

Thionylchloride catalyzed aldol condensation: Synthesis, spectral correlation and antibacterial activities of some 3,5-dichloro-2-hydroxyphenyl chalcones

**R. Arulkumaran¹, S. Vijayakumar¹, R. Sundararajan¹, S P. Sakthinathan¹,
D. Kamalakkannan¹, R. Suresh¹, K. Ranganathan¹,
G. Vanangamudi¹, G. Thirunarayanan^{2,*}**

¹ PG & Research Department of Chemistry, Government Arts College, C-Mutlur,
Chidambaram-608102, India.

² Department of Chemistry, Annamalai University, Annamalainagar-608002, India.

*E-mail address: drgtnarayanan@gmail.com

ABSTRACT

A series of substituted styryl 3,5-dichloro-2-hydroxyphenyl ketones [1-(3, 5-dichloro-2-hydroxy)-3-phenylprop-2-en-1-one] were synthesized using thionyl chloride assisted Crossed-Aldol reaction. The yields of chalcones were more than 80%. The synthesized chalcones were characterized by analytical and spectroscopic data. From the spectroscopic data the group frequencies were correlated with Hammett substituent constants, F and R parameters. From the results of statistical analysis the effect of substituents were discussed. The antibacterial activities of these chalcones have been evaluated using Bauer-Kirby method.

Keywords:

Thionylchloride; Styryl 3,5-dichloro-2-hydroxyphenyl ketones; IR and NMR spectra; Hammett correlation; Substituent effects; Antimicrobial activities

1. INTRODUCTION

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 have been synthesized [1] and extracted from natural plants [2] by organic chemists. Various methods available for synthesizing chalcones such as Aldol, Crossed-Aldol, Claisen-Schmidt, Knoevenagel, Greener methods-Grinding of reactants, solvent free and oxides of nanoparticles with microwave heating. Also microwave assisted solvent free Aldol and Crossed-Aldol condensation [3, 4, 5] were useful synthesis of carbonyl compounds. Due to C-C single bond rotation [6] 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.

Chalcones possess various biological activities such as antibacterial [7, 8], antifungal [9], antioxidant [10], antiviral [11], antimalarial [12], antiplasmodial [13], antituberculosis [14], antiproliferative [15], antileishmanial [16], anti-inflammatory [17], antianalgesic and sedative [18], insect, antifeedants [19]. Halogenated chalcones possess insect antifeedant activities [20]. The presence of a reactive α , β -unsaturated keto function in chalcones was found to be responsible for their antimicrobial activity. At present, scientists have paid more interest to correlate the group frequencies of spectral data with Hammett substituent constants to explain the substituent effects of organic compounds. There is no information available in the literature regarding Thionylchloride catalyzed aldol condensation between aryl ketones and aldehydes, spectral and antimicrobial activities. Therefore the authors have taken efforts for synthesizing some chalcones by thionylchloride assisted Aldol condensation, studied the spectral correlation and antimicrobial activities.

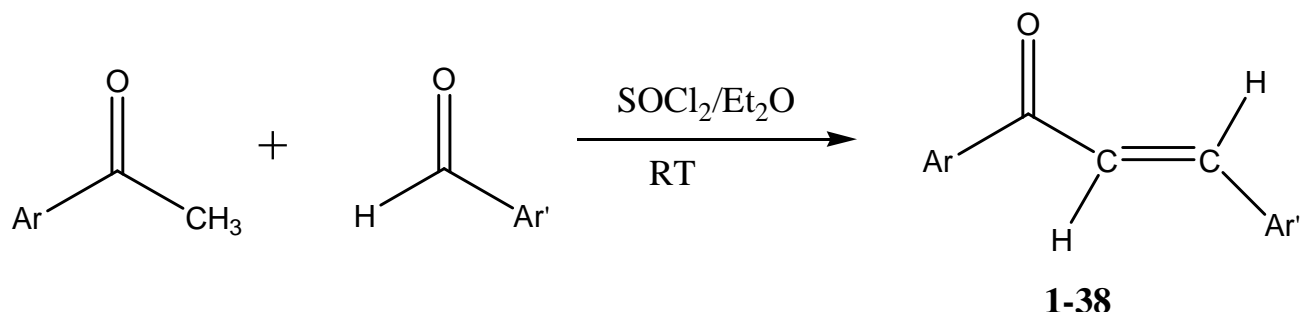
2. EXPERIMENTAL

2.1. General

All chemicals used were purchased from Sigma-Aldrich chemical company Bangalore. Melting points of all chalcones have been determined in open glass capillaries on Suntex melting point apparatus and are uncorrected. The ultra violet spectra of the chalcones synthesized have been recorded using ELICO-double beam BL222 Bio- Spectrophotometer. Infrared spectra (KBr, $4000-400\text{cm}^{-1}$) have been recorded on AVATAR-300 Fourier transform spectrophotometer. BRUKER-500MHz NMR spectrometers have been utilized for recording ^1H and ^{13}C spectra in CDCl_3 solvent using TMS as internal standard.

2.2. Synthesis of chalcones

Appropriate mixture of 3,5-dichloro-2-hydroxyacetophenone (100 mmol) and substituted benzaldehydes (100 mmol), 15mL of diethyl ether and (100 mmol) of thionylchloride were added. The reaction mixture was vigorously stirred at room temperature for 30 minutes (Scheme 1). After complete conversion of the ketones as monitored by TLC, the mixture was allowed to stand 20 minutes. The reagents were removed by filtration. The filtrate was washed with distilled water and recrystallized from absolute ethanol, dried well and kept in a desiccator.



Scheme 1. Thionyl chloride catalyzed aldol condensation between 3,5-dichloro-2-hydroxyacetophenone and benzaldehydes (entries 27-36).

3. RESULTS AND DISCUSSION

In our organic chemistry research laboratory, we attempted to synthesize aryl chalcone derivatives by Crossed-Aldol condensation of electron withdrawing as well as electron donating group substituted aryl methyl ketones and benzaldehydes in the presence of vigorous acidic catalyst thionyl chloride in diethyl ether except acid or base or its salt in atmospheric temperature condition. Hence the authors have synthesized the chalcone derivatives by the reaction between 100 mmol of aryl methyl ketones 100 mmol substituted benzaldehydes, 100 mmol of thionyl chloride and 15 mL of ether at room temperature (Scheme 1). During the course of this reaction the acidic thionyl chloride catalyzes Aldol reaction between aryl ketone and aldehydes and elimination of water gave the chalcones. The yields of the chalcones in this reaction are more than 80%. The proposed general mechanism of this reaction is given in Fig. 1. Further we investigated this reaction with equimolar quantities of the 3,5-dichloro-2-hydroxyacetophenone and benzaldehyde (entry 27). In this reaction the obtained yield is 83%. The physical constants yield and mass spectral data are presented in Table 1. We have studied the effect of solvent for this Aldol condensation by observing the yield of the products. The solvents such as ethanol, methanol, dichloromethane, dimethyl formamide and water have been used for this Aldol reaction with 3,5-dichloro-2-hydroxyacetophenone and benzaldehyde. Carrying out this Aldol reaction with above solvents the resulting yields are 73%, 68%, 65%, 66% and 65% of chalcones respectively. The same reaction was carried out with reflux conditions and there is no improvement for the yield of the products. Here the authors have achieved the aim of this synthetic method with the observation of more than 82% yields of aryl chalcones by condensation of 3,5-dichloro-2-hydroxyacetophenone and benzaldehyde in presence of $\text{SOCl}_2/\text{Et}_2\text{O}$ in room temperature.

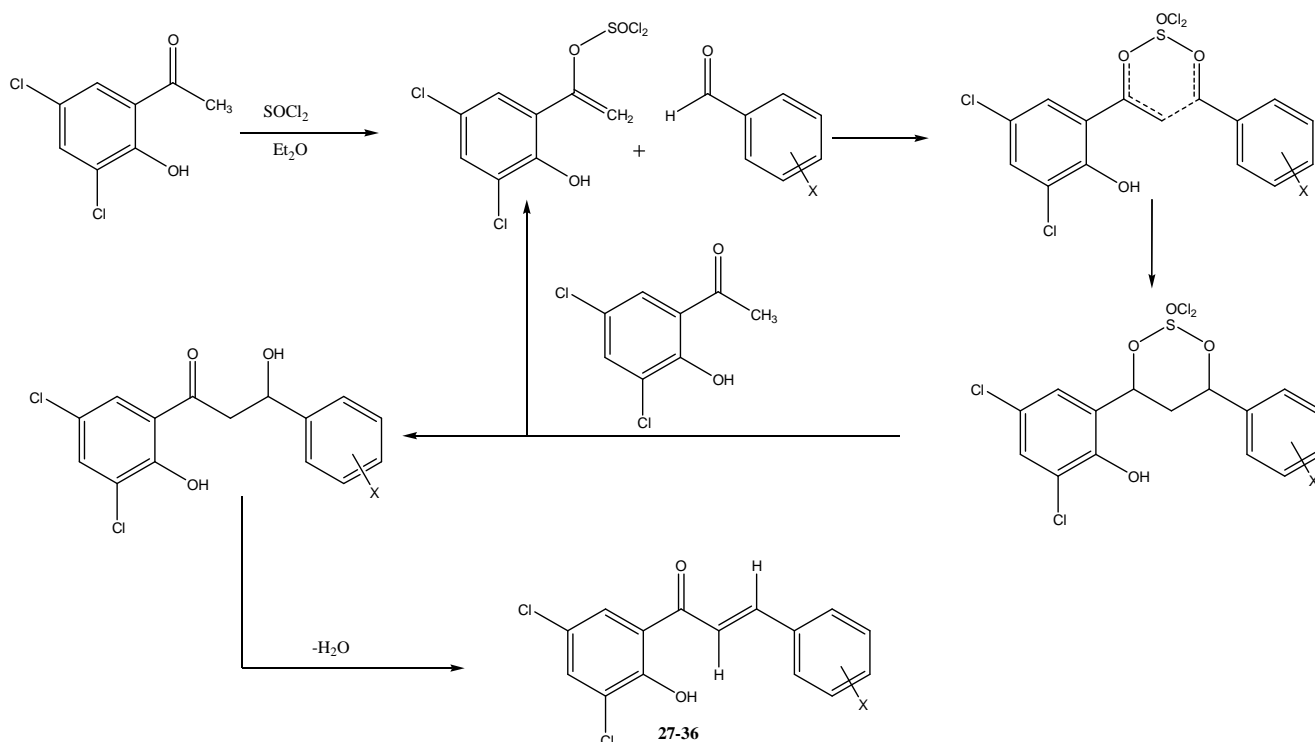


Fig. 1. Proposed mechanism for the synthesis of substituted styryl 3,5-dichloro-2-hydroxyphenyl ketones by solfonyl chloride catalyzed Aldol reaction.

Table 1. Analytical and mass spectral data of chalcones synthesized by $\text{SOCl}_2/\text{Et}_2\text{O}$ catalyzed aryl methyl ketones and substituted benzaldehydes reaction of the type
 $\text{Ar-CO-CH}_3 + \text{Ar}'\text{-CHO} \rightarrow \text{Ar-CO-CH=CH-Ar}'$.

Entry	Ar	Ar'	Product	M. W.	Yield (%)	m.p. (°C)	Mass
1	C_6H_5	C_6H_5	$\text{C}_6\text{H}_5\text{COCH=CHC}_6\text{H}_5$	208	81	55-56 (55-58)[21]	---
2	4- $\text{N}(\text{CH}_3)_2\text{C}_6\text{H}_4$	C_6H_5	4- $\text{N}(\text{CH}_3)_2\text{C}_6\text{H}_4\text{COCH=CHC}_6\text{H}_5$	294	80	87-88 (87-88) [21]	---
3	C_6H_5	C_{10}H_7 (1-Naph)	$\text{C}_6\text{H}_5\text{COCH=CHC}_{10}\text{H}_7$	273	85	104-105 (104-105)[21]	---
4	C_6H_5	$\text{C}_8\text{H}_6\text{N}$ (3-Ind)	$\text{C}_6\text{H}_5\text{COCH=CHC}_8\text{H}_6\text{N}$	262	80	140-141 (140)[21]	---
5	C_6H_5	4-OHC $_6\text{H}_4$	$\text{C}_6\text{H}_5\text{COCH=CHC}_6\text{H}_4\text{OH}$	291	82	122-123 (122)[21]	--
6	C_6H_5	4-OCH $_3\text{C}_6\text{H}_4$	$\text{C}_6\text{H}_5\text{COCH=CHC}_6\text{H}_4\text{OCH}_3$	291	80	164-165 (164)[21]	---
7	4-NH $_2\text{C}_6\text{H}_5$	C_4H_3 (3-Furyl)	4-NH $_2\text{C}_6\text{H}_5\text{COCH=CHC}_4\text{H}_3$	213	81	120-121 (119-120) [21]	---
8	4-NH $_2\text{C}_6\text{H}_4$	C_6H_5	4-NH $_2\text{C}_6\text{H}_4\text{COCH=CHC}_6\text{H}_5$	223	82	98-99 (98-99) [21]	---
9	4-NH $_2\text{C}_6\text{H}_4$	2,6-Cl $_2\text{C}_6\text{H}_3$	4-NH $_2\text{C}_6\text{H}_4\text{COCH=CHC}_6\text{H}_3\text{Cl}_2$	291	80	98-99 (98-99) [21]	---
10	4-FC $_6\text{H}_4$	C_6H_5	4-FC $_6\text{H}_4\text{COCH=CHC}_6\text{H}_5$	226	81	49-50 (49-50) [21]	---
11	2,4-Cl $_2\text{C}_6\text{H}_3$	C_6H_5	2,4-Cl $_2\text{C}_6\text{H}_3\text{COCH=CHC}_6\text{H}_5$	276	84	80-82 (80-81) [21]	
12	3,4-Cl $_2\text{C}_6\text{H}_3$	C_6H_5	3,4-Cl $_2\text{C}_6\text{H}_3\text{COCH=CHC}_6\text{H}_5$	276	82	100-101 (100-101) [21]	
13	4-(OH) C_6H_4	C_6H_5	4-(OH) $\text{C}_6\text{H}_3\text{COCH=CHC}_6\text{H}_5$	226	80	63-64 (63-64) [21]	
14	C_{10}H_7 (1-Naph)	C_6H_5	$\text{C}_{10}\text{H}_7\text{COCH=CHC}_6\text{H}_5$	258	80	100-102 (100-102) [21]	
15	4-Br C_{10}H_6 (1-Naph)	C_6H_5	4-Br $\text{C}_{10}\text{H}_6\text{COCH=CHC}_6\text{H}_5$	396	82	103-104 (103-104) [21]	
16	4-Cl C_{10}H_6 (1-Naph)	C_6H_5	4-Cl $\text{C}_{10}\text{H}_6\text{COCH=CHC}_6\text{H}_5$	292	83	122-123 (122-123) [21]	
17	C_{10}H_7 (2-Naph)	C_6H_5	$\text{C}_{10}\text{H}_7\text{COCH=CHC}_6\text{H}_5$	258	81	104-105 (104-105) [21]	
18	C_{13}H_9 (2-Fluorene)	C_6H_5	$\text{C}_{13}\text{H}_9\text{COCH=CHC}_6\text{H}_5$	296	80	150-151 (150-151) [21]	---

19	C ₁₂ H ₉ (Biphenyl)	C ₆ H ₅	C ₁₂ H ₉ COCH=CHC ₆ H ₅	284	83	153-154 (153-154[21])	---
20	C ₄ H ₃ O(2-Furyl)	C ₆ H ₅	C ₄ H ₃ OCOCH=CHC ₆ H ₅	198	80	80-81 (80-81) [21]	---
21	C ₄ H ₃ S(2-Thienyl)	C ₆ H ₅	C ₄ H ₃ SCOCH=CHC ₆ H ₅	204	83	112-113 (112-113) [21]	---
22	C ₁₄ H ₁₀ (Anthracene)	C ₆ H ₅	C ₁₄ H ₉ COCH=CHC ₆ H ₅	308	82	124-125 (124-125) [21]	---
23	5-BrC ₄ H ₂ S(2-Thyl)	C ₆ H ₅	5-BrC ₄ H ₂ SCOCH=CHC ₆ H ₅	292	83	107-110 (107-110) [21]	---
24	5-BrC ₄ H ₂ S(2-Thyl)	4-BrC ₆ H ₄	5-BrC ₄ H ₂ SCOCH=CHC ₆ H ₄ Br	371	82	173-174 (173-174) [21]	---
25	4-Cyclohexylphenyl	C ₆ H ₅	4-C ₆ H ₁₁ C ₆ H ₄ CO CH=CHC ₆ H ₅	290	83	105-106 (104-105) [21]	---
26	4-Cyclohexylphenyl	3-BrC ₆ H ₄	4-C ₆ H ₁₁ C ₆ H ₄ CO CH=CHC ₆ H ₄ Br	369	80	110-111 (110-111) [21]	---
27	3,5-Cl ₂ -2-OHC ₆ H ₂	C ₆ H ₅	3,5-Cl ₂ -2-OH-C ₆ H ₂ COCH=CHC ₆ H ₄	293	83	110-111	293[M ⁺], 295[M ²⁺], 297[M ⁴⁺], 214, 201, 188, 103, 91, 77
28	3,5-Cl ₂ -2-OHC ₆ H ₂	3-BrC ₆ H ₄	3,5-Cl ₂ -2-OHC ₆ H ₂ COCH=CHC ₆ H ₄ Br	372	86	262-263	372[M ⁺], 374[M ²⁺], 376[M ⁴⁺], 378[M ⁶⁺], 214,201,1 88, 180, 154,78,77.
29	3,5-Cl ₂ -2-OHC ₆ H ₂	4-BrC ₆ H ₄	3,5-Cl ₂ -2-OHC ₆ H ₂ COCH=CHC ₆ H ₄ Br	372	84	251-252	372[M ⁺], 374[M ²⁺], 376[M ⁴⁺], 378[M ⁶⁺], 214,201, 188, 180, 154,78,77.
30	3,5-Cl ₂ -2-OHC ₆ H ₂	2-ClC ₆ H ₄	3,5-Cl ₂ -2-OHC ₆ H ₂ CO CH=CHC ₆ H ₄ Cl	327	86	261-262	327[M ⁺], 329[M ²⁺], 331[M ⁴⁺], 333[M ⁶⁺], 214,201, 188, 180, 137,124, 111,77,34.

31	3,5-Cl ₂ -2-OHC ₆ H ₂	3-ClC ₆ H ₄	3,5-Cl ₂ -2-OHC ₆ H ₂ CO CH=CHC ₆ H ₄ Cl	327	85	116-117	327[M ⁺], 329[M ²⁺], 331[M ⁴⁺], 333[M ⁶⁺], 214,201,188, 180, 137,124, 111,77,34.
32	3,5-Cl ₂ -2-OHC ₆ H ₂	4-ClC ₆ H ₄	3,5-Cl ₂ -2-OHC ₆ H ₂ COCH=CHC ₆ H ₄ Cl	327	87	149-150	327[M ⁺], 329[M ²⁺], 331[M ⁴⁺], 333[M ⁶⁺], 214,201,188, 180, 137,124, 111,77,34.
33	3,5-Cl ₂ -2-OHC ₆ H ₂	4-FC ₆ H ₄	3,5-Cl ₂ -2-OHC ₆ H ₂ COCH=CHC ₆ H ₄ F	311	84	110-111	311[M ⁺], 313[M ²⁺], 315[M ⁴⁺], 214, 201,188, 121, 108, 95, 77, 18.
34	3,5-Cl ₂ -2-OHC ₆ H ₂	4-CH ₃ C ₆ H ₄	3,5-Cl ₂ -2-OHC ₆ H ₂ COCH=CHC ₆ H ₄ CH ₃	307	85	201-202	307[M ⁺], 309[M ²⁺], 311[M ⁴⁺], 214, 201,188, 117,104, 91, 77, 15.
35	3,5-Cl ₂ -2-OHC ₆ H ₂	3-NO ₂ C ₆ H ₄	3,5-Cl ₂ -2-OHC ₆ H ₂ COCH=CHC ₆ H ₄ -NO ₂	338	87	232-233	338[M ⁺], 340[M ²⁺], 342[M ⁴⁺], 214, 201,188, 148,135, 122, 7, 45.
36	3,5-Cl ₂ -2-OHC ₆ H ₂	4-NO ₂ C ₆ H ₄	3,5-Cl ₂ -2-OHC ₆ H ₂ CO CH=CHC ₆ H ₄ -NO ₂	338	88	221-222	338[M ⁺], 340[M ²⁺], 342[M ⁴⁺], 214,201,188,148,135, 5,122,77, 45.

The Ultra-violet, infrared and NMR spectral data of unknown chalcones, substituted 3,5-dichloro-2-hydroxy phenyl ketones were summarized below (27-36).

(2E)-1-(3,5-Dichloro-2-hydroxyphenyl)-3-phenyl-2-propen-1-one (27): IR (KBr, cm^{-1}): $\nu=1639.17(\text{CO}_{s\text{-}cis})$, $1570.68(\text{CO}_{s\text{-}trans})$, $1044.36(\text{CH}=\text{CH})$, $3438.55(\text{OH})$; ^1H NMR (CDCl_3 , ppm): $\delta=7.580(d, 1\text{H}, \alpha)$, $8.020(d, 1\text{H}, \beta)$, $7.479\text{-}7.849(m, 7\text{H Ar-H})$, $1.851(s, 1\text{H -OH})$; ^{13}C NMR(CDCl_3 , ppm): $\delta=121.068(\text{C}_\alpha)$ $147.619(\text{C}_\beta)$, $192.607(\text{CO})$, $134.110(\text{C}_1)$, $127.430(\text{C}_2, \text{C}_6)$, $127.646(\text{C}_3, \text{C}_4, \text{C}_5)$, $124.174(\text{C}_1')$, $157.998(\text{C}_2')$, $127.430(\text{C}_3')$, $135.766(\text{C}_4')$, $128.992(\text{C}_5')$, $129.182(\text{C}_6')$.

(2E)-1-(3,5-Dichloro-2-hydroxyphenyl)-3-(3-bromophenyl)-2-propen-1-one (28): IR (KBr, cm^{-1}): $\nu=1648.64(\text{CO}_{s\text{-}cis})$, $1583.65(\text{CO}_{s\text{-}trans})$, $1026.02(\text{CH}=\text{CH})$, $3423.39(\text{OH})$; ^1H NMR (CDCl_3 , ppm): $\delta=7.554(d, 1\text{H}, \alpha)$, $7.916(d, 1\text{H}, \beta)$, $7.281\text{-}7.931(m, 6\text{H Ar-H})$, $3.535(s, 1\text{H -OH})$; ^{13}C NMR(CDCl_3 , ppm): $\delta=131.155(\text{C}_\alpha)$ $141.319(\text{C}_\beta)$, $192.541(\text{CO})$, $135.995(\text{C}_1)$, $131.155(\text{C}_2)$, $131.155(\text{C}_3)$, $131.155(\text{C}_4)$, $131.155(\text{C}_5)$, $131.155(\text{C}_6)$, $131.155(\text{C}_1')$, $150.030(\text{C}_2')$, $131.155(\text{C}_3')$, $135.995(\text{C}_4')$, $134.301(\text{C}_5')$, $134.301(\text{C}_6')$.

(2E)-1-(3,5-Dichloro-2-hydroxyphenyl)-3-(4-bromophenyl)-2-propen-1-one (29): IR (KBr, cm^{-1}): $\nu=1643.77(\text{CO}_{s\text{-}cis})$, $1574.29(\text{CO}_{s\text{-}trans})$, $1045.73(\text{CH}=\text{CH})$, $3459.64(\text{OH})$; ^1H NMR (CDCl_3 , ppm): $\delta=7.555(d, 1\text{H}, \alpha)$, $7.934(d, 1\text{H}, \beta)$, $7.285\text{-}7.857(m, 6\text{H Ar-H})$, $4.707(s, 1\text{H -OH})$; ^{13}C NMR(CDCl_3 , ppm): $\delta=120.957(\text{C}_\alpha)$ $146.090(\text{C}_\beta)$, $192.351(\text{CO})$, $135.912(\text{C}_1)$, $127.627(\text{C}_2, \text{C}_6)$, $132.155(\text{C}_3, \text{C}_5)$, $123.363(\text{C}_4)$, $126.086(\text{C}_1')$, $158.017(\text{C}_2')$, $127.365(\text{C}_3')$, $135.912(\text{C}_4')$, $127.627(\text{C}_5')$, $130.253(\text{C}_6')$.

(2E)-1-(3,5-Dichloro-2-hydroxyphenyl)-3-(2-chlorophenyl)-2-propen-1-one (30): IR (KBr, cm^{-1}): $\nu=1644.06(\text{CO}_{s\text{-}cis})$, $1579.14(\text{CO}_{s\text{-}trans})$, $1026.37(\text{CH}=\text{CH})$, $3429.16(\text{OH})$; ^1H NMR (CDCl_3 , ppm): $\delta=7.566(d, 1\text{H}, \alpha)$, $8.413(d, 1\text{H}, \beta)$, $7.285\text{-}7.688(m, 6\text{H Ar-H})$, $3.046(s, 1\text{H -OH})$; ^{13}C NMR(CDCl_3 , ppm): $\delta=129.703(\text{C}_\alpha)$ $146.642(\text{C}_\beta)$, $193.603(\text{CO})$, $135.995(\text{C}_1)$, $131.155(\text{C}_2)$, $131.155(\text{C}_3)$, $131.155(\text{C}_4)$, $131.155(\text{C}_5)$, $131.155(\text{C}_6)$, $131.155(\text{C}_1')$, $150.030(\text{C}_2')$, $131.155(\text{C}_3')$, $135.995(\text{C}_4')$, $134.301(\text{C}_5')$, $134.301(\text{C}_6')$.

(2E)-1-(3,5-Dichloro-2-hydroxyphenyl)-3-(3-chlorophenyl)-2-propen-1-one (31): IR (KBr, cm^{-1}): $\nu=1645.69(\text{CO}_{s\text{-}cis})$, $1585.31(\text{CO}_{s\text{-}trans})$, $1034.67(\text{CH}=\text{CH})$, $3455.43(\text{OH})$; ^1H NMR (CDCl_3 , ppm): $\delta=7.561(d, 1\text{H}, \alpha)$, $7.927(d, 1\text{H}, \beta)$, $7.369\text{-}7.701(m, 6\text{H Ar-H})$, $5.556(s, 1\text{H -OH})$; ^{13}C NMR (CDCl_3 , ppm): $\delta=120.323(\text{C}_\alpha)$ $145.742(\text{C}_\beta)$, $192.322(\text{CO})$, $136.004(\text{C}_1)$, $127.139(\text{C}_2)$, $134.995(\text{C}_3)$, $128.354(\text{C}_4)$, $130.415(\text{C}_5)$, $124.307(\text{C}_6)$, $125.139(\text{C}_1')$, $158.018(\text{C}_2')$, $126.182(\text{C}_3')$, $136.004(\text{C}_4')$, $129.152(\text{C}_5')$, $130.279(\text{C}_6')$.

(2E)-1-(3,5-Dichloro-2-hydroxyphenyl)-3-(4-chlorophenyl)-2-propen-1-one (32): IR (KBr, cm^{-1}): $\nu=1638.60(\text{CO}_{s\text{-}cis})$, $1581.57(\text{CO}_{s\text{-}trans})$, $1015.80(\text{CH}=\text{CH})$, $3450.09(\text{OH})$; ^1H NMR (CDCl_3 , ppm): $\delta=7.536(d, 1\text{H}, \alpha)$, $7.948(d, 1\text{H}, \beta)$, $7.284\text{-}7.964(m, 6\text{H Ar-H})$, $4.696(s, 1\text{H -OH})$; ^{13}C NMR(CDCl_3 , ppm): $\delta=120.962(\text{C}_\alpha)$ $146.007(\text{C}_\beta)$, $192.338(\text{CO})$, $132.566(\text{C}_1)$, $127.352(\text{C}_2, \text{C}_6)$, $129.191(\text{C}_3)$, $134.927(\text{C}_4)$, $129.504(\text{C}_5)$, $124.245(\text{C}_1')$, $158.013(\text{C}_2')$, $125.124(\text{C}_3')$, $137.642(\text{C}_4')$, $127.062(\text{C}_5')$, $129.504(\text{C}_6')$.

(2E)-1-(3,5-Dichloro-2-hydroxyphenyl)-3-(4-fluorophenyl)-2-propen-1-one (33): IR (KBr, cm^{-1}): $\nu=1645.58(\text{CO}_{s\text{-}cis})$, $1582.36(\text{CO}_{s\text{-}trans})$, $1020.64(\text{CH}=\text{CH})$, $3431.29(\text{OH})$; ^1H NMR (CDCl_3 , ppm): $\delta=7.503(d, 1\text{H}, \alpha)$, $7.981(d, 1\text{H}, \beta)$, $7.162\text{-}7.997(m, 6\text{H Ar-H})$, $3.921(s, 1\text{H -OH})$; ^{13}C NMR(CDCl_3 , ppm): $\delta=127.365(\text{C}_\alpha)$ $146.400(\text{C}_\beta)$, $192.417(\text{CO})$, $130.999(\text{C}_1)$, $127.365(\text{C}_2, \text{C}_6)$, $116.636(\text{C}_3, \text{C}_5)$, $164.307(\text{C}_4)$, $127.365(\text{C}_1')$, $164.307(\text{C}_2')$, $127.365(\text{C}_3')$, $135.995(\text{C}_4')$, $127.365(\text{C}_5')$, $130.999(\text{C}_6')$.

(2E)-1-(3,5-Dichloro-2-hydroxyphenyl)-3-(4-methylphenyl)-2-propen-1-one (34): IR (KBr, cm^{-1}): $\nu=1636.89(\text{CO}_{s\text{-}cis})$, $1590.49(\text{CO}_{s\text{-}trans})$, $1054.97(\text{CH}=\text{CH})$, $3435.69(\text{OH})$; ^1H NMR (CDCl_3 , ppm): $\delta=7.386(d, 1\text{H}, \alpha)$, $7.641(d, 1\text{H}, \beta)$, $6.951\text{-}7.657(m, 6\text{H Ar-H})$, $3.873(s, 1\text{H - OH})$, $2.402(s, 3\text{H -CH}_3)$; ^{13}C NMR(CDCl_3 , ppm): $\delta=118.947(\text{C}_\alpha)$ $143.564(\text{C}_\beta)$, $192.645(\text{CO})$, $132.411(\text{C}_1)$, $126.010(\text{C}_2, \text{C}_6)$, $129.634(\text{C}_3, \text{C}_5)$, $140.771(\text{C}_4)$, $126.010(\text{C}_1', \text{C}_3')$, $153.654(\text{C}_2')$, $132.411(\text{C}_4')$, $128.456(\text{C}_5')$, $129.901(\text{C}_6')$, $21.501(\text{CH}_3)$.

(2E)-1-(3,5-Dichloro-2-hydroxyphenyl)-3-(3-nitrophenyl)-2-propen-1-one (35): IR (KBr, cm^{-1}): $\nu=1650.15(\text{CO}_{s\text{-}cis})$, $1585.00(\text{CO}_{s\text{-}trans})$, $1045.68(\text{CH}=\text{CH})$, $3452.09(\text{OH})$; ^1H NMR (CDCl_3 , ppm): $\delta=7.865(d, 1\text{H}, \alpha)$, $8.027(d, 1\text{H}, \beta)$, $7.600\text{-}8.584(m, 6\text{H Ar-H})$, $2.682(s, 1\text{H - OH})$; ^{13}C NMR(CDCl_3 , ppm): $\delta=122.928(\text{C}_\alpha)$ $140.835(\text{C}_\beta)$, $192.873(\text{CO})$, $140.835(\text{C}_1)$, $122.928(\text{C}_2)$, $140.835(\text{C}_3)$, $122.928(\text{C}_4)$, $122.928(\text{C}_5)$, $140.835(\text{C}_6)$, $122.928(\text{C}_1')$, $169.147(\text{C}_2')$, $122.928(\text{C}_3')$, $140.835(\text{C}_4')$, $122.928(\text{C}_5')$, $122.958(\text{C}_6')$.

(2E)-1-(3,5-Dichloro-2-hydroxyphenyl)-3-(4-nitrophenyl)-2-propen-1-one (36): IR (KBr, cm^{-1}): $\nu=1647.51(\text{CO}_{s\text{-}cis})$, $1586.57(\text{CO}_{s\text{-}trans})$, $1041.17(\text{CH}=\text{CH})$, $3435.07(\text{OH})$; ^1H NMR (CDCl_3 , ppm): $\delta=7.864(d, 1\text{H}, \alpha)$, $8.013(d, 1\text{H}, \beta)$, $7.652\text{-}7.879(m, 6\text{H Ar-H})$, $3.097(s, 1\text{H - OH})$; ^{13}C NMR(CDCl_3 , ppm): $\delta=124.374(\text{C}_\alpha)$ $152.692(\text{C}_\beta)$, $193.435(\text{CO})$, $134.301(\text{C}_1)$, $129.446(\text{C}_2, \text{C}_6)$, $124.374(\text{C}_3, \text{C}_5)$, $152.692(\text{C}_4)$, $114.459(\text{C}_1')$, $159.226(\text{C}_2')$, $124.374(\text{C}_3')$, $134.301(\text{C}_4')$, $129.446(\text{C}_5', \text{C}_6')$.

In the present investigation UV absorption maxima from UV spectra, the spectral linearity of chalcones has been studied by evaluating the effect of substituents. 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 $\text{>C}=\text{C}<$ *out of planes* (cm^{-1}), the vinyl hydrogen from IR spectra and chemical shifts $\delta(\text{ppm})$, of H_α , H_β , C_α , C_β and CO from ^1H and ^{13}C NMR spectra have been correlated with various substituent constants.

3.1. Ultra violet spectral study

The UV spectra of all synthesized chalcones were recorded in SHIMADZU-1650 SPECTROMETER (λ_{max} nm) in spectral grade methanol. The measured absorption maxima (λ_{max} nm) of these chalcones are presented in Table 2. These values are correlated with Hammett substituent constants and F and R parameters using single and multi-linear regression analysis. Hammett correlation involving the group frequencies and absorption maxima, the form of the Hammett equation employed is

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

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

The results of statistical analysis of these values with Hammett substituent constants are presented in Table 3. From Table 3, Hammett substituent constants σ , σ^+ , σ_I , σ_R , F and R values gave poor correlations with λ_{max} . All constants gave negative ρ values. This is due to

Table 2. The UV λ_{\max} (nm), IR $\nu(\text{cm}^{-1})$, and NMR $\delta(\text{ppm})$ frequencies of substituted styryl 3,5-dichloro-2-hydroxyphenyl ketones (entries 27-36).

Entry	Substt.	λ_{\max}	$\nu\text{CO}_{s\text{-}cis}$	$\nu\text{CO}_{s\text{-}trans}$	νCH_{ip}	νCH_{op}	$\nu\text{CH}=\text{CH}_{op}$	$\nu\text{C}=\text{C}_{op}$	δH_{α}	δH_{β}	δCO	δC_{α}	δC_{β}
27	H	318.0	1639.17	1570.68	1169.73	770.42	1044.36	590.98	7.580	8.020	192.60	121.06	147.61
28	3-Br	275.2	1648.64	1583.65	1144.22	749.71	1026.02	573.75	7.554	7.916	192.54	131.15	141.31
29	4-Br	322.0	1643.77	1574.29	1167.94	745.78	1045.73	601.71	7.555	7.934	192.35	120.95	146.09
30	2-Cl	285.9	1644.06	1579.14	1139.97	749.09	1026.37	581.89	7.566	8.413	193.60	129.70	146.64
31	3-Cl	270.8	1645.69	1585.31	1167.76	786.84	1034.67	602.94	7.561	7.927	192.32	120.32	145.74
32	4-Cl	329.4	1638.60	1581.57	1168.64	749.84	1015.8	534.47	7.536	7.948	192.33	120.96	146.00
33	4-F	327.0	1645.58	1582.36	1157.51	755.68	1020.64	542.47	7.503	7.981	192.41	127.36	146.40
34	4-CH ₃	334.2	1636.89	1590.49	1172.62	738.87	1054.97	571.86	7.386	7.641	192.64	118.94	143.56
35	3-NO ₂	270.6	1650.15	1585.00	1149.89	751.69	1045.68	546.72	7.865	8.027	192.87	122.92	140.83
36	4-NO ₂	315.6	1647.51	1586.57	1164.22	745.76	1041.17	558.90	7.864	8.013	193.43	124.37	152.69

Table 3. Results of statistical analysis of substituted styryl 3,5-dichloro-2-hydroxyphenyl ketones (entries 27-36).

Frequency	Constants	r	I	ρ	s	n	Correlated derivatives
$UV\lambda_{max}$	σ	0.854	318.12	-47.119	23.12	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.862	318.38	-46.439	21.52	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.842	323.76	-45.759	25.05	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.620	301.43	-28.622	27.04	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.727	317.20	-29.303	26.53	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.725	299.91	-31.580	26.71	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
νCO_{s-cis} (cm-1)	σ	0.980	1640.66	11.833	2.84	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.979	1641.07	10.085	2.89	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.900	1637.80	15.019	2.81	9	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.819	1644.56	4.658	4.65	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.710	1638.08	14.073	2.96	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.715	1644.52	3.281	4.68	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂

$\nu\text{CO}_{s\text{-trans}}$ (cm-1)	σ	0.725	1580.51	4.939	6.03	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.705	1581.65	0.854	6.23	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.718	1580.07	4.428	6.13	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.710	1582.29	3.234	6.20	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.722	1579.66	5.318	6.08	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.804	1582.11	1.334	6.23	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
νCH_{ip} (cm-1)	σ	0.833	1163.88	-12.881	11.67	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.845	1164.59	-14.944	11.06	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.748	1170.02	-23.659	10.82	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.712	1161.18	7.773	12.29	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.844	1169.09	-21.010	11.08	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.809	1161.05	5.141	12.33	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
νCH_{op} (cm-1)	σ	0.800	754.32	0.100	14.91	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.701	754.18	0.635	14.91	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.706	755.84	-3.587	14.88	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.709	753.47	-7.414	14.83	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.809	756.61	-5.340	14.83	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.502	754.11	-1.608	14.90	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂

$\nu_{CH=CH_{op}}$ (cm-1)	σ	0.700	1035.61	-0.275	13.60	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.601	1035.41	0.441	13.60	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.743	1045.14	-23.248	12.25	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.961	1040.58	42.062	10.73	7	H, 3-Br, 2-Cl, 3-Cl, 4-F, 3-NO ₂ , 4-NO ₂
	F	0.744	1045.25	-23.068	12.17	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.645	1040.76	33.295	11.37	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
$\nu_{C=C_{op}}$ (cm-1)	σ	0.720	575.29	-16.765	25.34	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.703	569.80	2.613	25.89	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.735	585.36	-35.829	24.25	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.705	570.83	2.249	25.90	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.746	589.72	-45.506	22.97	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.705	571.57	6.382	25.87	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
ν_{OH} (cm-1)	σ	0.742	3437.72	17.768	12.10	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.740	3438.55	14.365	12.26	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.629	3436.39	15.337	12.79	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.643	3446.24	29.244	12.05	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.718	3438.75	9.439	13.14	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.634	3446.81	25.970	12.05	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂

$\delta_{H\alpha}$ (ppm)	σ	0.914	7.468	0.457	0.06	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.905	7.490	0.367	0.08	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.638	7.432	0.398	0.12	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.730	7.668	0.590	0.10	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.544	7.457	0.332	0.13	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.728	7.678	0.518	0.11	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
$\delta_{H\beta}$ (ppm)	σ	0.726	7.935	0.165	0.19	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.947	7.907	0.255	0.17	8	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 3-NO ₂ , 4-NO ₂
	σ_I	0.420	7.846	0.328	0.18	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.707	7.972	-0.079	0.19	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.732	7.877	0.248	0.18	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.704	7.988	0.036	0.19	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
δ_{CO} (ppm)	σ	0.838	192.54	0.582	0.44	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.749	192.52	0.641	0.42	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.723	192.52	0.444	0.47	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.735	192.81	0.878	0.45	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.760	192.58	0.296	0.48	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.741	192.85	0.904	0.44	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂

$\delta C\alpha(\text{ppm})$	σ	0.728	122.95	2.920	4.40	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.829	122.75	3.515	4.30	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.634	120.58	7.726	4.04	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.731	122.91	-7.169	4.26	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.745	120.47	7.836	3.99	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.730	122.80	-6.197	4.28	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
$\delta C\beta(\text{ppm})$	σ	0.711	145.33	1.274	3.54	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.713	145.30	1.319	3.52	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.808	145.20	1.177	3.55	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.808	145.88	1.607	3.54	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.810	145.18	1.196	3.55	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.712	146.01	2.046	3.53	10	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂

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

The inability of effect of substituents on absorption and the resonance conjugative structure shown in Fig. 2. regression analysis of these frequencies of all ketones with inductive, resonance and Swain – Lupton's [22] constants produce satisfactory correlations as evident in equations 2 and 3.

$$\lambda_{(nm)} = 320.28(\pm 18.167) - 45.151(\pm 36.359)\sigma_I - 26.949(\pm 46.585)\sigma_R \quad \dots(2)$$

$(R = 0.946, n = 10, P > 90\%)$

$$\lambda_{(nm)} = 313.31(\pm 18.011) - 34.042(\pm 36.579)F - 37.516(\pm 42.981)R \quad \dots(3)$$

$(R = 0.941, n = 10, P > 90\%)$

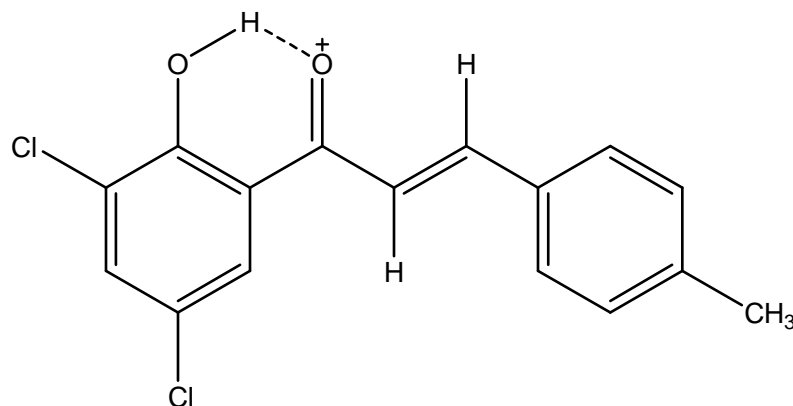


Fig. 2. The resonance-conjugative structure

3.2. IR spectral study

The carbonyl stretching frequencies (cm^{-1}) of *s-cis* and *s-trans* isomers of present study are presented in Table 2. The stretching frequencies for carbonyl absorption are assigned based on the assignments made by Hays and Timmons [23] 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 withdrawing group is present in phenyl ring while highest frequency is noted when strongest electro attracting group present in phenyl ring. A similarly trend in absorption was earlier noted by Perjessy and Hrniciar [24] too whose investigated on chalcones demonstrates that *s-trans* conformers transmit more effectively than *s-cis* conformers due to reason stated earlier. The difference in carbonyl frequencies between the *s-cis* and *s-trans* conformers is higher in this study than the difference observed by Silver and Boykin [25] between similar conformers in phenyl styryl ketones. These data have been correlated with Hammett substituent constants and Swain-Lupton constants [22]. In this correlation the structure parameter Hammett equation employed is as shown in the following equation:

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

Where ν is the carbonyl frequencies of substituted system and ν_0 is the corresponding quantity of unsubstitued 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.

From Table 2, the *s-cis* conformers gave satisfactory correlation with Hammett σ , σ^+ , and σ_I constants. And the *s-trans* conformers, the correlation $\nu_{\text{C=O}}$ fails with Hammett σ parameters. All correlations gave positive ρ values and it implies that there is a normal substituent effects operates in all systems.

The correlation of CH *in-plane* and *out of plane* modes with Hammett σ constants were fails in correlation. The CH *in-plane* modes gave negative ρ values in all correlations.

A satisfactory correlation obtained for CH=CH *out of plane* modes with Hammett σ_R constants. Also all correlation were fails with C=C *out of plane* modes with Hammett constants. Similarly the ν_{OH} stretches also fail in correlations. This is due to the inability polar, resonance and inductive effects substituent constant to predict the reactivity of the frequencies along with the resonance conjugative structure shown in Fig. 2. The correlation of ν_{OH} stretches were fails in correlation with Hammett substituent constants, F and R parameters..

Some of the individual single parameter correlations were fails with hammett substituent constants and F and R parameters. While the multi-regression analysis seems worthwhile with Swain- Luptons[22] constants and the generated equations are shown in 5-18.

$$\nu_{CO_{s-cis}} (\text{cm}^{-1}) = 1638.33(\pm 1.996) + 14.926(\pm 3.994)\sigma_I + 4.105(\pm 5.118) \sigma_R \quad \dots(5)$$

$$(R = 0.982, n = 10, P > 95\%)$$

$$\nu_{CO_{s-cis}} (\text{cm}^{-1}) = 1638.69(\pm 1.904) + 14.813(\pm 3.868)F + 5.864(\pm 4.545) R \quad \dots(6)$$

$$(R = 0.982, n = 10, P > 95\%)$$

$$\nu_{CO_{s-trans}} (\text{cm}^{-1}) = 1580.47(\pm 4.533) + 4.359(\pm 9.073)\sigma_I + 3.073(\pm 11.624) \sigma_R \quad \dots(7)$$

$$(R = 0.920, n = 10, P > 90\%)$$

$$\nu_{CO_{s-trans}} (\text{cm}^{-1}) = 1579.90(\pm 4.332) + 5.610(\pm 8.798)F + 2.313(\pm 10.338) R \quad \dots(8)$$

$$(R = 0.923, n = 10, P > 90\%)$$

$$\nu_{CH_{ip}} (\text{cm}^{-1}) = 1171.14(\pm 7.932) - 23.854(\pm 15.875)\sigma_I + 8.657(\pm 20.340) \sigma_R \quad \dots(9)$$

$$(R = 0.950, n = 10, P > 95\%)$$

$$\nu_{CH_{ip}} (\text{cm}^{-1}) = 1169.25(\pm 7.919) - 20.819(\pm 16.083)F + 1.511(\pm 18.898) R \quad \dots(10)$$

$$(R = 0.944, n = 10, P > 90\%)$$

$$\nu_{CH_{op}} (\text{cm}^{-1}) = 754.90(\pm 10.995) - 3.422(\pm 22.004)\sigma_I - 7.287(\pm 28.193) \sigma_R \quad \dots(11)$$

$$(R = 0.911, n = 10, P > 90\%)$$

$$\nu_{CH_{op}} (\text{cm}^{-1}) = 756.34(\pm 10.604) - 5.667(\pm 21.536)F - 2.596(\pm 25.305) R \quad \dots(12)$$

$$(R = 0.910, n = 10, P > 90\%)$$

$$\nu_{CH=CH_{op}} (\text{cm}^{-1}) = 1050.69(\pm 6.525) - 24.218(\pm 13.058)\sigma_I + 42.959(\pm 16.731) \sigma_R \quad \dots(13)$$

$$(R = 0.976, n = 10, P > 95\%)$$

$$\nu_{CH=CH_{op}} (\text{cm}^{-1}) = 1048.36(\pm 7.297) - 19.288(\pm 14.821)F + 29.932(\pm 17.415) R \quad \dots(14)$$

$$(R = 0.966, n = 10, P > 95\%)$$

$$\nu_{C=C_{op}} (\text{cm}^{-1}) = 585.82(\pm 17.994) - 35.910(\pm 36.012)\sigma_I + 3.579(\pm 46.140) \sigma_R \quad \dots(15)$$

$$(R = 0.935, n = 10, P > 90\%)$$

$$\nu_{C=C_{op}} (\text{cm}^{-1}) = 589.56(\pm 16.422) - 45.707(\pm 33.352)F - 1.587(\pm 39.189) R \quad \dots(16)$$

$$(R = 0.946, n = 10, P > 90\%)$$

$$\nu_{OH} (\text{cm}^{-1}) = 3440.11(\pm 8.506) + 14.690(\pm 17.023)\sigma_I + 28.700(\pm 21.811) \sigma_R \quad \dots(17)$$

$$(R = 0.951, n = 10, P > 95\%)$$

$$\nu_{\text{OH}} (\text{cm}^{-1}) = 3441.69(\pm 8.267) + 13.006(\pm 16.789)F + 28.238(\pm 19.728)R \quad \dots(18)$$

$(R = 0.940, n = 10, P > 90\%)$

3.3. ¹H NMR spectral correlation

In the present study the ¹H NMR spectra of the chalcones under investigation have been recorded in deuterated chloroform employing tetramethylsilane (TMS) as internal standard. The signals of the ethylenic protons have been assigned. They are calculated as AB or AA' BB' systems respectively [26, 27]. The chemical shifts of H_α are found 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 shift δ (ppm) depends on the electronic environment of the nuclei concerned. These shifts have been correlated with reactivity parameters. Thus the Hammett equation employed for the analysis in the form as is as shown below:

$$\text{Log } \delta = \text{Log } \delta_0 + \rho\sigma \quad \dots (19)$$

where δ₀ is the chemical shift in the corresponding parent compound.

The assigned ¹H NMR chemical shifts (δ ppm) of H_α and H_β of substituted styryl 3,5-dichloro-2-hydroxyphenyl ketones are presented in Table 2. These chemical shifts are correlated with Hammett substituent constants and F and R parameters. The results of statistical analysis these chemical shifts (ppm) are shown in Table 3. Hammett σ and σ⁺, parameters gave satisfactory correlations with δH_α chemical shifts with positive ρ values. The δH_β chemical shifts gave satisfactory correlation with Hammett σ⁺ constant. The remaining Hammett substituent constants, F and R parameters were fail correlations. This is due to the reasons stated earlier and associated with the resonance conjugative structure. The degree of transmission of substituent effects on δH_α is higher than δH_β chemical shifts.

Some of the single parameter correlations of δH_α and δH_β chemical shifts fail with Hammett sigma constants and F and R parameters. While seeking the multi regression analysis, there is satisfactorily correlations observed with Swain-Lupton and F and R parameters[22]. The correlation multi regression equations are shown below (20-23)

$$\delta H_{\alpha}(\text{ppm}) = 7.507(\pm 0.036) + 0.385(\pm 0.073)\sigma_1 + 0.576(\pm 0.094)\sigma_R \quad \dots(20)$$

$(R = 0.951, n = 10, P > 95\%)$

$$\delta H_{\alpha}(\text{ppm}) = 7.578(\pm 0.023) + 0.406(\pm 0.048)F + 0.589(\pm 0.057)R \quad \dots(21)$$

$(R = 0.978, n = 10, P > 95\%)$

$$\delta H_{\beta}(\text{ppm}) = 7.834(\pm 0.133) + 0.330(\pm 0.267)\sigma_1 - 0.092(\pm 0.342)\sigma_R \quad \dots(22)$$

$(R = 0.943, n = 10, P > 90\%)$

$$\delta H_{\beta}(\text{ppm}) = 7.886(\pm 0.133) + 0.258(\pm 0.271)F + 0.081(\pm 0.319)R \quad \dots(23)$$

$(R = 0.934, n = 10, P > 90\%)$

3.4. ^{13}C NMR spectral correlation

The assigned carbonyl carbon chemical shifts (δ ppm) of CO, C_α and C_β of 3,4-dichloro-2-hydroxyphenyl chalcones are presented in Table 2 and these chemical shifts are correlated with Hammett sigma constants and F and R parameters. The results of statistical analysis are shown in Table 3. From the table, the CO, C_α and C_β carbon chemical shifts are found to show poor correlation with Hammett σ constants, F and R parameters along with positive ρ values.

This shows that the normal substituent effect gets reversed in all ketones. The polar, resonance and Field effects of the substituents also fail in correlation. This is due to the reason stated earlier and it is attributed to conjugated structure shown in Figure 2.

Single parameter correlations of the chemical shifts of ^{13}C NMR of C_α and C_β (δ ppm) from ^{13}C NMR spectral data with Hammett sigma constants and F and R parameters fail. While seeking the multi regression analysis, there is a satisfactorily correlations observed with Swain-Lupton and F and R parameters. The correlated multi regression equations are given in 24-29.

$$\delta\text{CO}(\text{ppm}) = 192.64(\pm 0.327) + 0.424(\pm 0.655)\sigma_I + 0.863(\pm 0.840)\sigma_R \quad \dots(24)$$

$(R = 0.942, n = 10, P > 90\%)$

$$\delta\text{CO}(\text{ppm}) = 192.68(\pm 0.306) + 0.420(\pm 0.622)F + 0.977(\pm 0.731)R \quad \dots(25)$$

$(R = 0.947, n = 10, P > 90\%)$

$$\delta\text{C}_\alpha(\text{ppm}) = 119.62(\pm 2.795) + 7.895(\pm 5.593)\sigma_I - 7.461(\pm 7.167)\sigma_R \quad \dots(26)$$

$(R = 0.954, n = 10, P > 95\%)$

$$\delta\text{C}_\alpha(\text{ppm}) = 119.96(\pm 2.749) + 7.212(\pm 5.583)F - 4.939(\pm 6.560)R \quad \dots(27)$$

$(R = 0.951, n = 10, P > 95\%)$

$$\delta\text{C}_\beta(\text{ppm}) = 145.40(\pm 2.658) + 1.142(\pm 5.254)\sigma_I + 1.564(\pm 6.732)\sigma_R \quad \dots(28)$$

$(R = 0.912, n = 10, P > 90\%)$

$$\delta\text{C}_\beta(\text{ppm}) = 145.42(\pm 2.511) + 1.487(\pm 5.100)F + 2.305(\pm 5.992)R \quad \dots(29)$$

$(R = 0.916, n = 10, P > 90\%)$

3.5. Antimicrobial activities

Chalcones possess a wide range of biological activities such as antibacterial [7, 8], antifungal [9], antiviral [11], antifeedant [19], antimalarial [12], antituberculosis [14], and antioxidant [10] activities. These multipronged activities present in different chalcones are examined against respective microbes-bacteria's.

3.5.1. Antibacterial sensitivity assay

Antibacterial sensitivity assay was performed using Kirby-Bauer [28] 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 Whatman No.1 filter paper, impregnated with the solution of the compound were 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.

The antibacterial screening effect of synthesized chalcones is shown in Figure 4. (Plates 1-10). The zone of inhibition is compared using Table 4 and the Clustered column Chart is shown in Figure 5. A good antibacterial activity was possessed by all substituents on the microorganisms in general. All the compounds showed excellent activity against *B.subtilis* and *P.aeruginosa* species. The substituent 4-Cl, 4-CH₃ and 3-NO₂ have high activity against *B.subtilis*. The substituent 4-Br and 4-Cl have high activity against *E.Coli*. The substituent 3-NO₂ has improved antibacterial activity against *S.aureus* than other species.

Table 4. Antibacterial activity of 3,5-dichloro-2-hydroxyphenyl chalcones(entries 27-36).

Entry	Substt.	Zone of Inhibition (mm)				
		Gram positive Bacteria			Gram negative Bacteria	
		<i>B.subtilis</i>	<i>M.luteus</i>	<i>S.aureus</i>	<i>E.coli</i>	<i>P.aeruginosa</i>
27	H	6	7	7	6	6
28	3-Br	6	7	6	6	6
29	4-Br	6	8	6	8	8
30	2-Cl	6	6	6	7	6
31	3-Cl	6	6	-	7	6
32	4-Cl	7	6	6	8	6
33	4-F	6	6	7	6	7
34	4-Me	7	6	6	6	7
35	3-NO ₂	9	6	9	7	6
36	4-NO ₂	6	7	7	7	7
Standard	Ampicillin	8	8	7	9	9
Control	DMSO	-	-	-	-	-

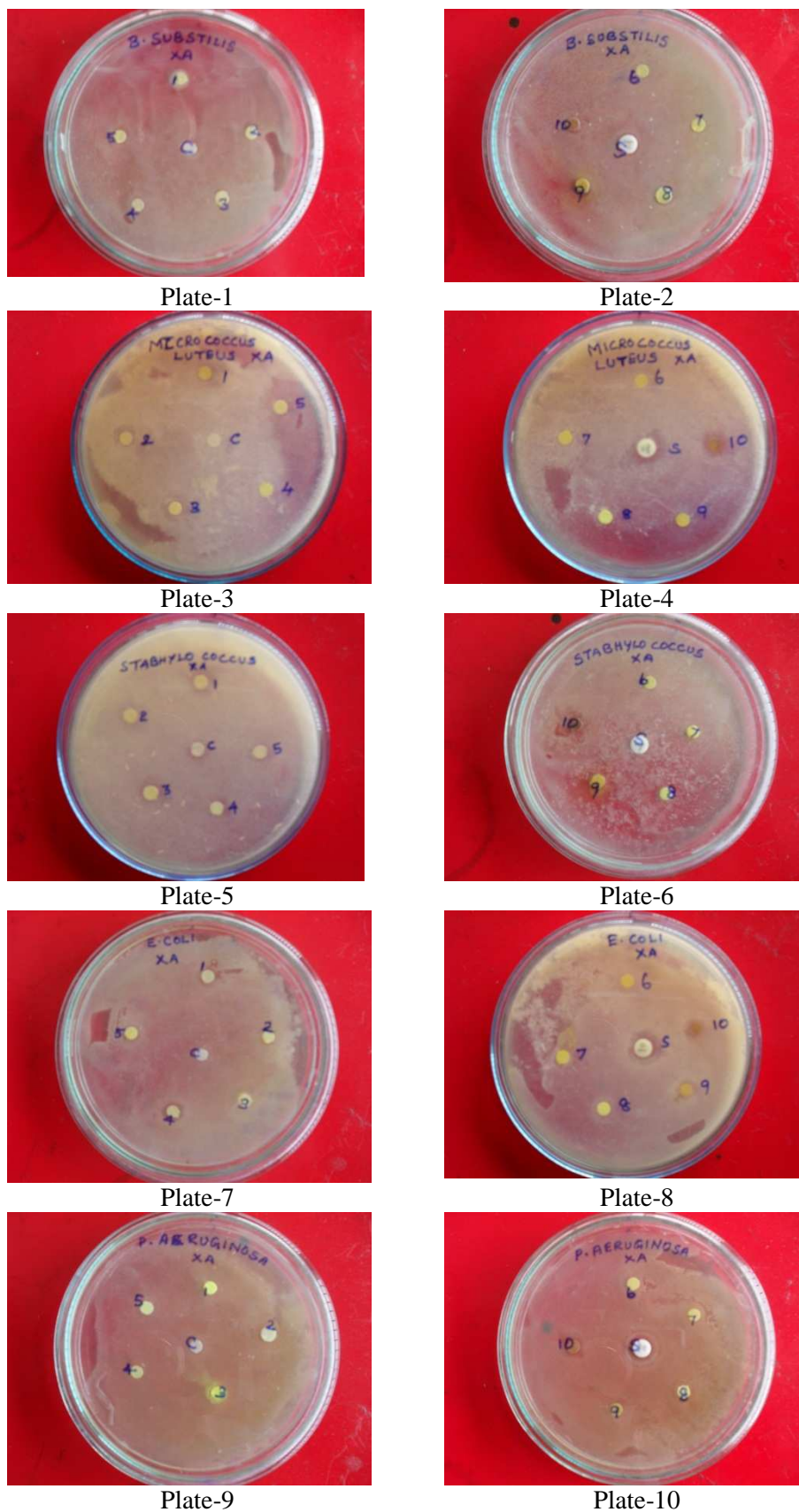


Fig. 5. Antibacterial activity of 3,5-dichloro-2-hydroxyphenyl chalcones (entries 27-36).

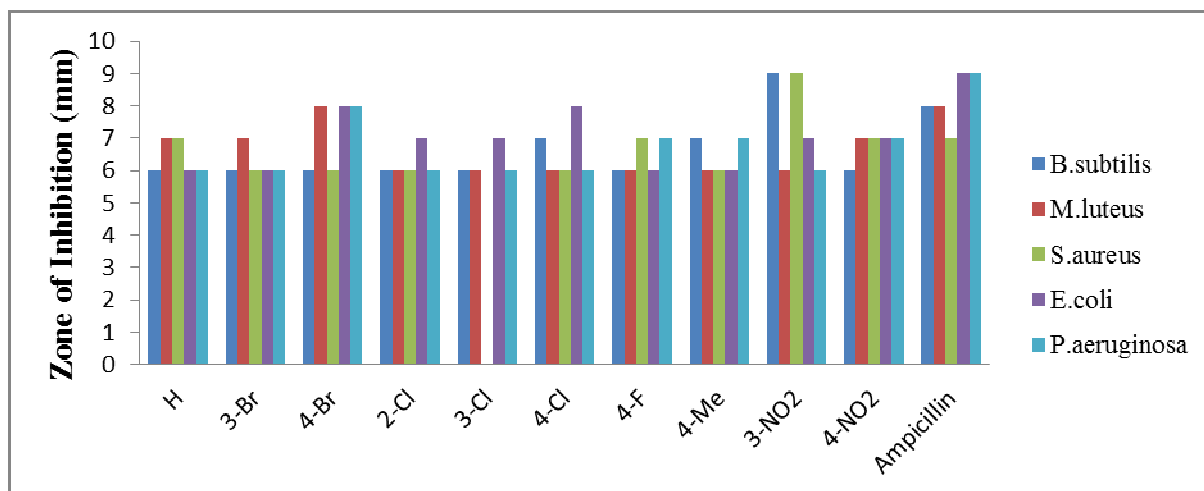


Fig. 6. Antibacterial activity of 3, 5-dichloro-2-hydroxyphenyl chalcones (entries 27-36): clustered column chart.

4. CONCLUSION

We have developed an efficient Crossed-Aldol condensation for synthesis of chalcones using thionyl chloride catalyst. The yield of the reaction is more than 80%. The purities of these synthesised chalcones are checked by their physical constants, analytical and spectral data. The spectroscopic data of the chalcones were correlated with Hammett substituent constants, F and R parameters. The antibacterial activities of all synthesized chalcones have been studied using Bauer- Kirby method.

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