

## **Solid Fly-ash:PTS catalyzed synthesis, spectral studies and antimicrobial activities of some 1,3-diarylpropenones**

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The green catalyst Fly-ash:PTS has been prepared and characterized by IR and SEM analysis. Using this catalyst some aryl chalcones have been synthesized by aldol condensation of aryl methyl ketone and substituted benzaldehydes. It has been observed that this reaction yields more than 85% of the product. These chalcones have been characterized by their physical constants and spectral data following the procedures published in literature. The effect of substituents on the spectral data of the chalcones, synthesized, has been studied using single and multi-regression analysis with Hammett equation. The antibacterial and antifungal activities of these chalcones have been studied using Bauer-Kirby method.

**Keywords:** Chalcones; Greener synthesis, Fly-ash:PTS; UV spectra, IR spectra, NMR spectra, Hammett correlation, antibacterial activity, antifungal activity.

### 1. INTRODUCTION

Numerous greener and solvent-free [1,2] synthetic methods are available in the literature for the synthesis of organic compounds. The reactions involving the formation of carbon-carbon bond and carbon-

heteroatom bond are becoming important and in fact very interesting in green synthesis. Based on this fact, the Aldol [3], Crossed-aldol [4], Knoevenagel [5], Mannich [6], Michael [7], Suzuki [8], Darzen's [9] and Wittig [10] reactions have been applied for synthesizing isomeric biologically active compounds such as chalcones, alkenes and Mannich bases. Thermal condensation reactions have been found to be sluggish and time-consuming with poor yields. However in the microwave conditions, the reaction becomes faster, giving appreciable yield involving easier process of isolation of the products. Scientists and researchers in Chemistry have used microwave irradiation technique for solid phase green synthesis [5,11,12]. Numerous green Catalysts such as Fly-ash: sulphuric acid [13], anhydrous zinc chloride [14], ground chemistry catalysts-grinding the reactants with sodium hydroxide [16], aqueous alkali in lower temperature [17], solid sulphonic acid from aqueous alkali in lower temperature [17], solid sulphonic acid from bamboo [18], barium hydroxide [19] anhydrous sodium bicarbonate [20], microwave assisted synthesis [21], Fly-ash:water [1], triphenylphosphite [22], alkali earth metals [23], KF/Al<sub>2</sub>O<sub>3</sub> [24], silica-sulphuric acid [2, 25] and sulfated titania [26], have been reported in the literature, for the synthesis of many number of organic compounds. The effect of substituents have been studied, through UV-Vis, IR, <sup>1</sup>H and <sup>13</sup>C NMR spectral data observed for ketones [21], unsaturated ketones [22-24], acid chlorides [14], acyl bromides and esters [25]. However, it is worthwhile to mention that only a little work has been done so far and published in the literature regarding the study of the effect of substituents with respect to chalcone derivatives, using UV, infrared, proton and carbon-13 spectral data. Also, no information has been found in literature in the recent past, regarding the synthesis of chalcones using Fly-ash:PTS catalyzed aldol reaction. Hence the authors have taken efforts to synthesize some aryl chalcones using solvent free Fly-ash:PTS catalyzed aldol condensation with the help of microwave irradiation technique. Also the effect of substituents has been studied with Hammett equation followed by the study of antimicrobial activities with regard to the synthesized chalcone derivatives.

## 2. MATERIAL AND METHODS

All chemicals have been procured from E-Merck brand. Melting points of all chalcones have been determined in open glass capillaries on Mettler FP51 melting point apparatus and are uncorrected. UV spectra

have been recorded on ELICO BL 222 spectrophotometer. Avatar-300 Fourier transform spectrophotometer has been utilized for recording Infrared spectra ( $\text{KBr}$ ,  $4000\text{--}400\text{cm}^{-1}$ ) and the NMR spectra all synthesized chalcones have been recorded in Bruker 400MHz spectrometer. With the help of SIMADZU GC-MS2010 Spectrometer, using Electron Impact (EI) techniques, mass spectra have been recorded

### Preparation and characterization of catalyst

In a  $50\text{ cm}^3$  Borosil beaker, 1g of Fly-ash and  $0.8\text{ cm}^3$  ( $0.5\text{ mol}$ ) of *p*-toluenesulphonic acid have been taken and mixed thoroughly with glass rod. This mixture has been heated on a hot air oven at  $85^\circ\text{C}$  for 1h, cooled to room temperature, stored in a Borosil bottle and tightly capped. The product has been characterized by infrared spectra and SEM analysis.

Infrared spectral data of Fly-ash:PTS is  $\nu(\text{cm}^{-1})$ : 3450(OH); 3012 (C-H); 1496, 1385(C-S); 1346, 1155(S=O); and *op* modes: 1133, 1100, 965, 890, 851, 834, 663, 658, 620, 578, 468, 425.

The SEM images of Fly-ash and Fly-ash:PTS at two different magnifications have been shown in Figs. 1(a–d). It has been observed from Figures 1a and 1b, that the crystallinity is more in Fly-ash. The spherical shaped particles are clearly seen at both magnifications in

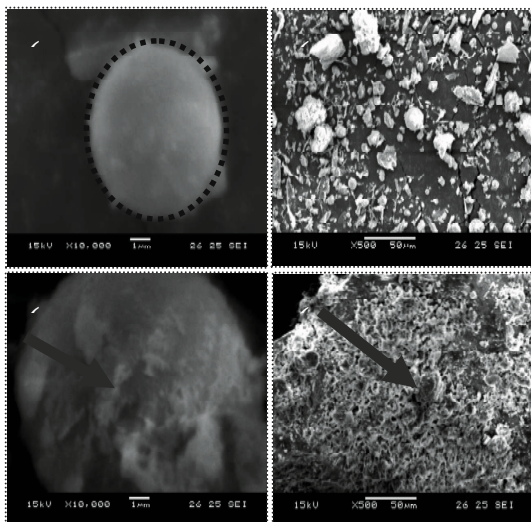
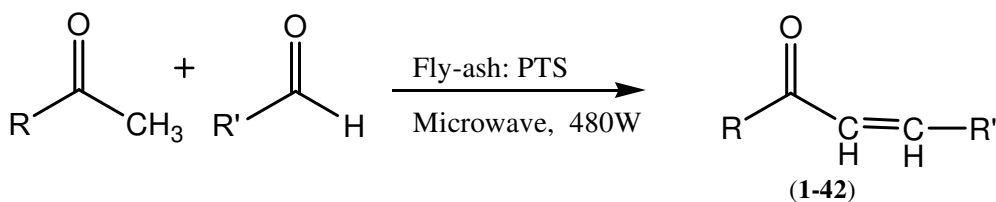


Fig 1. SEM images of pure fly ash and PTSA-fly ash; a) pure fly ash ( $1\mu\text{m}$ ), b) pure fly ash ( $50\mu\text{m}$ ), c) PTSA – fly ash ( $1\mu\text{m}$ ) ( $\Rightarrow$  – corroded), d) PTSA – fly ash ( $50\mu\text{m}$ ) ( $\Rightarrow$  – corroded).

Fig. 1a and 1b. Fig. 1a reveals and evidences the globular structure of pure Fly-ash (round shaped particle). Also, it is observable from Fig. 1c and 1d that some of the particles are slightly corroded by *p*-toluene sulphonic acid (shown by arrow mark) and this may be due to dissolution of Fly-ash by *p*-toluene sulphonic acid. This has been further confirmed by Fig 1d, showing the well-shaped particles of pure Fly-ash.

## Synthesis of chalcones

An appropriate equimolar quantities of aryl methyl ketone (2 mmol), substituted benzaldehydes (2 mmol) and Fly-ash:PTS (0.75 g) have been taken in Borosil tube and tightly capped. The mixture has been exposed to microwave irradiation for 8-10 minutes in a microwave oven (Scheme 1) (LG Grill, Intellwave, Microwave Oven, 160-800W) and then cooled to room temperature. The organic layer has been separated with dichloromethane, which, on evaporation, yields a solid product. The solid, on recrystallization with benzene-hexane mixture gives glittering solid. The insoluble catalyst has been recycled by washing the solid reagent remained on the filter by ethyl acetate (8 cm<sup>3</sup>) followed by drying in an oven at 100°C for 1h. This recycled catalyst has been reused for further reactions.



Scheme 1. Synthesis of aryl chalcones

## 3. RESULTS AND DISCUSSION

The Fly-ash has been converted to useful green catalyst Fly-ash:PTS by mixing fly-ash and *p*-toluene sulphuric acid. It is worthwhile to mention that the enhancement of the catalytic activity is attributed to the sulphonic acid group and chemical species present in the Fly-ash. During the course of the reaction, these species promote the catalytic effect on condensation between the aryl methyl ketones and aryl aldehydic groups leading to the formation of chalcones. The proposed general reaction mechanism is shown in (Fig. 2).

After the completion of the reaction, the products have been isolated followed by washing the catalyst with ethyl acetate. To make this catalyst reusable for further reactions, it has been heated to 100°C. It is interesting to note that during the condensation there has been no appreciable change in the percentage of the yield of chalcones, on reusing the same catalyst. The analytical and mass spectral data recorded for the chalcones, synthesized, are presented in Table 1. The UV-visible, IR and NMR data for these compounds are provided in Tables 2 and 3.

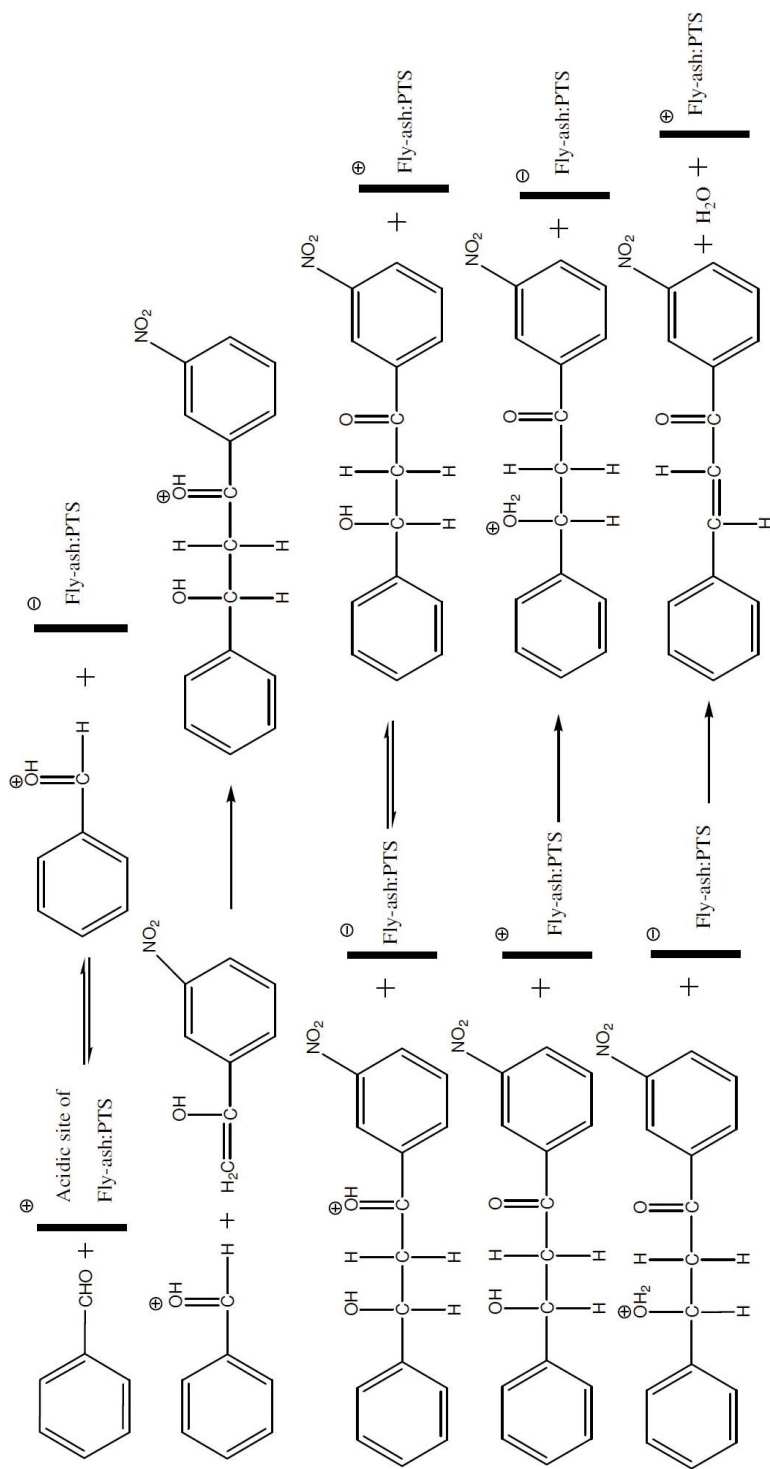


Fig. 2. The proposed mechanism of crossed aldol condensation catalyzed by Fly-ash:PTS for 3-nitroacetophenone and benzaldehydes.

Table 1. Analytical and mass spectral data of chalcones synthesized by fly-ash: PTS catalyzed aryl methyl ketones and substituted benzaldehydes reaction of the type  $R-CO-CH_3 + R'-CHO \rightarrow R-CO-CH=CH-R'$  under microwave irradiation.

Entry	R	R'	Product	M.W.	Yield [%]	M.p. [°C]	Mass (m/z)
1	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> COCH=CHC <sub>6</sub> H <sub>5</sub>	208	87	55-56 (55-58)[13]	-
2	C <sub>6</sub> H <sub>5</sub>	4-OHC <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub> COCH=CHC <sub>6</sub> H <sub>4</sub> OH	291	85	122-123 (122)[13]	-
3	C <sub>6</sub> H <sub>5</sub>	4-OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub> COCH=CHC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub>	291	86	164-165 (164)[13]	-
4	4-NH <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	4-NH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> COCH=CHC <sub>6</sub> H <sub>5</sub>	223	85	98-99 (98-99)[13]	-
5	4-F-C <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	4-F-C <sub>6</sub> H <sub>4</sub> COCH=CHC <sub>6</sub> H <sub>5</sub>	226	86	49-50 (49-50)[13]	-
6	2,4-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	2,4-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> COCH=CHC <sub>6</sub> H <sub>5</sub>	276	87	80-82 (80-81)[13]	-
7	3,4-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	3,4-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> COCH=CHC <sub>6</sub> H <sub>5</sub>	276	87	100-101 (100-101)[13]	-
8	4-(OH)C <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	4-OHC <sub>6</sub> H <sub>3</sub> COCH=CHC <sub>6</sub> H <sub>5</sub>	226	87	(63-64)[13]	-
9	3-(NO <sub>2</sub> )C <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> COCH=CHC <sub>6</sub> H <sub>5</sub>	253	87	204-205 (203)[27]	253[M+]
10	3-(NO <sub>2</sub> )C <sub>6</sub> H <sub>4</sub>	3-BrC <sub>6</sub> H <sub>5</sub>	3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> COCH=CHC <sub>6</sub> H <sub>4</sub> Br	332	86	139-140	332[M+], 334[M2+]
11	3-(NO <sub>2</sub> )C <sub>6</sub> H <sub>4</sub>	4-BrC <sub>6</sub> H <sub>5</sub>	3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> COCH=CHC <sub>6</sub> H <sub>4</sub> Br	332	87	166-167	332[M+], 334[M2+]

cont. Table 2.

Entry	R	R'	Product	M.W.	Yield [%]	M.p. [°C]	Mass (m/z)
12	3-(NO <sub>2</sub> )C <sub>6</sub> H <sub>4</sub>	3-ClC <sub>6</sub> H <sub>5</sub>	3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> COCH=CHC <sub>6</sub> H <sub>4</sub> Cl	287	87	226-227	287[M+],289[M2+]
13	3-(NO <sub>2</sub> )C <sub>6</sub> H <sub>4</sub>	4-ClC <sub>6</sub> H <sub>5</sub>	3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> COCH=CHC <sub>6</sub> H <sub>4</sub> Cl	287	87	172-173	287[M+],289[M2+]
14	3-(NO <sub>2</sub> )C <sub>6</sub> H <sub>4</sub>	4-FC <sub>6</sub> H <sub>5</sub>	3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> COCH=CHC <sub>6</sub> H <sub>4</sub> F	271	86	150-151	271[M+],273[M2+]
15	3-(NO <sub>2</sub> )C <sub>6</sub> H <sub>4</sub>	2-OHC <sub>6</sub> H <sub>5</sub>	3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> COCH=CHC <sub>6</sub> H <sub>4</sub> OH	269	86	126-126	269[M+]
16	3-(NO <sub>2</sub> )C <sub>6</sub> H <sub>4</sub>	4-OHC <sub>6</sub> H <sub>5</sub>	3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> COCH=CHC <sub>6</sub> H <sub>4</sub> OH	269	85	141-142	269[M+]
17	3-(NO <sub>2</sub> )C <sub>6</sub> H <sub>4</sub>	2-OCH <sub>3</sub> C <sub>6</sub> H <sub>5</sub>	3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> COCH=CHC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub>	283	85	132-133	283[M+]
18	3-(NO <sub>2</sub> )C <sub>6</sub> H <sub>4</sub>	4-OCH <sub>3</sub> C <sub>6</sub> H <sub>5</sub>	3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> COCH=CHC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub>	283	86	151-152	283[M+]
19	3-(NO <sub>2</sub> )C <sub>6</sub> H <sub>4</sub>	2-CH <sub>3</sub> C <sub>6</sub> H <sub>5</sub>	3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> COCH=CHC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	267	86	81-82	267[M+]
20	3-(NO <sub>2</sub> )C <sub>6</sub> H <sub>4</sub>	4-CH <sub>3</sub> C <sub>6</sub> H <sub>5</sub>	3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> COCH=CHC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	267	86	122-123 149-150[28]	267[M+]
21	3-(NO <sub>2</sub> )C <sub>6</sub> H <sub>4</sub>	3-NO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> COCH=CHC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	298	86	198-199 (204)[29]	298[M+]
22	3-(NO <sub>2</sub> )C <sub>6</sub> H <sub>4</sub>	4-NO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> COCH=CHC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	298	86	248-249 (247)[30]	298[M+]
23	C <sub>10</sub> H <sub>7</sub> (1-Naph)	C <sub>6</sub> H <sub>5</sub>	C <sub>10</sub> H <sub>7</sub> COCH=CHC <sub>6</sub> H <sub>5</sub>	258	85	100-102 (100-102)[13]	-
24	4-BrC <sub>10</sub> H <sub>6</sub> (1-Naph)	C <sub>6</sub> H <sub>5</sub>	4-BrC <sub>10</sub> H <sub>6</sub> COCH=CHC <sub>6</sub> H <sub>5</sub>	396	87	103-104 (103-104)[13]	-



cont. Table 2.

Entry	R	R'	Product	M.W.	Yield [%]	M.p. [°C]	Mass (m/z)
25	4-ClC <sub>10</sub> H <sub>6</sub> (1-Naph)	C <sub>6</sub> H <sub>5</sub>	4-ClC <sub>10</sub> H <sub>6</sub> COCH=CHC <sub>6</sub> H <sub>5</sub>	292	86	122-123 (122-123)[13]	-
26	2-OHC <sub>10</sub> H <sub>6</sub> (1-Naph)	C <sub>6</sub> H <sub>5</sub>	2-OHC <sub>10</sub> H <sub>6</sub> COCH=CHC <sub>6</sub> H <sub>5</sub>	274	85	101-102 (101-102)[31]	-
27	4-OCH <sub>3</sub> C <sub>10</sub> H <sub>6</sub> (1-Naph)	C <sub>6</sub> H <sub>5</sub>	4-OCH <sub>3</sub> C <sub>10</sub> H <sub>6</sub> COCH=CHC <sub>6</sub> H <sub>5</sub>	310	86	113-114 (113-114)[13]	-
28	4-CH <sub>3</sub> C <sub>10</sub> H <sub>6</sub> (1-Naph)	C <sub>6</sub> H <sub>5</sub>	4-CH <sub>3</sub> C <sub>10</sub> H <sub>6</sub> COCH=CHC <sub>6</sub> H <sub>5</sub>	284	87	98-99 (98)[13]	-
29	C <sub>10</sub> H <sub>7</sub> (2-Naph)	C <sub>6</sub> H <sub>5</sub>	C <sub>10</sub> H <sub>7</sub> COCH=CHC <sub>6</sub> H <sub>5</sub>	258	87	104-105 (104-105)[13]	-
30	6-OCH <sub>3</sub> C <sub>10</sub> H <sub>6</sub> (2-Naph)	C <sub>6</sub> H <sub>5</sub>	6-OCH <sub>3</sub> C <sub>10</sub> H <sub>6</sub> COCH=CHC <sub>6</sub> H <sub>5</sub>	310	86	67-68 (67-68)[13]	-
31	6-CH <sub>3</sub> C <sub>10</sub> H <sub>6</sub> (2-Naph)	C <sub>6</sub> H <sub>5</sub>	6-CH <sub>3</sub> C <sub>10</sub> H <sub>6</sub> COCH=CHC <sub>6</sub> H <sub>5</sub>	284	86	123-124 (123-124)[13]	-
32	C <sub>13</sub> H <sub>9</sub> (2-Fluorene)	C <sub>6</sub> H <sub>5</sub>	C <sub>13</sub> H <sub>9</sub> COCH=CHC <sub>6</sub> H <sub>5</sub>	296	87	150-151 (153-154)[13]	-
33	C <sub>12</sub> H <sub>9</sub> (Biphenyl)	C <sub>6</sub> H <sub>5</sub>	C <sub>12</sub> H <sub>9</sub> COCH=CHC <sub>6</sub> H <sub>5</sub>	284	87	153-154 (153-154)[13]	-
34	C <sub>4</sub> H <sub>3</sub> O(2-Furyl)	C <sub>6</sub> H <sub>5</sub>	C <sub>4</sub> H <sub>3</sub> OCOCH=CHC <sub>6</sub> H <sub>5</sub>	198	87	80-81 (80-81)[13]	-



cont. Table 2.

Entry	R	R'	Product	M.W.	Yield [%]	M.p. [°C]	Mass (m/z)
35	C <sub>4</sub> H <sub>3</sub> S(2-Thienyl)	C <sub>6</sub> H <sub>5</sub>	C <sub>4</sub> H <sub>3</sub> SCOCH=CHC <sub>6</sub> H <sub>5</sub>	204	87	112-113 (112-113)[13]	-
36	C <sub>14</sub> H <sub>10</sub> (Anthracene)	C <sub>6</sub> H <sub>5</sub>	C <sub>14</sub> H <sub>9</sub> COCH=CHC <sub>6</sub> H <sub>5</sub>	308	87	124-125 (124-125)[13]	-
37	5-BrC <sub>4</sub> H <sub>2</sub> S(2-Thienyl)	C <sub>6</sub> H <sub>5</sub>	5-BrC <sub>4</sub> H <sub>2</sub> SCOCH=CHC <sub>6</sub> H <sub>5</sub>	292	87	107-110 (107-110)[13]	-
38	5-ClC <sub>4</sub> H <sub>2</sub> S(2-Thienyl)	C <sub>6</sub> H <sub>5</sub>	5-ClC <sub>4</sub> H <sub>2</sub> SCOCH=CHC <sub>6</sub> H <sub>5</sub>	248	87	161-162	-
39	5-CH <sub>3</sub> C <sub>4</sub> H <sub>2</sub> O(2-Furyl)	C <sub>6</sub> H <sub>5</sub>	5-CH <sub>3</sub> C <sub>4</sub> H <sub>2</sub> OCOCH=CHC <sub>6</sub> H <sub>5</sub>	212	87	111-112 (110)[32]	-
40	1-CH <sub>3</sub> C <sub>4</sub> H <sub>3</sub> N(2-Pyrrol)	C <sub>6</sub> H <sub>5</sub>	1-CH <sub>3</sub> C <sub>4</sub> H <sub>3</sub> COCH=CHC <sub>6</sub> H <sub>5</sub>	212	87	209-210 (209-210)[33]	-
41	2,5-(CH <sub>3</sub> ) <sub>2</sub> C <sub>4</sub> HS(3-Thienyl)	C <sub>6</sub> H <sub>5</sub>	2,5-(CH <sub>3</sub> ) <sub>2</sub> C <sub>4</sub> HSCOCH=CHC <sub>6</sub> H <sub>5</sub>	230	87	322-323 (322-323)[33]	-
42	2,5-(CH <sub>3</sub> ) <sub>2</sub> C <sub>4</sub> HO(3-Furyl)	C <sub>6</sub> H <sub>5</sub>	2,5-(CH <sub>3</sub> ) <sub>2</sub> C <sub>4</sub> HOCOCH=CHC <sub>6</sub> H <sub>5</sub>	242	87	125-126 (125-126) [33]	-

Table 2. The Uv-Visible absorption  $\lambda_{\max}$ (nm) and infrared spectral data ( $\nu$ ,  $\text{cm}^{-1}$ ) of substituted styryl-3-nitrophenyl ketones(9-22).

Entry	$\lambda_{\max}$ [nm]	CO ( <i>s-cis</i> )	CO ( <i>s-trans</i> )	$\text{CH}_{ip}$	$\text{CH}_{op}$	$\text{CH}=\text{CH}_{op}$	$\text{C}=\text{C}_{op}$
9	315	1608.97	1527.28	1083.81	739.31	1047.04	565.81
10	307	1605.10	1528.60	1086.59	710.64	1047.70	575.82
11	320	1604.17	1527.28	1076.77	711.59	1046.56	493.34
12	306	1606.60	1528.89	1088.58	784.36	1048.88	577.36
13	319	1600.94	1528.44	1084.75	715.94	1045.10	463.75
14	315	1665.42	1525.87	1086.55	718.62	1049.26	463.68
15	303	1651.37	1531.70	1108.62	734.16	1023.49	463.32
16	350	1665.79	1518.13	1080.14	754.93	1024.26	462.16
17	348	1656.14	1519.77	1081.36	755.89	1026.31	462.33
18	346	1665.91	1517.87	1080.67	722.87	1028.5	463.40
19	321	1659.69	1527.82	1086.82	741.87	1023.32	460.91
20	326	1658.34	1525.61	1085.26	689.76	1043.92	499.15
21	301	1605.48	1525.18	1086.76	731.43	1022.44	463.27
22	316	1662.82	1534.91	1116.53	739.73	1020.40	560.51

Table 3. The NMR spectral data  $\delta$ (ppm) of substituted styryl-3-nitrophenyl ketones.

Entry	Vinyl $\text{H}_{\alpha}$	Vinyl $\text{H}_{\beta}$	CO	Vinyl $\text{C}_{\alpha}$	Vinyl $\text{C}_{\beta}$
9	7.560	7.919	188.04	120.64	146.82
10	7.543	7.837	187.66	121.84	144.89
11	6.956	8.634	187.75	121.04	145.35
12	7.769	8.377	187.67	121.77	145.01
13	7.783	7.893	187.77	121.04	145.24
14	7.511	7.915	187.83	120.34	145.49

cont. Table 3.

Entry	Vinyl H <sub>α</sub>	Vinyl H <sub>β</sub>	CO	Vinyl C <sub>α</sub>	Vinyl C <sub>β</sub>
15	7.692	8.183	195.73	121.82	148.57
16	7.455	7.914	187.99	123.21	146.68
17	7.669	7.760	187.26	122.60	145.80
18	7.457	7.915	188.01	123.22	146.71
19	7.509	8.259	188.05	121.66	144.39
20	7.538	7.924	188.13	123.27	146.95
21	7.978	8.567	187.37	122.78	143.59
22	7.703	7.919	182.15	123.37	141.13

We have investigated the catalytic effect of Fly-ash:PTS during the condensation reaction of 3-nitrophenyl methyl ketone and benzaldehyde (**Entry 9**) by varying the quantity of catalyst from 0.5 g to 1.5g. As the quantity of catalyst is increased from 0.5g to 0.75g, the percentage of yield of the product is found to increase from 85 to 87%. Further increase in the quantity of catalyst shows no significant increase in the percentage of the product. This catalytic effect is shown in (Fig. 3). The optimum

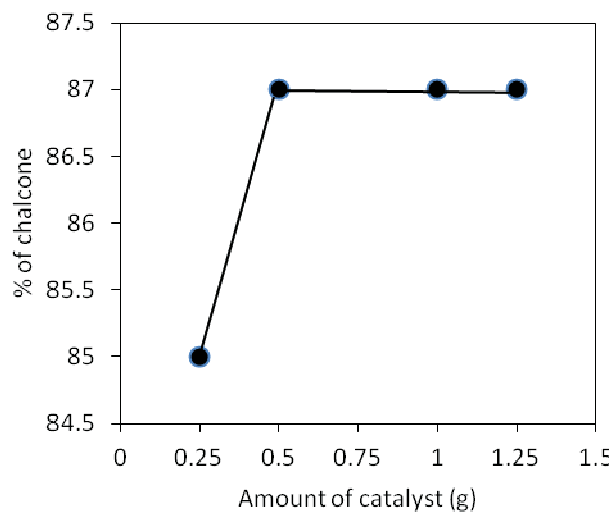


Fig. 3. Effects of catalyst loading.

quantity of catalyst is observed to be 0.75g. This catalyst has been reused for the condensation reaction between 3-nitrophenyl methyl ketone and benzaldehyde and the percentage of yield on reusing the catalyst is given in Table 4. From the Table 4, the yield of the product is found to be 87 % for the first two runs; however, the yield of the product is found to be 86.5%,

86% and 86 % for the third, fourth and fifth runs of reactions respectively. It is observed that there is no appreciable loss in the catalytic activity up to the fifth run.

Table 4. Reusability of catalyst on condensation of 3-nitrophenyl ketone (2 mmol) and benzaldehydes (2 mmol) (**Entry 9**) under microwave irradiation.

Run	1	2	3	4	5
Yield	87	87	86	85	85

### Spectral linearity

In the present study, the spectral linearity of chalcones has been investigated by evaluating the substituent effects. For all the chalcones, synthesized, the UV spectral data, assigned group frequencies like carbonyl stretches  $\nu_{\text{CO}}$ , the deformation modes of vinyl part CH *out of plane*, *in-plane*, CH=CH and  $>C=C<$  *out of planes* ( $\text{cm}^{-1}$ ), the vinyl hydrogen and observed chemical shifts  $\delta(\text{ppm})$ , of  $H_{\alpha}$ ,  $H_{\beta}$ ,  $C_{\alpha}$ ,  $C_{\beta}$  and CO are correlated with various substituent constants.

#### UV-Vis and IR spectral study

The UV spectra of all synthesized chalcones have been recorded in ELICO BL 222 spectrophotometer, in spectral grade methanol. The measured absorption maxima ( $\lambda_{\text{max}}$  nm) of these chalcones are presented in Table 2. These values have been correlated with Hammett substituent constants and F and R parameters using single and multi-linear regression analysis [11, 12, 26, 31, 32]. The form of the Hammett equation involving the absorption maxima, employed is shown in equation (1),

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

where  $\lambda_0$  is the frequency for the parent member of the series.

The results of statistical analysis [1, 5, 11, 12, 26, 31, 32] of these values with Hammett substituent constants are presented in Table 5. From Table 5, Hammett substituent constants  $\sigma$  and  $\sigma^+$  constants are found to give satisfactory correlations. But  $\sigma^{\text{R}}$ ,  $\sigma^{\text{I}}$  and R have shown poor correlations with  $\lambda_{\text{max}}$ . For all these parameters, negative  $\rho$  values are observed. This is due to the weak polar, resonance and inductive effects of the substituents for predicting the reactivity on the absorption. This is

attributed to the resonance conjugative structure shown in Fig. 4. The multi regression analysis of these data for all ketones with inductive, resonance and Swain-Lupton's [34] constants produce satisfactory correlations as shown in equations (2 and 3).

$$UV(\lambda_{\max}) = 320.83 (\pm 9.104) - 17.143 (\pm 18.746)\sigma_I - 27.403 (\pm 17.485) \sigma_R \quad (2)$$

(r = 0.951, n = 14, P > 95%)

$$UV(\lambda_{\max}) = 320.30 (\pm 8.416) - 20.479 (\pm 17.055)F - 28.902 (\pm 14.019) R \quad (3)$$

(r = 0.982, n = 14, P > 95%)

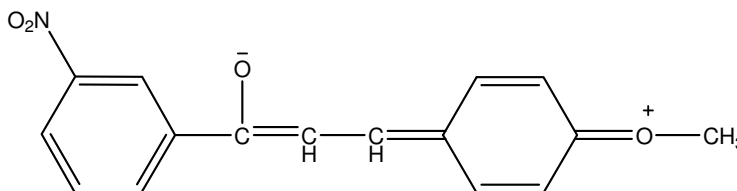


Fig. 4. The resonance-conjugative structure.

The synthesized chalcones exist as *s-cis* and *s-trans* conformers. These conformers have been confirmed by the carbonyl group doublets observed in the range of  $1600-1700\text{cm}^{-1}$  in IR spectra. They are shown in Fig. 5 and the corresponding carbonyl frequencies ( $\text{cm}^{-1}$ ) of the conformers are presented in Table 2. The *s-cis* conformers are found to absorb at higher vibrational frequencies than *s-trans* conformers. Generally, carbonyl doublets are observed at lower absorption frequencies in chalcones with electron donating substituents, whereas they are observed at higher frequencies in both the conformers of chalcones with the electron withdrawing substituents. The same trend has been observed in the present investigation as well. These frequencies have been correlated with various Hammett sigma constants and Swain-Lupton's parameters [34] by single and multi linear regression analysis [1, 5, 11, 12, 26, 31, 32]. While seeking Hammett correlation involving group frequencies, the form of the Hammett equation employed is shown in equation (4).

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

where  $\nu_0$  is the frequency for the parent member of the series.

Table 5. Results of statistical analysis of Uv-Vis and IR spectral frequencies of substituted styryl-3-nitrophenyl ketones with Hammett substituent constants.

Frequency	Constants	r	I	$\rho$	s	n	Correlated derivatives
UV <sub>max</sub>	$\sigma$	0.968	323.78	-29.267	12.58	12	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub>
	$\sigma^+$	0.975	320.67	-23.440	11.32	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_I$	0.324	329.07	-23.089	16.24	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_R$	0.461	314.31	-30.639	15.24	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	F	0.310	329.09	-21.736	16.32	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	R	0.512	312.75	-29.503	14.74	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
vCO <sub>3, cis</sub> (cm <sup>-1</sup> )	$\sigma$	0.853	1640.34	-39.987	25.36	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.620	1636.06	-33.754	23.50	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_I$	0.290	1649.11	-36.124	28.67	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_R$	0.473	1624.44	-54.913	26.39	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>

cont. Table 5.

Frequency	Constants	r	I	$\rho$	s	n	Correlated derivatives
	F	0.120	1642.22	-14.739	29.75	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	R	0.524	1621.70	-52.699	25.51	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
$\nu\text{CO}_{s\text{-trans}}(\text{cm}^{-1})$	$\sigma$	0.825	1525.56	7.887	3.95	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.907	1526.40	6.452	3.59	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_1$	0.239	1524.54	5.021	4.90	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_R$	0.463	1528.29	9.047	4.47	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	F	0.820	1524.71	4.257	4.94	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	R	0.852	1528.81	8.918	4.29	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
$\nu\text{CH}_{\beta}(\text{cm}^{-1})$	$\sigma$	0.935	1087.13	11.180	10.52	12	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub>
	$\sigma^+$	0.934	1088.26	7.059	10.74	12	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub>
	$\sigma_1$	0.925	1084.05	11.958	11.05	12	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub>



cont. Table 5.

Frequency	Constants	r	I	$\rho$	s	n	Correlated derivatives
	$\sigma_R$	0.915	1089.67	6.974	11.28	12	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub>
	F	0.929	1083.33	13.210	10.96	12	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub>
	R	0.918	1090.15	7.158	11.22	12	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub>
$\nu_{CH_{mp}}(cm^{-1})$	$\sigma$	0.021	732.33	-1.343	24.54	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.040	732.17	-1.797	24.52	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_1$	0.090	729.12	9.232	24.44	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_R$	0.810	729.19	-13.310	24.30	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	F	0.032	731.06	3.216	24.53	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	R	0.814	730.10	-7.349	24.44	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
$\nu_{CH=CH_{mp}}(c^{-1})$	$\sigma$	0.109	1035.22	3.444	12.46	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.225	1035.64	5.127	12.21	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>

cont. Table 5.

Frequency	Constants	r	I	$\rho$	s	n	Correlated derivatives
$\nu\text{C}=\text{C}_{\text{sp}}(\text{cm}^{-1})$	$\sigma_{\text{I}}$	0.005	1035.61	-0.301	12.53	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_{\text{R}}$	0.780	1035.46	4.187	12.49	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	F	0.012	1035.75	-0.654	12.53	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	R	0.801	1035.77	4.368	12.47	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma$	0.389	458.63	128.186	121.03	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.378	471.91	90.387	121.61	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_{\text{I}}$	0.144	442.96	78.918	130.03	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_{\text{R}}$	0.858	536.94	296.337	106.74	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	F	0.029	463.89	15.934	131.36	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	R	0.853	539.84	243.322	109.52	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>

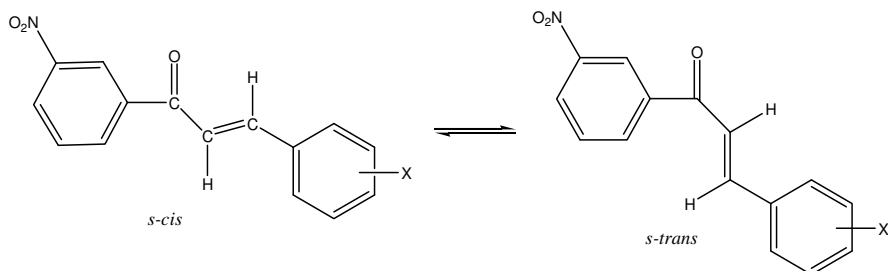


Fig. 5. The *s-cis* and *s-trans* conformers of 3-nitrophenyl chalcones.

The results of single regression analysis of carbonyl frequencies with substituent constants are presented in Table 5. From Table 5, it is evident that the correlation for  $\nu_{\text{C=O}}$  of both conformers fails with Hammett  $\sigma$  constants and F and R parameters. The  $\sigma^+$  constants have shown satisfactory correlation with *s-trans* conformers. The remaining constants are found to produce poor correlations with both the conformers. The failure in correlation is attributed to the conjugation between the substituent and the carbonyl group in chalcones as shown in Fig. 4. Positive  $\rho$  values are observed for *s-trans* and negative  $\rho$  values for *s-cis* conformers, in all correlations. This observation implies that there is a normal substituent effect operating in all systems.

The correlation of CH *in-plane* modes with Hammett sigma constants is found to be satisfactory with positive  $\rho$  values in all cases and this implies that the normal substituent effect operates in all ketones.

All correlations of CH *out of plane*, CH=CH *out of plane* and C=C *out of plane* modes with Hammett constants, F and R parameters are found to fail. Positive  $\rho$  values are observed in all correlations and this reveals that there operates a normal substituent effect in all ketones. In view of the inability of some of the  $\sigma$  constants to produce individually satisfactory correlations, the authors feel that it is worthwhile to seek multiple correlations involving either  $\sigma_1$  and  $\sigma_R$  constants or Swain-Lupton's [34], F and R parameters. The correlation equations for *s-cis*, *s-trans* and deformation modes are given equations 5-16.

$$\nu_{\text{CO}_{s-cis}}(\text{cm}^{-1}) = 1634.05(\pm 15.932) - 25.243(\pm 3.806)\sigma_1 - 50.148(\pm 30.598)\sigma_R \quad (5)$$

$(R = 0.914, n = 14, P > 90\%)$

$$\nu_{\text{CO}_{s-cis}}(\text{cm}^{-1}) = 1626.3(\pm 15.372) - 12.463(\pm 3.153)F - 52.333(\pm 25.606)R \quad (6)$$

$(R = 0.934, n = 14, P > 90\%)$

$$\nu\text{CO}_{s\text{-trans}}(\text{cm}^{-1}) = 1527.08(\pm 2.7356) + 3.189(\pm 1.632)\sigma_{\text{I}} + 8.445(\pm 5.259)\sigma_{\text{R}} \quad (7)$$

$$(R = 0.948, n = 14, P > 90\%)$$

$$\nu\text{CO}_{s\text{-trans}}(\text{cm}^{-1}) = 1527.39(\pm 2.542) + 3.874(\pm 1.151)F + 8.804(\pm 4.234)R \quad (8)$$

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

$$\nu\text{CH}_{\text{ip}}(\text{cm}^{-1}) = 1085.52(\pm 6.810) + 10.891(\pm 4.022)\sigma_{\text{I}} + 4.919(\pm 3.078)\sigma_{\text{R}} \quad (9)$$

$$(R = 0.927, n = 14, P > 90\%)$$

$$\nu\text{CH}_{\text{ip}}(\text{cm}^{-1}) = 1085.39(\pm 6.537) + 12.916(\pm 3.246)F + 6.778(\pm 1.889)R \quad (10)$$

$$(R = 0.933, n = 14, P > 90\%)$$

$$\nu\text{CH}_{\text{op}}(\text{cm}^{-1}) = 724.38(\pm 14.946) + 12.637(\pm 3.776)\sigma_{\text{I}} - 15.696(\pm 8.705)\sigma_{\text{R}} \quad (11)$$

$$(R = 0.918, n = 14, P > 90\%)$$

$$\nu\text{CH}_{\text{op}}(\text{cm}^{-1}) = 728.79(\pm 14.826) + 3.540(\pm 1.048)F - 7.453(\pm 4.698)R \quad (12)$$

$$(R = 0.933, n = 14, P > 90\%)$$

$$\nu\text{CH}=\text{CH}_{\text{op}}(\text{cm}^{-1}) = 1036.94(\pm 7.739) - 1.261(\pm 0.935)\sigma_{\text{I}} + 4.426(\pm 1.862)\sigma_{\text{R}} \quad (13)$$

$$(R = 0.908, n = 14, P > 90\%)$$

$$\nu\text{CH}=\text{CH}_{\text{op}}(\text{cm}^{-1}) = 1037.09(\pm 7.566) - 0.845(\pm 0.335)F + 4.393(\pm 1.604)R \quad (14)$$

$$(R = 0.916, n = 14, P > 90\%)$$

$$\nu\text{C}=\text{C}_{\text{op}}(\text{cm}^{-1}) = 531.13(\pm 66.109) + 15.245(\pm 6.124)\sigma_{\text{I}} + 293.46(\pm 26.963)\sigma_{\text{R}} \quad (15)$$

$$(R = 0.908, n = 14, P > 90\%)$$

$$\nu\text{C}=\text{C}_{\text{op}}(\text{cm}^{-1}) = 537.86(\pm 66.462) + 5.361(\pm 1.691)F + 243.164(\pm 110.71)R \quad (16)$$

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

### <sup>1</sup>H NMR spectral study

The <sup>1</sup>H NMR spectra of the chalcones, synthesized, have been recorded in deuteriochloroform solution employing tetramethylsilane (TMS) as internal standard. The signals of the ethylenic protons have been assigned from the NMR spectra. They have been calculated as AB or AA' or BB' systems respectively. In this series of ketones, lower chemical shifts (ppm) are observed for H<sub>α</sub>, and higher chemical shifts (ppm) are observed for H<sub>β</sub>. The vinyl protons are observed to give an AB pattern. The β-proton doublets are well separated from the signals of the aromatic protons. The assigned vinyl proton chemical shifts δ(ppm) of all ketones are presented in Table 3.

In nuclear magnetic resonance spectra, the <sup>1</sup>H or the <sup>13</sup>C chemical shift (δ) values depend 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 shown in equation (17).

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

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

The assigned  $H_\alpha$  and  $H_\beta$  proton chemical shifts (ppm) have also been correlated with various Hammett sigma constants. The results of statistical analysis [1, 5, 11, 12, 26, 31, 32] are presented in Table 6. All correlations with Hammett sigma constants, F and R parameters are found to be satisfactory only for  $H_\alpha$  proton chemical shifts (ppm) and not for  $H_\beta$  proton chemical shifts (ppm). The positive  $\rho$  values observed in all the correlations evidence the operation of normal substituent effect in all chalcones. Also, the failure in correlation for  $H_\beta$  proton chemical shifts is attributed to the conjugative structure shown in Fig. 4.

Application of Swain-Lupton [34] treatment to the relative chemical shifts of  $H_\alpha$  and  $H_\beta$  with F and R parameters is successful with resonance and inductive effects and found unsuccessful with F & R parameters in the multi regression analysis as shown in equations 18-21.

$$\delta H_\alpha(\text{ppm}) = 7.545(\pm 0.144) + 0.197(\pm 0.029)\sigma_I + 0.138(\pm 0.027)\sigma_R \quad (18)$$

$(R = 0.983, n = 14, P > 95\%)$

$$\delta H_\alpha(\text{ppm}) = 7.575(\pm 0.139) + 0.182(\pm 0.028)F + 0.209(\pm 0.023)R \quad (19)$$

$(R = 0.982, n = 14, P > 95\%)$

$$\delta H_\beta(\text{ppm}) = 8.074(\pm 0.168) + 0.213(\pm 0.034)\sigma_I + 0.325(\pm 0.032)\sigma_R \quad (20)$$

$(R = 0.936, n = 14, P > 90\%)$

$$\delta H_\beta(\text{ppm}) = 8.090(\pm 0.165) + 0.197(\pm 0.033)F + 0.306(\pm 0.027)R \quad (21)$$

$(R = 0.908, n = 14, P > 90\%)$

Table 6. Results of statistical analysis of NMR spectral frequencies of 3-nitrophenyl chalcones with Hammett substituent constants.

Frequency	Constants	r	I	$\rho$	s	n	Correlated derivatives
$\delta_{\text{HC}}(\text{ppm})$	$\sigma$	0.932	7.563	0.198	0.22	13	H, 3-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.923	7.583	0.104	0.23	13	H, 3-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_1$	0.922	7.503	0.227	0.23	13	H, 3-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_R$	0.918	7.620	0.176	0.23	13	H, 3-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	F	0.919	7.511	0.191	0.23	13	H, 3-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	R	0.926	7.642	0.214	0.23	13	H, 3-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
$\delta_{\text{HP}}(\text{ppm})$	$\sigma$	0.837	8.049	0.277	0.27	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.442	8.078	0.235	0.26	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_1$	0.233	7.977	0.283	0.28	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_R$	0.323	8.156	0.365	0.27	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	F	0.176	7.997	0.210	0.28	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>

cont. Table 6.

Frequency	Constants	r	I	$\rho$	s	n	Correlated derivatives
$\delta C_{\alpha}$ (ppm)	R	0.317	8.162	0.312	0.27	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma$	0.803	122.03	-0.098	1.10	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.819	122.01	-0.401	1.08	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_1$	0.701	122.00	0.073	1.10	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_R$	0.706	122.08	0.262	1.10	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	F	0.702	122.06	-0.120	1.10	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
$\delta C_{\beta}$ (ppm)	R	0.801	122.01	-0.052	1.10	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma$	0.978	145.78	-3.624	1.14	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.973	145.41	-2.450	1.25	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_1$	0.605	147.03	-4.631	1.46	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_R$	0.906	144.38	-4.811	1.36	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>



cont. Table 6.

Frequency	Constants	r	I	$\rho$	s	n	Correlated derivatives
	F	0.508	146.85	-3.829	1.58	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	R	0.967	144.26	-4.202	1.35	13	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub>
	$\sigma$	0.506	188.26	-3.574	2.42	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub>
	$\sigma^+$	0.439	187.90	-2.249	2.53	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_I$	0.369	189.41	-4.311	2.61	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma_R$	0.595	186.48	-6.491	2.26	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	F	0.275	189.09	-3.168	2.70	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>
	R	0.564	186.41	-5.334	2.32	14	H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 2-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 2-CH <sub>3</sub> , 4-CH <sub>3</sub> , 3-NO <sub>2</sub> , 4-NO <sub>2</sub>

*<sup>13</sup>C NMR spectral study*

Spectral analysts, organic chemists and researchers[[1, 5, 11, 12, 26, 31, 32] have made extensive study of <sup>13</sup>C NMR spectra for a large number of different ketones and styrenes. The assigned vinyl C<sub>α</sub>, C<sub>β</sub> and carbonyl carbon chemical shifts are presented in Table 3. The results of statistical analysis are given in Table 6. They have been observed a correlation linear for. The correlations of C<sub>α</sub> carbon chemical shifts(ppm) with Hammett σ constants, F and R parameters are found to be poor. A satisfactory correlation is observed for C<sub>β</sub> carbon chemical shifts(ppm) with Hammett sigma constants and R parameters with positive ρ values. The remaining inductive and fielded parameters fail in correlations. This is due to the reasons stated earlier and attributed to the resonance conjugative structure shown in Fig. 4.

The assigned carbonyl carbon chemical shifts (ppm) have been correlated with Hammett constants using single and multi linear regression analysis and they are presented in Table 6. The Hammett sigma constants correlate poorly with carbonyl carbon chemical shifts of these ketones. All correlations give positive ρ values which evidence the operation of normal substituent effects in all the ketones. The failure in correlation is due to the conjugation existing between the substituent and the carbonyl group as shown in Fig. 4.

The Swain-Luptons' [34] parameter correlations are found to be satisfactory with the carbon chemical shifts and the regression equations are given in (22)-(27).

$$\delta C_{\alpha} \text{ (ppm)} = 122.67 (\pm 0.686) + 0.017(\pm 1.413)\sigma_I + 0.259(\pm 1.318) \sigma_R \quad (22)$$

$$(R = 0.906, n = 14, P > 90\%)$$

$$\delta C_{\alpha} \text{ (ppm)} = 122.06 (\pm 0.673) - 0.118(\pm 1.364)F - 0.048(\pm 1.121) R \quad (23)$$

$$(R = 0.907, n = 14, P > 90\%)$$

$$\delta C_{\beta} \text{ (ppm)} = 145.80 (\pm 0.642) - 3.741(\pm 1.323)\sigma_I - 4.105(\pm 1.234) \sigma_R \quad (24)$$

$$(R = 0.982, n = 14, P > 95\%)$$

$$\delta C_{\beta} \text{ (ppm)} = 145.60 (\pm 0.616) - 3.651(\pm 1.249)F - 4.095(\pm 1.027) R \quad (25)$$

$$(R = 0.983, n = 14, P > 95\%)$$

$$\delta CO \text{ (ppm)} = 187.63(\pm 1.330) - 3.026(\pm 2.739)\sigma_I - 5.920(\pm 2.555) \sigma_R \quad (26)$$

$$R = 0.906, n = 14, P > 90\%$$

$$\delta CO \text{ (ppm)} = 187.50(\pm 1.341) - 2.940(\pm 2.718)F - 5.247(\pm 2.234)R \quad (27)$$

$$(R = 0.962, n = 14, P > 95\%)$$

## Antimicrobial activities

Chalcones possess a wide range of biological activities such as antibacterial [35, 36], antifungal [35, 36], antiviral [37], antifeedant [38, 39], anticancer [35, 36], antimalarial [40], antituberculosis [41], antiAIDS [42] and antioxidant [43] effects. These multiprolonged activities present in different chalcones have been examined against respective microbes-bacteria's and fungi.

### *Antibacterial sensitivity assay*

Antibacterial sensitivity assay has been performed using Kirby-Bauer [44] disc diffusion technique. In each Petri plate about 0.5 cm<sup>3</sup> of the test bacterial sample is 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 are placed on the medium using sterile forceps. The plates are 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 are visually examined and the diameter values of the zone of inhibition are measured. Triplicate results were recorded by repeating the same procedure.

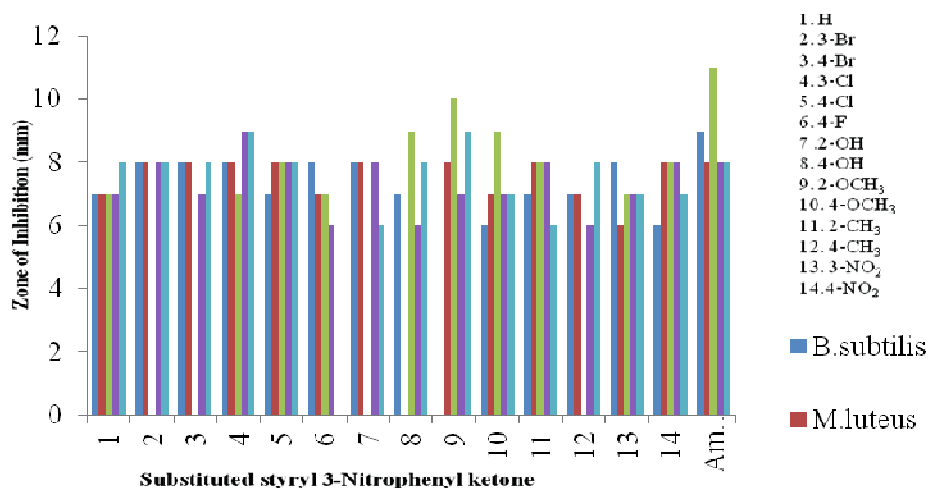


Fig. 7. The antibacterial activities of 3-nitrophenyl chalcones-clustered column chart.

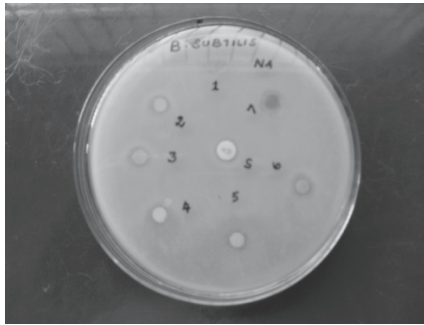


Plate-1

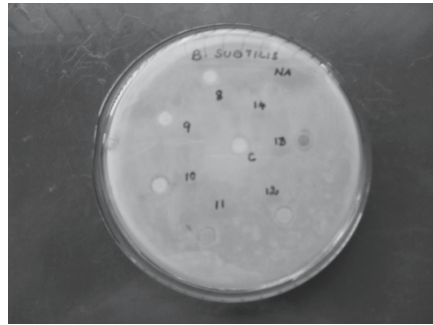


Plate-2

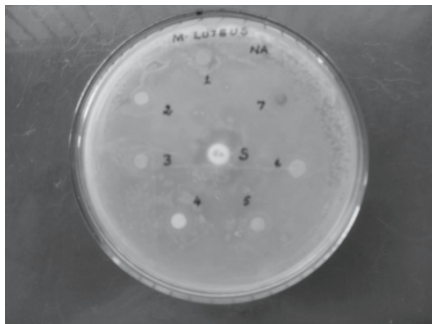


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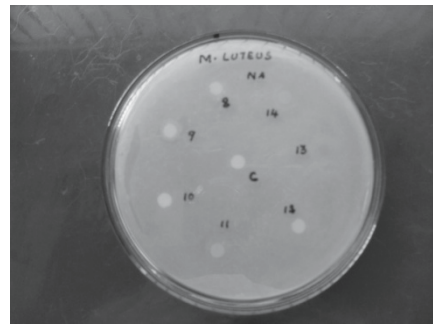


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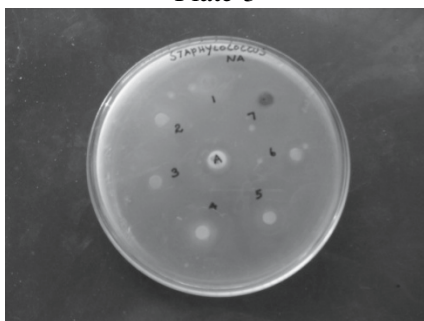


Plate-5

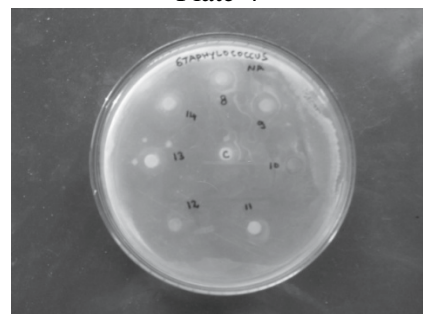


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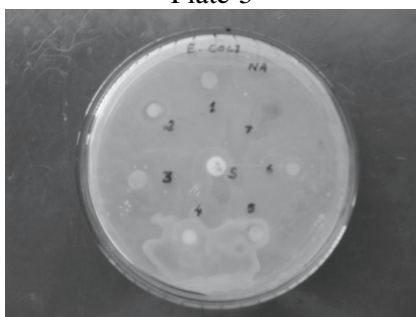


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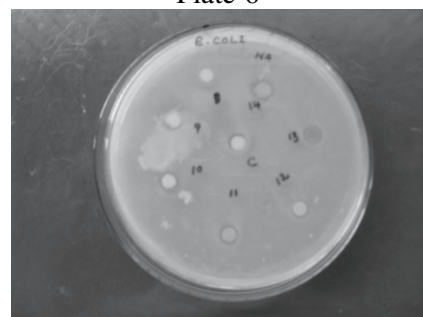


Plate-8

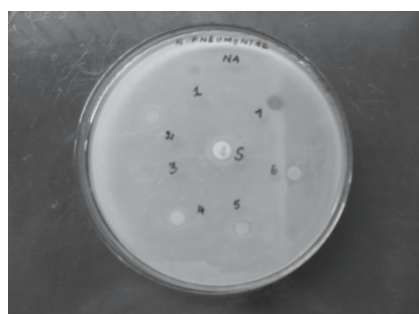


Plate-9

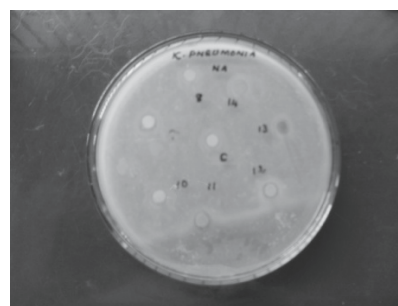


Plate-10

Fig. 6. Antibacterial activity of substituted styryl 3-nitrophenyl chalcones.

Table 7. The antibacterial activities of 3-nitrophenyl chalcones.

S. No.	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>K.pneumoniae</i>
1	H	7	7	7	7	8
2	3-Br	8	8	–	8	8
3	4-Br	8	8	–	7	8
4	3-Cl	8	8	7	9	9
5	4-Cl	7	8	8	8	8
6	4-F	8	7	7	6	–
7	2-OH	8	8	–	8	6
8	4-OH	7	–	9	6	8
9	2-OCH <sub>3</sub>	–	8	10	7	9
10	4-OCH <sub>3</sub>	6	7	9	7	7
11	2-CH <sub>3</sub>	7	8	8	8	6
12	4-CH <sub>3</sub>	7	7	–	6	8
13	3-NO <sub>2</sub>	8	6	7	7	7
14	4-NO <sub>2</sub>	6	8	8	8	7
Standard	Ampicillin	9	8	11	8	8
Control	DMSO	–	–	–	–	–

All substituents are found to possess an appreciable antibacterial activity on the microorganisms in general. All the compounds show excellent activities on *E.coli*, *K.pneumoniae* and *M.Luteus* species. The substituent 3-Cl and 2-OCH<sub>3</sub> have shown higher activity than ampicillin against *K.pneumoniae*. The substituent 4-OH and 2-OCH<sub>3</sub> have shown high activity against *S.aureus*.

### Antifungal sensitivity assay

Antifungal sensitivity assay has been performed using Kirby-Bauer [44] disc diffusion technique. PDA medium is prepared and sterilized as stated earlier. It is poured into the Petri-plate (ear bearing heating condition) which has been already filled with 1 ml of the fungal species. The plate is rotated clockwise and counter-clockwise for uniform spreading of the species. The discs are impregnated with the test solution. The test solution is prepared by dissolving 15 mg of the chalcone in 1ml of DMSO solvent. The medium is allowed to solidify and kept for 24 hours. Then the plates are visually examined and the diameter values of zone of inhibition are measured. Triplicate results are recorded by repeating the same procedure.

The clustered column chart, shown in Fig. 9 reveals that all the compounds have excellent antifungal activity against all the three fungal species namely *A.niger*, *M.spp* and *T.viride* except 4-Br substituent. The chalcones with H, 2-OH and 4-OH substituents have shown greater antifungal activity than those with the other substituents present in the series.

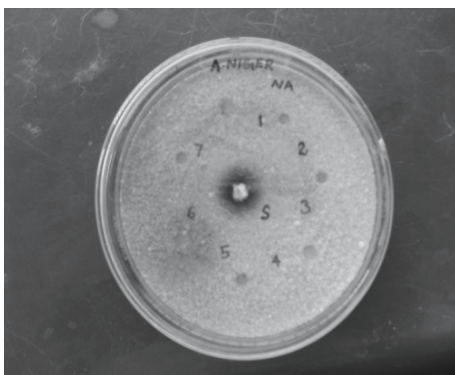


Plate-1

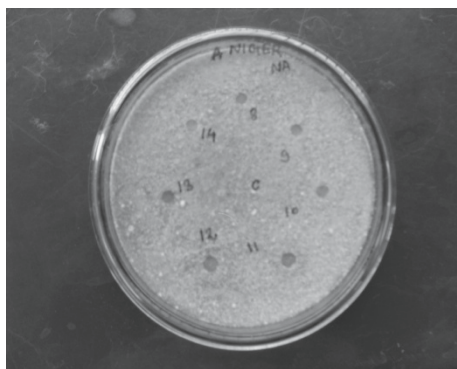


Plate-2



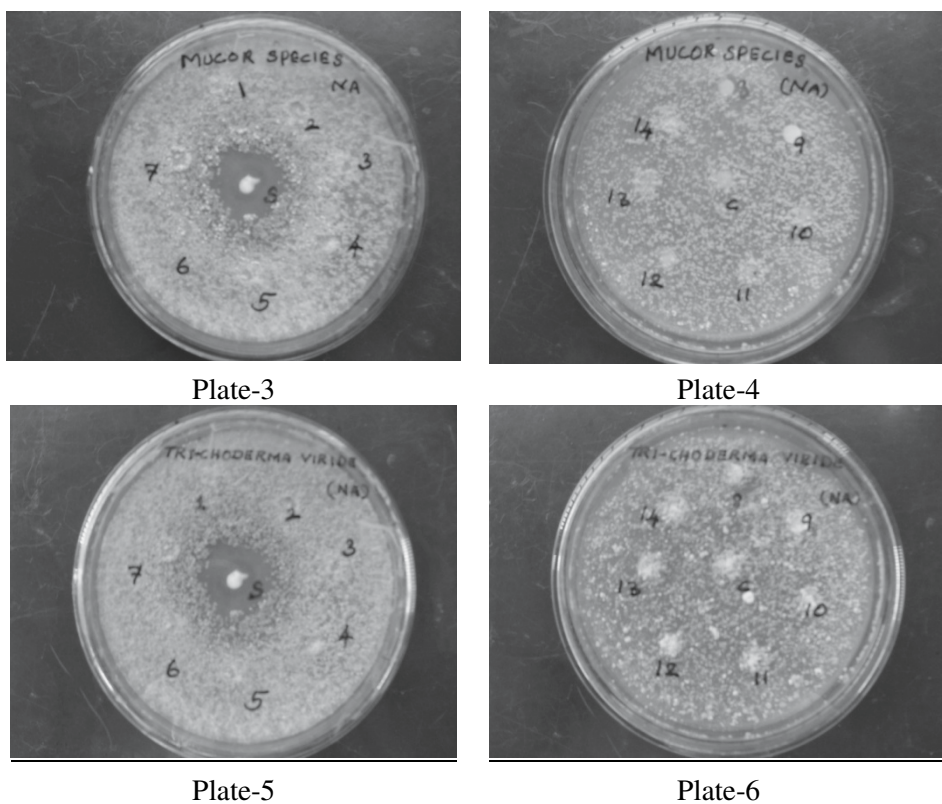


Fig. 8. Antifungal activities of 3-nitrophenyl chalcones.

Table 8. Antifungal activities of 3-nitrophenyl chalcones.

S.No.	X	Zone of Inhibition (mm)		
		<i>A.niger</i>	<i>M.spp</i>	<i>T.viride</i>
1	H	6	6	6
2	3-Br	–	6	6
3	4-Br	–	–	–
4	3-Cl	7	–	6
5	4-Cl	6	–	–
6	4-F	6	–	–
7	2-OH	6	6	6
8	4-OH	6	7	7



cont. Table 8.

S.No.	X	Zone of Inhibition (mm)		
9	2-OCH <sub>3</sub>	–	6	6
10	4-OCH <sub>3</sub>	–	–	6
11	2-CH <sub>3</sub>	6	6	–
12	4-CH <sub>3</sub>	6	–	6
13	3-NO <sub>2</sub>	–	–	6
14	4-NO <sub>2</sub>	–	6	–
Standard	Miconazole.	11	13	12

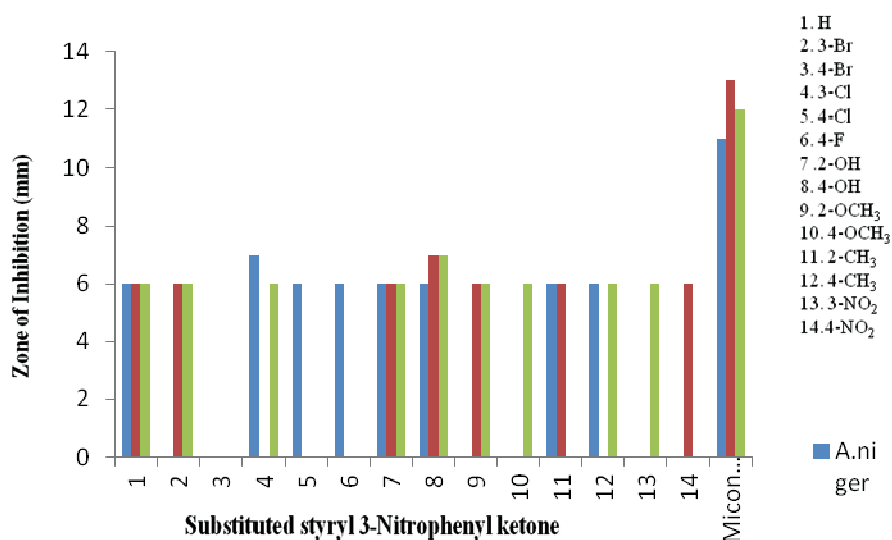


Fig. 9. Antifungal activities of 3-nitrophenyl chalcones-clustered column chart.

#### 4. CONCLUSIONS

The authors have developed an efficient catalytic method for the synthesis of chalcones by Crossed-Aldol reaction between aryl ketones and aldehydes, using a solvent free environmentally greener catalyst Fly-ash:PTS under microwave irradiation. This reaction protocol offers a simple, economical, environmentally friendly, non-hazardous, easier work-up procedure and good yields. The effect of substituents on the

spectral data and the antimicrobial activities of all the chalcones, synthesized, have been studied, in the present investigation.

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