

Synthesis and assessment of substituent effect on (*E*)-1-(4-fluoro-3-methylphenyl)-3-phenylprop-2-en-1-one compounds

S. Balaji¹, M. Rajarajan¹, R. Vijayakumar¹, V. Manikandan¹, R. Senbagam¹
G. Vanangamudi^{1*}, G. Thirunarayanan²,

¹PG & Research Department of Chemistry, Government Arts College, C-Mutlur,
Chidambaram-608 102, India

²Department of Chemistry, Annamalai University, Annamalainagar-608 002, India

*E-mail address: drgvsibi@gmail.com

Keywords: Synthesis, 4-fluoro-3-methyl acetophenone, UV, IR and NMR spectra, Spectral correlation analysis and substituent effect.

ABSTRACT. In the present investigation, a series of substituted (*E*)-1-(4-fluoro-3-methylphenyl)-3-phenylprop-2-en-1-one compounds were synthesized by condensation reaction of 4-fluoro-3-methyl acetophenone with substituted benzaldehydes in the presence of alkali. The yields of synthesized compounds are more than 80%. The structures of all the synthesized compounds were confirmed by their physical constants, UV, IR and NMR spectral data. All the observed spectral data of substituted (*E*)-1-(4-fluoro-3-methylphenyl)-3-phenylprop-2-en-1-one compounds have been correlated with Hammett substituent constants and *F* and *R* parameters using single and multi-linear regression analyses. From the results of statistical analysis the effects of substituents have been discussed.

1. INTRODUCTION

Chalcones are 3-phenylprop-2-en-1-one compounds, in which two aromatic rings are linked by a three carbon α , β -unsaturated carbonyl system. These are abundant in edible plants and are considered to be precursors of flavonoids and isoflavonoids. The compounds with the backbone of chalcones have been reported to possess various properties by which they find many applications in different fields. Molecules possessing such system have relatively low redox potentials and have a greater probability of undergoing electron transfer reactions. 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 chalcones have been used as agro chemicals and drugs [2-6]. Various methods are available for the synthesis of chalcone, the most convenient method is the one that involves the Crossed-Aldol condensation of equimolar quantities of acetylated aliphatic or aromatic compounds with substituted benzaldehydes in the presence of aqueous alcoholic alkali [7]. Spectroscopic data is useful for study of effect of substituents using Hammett substituent constants, *F* and *R* parameters by single and multi-regression analysis. Recently chemists [8-9] has synthesized and studied spectral correlations of some aryl chalcones and they observed satisfactory correlations using spectral data with Hammett substituent constants, *F* and *R* parameters. Literature survey shows that there is no information available regarding the study of UV, IR and NMR spectral correlation of substituted (*E*)-1-(4-fluoro-3-methylphenyl)-3-phenylprop-2-en-1-one compounds. Therefore the authors have taken efforts to synthesis these 3-phenylprop-2-en-1-one compounds 4-fluoro-3-methyl acetophenone with various substituted benzaldehydes by condensation reaction. The various spectral data of these 3-phenylprop-2-en-1-one compounds have been utilized for studying the quantitative structure activity relationships through Hammett correlations.

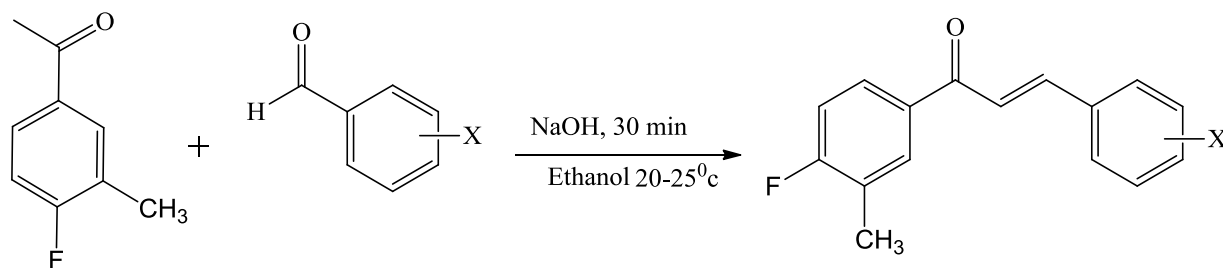
2. EXPERIMENTAL

2.1. Materials and Methods

All the chemicals used in this investigation were purchased from Sigma-Aldrich and E-Merck chemical companies. Melting points of all synthesized chalcones were determined in open glass capillaries on Mettler FP51 melting point apparatus and are uncorrected. The Shimadzu-1650 ultraviolet spectrophotometer was utilized for recording the absorption maxima (λ_{\max} , nm), of all chalcones in spectral grade methanol. Infrared spectra (KBr, 4000–400 cm^{-1}) of all chalcones were recorded in Avatar-300 Fourier transform spectrophotometer. The NMR spectra of all chalcones were recorded in Bruker AV400 NMR spectrometer, operating 400 MHz and 500 MHz for ^1H and 100 MHz for ^{13}C spectra in CDCl_3 solvent using TMS as internal standard.

2.2. General procedure for crossed-aldol condensation of (*E*)-1-(4-fluoro-3-methylphenyl)-3-phenylprop-2-en-1-one compounds:

A mixture of 4-fluoro-3-methyl acetophenone (0.05 mol) and various substituted benzaldehydes (0.05 mol) was dissolved in 50 ml absolute ethanol in a 250 ml round-bottom flask equipped with a magnetic stirrer. Then 50 ml NaOH solution (1 g in 50 ml H_2O) was added drop wise to the reaction mixture on vigorous stirring for 30 minutes when solution became turbid. The reaction mixture was neutralized by 0.1N HCl by the precipitation occurred [10-11]. On filtering off, the crude chalcone was dried in air and recrystallized using ethanol to get glittering color solid, and their melting points were observed. The general reaction is shown in **Scheme-1**. The physical constants are presented in Table-1. The UV, IR and NMR spectral data of these chalcones are presented in Table-2.



Scheme 1. Synthesis of substituted (*E*)-1-(4-fluoro-3-methylphenyl)-3-phenylprop-2-en-1-one.

Table 1. Physical constants of substituted (*E*)-1-(4-fluoro-3-methylphenyl)-3-phenylprop-2-en-1-one compounds.

Entry	X	M. F.	M. W.	Yield (%)	m.p. (°C)
1	H	$\text{C}_{16}\text{H}_{13}\text{FO}$	240.27	86	58-60
2	3-Br	$\text{C}_{16}\text{H}_{12}\text{FBrO}$	319.17	81	57-59
3	4-Br	$\text{C}_{16}\text{H}_{12}\text{FBrO}$	319.17	90	91-93
4	2-Cl	$\text{C}_{16}\text{H}_{12}\text{FClO}$	274.72	83	60-62
5	3-Cl	$\text{C}_{16}\text{H}_{12}\text{FClO}$	274.72	92	61-63
6	4-Cl	$\text{C}_{16}\text{H}_{12}\text{FClO}$	274.72	93	99-101

7	3-F	C ₁₆ H ₁₂ F ₂ O	258.26	82	80-82
8	4-F	C ₁₆ H ₁₂ F ₂ O	258.26	94	88-91
9	4-OCH ₃	C ₁₇ H ₁₅ FO ₂	270.30	91	49-51
10	4-CH ₃	C ₁₇ H ₁₅ FO	254.30	82	97-99
11	3-NO ₂	C ₁₆ H ₁₂ FNO ₃	285.27	85	121-123

Table 2. The ultraviolet absorption maxima (λ_{max} , nm), infrared absorptions (ν , cm⁻¹) and NMR chemical shifts (δ , ppm) spectral data of substituted (*E*)-1-(4-fluoro-3-methylphenyl)-3-phenylprop-2-en-1-one compounds.

Entry	X	λ_{max}	ν CO	ν CO	ν CH _{ip}	ν CH _{op}	ν CH=CH _{op}	ν C=C _{op}	δ H _{α}	δ H _{β}	δ C _{α}	δ C _{β}	δ CO
			(<i>s-cis</i>)	(<i>s-trans</i>)									
1	H	309.0	1662.64	1597.06	1244.09	761.88	1051.20	557.43	7.523	7.822	121.71	144.78	189.02
2	3-Br	301.5	1658.78	1600.92	1240.23	783.10	1060.85	538.14	7.490	7.705	122.89	142.83	188.47
3	4-Br	315.0	1662.64	1595.13	1242.16	812.03	1047.35	530.42	7.508	7.747	122.15	143.32	188.73
4	2-Cl	302.5	1664.57	1593.20	1244.09	817.82	1043.49	551.64	7.467	8.182	124.59	140.60	189.03
5	3-Cl	306.0	1666.50	1597.06	1244.09	792.74	1051.20	567.07	7.505	7.727	122.85	142.97	188.53
6	4-Cl	312.5	1664.57	1597.06	1244.09	819.75	1047.35	553.57	7.485	7.750	122.06	143.25	188.69
7	3-F	303.0	1660.71	1591.27	1242.16	815.89	1049.28	551.64	7.497	7.749	122.84	143.18	188.61
8	4-F	310.5	1664.57	1595.13	1236.37	823.60	1049.28	565.14	7.447	7.782	121.45	143.43	188.80
9	4-OCH ₃	326.0	1664.57	1597.06	1247.94	825.53	1043.49	551.64	7.370	7.763	119.34	144.63	189.04
10	4-CH ₃	324.5	1658.78	1597.06	1238.30	813.96	1045.42	555.50	7.481	7.807	120.74	144.91	189.19
11	3-NO ₂	301.0	1666.50	1598.99	1246.02	810.10	1047.35	542.00	7.117	7.847	122.27	141.60	188.18

Table 3. Results of statistical analysis of ultraviolet absorption maxima (λ_{max} , nm), infrared absorptions (ν , cm^{-1}) and NMR chemical shifts (δ , ppm) of substituted (*E*)-1-(4-fluoro-3-methylphenyl)-3-phenylprop-2-en-1-one compounds with Hammett σ , σ^+ , σ_I , σ_R and *F* and *R* parameters.

Frequency	Constants	R	I	ρ	s	n	Correlated derivatives
λ_{max} nm	σ	0.983	315.11	-26.17	5.05	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	σ^+	0.968	312.88	-17.91	4.63	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	σ_I	0.906	319.68	-24.47	7.28	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	σ_R	0.821	308.23	-9.29	9.06	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	<i>F</i>	0.905	318.02	-18.73	7.78	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	<i>R</i>	0.827	307.50	-10.10	8.91	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
$\nu\text{CO}_{s-cis}(\text{cm}^{-1})$	σ	0.821	1662.68	2.54	2.78	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	σ^+	0.812	1663.00	1.03	2.85	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	σ_I	0.844	1661.04	5.44	2.59	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	σ_R	0.808	1663.39	1.12	2.88	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	<i>F</i>	0.818	1661.85	3.11	2.76	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	<i>R</i>	0.814	1663.59	1.65	2.86	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
$\nu\text{CO}_{s-trans}(\text{cm}^{-1})$	σ	0.814	1596.09	1.36	2.74	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	σ^+	0.802	1596.38	-0.13	2.76	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	σ_I	0.813	1596.99	-1.64	2.74	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	σ_R	0.806	1598.05	8.05	2.21	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	<i>F</i>	0.832	1597.78	-3.38	2.61	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	<i>R</i>	0.905	1597.90	5.94	2.33	9	H, 4-Br, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
$\nu\text{CH}_{ip}(\text{cm}^{-1})$	σ	0.812	1242.40	1.48	3.50	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	σ^+	0.800	1242.67	0.05	3.53	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	σ_I	0.781	1242.19	1.25	3.52	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	σ_R	0.825	1243.56	4.29	3.41	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	<i>F</i>	0.811	1243.34	-1.55	3.50	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	<i>R</i>	0.827	1243.69	3.89	3.39	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
$\nu\text{CH}_{op}(\text{cm}^{-1})$	σ	0.811	808.97	-10.68	20.49	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	σ^+	0.823	808.59	-10.72	20.17	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	σ_I	0.831	794.08	32.98	19.24	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	σ_R	0.905	796.26	-52.21	17.71	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	<i>F</i>	0.844	792.43	34.48	18.56	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	<i>R</i>	0.905	795.48	-44.06	17.58	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
$\nu\text{CH}=\text{CH}_{op}(\text{cm}^{-1})$	σ	0.903	1047.50	6.53	4.68	10	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	σ^+	0.902	1048.15	3.90	4.75	10	H, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	σ_I	0.792	1047.63	2.86	5.02	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	σ_R	0.715	1049.48	3.59	5.01	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	<i>F</i>	0.791	1047.85	2.12	5.03	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	<i>R</i>	0.812	1049.39	2.46	5.03	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
$\nu\text{C}=\text{C}_{op}(\text{cm}^{-1})$	σ	0.903	553.72	-12.83	10.88	9	H, 3-Br, 2-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	σ^+	0.903	552.67	-8.99	10.80	9	H, 3-Br, 2-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	σ_I	0.729	556.00	-12.09	11.17	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	σ_R	0.832	547.53	-18.37	10.88	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂

	<i>F</i>	0.811	553.20	-4.55	11.46	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	<i>R</i>	0.825	548.18	-11.95	11.13	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
$\delta H_a(\text{ppm})$	σ	0.824	7.477	-0.174	0.110	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	σ^+	0.818	7.452	-0.05	0.120	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	σ_I	0.837	7.521	-0.196	0.113	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	σ_R	0.831	7.397	-0.23	0.112	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	<i>F</i>	0.830	7.503	-0.139	0.116	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	<i>R</i>	0.832	7.403	-0.157	0.115	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
$\delta H_b(\text{ppm})$	σ	0.901	7.811	-0.069	0.137	10	H, 3-Br, 4-Br 3-Cl,4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	σ^+	0.801	7.793	0.028	0.138	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	σ_I	0.797	7.815	-0.042	0.138	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	σ_R	0.800	7.790	-0.039	0.138	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	<i>F</i>	0.810	7.829	-0.074	0.137	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	<i>R</i>	0.805	7.806	0.03	0.138	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
$\delta CO(\text{ppm})$	σ	0.991	188.93	-0.97	0.12	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	σ^+	0.972	188.83	-0.51	0.21	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	σ_I	0.907	188.15	-1.03	0.20	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	σ_R	0.803	188.65	-0.46	0.30	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	<i>F</i>	0.906	189.08	-0.78	0.23	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	<i>R</i>	0.821	188.66	-0.35	0.30	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
$\delta Ca(\text{ppm})$	σ	0.965	121.48	3.11	1.07	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	σ^+	0.913	120.94	2.92	1.23	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	σ_I	0.848	120.94	2.92	1.23	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	σ_R	0.814	122.27	0.96	1.40	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	<i>F</i>	0.835	121.29	1.85	1.32	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	<i>R</i>	0.825	121.45	1.44	1.36	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
$\delta Cb(\text{ppm})$	σ	0.907	142.85	-3.30	0.96	10	H, 3-Br, 4-Br 3-Cl,4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	σ^+	0.907	143.58	-2.34	0.88	10	H, 3-Br, 4-Br 3-Cl,4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	σ_I	0.907	144.92	-4.35	0.92	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	σ_R	0.811	143.04	-0.90	1.36	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	<i>F</i>	0.904	144.43	-2.86	1.14	10	H, 3-Br, 4-Br 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂
	<i>R</i>	0.821	142.91	-1.20	1.34	11	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 3-F, 4-F, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂

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

3. RESULT AND DISCUSSION

3. 1. Spectral linearity

The spectral linearity of chalcones was studied by evaluating the substituent effects [12-13] with respect to various spectral data. The assigned spectral data of all chalcones such as absorption maximum λ_{max} (nm) of carbonyl groups, infrared carbonyl stretches of νCO_{s-cis} and $s-trans$, the deformation modes of vinyl part CH *out of plane*, *in-plane*, CH=CH and $>\text{C}=\text{C}<$ *out of planes* (cm^{-1}), NMR chemical shifts $\delta(\text{ppm})$ of H_α , H_β , C_α , C_β , CO are assigned and these data are correlated with various substituent constants.

3. 1. 1. UV spectral study

The absorption maxima (λ_{max} nm) of synthesized substituted (E)-1-(4-fluoro-3-methylphenyl)-3-phenylprop-2-en-1-one compounds were assigned and presented in Table 2. These absorption maxima (λ_{max} nm) of these chalcones were correlated with Hammett substituent constants [14-20] and F and R parameters [21] using single and multi-linear regression analysis. Hammett correlation involving the group frequencies and absorption maxima, the form of the Hammett equation employed is

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

where λ_0 is the frequency for the parent member of the series.

From the Table-3, it is evident that the UV absorption maximum $\lambda_{max}(\text{nm})$ values of all substituted 3-phenylprop-2-en-1-one compounds, have shown satisfactory correlations with σ ($r = 0.983$), σ^+ ($r=0.968$), σ_I ($r=0.906$) and F parameter ($r = 0.905$). However UV absorption maximum $\lambda_{max}(\text{nm})$ values of all substituted (E)-1-(4-fluoro-3-methylphenyl)-3-phenylprop-2-en-1-one compounds, have shown poor correlations ($r < 0.900$) with the Hammett substituent constant σ_R and R parameter. This is attributed to the weak resonance effect of the substituents for predicting the reactivity on the UV absorption through resonance as per the conjugative structure as shown in Fig.1.

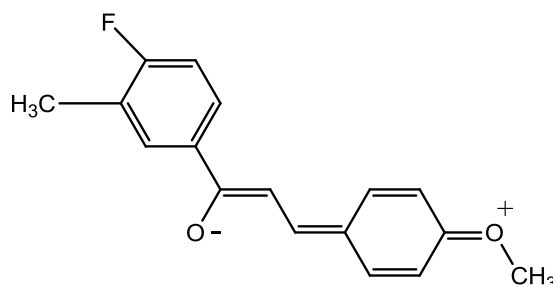


Fig. 1. Resonance conjugative structure

All the correlations have shown negative ρ values. This indicates the operation of reverse substituent effect with respect to UV absorption maximum $\lambda_{max}(\text{nm})$ values in all substituted 3-phenylprop-2-en-1-one compounds. Since some of the single parameter correlations failed for the UV absorption maximum $\lambda_{max}(\text{nm})$ values with Hammett constant σ_R and R parameter, it is decided to go for multi regression analysis. While seeking the multi regression analysis there is satisfactory correlations are observed as shown in the following equations (2) and (3).

$$\lambda_{max}(\text{nm}) = 317.574(\pm 4.760) - 26.741(\pm 9.207)\sigma_I - 14.624(\pm 4.867)\sigma_R \quad (2)$$

$(R = 0.969, n=11, P>95\%)$

$$\lambda_{max}(\text{nm}) = 315.793(\pm 3.959) - 26.832(\pm 8.935)F - 21.678(\pm 7.280)R \quad (3)$$

$(R = 0.976, n=11, P>95\%)$

3. 2. IR spectral study

The carbonyl stretching frequencies (cm^{-1}) of *s-cis* and *s-trans* conformers are shown in Fig. 2. The IR frequency values are presented in Table 2.

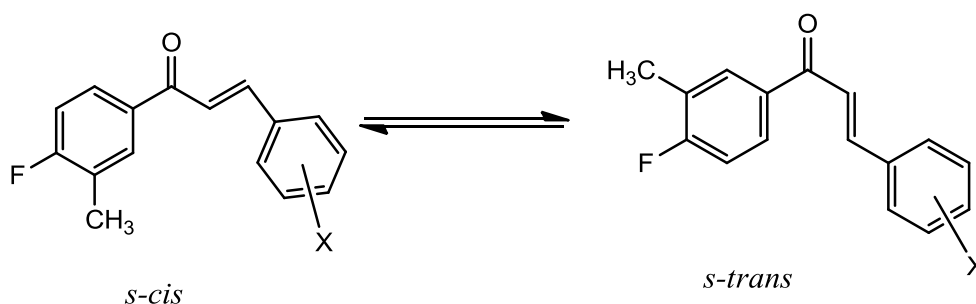


Fig. 2. The *s-cis* and *s-trans* conformers of (E)-1-(4-fluoro-3-methylphenyl)-3-phenylprop-2-en-1-one compounds.

The IR frequency values are correlated with Hammett substituent constants [14-20] and Swain-Lupton's parameters [21]. While seeking Hammett correlation involving group frequencies, the form of the Hammett equation employed is

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

where ν_0 is the carbonyl frequencies of substituted system.

3. 2. 1. IR Spectral Correlation of $\nu\text{CO}_{s-cis}(\text{cm}^{-1})$

The IR frequency $\nu\text{CO}_{s-cis}(\text{cm}^{-1})$ values of all substituted 3-phenylprop-2-en-1-one compounds have shown poor correlations ($r < 0.900$) with all Hammett substituent constants and *F* and *R* parameters. This is attributed to the weak polar, inductive, field and resonance effects of the substituents. All the correlations have shown positive ρ values. This indicates the operation of normal substituent effect with respect to IR frequency $\nu\text{CO}_{s-trans}(\text{cm}^{-1})$ values in all substituted 3-phenylprop-2-en-1-one compounds.

3. 2. 2. IR Spectral Correlation of $\nu\text{CO}_{s-trans}(\text{cm}^{-1})$

The IR frequency $\nu\text{CO}_{s-trans}(\text{cm}^{-1})$ values of all substituted 3-phenylprop-2-en-1-one compounds except that with 3-Br and 2-Cl substituent have shown satisfactory correlations with *R* parameter ($r=0.905$). When the substituent that has been given exception is included in regression it reduces the correlations considerably. The IR frequency $\nu\text{CH}_{IP}(\text{cm}^{-1})$ values of all substituted 3-phenylprop-2-en-1-one compounds have shown poor correlations ($r < 0.900$) with all Hammett substituent constants and *F* parameter. This is attributed to the weak polar, inductive, resonance and field effects of the substituents. All the correlations except Hammett substituent constants σ^+ , σ_I and *F* parameter have shown positive ρ values. This indicates the operation of normal substituent effect with respect to IR frequency $\nu\text{CO}_{s-trans}(\text{cm}^{-1})$ values in all substituted 3-phenylprop-2-en-1-one compounds.

3. 2. 3. IR Spectral Correlation of $\nu\text{CH}_{IP}(\text{cm}^{-1})$

The IR frequency $\nu\text{CH}_{IP}(\text{cm}^{-1})$ values of all substituted 3-phenylprop-2-en-1-one compounds have shown poor correlations ($r < 0.900$) with all Hammett substituent constants and *F* and *R* parameters. This is attributed to the weak polar, inductive, field and resonance effects of the substituents. All the correlation (except *F* parameter) have shown positive ρ values. This indicates the operation of normal substituent effect with respect to IR frequency $\nu\text{CO}_{s-trans}(\text{cm}^{-1})$ values in all substituted 3-phenylprop-2-en-1-one compounds.

3. 2. 4. IR Spectral Correlation of $\nu\text{CH}_{OP}(\text{cm}^{-1})$

The IR frequency $\nu\text{CH}_{OP}(\text{cm}^{-1})$ values of all substituted 3-phenylprop-2-en-1-one compounds, except that with the H(parant) and 3-Br substituents has shown satisfactory correlations with Hammett substituent constant σ_R ($r = 0.905$). The IR frequency $\nu\text{CH}_{OP}(\text{cm}^{-1})$ values of all substituted 3-phenylprop-2-en-1-one compounds, except that with the H(parant) substituent has shown satisfactory correlations with *R* parameter ($r = 0.905$). When these substituents that have been

given exception are included in regression they reduce the correlations considerably. The IR frequency $\nu\text{CH}_{OP}(\text{cm}^{-1})$ values of all substituted 3-phenylprop-2-en-1-one compounds have shown poor correlations with remaining Hammett substituent constant σ , σ^+ , σ_I , and F parameter. This is attributed to the weak polar, inductive, and field effects of the substituents. All the correlations have shown (except σ_I , and F parameter) negative ρ values. This indicates the operation of reverse substituent effect with respect to IR frequency $\nu\text{CH}_{OP}(\text{cm}^{-1})$ values in all substituted 3-phenylprop-2-en-1-one compounds.

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

The IR frequency $\nu\text{CH}=\text{CH}_{OP}(\text{cm}^{-1})$ values of all substituted 3-phenylprop-2-en-1-one compounds except that with the 3-Br substituent has shown satisfactory correlations with Hammett substituent constant σ ($r=0.903$) and σ^+ ($r = 0.902$). When these substituent that have been given exception are included in regression they reduce the correlations considerably. The IR frequency $\nu\text{CH}=\text{CH}_{OP}(\text{cm}^{-1})$ values of all substituted 3-phenylprop-2-en-1-one compounds have shown poor correlations with the remaining Hammett substituent constant σ_R , σ_I , and F and R parameters. This is attributed to the weak polar, inductive, field and resonance effects of the substituents. All the correlations (except σ_R and σ_I) have shown positive ρ values. This indicates the operation of normal substituent effect with respect to IR frequency $\nu\text{CH}=\text{CH}_{OP}(\text{cm}^{-1})$ values in all substituted 3-phenylprop-2-en-1-one compounds.

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

The IR frequency $\nu\text{C}=\text{C}_{OP}(\text{cm}^{-1})$ values of all substituted 3-phenylprop-2-en-1-one compounds except 4-Br and 3-Cl substituents has shown satisfactory correlations with Hammett substituent constants σ ($r=0.903$) and σ^+ ($r = 0.903$). When these substituents that have been given exception are included in regression they reduce the correlations considerably. The IR frequency $\nu\text{C}=\text{C}_{OP}(\text{cm}^{-1})$ values of all substituted 3-phenylprop-2-en-1-one compounds have shown poor correlations with the remaining Hammett substituent constants and F and R parameters. This is attributed to the inductive, field and resonance effects of the substituents. All the correlations have shown negative ρ values. This indicates the operation of reverse substituent effect with respect to IR frequency $\nu\text{C}=\text{C}_{OP}(\text{cm}^{-1})$ values in all substituted 3-phenylprop-2-en-1-one compounds. Most of the single regression analyses have shown poor correlation, it is decided to go for multi-regression analyses. The multi-regression produced satisfactory correlations with Hammett substituent constants and F and R parameters [21]. The multi correlation equations are given in (5) - (16).

$$\nu\text{CO}_{s-cis}(\text{cm}^{-1}) = 1661.37(\pm 1.826) + 5.759(\pm 1.917)\sigma_I + 2.279(\pm 0.758)\sigma_R \quad (5)$$

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

$$\nu\text{CO}_{s-cis}(\text{cm}^{-1}) = 166.22(\pm 1.743) + 4.453(\pm 1.484)F + 3.571(\pm 1.190)R \quad (6)$$

$(R = 0.940, n=11, P>90\%)$

$$\nu\text{CO}_{s-trans}(\text{cm}^{-1}) = 1598.148(\pm 1.584) - 0.407(\pm 0.135)\sigma_I + 7.972(\pm 2.657)\sigma_R \quad (7)$$

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

$$\nu\text{CO}_{s-trans}(\text{cm}^{-1}) = 1598.333(\pm 1.525) - 1.384(\pm 0.461)F + 5.532(\pm 1.844)R \quad (8)$$

$(R = 0.964, n=11, P>95\%)$

$$\nu\text{CH}_{ip}(\text{cm}^{-1}) = 1242.872(\pm 2.424) - 1.983(\pm 0.661)\sigma_I + 4.692(\pm 1.564)\sigma_R \quad (9)$$

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

$$\nu\text{CH}_{ip}(\text{cm}^{-1}) = 1243.734(\pm 2.240) - 0.120(\pm 0.040)F + 3.839(\pm 1.279)R \quad (10)$$

$(R = 0.927, n=11, P>90\%)$

$$\nu\text{CH}_{op}(\text{cm}^{-1}) = 787.298(\pm 11.950) + 25.673(\pm 8.557)\sigma_I - 47.098(\pm 15.699)\sigma_R \quad (11)$$

$(R = 0.959, n=11, P>95\%)$

$$\nu\text{CH}_{op}(\text{cm}^{-1}) = 788.856(\pm 11.060) + 21.485(\pm 7.161)F - 34.791(\pm 11.597)R \quad (12)$$

$(R = 0.958, n=11, P>95\%)$

$$\nu\text{CH}=\text{CH}_{op}(\text{cm}^{-1}) = 1048.253(\pm 3.541) + 3.529(\pm 1.176)\sigma_I + 4.297(\pm 1.432)\sigma_R \quad (13)$$

$(R = 0.925, n=11, P>90\%)$

$$\nu_{\text{CH}=\text{CH}_{op}} (\text{cm}^{-1}) = 11048.270(\pm 3.265) + 3.637(\pm 1.212)F + 4.038(\pm 1.346)R \quad (14)$$

($R = 0.923$, $n=11$, $P>90\%$)

$$\nu_{\text{C}=\text{C}_{op}} (\text{cm}^{-1}) = 552.916(\pm 7.365) - 15.421(\pm 5.140)\sigma_1 - 21.451(\pm 7.150)\sigma_R \quad (15)$$

($R = 0.954$, $n=11$, $P>95\%$)

$$\nu_{\text{C}=\text{C}_{op}} (\text{cm}^{-1}) = 551.500(\pm 7.136) - 10.749(\pm 3.583)F - 16.592(\pm 5.530)R \quad (16)$$

($R = 0.935$, $n=11$, $P>90\%$)

3.3. NMR Spectral study

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 vinyl proton chemical shifts (ppm) have been correlated with reactivity parameters using Hammett equation in the form of

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

where δ_0 is the chemical shift of unsubstituted system.

3.3.1. ^1H NMR Spectral correlation

3.3.2. ^1H NMR Spectral Correlations of H_α (ppm)

The assigned H_α chemical shifts (δ , ppm) values are correlated with Hammett constants [14-20] and F and R parameters [21], all substituents have shown poor correlation with all Hammett substituent constants and F and R parameters. This is attributed to the weak polar, inductive, resonance and field effects of the substituents. The substituents effect for predicting the reactivity on the chemical shifts through resonance as per the conjugative structure shown in Fig. 1. All the correlations have shown negative ρ values. This indicates the operation of reverse substituent effect.

3.3.3. ^1H NMR Spectral Correlations of H_β (ppm)

The assigned H_β chemical shifts (δ , ppm) values are correlated with Hammett constants and F and R parameters, except 2-Cl substituent have shown satisfactory correlation with Hammett substituent Constant σ ($r=0.901$). When the substituent that has been given exception is included in regression it reduces the correlations considerably. The IR frequency $\nu_{\text{C}=\text{C}_{OP}}(\text{cm}^{-1})$ values of all substituted 3-phenylprop-2-en-1-one compounds have shown poor correlations with the remaining Hammett substituent constants and F and R parameters. This is attributed to the polar effects, inductive effects, resonance effects and field effect. All the correlations except σ^+ and R parameter have shown negative ρ values. This indicates the operation of reverse substituent effect.

Some of the single regression analyses have shown poor correlations with Hammett substituent constants and swain-Lupton's parameters [21]. It is decided to go for multi-regression, the multi-regression analysis produced satisfactory correlations with the chemical shifts of (δ , ppm) H_α and H_β . The multi-correlation equations are given in (18)-(21).

$$\delta_{\text{H}_\alpha}(\text{ppm}) = 7.481(\pm 0.070) - 0.238(\pm 0.793)\sigma_1 - 0.277(\pm 0.092)\sigma_R \quad (18)$$

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

$$\delta_{\text{H}_\alpha}(\text{ppm}) = 7.476(\pm 0.066) - 0.237(\pm 0.079)F - 0.260(\pm 0.086)R \quad (19)$$

($R = 0.957$, $n=11$, $P>95\%$)

$$\delta_{\text{H}_\beta}(\text{ppm}) = 7.807(\pm 0.098) - 0.050(\pm 0.016)\sigma_1 - 0.049(\pm 0.016)\sigma_R \quad (20)$$

($R = 0.910$, $n=11$, $P>90\%$)

$$\delta_{\text{H}_\beta}(\text{ppm}) = 7.829(\pm 0.090) - 0.074(\pm 0.024)F - 0.001(\pm 0.0003)R \quad (21)$$

($R = 0.914$, $n=11$, $P>90\%$)

3.4. ^{13}C NMR spectral correlation

3.4.1. ^{13}C NMR spectral correlation of δC_α carbon

The assigned C_α chemical shifts (δ , ppm) correlated with Hammett constants [14-20] and F and R parameters, except that with 2-Cl substituent have shown satisfactory correlation with Hammett substituent constant σ ($r = 0.965$) σ^+ ($r=0.913$). When the substituent that has been given exception is included in regression it reduces the correlations considerably. The remaining few

Hammett substituent constants σ_I , σ_R and F and R parameters have shown poor correlations ($r < 0.900$). This is attributed to the inductive and resonance effects of the substituent. All the correlations have shown positive ρ values. This indicates the operation of normal substituent effect.

3. 4. 2. ^{13}C NMR spectral correlation of δC_β carbon

The assigned C_β chemical shifts (δ , ppm) correlated with Hammett constants and F and R parameters, All substituent have shown satisfactory correlation with Hammett substituent constant σ_I ($r = 0.907$). C_β chemical shifts (δ , ppm) correlated with Hammett constants and F and R parameters, expect that with 2-Cl substituent have shown satisfactory correlation with Hammett substituent constant σ ($r = 0.907$), σ^+ ($r = 0.907$) and F ($r = 0.904$) parameter. When the substituent that has been given exception is included in regression it reduces the correlations considerably. The remaining one Hammett substituent constants σ_R and R parameters [21] have shown poor correlations ($r < 0.900$). This is attributed to the resonance effects of the substituent. All the correlations have shown negative ρ values. This indicates the operation of reverse substituent effect.

3. 4. 3. ^{13}C NMR spectral correlation of δCO carbon

The assigned CO chemical shifts (δ , ppm) correlated with Hammett constants and F and R parameters, all the substituent have shown satisfactory correlation with Hammett substituent constants σ ($r = 0.991$), σ^+ ($r=0.972$), σ_I ($r = 0.907$) F parameter ($r=0.906$). When the substituent that has been given exception is included in regression it reduces the correlations considerably. The remaining one Hammett substituent constants σ_R and R parameter have shown poor correlations ($r < 0.900$). This is attributed to the resonance effect of the substituents. All the correlations have shown negative ρ values. This indicates the operation of reverse substituent effect. Some of the single regression analyses have shown poor correlations with Hammett substituent constants and swain-Lupton's parameters [21]. It is decided to go for multi-regression, the multi-regression analysis produced satisfactory correlations with the chemical shifts of (δ , ppm) C_α , C_β and CO. The multi correlation equations are given in (22)-(27).

$$\delta\text{CO}(\text{ppm}) = 189.058(\pm 0.105) - 1.146(\pm 0.382) \sigma_I - 0.694(\pm 0.231) \sigma_R \quad (22)$$

$(R = 0.988, n=11, P>95\%)$

$$\delta\text{CO}(\text{ppm}) = 189.998(\pm 0.097) - 1.086(\pm 0.362)F - 0.818(\pm 0.272)R \quad (23)$$

$(R = 0.988, n=11, P>95\%)$

$$\delta\text{C}_\alpha(\text{ppm}) = 121.170(\pm 0.854) + 3.173(\pm 1.057)\sigma_I + 1.601(\pm 0.533)\sigma_R \quad (24)$$

$(R = 0.953, n=11, P>95\%)$

$$\delta\text{C}_\alpha(\text{ppm}) = 121.574(\pm 0.774) + 2.856(\pm 0.952) F + 2.678(\pm 0.892) R \quad (25)$$

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

$$\delta\text{C}_\beta(\text{ppm}) = 144.662(\pm 0.604) - 4.641(\pm 1.547) \sigma_I - 1.832(\pm 0.610) \sigma_R \quad (26)$$

$(R = 0.978, n=11, P>95\%)$

$$\delta\text{C}_\beta(\text{ppm}) = 144.135(\pm 0.610) - 3.958(\pm 1.330) F - 2.914(\pm 0.971) R \quad (27)$$

$(R = 0.974, n=11, P>95\%)$

4. CONCLUSION

A series of ten numbers of substituted (*E*)-1-(4-fluoro-3-methylphenyl)-3-phenylprop-2-en-1-one compounds have been synthesized by condensation of 4-fluoro-3-methyl acetophenone with substituted benzaldehydes. These synthesized substituted (*E*)-1-(4-fluoro-3-methylphenyl)-3-phenylprop-2-en-1-one compounds have been characterized by their physical constants, UV, IR and NMR spectral data. These UV, IR, NMR spectral data of these chalcones has been correlated with Hammett substituent constants, F and R parameters. From the results of statistical analyses the effects of substituent on the spectral data have been studied. UV and ^{13}C NMR spectral correlations produced more number of satisfactory correlations. Some of the Hammett substituent constants and swain-Lupton's parameters have shown poor correlation. However, all the multi-regression analyses have shown satisfactory correlations.

Acknowledgement

The authors thank DST NMR facility, Department of Chemistry, Annamalai University, Annamalainagar-608 002, for recording NMR spectra of ten synthesized compounds.

References

- [1] Di Carlo G., Mascolo N., Izzo A.A., Capasso F., *Life Sci* 65 (1999) 122.
- [2] Majinda R.R.T., Abegaz B.M., Bezabih M., Ngadjui B.T., Wanjala C.C.W., Mdee L.L., Bojase G., Sialyo A., Masesane I., Yeboah S.O., *Pure Appl Chem* 73 (2001)1197.
- [3] Mirinda C. L., Aponso G. L., Stevens J. F., Denizer M. L., Buhler D. R., *Cancer Lett* 149 (2000) 21–29.
- [4] Monostory K., Tamasi, V., Vereckey, L., Perjesi, P., *Toxicology* 184 (2003) 203.
- [5] Modzelewska A., Pettit C., Achanta G., Davidson N.E., Huang P., Khan S.R., *Bioorg Med Chem* 14 (2006) 3491.
- [6] Sitaram Kumar M., Das J., Iqbal J., Trehan S., *Eur J Med Chem* 42 (2007) 538.
- [7] Thirunarayanan, G., Ananthakrishna Nadar, P., *Asian J Chem* 14 (2002) 1518.
- [8] Thirunarayanan G., Vanangamudi G., *E-J. Chem* 4 (1) (2007) 90.
- [9] Subramanian M., Vanangamudi G., Thirunarayanan G., *Spectrochim Acta* 110A (2013) 116.
- [10] Shendarkar G.R., Savant D.M., Badole K.D., Waghmare G.S., *Int. J Phar Tech Res* Vol.4, No.3, pp 1129-1135.
- [11] GiasuddinAhmed M., Romman U. K. R., Mosaddeq Ahmed S., Kawsari Akhter.,and Ershad Halim Md., *Bangladesh J. Sci. Ind. Res.* 42(1), 2007, 45-52
- [12] Vanangamudi G., Ranganathan K., Thirunaryanan G., *World J Chem* 7 (2012) 22
- [13] Kamalakkannan D., Vanangamudi G., Arulkumaran R., Thirumurthy K., Mayavel P., Thirunarayanan G., *Elixir OrgChem* 46 (2012) 157.
- [14] Sakthinathan S. P., Suresh R., Mala V., Sathiyamoorthi K., Kamalakkannan D., Ranganathan K., Arulkumaran R., Vijayakumar S., Sundararajan R., Vanangamudi G., Thirunarayanan G., *Int Lett Chem Phy Astro* 6 (2013) 77.
- [15] Sekar K. G., Thirunarayanan G., *Int Lett Chem Phy Astro* 8(2) (2013) 160
- [16] Senbagam R., Rajarajan M., Vijayakumar R., Manikandan V., Balaji S., Vanangamudi G.,Thirunarayanan G., *W S N 3* (2015) 155.
- [17] Vijayakumar R., Rajarajan M., Balaji S., Manikandan V., Senbagam R., Vanangamudi G.,Thirunarayanan G., *W S N 3* (2015) 81.
- [18] Rajarajan M., Senbagam R., Vijayakumar R., Manikandan V., Balaji S., Vanangamudi G.,Thirunarayanan G., *W S N 3* (2015) 155.
- [19] Senbagam R., Rajarajan M., Vijayakumar R., Manikandan., Balaji S., Vanangamudi G., Thirunarayana G., *Int Lett Chem Phy Astro* 53 (2015) 154.
- [20] Thirunarayanan G., Sathiyendiran V., Vanangamudi G., Arulkumaran R., Manikandan V., Suresh R., Kamalakkannan D., Sakthinathan S. P., Sundararajan R., Sathiyamorthi K., Balaji S., Vijayakumar R., Senbagam R. *Int Lett Chem Phy Astro*50 (2015) 9.
- [21] Swain C. G., Lupton E. C. Jr., *Am. Chem. Soc* 90 (1968) 4328.