



Spectral Linearity of some (E)-3-Thienyl Chalcones

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ABSTRACT

A series containing nine 3-thienyl chalcones have been synthesized solvent-free crossed aldol condensation of 3-acetyl thiophene and substituted benzaldehydes. The purities of these synthesized chalcones were checked by their physical constants and spectral data published earlier in literature. The spectral data such as UV λ_{max} (nm), infrared ν (cm^{-1}) COs-cis and s-trans, stretches, CH, CH=CH, C=C deformation modes, NMR chemical shifts (δ , ppm) of vinyl proton, carbon and carbonyl carbon of these chalcones were correlated with Hammett substituent constants, F and R parameters using single and multi-linear regression analyses. From the results of statistical analyses the effect of substituents on the above spectral data has been studied.

Key words: 3-Thienyl chalcones, Crossed-Aldol condensation, Infrared spectra, NMR spectra, Spectral correlation, Hammett equation.

1. INTRODUCTION

The quantitative structure-activity relationship (QSAR), quantitative structure-property relationship (QSPR), and quantitative structure relationships (QSR) were employed for determination of structure, qualitative and quantitative analysis of organic molecules [1,2]. Spectroscopic data were useful and utilized for prediction of ground state equilibration of organic molecules [3]. From infrared spectroscopic data, the E, Z, s-cis and s-trans conformers of alkenes, alkynes, unsaturated compounds, anti- and gauche form of acyl halides has been predicted [4,5]. From NMR spectra, the E and Z configuration of the above said molecules have been established using the coupling constant J, in Hz values [6-8]. Also these spectroscopic data were used for the study of structure parameter correlations in biological active molecules[9], analysis of normal co-ordination[10], reaction mechanism in transition states [11], qualitative and quantitative analysis [4, 12, 13], finding the nature, concentration and structure of samples [12,14], effect of substituents on long range β -sheet structure of oligopeptides [15], enol-enone mechanisms [16], density functional theory [17], gas phase reactivity of sulphides [18], and rotational barriers in selenomides [19]. The correlation of half wave reduction potential of unsaturated ketones gave the QSR relationships [20]. Chalcones possess multipronged activities, due the -CO-CH=CH- moiety and substituents in phenyl rings. The important biological activities of

chalcones are antimicrobial [21], anti-viral [22], anti-plasmodial [23], anti-tuberculosis [24], anti-oxidant [25], and insect antifeedants [26,27]. Now-a-days chemists and scientists have paid much more interest to correlate the spectral data with Hammett substituent constants for studied the effect of substituents of organic molecules [4, 28-31]. Recently, Sekar and Thirunarayanan [31] have studied the effect of substituents in heterocyclic compounds. Within the above view, there is no information available for the study of correlation of spectral data with Hammett substituent constants in 3-thienyl chalcones. Therefore, the authors have taken efforts to studying the effect of substituents on the spectral data of 3-thienyl chalcones by synthesize and record their UV-visible, infrared and NMR spectra.

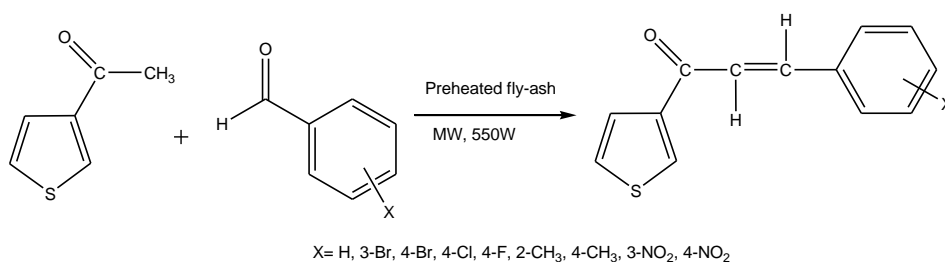
2. EXPERIMENTAL

2.1. Materials and Methods

All chemicals used were purchased from Sigma-Aldrich and E-Merck chemical company. Fly-ash was collected from the Thermal Power Plant II, Neyveli Lignite Corporation, Tamilnadu, India. Melting points of all chalcones were determined in open glass capillaries on Mettler FP51 melting point apparatus and are uncorrected. Infrared spectra (KBr, 4000-400 cm^{-1}) were recorded on AVATAR-300 Fourier transform spectrophotometer. INSTRUM AV300 operating at 500MHz was used for ¹H spectra and 125.46 MHz for ¹³C spectra in DMSO solvent using TMS as

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**Scheme 1:** Synthesis of 3-thienyl chalcones**Table 1.** Analytical and mass spectral data of 3-thienyl chalcones

Entry	X	M.F.	M.W.	Yield (%)	M.p. (°C)	Mass (m/z)
1	H	C ₁₃ H ₁₀ SO	214	67	107-108(105-106) ^[32]	214[M ⁺]
2	3-Br	C ₁₃ H ₉ SOBr	291	65	93-94(91-92) ^[32]	291[M ⁺], 294[M ²⁺]
3	4-Br	C ₁₃ H ₉ SOBr	291	66	130-131(132-133) ^[32]	291[M ⁺], 294[M ²⁺]
4	4-Cl	C ₁₃ H ₉ SOCl	248	66	124-125(124-125) ^[32]	248[M ⁺], 250[M ²⁺]
5	4-F	C ₁₃ H ₉ SOF	231	65	76-77(76-77) ^[32]	231[M ⁺], 233[M ²⁺]
6	2-CH ₃	C ₁₄ H ₁₂ SO	228	66	71-72 (69-70) ^[32]	227[M ⁺]
7	4-CH ₃	C ₁₄ H ₁₂ SO	228	65	119-120 (118-119) ^[32]	227[M ⁺]
8	3-NO ₂	C ₁₃ H ₉ SO ₃ N	259	65	144-145 (144-145) ^[32]	259[M ⁺]
9	4-NO ₂	C ₁₃ H ₉ SO ₃ N	259	65	133-134 (133-134) ^[32]	259[M ⁺]

internal standard. Mass spectra were recorded on a SIMADZU GC-MS2010 Spectrometer using Electron Impact (EI) techniques.

2.2. Preparation of Preheated Fly-Ash

The preheated fly-ash was prepared by literature method [32]. The fly-ash was heated on hot air oven at 110 °C for 2h. During the heating demoisturising takes place. This preheating helps for avoiding colloidal formation during the reaction.

2.3. General Procedure for Synthesis of Substituted Styryl 3-thienylketones

The substituted styryl 3-thienyl ketones were prepared using procedure published in literature [32]. Appropriate mixture of 3-acetyl thiophene (2 mmol), substituted benzaldehydes (2 mmol) and preheated fly-ash (0.5 g) were taken in 50 mL corning glass tube and tightly capped. The reaction mixture was subjected to microwave irradiation for 6-8 minutes in a microwave oven at 550W (Scheme 1) (Samsung Grill, GW73BD Microwave oven, 230 V A/c, 50 Hz, 2450 Hz, 100- 750 W (IEC-705) and then cooled to room temperature. Added 10 mL of dichloromethane, the organic layer has been separated which on evaporation yields the solid product. The solid, on recrystallization with benzene-hexane mixture gives glittering pale yellow solid. The analytical and mass fragments of these chalcones were presented in Table 1. The spectroscopic data such as UV λ_{max} (nm), infrared

ν (cm⁻¹) COs-*cis* and *s-trans*, stretches, CH, CH=CH, C=C deformation modes, NMR chemical shifts (δ , ppm) of vinyl proton, carbon and carbonyl carbon of these chalcones are presented in Table 2.

3. RESULTS AND DISCUSSION

3.1. UV Spectral Study

The measured ultra-violet absorption maxima λ_{max} , (nm) of the synthesized 3-thienyl chalcones were presented in Table 3. The results of the statistical analysis of ultra-violet absorption maxima λ_{max} , (nm) of substituted styryl 3-thienyl ketones with Hammett substituent constants, F and R parameters were presented in Table-3. These absorption λ_{max} , (nm) maxima were correlated with Hammett substituent constants, F and R parameters [4,28-33]. While seeking Hammett correlation, involving the ultra-violet absorption maxima λ_{max} , (nm) values, the form of the Hammett equation employed is as given in equation.

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

where λ is the absorption maxima of the 3-thienyl chalcone series, ρ is the slope with the meaning of linear coefficient, σ is the constant in the Hammett equation and λ_0 is the maxima of parent member of the chalcone series.

From Table 3, all correlations of the absorption maxima λ_{max} , (nm) of these chalcones with Hammett substituent constants, F and R parameters were fail. The obtained ρ values are negative for all

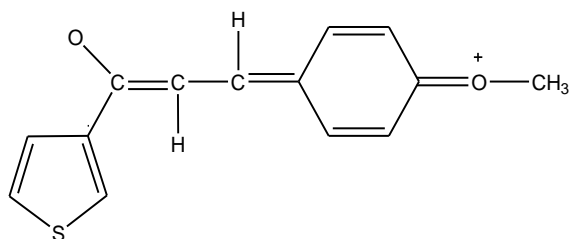


Figure.1: The resonance-conjugative structure.

correlations. This is due to the reversal substituent effects operate in all systems. Also the inability of the effect of substituents in phenyl ring and is associated with the resonance-conjugative structure as shown in Figure. 1.

The multi-regression analysis of ultra-violet absorption maxima λ_{max} , (nm) of these chalcones with σ_I and σ_R or Swain-Lupton's F and R parameters [34] gave satisfactory correlations. The generated correlation equations are shown in (2-3).

$$\lambda_{max}(nm) = 321.280(\pm 9.964) - 34.35(\pm 20.597)\sigma_I - 33.71(\pm 10.863)\sigma_R \quad (R=0.955, n=14, P>95\%) \quad (2)$$

$$\lambda_{max}(nm) = 321.09(\pm 9.541) - 36.76(\pm 19.418)F - 35.91(\pm 15.940)R \quad (R=0.968, n=14, P>95\%) \quad (3)$$

3.2. IR Spectral Study

The synthesized chalcones in the present study are shown in Scheme 1. The assigned $\nu_{C=O}$ (cm^{-1}) stretches of the *s-cis* and *s-trans* conformers and $\nu_{CH_{ip}}$, $\nu_{CH_{op}}$, $\nu_{CH=CH_{op}}$ and $\nu_{C=C_{op}}$ (cm^{-1}) modes of all the substituted styryl 3-thienyl ketones are presented in Table 2. The carbonyl *s-cis* and *s-trans* conformers of present study are shown in Figure. 2.

The stretching frequencies for carbonyl absorption are assigned based on the assignments made by Hays and Timmons, [35] (Hays and Timmons 1968) for *s-cis* and *s-trans* conformers at 1690 and 1670 cm^{-1} , respectively. As anticipated the lowest carbonyl frequency is observed in both the conformers when strongest electron donating group is present in phenyl ring while highest frequency is noted when strongest electro withdrawing group present in phenyl ring. A similar trend in absorption of chalcones demonstrates that *s-trans* conformers transmit more effectively than *s-cis* conformers due to reason stated earlier.

These data have been correlated with Hammett substituent constants and [34] constants. In this correlation the structure parameter Hammett equation employed is as shown in the following equation:

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

Where ν is the carbonyl frequencies of substituted system and ν_0 is the corresponding quantity of un substituted system; σ is a Hammett substituent constant, which in principle is characteristics of the substituent and ρ is a reaction constant which is depend upon the nature of the reaction. Hammett equation is one of the important tools for studying linear free energy relationships and it has been widely used in structures of the chemical reactivity of substituted aromatic system.

The assigned $\nu_{C=O}$ (cm^{-1}) stretches of the *s-cis* and *s-trans* conformers and $\nu_{CH_{ip}}$, $\nu_{CH_{op}}$, $\nu_{CH=CH_{op}}$ and $\nu_{C=C_{op}}$ (cm^{-1}) modes of all the substituted styryl 3-thienyl ketones are correlated with Hammett substituent constants, F and R parameters. The results of statistical analyses are presented in Table 3. From Table 3, all substituents have shown satisfactory correlations for $\nu_{C=O_{s-cis}}$ (cm^{-1}) stretches with Hammett substituent constants σ ($r=0.906$) and σ^+ ($r=0.905$).

All substituents have shown poor correlations ($r<0.900$) for $\nu_{C=O_{s-cis}}$ (cm^{-1}) stretches with Hammett constants σ_I , σ_R , F and R parameters. This is due to the incapability of inductive, field and resonance effects of the substituents for predicting the reactivity on the frequency through resonance as per conjugative structure as shown in Figure. 1. All substituents have shown positive ρ values with Hammett constants and F and R parameters. It indicates that the normal substituent effect operates in all substituents. From Table 3, all the substituents except 3- NO_2 have shown satisfactory correlations ($r=0.957$) for $\nu_{C=O_{s-trans}}$ (cm^{-1}) stretches with F parameter only. This substituent 3- NO_2 reduces correlations considerably when it is included in the regression. All substituents have shown poor correlations ($r<0.900$) for $\nu_{C=O_{s-trans}}$ (cm^{-1}) stretches with Hammett substituent constants σ , σ^+ , σ_I , σ_R and R parameter. This is due to the incapability of polar, inductive and resonance effects of the substituents for predicting the reactivity on the frequency through resonance as per conjugative structure as shown in Figure. 1.

From Table 3, all substituents have shown poor correlations ($r<0.900$) for the $\nu_{CH_{ip}}$ (cm^{-1}), $\nu_{CH_{op}}$ (cm^{-1}), $\nu_{CH=CH_{op}}$ (cm^{-1}) and $\nu_{C=C_{op}}$ (cm^{-1}) modes with Hammett substituent constants σ , σ^+ , σ_I , σ_R , F and R parameters. This is due to the incapability of polar, inductive, field and resonance effects of the substituents for predicting the reactivity on the frequency through resonance as per conjugative structure as shown in Figure. 1.

Since some of the single parameter correlations failed for the $\nu_{C=O_{s-cis}}$ (cm^{-1}), $\nu_{C=O_{s-trans}}$ (cm^{-1}), $\nu_{CH_{ip}}$ (cm^{-1}), $\nu_{CH_{op}}$ (cm^{-1}), $\nu_{CH=CH_{op}}$ (cm^{-1}) and

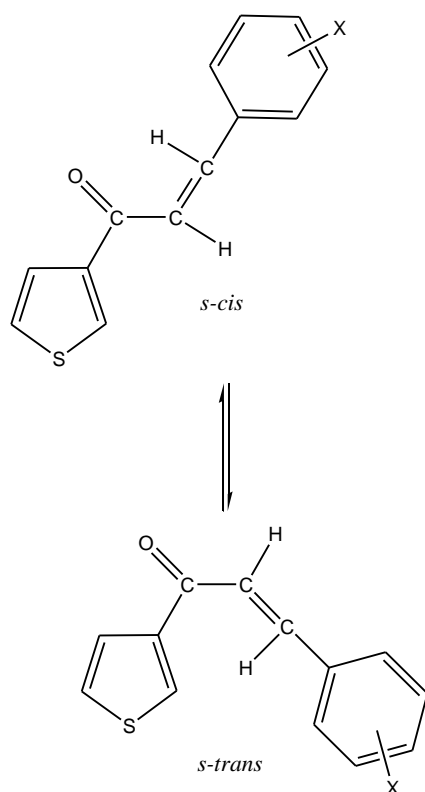


Figure 2: The *s-cis* and *s-trans* conformers of 3-thienyl chalcones.

$\nu\text{C}=\text{C}_{op}(\text{cm}^{-1})$ modes with Hammett constants and F and R parameters, it is decided to go for multi regression analysis. While seeking the multi regression analysis there is satisfactory correlations are observed for these chemical shifts with Swain-Lupton's, F and R parameters. The correlated multi regression equations are given in (5) - (16).

$$\nu\text{CO}_{s-cis}(\text{cm}^{-1}) = 1652.25(\pm 1.307) + 5.044(\pm 2.703)\sigma_I + 0.751(\pm 0.050)\sigma_R \quad (R=0.961, n=9, P>95\%) \quad (5)$$

$$\nu\text{CO}_{s-cis}(\text{cm}^{-1}) = 1652.29(\pm 1.295) + 4.979(\pm 2.613)F + 1.386(\pm 0.049)R \quad (R=0.961, n=9, P>95\%) \quad (6)$$

$$\nu\text{CO}_{s-trans}(\text{cm}^{-1}) = 1590.45(\pm 4.875) - 2.15(\pm 0.077)\sigma_I - 25.33(\pm 15.100)\sigma_R \quad (R=0.957, n=9, P>95\%) \quad (7)$$

$$\nu\text{CO}_{s-trans}(\text{cm}^{-1}) = 1590.71(\pm 4.814) - 4.440(\pm 0.798) - 22.006(\pm 13.090)R \quad (R=0.957, n=9, P>95\%) \quad (8)$$

$$\nu\text{CH}_{ip}(\text{cm}^{-1}) = 1175.60(\pm 8.104) + 7.101(\pm 1.752)\sigma_I + 5.262(\pm 2.102)\sigma_R \quad (R=0.919, n=9, P>90\%) \quad (9)$$

$$\nu\text{CH}_{ip}(\text{cm}^{-1}) = 1175.80(\pm 7.988) + 6.836(\pm 1.259)F + 5.372(\pm 1.720)R \quad (R=0.918, n=9, P>90\%) \quad (10)$$

$$\nu\text{CH}_{op}(\text{cm}^{-1}) = 779.615(\pm 10.582) - 47.30(\pm 21.874)\sigma_I + 21.69(\pm 13.777)\sigma_R \quad (R=0.966, n=9, P>95\%) \quad (11)$$

$$\nu\text{CH}_{op}(\text{cm}^{-1}) = 779.697(\pm 9.831) - 48.892(\pm 20.010)F + 4.925(\pm 2.731)R \quad (R=0.971, n=9, P>95\%) \quad (12)$$

$$\nu\text{CH}=\text{CH}_{op}(\text{cm}^{-1}) = 1073.77(\pm 2.964) - 2.00(\pm 0.127)\sigma_I + 6.46(\pm 3.181)\sigma_R \quad (R=0.929, n=9, P>90\%) \quad (13)$$

$$\nu\text{CH}=\text{CH}_{op}(\text{cm}^{-1}) = 1073.15(\pm 2.967) - 0.232(\pm 0.039)F + 4.574(\pm 1.068)R \quad (R=0.922, n=9, P>90\%) \quad (14)$$

$$\nu\text{C}=\text{C}_{op}(\text{cm}^{-1}) = 577.75(\pm 5.900) - 7.965(\pm 2.195)\sigma_I + 2.758(\pm 1.274)\sigma_R \quad (R=0.925, n=9, P>90\%) \quad (15)$$

$$\nu\text{C}=\text{C}_{op}(\text{cm}^{-1}) = 577.65(\pm 5.803) - 7.581(\pm 1.812)F + 1.089(\pm 0.779)R \quad (R=0.925, n=9, P>90\%) \quad (16)$$

3.3. NMR Spectral study

The ^1H and ^{13}C NMR spectra of nine chalcones under investigation are recorded in deuterated dimethyl sulphoxide employing tetramethylsilane (TMS) as internal standard. The signals of the ethylenic protons were assigned. They are calculated as AB or AA' BB' systems respectively. The chemical shifts of H_α are at higher field than those of H_β in this series of ketones. The ethylenic protons give an AB pattern and the β -proton doublet in most cases is well separated from the signals of the aromatic protons. The assigned chemical shifts of the ethylenic protons are presented in Table 2.

In nuclear magnetic resonance spectra, the proton chemical shifts δ (ppm) depends on the electronic environment of the nuclei concerned. These shifts can be correlated with reactivity parameters. Thus the Hammett equation may be used in the form as

$$\text{Log } \delta = \text{Log } \delta_0 + \rho\sigma \quad (17)$$

where δ_0 is the chemical shift in the corresponding parent compound.

The assigned vinyl proton, carbon and carbonyl carbon of the 3-thienyl chalcones were correlated with Hammett substituent constants, F and R parameters. The results of statistical analyses were shown in Table 3. From Table 3, all substituents have shown satisfactory correlations ($r>0.900$) for the δH_α chemical shifts (ppm) with Hammett constants σ , σ^+ , σ_R and R parameter. All substituents have shown poor correlations ($r<0.900$) for δH_α chemical shifts (ppm) with Hammett substituent constant σ_I and F parameter. This is due to the reason stated earlier and it is associated with the conjugative structure as shown in Figure. 1. All correlations have shown positive ρ values with Hammett constants σ , σ^+ , σ_I , σ_R and F and R parameters. This indicates that all normal substituents effect operates in all chalcones.

From Table-3, all substituents have shown poor correlations ($r<0.900$) for δH_β chemical shifts (ppm) with Hammett substituent constant σ , σ^+ , σ_I , σ_R and F and R parameters. The reason for these poor correlations was stated earlier and it is

Table 2: The uv-visible absorption maxima (λ_{max} , nm), infrared spectral data (ν , cm^{-1}), ^1H and ^{13}C NMR spectral data (δ , ppm) of substituted styryl-3-thienyl ketones.

Entry	X	λ_{max}	$\text{CO}_{(s-cis)}$	$\text{CO}_{(s-trans)}$	CH_{ip}	CH_{op}	$\text{CH}=\text{CH}_{op}$	$\text{C}=\text{C}_{op}$	H_α	H_β	CO	C_α	C_β
1	H	310.40	1653.00	1598.00	1154.00	762.00	1073.00	564.00	7.399	7.816	183.94	122.74	144.08
2	3-Br	315.20	1658.00	1599.00	1179.00	782.00	1071.00	575.00	7.394	7.768	183.50	123.11	142.88
3	4-Br	314.40	1654.00	1596.00	1176.00	753.00	1068.00	570.00	7.393	7.749	183.67	123.21	142.96
4	4-Cl	315.20	1651.00	1596.00	1176.00	759.00	1068.00	571.00	7.389	7.763	183.68	123.12	142.97
5	4-F	310.60	1655.00	1599.00	1173.00	729.00	1073.00	570.00	7.337	7.786	183.77	122.42	143.04
6	2-CH ₃	339.70	1652.70	1589.06	1191.79	767.53	1072.23	595.89	7.332	8.121	183.99	123.84	143.17
7	4-CH ₃	322.40	1650.77	1589.06	1180.22	798.38	1076.08	574.68	7.371	7.806	184.12	121.73	144.25
8	3-NO ₂	267.80	1654.62	1571.70	1195.65	742.46	1081.87	576.61	7.525	7.846	183.07	122.27	141.03
9	4-NO ₂	317.60	1656.55	1592.91	1172.51	752.10	1068.37	574.68	7.511	7.827	183.03	124.26	142.62

Table 3: Results of statistical analysis of ultra-violet, infrared (cm^{-1}) and nuclear magnetic resonance (δ ppm) spectral data of substituted styryl 3-thienyl ketones with Hammett σ , σ^+ , σ_I , σ_R constants and F and R parameters

Frequency	Constants	r	I	ρ	s	n	Correlated derivatives
UV λ_{max}	σ	0.861	320.31	-33.408	15.95	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.895	318.22	-28.025	16.34	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.855	325.62	-36.781	16.87	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.839	308.53	-39.274	18.64	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.852	325.30	-33.868	17.23	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.835	308.06	-30.618	18.96	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
vCO _{s-cis} (cm^{-1})	σ	0.906	1652.96	4.321	1.98	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.905	1653.17	3.922	1.92	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.861	1652.15	5.098	2.02	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.712	1654.12	1.567	2.54	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.860	1652.13	4.867	2.04	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.706	1654.05	0.669	2.55	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
vCO _{s-trans} (cm^{-1})	σ	0.836	1594.35	-8.850	8.59	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.730	1593.63	-6.630	8.76	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.713	1593.71	-3.984	9.14	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.757	1589.64	-25.688	7.56	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.957	1593.30	-2.663	9.18	8	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 4-NO ₂
	R	0.809	1589.14	-21.366	7.70	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
10 vCH _{ip} (cm^{-1})	σ	0.817	1176.19	5.953	12.59	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.812	1176.81	3.784	12.68	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂

vCH _{op} (cm ⁻¹)	σ _I	0.717	1174.92	7.480	12.58	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ _R	0.810	1178.23	6.411	12.72	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.715	1175.17	6.402	12.62	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.808	1178.22	4.387	12.74	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ	0.739	766.01	-23.402	20.18	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ ⁺	0.838	764.60	-19.889	20.29	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ _I	0.863	776.82	-45.739	16.95	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ _R	0.713	762.05	14.039	21.83	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.710	779.11	-49.289	15.50	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.712	762.37	11.970	21.83	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
vCH=CH _{op} (cm ⁻¹)	σ	0.805	1072.24	0.658	4.78	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ ⁺	0.801	1072.43	0.180	4.79	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ _I	0.809	1072.94	1.539	4.77	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ _R	0.726	1073.02	6.738	4.62	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.703	1072.62	-0.601	4.79	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.722	1073.07	4.608	4.66	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
vC=C _{op} (cm ⁻¹)	σ	0.816	575.62	-4.212	9.31	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ ⁺	0.719	575.53	-4.382	9.25	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ _I	0.825	577.40	-7.766	9.14	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ _R	0.803	574.80	1.469	9.44	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.825	577.53	-7.669	9.13	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.805	574.97	2.182	9.43	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
δ _{Ha} (ppm)	σ	0.959	7.365	0.174	0.03	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ ⁺	0.958	7.376	0.148	0.03	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ _I	0.858	7.356	0.138	0.05	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ _R	0.908	7.437	0.301	0.03	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.846	7.365	0.107	0.06	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.908	7.442	0.249	0.04	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
δ _{Hβ} (ppm)	σ	0.831	7.854	-0.100	0.11	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ ⁺	0.833	7.850	-0.093	0.11	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ _I	0.846	7.895	-0.181	0.10	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ _R	0.807	7.836	0.046	0.12	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.844	7.894	-0.168	0.10	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.712	7.841	0.065	0.12	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
δCO(ppm)	σ	0.992	183.891	-1.081	0.05	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ ⁺	0.958	183.825	-0.914	0.11	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ _I	0.908	184.046	-1.144	0.21	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ _R	0.857	183.522	-1.147	0.33	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.876	184.013	-0.991	0.26	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂

δC_a (ppm)	R	0.853	183.505	-0.918	0.34	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ	0.831	122.80	0.069	0.79	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.735	122.82	0.686	0.78	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.721	122.75	0.583	0.81	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.720	123.05	0.891	0.81	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.811	122.85	0.309	0.83	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
δC_p (ppm)	R	0.825	123.10	0.903	0.80	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ	0.785	143.47	-2.050	0.06	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.754	143.34	-1.726	0.64	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.776	143.88	-2.490	0.62	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.835	142.82	-1.722	0.92	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.715	143.83	-2.225	0.68	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.833	142.79	-1.377	0.92	9	H, 3-Br, 4-Br, 4-Cl, 4-F, 2-CH 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
 r =correlation co-efficient; ρ =slope; I=intercept; s=standard deviation; n=number of substituents

associated with conjugative structure shown in Figure. 1. All substituents have shown negative ρ values with Hammett constants σ , σ^+ , σ_1 and F parameter. This indicates that the substituent effect reverses in all substituents.

From Table-3, all substituents have shown good correlations ($r=0.992$) for the δCO chemical shifts (ppm) with Hammett constant σ . All substituents have shown satisfactory correlations for the δC_α chemical shifts (ppm) with Hammett constants σ^+ ($r=0.958$) and σ_1 ($r=0.908$). All substituents have shown poor correlations ($r<0.900$) for δC_α chemical shifts (ppm) with Hammett substituent constant σ_R , F and R parameters.

From Table-3, all substituents have shown poor correlations ($r<0.900$) for δC_α and δC_β chemical shifts (ppm) with Hammett constants and F and R parameters.

This is due to the incapability of polar, inductive, field and resonance effect of the substituents for predicting the reactivity on the chemical shift through resonance as per conjugative structure as shown in Figure. 1. All the substituents have shown negative ρ values with Hammett constants and F and R parameters. This indicates that the substituent effect reverses in all substituents.

Since some of the single parameter correlations failed for the ^{13}C NMR of δC_α chemical shifts (ppm) with Hammett constants and F and R parameters, it is decided to go for multi regression analysis. While seeking the multi regression analysis there is satisfactory correlations are observed for these chemical shifts with Swain-Lupton's, F and R [34] parameters. The correlated multi regression equations are given in (18) - (27).

$$\delta H_\alpha(\text{ppm}) = 7.393(\pm 0.008) + 0.118(\pm 0.017)\sigma_1 + 0.282(\pm 0.026)\sigma_R \quad (R=0.998, n=9, P>95\%) \quad (18)$$

$$\delta H_\alpha(\text{ppm}) = 7.316(\pm 0.007) + 0.129(\pm 0.015)F + 0.267(\pm 0.021)R \quad (R=0.998, n=9, P>95\%) \quad (19)$$

$$\delta H_\beta(\text{ppm}) = 7.9058(\pm 0.068) - 0.186(\pm 0.042)\sigma_1 + 0.076(\pm 0.012)\sigma_R \quad (R=0.947, n=9, P>90\%) \quad (20)$$

$$\delta H_\beta(\text{ppm}) = 7.899(\pm 0.068) - 0.165(\pm 0.013)F + 0.413(\pm 0.186)R \quad (R=0.944, n=9, P>90\%) \quad (21)$$

$$\delta\text{CO}(\text{ppm}) = 183.921(\pm 0.047) - 1.074(\pm 0.097)\sigma_1 - 0.973(\pm 0.146)\sigma_R \quad (R=0.998, n=9, P>95\%) \quad (22)$$

$$\delta\text{CO}(\text{ppm}) = 183.88(\pm 0.045) - 1.078(\pm 0.092)F - 1.073(\pm 0.123)R \quad (R=0.998, n=9, P>95\%) \quad (23)$$

$$\delta\text{C}_\alpha(\text{ppm}) = 122.86(\pm 0.517) + 0.525(\pm 0.070)\sigma_1 + 0.807(\pm 0.603)\sigma_R \quad (R=0.929, n=9, P>90\%) \quad (24)$$

$$\delta\text{C}_\alpha(\text{ppm}) = 122.96(\pm 0.508) + 0.386(\pm 0.034)F + 0.959(\pm 0.382)R \quad (R=0.929, n=9, P>90\%) \quad (25)$$

$$\delta\text{C}_\beta(\text{ppm}) = 143.710(\pm 0.360) - 2.394(\pm 0.746)\sigma_1 - 1.334(\pm 0.117)\sigma_R \quad (R=0.982, n=9, P>95\%) \quad (26)$$

$$\delta\text{C}_\beta(\text{ppm}) = 143.63(\pm 0.353) - 2.363(\pm 0.718)F - 1.718(\pm 0.960)R \quad (R=0.982, n=9, P>95\%) \quad (27)$$

4. CONCLUSIONS

Totally nine 3-thienyl chalcones have been synthesized by solvent-free Crossed-Aldol condensation under microwave irradiation. The spectral group frequencies of these chalcones were assigned and correlated with Hammett substituent constants, F and R parameters. Most of the single parameter correlations shown satisfactory correlation coefficients. The multi-regression analyses shows the r values are greater than 0.900 in all correlations.

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***Bibliographic Sketch**



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