Spectral correlation analysis of Hammett substituent constants and biological activities of some (E)-1-(4-phenoxyphenyl)-3-phenylprop-2-en-1-ones

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ABSTRACT

A series of aryl chalcones have been synthesized from 4-phenoxyacetophenone with various substituted benzaldehydes. The purity of all chalcones has been checked using their physical constants and spectral data. These spectral data have been correlated with Hammett substituent constants and F and R parameters using single and multi-linear regression analysis. From the results of statistical analysis, the effect of substituents on the above spectral data has been studied. The single parameter correlation with few Hammett constants and F and R parameters gave satisfactory correlation coefficients whereas all multiple correlations gave satisfactory correlation coefficients with Resonance, Field and Swain-Lupton’s parameters. The antimicrobial activities of all chalcones have been studied using Bauer-Kirby method.

Keywords: substituted styryl 4-phenoxyphenylketones; UV-spectra; IR-spectra; NMR-spectra; Hammett constants; substituent effects; regression analysis and antimicrobial activities

1. INTRODUCTION

The quantitative structure activity relationship and quantitative structure property relationships were used for finding the structure of molecule, quantitative and qualitative analysis. Spectral data of organic compounds are useful for prediction of structure, stereo chemical and physicochemical properties [1]. There is considerable information avail in literature concerning the transmission of electronic effects in molecule undergoing isomer equilibration in ground state. For example enol and enones, α, β-unsaturated ketones [2]. The 2E chalcones are α, β-unsaturated ketones possess methylene structural moieties and they belongs to biomolecules. Many alkyl-alkyl, alkyl-aryl and aryl-aryl categories of chalcones were synthesized [3] and extracted from natural plants [4] by organic chemists. Due to C-C single bond rotation [5] of carbonyl and alkene carbons, they exist as E s-cis and s-trans and Z s-cis and Z s-trans conformers. These structural conformers of chalcones have been confirmed by NMR and IR spectroscopy. the aldol condensation is useful for the formation of
carbon-carbon bonds in many kinds of carbonyl compounds [6], due to the importance of the methylene structural unit, which is found in many naturally occurring compounds, antibiotics, and the use of cyclic and acyclic ketones as precursors for the synthesis of pyrimidine derivatives [7]. The basic skeleton of chalcones figures widely in natural products which are known to have multi-pronged activity [8]. Many of the chalcones are used as agrochemicals and drugs [9]. The condensation of ketones with aldehydes is of special interest, and the crossed-aldol condensation is an effective pathway for those preparations. Generally chalcones possess various multipronged activities [10] such as anticancer, antimicrobial [11], antioxidant [12] antiviral [13], anti-aids [14], insect antifeedant [10], antimalarial [15], antiplasmodial [16] agrochemicals and drugs [17]. These potentials are also applied for the study of structure activity relationships [18]. From through literature survey it is observed that there is no report on the effect of substituents- QSAR or QPR study with these compounds, in the past. Therefore the authors take effort to synthesis some substituted styryl 4-Phenoxy phenyl ketones and study the correlation analysis with their UV, IR and NMR data and their antimicrobial activities by using Kirby-Bauer [19] disc diffusion technique.

2. EXPERIMENTAL
2.1 General

All chemicals used were purchased from Sigma-Aldrich and E-Merck chemical companies. Melting points of all chalcones were determined in open glass capillaries on Mettler FP51 melting point apparatus and are uncorrected. The ultraviolet spectrophotometer was utilized for recording the absorption maxima ($\lambda_{\text{max}}$, nm), of all chalcones in spectral grade solvent. Infrared spectra (KBr, 4000-400 cm$^{-1}$) were recorded AVATAR-300 Fourier transform spectrophotometer. BRUKER-300 MHz NMR spectrometer was used for recording NMR spectra operating at 300 MHz for $^1$H spectra and 125.46 MHz for $^{13}$C spectra in CDCl$_3$ solvent using TMS as internal standard.

2.2. Synthesis of chalcones

A solution of benzaldehyde (0.01 mol) and 4-phenoxyacetophenone (0.01 mol), sodium hydroxide (0.5 g) and 10 ml of ethanol were shaken occasionally for 1 hour [3]. The completion of the reaction was monitored by TLC. The resulting precipitate was filtered and washed with cold water. The product appeared as pale yellow solid. Then the products are

![Scheme 1](image-url)
recrystallized using ethanol to obtain pale yellow glittering solid melting at 88-90 °C. The physical constants are presented in Table 1.

**Table 1.** Physical constants of substituted styryl 4-phenoxyphenyl ketones.

| Entry | X   | M. F.       | M. W. | Yield (%) | m.p. (°C)     |
|------|-----|-------------|-------|-----------|---------------|
| 1    | H   | C_{21}H_{16}O_{2} | 300   | 93        | 88-90 (85-86) [20] |
| 2    | 3-Br| C_{21}H_{15}BrO_{2} | 379   | 91        | 117-119       |
| 3    | 4-Br| C_{21}H_{15}BrO_{2} | 379   | 88        | 124-126       |
| 4    | 4-Cl| C_{21}H_{15}ClO_{2} | 334   | 89        | 134-136       |
| 5    | 4-F | C_{21}H_{15}FO_{2} | 318   | 88        | 110-112       |
| 6    | 2-OCH_{3} | C_{22}H_{18}O_{3} | 330   | 87        | 105-107       |
| 7    | 4-OCH_{3} | C_{22}H_{18}O_{3} | 330   | 89        | 108-110 (97) [20] |
| 8    | 4-CH_{3} | C_{22}H_{18}O_{2} | 314   | 90        | 125-127       |
| 9    | 3-NO_{2} | C_{21}H_{15}NO_{4} | 345   | 89        | 128-130       |
| 10   | 4-NO_{2} | C_{21}H_{15}NO_{4} | 345   | 84        | 132-134       |

3. RESULTS AND DISCUSSION

In the present study the spectral linearity of chalcones has been studied by evaluating the substituent effects. The assigned group frequencies of all chalcones like carbonyl stretches νCO, the deformation modes of vinyl part CH out of plane, in-plane, CH=CH and >C=C< out of planes (cm⁻¹), the vinyl hydrogen and chemical shifts δ(ppm), of Hα, Hβ, Cα, Cβ, CO are assigned and these frequencies are correlated with various substituent constants.

3.1. UV spectral study

The measured absorption maxima (λmax nm) values of the synthesized chalcones have been recorded and presented in Table 2. These data are correlated with Hammett substituent constants and F and R parameters using single and multi-linear regression analysis Hammett equation employed, for the correlation analysis, involving the absorption maxima as is shown below in equation (1).

\[ \lambda = \rho \sigma + \lambda_o \]  

where \( \lambda_o \) is the frequency for the parent member of the series.

The results of statistical analysis [21-23] are presented in Table 3. From the Table 3, the results of statistical analysis of these UV absorption maxima (λmax, nm) values with Hammett substituent constants, except that with 4-NO₂ substituent have shown satisfactory
correlations with Hammett substituent constant $\sigma$ ($r = 0.973$) and $\sigma^+$ ($r = 0.977$). The absorption values except those with 4-F and 4-NO$_2$ substituents have shown satisfactory correlations with Hammett substituent constant $\sigma_R$ ($r = 0.966$) and $R$ ($r = 0.960$) parameter. The absorption values except those with H(parent) and 4-CH$_3$ substituents have shown satisfactory correlations with Hammett substituent constant $\sigma_I$ ($r = 0.936$) and except those with H (parent) 2-OCH$_3$ and 4-OCH$_3$ substituents have shown satisfactory correlations with $F$ ($r = 0.903$) parameter.

Also, the multi-regression produced satisfactory correlations with Hammett substituent constants and $F$ and $R$ parameters [24]. The multi correlation equations are given in (2) and (3).

\[
\lambda_{\text{max}} \text{ (nm)} = 332.507(\pm 6.526) - 12.374(\pm 13.156)\sigma_I - 28.973(\pm 12.696)\sigma_R \quad ...(2)
\]
\[
R = 0.976, \ n = 10, \ P > 95 \%
\]

\[
\lambda_{\text{max}} \text{ (nm)} = 323.217 \ (\pm 6.241) - 16.087(\pm 12.158)F - 27.037(\pm 11.324)R \quad ...(3)
\]
\[
R = 0.972, \ n = 10, \ P > 95 \%
\]

Fig. 1. The resonance-conjugated structure.
Table 2. The ultraviolet absorption maxima ($\lambda_{\text{max}}$, nm), infrared absorptions ($\nu$, cm$^{-1}$) and NMR chemical shifts ($\delta$, ppm) of substituted styryl 4-phenoxy phenyl ketones.

| Entry | X       | $\lambda_{\text{max}}$ | CO$_{\text{cis}}$ | CO$_{\text{trans}}$ | CH$_{\alpha}$ | CH$_{\beta}$ | CH=CH | C=O | $\delta$H$_{\alpha}$ (ppm) | $\delta$H$_{\beta}$ (ppm) | $\delta$C$_{\alpha}$ (ppm) | $\delta$C$_{\beta}$ (ppm) | $\delta$CO (ppm) |
|-------|---------|------------------------|-------------------|---------------------|--------------|-------------|--------|-----|--------------------------|--------------------------|--------------------------|--------------------------|--------------|
| 1     | H       | 316                    | 1654.92           | 1656.85             | 1597.06      | 1247.94     | 754.17 | 991.41 | 7.092                     | 8.208                    | 121.91                   | 143.62                   | 187.57       |
| 2     | 3-Br    | 314                    | 1656.85           | 1598.99             | 1249.87      | 783.10      | 991.41 | 499.56 | 7.057                     | 8.234                    | 119.99                   | 141.82                   | 187.40       |
| 3     | 4-Br    | 321                    | 1654.92           | 1597.06             | 1247.94      | 783.10      | 991.41 | 499.56 | 7.057                     | 8.234                    | 119.99                   | 141.82                   | 187.40       |
| 4     | 3-Cl    | 321                    | 1656.85           | 1598.99             | 1249.87      | 783.10      | 991.41 | 499.56 | 7.057                     | 8.234                    | 119.99                   | 141.82                   | 187.40       |
| 5     | 4-Cl    | 321                    | 1656.85           | 1598.99             | 1249.87      | 783.10      | 991.41 | 499.56 | 7.057                     | 8.234                    | 119.99                   | 141.82                   | 187.40       |
| 6     | 4-F     | 343                    | 1654.92           | 1656.85             | 1597.06      | 1247.94     | 783.10 | 991.41 | 7.092                     | 8.208                    | 121.91                   | 143.62                   | 187.57       |
| 7     | 4-CH$_3$| 343                    | 1654.92           | 1656.85             | 1597.06      | 1247.94     | 783.10 | 991.41 | 7.092                     | 8.208                    | 121.91                   | 143.62                   | 187.57       |
| 8     | 2-OCH$_3$| 343                  | 1654.92          | 1656.85            | 1597.06      | 1247.94     | 783.10 | 991.41 | 7.092                     | 8.208                    | 121.91                   | 143.62                   | 187.57       |
| 9     | 4-OCH$_3$| 343                  | 1654.92          | 1656.85            | 1597.06      | 1247.94     | 783.10 | 991.41 | 7.092                     | 8.208                    | 121.91                   | 143.62                   | 187.57       |
| 10    | 4-NO$_2$| 343                    | 1654.92           | 1656.85             | 1597.06      | 1247.94     | 783.10 | 991.41 | 7.092                     | 8.208                    | 121.91                   | 143.62                   | 187.57       |
| 11    | 3-NO$_2$| 343                    | 1654.92           | 1656.85             | 1597.06      | 1247.94     | 783.10 | 991.41 | 7.092                     | 8.208                    | 121.91                   | 143.62                   | 187.57       |
| 12    | 4-NO$_2$| 343                    | 1654.92           | 1656.85             | 1597.06      | 1247.94     | 783.10 | 991.41 | 7.092                     | 8.208                    | 121.91                   | 143.62                   | 187.57       |
Table 3. Results of statistical analysis of ultraviolet absorption maxima ($\lambda_{\text{max}}, \text{nm}$), infrared absorptions ($\nu \text{ cm}^{-1}$) and NMR chemical shifts ($\delta, \text{ppm}$) of substituted styryl 4-phenoxy phenyl ketones with Hammett $\sigma$, $\sigma^+$, $\sigma_I$, $\sigma_R$ and F and R parameters.

| Frequency | Constants | r   | I       | $\rho$     | s   | n   | Correlated derivatives                        |
|-----------|-----------|-----|---------|------------|-----|-----|-----------------------------------------------|
| $\lambda_{\text{max}}$ | $\sigma$  | 0.973 | 326.438 | -21.751    | 8.545 | 9   | H,3-Br,4-Br,4-Cl,4-F,2-OCH$_3$, 4-OCH$_3$,4-CH$_3$,3-NO$_2$ |
|           | $\sigma^+$ | 0.977 | 324.446 | -17.95     | 7.870 | 9   | H,3-Br,4-Br,4-Cl,4-F,2-OCH$_3$, 4-OCH$_3$,4-CH$_3$,3-NO$_2$ |
|           | $\sigma_I$ | 0.936 | 329.653 | -17.647     | 11.683 | 8   | 3-Br,4-Br,4-Cl,4-F,2-OCH$_3$, 4-OCH$_3$,3-NO$_2$,4-NO$_2$ |
|           | $\sigma_R$ | 0.966 | 317.469 | -31.071     | 9.697 | 8   | H,3-Br,4-Br,4-Cl,2-OCH$_3$, 4-OCH$_3$,4-CH$_3$,3-NO$_2$ |
|           | F         | 0.903 | 329.671 | -16.8886    | 11.683 | 7   | 3-Br,4-Br,4-Cl,4-F,4-CH$_3$,3-NO$_2$,4-NO$_2$ |
|           | R         | 0.963 | 316.788 | -27.4512    | 9.697  | 8   | H,3-Br,4-Br,4-Cl,2-OCH$_3$, 4-OCH$_3$,4-CH$_3$,3-NO$_2$ |
| CO$_{\text{cis}}$ | $\sigma$  | 0.817 | 1640.17 | 10.30767    | 26.524 | 10  | H,3-Br,4-Br,4-Cl,4-F,2-OCH$_3$,4-OCH$_3$,4-CH$_3$,3-NO$_2$,4-NO$_2$ |
|           | $\sigma^+$ | 0.812 | 1640.50  | 16.12202    | 25.406 | 10  | H,3-Br,4-Br,4-Cl,4-F,2-OCH$_3$, 4-OCH$_3$,4-CH$_3$,3-NO$_2$,4-NO$_2$ |
|           | $\sigma_I$ | 0.708 | 1644.06  | -5.98854    | 26.832  | 10  | H,3-Br,4-Br,4-Cl,4-F,2-OCH$_3$, 4-OCH$_3$,4-CH$_3$,3-NO$_2$,4-NO$_2$ |
|           | $\sigma_R$ | 0.8   | 1644.62   | 15.82122    | 26.542  | 10  | H,3-Br,4-Br,4-Cl,4-F,2-OCH$_3$, 4-OCH$_3$,4-CH$_3$,3-NO$_2$,4-NO$_2$ |
|      | F   | 0.702 | 1642.95  | -2.91977  | 26.8651  | 10  | H,3-Br,4-Br,4-Cl,4-F,2-OCH₃, 4-OCH₃,4-CH₃,3-NO₂,4-NO₂ |
|------|------|--------|----------|-----------|----------|-----|------------------------------------------------------|
| R    | 0.751| 1645.50| 16.319   | 26.4582   | 36.9488  | 10  | H,3-Br,4-Br,4-Cl,4-F,2-OCH₃, 4-OCH₃,4-CH₃,3-NO₂,4-NO₂ |
| $\sigma$ | 0.804 | 1579.15 | 4.616102 | 18.148888 | 35.6593  | 10  | H,3-Br,4-Br,4-Cl,4-F,2-OCH₃, 4-OCH₃,4-CH₃,3-NO₂,4-NO₂ |
| $\sigma^+$ | 0.801 | 1578.42 | 12.5581  | 36.8578   | 36.8005  | 10  | H,3-Br,4-Br,4-Cl,4-F,2-OCH₃, 4-OCH₃,4-CH₃,3-NO₂,4-NO₂ |
| $\sigma_1$ | 0.702 | 1584.61 | -12.5581 | 36.8578   | 36.8005  | 10  | H,3-Br,4-Br,4-Cl,4-F,2-OCH₃, 4-OCH₃,4-CH₃,3-NO₂,4-NO₂ |
| $\sigma_R$ | 0.765 | 1580.68 | 4.502829 | 36.8002   | 36.7876  | 10  | H,3-Br,4-Br,4-Cl,4-F,2-OCH₃, 4-OCH₃,4-CH₃,3-NO₂,4-NO₂ |
| CH₁₂p | $\sigma$ | 0.920 | 1246.34  | -4.539665 | 9.29186  | 6   | H,3-Br,4-Cl,4-F,4-CH₃,3-NO₂                     |
| $\sigma^+$ | 0.903 | 1246.11 | -5.96681 | 8.91497   | 7       |     | H,3-Br,4-Cl,4-F,2-OCH₃, 4-CH₃,3-NO₂               |
| $\sigma_1$ | 0.965 | 1247.90 | -6.02639 | 9.35878   | 10      |     | H,3-Br,4-Br,4-Cl,4-F,2-OCH₃, 4-OCH₃,4-CH₃,3-NO₂,4-NO₂ |
| $\sigma_R$ | 0.901 | 1244.71 | -5.14126 | 9.38699   | 7       |     | H,3-Br,4-Cl,2-OCH₃,4-OCH₃, 4-CH₃,4-NO₂           |
|     | F          | 0.901 | 1248.37 | -6.95774 | 9.29975 | 7          | H$_3$Br,4-Cl,2-OCH$_3$,4-OCH$_3$,4-CH$_3$,3-NO$_2$ |
|-----|------------|-------|---------|----------|---------|------------|--------------------------------------------------|
|     | R          | 0.909 | 1244.95 | -2.97338 | 9.4486  | 6          | H$_3$Br,4-Cl,4-F,4-CH$_3$,3-NO$_2$                |

| CH$_{op}$ | σ        | 0.8     | 765.400 | 9.275061 | 24.7633 | 10         | H$_3$Br,4-Br,4-Cl,4-F,2-OCH$_3$,4-OCH$_3$,4-CH$_3$,3-NO$_2$,4-NO$_2$ |
|------------|----------|---------|---------|----------|---------|------------|--------------------------------------------------|
| σ$^+$      | 0.8      | 766.433 | 5.37808 | 24.8940  | 10      | H$_3$Br,4-Br,4-Cl,4-F,2-OCH$_3$,4-OCH$_3$,4-CH$_3$,3-NO$_2$,4-NO$_2$ |
| σ$_I$      | 0.812    | 772.290 | -14.3862| 24.7940  | 10      | H$_3$Br,4-Br,4-Cl,4-F,2-OCH$_3$,4-OCH$_3$,4-CH$_3$,3-NO$_2$,4-NO$_2$ |
| σ$_R$      | 0.798    | 772.675 | 32.63249| 23.7416  | 10      | H$_3$Br,4-Br,4-Cl,4-F,2-OCH$_3$,4-OCH$_3$,4-CH$_3$,3-NO$_2$,4-NO$_2$ |
| F          | 0.814    | 772.476 | -14.2001| 24.7763  | 10      | H$_3$Br,4-Br,4-Cl,4-F,2-OCH$_3$,4-OCH$_3$,4-CH$_3$,3-NO$_2$,4-NO$_2$ |
| R          | 0.823    | 773.18  | 27.8106 | 23.7416  | 10      | H$_3$Br,4-Br,4-Cl,4-F,2-OCH$_3$,4-OCH$_3$,4-CH$_3$,3-NO$_2$,4-NO$_2$ |
| CH=CH$_{op}$ | σ        | 0.919   | 1003.03 | 9.416676 | 20.4015 | 6          | H$_4$Br,4-Cl,4-F,4-OCH$_3$,4-CH$_3$               |
| σ$^+$      | 0.902    | 1004.56 | -0.45712| 20.4055  | 6       | H$_4$Br,4-Cl,4-F,4-OCH$_3$,4-CH$_3$               |
| σ$_I$      | 0.804    | 1003.19 | 3.524465| 20.3868  | 10      | H$_3$Br,4-Br,4-Cl,4-F,2-OCH$_3$,4-OCH$_3$,4-CH$_3$,3-NO$_2$,4-NO$_2$ |
|       | σR     | C=C_{op} σ | F | R | δHα σ | σ^+ | σI | F | R | δHα σ |
|-------|--------|------------|---|---|-------|-----|----|---|---|-------|
| σR    | 0.792  | 0.939      | 0.825 | 0.824 | 0.905 | 0.904 | 0.712 | 0.802 | 0.812 | 0.811 |
|       | 1007.44 | 503.824    | 1001.99 | 1006.24 | 7.36938 | 1.83435 | 497.894 | 502.342 | 502.311 | 498.290 |
|       | 16.41204 | -13.9563 | 6.398419 | 7.569515 | -28.8871 | 1.83435 | -28.8871 | -28.8871 | -28.8871 | -28.8871 |
|       | 19.9291 | 20.3890 | 20.3339 | 13.5194 | 13.5194 | 13.5194 | 13.5194 | 13.5194 | 13.5194 | 13.5194 |
|       | 10     | 8        | 8    | 8    | 8      | 8    | 8    | 8    | 8    | 8      |
|       | H_3-Br,4-Br,4-Cl,4-F,2-OCH_3,4-OCH_3,4-CH_3,3-NO_2,4-NO_2 | H_3-Br,4-Br,4-Cl,4-F,2-OCH_3,4-OCH_3,4-CH_3,3-NO_2,4-NO_2 | H_3-Br,4-Br,4-Cl,4-F,2-CH_3,3-NO_2,4-NO_2 | H_3-Br,4-Br,4-Cl,4-F,2-CH_3,3-NO_2,4-NO_2 | H_3-Br,4-Br,4-Cl,4-F,2-CH_3,3-NO_2,4-NO_2 | H_3-Br,4-Br,4-Cl,4-F,2-CH_3,3-NO_2,4-NO_2 | H_3-Br,4-Br,4-Cl,4-F,2-CH_3,3-NO_2,4-NO_2 | H_3-Br,4-Br,4-Cl,4-F,2-CH_3,3-NO_2,4-NO_2 | H_3-Br,4-Br,4-Cl,4-F,2-CH_3,3-NO_2,4-NO_2 | H_3-Br,4-Br,4-Cl,4-F,2-CH_3,3-NO_2,4-NO_2 |
| Chemical shifts | Constants | r   | I     | ρ     | s     | n  | Correlated derivatives                          |
|-----------------|-----------|-----|-------|-------|-------|----|-----------------------------------------------|
| $\delta_{H\beta}$ | $\sigma$  | 0.917 | 8.207 | 0.08287 | 0.02885 | 9  | H$_3$-Br$_3$-Br$_3$-Cl$_4$-F$_2$-OCH$_3$$_3$-4-CH$_3$-3-NO$_2$, 4-NO$_2$ |
| $\sigma^+$       |           | 0.917 | 8.215 | 0.05945 | 0.03177 | 9  | H$_3$-Br$_3$-Br$_3$-Cl$_4$-F$_2$-OCH$_3$$_3$-4-CH$_3$-3-NO$_2$, 4-NO$_2$ |
| $\sigma_i$       |           | 0.925 | 8.184 | 0.096313 | 0.03790 | 9  | H$_3$-Br$_3$-Br$_3$-Cl$_4$-F$_2$-OCH$_3$$_3$-4-CH$_3$-3-NO$_2$, 4-NO$_2$ |
| $\sigma_R$       |           | 0.916 | 8.240 | 0.11087 | 0.03428 | 9  | H$_3$-Br$_3$-Br$_3$-Cl$_4$-F$_2$-OCH$_3$$_3$-4-CH$_3$-3-NO$_2$, 4-NO$_2$ |
| F               | 0.914     | 8.187 | 0.082544 | 0.03948 | 9  | H$_3$-Br$_3$-Br$_3$-Cl$_4$-F$_2$-OCH$_3$$_3$-4-CH$_3$-3-NO$_2$, 4-NO$_2$ |
| R               | 0.906     | 8.243 | 0.1000915 | 0.03465 | 9  | H$_3$-Br$_3$-Br$_3$-Cl$_4$-F$_2$-OCH$_3$$_3$-4-CH$_3$-3-NO$_2$, 4-NO$_2$ |
| $\delta C_a$     | $\sigma$  | 0.814 | 120.509 | -0.45927 | 0.81457 | 10 | H$_3$-Br$_3$-Br$_3$-Cl$_4$-F$_2$-OCH$_3$$_3$-4-CH$_3$-3-NO$_2$, 4-NO$_2$ |
| \( \sigma^+ \) | 0.758 | 120.458 | -0.26364 | 0.82493 | 10 | H,3-Br,4-Br,4-Cl,4-F, 2-OCH,4-OCH,4-CH, 3-NO,4-NO |
| \( \sigma_I \) | 0.715 | 120.970 | -1.41612 | 0.75326 | 10 | H,3-Br,4-Br,4-Cl,4-F, 2-OCH,4-OCH,4-CH, 3-NO,4-NO |
| \( \sigma_R \) | 0.704 | 120.412 | -1.13787 | 0.83649 | 10 | H,3-Br,4-Br,4-Cl,4-F, 2-OCH,4-OCH,4-CH, 3-NO,4-NO |
| \( F \) | 0.725 | 120.732 | -0.74882 | 0.81257 | 10 | H,3-Br,4-Br,4-Cl,4-F, 2-OCH,4-OCH,4-CH, 3-NO,4-NO |
| \( R \) | 0.801 | 120.393 | -1.09333 | 0.83548 | 10 | H,3-Br,4-Br,4-Cl,4-F, 2-OCH,4-OCH,4-CH, 3-NO,4-NO |
| \( \delta C_\beta \) | 0.914 | 142.684 | -2.45457 | 0.34984 | 10 | H,3-Br,4-Br,4-Cl,4-F, 2-OCH,4-OCH,4-CH, 3-NO,4-NO |
| \( \sigma^+ \) | 0.914 | 142.684 | -1.81335 | 0.47158 | 10 | H,3-Br,4-Br,4-Cl,4-F, 2-OCH,4-OCH,4-CH, 3-NO,4-NO |
| \( \sigma_I \) | 0.992 | 143.956 | -3.76242 | 0.50149 | 8 | 3-Br,4-Br,4-Cl,4-F,2-OCH, 4-OCH,3-NO,4-NO |
| \( \sigma_R \) | 0.904 | 142.122 | -2.33418 | 0.89724 | 8 | 3-Br,4-Br,4-Cl,4-F,2-OCH, 4-OCH,3-NO,4-NO |
| \( F \) | 0.914 | 143.848 | -3.3169 | 0.62812 | 9 | H,3-Br,4-Br,4-Cl,2-OCH, 4-OCH,4-CH,3-NO, 4-NO |
| \( R \) | 0.951 | 142.069 | -2.0656 | 0.91494 | 7 | 3-Br,4-Br,4-Cl,2-OCH, 4-OCH,3-NO,4-NO |
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.

\[
\delta_{\text{CO}} \quad \sigma \quad 0.905 \quad 187.456 \quad -0.07644 \quad 0.06033 \quad 8 \quad \text{H}_3\text{-Br},4\text{-Br},4\text{-Cl},4\text{-F},4\text{-CH}_3,3\text{-NO}_2,4\text{-NO}_2
\]

\[
\sigma^+ \quad 0.903 \quad 187.447 \quad -0.04353 \quad 0.06418 \quad 8 \quad \text{H}_3\text{-Br},4\text{-Br},4\text{-Cl},4\text{-F},4\text{-CH}_3,3\text{-NO}_2,4\text{-NO}_2
\]

\[
\sigma_1 \quad 0.907 \quad 187.520 \quad -0.20307 \quad 0.04394 \quad 10 \quad \text{H}_3\text{-Br},4\text{-Br},4\text{-Cl},4\text{-F},2\text{-OCH}_3,4\text{-OCH}_3,4\text{-CH}_3,3\text{-NO}_2,4\text{-NO}_2
\]

\[
\sigma_R \quad 0.9 \quad 187.442 \quad -0.00905 \quad 0.06836 \quad 8 \quad \text{H}_3\text{-Br},4\text{-Br},4\text{-Cl},4\text{-F},2\text{-OCH}_3,4\text{-OCH}_3,3\text{-NO}_2,4\text{-NO}_2
\]

\[
F \quad 0.916 \quad 187.511 \quad -0.16674 \quad 0.05083 \quad 9 \quad \text{H}_3\text{-Br},4\text{-Br},4\text{-Cl},2\text{-OCH}_3,4\text{-OCH}_3,4\text{-CH}_3,3\text{-NO}_2,4\text{-NO}_2
\]

\[
R \quad 0.902 \quad 187.442 \quad -0.00644 \quad 0.06838 \quad 8 \quad \text{H}_3\text{-Br},4\text{-Br},4\text{-Cl},4\text{-F},2\text{-OCH}_3,4\text{-OCH}_3,4\text{-CH}_3,3\text{-NO}_2,4\text{-NO}_2
\]

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

where \(\nu\) is the carbonyl frequencies of substituted system.

**Fig. 2.** The \(s\)-cis and \(s\)-trans conformers of 4-phenoxy phenyl ketones.
From Table 3, the IR frequency COs-cis and COs-trans values have shown poor correlations \( (r < 0.900) \) with Hammett substituent constants and \( F \) and \( R \) parameters. This is attributed to weak polar, inductive, field and resonance effects of the substituents for predicting the reactivity on the IR frequency through resonance. This is evident with resonance conjugative structure shown in Fig. 1.

The infrared frequency of CH\(_{ip}\), except those with 4-Br, 2-OCH\(_3\), 4-OCH\(_3\) and 4-NO\(_2\) substituents have shown satisfactory correlation with Hammett substituent constant \( \sigma \) \( (r = 0.920) \) and \( R \) \( (r = 0.909) \) parameter, except those with 4-Br, 2-OCH\(_3\) and 4-NO\(_2\) substituents have shown satisfactory correlation with Hammett substituent constant \( \sigma^+ \) \( (r = 0.903) \), except those with 4-Br, 4-F and 4-NO\(_2\) substituents have shown satisfactory correlation with Hammett substituent constant \( \sigma_R \) \( (r = 0.901) \) and except those with 4-Br, 4-F and 3-NO\(_2\) substituents have shown satisfactory correlation with \( F \) \( (r = 0.901) \) parameter. The remaining Hammett substituent constant \( \sigma_I \) have shown poor correlations \( (r < 0.900) \) This is attributed to the weak field and resonance effects of the substituents for predicting the reactivity on the infrared frequency through resonance as per the conjugative structure as shown in Fig. 1.

The infrared frequency of CH\(_{op}\), with all Hammett substituent constants and \( F \) and \( R \) parameters has shown poor correlation \( (r < 0.900) \). The infrared frequency of CH=CH\(_{op}\), except those with 3-Br, 2-OCH\(_3\), 3-NO\(_2\) and 4-NO\(_2\) substituents have shown satisfactory correlation with Hammett substituent constant \( \sigma \) \( (r = 0.919) \) and \( \sigma^+ \) \( (r = 0.909) \) and C=C\(_{op}\), except those with 2-OCH\(_3\) and 3-NO\(_2\) substituents have shown satisfactory correlation with Hammett substituent constant \( \sigma \) \( (r = 0.939) \) and \( \sigma^+ \) \( (r = 0.936) \). The remaining Hammett substituent constants and \( F \) and \( R \) parameters have shown poor correlations \( (r < 0.900) \) This is attributed to the weak field and resonance effects of the substituent for predicting the reactivity on the infrared frequency through resonance as per the conjugative structure as shown in Fig. 1.

Some 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 [24]. The multi correlation equations are given in (5) - (16).

\[
v\text{CO}_{s-cis} (\text{cm}^{-1}) = 1648.347(\pm19.504) - 9.151(\pm3.319)\sigma_I + 17.372(\pm2.944)\sigma_R \quad \text{(5)}
\]

\[
v\text{CO}_{s-cis} (\text{cm}^{-1}) = 1646.873(\pm19.027) - 3.406(\pm1.066)F + 16.399(\pm2.522)R \quad \text{(6)}
\]

\[
v\text{CO}_{s-trans} (\text{cm}^{-1}) = 1586.305(\pm27.157) - 13.803(\pm1.747)\sigma_I + 6.843(\pm1.833)\sigma_R \quad \text{(7)}
\]

\[
v\text{CO}_{s-trans} (\text{cm}^{-1}) = 1587.387(\pm26.385) - 10.977(\pm2.401)F + 13.955(\pm2.873)R \quad \text{(8)}
\]

\[
v\text{CH}_{ip} (\text{cm}^{-1}) = 1246.853(\pm6.854) - 5.253(\pm1.818)\sigma_I - 4.251(\pm1.335)\sigma_R \quad \text{(9)}
\]

\[
v\text{CH}_{ip} (\text{cm}^{-1}) = 1247.71(\pm6.666) - 6.875(\pm1.987)F - 2.797(\pm1.095)R \quad \text{(10)}
\]
3. 3. NMR Spectral study

3. 3.1. $^1$H NMR spectra

The $^1$H NMR spectra of the chalcones under investigation have been recorded in deuterated dimethyl sulphoxide employing tetramethylsilane (TMS) as internal standard. The signals of the ethylenic protons have been assigned. They are calculated as AB or AA$^0$ BB$^0$ systems respectively. The assigned chemical shifts values are presented in Table 2. In nuclear magnetic resonance spectra, the proton or the $^{13}$C chemical shifts ($\delta$) 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

$$
\delta = \delta_0 + \rho \sigma
$$

where $\delta_0$ is the chemical shift of unsubstituted system.

The assigned H$\alpha$ and H$\beta$ proton chemical shifts (ppm) are correlated with various Hammett sigma constants. The results of statistical analysis [20-23] are presented in Table 3. The H$\alpha$ chemical shifts ($\delta$, ppm) correlated with Hammett constants and F and R parameters, except those with H (parent) and 4-Br have shown satisfactory correlations with a few Hammett substituent constants $\sigma$ (r = 0.905) and $\sigma^+$ (r = 0.904) and except those with 3-Br and 4-Br substituents have shown satisfactory correlations with Hammett substituent constant $\sigma_R$ (r = 0.905) and R (r = 0.905) parameter.

The H$\beta$ chemical shifts ($\delta$, ppm) correlated with Hammett constants and F and R parameters, except that with 3-NO$_2$ substituent have shown satisfactory correlation with Hammett substituent constant $\sigma$ (r = 0.917), $\sigma^+$ (r = 0.919), $\sigma_f$ (r = 0.925), $\sigma_R$ (0.916), F (0.914) and R (r = 0.906) parameters.

The remaining few Hammett substituent constants and swain-Lupton’s parameters [24] have shown poor correlations (r < 0.900). This is attributed to the weak polar and resonance
effects of the substituent for predicting the reactivity on the chemical shifts through resonance as per the conjugative structure shown in Fig. 1.

Some of the single regression analyses have shown poor correlations with Hammett substituent constants and swain-Lupton’s parameters [24]. It is decided to go for multi-regression, the multi-regression analysis produced satisfactory correlations with the chemical shifts of (δ, ppm) Hα and Hβ. The multi correlation equations are given in (18)-(21).

\[
\begin{align*}
\delta H_\alpha(\text{ppm}) &= 7.258(\pm 0.141) - 0.035(\pm 0.284)\sigma_I - 0.453(\pm 0.274)\sigma_R \\
(R &= 0.942, \ n = 10, \ P > 90 \%) \\
\delta H_\alpha(\text{ppm}) &= 7.227(\pm 0.133) - 0.012(\pm 0.259)F - 0.454(\pm 0.242)R \\
(R &= 0.957, \ n = 10, \ P > 95 \%) \\
\delta H_\beta(\text{ppm}) &= 8.208(\pm 0.020) + 0.078(\pm 0.41)\sigma_I + 0.097(\pm 0.040)\sigma_R \\
(R &= 0.997, \ n = 10, \ P > 95 \%) \\
\delta H_\beta(\text{ppm}) &= 8.211(\pm 0.019) + 0.080(\pm 0.038)F + 0.099(\pm 0.035)R \\
(R &= 0.997, \ n = 10, \ P > 95 \%)
\end{align*}
\]

3. 3. 2. $^{13}$C NMR spectra

From Table 3, the $\delta C_\alpha$ chemical shifts values have shown poor correlations ($r < 0.900$) with Hammett substituent constants and $F$ and $R$ parameters. This is attributed to weak polar, inductive, field and resonance effects of the substituents for predicting the reactivity on the chemical shift through resonance. This is evident with resonance conjugative structure shown in Fig. 1.

The $\delta C_\beta$ chemical shift, with all the substituents have shown satisfactory correlations with Hammett substituent constants namely $\sigma$ ($r = 0.947$) and $\sigma^+$ ($r = 0.914$). The $\delta C_\beta$ chemical shift values, except those with H (parent) and 4-CH$_3$ substituents have shown satisfactory correlations with Hammett substituent constants $\sigma_I$ ($r = 0.992$) and $\sigma_R$ ($r = 0.904$), except that with 4-F substituent have shown satisfactory correlations with $F$ ($r = 0.914$) parameter and except those with H (parent), 4-F and 4-CH$_3$ substituents have shown satisfactory correlations with $R$ ($r = 0.951$) parameter.

The $\delta CO$ chemical shifts, except those with 2-OCH$_3$ and 4-OCH$_3$ substituents have shown satisfactory correlations with Hammett substituent constants namely $\sigma$ ($r = 0.905$) and $\sigma^+$ ($r = 0.903$), except that with 4-CH$_3$ substituent have shown satisfactory correlations with Hammett substituent constant namely $\sigma_R$ ($r = 0.907$), except that with 4-F substituent have shown satisfactory correlations with $F$ ($r = 0.914$) parameter and except those with 3-NO$_2$ and 4-NO$_2$ substituents have shown satisfactory correlations with $R$ parameter. The remaining Hammett substituents have shown poor correlations ($r < 0.900$). This is due to the weak polar effect of the substituents for predicting the reactivity on the chemical shift through resonance as per the conjugative structure shown in Fig-1.

Some of the single parameter correlation was fails in regression, while seeking the multi-regression analysis correlations were satisfactorily obtained within these carbon chemical shifts and the multi-regression equations are given in (22)-(27).

\[
\begin{align*}
\delta CO(\text{ppm}) &= 187.527(\pm 0.032) - 0.208(\pm 0.064)\sigma_I + 0.026(\pm 0.062)\sigma_R \\
(R &= 0.977, \ n = 10, \ P > 90 \%)
\end{align*}
\]
\[
\delta CO(\text{ppm}) = 187.510(\pm 0.036) - 0.170(\pm 0.071)F - 0.002(\pm 0.066)R \\
(R = 0.966, n = 10, P > 95 \%) 
\]

\[
\delta C_\alpha(\text{ppm}) = 120.997(\pm 0.555) - 1.435(\pm 0.119)\sigma I + 0.105(\pm 1.080)\sigma R \\
(R = 0.943, n = 10, P > 95 \%) 
\]

\[
\delta C_\alpha(\text{ppm}) = 120.692(\pm 0.584) - 0.744(\pm 0.137)F - 0.171(\pm 1.059)R \\
(R = 0.924, n = 10, P > 95 \%) 
\]

\[
\delta C_\beta(\text{ppm}) = 143.525(\pm 0.146) - 3.444(\pm 0.294)\sigma I - 1.750(\pm 0.283)\sigma R \\
(R = 0.998, n = 10, P > 95 \%) 
\]

\[
\delta C_\beta(\text{ppm}) = 143.375(\pm 0.184) - 3.258(\pm 0.358)F - 1.982(\pm 0.334)R \\
(R = 0.997, n = 10, P > 95 \%) 
\]

3.4. Antimicrobial activities

3.4.1. Antibacterial sensitivity assay

Antibacterial sensitivity assay was performed using Kirby-Bauer [19] disc diffusion technique. In each Petri plate about 0.5 mL of the test bacterial sample was spread uniformly over the solidified Mueller Hinton agar using sterile glass spreader. Then the discs with 5mm diameter made up of Whatmann No.1 filter paper, impregnated with the solution of the compound was placed on the medium using sterile forceps. The plates were incubated for 24 hours at 37 °C by keeping the plates upside down to prevent the collection of water droplets over the medium. After 24 hours, the plates were visually examined and the diameter values of the zone of inhibition were measured. Triplicate results were recorded by repeating the same procedure.

3.4.2. Antifungal sensitivity assay

Antifungal sensitivity assay was performed using Kirby-Bauer [19] disc diffusion technique. PDA medium was prepared and sterilized as above. It was poured (ear bearing heating condition) in the Petri-plate which was already filled with 1 ml of the fungal species. The plate was rotated clockwise and counter clock-wise for uniform spreading of the species.

The discs were impregnated with the test solution. The test solution was prepared by dissolving 15 mg of the chalcone in 1 mL of DMSO solvent. The medium was allowed to solidify and kept for 24 hours. Then the plates were visually examined and the diameter values of zone of inhibition were measured. Triplicate results were recorded by repeating the same procedure.
Plate - 1

Fig. 2. Petri-dishes for Anti-bacterial activity of substituted 4-phenoxy phenyl ketones.

Plate – 2
Fig. 2(continue). Petri-dishes for Anti-bacterial activity of substituted 4-phenoxy phenyl ketones.
Fig. 2(continue). Petri-dishes for Anti-bacterial activity of substituted 4-phenoxy phenyl ketones.

Table 4. Antibacterial activity of substituted styryl 4-phenoxy phenyl ketones.

| S. No. | Substituent | Zone of Inhibition (mm) |
|--------|-------------|------------------------|
|        |             | Gram positive Bacteria | Gram negative Bacteria |
|        |             | B. subtilis | M. luteus | S. aureus | E. coli | P. aeruginosa |
| 1      | H           | 8 | - | 9 | - | 7 |
| 2      | 3-Br        | 7 | 7 | 7 | 8 | 7 |
| 3      | 4-Br        | 7 | - | 9 | 7 | - |
| 4      | 4-Cl        | 7 | 7 | 10 | - | - |
| 5      | 4-F         | - | 7 | 7 | - | 8 |
| 6      | 2-OCH₃      | - | - | 8 | 8 | - |
The antibacterial effect of the styryl 4-phenoxy phenyl chalcones is shown in Fig. 3 for Plates (1)-(5). Analysis of the zone of inhibition values are given in Table 4 and the Clustered column Chart Fig.-3. H(parent), 4-Cl and 4-Br substituent has shown markable antibacterial activity against *S. aureus*. All the substituents except 4-Cl have shown moderate antibacterial activity against *E. coli* and *P. aeruginosa*. All the substituents except 4-F, 2-OCH3 and 4-CH3 have shown moderate antibacterial activity against *B. subtilis*.

The antifungal effect of the styryl 4-phenoxy phenyl ketones is shown in Fig. 5 for Plates (11-14). Analysis of the zone of inhibition values is given Table 5 and the Clustered column Chart Fig. 6. Analysis of the Zone of inhibition (mm) values reveals that only four substituent compounds with H (parent), 4-Cl, 3-NO2 and 4-NO2 have shown moderate

| Substituents | Activity |
|--------------|----------|
| 1. H         |          |
| 2. 3-Br      |          |
| 3. 4-Br      |          |
| 4. 4-Cl      |          |
| 5. 4-F       |          |
| 6. 2-OCH3    |          |
| 7. 4-OCH3    |          |
| 8. 8-CH3     |          |
| 9. 9-NO2     |          |
| 10. 10-4-NO2 |          |

**Fig. 3.** Chart for Antibacterial activity of substituted styryl 4-phenoxy phenyl ketones.

**Table 4.** Analysis of the Zone of inhibition values

| Substituents | Activity |
|--------------|----------|
| 1. H         |          |
| 2. 3-Br      |          |
| 3. 4-Br      |          |
| 4. 4-Cl      |          |
| 5. 4-F       |          |
| 6. 2-OCH3    |          |
| 7. 4-OCH3    |          |
| 8. 8-CH3     |          |
| 9. 9-NO2     |          |
| 10. 10-4-NO2 |          |

**Fig. 5.** Chart for Antifungal activity of substituted styryl 4-phenoxy phenyl ketones.
antifungal activities against *A. niger*. The compounds with 4-CH$_3$, 3-NO$_2$ and 4-NO$_2$ substituents have shown good antifungal activities against *T. viride*. The remaining substituents have shown moderate antifungal activities against *T. viride*.

![Figure 4. Antifungal activities substituted styryl 4-phenoxyphenyl ketones.](Plate-6-Plate-7-Plate-8-Plate-9)
Table 5. Antifungal activity of substituted styryl 4-phenoxyphenyl ketones.

| S. No | Substituents | Zone of Inhibition (mm) |
|-------|--------------|-------------------------|
|       |              | A. niger    | T. viride    |
| 1     | H            | 7           | 9           |
| 2     | 3-Br         | -           | 9           |
| 3     | 4-Br         | 7           | 7           |
| 4     | 4-Cl         | 8           | 8           |
| 5     | 4-F          | 7           | 8           |
| 6     | 2-OMe        | -           | 7           |
| 7     | 4-OMe        | 7           | 7           |
| 8     | 4-Me         | 7           | 11          |
| 9     | 3-NO₂        | 9           | 11          |
| 10    | 4-NO₂        | 9           | 11          |
| Standard | Miconazole | 14          | 13          |
| Control | DMSO        | -           | -           |

Fig. 6. Chart for antifungal activity of substituted 4-phenoxy phenyl ketones.
4. CONCLUSIONS

Some chalcones have been synthesized by condensation of ketone and benzaldehydes. These chalcones have been characterized by their physical constants, spectral data. The 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. The antimicrobial activities of all synthesized imines have been studied using Bauer-Kirby method.

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