Microwave assisted synthesis, spectral studies and antimicrobial activities of some 2',4'-difluorophenyl chalcones

S. Vijayakumar¹, R. Arulkumaran¹, R. Sundararajan¹, S. P. Sakthinathan¹,
R. Suresh¹, D. Kamalakkannan¹, K. Ranganathan¹, K. Sathiyamoorthy¹,
V. Mala¹, G. Vanangamudi^{1,*}, G. Thirunarayanan²

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

²Department of Chemistry, Annamalai University, Annamalai Nagar - 608002, India

*E-mail address: drgvsibi@gmail.com

ABSTRACT

Some 2',4'-difluorophenyl chalcones have been synthesized under microwave irradiation using aldol condensation between 2,4-difluoroacetophenone and substituted benzaldehydes using catalytic amount of hydroxyapatite. The yields of the chalcones are more than 85 %. The purities of these synthesized chalcones were examined by their physical constants and spectroscopic data. The UV absorption maxima (λ_{max} , nm), infrared stretches (ν , cm^{-1}) of CO, fingerprint region of $\text{CH}_{\text{ip/op}}$, $\text{CH}=\text{CH}_{\text{op}}$, $\text{C}=\text{C}_{\text{op}}$ modes, NMR chemical shifts (δ , ppm) of vinyl proton, carbon and carbonyl carbons have been assigned and correlated with Hammett substituent constants, F and R parameters using single and multi-regression analysis. From the statistical analysis the effect of substituent on the above spectral frequencies can be discussed. The antimicrobial activities of these synthesized chalcones have been screened using Bauer-Kirby method.

Keywords: Microwave irradiation; Aldol condensation; Hydroxyapatite; Spectral correlations; Hammett σ constants; Antimicrobial activities

1. INTRODUCTION

Chalcones are, α , β unsaturated ketones, possess methylene structural moieties and they belong 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 reactions, Greener methods-Grinding of reactants, solvent free and oxides of nanoparticles with microwave heating. Also microwave assisted solvent free Aldol and Crossed-Aldol condensation [3-5] were useful for 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. Compounds with the backbone of chalcone possess various biological activities such as anti-microbial [7], anti-inflammatory [8],

analgesic [9], anti-ulcerative [10], immune-modulatory [11], anti-malarial [12], anti-cancer [13], anti-viral [14], anti-leishmanial [15], anti-oxidant [16], anti-tubercular [17], anti-hyperglycemic [18] etc. A compound having anti-oxidant activity prevents and counteracts the damage of the human tissue by the normal effects of physiological oxidation [19].

Presence of the reactive keto group and the vinylenic group in the chalcone and their analogues possesses the antioxidant activity [20]. Compounds that associated with the antioxidant properties are hydroxyl and phenyl group. Oxidative stress which is caused by the free radical damage is help to deal with the antioxidants [21]. Spectroscopic data is useful for study of effects of substituents on the specified spectral group frequencies using Hammett substituent constants, F and R parameters by single and multi-regression analysis.

From the results the ground state molecular equilibration can be predicted. Recently Subramanian et. al. [22, 23] have studied the synthesis and spectral correlations of some heterocyclic chalcones and they observed satisfactory correlations. Sathiyamoorthy et al., [24-26] also studied the same with the some iodo and hydroxy substituted phenyl chalcones. With a view to above there is no report available for microwave assisted synthesis, the study of substituent effects and screening of antimicrobial activities of 2',4'-difluorophenyl chalcones in the past in literature. Therefore the authors have taken efforts for microwave assisted synthesis of 2',4'-difluorophenyl chalcones, study of substituent effects and screening of antimicrobial activities using Bauer-Kirby [27] method.

2. EXPERIMENTAL

2. 1. Materials and Methods

All the chemicals involved in the present investigation, have been procured from Sigma-Aldrich and E-Merck chemical companies. Melting points of all chalcones have been determined in open glass capillaries on SUNTEX melting point apparatus and are uncorrected. The UV spectra of all the chalcone, synthesized, have been recorded with ELICO-BL222 spectrophotometer ($\lambda_{\max}$ nm) in spectral grade methanol solvent. Infrared spectra (KBr, 4000-400 cm^{-1}) have been recorded on AVATAR-300 Fourier transform spectrophotometer. The NMR spectra were recorded in Bruker AV400 NMR spectrometer operating at 400 MHz has been utilized for recording ^1H NMR spectra and 100 MHz for ^{13}C spectra in CDCl_3 solvent using TMS as internal standard.

2. 2. Synthesis of 2',4'-fluorophenyl chalcones

An appropriate equimolar quantities of 2,4-difluoroacetophenone (2 mmol), substituted benzaldehydes (2 mmol), methanol (10 mL) and 1 g hydroxyapatite was added and the mixture was stirred at room temperature for 5 min. Methanol was evaporated to give a homogeneous solid. About 5 mL of water was added to this solid and the mixture was irradiated by microwave for 5-6 minutes (Scheme 1) [22]. After completion of reaction, dichloromethane (20 mL) was added, followed by simple filtration. The solution was concentrated and to purified by re-crystallization. The synthesized chalcones are characterized by their physical constants, IR, ^1H and ^{13}C NMR and Mass spectral data. Analytical and Mass spectral data are presented in Table 1.

Scheme 1. Synthesis of substituted styryl-2,4-difluorophenyl ketone.

Table 1. The physical analytical and melting point of substituted styryl-2,4-difluorophenyl ketones.

Entry	X	M. F.	M. W.	Yield (%)	m. p. (°C)
1	H	C ₁₅ H ₁₀ F ₂ O	244	87	95-96
2	3-Br	C ₁₅ H ₉ F ₂ OBr	323	85	101-102(98)[28], 95[39], 105[30]
3	4-Br	C ₁₅ H ₉ F ₂ OBr	323	86	103-104(102)[29], 102[30]
4	4-Cl	C ₁₅ H ₉ F ₂ OCl	278	85	99-100(102) [28], 102[39], 102[30]
5	2-OCH ₃	C ₁₆ H ₁₂ F ₂ O ₂	274	87	78-79
6	4-OCH ₃	C ₁₆ H ₁₂ F ₂ O ₂	274	89	87-88(84)[28], 83[29]
7	4-CH ₃	C ₁₆ H ₁₂ F ₂ O	258	87	81-82(80)[28], 64[29]
8	3-NO ₂	C ₁₅ H ₉ NF ₂ O ₃	289	85	140-141(141)[28], 141[29], 144[30]
9	4-NO ₂	C ₁₅ H ₉ NF ₂ O ₃	289	85	138-139

3. RESULT AND DISCUSSION

3. 1. Spectral linearity

In the present investigation the Hammett spectral linearity of these synthesized chalcones has been studied by evaluating the substituent effects on the group frequencies. The assigned spectroscopic data of all chalcones such as absorption maximum λ_{max} (nm) of carbonyl groups, infrared carbonyl stretches of *ν*COs-*cis* and *s-trans*, the deformation modes of vinyl part CH_{out of plane}, *in-plane*, CH=CH and >C=C< *out of planes* (cm⁻¹), NMR chemical shifts δ (ppm) of H _{α} , H _{β} , C _{α} , C _{β} , CO are assigned and these data are correlated with various substituent constants.

3. 1. 1. UV spectral study

The absorption maxima ($\lambda_{\max}$ nm) of synthesized 2',4'-difluorophenyl chalcones were assigned and presented in Table 2. These absorption maxima ($\lambda_{\max}$ nm) of these chalcones were correlated with Hammett substituent constants and F and R parameters using single and multi-linear regression analysis [1, 4, 22-26, 31-35]. 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.

Table 2. The ultraviolet absorption maxima ($\lambda_{\max}$, nm), infrared absorptions (ν , cm^{-1}) and NMR chemical shifts (δ , ppm) of substituted styryl 2,4-difluorophenyl ketones.

Entry	X	$\lambda_{\max}$	$\text{CO}_{(s-cis)}$	$\text{CO}_{(s-trans)}$	CH_{ip}	CH_{op}	$\text{CH}=\text{CH}_{op}$	$\text{C}=\text{C}_{op}$	H_a	H_β	C_a	C_β	CO
1	H	328.0	1675.34	1598.99	1190.08	742.59	1093.64	545.85	7.116	7.774	125.44	143.35	188.95
2	3-Br	299.6	1676.14	1604.77	1188.15	802.39	1093.64	540.07	7.429	7.707	126.24	146.35	186.88
3	4-Br	314.2	1664.00	1598.99	1207.44	740.67	1085.92	559.36	7.377	7.894	125.55	143.50	189.95
4	4-Cl	312.8	1656.85	1602.85	1192.01	731.02	1085.92	557.43	7.380	7.917	125.53	143.44	186.95
5	2-OCH ₃	339.6	1627.92	1600.00	1143.79	740.67	1022.27	559.36	7.763	7.909	122.94	145.01	187.36
6	4-OCH ₃	342.6	1662.64	1593.20	1161.15	744.52	1008.77	596.00	7.402	7.806	119.23	144.90	188.84

7	4-CH ₃	334.4	1654.92	1602.85	1193.94	732.95	1097.50	551.64	7.269	7.778	120.73	144.34	188.40
8	3-NO ₂	263.8	1670.00	1606.70	1188.15	734.88	1033.85	534.28	7.557	7.722	122.58	143.99	189.00
9	4-NO ₂	278.4	1658.78	1608.63	1170.79	699.30	1028.06	565.14	7.572	7.997	123.06	144.66	188.80

The results of statistical analysis [1, 4, 22-26, 31-35] of these UV absorption maxima ($\lambda_{\max}$, nm) data with Hammett substituent constants, F and R parameters are presented in Table 3. The Hammett σ and σ^+ constants gave satisfactory correlation.

The Hammett σ_I , σ_R constants, F and R parameters produced satisfactory correlations excluding H and 4-CH₃ substituents. When included these substituents in correlations, they reduced the correlation coefficients considerably and leads to fail.

The failure in correlation is due to the incapable of inductive and resonance effects of substituents on the absorption and is associated with the resonance-conjugative structure shown in Figure 1.

Fig. 1. The resonance-conjugative structure.

The multi regression analysis of these frequencies of all ketones with inductive, resonance and Swain – Lupton's [36] constants produce satisfactory correlations as evident in equations (2 and 3).

$$\text{UV}(\lambda_{\max}, \text{nm}) = 326.96 (\pm 5.360) - 66.966 (\pm 11.056) \sigma_I - 66.935 (\pm 11.430) \sigma_R \quad \dots(2)$$

$(R = 0.997, n = 9, P > 95 \%)$

$$\text{UV}(\lambda_{\max}, \text{nm}) = 326.28 (5.033) - 71.347 (\pm 10.217) F - 63.381 (\pm 9.535) R \quad \dots(3)$$

$(R = 0.997, n = 9, P > 95 \%)$

Table 3. Results of statistical analysis of infrared $\nu(\text{cm}^{-1})$ $\text{CO}_{s\text{-}cis}$, $\text{CO}_{s\text{-}trans}$, CH_{ip} , CH_{op} , $\text{CH}=\text{CH}_{op}$ and $\text{C}=\text{C}_{op}$ substituted styryl-2,4-difluorophenyl ketones with Hammett σ , σ^+ , σ_I , σ_R constants and F and R parameters.

Frequency	Constants	r	I	ρ	s	n	Correlated derivatives
λ_{max}	σ	0.996	323.35	-63.634	6.97	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.992	317.18	-47.069	11.19	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.997	343.87	-87.133	17.88	7	3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.907	299.81	-88.501	18.41	7	3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.908	346.10	-93.926	17.30	7	3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.992	296.73	-85.519	18.07	7	3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 3-NO ₂ , 4-NO ₂
$\text{CO}_{s\text{-}cis}$	σ	0.750	1651.82	17.258	13.41	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.745	1659.56	12.057	13.83	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.709	1658.84	5.262	15.42	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.673	1666.31	38.606	11.81	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.690	1658.74	5.576	15.42	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.653	1666.46	30.852	13.03	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
$\text{CO}_{s\text{-}trans}$	σ	0.907	1600.39	8.856	3.01	7	H, 3-Br, 4-Br, 4-Cl, 4-OCH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.908	1601.21	6.968	2.95	7	H, 3-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.905	1598.32	9.924	4.22	7	3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.906	1603.79	13.194	3.63	7	3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.905	1598.43	10.791	4.17	7	3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 3-NO ₂ , 4-NO ₂

	R	0.907	1604.43	13.690	3.33	6	4-Br, 4-Cl, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
CH _{ip}	σ	0.831	1178.71	17.844	19.27	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.841	1180.04	17.276	18.32	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.732	1182.09	-1.012	20.87	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.751	1188.57	47.381	16.87	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.642	1182.50	-2.191	20.86	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.652	1189.25	40.569	17.73	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
CH _{op}	σ	0.901	742.81	-10.728	28.18	7	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.901	741.57	-5.925	28.39	7	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.600	745.13	-11.512	28.43	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.732	736.42	-31.694	27.38	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.532	746.50	-15.694	28.32	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.734	734.49	-35.035	26.96	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
CH=CH _{op}	σ	0.732	1060.88	1.104	39.19	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.712	1059.90	11.933	38.58	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.734	1080.96	-55.446	36.26	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.723	1066.80	39.729	37.81	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.742	1083.98	-64.265	35.65	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.725	1067.98	37.302	37.86	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
C=C _{op}	σ	0.743	559.72	-18.680	17.15	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ ,

							4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.758	558.46	-19.439	15.43	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.809	558.91	-6.523	19.01	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.751	551.10	-37.818	16.38	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.707	558.57	-5.628	19.31	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.759	548.77	-41.993	15.31	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
$\delta_{H\alpha}$ (ppm)	σ	0.814	7.418	0.062	0.19	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.811	7.425	0.039	0.19	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.906	0.726	0.451	0.15	7	H, 3-Br, 4-Br, 4-Cl, 4-OCH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.903	7.390	-0.233	0.18	6	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-CH ₃ ,
	F	0.906	7.256	0.485	0.15	8	H, 3-Br, 4-Br, 4-Cl, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.902	7.398	-0.166	0.19	6	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-CH ₃
$\delta_{H\beta}$ (ppm)	σ	0.805	7.831	0.012	0.10	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.807	7.832	0.014	0.10	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.902	7.792	0.114	0.10	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.811	7.826	-0.050	0.10	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.902	7.792	0.114	0.10	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.805	7.829	-0.021	0.10	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
δ_{CO} (ppm)	σ	0.815	188.28	0.395	1.11	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.817	188.31	0.342	1.10	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.708	188.36	-0.054	1.12	9	H, 3-Br, 4-Br, 4-Cl,

							2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.737	188.58	1.628	1.04	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.802	188.31	1.107	1.12	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.832	188.58	1.254	1.07	9	H, 3-Br, 4-Br, 4-Cl, 2- OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3- NO ₂ , 4-NO ₂
$\delta C\alpha$ (ppm)	σ	0.831	123.13	2.043	2.41	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.906	123.24	2.399	2.18	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.823	122.64	2.308	2.51	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.823	123.81	2.359	2.51	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.726	122.87	1.705	2.55	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.732	124.03	3.001	2.45	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
$\delta C\beta$ (ppm)	σ	0.707	144.40	-0.075	1.03	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.712	144.41	-0.183	1.02	9	H, 3-Br, 4-Br, 4-Cl, 2- OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3- NO ₂ , 4-NO ₂
	σ_I	0.715	144.18	0.588	1.02	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.830	144.21	-1.229	0.98	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.713	144.14	0.699	1.01	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.832	144.14	-1.336	0.96	9	H, 3-Br, 4-Br, 4-Cl, 2-OCH ₃ , 4-OCH 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

3. 1. 2. IR spectral study

The assigned carbonyl stretching frequencies (cm^{-1}) of *s-cis* and *s-trans* isomers of present study are presented in Table 2 and the corresponding conformers are shown in Fig. 2. The stretching frequencies for carbonyl absorption are assigned based on the assignments made by Hays and Timmons [37] for *s-cis* and *s-trans* conformers at 1690 and 1670 cm^{-1} , respectively. These data have been correlated with Hammett substituent constants and Swain-

Lupton's constants [36] and are presented in Table 3. 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 unsubstituted 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.

Fig. 2. The *s-cis* and *s-trans* conformers of 2',4'-difluorophenyl chalcones.

The results of single parameter statistical analysis of carbonyl frequencies of *s-cis* conformers with all Hammett substituent constants, F and R parameters were poor correlated. The failure in correlation is due the conjugation between the substituent and the carbonyl group in chalcones and is associated with the resonance conjugative structure shown in Figure 1. The *s-trans* conformer gave satisfactory correlation for constants, F and R parameters excluding H, 3-Br, 2-OCH₃, 4-CH₃ substituents. If these substituents were included in the correlation, they reduced the correlation significantly.

The correlation of CH *in-plane* with Hammett substituent constants, F and R parameters were poor correlated and *out of plane* modes with Hammett σ and σ^+ constants shown satisfactory correlations. The σ_I , σ_R constants and F and R parameters has poorly correlated. The CH=CH and C=C *out of plane* modes with all Hammett substituent constants, F and R parameters were fail in correlation, This is due to the conjugation between the substituent and the vinyl group in chalcones as shown in Figure 1.

In view of the inability of some of the σ constants to produce individually satisfactory correlations, it was thought that worthwhile to seek multiple correlations involving either σ_I and σ_R constants or Swain-Lupton's [36] F and R parameters. The correlation equations for *s-cis*, *s-trans* and *deformation modes* are given in equations 5-16.

$$\nu_{\text{CO}_{s\text{-cis}}}(\text{cm}^{-1}) = 1669.17(\pm 9.078) - 7.053(\pm 18.710)\sigma_I - 40.877(\pm 19.344)\sigma_R \quad \dots (5)$$

($R = 0.965$, $n = 9$, $P > 95\%$)

$$\nu_{\text{CO}_{s\text{-cis}}}(\text{cm}^{-1}) = 1668.98(\pm 10.894) - 6.087(\pm 22.114)F + 32.740(\pm 20.638)R \quad \dots (6)$$

($R = 0.954$, $n = 9$, $P > 95\%$)

$$\nu_{\text{CO}_{s\text{-trans}}}(\text{cm}^{-1}) = 1601.12(\pm 2.504) + 6.581(\pm 5.166)\sigma_I + 11.073(\pm 5.341)\sigma_R \quad \dots (7)$$

($R = 0.976$, $n = 9$, $P > 95\%$)

$$\nu\text{CO}_{\text{s-trans}}(\text{cm}^{-1}) = 1601.67(\pm 2.465) + 6.649(\pm 5.005)F + 11.627(\pm 5.341)R \quad \dots(8)$$

$$(R = 0.987, n = 9, P > 95 \%)$$

$$\nu\text{CH}_{\text{ip}}(\text{cm}^{-1}) = 1195.43(\pm 12.664) - 16.930(\pm 26.123)\sigma_{\text{I}} + 52.833(\pm 27.008)\sigma_{\text{R}} \quad \dots(9)$$

$$(R = 0.925, n = 9, P > 90 \%)$$

$$\nu\text{CH}_{\text{ip}}(\text{cm}^{-1}) = 1197(\pm 14.434) - 18.711(\pm 29.298)F + 46.37(\pm 27.343)R \quad \dots(10)$$

$$(R = 0.956, n = 9, P > 95 \%)$$

$$\nu\text{CH}_{\text{op}}(\text{cm}^{-1}) = 737.30(\pm 21.262) - 2.173(\pm 43.858)\sigma_{\text{I}} - 30.994(\pm 45.343)\sigma_{\text{R}} \quad \dots(11)$$

$$(R = 0.920, n = 9, P > 90 \%)$$

$$\nu\text{CH}_{\text{op}}(\text{cm}^{-1}) = 735.88(\pm 22.678) - 3.338(\pm 46.030)F + 30.994(\pm 45.343)R \quad \dots(12)$$

$$(R = 0.933, n = 9, P > 90 \%)$$

$$\nu\text{CH}=\text{CH}_{\text{op}}(\text{cm}^{-1}) = 1097.07(\pm 25.374) - 74.660(\pm 52.341)\sigma_{\text{I}} + 63.774(\pm 54.114)\sigma_{\text{R}} \quad \dots(13)$$

$$(R = 0.955, n = 14, P > 95 \%)$$

$$\nu\text{CH}=\text{CH}_{\text{op}}(\text{cm}^{-1}) = 1104.10(\pm 25.594) - 87.191(\pm 53.981)F + 64.355(\pm 50.379)R \quad \dots(14)$$

$$(R = 0.959, n = 9, P > 95 \%)$$

$$\nu\text{C}=\text{C}_{\text{op}}(\text{cm}^{-1}) = 548.54(\pm 12.675) + 5.394(\pm 26.146)\sigma_{\text{I}} - 39.555(\pm 27.032)\sigma_{\text{R}} \quad \dots(15)$$

$$(R = 0.947, n = 9, P > 90 \%)$$

$$\nu\text{C}=\text{C}_{\text{op}}(\text{cm}^{-1}) = 544.43(\pm 12.711) + 10.490(\pm 25.801)F - 45.248(\pm 24.079)R \quad \dots(16)$$

$$(R = 0.961, n = 9, P > 95 \%)$$

3. 1. 3. ^1H NMR spectral study

The ^1H NMR spectra of synthesized chalcones have been recorded using deuteriochloroform employing tetramethylsilane (TMS) as internal standard. The ethylenic protons signals of the chalcones were assigned from their spectra. They were calculated as AB or AA' or BB' systems respectively. The lower chemical shifts (ppm) obtained for H_α and higher chemical shifts (ppm) obtained for H_β in this series of ketones. The vinyl protons give an AB pattern and the β -proton doublets were well separated from the signals of the aromatic protons. The assigned vinyl proton chemical shifts $\delta(\text{ppm})$ of all ketones were presented in Table 2. In nuclear magnetic resonance spectra, the proton or the ^{13}C chemical shifts (δ) depends on the electronic environment of the nuclei concerned. The assigned vinyl proton chemical shifts (ppm) have been correlated with reactivity parameters using Hammett equation in the form of

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

where δ_0 is the chemical shift of unsubstituted ketones.

The assigned H_α and H_β proton chemical shifts (ppm) are correlated with various Hammett sigma constants. The results of statistical analysis [1, 4, 25, 26, 28, 32-36] are presented in Table 3. The obtained correlation is satisfactory for H_α with Hammett σ_{I} , σ_{R} constants, F and R parameters excluding 2-OCH₃, 4-OCH₃, 4-CH₃ and NO₂ substituents. The Hammett σ and σ^+ substituent constants were fail in correlation. A fair degree of correlation is obtained for H_β proton chemical shifts (ppm) with Hammett σ_{I} and F parameter.

The remaining Hammett sigma constants and R parameters were fail correlations. The failure in correlation is due to the reason stated earlier.

Some of the single parameter correlation were fail in correlation for vinyl protons. While seeking the multi-correlation by the application of Swain-Lupton's[36] treatment to the relative chemical shifts of H_α and H_β with F and R values is successful with resonance, inductive effect generates the multi regression equations 18-21.

$$\delta H_\alpha(\text{ppm}) = 7.161(\pm 0.093) + 0.577(\pm 0.191)\sigma_I - 0.419(\pm 0.198)\sigma_R \quad \dots(18)$$

$$(R = 0.979, n = 9, P > 95 \%)$$

$$\delta H_\alpha(\text{ppm}) = 7.144(\pm 0.107) + 0.612(\pm 0.217)F - 0.357(\pm 0.202)R \quad \dots(19)$$

$$(R = 0.976, n = 9, P > 95 \%)$$

$$\delta H_\beta(\text{ppm}) = 7.768(\pm 0.076) + 0.143(\pm 0.158)\sigma_I - 0.096(\pm 0.163)\sigma_R \quad \dots(20)$$

$$(R = 0.936, n = 9, P > 90 \%)$$

$$\delta H_\beta(\text{ppm}) = 7.728(\pm 0.084) + 0.137(\pm 0.172)F - 0.064(\pm 0.160)R \quad \dots(21)$$

$$(R = 0.931, n = 9, P > 90 \%)$$

3. 1. 4. ^{13}C NMR spectral study

Scientists and physical organic chemists [1, 4, 22-26, 31-35], have made extensive study of ^{13}C NMR spectra for a large number of different ketones and styrenes. The assigned vinyl C_α , C_β and carbonyl carbon chemical shifts are presented in Table 2. The results of statistical analysis are given in Table 3. The C_α chemical shifts (ppm) gave satisfactory correlation with Hammett σ^+ constants. The correlation of these chemical shifts with remaining Hammett constant, F and R parameters gave poor correlation. The chemical shifts (ppm) of C_β and CO carbons with Hammett substituent constants, F and R parameters gave poor correlation. This is due to the reason stated earlier and associated with resonance conjugative structure shown in Figure. 1.

Some of the single parameter correlation were fails in regression, while seeking the multi-regression analysis through Swain Lupton's [36] parameter correlations were satisfactorily obtained within these carbon chemical shifts and the regression equations are given in 22-27.

$$\delta \text{CO}(\text{ppm}) = 188.82(\pm 0.802) - 0.603(\pm 1.654)\sigma_I + 1.822(\pm 1.710)\sigma_R \quad \dots(22)$$

$$(R = 0.939, n = 9, P > 90 \%)$$

$$\delta \text{CO}(\text{ppm}) = 188.73(\pm 0.900) - 0.381(\pm 1.827)F + 1.372(\pm 1.705)R \quad \dots(23)$$

$$(R = 0.931, n = 9, P > 90 \%)$$

$$\delta C_\alpha(\text{ppm}) = 123.101(\pm 1.920) + 1.769(\pm 3.960)\sigma_I + 1.789(\pm 4.094)\sigma_R \quad \dots(24)$$

$$(R = 0.929, n = 9, P > 90 \%)$$

$$\delta C_\alpha(\text{ppm}) = 123.73(\pm 2.060) + 0.715(\pm 4.182)F + 2.779(\pm 3.903)R \quad \dots(25)$$

$$(R = 0.932, n = 9, P > 90 \%)$$

$$\delta C_\beta(\text{ppm}) = 143.78(\pm 0.735) + 1.061(\pm 1.516)\sigma_I - 1.570(\pm 1.567)\sigma_R \quad \dots(26)$$

$$(R = 0.942, n = 9, P > 90 \%)$$

$$\delta C_\beta(\text{ppm}) = 143.59(\pm 0.770) + 1.321(\pm 1.564)F - 1.746(\pm 1.460)R \quad \dots(27)$$

$$(R = 0.942, n = 9, P > 90 \%)$$

3. 2. Microbial activities

3. 2. 1. Antibacterial sensitivity assay

Antibacterial sensitivity assay was performed using Kirby-Bauer [27] disc diffusion technique. In each Petri plate about 0.5ml 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 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.

Table 4. Antibacterial activity of substituted styryl 2,4-difluorophenyl ketones.

Entry	X	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>	<i>K. pneumoniae</i>
1	H	6	6	6	6	6	7
2	3-Br	6	6	7	---	---	6
3	4-Br	6	---	8	---	---	7
4	4-Cl	6	6	7	6	---	8
5	2-OCH ₃	6	---	8	6	---	7
6	4-OCH ₃	---	---	6	6	---	6
7	4-CH ₃	6	6	7	6	6	7
8	3-NO ₂	7	7	8	6	7	8
9	4-NO ₂	8	---	7	6	8	6
10	Ampicillin	9	6	7	7	7	9
11	DMSO	---	---	---	---	---	---

Fig. 4. Antibacterial activities of 2',4'-difluorophenyl chalcones-clustered column chart.

Fig. 3. Antibacterial activities of 2',4'-difluorophenyl chalcones-petri dish plates.

3. 2. 2. Antifungal activity

The antifungal activity of the substituted styryl 2,4-difluorophenyl ketones have been measured using Baue-Kirby zone of inhibition method [27]. The measured antifungal activity of the synthesized chalcones were shown in Fig. 5, for Plates (1-4). Analysis of the zone of inhibition as given in Table 5 and the Clustered column Chart given in Fig. 6. The 2-OCH₃ substituted compound has shown more antifungal activity than other substituents against the fungal specie *Mucor species*, under investigation. The 3-NO₂ substituent compound has shown equal antifungal activity against the above two fungal species.

Fig. 5. Antifungal activities of 2',4'-difluorophenyl chalcones-petri dish plates.

Fig. 6. Antifungal activities of 2',4'-difluorophenyl chalcones-clustered column chart.

Table 5. Antifungal activity of substituted styryl 2,4-difluorophenyl ketones.

S. NO.	X	Zone of inhibition (mm)	
		<i>A. niger</i>	<i>M. species</i>
1	H	5	7
2	3-Br	5	8
3	4-Br	5	7
4	4-Cl	6	5
5	2-OCH ₃	5	9
6	4-OCH ₃	7	5
7	4-CH ₃	5	6
8	3-NO ₂	7	7
9	4-NO ₂	5	6
Standard	Miconazole	11	13
control	DMSO	---	---

4. CONCLUSION

Some 2',4'-difluorophenyl chalcones have been synthesized by condensation of 2,4-difluoroacetophenone and substituted benzaldehydes using microwave irradiation in the presence of hydroxyapatite catalyst. This reaction protocol offers a simple, easier work-up procedure and good yields. The 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 chalcone have been studied using Bauer-Kirby method.

ACKNOWLEDGEMENT

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

References

- [1] Arulkumaran R., Vijayakumar S., Sakthinathan S. P., Kamalakkannan D., Ranganathan K., Suresh R., Sundararajan R., Vanangamudi G., Thirunarayanan G., *J. Chil. Chem. Soc.* 58(2) (2013) 1553-1559.
- [2] (a) Yankep E., Fomumand Z. T., Dangne E., *Phytochem.* 46 (1997) 591-593.
- [3] Thirunarayanan G., Vanangamudi G., *E-J. Chem.* 4 (1) (2007) 90-97.

-
- [4] Ranganathan K., Arulkumaran R., Kamalakkannan D., Sundararajan R., Sakthinathan S. P., Vijayakumar S., Suresh R., Vanangamudi G., Thirumurthy K., Mayavel P., Thirunarayanan G., *Int. J. Pharm. Med. and Bio. SC* 1(1) (2012) 62-85.
- [5] Venkat Reddy G, Maitraie G, Narsaiah D, Rambahu B, Rao R, *Synth. Commun.* 31(18) (2001) 2881-2884.
- [6] Mulliken R. S., *J. Chem. Phys.* 7 (1939) 121-131.
- [7] Hsieh H. K., Tsao L. T., Wang J. P., *J. Pharm. Pharmacol.* 52(2) (2000) 163-171.
- [8] Viana G. S., Bandeira M. A., Matos F., *J. Phytomed.* 10 (2003) 189-195.
- [9] Zhao L. M., Jin H. S., Sun L. P., Piao H. R., Quan Z. S., *Bioorg. Med. Chem. Lett.* 15(22) (2005) 5027-5029.
- [10] Mukarami S., Muramatsu M., Aihara H., Otomo S., *Biochem. Pharmacol.* 42(7) (1991) 1447-1451.
- [11] Liu M., Wilairat P., Go L. M., *J. Med. Chem.* 44(5) (2001) 4443-4452.
- [12] Francesco E., Salvatore G., Luigi M., *Phytochem.* 68(7) (2007) 939-953.
- [13] Onyilagna J. C., Malhotra B., Elder M., Towers G. H. N., *Can. J. Plant. Pathol.* 19 (1997) 133-137.
- [14] Nielsen S. F., Chen M., Theander T. G., Kharazmi A., *Bioorg. Med. Chem. Lett.* 5 (1995) 449-452.
- [15] Miranda C. L., Aponso G. L. M., *J. Agricul Food Chem.* 48 (2000) 3876-3884.
- [16] Siva Kumar P. M., Geetha Babu S. K., Mukesh D, *Chem. Pharm. Bull.* 55(1) (2007) 44-49.
- [17] Satyanarayana M., Tiwari P., Tripathi K., Srivastava A. K., Pratap R., *Bioorg. Med. Chem. Lett.* 12 (2004) 883-889.
- [18] Barford L., Kemp K., Hansen M., Kharazmi A., *Inter Immunopharmacol.* 2 (2007) 545.
- [19] Maria J., Moa G., Mandado M., *Chem. Phy. Lett.* 446 (2007) 1-7.
- [20] Anto R. J., Sukumaran K., Kuttan G., Rao M. A., *Cancer Lett.* 97 (1995) 33.
- [21] Utpal B, Sahu A, Ali S S, Kasoju L, Singh A, *Food Res. Inter.* 41 (2008) 1-15.
- [22] Subramanian M., Vanangamudi G., Thirunarayanan G., *Spectrochim. Acta* 110A (2013) 116-123.
- [23] Vanangamudi G., Subramanian M., Thirunarayanan G., *Arabian J. Chem.*, 2013. DOI: 10.1016/j.arabjc.2013.03.006.
- [24] Sathiyamoorthi K., Mala V., Suresh R., Sakthinathan S. P., Kamalakkannan D., Ranganathan K., Arulkumaran R., Sundararajan R., Vijayakumar S., Vanangamudi G., Thirunarayanan G., *International Letters of Chemistry, Physics and Astronomy* 7(2) (2013) 102-119.
- [25] Sathiyamoorthi K., Mala V., Suresh R., Sakthinathan S. P., Kamalakkannan D., Vanangamudi G., Thirunarayanan G., *Spectrochim Acta*, 2013. DOI: <http://dx.doi.org/10.1016/j.saa.2013.04.048>.

-
- [26] Mala V., Sathiyamoorthy K., Sakthinathan S. P., Kamalakkannan D., Suresh R., Vanangamudi G., Thirunarayanan G., *Q-Science Connect*. 2013.
DOI: <http://dx.doi.org/10.5339/connect.2013>.
- [27] Bauer A. W., Kirby W. M. M., Sherris J. C., Truck M., *Am. J. Clin. Pathol* 45 (1966) 493-498.
- [28] Dhanaji H., Jadhav Ramaa C.S., *Indian J. Chem.* 46 (2007) 2064-2067.
- [29] Sachin I., Tabreskhan P., Rhea M., Ramaa C. S., *Int. J. Drug Desgn. Discov.* 1(3) (2010) 209-215.
- [30] Arpita H. More, Jadhav Ramaa C. S., *Ind. J. Chem.* 49B (2010) 364-367.
- [31] Sekar K. G., Thirunarayanan G., *International Letters of Chemistry, Physics and Astronomy* 8(3) (2013) 249-258.
- [32] Ranganathan K., Suresh R., Kamalakkannan D., Arulkumaran R., Sundararajan R., Sakthinathan S. P., Vijayakumar S., Vanangamudi G., Thirumurthy K., Mayavel P., Thirunarayanan G., *International Letters of Chemistry, Physics and Astronomy* 4 (2012) 66-75.
- [33] Arulkumaran R., Vijayakumar S., Sundararajan R., Sakthinathan S. P., Kamalakkannan D., Suresh R., Ranganathan K., Rajakumar P. R., Vanangamudi G., Thirunarayanan G., *International Letters of Chemistry, Physics and Astronomy* 5 (2013) 21-38.
- [34] Sakthinathan S. P., Suresh R., Mala V., Sathiyamoorthi K., Kamalakkannan D., Ranganathan K., Arulkumaran R., Vijayakumar S., Sundararajan R., Vanangamudi G., Thirunarayanan G., *International Letters of Chemistry, Physics and Astronomy* 6 (2013) 77-90.
- [35] Sekar K. G., Thirunarayanan G., *International Letters of Chemistry, Physics and Astronomy* 8(2) (2013) 160-174.
- [36] Swain C. G., Lupton E. C. Jr., *J. Am. Chem. Soc.* 90 (1968) 4328-4337.
- [37] Hays W. P., Timmons C. J., *Spectrochim. Acta.* 24A (1968) 323-334.

(Received 26 April 2013; accepted 29 April 2013)