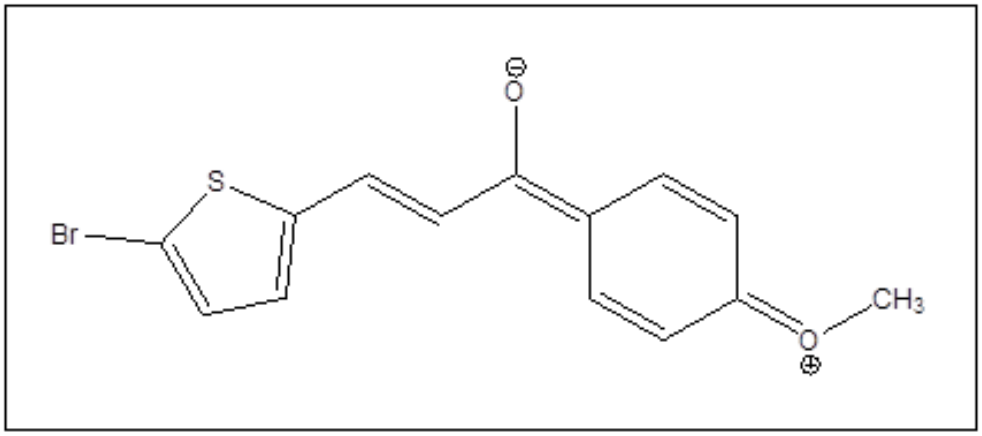


Figure 1. Resonance conjugative structure

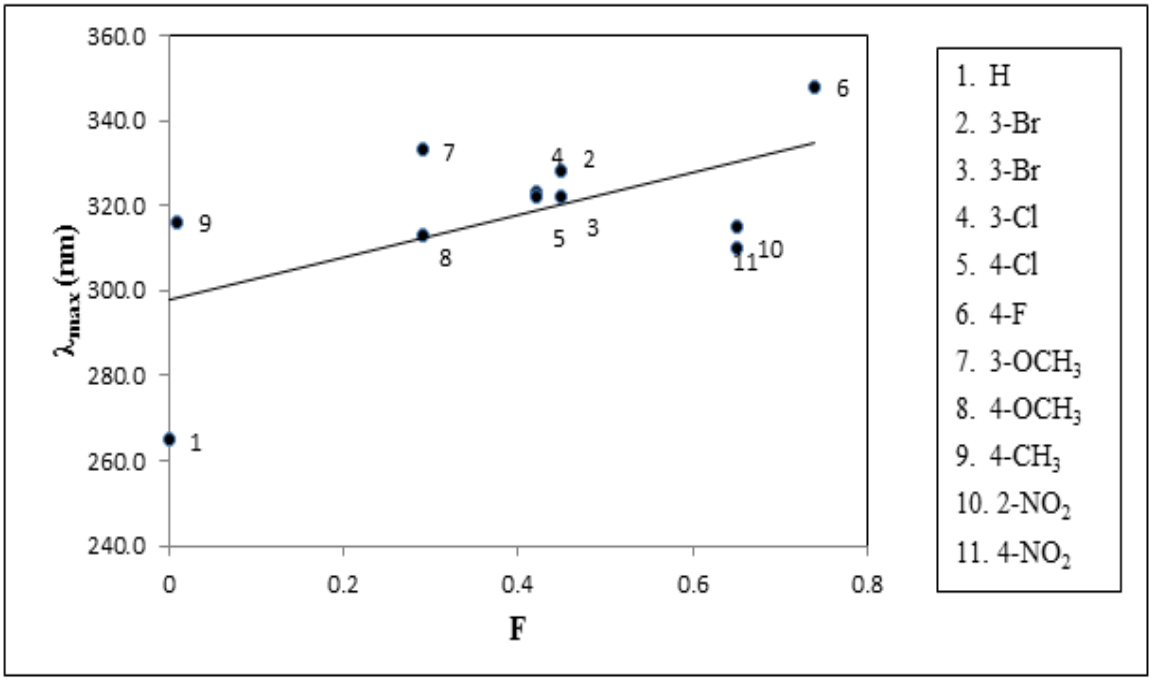


Figure 2. Plot of UV ($\lambda_{max,}$ nm) values of substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds Vs *F*

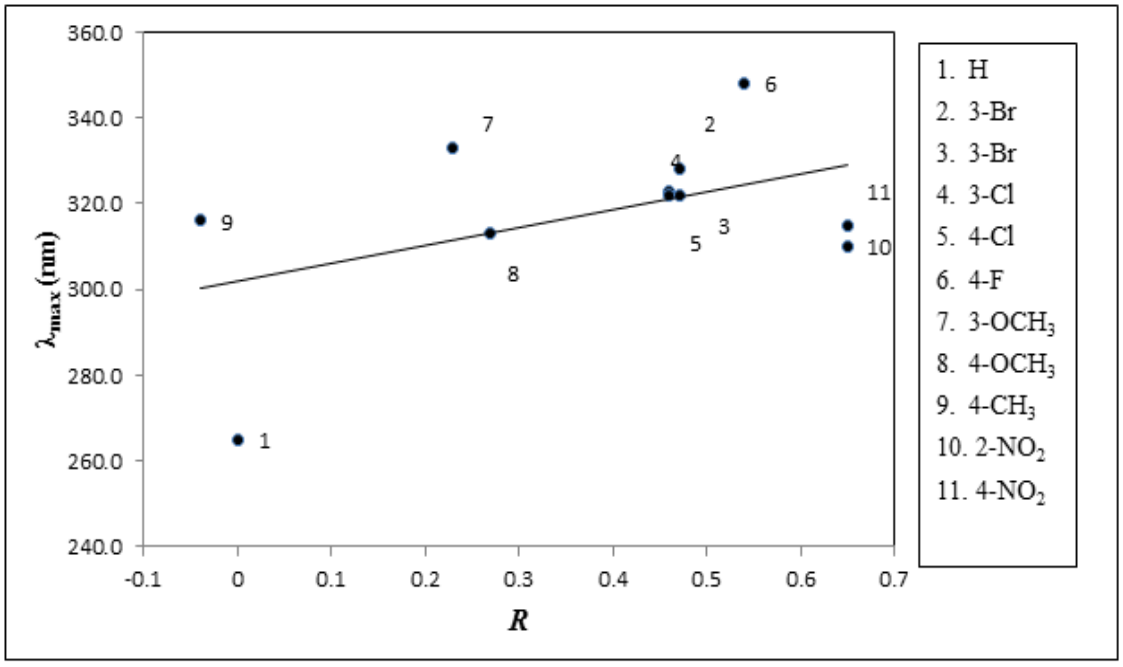


Figure 3. Plot of UV ($\lambda_{max,}$ *nm)* values of substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds Vs *R*

$$\lambda max\ (nm) = 287.11(\pm 9.067) + 53.203(\pm 18.113)\sigma_I - 64.4864(\pm 19.935)\sigma_R \quad \ldots(2)$$
$$(r = 0.908,\ n = 11,\ P > 90\%)$$
$$\lambda max\ (nm) = 286.9115(\pm 8.482) + 5\ 1.5565(\pm 16.671)F - 46.2081(\pm 15.520)R \quad \ldots(3)$$
$$(r = 0.983,\ n = 11,\ P > 95\%)$$

3. 2. IR spectral study

The assigned infrared frequencies (cm^{-1}) of νCO *s-trans* and *s-cis* conformers, νC-H*ip*, νC-H*op*, νCH=CH*op*, νC=C*op*, of substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-ones are given in **Table 1**. The measured infrared frequency values are correlated [20-23] with substituent constants of Hammett and *F* and *R* parameters using regression of single and multi-linear analysis. For the correlation analysis, an absorption maximum of employing Hammett equation is shown below in equation (4).

$$\upsilon = \rho\sigma + \upsilon_o \quad \ldots(4)$$

where υ_o is the frequency for the parent member of the series.

3. 2. 1. IR Spectral Correlation of υCO*s-cis* (cm^{-1})

From the **Table 3**, it is evident that the IR frequency υCO*s-cis* (cm^{-1}) values of all substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds with Hammett substituent σ(r = 0.943) constant give satisfactory correlations. Except 4-Fluoro substituent the IR frequency υCO*s-cis* (cm^{-1}) values of all substituted (*E*)-3-(5-

bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds with Hammett substituent σ^+ (r = 0.903), σ_I (r = .901), σ_R (r = 0.904) constants and F parameter (r = 0.900) and R parameter (r = 0.904) give satisfactory correlations. Except those with F parameter all the correlations give negative ρ values. This indicates the operation of reverse substituent effect with respect to IR frequency υCO*s-cis* (cm^{-1}) values in all substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds.

3. 2. 2. IR Spectral Correlation of υCO*s-trans* (cm^{-1})

From the **Table 3**, it is evident that the IR frequency υCO*s-trans* (cm^{-1}) values of except, 3-NO_2, 4-NO_2 and 4-CH_3 substituents of all substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds of Hammett substituent constant σ (r = 0.908) give satisfactory correlations. Except 4-CH_3 and 3-NO_2 substituents of the IR frequency υCO*s-trans*(cm^{-1}) values of all substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds of Hammett substituent constant σ^+ (r = 0.902) give satisfactory correlations.

Except Parent compound, 4-NO_2 and 4-OCH_3 substituents of the IR frequency υCO*s-trans* (cm^{-1}) values of all substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds of Hammett substituent constant σ_I (r = 0.903) give satisfactory correlations. Except 3-OCH_3 and 3-NO_2 substituents of the IR frequency υCO*s-trans* (cm^{-1}) values of all substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds of Hammett substituent constant σ_R (r = 0.901) give satisfactory correlations.

Except Parent compound, 4-NO_2 and 4-OCH_3 substituents of the IR frequency υCO*s-trans* (cm^{-1}) values of all substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds give satisfactory correlations with F parameter (r = 0.903).

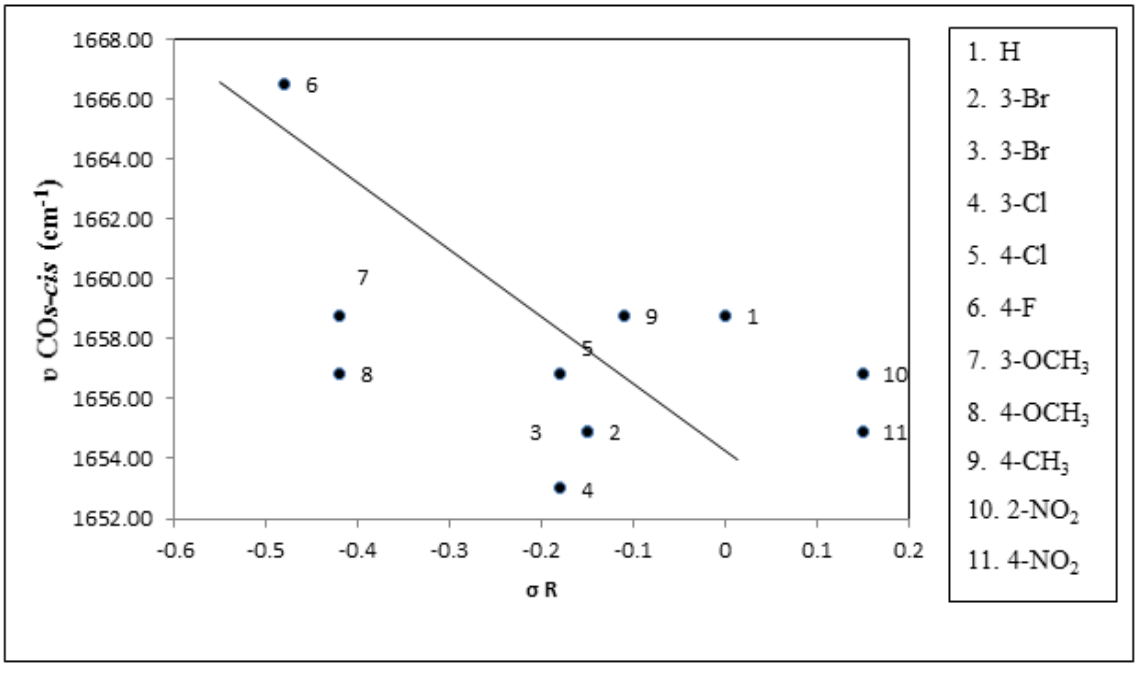


Figure 4. Plot of IR CO*s-cis* (cm^{-1}) values of substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds Vs σ_R

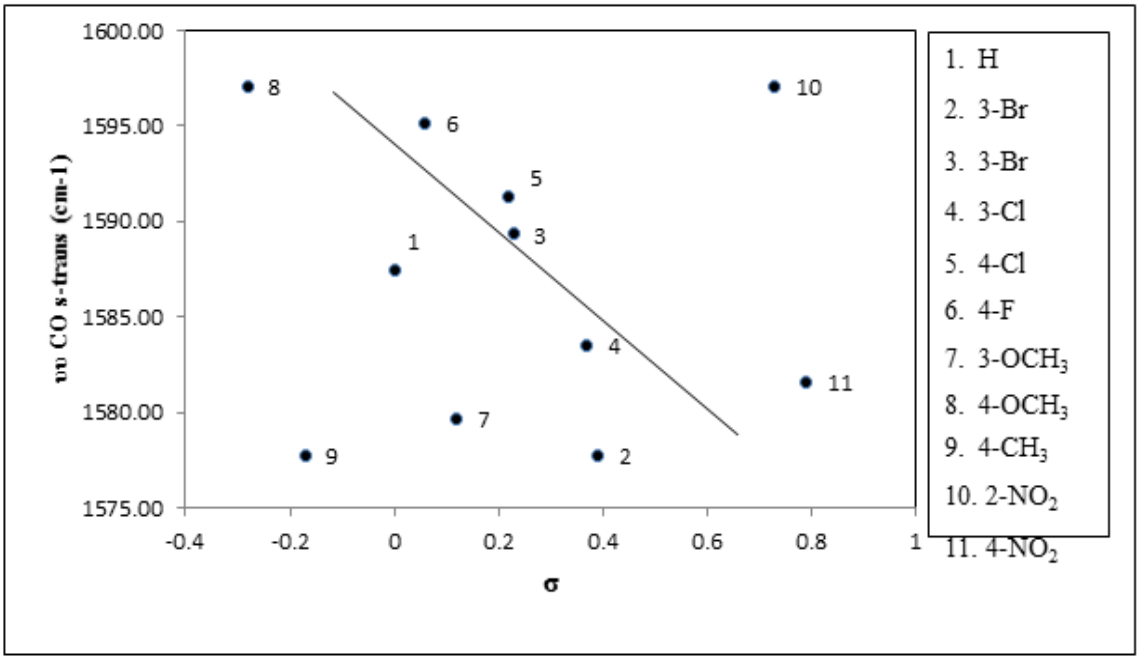


Figure 5. Plot of IR CO*s-trans* (cm^{-1}) values of
Substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds Vs σ

Except 4-F, 4-NO_2 and 4-OCH_3 substituents of the IR frequency υCO*s-trans* (cm^{-1}) values of all substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds give satisfactory correlations with R parameter (r = 0.901). Except σ_I constant and F parameter all the correlations give negative ρ values. This indicates the operation of reverse substituent effect with respect to IR frequency υCO*s-trans* (cm^{-1}) values in all substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds.

3. 2. 3. IR Spectral Correlation of υC-H*ip* (cm^{-1})

From the **Table 3**, it is evident that the IR frequency υC-H*ip* (cm^{-1}) values of all substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds of Hammett substituent constants and *F* and *R* parameters give poor correlations (r < 0.900). The inductive, resonance, weak polar and field effects is attributed for substituents give the reactivity on the IR frequency υC-H*ip* (cm^{-1}) **Figure 1** shows conjugative structure of resonance. Except with σ_I constant and F parameter all the correlations give negative ρ values. This indicates the operation of reverse substituent effect with respect to IR frequency υC-H*ip* (cm^{-1}) values in all substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds.

3. 2. 4. IR Spectral Correlation of υC-H*op* (cm^{-1})

From the **Table 3**, it is evident that the IR frequency υC-H*op* (cm^{-1}) values of all substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds of Hammett substituent constants and *F* and *R* parameters give poor correlations (r < 0.900).

This is attributed to the resonance effect, inductive, weak polar and field effects of substituents for predicting the reactivity on the IR frequency υC-H*op* (cm^{-1}) **Figure 1** shows conjugative structure of resonance**.**

Except σ^+ constant all the correlations give positive ρ values. This indicates the operation of normal substituent effect with respect to IR frequency υC-H*op* (cm^{-1}) values in all substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds.

3. 2. 5. IR Spectral Correlation of υ-CH=CH-*op* (cm^{-1})

From the **Table 4**, it is evident that the IR frequency υ-CH=CH-*op* (cm^{-1}) values of all substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds of Hammett substituent constants and *F* and *R* parameters give poor correlations (r < 0.900).

This is attributed to the resonance, inductive, weak polar and field effects of substituents for predicting the reactivity on the IR frequency υ-CH=CH-*op* (cm^{-1}) **Figure 1** shows conjugative structure of resonance**.**

Except σ, σ_I constant and R parameter all the correlations give positive ρ values. This indicates the operation of normal substituent effect with respect to IR frequency υ-CH=CH-*op* (cm^{-1}) values in all substituted (E)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds.

3. 2. 6. IR Spectral Correlation of υ-C=C-*op* (cm^{-1})

From the **Table 3**, it is evident that the IR frequency υ-C=C-*op* (cm^{-1}) values of all substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds of Hammett substituent constants and *F* and *R* parameters give poor correlations (r < 0.900).

This is attributed to the resonance, inductive, weak polar and field effects of substituents for predicting the reactivity on the IR frequency υC=C-*op* (cm^{-1}) **Figure 1** shows conjugative structure of resonance.

All the correlations have shown negative ρ values. This indicates the operation of reverse substituent effect with respect to IR frequency υC=C-*op* (cm^{-1}) values in all substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds.

Some correlations of single parameter failed for the IR frequency υCO*s-cis*, υCO*s-trans*, υC-H*ip*, υC-H*op*, υCH=CH-*op*, υC=C-*op* (cm^{-1}) values with Hammett constants and *F* and *R* parameter, it is concluded to drive for multi regression analysis with Swain-Lupton's [23] parameters. While looking for the multi regression analysis there is satisfactory correlations are observed as give in the following equations (5) to (16).

$$\nu CO_{s\text{-}cis}\ (cm^{-1}) = 1656.55(\pm 2.375) - 1.1960(\pm 4.745)\ \sigma_I - 7.8643(\pm 5.223)\sigma_R \quad \ldots(5)$$
$$(r = 0.949,\ n = 11,\ P > 90\%)$$

$$\nu CO_{s\text{-}cis}\ (cm^{-1}) = 1655.205(\pm 2.290) + 1.5999(\pm 4.502)F\text{-}6.8727(\pm 4.191)R \quad \ldots(6)$$
$$(r = 0.955,\ n = 11,\ P > 95\%)$$

$$\nu CO_{s\text{-}trans}\ (cm^{-1}) = 1581.4(\pm 5.262) + 11.6792(\pm 10.513)\ \sigma_I - 7.6663(\pm 11.570)\sigma_R \quad \ldots(7)$$
$$(r = 0.939\ n = 11\ p > 90\%)$$

$$\nu CO_{s\text{-}trans}\ (cm^{-1}) = 1581.47(\pm 5.093) + 11.6979(\pm 10.010)F - 4.2353(\pm 9.319)R \quad \ldots(8)$$
$$(r = 0.945\ n = 11\ P > 90\%)$$

$$\nu CH_{ip}\ (cm^{-1}) = 1090.533(\pm 93.916) + 149.571(\pm 187.612)\ \sigma_I - 420.618(\pm 206.483)\sigma_R \quad \ldots(9)$$
$$(r = 0.915,\ n = 11,\ P > 95\%)$$

$\nu CH_{ip}\,(cm^{-1}) = 1051.58(\pm86.571) + 235.1611(\pm170.150)F - 315.424(\pm158.401)R$ …(10)
(r = 0.964, n = 11, P > 95%)
$\nu CH_{op}\,(cm^{-1}) = 1780.2611(\pm15.496) + 27.9124(\pm30.956)\sigma_I + 30.2170(\pm34.070)\sigma_R$ …(11)
(r = 0.944, n = 11, P > 90%)
$\nu CH_{op}\,(cm^{-1}) = 782.2070(\pm14.845) + 27.2592(\pm29.176)F + 31.9106(\pm27.162)R$ …(12)
(r = 0.947, n = 11, P > 90%)
$\nu CH{=}CH_{op}\,(cm^{-1}) = 1028.2339(\pm12.256) + 5.7624(\pm24.484)\,\sigma_I - 4.9247(\pm26.947)\sigma_R$ ..(13)
(r = 0.909, n = 11, P > 90%)
$\nu CH{=}CH_{op}\,(cm^{-1}) = 1026.9681(\pm11.865) + 8.1516(\pm23.319)\,F - 4.5070(\pm21.709)R$ ..(14)
(r = 0.904, n = 11, P > 90%)
$\nu C{=}C_{op}\,(cm^{-1}) = 554.6402(\pm20.059) - 8.1417(\pm40.071)\,\sigma_I - 23.1157(\pm44.101)\sigma_R$ …(15)
(r = 0.921, n = 11, P > 90%)
$\nu C{=}C_{op}\,(cm^{-1}) = 546.4315(\pm19.208) + 6.7503(\pm37.753)F - 27.7658(\pm35.146)R$ …(16)
(r = 0.927, n = 11, P > 90%)

3. 3. The spectral study of NMR

In nuclear magnetic resonance spectra, the proton and the ^{13}C chemical shifts (δ) depends on the electronic environment of the nuclei concerned. The assigned chemical shifts (ppm) have been correlated with reactivity parameters using Hammett equation [20-23] in the form of

$$\delta = \rho\sigma + \delta_o \quad \ldots(17)$$

where δ_o is the frequency for the parent participant of the series.

3. 3. 1. Spectral ^{1}H NMR Correlation

3. 3. 1. 1. Spectral ^{1}H NMR Correlations of Hα (ppm)

From the **Table 3**, the assigned Hα chemical shifts (δ, ppm) values of except, 3-NO_2, 4-NO_2 and 4-F substituents all the substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds of Hammett substituent constant σ (r = 0.901) give satisfactory correlations. Except 4 and 3-NO_2 substituents Hα chemical shifts (δ ppm) data of the substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds of Hammett substituent constant σ^+ (r = 0.902) give satisfactory correlations. Except 4-NO_2 and 3-NO_2 substituents Hα chemical shifts (δ, ppm) data of the substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds of F parameter (r = 0.905) give satisfactory correlations. Except 4-NO_2 and 3-NO_2 substituents Hα chemical shifts (δ ppm) data of the substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds of R parameter (r = 0.902) give satisfactory correlations. However, (δ, ppm) ^{1}H NMR values of (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds, give poor correlation (r < 0.900) with balance Hammett substituent constants σ_I and σ_R. This is attributed to the resonance, inductive, weak polar effects of substituents. The substituents effect of reactivity on the chemical shifts **Figure 1** shows conjugative structure of resonance**.** Except σ_R and R parameter all the correlations give negative ρ values. This indicates the operation of reverse substituent effect with respect to NMR spectral values (ppm) values in all substituted (E)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds.

3. 3. 1. 2. Spectral ^{1}H NMR Correlations of H_β (ppm)

From the **Table 3**, the assigned Hβ chemical shifts (δ, ppm) values of all the substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds Hammett substituent constants σ (r = 0.987), σ^+ (r = 0.974), σ_I (r = 0.974) and σ_R (r = 0.965) give satisfactory correlations. Except 3-NO_2 and 4-F substituents all the substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds of F parameter (r = 0.967) give satisfactory correlation. Except Parent(H), 4-CH_3 and 3-NO_2 substituents all the substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds of R parameter (r = 0.901) give satisfactory correlation. All the correlations give positive ρ values. This indicates the operation of normal substituent effect with respect to NMR spectral values (ppm) values in all substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds.

Some correlations of single parameter failed for the ^{1}HNMR Spectral Correlations Hα (ppm) and H_β (ppm) values with Hammett constants and *F* and *R* parameter, it is concluded to go for regression of multi analysis with Swain-Lupton's [24] parameters. While looking for the multi regression analysis there is satisfactory correlations are observed as give in the following equations (18) to (21).

$$\delta H_\alpha \text{ (ppm)} = 7.2392(\pm0.028) - 0.1115(\pm0.057)\sigma_I + 0.0952(\pm0.062)\sigma_R \quad \ldots(18)$$
$$(r = 0.962,\ n = 11,\ P > 95\%)$$

$$\delta H_\alpha \text{ (ppm)} = 7.2384(\pm0.027) - 0.1128(\pm0.054)F + 0.0541(\pm0.050)R \quad \ldots(19)$$
$$(r = 0.963,\ n = 11,\ P > 95\%)$$

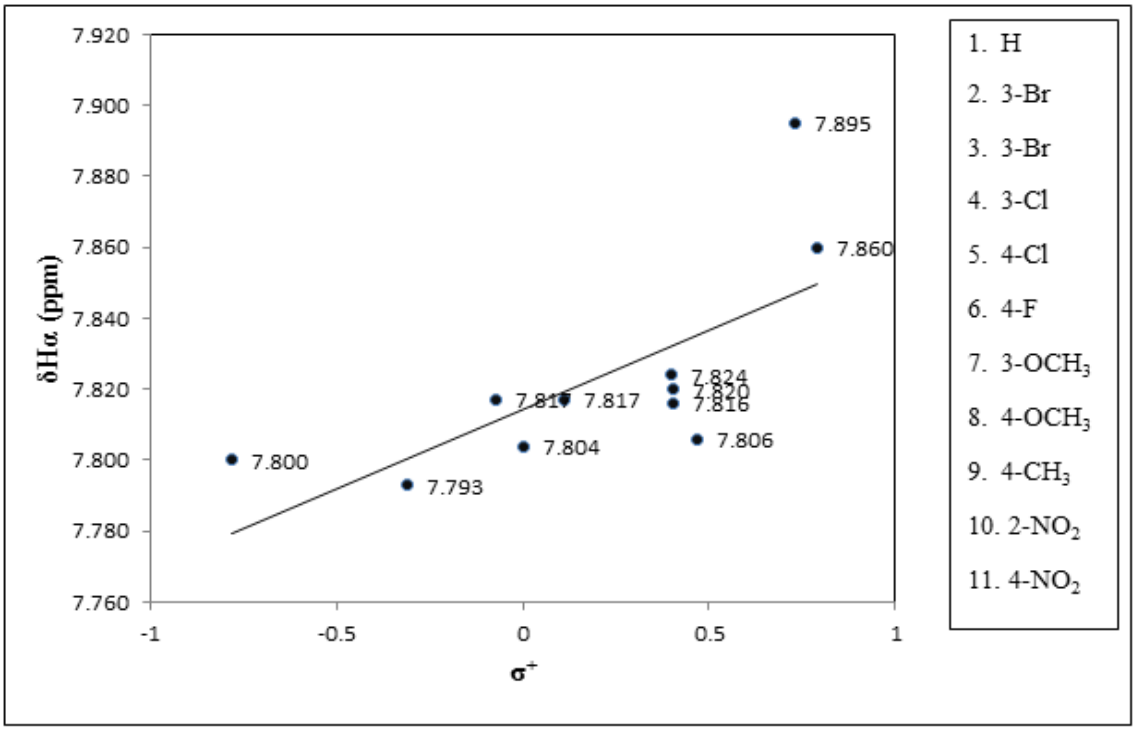


Figure 6. Plot of ^{1}H NMR H_α (ppm) values of substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds Vs σ^+

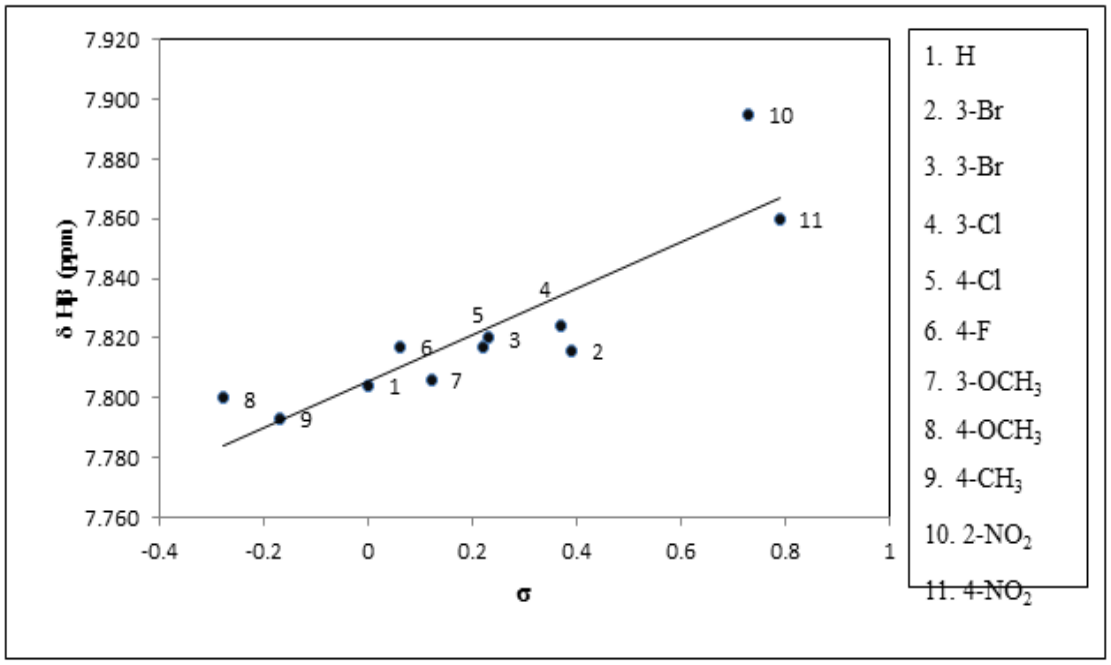


Figure 7. Plot of ^{1}H NMR H_β (ppm) values of substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds Vs σ

$$\delta H_\beta \text{ (ppm)} = 7.8043(\pm 0.009) + 0.0804(\pm 0.018)\sigma_I + 0.0729(\pm 0.020)\sigma_R \quad \ldots(20)$$
$$(r = 0.990,\ n = 11,\ P > 95\%)$$
$$\delta H_\beta \text{ (ppm)} = 7.8064(\pm 0.009) + 0.0807(\pm 0.017)F + 0.0699(\pm 0.016)R \quad \ldots(21)$$
$$(r = 0.991,\ n = 11,\ P > 95\%)$$

3. 3. 2. ^{13}CNMR Correlation

3. 3. 2. 1. ^{13}CNMR Correlations of C=O (ppm)

From the **Table 4**, the assigned C=O chemical shifts (δ, ppm) values of (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds of Hammett substituent constants σ_I (r = 0.907) and F parameter (r = 0.907) give satisfactory correlations. The C=O chemical shifts(δ ppm) values of (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds of Hammett substituent constants σ, σ^+, σ_R and *R* parameter give poor correlations (r < 0.900). This is attributed to the resonance and weak polar effects of substituents. The substituents effect of reactivity on chemical shifts **Figure 1** shows conjugative structure of resonance**.** All the correlations give negative ρ values. This indicates the operation of reverse substituent effect with respect to NMR spectral values (ppm) values in all substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds.

3. 3. 2. 2. ^{13}CNMR Spectral Correlations of C_α (ppm)

From the **Table 4**, the assigned Cα chemical shifts (δ, ppm) values of (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds of Hammett substituent constants σ_R (r = 0.908) and R parameter (r = 0.906) give satisfactory correlations.

The remaining Hammett substituent constants σ, σ^+, σ_I and *F* parameter give poor correlations (r < 0.900). This is due to the, field, inductive and weak polar effects of substituents. The substituents effects of the reactivity on the chemical shifts **Figure 1** shows conjugative structure of resonance. All the correlations give positive ρ values. This indicates the operation of normal substituent effect with respect to NMR spectral values (ppm) values in all substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds.

3. 3. 2. 3. ^{13}CNMR Spectral Correlations of Cβ (ppm)

From the **Table 4**, the assigned Cβ chemical shifts (δ, ppm) values of (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds of Hammett substituent constants *F* and *R* parameter give poor correlations (r < 0.900). This is due to the field, resonance, inductive and weak polar effects of substituents. The substituents effect of the reactivity on the chemical shifts **Figure 1** shows conjugative structure of resonance. All the correlations have shown positive ρ values. This indicates the operation of normal substituent effect with respect to NMR spectral values (ppm) values in all substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds. Some correlations of single parameter failed for the ^{13}CNMR Spectral Correlations C=O (ppm), C_α (ppm) and C_β (ppm) values with Hammett constants and *F* and *R* parameter, it is concluded to go for multi regression analysis with Swain-Lupton's [24] parameters. While looking for the multi regression analysis there is satisfactory correlations are observed as give in the following equations (22) to (27).

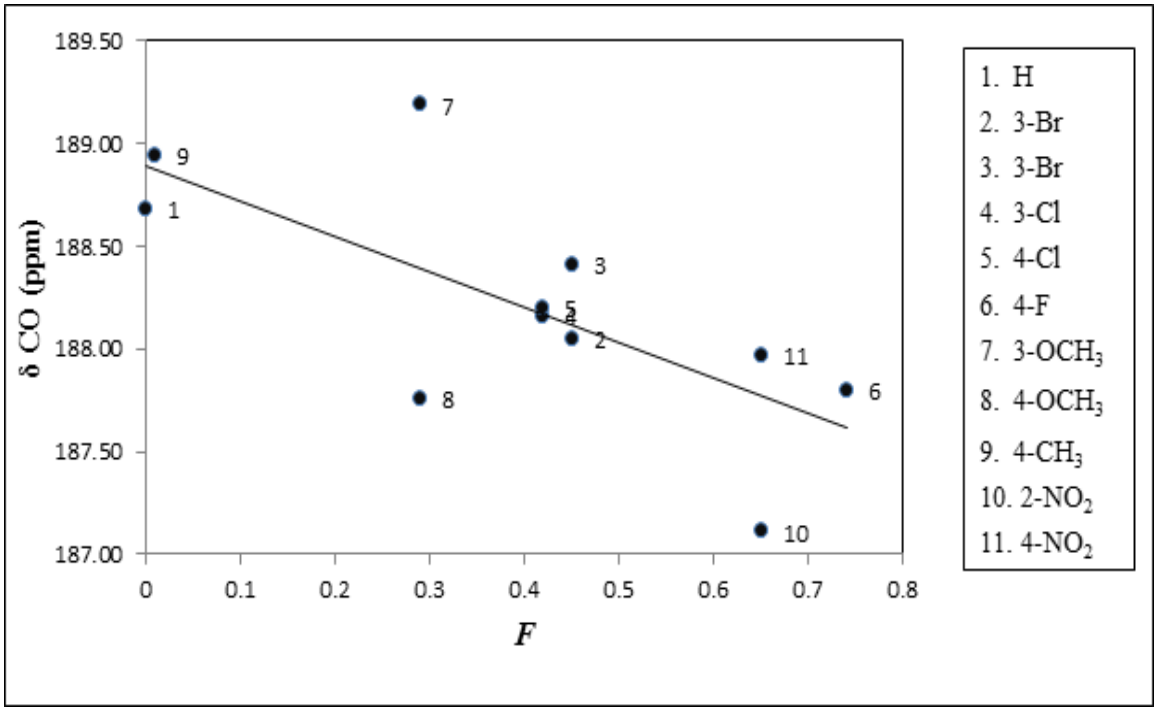


Figure 8. Plot of ^{13}C NMR CO (ppm) values of substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds Vs *F*

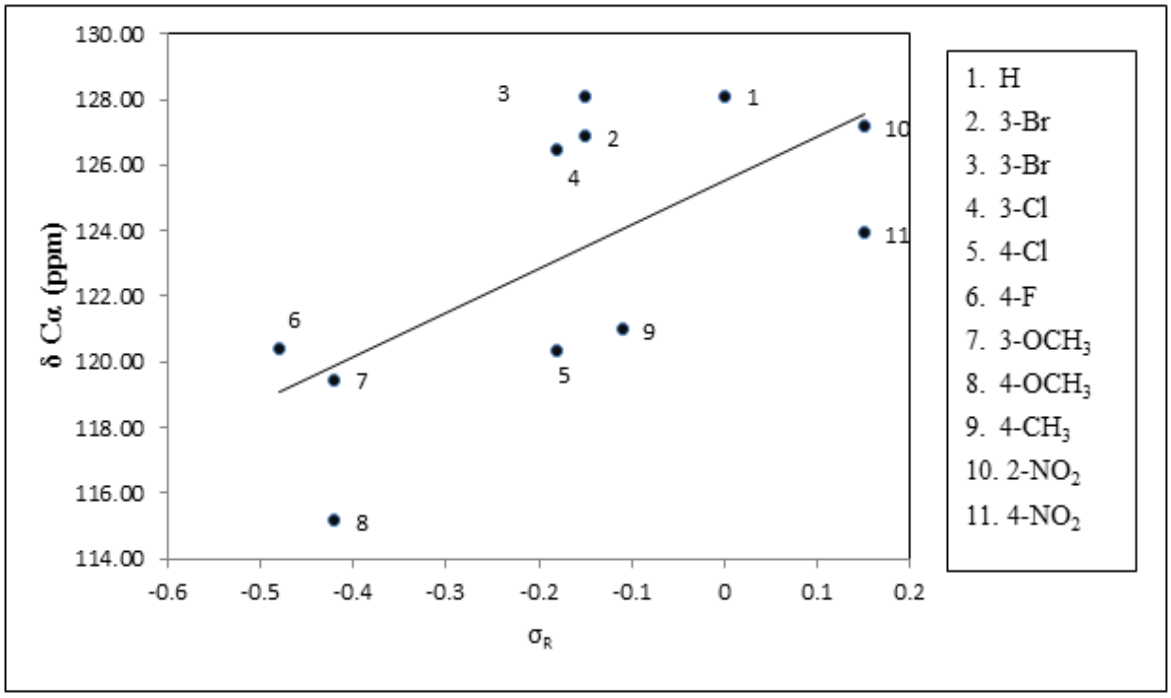


Figure 9. Plot of ^{13}C NMR C_α (ppm) values of substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds Vs σ_R

$$\delta CO\ (ppm) = 188.8285(\pm 0.301) - 1.7681(\pm 0.601)\sigma_I - 0.2855(\pm 0.661)\sigma_R \quad \ldots(22)$$
$$(r = 0.974,\ n = 11,\ P > 95\%)$$

$$\delta CO\ (ppm) = 188.7749(\pm 0.291) - 1.7091(\pm 0.572)F - 0.5720(\pm 0.532)R \quad \ldots(23)$$
$$(r = 0.974\ n = 11,\ P > 95\%)$$

$$\delta C_\alpha\ (ppm) = 124.9479(\pm 2.469) + 1.4548(\pm 4.932)\sigma_I + 13.1562(\pm 5.428)\sigma_R \quad \ldots(24)$$
$$(r = 0.966\ n = 11,\ P > 95\%)$$

$$\delta C_\alpha\ (ppm) = 125.4846(\pm 2.341) + 1.1047(\pm 4.602)F + 11.4752(\pm 4.284)R \quad \ldots(25)$$
$$(r = 0.969\ n = 11,\ P > 95\%)$$

$$\delta C_\beta\ (ppm) = 134.8425(\pm 1.512) + 1.0614(\pm 3.022)\sigma_I + 0.9292(\pm 3.326)\sigma_R \quad \ldots(26)$$
$$(r = 0.817\ n = 11,\ P > 90\%)$$

$$\delta C_\beta\ (ppm) = 134.9904(\pm 1.477) + 0.7779(\pm 2.903)F + 0.9245(\pm 2.703)R \quad \ldots(27)$$
$$(r = 0.915\ n = 11,\ P > 90\%)$$

4. CONCLUSIONS

Series of eleven numbers of substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds has been synthesized by condensation of bromothiophene-2-carbaldehyde and substituted acetophenones. These synthesized substituted (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one compounds has been characterized by their physical constants, spectral data. The UV, IR, proton and ^{13}C nuclear magnetic resonance spectral value of these (*E*)-3-(5-bromothiophen-2-yl)-1-phenylprop-2-en-1-one has been

correlated with the substituent constants of Hammett and *F* and *R* parameters. Substituent effect studied through statistical analyses from the spectral values. UV, ^{1}H and ^{13}C NMR spectral correlations produced more number of satisfactory correlations. But IR spectral values give poor correlation with all Hammett substituents constants and Swain-Lupton's (*F* and *R*) parameters. However, all the multi-regression analyses give satisfactory correlations.

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References

[1] G. Di Carlo. N. Mascolo. A. A. Izzo and F. Capasso, *Life Sci*, 65 (1999) 337-353

[2] G. Thirunaryanan, and G. Vanangamudi, *Arkivoc*, 12 (2006) 58-64

[3] N. Iranpoor, B. Zeynizadeli, and A. Aghapour, *J. Chem. Res, S.* (1999) 554-555

[4] F. Winternitz,G. Conder, and P. Vassort, *Tetrahedron Lett*, 26 (1986) 5981-5985

[5] S. S. Misra, and R. S. Tewari, *J Indian Chem. Soc* 50 (1973) 51-68

[6] L. Lafen, Ger. (1970). *2010180, Chem. Abstr,* 73 (1970) 120342s

[7] K. Ranganathan, G. Vanangamudi, K. Thirumuruthy, and G. Thirunarayanan, *Bull. Chem. Soc. Ethiop.* 28(2) (2014) 271-288

[8] G. Thirunarayanan, *J. Kor. Chem. Soc.* 52(4) (2008) 369-379

[9] G. Thirunarayanan and P. Ananthakrishna Nadar, *A. J. Chem.* 14(3-4) (2002) 1518-1522

[10] G. Thirunarayanan, G. Vanangamudi, V. Sathiyendiran and K. Ravi. *Ind. J. Chem.* 14 (50B) (2011) 593-604

[11] D. Morealeda, D. E. Abed, H. Pellissier, and M. Santelli, *J. Mol. Struct.(TheoChem)* 760 (1-3) (2006) 113-119

[12] P. R. Griffiths, J. M. Chalmers, *Handbook of Vibrational Spectroscopy*, Chinchester, John-Wiley & Sons, 4 (2002) 2576-2592

[13] B. Utpal, A. Sahu, S. S. Ali, L. Kasoju and A. Singh, *Food. Res. Inter.* 41 (2008) 1-15

[14] G. Vanangamudi, K. Ranganathan and G. Thirunaryanan, *Wor. J. Chem.* 7 (2012) 1-12

[15] V. Horvath, Z. Varga and A. Kov´acs, *J. Mol. Struct. Theochem* 755 (1-3) (2005) 247-251

[16] R. J. Anto, K. Sukumaran, G. Kuttan and M. A. Rao, *Cancer. Lett.* 97 (1995) 33-37

[17] G. Thirunarayanan, S. Surya, S. Srinivasan, G. Vanangamudi and V. Sathyendiran, *Spectrochim Acta* 75A (2010) 152-156

[18] S. G. Kucukguzel, A. Mazi, F. Sahin, S. Ozturk and J. Stables, *Eur. J. Med. Chem.* 38 (2003) 1005-1009

[19] P. Christuraj, P. R. Rajakumar, C. Geetha, G. Vanangamudi, R. Arulkumran, R. Sundararajan, G. Thirunarayanan, *Int. J. Bioorg. Chem.* 1(1) (2016) 22-31

[20] S. P. Sakthinathan, R. Suresh, V. Mala, K. Sathiyamoorthi, D. Kamalakkannan, K. Ranganathan, S. John Joseph, G. Vanangamudi and G. Thirunarayanan., *Int. J. Sci. Res. Know*. 1(11) (2013) 472-483

[21] S. P. Sakthinathan, R. Suresh, V. Mala, K. Sathiyamoorthi, D. Kamalakkannan, K. Ranganathan, R. Arulkumaran, S. Vijayakumar, R. Sundararajan, G. Vanangamudi and G. Thirunarayanan. *Inter. Lett. Chem. Phy. Astro.* 6 (2013) 77-90

[22] R. Suresh, D. Kamalakkannan, K. Ranganathan, R. Arulkumaran, R. Sundararajan, S. P. Sakthinathan, S. Vijayakumar, K. Sathiyamoorthi, V. Mala, G. Vanangamudi, K. Thirumurthy, P. Mayavel and G. Thirunarayanan, *Spectrochim. Acta.* 101A (2013) 239-248

[23] R. Arulkumaran, S. Vijayakumar, S. P. Sakthinathan, D. Kamalakkannan, K. Ranganathan, R. Suresh, R. Sundararajan, G. Vanangamudi and G. Thirunarayanan, *J. Chil. Chem. Soc.* 58(2) (2013) 1670-1684

[24] C. G. Swain and E. C. Lupton, *J. Am. Chem. Soc.* 90 (1968) 4328-4337.

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