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

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ABSTRACT

A series of substituted of *(E)*-1-(5-chloro-2-hydroxyphenyl)-3-phenylprop-2-en-1-one compounds by cross-aldol condensation reaction of 5-chloro-2-hydroxy acetophenone with various substituted benzaldehyde in the presence sodium hydroxide (base). The synthesized substituted (*E*)-1-(5-chloro-2-hydroxyphenyl)-3-phenylprop-2-en-1-one compounds was characterized by physical constants, UV, FT-IR, ^{1}H & ^{13}C-NMR spectral data. All the spectral data of substituted (*E*)-1-(5-chloro-2-hydroxyphenyl)-3-phenylprop-2-en-1-one compounds has been Hammett correlation with linear regression analyses.

***Keywords*:** (*E*)-5-Chloro-2-hydroxyphenyl chalcones; synthesis; UV; IR and NMR spectra; Hammett correlation analysis; Substituent effect

1. INTRODUCTION

Chalcones are very interesting compound, moreover, natural and synthetic compound of chalcones have role as precursors for other compound, therefore, many chalcones become

model structure of target compound by researcher [1]. Recently, chalcones compound doped polymers [2-4] are gaining attention of researchers due to their interesting properties and potential applications. Chalcones are group of compounds with various substitution patterns on the two aromatic rings of 1,3-diphenyl-2-propen-1-one. Chalcones constitute an important class of natural products belonging to the flavonoid family. Aldol condensation represents an important class of carbon-carbon bond formation reactions.

Chalcones constitute an important group of natural compounds that are especially abundant in fruits (e.g., citruses, apples), vegetables (e.g., tomatoes, shallots, bean sprouts, potatoes) and various plants and spices (e.g., licorice) many of which have been used for centuries in traditional herbal medicine [5]. The α,β-unsaturated ketones are the major content in citrus fruits and various plants. Chalcones as very good synthons for the production of five and six-member ring systems [6,7] such as pyrazoles [8], pyrazolines [9], isoxazolines [10], aurones [11], pyrimidine [12], falvanones [13] and di-aryl cyclohexenones [14] and so on.

In the present study we report the synthesis of substituted *(E)*-1-(5-chloro-2-hydroxyphenyl)-3-phenylprop-2-en-1-one compounds by cross-aldol condensation reaction of 5-chloro-2-hydroxy acetophenone with various substituted benzaldehyde. The UV, IR and NMR spectral data of these substituted *(E)*-1-(5-chloro-2-hydroxyphenyl)-3-phenylprop-2-en-1-one compounds have been utilized for studying the quantitative structure activity relationships through Hammett correlations.

2. EXPERIMENTAL

2. 1. Material and methods

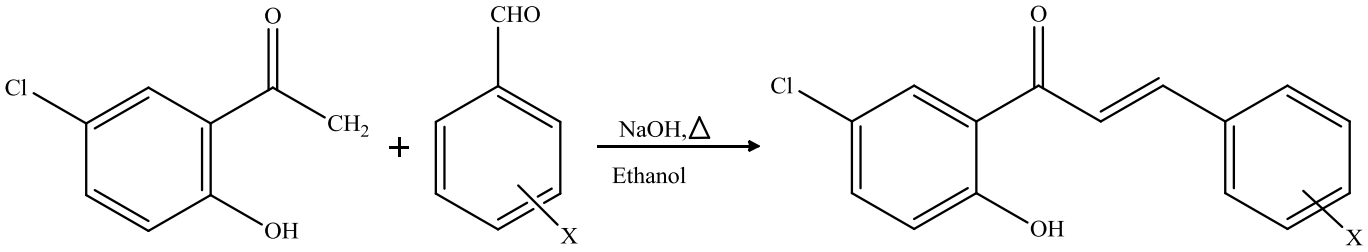
All the used chemicals and materials were purchased from Aldrich and Merck chemical companys. Melting points of all the synthesized substituted (*E*)-1-(5-chloro-2-hydroxyphenyl)-3-phenylprop-2-en-1-one compounds were observed in open glass capillaries on Mettler FP51 and were uncorrected. The UV spectra of all substituted (*E*)-1-(5-chloro-2-hydroxyphenyl)-3-phenylprop-2-en-1-one have been recorded using SHIMADZU- 1650 SPECTROMETER in spectral grade methanol. IR spectra (KBr, 4000-400 cm^{-1}) have been recorded on SHIMADZU-2010 Fourier transform spectrophotometer. The NMR spectra have been recorded in BRUKER 400 spectrometer operating at 400 MHz for ^{1}H NMR spectra and 100 MHz for ^{13}C NMR spectra in $CDCl_3$ solvent using TMS as internal standard.

2. 2. General procedure for crossed-aldol condensation of synthesis substituted (*E*)-1-(5-chloro-2-hydroxyphenyl)-3-phenylprop-2-en-1-one compounds:

Equi-molar quantities of 5-chloro-2-hydroxy acetophenone (0.05 mol) and various substituted benzaldehydes (0.05 mol) were dissolved in 20 ml rectified ethanol in a 250 ml round-bottom flask equipped with a magnetic stirrer. Then 10 mL NaOH solution (1.0 g in 10 mL H_2O) was added drop wise to the reaction mixture on vigorous stirring for 20 minutes [15,16].

The reaction mixture was neutralized by the addition of 0.1 N HCl, and then the precipitate was obtained. On filtering off, the crude substituted (*E*)-1-(5-chloro-2-hydroxyphenyl)-3-phenylprop-2-en-1-one compounds was dried in air-oven and recrystallized from rectified ethanol to get glittering yellow color solid, and their melting points were been

observed. The general reaction is shown in **Scheme 1.** The physical constants are presented in **Table 1**. The UV, IR and NMR spectral value of these substituted (*E*)-1-(5-chloro-2-hydroxyphenyl)-3-phenylprop-2-en-1-one compounds is presented in **Table 2**.



X= H, 3-Br, 4-Br, 3-Cl, 3-F, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5

Scheme 1. Synthesis of substituted (*E*)-1-(5-chloro-2-hydroxyphenyl)-3-phenylprop-2-en-1-ones.

Table 1. Physical constants and analytical data of substituted (*E*)-1-(5-chloro-2-hydroxyphenyl)-3-phenylprop-2-en-1-one compounds.

Entry	X	M. F.	M. W.	Yield (%)	M.P. (°C)
1	H	$C_{15}H_{11}O_2Cl$	259	88	59-60
2	3-Br	$C_{15}H_{10}O_2BrCl$	337	86	97-98
3	4-Br	$C_{15}H_{10}O_2BrCl$	337	89	60-62
4	3-Cl	$C_{15}H_{10}O_2Cl_2$	293	83	129-130
5	3-F	$C_{15}H_{10}O_2FCl$	276	94	105-106
6	4-F	$C_{15}H_{10}O_2FCl$	276	92	158-160
7	4-OCH_3	$C_{16}H_{13}O_3Cl$	289	89	135-136
8	4-CH_3	$C_{16}H_{13}O_2Cl$	273	87	79-81
9	3-NO_2	$C_{15}H_{10}NO_4Cl$	304	90	162-163
10	3-OC_6H_5	$C_{21}H_{15}O_3Cl$	351	85	118-120

Table 2. The Ultraviolet absorption maxima (λ_{max}, nm), infrared absorptions (ν, cm^{-1}) and NMR chemical hifts (δ, ppm) spectral data of substituted (*E*)-1-(5-chloro-2-hydroxyphenyl)-3-phenylprop-2-en-1-one compounds.

Entry	X	UV λ_{max}	IR (ν, cm^{-1})					
			CO s-*cis*	CO s-*trans*	CH*ip*	CH*op*	CH=CH*op*	C=C*op*
1	**H**	316.5	1643.35	1577.77	1192.01	808.17	1024.20	522.71
2	**3-Br**	316.0	1643.35	1579.70	1190.08	806.25	1022.27	526.57
3	**4-Br**	314.5	1687.71	1600.92	1192.01	825.53	1025.42	530.42
4	**3-Cl**	315.0	1643.35	1575.84	1192.01	810.10	1024.20	538.14
5	**3-F**	321.0	1643.35	1577.77	1190.08	808.17	1022.27	538.14
6	**4-F**	319.5	1641.42	1579.70	1188.15	825.53	1026.13	511.14
7	**4-OCH_3**	370.5	1691.57	1573.91	1182.72	833.25	1022.27	532.35
8	**4-CH_3**	337.0	1695.43	1597.06	1188.86	837.11	1022.27	547.78
9	**3-NO_2**	304.0	1691.57	1589.34	1184.29	829.39	1024.20	542.00
10	**3-OPh**	290.0	1689.64	1593.20	1182.36	821.86	1022.27	545.85

Entry	X	^{1}H NMR (δ, ppm)		^{13}C NMR (δ, ppm)		
		Hα	Hβ	Cα	Cβ	CO
1	**H**	7.564	7.944	119.45	146.53	192.81
2	**3-Br**	7.586	7.852	120.35	144.67	192.51
3	**4-Br**	7.475	7.956	119.88	145.30	190.55
4	**3-Cl**	7.473	7.912	120.36	144.78	192.64
5	**3-F**	7.470	7.922	120.30	146.12	192.81
6	**4-F**	7.526	7.942	118.43	145.21	192.63
7	**4-OCH_3**	7.454	7.935	120.21	146.50	192.75
8	**4-CH_3**	7.581	7.981	119.94	146.72	192.87
9	**3-NO_2**	7.563	7.867	120.35	144.78	192.55
10	**3-OPh**	7.541	7.891	119.87	145.03	192.59

3. RESULT AND DISCUSSION

3. 1. Spectral linearity

The spectral linearity of substituted (*E*)-1-(5-chloro-2-hydroxyphenyl)-3-phenylprop-2-en-1-one compounds was evaluating the substituent effects [17,18] with respect to various spectral value. The assigned spectral data of all substituted (*E*)-1-(5-chloro-2-hydroxyphenyl)-3-phenylprop-2-en-1-one compounds such as absorption maximum λ_{max} (nm), infrared carbonyl stretches of ν*C*O *s-cis and* ν*C*O *s-trans*, the deformation modes of CH *out of plane*, *in-plane*, CH=CH and >C=C< *out of planes* (cm^{-1}), NMR chemical shifts δ (ppm) of H_α, H_β, C_α, C_β, CO are assigned and these data are correlated with Hammett substituent constants (σ, σ^+, σ_I & σ_R) [19,20] and Swain- Lupton's parameters (*F* & *R*) [21].

3. 1. 1. UV spectral study

The absorption maxima (λ_{max} nm) of synthesized substituted (*E*)-1-(5-chloro-2-hydroxyphenyl)-3-phenylprop-2-en-1-one compounds were assigned and presented in **Table 2**. These absorption maxima (λ_{max} nm) of these substituted (*E*)-1-(5-chloro-2-hydroxyphenyl)-3-phenylprop-2-en-1-one compounds were correlated with Hammett substituent constants (σ, σ^+, σ_I & σ_R) and Swain-Lupton's parameters (*F* & *R*) using single and multi-linear regression analysis. Hammett correlation involving the group frequencies and absorption maxima (λ_{max} nm), the form of the Hammett equation employed is

$$\lambda = \rho\sigma + \lambda_o \qquad \text{……..…. (1)}$$

where: λ_o is the absorption maximum of the unsubstituted system.

From the **Table 3**, it is evident that the UV absorption maximum λ_{max} (nm) values of all substituted (*E*)-1-(5-chloro-2-hydroxyphenyl)-3-phenylprop-2-en-1-one compounds, all the substituents have shown good correlations with σ (r = 0.907), σ^+ (r = 0.905), σ_I (r = 0.939), F (r = 0.921), and R (r = 0.906) parameters. Except that with the 4-OCH_3 substituent has shown good correlations with σ_R (r = 0.917) parameter. When the 4-OCH_3 substituent that has been given exception is included in regression it reduces the correlations considerably. The UV absorption through resonance as per the conjugative structure shown in **Fig. 1**.

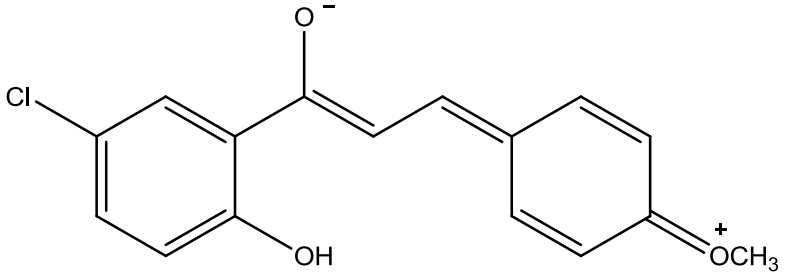


Fig.1 - Resonance conjugative structure

All the correlations have shown negative ρ values. This indicates the operation of reverse substituent effect with respect to UV absorption maximum λ_{max} (nm) values in all substituted

(*E*)-1-(5-chloro-2-hydroxyphenyl)-3-phenylprop-2-en-1-one compounds. Since all the single parameter correlations good (r>0.900) with Hammett constants (σ, σ^+, σ_I & σ_R) and **Table 3**. Results of statistical analysis of UV absorption maxima (λ_{max}, nm), IR frequencies (ν, cm^{-1}) and NMR chemical shifts (δ, ppm) of substituted (*E*)-1-(5-chloro-2-hydroxyphenyl)-3-phenylprop-2-en-1-one compounds with Hammett substituent constants (σ, σ^+, σI & σR) and *F* and *R* parameters.

Table 3. Results of statistical analysis of UV, IR and NMR.

Frequency	Constt.	r	I	ρ	s	n	Correlated derivatives
λ_{max}	σ	0.907	329.67	-53.93	15.38	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3- OC_6H_5
	σ^+	0.905	321.27	-23.11	19.43	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	σ_I	0.939	334.03	-36.36	20.75	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	σ_R	0.917	316.27	-16.98	22.22	9	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-CH_3, 3-NO_2, 3-OC_6H_5
	F	0.921	329.26	-21.61	21.72	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	R	0.906	311.56	-43.74	16.73	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
$\nu CO_{s\text{-}cis}$	σ	0.721	1667.09	-0.11	27.03	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	σ^+	0.726	1667.70	-16.62	25.74	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	σ_I	0.712	1673.98	-18.42	26.66	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	σ_R	0.665	1672.40	21.92	26.54	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5

	F	0.725	1677.89	-26.38	25.97	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	R	0.836	1673.18	30.27	24.92	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
$\nu CO_{s\text{-}trans}$	σ	0.639	1582.88	9.49	9.89	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	σ^+	0.658	1584.42	2.52	10.23	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	σ_I	0.800	1585.87	-3.61	10.27	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	σ_R	0.823	1587.29	11.40	9.95	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	F	0.818	1587.19	-6.52	10.14	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	R	0.905	1587.54	14.96	8.91	8	H, 3-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 3-NO_2, 3-OC_6H_5
νCH_{ip}	σ	0.820	1188.19	0.35	4.03	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	σ^+	0.847	1188.11	3.83	3.56	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	σ_I	0.815	1189.21	-2.55	3.98	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	σ_R	0.842	1189.28	4.24	3.91	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	F	0.811	1188.95	-1.69	4.00	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5

	R	0.824	1187.67	-2.87	3.91	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
νCH_{op}	σ	0.822	822.09	-9.04	11.85	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	σ^+	0.840	820.91	-9.87	11.13	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	σ_I	0.817	823.78	-8.66	11.98	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	σ_R	0.807	821.43	3.68	12.14	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	F	0.814	823.15	-6.38	12.03	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	R	0.800	820.60	0.33	12.17	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
$\nu CH{=}CH_{op}$	σ	0.826	1023.31	1.36	1.50	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	σ^+	0.834	1023.50	1.07	1.47	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	σ_I	0.828	1022.86	1.83	1.50	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	σ_R	0.821	1023.80	1.44	1.52	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	F	0.827	1022.91	1.53	1.50	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	R	0.810	1023.45	-0.46	1.55	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5

νC=C$_{op}$	σ	0.820	532.15	7.85	11.72	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	σ^+	0.808	533.58	-2.10	11.92	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	σ_I	0.810	535.52	-5.36	11.90	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	σ_R	0.791	535.85	9.65	11.75	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	F	0.813	536.87	-8.21	11.74	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	R	0.848	536.89	16.73	10.47	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
δH$_{α}$	σ	0.849	7.541	0.270	0.148	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	σ^+	0.809	7.587	0.030	0.169	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	σ_I	0.813	7.540	0.127	0.167	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	σ_R	0.806	7.634	0.189	0.164	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	F	0.840	7.577	0.026	0.170	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	R	0.781	7.670	0.403	0.097	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
δH$_{β}$	σ	0.905	7.934	-0.081	0.034	8	H, 4-Br, 3-Cl,4-Cl, 4-F, 4-CH_3, 3-NO_2, 3-OC_6H_5

	σ^+	0.842	7.921	-0.036	0.038	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	σ_I	0.906	7.960	-0.107	0.033	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	σ_R	0.807	7.916	-0.013	0.042	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	F	0.847	7.945	-0.061	0.039	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	R	0.812	7.911	-0.043	0.040	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
δCO	σ	0.956	192.29	0.00	0.83	8	H, 3-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 3-NO_2, 3-OC_6H_5
	σ^+	0.912	192.30	-0.17	0.83	8	H, 3-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 3-NO_2, 3-OC_6H_5
	σ_I	0.922	192.00	0.78	0.81	8	H, 3-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 3-NO_2, 3-OC_6H_5
	σ_R	0.923	192.08	-0.85	0.81	8	H, 3-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 3-NO_2, 3-OC_6H_5
	F	0.928	191.94	0.85	0.80	8	H, 3-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 3-NO_2, 3-OC_6H_5
	R	0.907	192.25	-0.19	0.83	8	H, 3-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 3-NO_2, 3-OC_6H_5
δC_α	σ	0.946	120.28	0.18	0.05	8	H, 3-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 3-NO_2, 3-OC_6H_5
	σ^+	0.962	120.31	0.09	0.06	9	H, 3-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5

	σ_I	0.815	120.24	0.19	0.06	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	σ_R	0.811	120.32	0.03	0.08	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	F	0.923	120.27	0.11	0.07	8	H, 3-Br, 3-Cl,4-Cl, 4-F, 4-CH_3, 3-NO_2, 3-OC_6H_5
	R	0.821	120.33	0.05	0.07	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
δC_β	σ	0.806	145.89	-1.92	0.63	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	σ^+	0.905	145.59	-0.89	0.73	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	σ_I	0.907	146.59	-2.74	0.54	8	H, 3-Br, 4-Br, 3-Cl, 4-F, 4-CH_3, 3-NO_2, 3-OC_6H_5
	σ_R	0.804	145.52	-0.15	0.86	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	F	0.815	146.26	-1.64	0.72	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
	R	0.894	145.40	-0.79	0.81	10	H, 3-Br, 4-Br, 3-Cl,4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 3-OC_6H_5
r = correlation co-efficient; ρ = slope; I = intercept; s = standard deviation; n = number of substituents							

Swain-Lupton's parameters (*F&R*), and go for multi regression analysis. While seeking the multi regression analysis, good correlations are observed as shown in the following equations (2) and (3).

$$\lambda_{max}\,(\text{nm}) = 329.659(\pm14.460) - 41.433(\pm3.142)\sigma_I - 25.836(\pm3.278)\sigma_R \quad (R = 0.947,\ n = 10,\ P > 90\%) \qquad \ldots(2)$$

$$\lambda_{max}\,(\text{nm}) = 327.564(\pm7.412) - 45.352(\pm16.338)F - 56.584(\pm3.421)R \quad (R = 0.987,\ n = 10,\ P > 95\%) \qquad \ldots(3)$$

3. 2. IR spectral study

The carbonyl stretching frequencies (cm^{-1}) of the entire substituted (*E*)-1-(5-chloro-2-hydroxyphenyl)-3-phenylprop-2-en-1-ones of *s-cis* and *s-trans* conformers are shown in **Fig. 2.** The IR frequency values are presented in **Table 2**

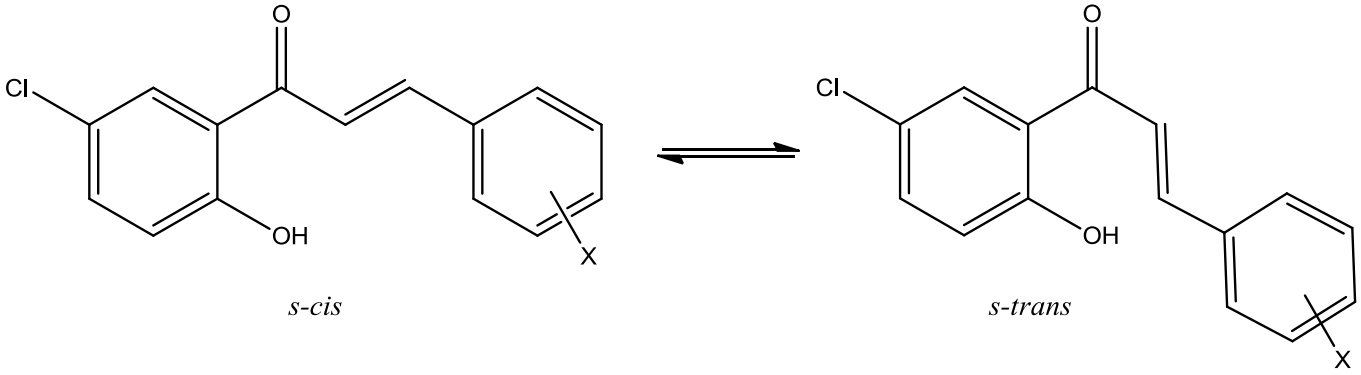


Fig.2. The *s-cis* and *s-trans* conformers of substituted (*E*)-1-(5-chloro-2-hydroxyphenyl)-3-phenylprop-2-en-1-one compounds.

The IR frequency values are correlated with Hammett substituent constants (σ, σ^+, σ_I & σ_R) and Swain- Lupton's parameters (*F* & *R*). While seeking Hammett correlation involving group frequencies, the form of the Hammett equation employed is

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

where ν_0 is the carbonyl frequencies of unsubstituted system.

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

The IR frequency $\nu CO_{s\text{-}cis}$ (cm^{-1}) values of all substituted (*E*)-1-(5-chloro-2-hydroxyphenyl)-3-phenylprop-2-en-1-one compounds. The all Hammett substituent constant (σ, σ^+, σ_I & σ_R) and Swain- Lupton's parameters (*F* & *R*) have shown poor correlations ($r < 0.900$). This is attributed to the weak resonance effect of the substituents for predicting the reactivity on the IR frequency $\nu CO_{s\text{-}cis}$ (cm^{-1}) values through resonance as per the conjugative structure stated earlier**.** All the correlations (except σ_R and *R*) have shown negative ρ values. This indicates the operation of reverse substituent effect with respect to IR frequency $\nu CO_{s\text{-}cis}$ (cm^{-1}) values in all substituted (*E*)-1-(5-chloro-2-hydroxyphenyl)-3-phenylprop-2-en-1-one compounds.

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

The IR frequency $\nu CO_{s\text{-}trans}$ (cm^{-1}) values of all substituted (*E*)-1-(5-chloro-2-hydroxyphenyl)-3-phenylprop-2-en-1-one compounds except those with 4-Br, 4-CH_3 substituent have shown good correlation with Swain- Lupton's parameter R ($r = 0.905$) parameter.

When these substituent that have been given exception are included in regression they reduce the correlations considerably, have shown poor correlations ($r < 0.900$) with remaining Hammett substituent constants (σ, σ^+, σ_I & σ_R) and Swain- Lupton's parameter (*F*). All the correlations (except σ_I and *F* parameter) have shown positive ρ values. This indicates the operation of normal substituent effect with respect to IR frequency $\nu CO_{s\text{-}trans}$ (cm^{-1}) values in all substituted (*E*)-1-(5-chloro-2-hydroxyphenyl)-3-phenylprop-2-en-1-one compounds.

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

The IR frequency νCH_{ip} (cm^{-1}) values of all substituted (*E*)-1-(5-chloro-2-hydroxyphenyl)-3-phenylprop-2-en-1-one compounds have shown poor correlations with the all Hammett substituent constants (σ, σ+, σ_I & σ_R) and Swain- Lupton's parameters (F & *R*). All the correlations (except σ_I and F and R) have shown positive ρ values. This indicates the operation of normal substituent effect with respect to IR frequency νCH_{ip} (cm^{-1}) values in all substituted (*E*)-1-(5-chloro-2-hydroxyphenyl)-3-phenylprop -2-en-1-one compounds.

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

The IR frequency νCH_{op} (cm^{-1}) values of all substituted (*E*)-1-(5-chloro-2-hydroxyphenyl)-3-phenylprop-2-en-1-one compounds have shown poor correlations with all Hammett substituent constant (σ, σ^+, σ_I, & σ_R) and Swain- Lupton's parameters (F&*R*). All the correlations (except σ_R and R) have shown negative ρ values. This indicates the operation of reverse substituent effect with respect to IR frequency νCH_{OP} (cm^{-1}) values in all substituted (*E*)-1-(5-chloro-2-hydroxyphenyl)-3-phenylprop-2-en-1-one compounds.

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

The IR frequency $\nu CH{=}CH_{OP}$ (cm^{-1}) values of all substituted (*E*)-1-(5-chloro -2-hydroxyphenyl)-3-phenylprop-2-en-1-one compounds have shown poor correlations with the all Hammett substituent constants (σ, σ+, σ_I & σ_R) and Swain- Lupton's parameters (F & *R*). All the correlations (except R) have shown positive ρ values. This indicates the operation of normal substituent effect with respect to IR frequency $\nu CH{=}CH_{OP}$ (cm^{-1}) values in all substituted (*E*)-1-(5-chloro-2-hydroxyphenyl)-3-phenylprop-2-en-1-one compounds.

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

The IR frequency $\nu C{=}C_{OP}$ (cm^{-1}) values of all substituted (*E*)-1-(5-chloro-2-hydroxyphenyl)-3-phenylprop-2-en-1-one compounds have shown poor correlations with the all Hammett substituent constants (σ, σ+, σ_I & σ_R) and Swain- Lupton's parameters (F & *R*). All the correlations (except σ^+,σ_I and F) have shown positive ρ values.

This indicates the operation of normal substituent effect with respect to IR frequency $\nu CH{=}CH_{OP}$ (cm^{-1}) values in all substituted (*E*)-1-(5-chloro-2-hydroxyphenyl)-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 good correlations with Hammett substituent constants (σ, σ^+, σ_I & σ_R) and Swain- Lupton's parameters (F & *R*) . The multi correlation equations are given in (5)-(16).

$\nu CO_{s\text{-}cis}\,(cm^{-1}) = 1677.163(\pm19.127) - 14.739(\pm4.156)\sigma_I + 18.773(\pm4.336)\,\sigma_R$
(R = 0.932, n = 10, P > 90%) …(5)

$\nu CO_{s\text{-}cis}\,(cm^{-1}) = 1678.668(\pm15.775) - 15.529(\pm3.477)\,F + 25.875(\pm2.856)\,R$
(R = 0.941, n = 10, P > 90%) …(6)

$\nu CO_{s\text{-}trans}\,(cm^{-1}) = 1587.756(\pm7.234) - 1.437(\pm0.1719)\,\sigma_I + 11.093(\pm1.640)\,\sigma_R$
(R = 0.926, n = 10, P > 90%) …(7)

$\nu\, CO_{s\text{-}trans}\,(cm^{-1}) = 1587.652(\pm 5.719) - 0.276(\pm0.002)\,F + 14.889(\pm5.356)\,R$
(R = 0.950, n = 10, P > 95%) …(8)

$\nu CH_{ip}\,(cm^{-1}) = 1189.869(\pm2.827) - 1.794(\pm0.014)\sigma_I + 3.863(\pm0.641)\,\sigma_R$
(R = 0.926, n = 10, P > 90%) …(9)

$\nu CH_{ip}\,(cm^{-1}) = 1188.838(\pm2.447) - 3.292(\pm0.539)\,F - 3.804(\pm0.443)R$
(R = 0.932, n = 10, P > 90%) …(10)

$\nu CH_{op}\,(cm^{-1}) = 824.117(\pm8.707) - 8.292(\pm1.892)\sigma_I + 1.917(\pm0.197)\sigma_R$
(R = 0.917, n = 10, P > 90%) …(11)

$\nu CH_{op}\,(cm^{-1}) = 823.104(\pm7.717) - 7.089\,(\pm1.701)\,F - 1.672(\pm0.397)\,R$
(R = 0.918, n = 10, P > 90%) …(12)

$\nu CH{=}CH_{op}\,(cm^{-1}) = 1023.187(\pm1.043) + 2.206(\pm0.226)\sigma_I + 1.912(\pm\,0.236)\sigma_R$
(R = 0.940, n = 10, P > 90%) …(13)

$\nu CH{=}CH_{op}\,(cm^{-1}) = 1022.918(\pm\,0.965) + 1.525(\pm0.212)F - 0.031(\pm0.017)R$
(R = 0.927, n = 10, P > 90%) …(14)

$\nu C{=}C_{op}\,(cm^{-1}) = 537.026(\pm8.524) - 3.617(\pm0.852)\sigma_I + 8.887(\pm1.932)\sigma_R$
(R = 0.920, n = 10, P > 90%) …(15)

$\nu C{=}C_{op}\,(cm^{-1}) = 537.368(\pm6.720) - 1.352(\pm0.481)F + 16.355(\pm3.169)R$
(R = 0.948, n = 10, P > 90%) …(16)

3. 3. NMR Spectral study

In Nuclear Magnetic Resonance spectra, the proton and the carbon chemical shifts (δ, ppm) depends on the electronic environment of the nuclei concerned. The assigned proton and carbon chemical shifts (δ, ppm) have been correlated with reactivity parameters using equation employed is shown in equation

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

where: δ_0 is the chemical shift of unsubstituted system.

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

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

The assigned H_{α} chemical shift (δ, ppm) values of all substituted (*E*)-1-(5-chloro-2-hydroxyphenyl)-3-phenylprop-2-en-1-one compounds have shown poor correlations ($r < 0.900$) with all Hammett substituent constants (σ, σ^{+}, σ_I & σ_R) and Swain- Lupton's parameters (F & *R*). This is attributed to weak inductive, resonance and field effects of the substituents for predicting the reactivity on the chemical shifts through resonance as per the conjugative structure shown in Fig. 1. All the correlations have shown positive ρ values. This indicates the operation of normal substituent effect with respect to H_{α} chemical shift (δ, ppm) values in all substituted (*E*)-1-(5-chloro-2-hydroxyphenyl)-3-phenylprop-2-en-1-one compounds.

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

The assigned H_{β} chemical shifts (δ, ppm) values are correlated with Hammett constants (σ, σ^{+}, σ_I & σ_R) and Swain- Lupton's parameter (F & *R*), except 3-Br and 4-OCH_3 substituents have shown good correlations with Hammett substituent constant σ ($r = 0.905$). When the substituent that has been given exception is included in regression it reduces the correlation considerably. This is due to incapability to the polar, inductive, resonance and field 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 remaining Hammett substituent constants (σ, σ^{+}, σ_I & σ_R) and swain-Lupton's parameters (F & R) . It is decided to go for multi-regression, the multi-regression analysis produced good correlations with the chemical shifts of (δ, ppm) H_{α} and H_{β}. The multi-correlation equations are given in (18)-(21).

$$\delta H_{\alpha}\,(\text{ppm}) = 7.579(\pm0.115) + 0.171(\pm0.025)\,\sigma_I - 0.226(\pm0.026)\,\sigma_R \quad (R = 0.935,\ n = 10,\ P > 90\%) \qquad \ldots(18)$$

$$\delta H_{\alpha}\,(\text{ppm}) = 7.591(\pm0.048) + 0.221(\pm0.009)\,F + 0.465(\pm0.089)\,R \quad (R = 0.989,\ n = 10,\ P > 95\%) \qquad \ldots(19)$$

$$\delta H_{\beta}\,(\text{ppm}) = 7.953(\pm0.023) - 0.114(\pm0.051)\,\sigma_I - 0.038(\pm0.005)\,\sigma_R \quad (R = 0.964,\ n = 10,\ P > 95\%) \qquad \ldots(20)$$

$$\delta H_{\beta}\,(\text{ppm}) = 7.943(\pm0.020) - 0.090(\pm0.005)\,F - 0.068(\pm0.037)\,R \quad (R = 0.966,\ n = 10,\ P > 95\%) \qquad \ldots(21)$$

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) of all substituted (*E*)-1-(5-chloro-2-hydroxyphenyl)-3-phenylprop-2-en-1-one compounds. Except 4-Cl and 3-NO_2 substituent have shown good correlations with Hammett substituent constant σ ($r = 0.946$). Except 4-Br substituent have shown good correlations with Hammett substituent constant σ^{+} ($r = 0.962$).

Except 4-Br and 4-OCH_3 substituent has shown good correlations with Swain- Lupton's parameter F (r = 0.923). When these substituent that have been given exception are included in regression they reduce the correlations considerably, have shown poor correlations (r < 0.900) with remaining Hammett substituent constants (σ_I & σ_R) and Swain- Lupton's parameter (R). All the correlations have shown positive ρ values. This indicates the operation of normal substituent effect with respect to C_α chemical shifts (δ, ppm) values in all substituted (*E*)-1-(5-chloro-2-hydroxyphenyl)-3-phenylprop-2-en-1-one compounds.

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

The assigned C_β chemical shifts (δ, ppm) of all substituted (*E*)-1-(5-chloro-2-hydroxyphenyl)-3-phenylprop-2-en-1-one compounds. All substituent have shown good correlations with Hammett substituent constant σ^+ (r = 0.905), except 4-Cl and 4-OCH_3 substituent have shown good correlations with Hammett substituent constant σ_I (r = 0.907). When these substituent that have been given exception are included in regression they reduce the correlations considerably, have shown poor correlations (r < 0.900) with remaining Hammett substituent constants (σ & σ_R) and Swain- Lupton's parameter (F & R). All the correlations have shown negative ρ values. This indicates the operation of reverse substituent effect with respect to C_β chemical shifts (δ, ppm) values in all substituted (*E*)-1-(5-chloro-2-hydroxyphenyl)-3-phenylprop-2-en-1-one compounds.

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

The assigned CO chemical shifts (δ, ppm) are correlated with Hammett constants (σ, σ^+, σ_I & σ_R) and *F* and *R* parameters, except 4-Br and 4-CH_3 substituents have shown good correlations with all Hammett substituent constant σ (r = 0.956) σ^+ (r = 0.912) σ_I (r = 0.922) σ_R (r = 0.923) and Swain- Lupton's parameters F (r = 0.928) and R (r = 0.907). When the substituent that has been given exception is included in regression it reduces the correlation considerably. All the correlations (except σ^+ σ_I and *F* parameters) have shown positive ρ values. This indicates the operation of normal substituent effect.

Some of the single regression analyses have shown poor correlations with Hammett substituent (σ, σ^+, σ_I, σ_R) constants and Swain-Lupton's parameters(F & R) . It is decided to go for multi-regression, the multi-regression analyses produced good correlations with the chemical shifts of (δ, ppm) C_α, C_β and CO. The multi correlation equations are given in (22)-(27).

$$\delta CO\ (ppm) = 191.878(\pm0.582) + 0.642(\pm0.126)\ \sigma_I - 0.717(\pm0.132)\ \sigma_R$$
(R = 0.963, n = 10, P > 95%) …(22)

$$\delta CO\ (ppm) = 191.947(\pm0.515) + 0.873(\pm0.113)\ F + 0.055(\pm0.009)R$$
(R = 0.948, n = 10, P > 90%) …(23)

$$\delta C_\alpha\ (ppm) = 120.259(\pm0.045) + 0.213(\pm0.099)\ \sigma_I + 0.085(\pm0.003)\sigma_R$$
(R = 0.963, n = 10, P > 95%) …(24)

$$\delta C_\alpha\ (ppm) = 120.276(\pm0.043)\ \ 0.154(\pm0.095)\ F + 0.103(\pm0.078)\ R$$
(R = 0.956, n = 10, P > 95%) …(25)

$$\delta C_\beta \text{ (ppm)} = 146.461(\pm 0.374) - 2.890(\pm 0.814)\ \sigma_I - 0.768(\pm 0.084)\ \sigma_R$$
(R = 0.980, n = 10, P > 95%) …(26)

$$\delta C_\beta \text{ (ppm)} = 146.197(\pm 0.356) - 2.249(\pm 0.785)\ F - 1.432(\pm 0.064)\ R$$
(R = 0.976, n = 10, P > 95%) …(27)

4. CONCLUSIONS

About ten numbers of substituted (*E*)-1-(5-chloro-2-hydroxyphenyl)-3-phenylprop-2-en-1-one compounds have been synthesized and their structure were confirmed by their physical constants, UV, IR and NMR spectral data. These spectral values have been correlated with Hammett substituent constant (σ, σ^+, σ_I & $\sigma_{R)}$ and Swain- Lupton's parameters (*F* & *R*). From the results of statistical analyses the effects of substituent on the spectral data have been studied. Single-regression analyses absorption maxima (λ_{max} nm), CO spectral data produced good correlations of all Hammett substituent constant (σ, σ^+, σ_I & σ_r) and Swain-Lupton's parameters (*F*&*R*). Most of the Hammett substituent constants and swain-Lupton's parameters have shown poor correlation. All the multi-regression analyses have shown good correlations.

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