

Solid Fly-Ash:PTS Catalyzed Green Aldol Condensation: Synthesis, Spectral Correlation, Antimicrobial and Insect Antifeedant Potent of Some Aryl Chalcones

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ABSTRACT

The waste harmful air pollutant fly-ash was converted into useful green catalyst fly-ash:PTS by mixing of appropriate quantity of fly-ash and *p*-toluene sulfonic acid. The prepared catalyst was characterised by infrared spectra and the morphology changes by SEM analysis. This solid fly-ash:PTS catalyst possess vigorous catalytic activity for aldol condensation of methyl ketones and substituted aldehydes in microwave irradiation. The yields of the chalcones are more than 80%. The purities of these chalcones were characterised by their physical constants and spectral data. The spectral frequencies of these chalcones have been correlated with Hammett substituent constants, F and R parameters. The Antimicrobial activities of these chalcones have been studied using Bauer-Kirby method. The insect antifeedant activities of these chalcones were measured using 4th instar Larvae *Achoea Janata L* with castor leaf discs.

Keywords: Solid fly-ash:PTS; Greener Aldol condensation; Spectral correlation.

INTRODUCTION

Homogeneous and heterogeneous catalytic Aldol and Crossed-Aldol condensation is a powerful tool for formation of carbon-carbon bond formation in many kinds of carbonyl compounds¹. Also microwave assisted solvent free Aldol and Crossed-Aldol condensation were useful synthesis of carbonyl compounds². Thermal aldol reaction is found to be sluggish and took longer time with low yields. However in the microwave heating conditions, the rate of reaction is fast as a result the reaction times are shorter and yield are high with easy isolation of products. Numerous green catalysts have been used for synthesizing chalcones such as silica-sulphuric acid^{1,3}, anhydrous zinc chloride⁴, Clay⁵, ground chemistry catalysts-grinding the reactants with sodium hydroxide⁶, aqueous alkali in lower temperature⁷, solid sulphonic acid from bamboo⁸, barium hydroxide⁹ anhydrous sodium bicarbonate¹⁰, microwave assisted

synthesis¹¹, fly-ash:water¹², fly-ash:H₂SO₄¹³ and sulfated titania¹⁴. Chalcones possess various multipronged activities such as antimicrobial¹⁵, antidepressants¹⁶, antiplosmodial¹⁷, anti-aids¹⁸ and insect antifeedant activities^{19, 20}. The infrared and nuclear magnetic resonance spectral data of these chalcones are useful for prediction of the ground state molecular equilibration and Hammett linearity. Recently Thirunarayanan et al have studied the effects of substituents on spectral group frequencies of pyrrolyl and furyl chalcones. Satisfactory and good Hammett correlations were observed in their work with these ketones. In the present investigation, the authors wish to report a new versatile catalyst fly-ash:PTS for efficient synthesizing chalcones by Crossed-Aldol condensation reaction. The yields of chalcones are more than 80%. The synthesized chalcones are characterized by their physical constants, Mass, IR and NMR spectral data as they

are unknown compounds so far. The purities of the known synthesized chalcones have been checked by their physical constants and their spectral data earlier published in literature. The spectral frequencies of these chalcones are correlated with Hammett substituent constants, F and R parameters. The antimicrobial activities of these chalcones have been studied using Bauer-Kirby²¹ method. The insect antifeedant activities of these chalcones were measured using 4th instar Larvae *Achoea Janata L* with Castor leaf discs^{19,20}.

EXPERIMENTAL

General

All chemicals used were purchased from Sigma-Aldrich Corporation (St. Louis, MO, USA) and E-Merck chemical company (Merck Limited, Mumbai, India). Fly ash was collected from Thermal Power Plant-II, Neyveli Lignite Corporation (NLC), Neyveli, Tamil Nadu, India. Melting points of all chalcones have been determined in open glass capillaries on Mettler FP51 melting point apparatus (Mettler-Toledo India Private Limited, Mumbai, India) and are uncorrected. The uv-visible absorption maxima of chalcones have been recorded in SHIMADZU-1650 spectrophotometer (λ_{max} , nm) in spectral grade methanol. Infrared spectra (KBr, 4000 to 400 cm^{-1}) have been recorded on AVATAR-300 Fourier transform spectrophotometer (Thermo Nicolet, USA). A BRUKER AMX-400 NMR spectrometer (BRUKER AXS GMBH, Krlsruhe, Germany) operating at 400 MHz has been utilized for recording ¹H spectra and 125.75 MHz for ¹³C spectra in CDCl₃ solvent using TMS as internal standard. Electron impact (70 eV) and chemical ionization mode FAB⁺ mass spectra have been recorded in SHIMADZU spectrometer.

Preparation of fly-ash:PTS catalyst

In a 50mL Borosil beaker, 1g of fly-ash and 0.8mL (0.5mol) 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°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 $\nu(cm^{-1})$: 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). Figures 1a and 1b evidence that the crystallinity is more in fly-ash. The spherical shaped particles are clearly seen at both magnifications in Fig 1a and 1b. Figure. 1a reveals and evidences the globular structure of pure fly-ash (round shaped particle). Also it is seen 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 (Figure 1).

Synthesis of chalcones

An appropriate equimolar quantities of aryl methyl ketones (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 for 8-10 minutes in a microwave oven (**Scheme 1**) (LG Grill, Intellowave, Microwave Oven, 160-800W) and then cooled to room temperature. The organic layer has been separated with dichloromethane which on evaporation yields the 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 mL) followed by drying in an oven at 100°C for 1h. This recycled catalyst has been made reusable for further reactions (scheme 1).

RESULTS AND DISCUSSION

Fly ash is a waste harmful air-pollutant sourced from the coal industries and thermal power plant and it has many chemical species^{10, 12, 13, 22} SiO₂, Fe₂O₃, Al₂O₃, CaO, MgO and insoluble residues. The waste fly-ash is converted into useful catalyst fly-ash: PTS by mixing of

appropriate quantity of fly-ash and *p*-toluene sulphonic acid. The sulphonic acid group and chemical species present in the fly-ash have enhanced the catalytic activity. During the course of the reactions these species are responsible for the promoting effects on condensation between the aryl ketone and aryl aldehydic groups leading to the formation of unsaturated ketone. The proposed general reaction mechanism is shown in Figure 2. In these experiments the products were isolated and the catalyst was washed with ethyl acetate, heated to 100°C then reusable for further five run reactions. There was no appreciable change in the percentage of yield of chalcones. In this protocol the reaction gave better yields of the chalcones during the condensation without any environmental discharge. The analytical and mass spectral data are presented in Table 1 (Figure 2 and Table 1).

We have investigated the catalytic effect of Fly-ash: PTS on the synthesis of substituted styryl 4'-cyclohexylphenyl ketone (**Entry 39**) by varying the catalyst quantity from 0.5 g to 1.5g. As the catalyst quantity is increased from 0.5g to 0.75g, the percentage of yield of product is increased from 86 to 87%. Further increase the catalyst amount there is no significant increasing of the percentage of product. This catalytic effect is shown in Figure 3. The optimum quantity of catalyst loading was found to be 0.75g. The reusability of this catalyst was studied the reaction of 4'-cyclohexyl phenyl methyl ketone and benzaldehyde. The reusability of catalyst on crossed-aldol reaction of 4'-cyclohexyl phenyl methyl ketone and benzaldehydes is given in Table 2. From the Table 2, first two runs gave 87% product. The third, fourth and fifth runs of reactions gave the yields 86.8%, 86.7% and 86.5 % of chalcones. There was no appreciable loss in its effect of catalytic activity was observed up to fifth run (Figure 3 and Table 2).

Spectral linearity

In the present study the spectral linearity of chalcones^{4, 17, 19, 22-26} has been studied by evaluating the substituent effects on the group frequencies. The assigned

group frequencies of all chalcones like UV-vis absorption λ_{\max} (nm), carbonyl stretches ν_{CO} -*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}), the vinyl hydrogen and chemical shifts δ (ppm), of H_{α} , H_{β} , C_{α} , C_{β} , CO are assigned and these frequencies are correlated with various substituent constants, Swain-Lupton's²⁷ F and R parameters.

UV-Vis and IR spectral study

The UV-Vis spectra of all synthesized chalcones were recorded in SHIMADZU-1650 spectrophotometer (λ_{\max} nm) in spectral grade methanol. The measured absorption maxima (λ_{\max} nm) of these chalcones (**Entries 39-50**) are presented in Table 3. These values are correlated with Hammett substituent constants, F and R parameters using single and multi-linear regression analysis^{4,17, 19, 22-26}. Hammett correlation involving the group frequencies and absorption maxima, the form of the Hammett equation employed is

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

where λ_0 is the frequency for the parent member of the series (Table 3).

The results of statistical analysis^{4,17,19,22-26} of these values with Hammett substituent constants are presented in Table 4. From Table 4, Hammett σ and σ^+ constants gave satisfactory correlations. The inductive, field and resonance parameters gave poor correlations with λ_{\max} of these chalcones. This is due to the inductive, field and resonances of the substituents were weak for predicting the reactivity on the absorption through resonance. This is evident with the resonance conjugative structure shown in Figure 4. (Table 4 and Figure 4).

The multi regression analysis of these frequencies of all ketones with inductive, resonance and Swain – Lupton's²⁷ constants produce satisfactory correlations as evident in equations (2 and 3).

$$\text{UV}(\lambda_{\max}) = 298.39 (\pm 12.924) + 8.853(\pm 2.029)\sigma_1 - 50.267(\pm 22.882) \sigma_R \dots(2)$$

($R = 0.959$, $n = 12$, $P > 95\%$)

$$\text{UV}(\lambda_{\max}) = 304.54 (\pm 11.518) + 1.752(\pm 0.475)F - 37.240(\pm 16.481)R \dots(3)$$

($R = 0.960$, $n = 12$, $P > 95\%$)

IR spectral study

The synthesized chalcones in the present study exist as *s-cis* and *s-trans* conformers respected with carbonyl and vinyl group and are shown in Figure 5. The carbonyl stretching frequencies (cm^{-1}) of these conformers of present study (**Entries 39-50**) are presented in Table 3. The stretching frequencies for carbonyl absorption are assigned based on the assignments made by Hays and Timmons²⁸ for *s-cis* and *s-trans* conformers at 1690 and 1670 cm^{-1} , respectively. As anticipated the lowest carbonyl frequency is observed in both the conformers when strongest electron withdrawing groups are present in phenyl ring while highest frequency is noted when strongest electro attracting group present in phenyl ring. A similar trend in absorption was earlier noted by Perjessy and Hrniciar²⁹ too whose investigated on chalcones demonstrates that *s-trans* conformers transmit more effectively than *s-cis* conformers due to reason stated earlier (Figure 5).

These data have been correlated with Hammett substituent constants and Swain-Lupton constants²⁷. In this correlation the structure parameter Hammett equation employed is as shown in the following equation:

$$v = \rho\sigma + v_0 \quad (4)$$

Where v is the carbonyl frequencies of substituted system and v_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. Hammett equation is one of the important tools for studying linear free energy relationships and it has been widely used in structures of the chemical reactivity of substituted aromatic system.

The results of single parameter statistical analysis of carbonyl frequencies with

substituent constants are presented in Table-4. From Table 4, the *s-cis* conformers the correlation of $\nu_{\text{C=O}}(\text{cm}^{-1})$ with Hammett σ , σ^+ and σ_1 constant is satisfactory. The remaining Hammett constants and F and R parameters fail in correlation. All correlations gave the positive ρ values except R parameter and it values implies that there is a normal substituent effects operates in all systems. This failure in correlation is due the conjugation between the substituent and the carbonyl group in chalcones as shown in Figure 5. In the *s-trans* conformers the correlation of $\nu_{\text{C=O}}(\text{cm}^{-1})$ with Hammett substituent constants, F and R parameters is satisfactory. All correlations gave the positive ρ values it values implies that there is a normal substituent effects operates in all systems. The correlation of CH *in-plane* modes with Hammett σ constant and R parameters were satisfactorily. The CH *in-plane* modes gave satisfactory correlation with Hammett σ^+ constant. The remaining substituent constants and F and R parameters were fail in the correlation of both the modes for all ketones. All correlation were fails for CH=CH *out of plane* and C=C *out of plane* modes with Hammett constants, F and R parameters. All correlation gave positive ρ values and this reveals that there is a normal substituent effects operated in all ketones. This failure in correlation is due the conjugation between the substituent and the carbonyl group in chalcones as shown in Figure 4.

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_1 and σ_R constants or Swain-Lupton's²⁷, F and R parameters. The correlation equations for *s-cis*, *s-trans* and *deformation modes* are given in equations 5-16.

$$\nu_{\text{CO}_{s-cis}}(\text{cm}^{-1}) = 1655.98(\pm 2.2614) + 3.418(\pm 1.554)\sigma_1 + 3.476(\pm 1.0039)\sigma_R \quad \dots(5)$$

($R = 0.938$, $n = 12$, $P > 90\%$)

$$\nu_{\text{CO}_{s-cis}}(\text{cm}^{-1}) = 1654.69(\pm 2.093) + 3.480(\pm 4.493)F - 2.030(\pm 2.996)R \quad \dots(6)$$

($R = 0.931$, $n = 12$, $P > 90\%$)

$$\nu\text{CO}_{s\text{-trans}}(\text{cm}^{-1}) = 1599.02(\pm 3.7807) + 8.197(\pm 7.614)\sigma_I + 15.167(\pm 6.69)\sigma_R \quad \dots(7)$$

($R = 0.967, n = 12, P > 95\%$)

$$\nu\text{CO}_{s\text{-trans}}(\text{cm}^{-1}) = 1597.12(\pm 3.409) + 9.952(\pm 7.244)F + 11.121(\pm 4.878)R \quad \dots(8)$$

($R = 0.927, n = 12, P > 90\%$)

$$\nu\text{CH}_{ip}(\text{cm}^{-1}) = 1174.62(\pm 6.092) + 4.152(\pm 12.270)\sigma_I + 19.116(\pm 10.786)\sigma_R \quad \dots(9)$$

($R = 0.953, n = 12, P > 95\%$)

$$\nu\text{CH}_{ip}(\text{cm}^{-1}) = 1170.09(\pm 6.429) + 2.659(\pm 13.662)F - 3.225(\pm 9.200)R \quad \dots(10)$$

($R = 0.913, n = 12, P > 90\%$)

$$\nu\text{CH}_{op}(\text{cm}^{-1}) = 783.211(\pm 18.06) + 35.374(\pm 36.380)\sigma_I - 62.233(\pm 31.982)\sigma_R \quad \dots(11)$$

($R = 0.956, n = 12, P > 95\%$)

$$\nu\text{CH}_{op}(\text{cm}^{-1}) = 802.960(\pm 19.066) + 25.581(\pm 40.515)F + 11.248(\pm 27.282)R \quad \dots(12)$$

($R = 0.924, n = 12, P > 90\%$)

$$\nu\text{CH}=\text{CH}_{op}(\text{cm}^{-1}) = 1025.42(\pm 2.784) - 7.040(\pm 5.608)\sigma_I - 5.469(\pm 4.930)\sigma_R \quad \dots(13)$$

($R = 0.952, n = 12, P > 95\%$)

$$\nu\text{CH}=\text{CH}_{op}(\text{cm}^{-1}) = 1025.07(\pm 2.208) - 6.444(\pm 4.691)F - 6.963(\pm 3.159)R \quad \dots(14)$$

($R = 0.966, n = 12, P > 95\%$)

$$\nu\text{C}=\text{C}_{op}(\text{cm}^{-1}) = 524.27(\pm 21.109) + 49.543(\pm 42.513)\sigma_I + 6.687(\pm 37.374)\sigma_R \quad \dots(15)$$

($R = 0.937, n = 12, P > 90\%$)

$$\nu\text{C}=\text{C}_{op}(\text{cm}^{-1}) = 528.30(\pm 19.634) + 36.695(\pm 41.722)F + 6.539(\pm 28.09)R \quad \dots(16)$$

($R = 0.929, n = 12, P > 90\%$)

¹H NMR spectral study

The ¹H NMR spectra of synthesized chalcones were recorded in deuteriochloroform solutions employing tetramethylsilane (TMS) as internal standard. The signals of the ethylenic protons 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 δ(ppm) of all ketones (**Entries 39-50**) were presented in Table 5 (Table 5).

In nuclear magnetic resonance spectra, the proton or the ¹³C 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 δ₀ 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 ^{4,17, 19, 22-26} are presented in Table 6. A satisfactory correlations obtained for H_α chemical shifts with Hammett σ, σ⁺, σ_R substituent constants and R parameters. A poor correlation is obtained for H_β proton chemical shifts (ppm) with Hammett sigma constants, F and R parameters. All correlations gave positive ρ values were obtained in all correlation and are evident for the normal substituent effect operates in all chalcones for both proton chemical shifts. The failure in the correlation is due to the reasons stated in earlier and the conjugative structure shown in Figure 4.

Here insert Table 6

Application of Swain-Lupton²⁷ treatment to the relative chemical shifts of H_α and H_β with F and R values is successful with resonance, inductive and fail with F & R parameter generates the multi regression equations 18-21.

$$\delta\text{H}_{\alpha}(\text{ppm}) = 7.561(\pm 0.057) + 0.436(\pm 0.115)\sigma_I + 0.330(\pm 0.101)\sigma_R \quad \dots(18)$$

($R = 0.974, n = 14, P > 95\%$)

$$\delta\text{H}_{\alpha}(\text{ppm}) = 7.747(\pm 0.074) + 0.101(\pm 0.059)F + 0.059(\pm 0.007)R \quad \dots(19)$$

($R = 0.927, n = 12, P > 90\%$)

$$\delta H_{\beta}(\text{ppm}) = 7.825(\pm 0.023) - 0.434(\pm 0.046)\sigma_1 + 0.056(\pm 0.001)\sigma_R \quad \dots(20)$$

($R = 0.945, n = 12, P > 90\%$)

$$\delta H_{\beta}(\text{ppm}) = 7.805(\pm 0.023) - 0.183(\pm 0.049)F + 0.433(\pm 0.033)R \quad \dots(21)$$

($R = 0.912, n = 12, P > 90\%$)

¹³C NMR spectral study

Spectral analysts, organic chemists and scientists^{4,17, 19, 22-26} have made extensive study of ¹³C 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 5. The results of statistical analysis are given in Table 6. A satisfactory correlations were obtained for CO carbon chemical shifts of these ketones with Hammett sigma substituent constants, F and R parameters. The Hammett σ, σ⁺,

σ₁ constants gave a satisfactory correlations with C_α chemical shifts. The C_β chemical shifts are failing in all correlation. The rho values are found to be positive for all correlations. The failure in correlations are due to reasons stated earlier with the resonance conjugative structure shown in Figure 4.

The Swain Lupton's²⁷ parameter correlations were satisfactorily obtained within these carbon chemical shifts and the regression equations are given in 22-27.

$$\delta \text{CO}(\text{ppm}) = 190.69(\pm 2.036) + 3.570(\pm 1.102)\sigma_1 + 3.686(\pm 1.606)\sigma_R \quad \dots(22)$$

($R = 0.944, n = 12, P > 90\%$)

$$\delta \text{CO}(\text{ppm}) = 190.21(\pm 1.944) + 3.297(\pm 2.132)F + 1.464(\pm 0.782)R \quad \dots(23)$$

($R = 0.930, n = 12, P > 90\%$)

$$\delta C_{\alpha}(\text{ppm}) = 121.93 (\pm 1.216) + 2.970(\pm 0.449)\sigma_1 + 4.184(\pm 2.153)\sigma_R \quad \dots(24)$$

($R = 0.964, n = 12, P > 95\%$)

$$\delta C_{\alpha}(\text{ppm}) = 121.38 (\pm 1.279) + 2.823(\pm 0.718)F + 1.862(\pm 0.830)R \quad \dots(25)$$

($R = 0.944, n = 12, P > 90\%$)

$$\delta C_{\beta}(\text{ppm}) = 143.86 (\pm 2.786) + 9.989(\pm 5.611)\sigma_1 + 1.729(\pm 0.933)\sigma_R \quad \dots(26)$$

($R = 0.953, n = 12, P > 95\%$)

$$\delta C_{\beta}(\text{ppm}) = 142.66 (\pm 2.399) + 11.130(\pm 5.098)F - 0.976(\pm 0.433)R \quad \dots(27)$$

($R = 0.958, n = 12, P > 95\%$)

Antimicrobial activities

Chalcones possess a wide range of biological activities such as antibacterial^{30, 31}, antifungal^{30, 31}, antiviral³², antifeedant^{20,34}, anticancer^{35,31}, antimalarial³⁵, antituberculosis³⁶, antiAIDS³⁷ and antioxidant³⁸ activities. These multipronged activities present in different chalcones are examined against respective microbes-bacteria's and fungi.

Antibacterial sensitivity assay

Antibacterial sensitivity assay was performed using Kirby-Bauer²¹ disc diffusion technique. In each Petri plate about 0.5 ml of the test bacterial sample was spread uniformly over the solidified Mueller Hinton agar using sterile glass spreader. Then the discs with 5mm diameter made up of Whatmann No.1 filter paper, impregnated with the solution of the compound were placed on the medium using sterile forceps. The plates were

incubated for 24 hours at 37°C by keeping the plates upside down to prevent the collection of water droplets over the medium. After 24 hours, the plates were visually examined and the diameter values of the zone of inhibition were measured. Triplicate results were recorded by repeating the same procedure.

The antibacterial activities of all prepared chalcones (**Entries 39-50**) have been studied against two gram positive pathogenic strains *Staphylococcus aureus*, *Enterococcus faecalis* and four gram negative strains *Escherichia coli*, *Klebsiella species*, *Pseudomonas* and *Proteus vulgaris*. The disc diffusion technique was followed using the Kirby-Bauer²¹ method, at a concentration of 250 µg/mL with Ampicillin and Streptomycin used as the standard drugs. The measured antibacterial activities of all chalcones are presented in Table 7. Four compounds **40, 41, 45** and **47** showed

maximum zone of inhibition against *Escherichia coli*, with greater than 20 mm compared to the chalcones **39**, **42**, **43**, **44**, **46**, **48**, **49**, and **50**. The chalcones **40**, **41**, **45** and **47** were active against *Staphylococcus*, showing maximum inhibition. The other epoxy ketones were found to be less effective against *S. aureus*. The oxirane derivatives **39** and **48** were more active against *Pseudomonas* showing greater than 20 mm zone of inhibition and the other derivatives showed the zone of inhibitions between 12-19 mm. The chalcones **39** and **48** are effective against *Klebsiella* with 20-24 mm zone of inhibition while the other keto chalcones showed a moderate activity. The chalcone **47** is active when it is screened against *P. vulgaris* and the other compounds are less effective. The chalcones **40**, **41** and **47** showed moderate activities against *E-faecalis* when they are screened with 20-24 mm zone of inhibition (Table 7).

Antifungal activity

Antifungal sensitivity assay was performed using Kirby-Bauer²¹ disc diffusion technique. PDA medium was prepared and sterilized as above. It was poured (ear bearing heating condition) in the Petri-plate which was already filled with 1 ml of the fungal species. The plate was rotated clockwise and counter clock-wise for uniform spreading of the species. The discs were impregnated with the test solution. The test solution was prepared by dissolving 15mg of the chalcone in 1ml of DMSO solvent. The medium was allowed to solidify and kept for 24 hours. Then the plates were visually examined and the diameter values of zone of inhibition were measured. Triplicate results were recorded by repeating the same procedure.

The study of antifungal activities of all chalcones (Entries **39-50**) has been done with *Candida albicans* as the fungal strain using the disc diffusion technique and the other two strains *Penicillium* species and *Aspergillus niger*, the dilution method was adopted. The drug dilution was kept as 50 µg/mL. *Griseofulvin* has been taken as the standard drug. The observed antifungal activities of all chalcones are

presented in Table 8. The study of antifungal activities of all chalcones against *C. albicans*, showed that the three compounds **41**, **42** and **47** are effective with 20 mm as the zone of inhibition in 250 µg/ disc while chalcones **45** and **46** are active with 13-19 mm zone of inhibition and the compounds **39**, **40**, **47-50** are the least active with 8-12 mm zone of inhibitions. Compounds **41**, **42**, **45** and **47** are visible against *Penicillium* species, in the development of the fungal colony and 2-3 colonies are recorded for the compound **47**. The inhibition of chalcones against *A.niger* was less in two compounds **41**, **42** and **45** being highly active followed by **46**. Presence of a methoxy, methyl, dimethyl and bromo substituents are responsible for antimicrobial activities of chalcones (Table 8).

Insect antifeedant activity

The multipronged activities present in different epoxy ketones are intended to examine their insect antifeedant activities against castor *semilooper*. The larvae of *Achoea Janata* L were reared as described on the leaves of castor *Ricinus communis* in the laboratory at the temperature range of 26°C ±1°C and a relative humidity of 75-85%. The leaf – disc bioassay method³⁸ was used against the 4th instar larvae to measure the antifeedant activity. The 4th instar larvae were selected for testing because the larvae at this stage feed very voraciously.

Measurement of insect antifeedant activity of chalcones

Leaf discs of a diameter of 1.85 cm were punched from castor leaves with the petioles intact. All chalcones. Insect antifeedant activities of substituted styryl 4'-cyclohexenyl ketones (Entries **39-50**) were dissolved in acetone at a concentration of 200 ppm dipped for 5 minutes. The leaf discs were air-dried and placed in one litre beaker containing little water in order to facilitate translocation of water. Therefore the leaf discs remains fresh throughout the duration of the test, 4th instar larvae of the test insect, which had been preserved on the leaf discs of all chalcones (Entries **39-50**) and allowed to

feed on them for 24 hours. The area of the leaf discs consumed were measured by Dethlers³⁷ method. The observed antifeedant activity of chalcones was presented in Table 9 (Table 9).

The results of the antifeedant activity of keto chalcones presented in Table 10 reveal that the compounds **40-43** are found to reflect remarkable antifeedant among all other chalcones. This test is performed with the insects which took only two-leaf disc soaked under the solution of this compound^{19,20}. Compounds **40** showed enough antifeedant activity but their activities are lesser than **41**. Further, compound **40** was subjected to measure the antifeedant activity at different 50, 100, 150 ppm concentrations and the observation reveals that as the concentrations are decreases, the activity also decreases. From the results in Table 8, it is observed that the chalcone **40**

showed an appreciable antifeedant activity at 150 ppm concentration (Table 10).

CONCLUSIONS

We have prepared a solid acidic fly-ash:PTS green catalyst from the waste pollutant fly-ash from thermal plant industry. We developed an efficient crossed-aldol condensation for synthesis of chalcones using a versatile fly-ash:PTS catalyst. This reaction protocol offers a simple, economical, environmentally friendly, non-hazards, easier work-up procedure and good yields. The effects of substituent on the group frequencies, antimicrobial and insect antifeedant activities of chalcones have been studied

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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 $\text{Ar}-\text{CO}-\text{CH}_3 + \text{Ar}'-\text{CHO} \rightarrow \text{Ar}-\text{CO}-\text{CH}=\text{CH}-\text{Ar}'$ under microwave irradiation

Entry	Ar	Ar'	Product	M.W.	Yield (%)	M.p (°C)	Mass (m/z)
1	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅ COCH=CHC ₆ H ₅	208	86	55-56 (55-58) ¹³	---
2	4-N(CH ₃) ₂ C ₆ H ₄	C ₆ H ₅	4-N(CH ₃) ₂ C ₆ H ₄ COCH=CHC ₆ H ₅	294	85	87-88 (87-88) ¹³	---
3	C ₆ H ₅	C ₁₀ H ₇ (1-Naph)	C ₆ H ₅ COCH=CHC ₁₀ H ₇	273	85	104-105 (104-105) ¹³	---
4	C ₆ H ₅	C ₈ H ₆ N(3-Indole)	C ₆ H ₅ COCH=CHC ₈ H ₆ N	262	86	140-141 (140) ¹³	---
5	C ₆ H ₅	4-OHC ₆ H ₄	C ₆ H ₅ COCH=CHC ₆ H ₄ OH	291	86	122-123 (122) ¹³	---
6	C ₆ H ₅	4-OCH ₃ C ₆ H ₄	C ₆ H ₅ COCH=CHC ₆ H ₄ OCH ₃	291	84	164-165 (164) ¹³	---
7	4-NH ₂ C ₆ H ₅	C ₄ H ₃ (3-Furyl)	C ₆ H ₅ COCH=CHC ₄ H ₃	213	82	120-121 (119-120) ¹³	---
8	4-NH ₂ C ₆ H ₄	C ₆ H ₅	4-NH ₂ C ₆ H ₄ COCH=CHC ₆ H ₅	223	82	98-99 (98-99) ¹³	---
9	4-NH ₂ C ₆ H ₄	4-N(C ₂ H ₅) ₂ C ₆ H ₄	4-NH ₂ C ₆ H ₄ COCH=CHC ₆ H ₄ N(CH ₃) ₂	294	83	90-91 (90-91) ¹³	---
10	4-NH ₂ C ₆ H ₄	2,6-Cl ₂ C ₆ H ₃	4-NH ₂ C ₆ H ₄ COCH=CHC ₆ H ₃ Cl ₂	291	80	98-99 (98-99) ¹³	---
11	4-NH ₂ C ₆ H ₄	C ₁₀ H ₇ (1-Naph)	4-NH ₂ C ₆ H ₄ COCH=CHC ₁₀ H ₇	273	83	124-125 (124-125) ¹³	---
12	4-F-C ₆ H ₄	C ₆ H ₅	4-FC ₆ H ₄ COCH=CHC ₆ H ₅	226	80	49-50 (49-50) ¹³	---
13	2, 4-Cl ₂ C ₆ H ₃	C ₆ H ₅	2,4-Cl ₂ C ₆ H ₃ COCH=CHC ₆ H ₅	276	84	80-82 (80-81) ¹³	---
14	3, 4-Cl ₂ C ₆ H ₃	C ₆ H ₅	3,4-Cl ₂ C ₆ H ₃ COCH=CHC ₆ H ₅	276	84	100-101 (100-101) ¹³	---
15	4-(OH)C ₆ H ₄	C ₆ H ₅	2,5-(OH)C ₆ H ₃ COCH=CHC ₆ H ₅	226	80	63-64 (63-64) ¹³	---
16	C ₁₀ H ₇ (1-Naph)	C ₆ H ₅	C ₁₀ H ₇ COCH:CHC ₆ H ₅	258	84	100-102 (100-102) ¹³	---
17	4-BrC ₁₀ H ₆ (1-Naph)	C ₆ H ₅	4-BrC ₁₀ H ₆ COCH=CHC ₆ H ₅	396	85	103-104 (103-104) ¹³	---
18	4-ClC ₁₀ H ₆ (1-Naph)	C ₆ H ₅	4-ClC ₁₀ H ₆ COCH=CHC ₆ H ₅	292	84	122-123	---

						(122-123) ¹³	
19	4-OCH ₃ C ₁₀ H ₆ (1-Naph)	C ₆ H ₅	4-OCH ₃ C ₁₀ H ₆ COCH=CHC ₆ H ₅	310	83	113-114 (113-114) ¹³	---
20	4-CH ₃ C ₁₀ H ₆ (1-Naph)	C ₆ H ₅	4-CH ₃ C ₁₀ H ₆ COCH=CHC ₆ H ₅	284	84	98-99 (98-99) ¹³	---
21	C ₁₀ H ₇ (2-Naph)	C ₆ H ₅	C ₁₀ H ₇ COCH=CHC ₆ H ₅	258	84	104-105 (104-105) ¹³	---
22	6-OCH ₃ C ₁₀ H ₆ (2-Naph)	C ₆ H ₅	6-OCH ₃ C ₁₀ H ₆ COCH=CHC ₆ H ₅	310	85	67-68 (67-68) ¹³	---
23	6-CH ₃ C ₁₀ H ₆ (2-Naph)	C ₆ H ₅	6-CH ₃ C ₁₀ H ₆ COCH=CHC ₆ H ₅	284	84	123-124 (123-124) ¹³	---
24	C ₁₃ H ₉ (2-Fluorene)	C ₆ H ₅	C ₁₃ H ₉ COCH=CHC ₆ H ₅	296	80	150-151 (150-151) ¹³	---
25	C ₁₂ H ₉ (Biphenyl)	C ₆ H ₅	C ₁₂ H ₉ COCH=CHC ₆ H ₅	284	85	153-154 (153-154) ¹³	---
26	C ₄ H ₃ O(2-Furyl)	C ₆ H ₅	C ₄ H ₃ OCOCH=CHC ₆ H ₅	198	85	80-81 (80-81) ¹³	---
27	5-CH ₃ C ₄ H ₂ N(2-Pyrrole)	C ₆ H ₅	5-CH ₃ C ₄ H ₂ NCOCH=CHC ₆ H ₅	210	84	137-138 (137-138) ¹³	---
28	C ₄ H ₃ S(2-Thienyl)	C ₆ H ₅	C ₄ H ₃ SCOCH=CHC ₆ H ₅	204	85	112-113 (112-113) ¹³	---
29	C ₁₄ H ₁₀ (Anthracene)	C ₆ H ₅	C ₁₄ H ₁₀ COCH=CHC ₆ H ₅	308	82	124-125 (124-125) ¹³	---
30	5-BrC ₄ H ₂ S(2-Thienyl)	C ₆ H ₅	5-BrC ₄ H ₂ SCOCH=CHC ₆ H ₅	292	86	107-110 (107-110) ¹³	---
31	5-BrC ₄ H ₂ S(2-Thienyl)	4-BrC ₆ H ₄	5-BrC ₄ H ₂ SCOCH=CHC ₆ H ₄ Br	371	84	173-174 (173-174) ¹³	---
32	5-BrC ₄ H ₂ S(2-Thienyl)	2-ClC ₆ H ₄	5-BrC ₄ H ₂ SCOCH=CHC ₆ H ₄ Cl	326	84	143-145 (143-145) ¹³	---
33	5-BrC ₄ H ₂ S(2-Thienyl)	4-ClC ₆ H ₄	5-BrC ₄ H ₂ SCOCH=CHC ₆ H ₄ Cl	326	85	156-157 (115-157) ¹³	---
34	5-BrC ₄ H ₂ S(2-Thienyl)	4-N(CH ₃) ₂ C ₆ H ₄	5-BrC ₄ H ₂ SCOCH=CHC ₆ H ₄ N(CH ₃) ₂	335	82	142-143 (142-143) ¹³	---
35	5-BrC ₄ H ₂ S(2-Thienyl)	4-FC ₆ H ₄	5-BrC ₄ H ₂ SCOCH=CHC ₆ H ₄ F	309	80	164-165 (164-165) ¹³	---
36	5-BrC ₄ H ₂ S(2-Thienyl)	4-IC ₆ H ₄	5-BrC ₄ H ₂ SCOCH=CHC ₆ H ₄ I	416	81	184-185 (184-185) ¹³	---
37	5-BrC ₄ H ₂ S(2-Thienyl)	4-OCH ₃ C ₆ H ₅	5-BrC ₄ H ₂ SCOCH=CHC ₆ H ₄ OCH ₃	322	83	148-149 (148-149) ¹³	---
38	5-BrC ₄ H ₂ S(2-Thienyl)	4-CH ₃ C ₆ H ₅ C ₆ H ₅	5-BrC ₄ H ₂ SCOCH=CHC ₆ H ₄ CH ₃	306	82	151-152 (151-152) ¹³	---
39	4-Cyclohexylphenyl	C ₆ H ₅	4-C ₆ H ₁₁ C ₆ H ₄ COCH=CHC ₆ H ₅	290	87		290M+, 289, 213, 207, 200, 187, 159, 131, 103, 90, 83, 77
40	4-Cyclohexylphenyl	3-BrC ₆ H ₄	4-C ₆ H ₁₁ C ₆ H ₄ COCH=CHC ₆ H ₄ Br	369	86		369M+, 371M2+, 289, 284, 213, 208, 200, 187, 180, 167, 159, 83, 77
41	4-Cyclohexylphenyl	3-ClC ₆ H ₄	4-C ₆ H ₁₁ C ₆ H ₄ COCH=CHC ₆ H ₄ Cl	325	85		325M+, 327M2+, 290, 289, 241, 200, 213, 187, 165, 159, 124, 111, 83, 77, 37, 35
42	4-Cyclohexylphenyl	4-ClC ₆ H ₄	4-C ₆ H ₁₁ C ₆ H ₄ COCH=CHC ₆ H ₄ Cl	325	84		325M+, 290, 327M2+, 241, 200, 189, 213, 187, 165, 159, 124, 111, 83, 77,
43	4-Cyclohexylphenyl	4-FC ₆ H ₄	4-C ₆ H ₁₁ C ₆ H ₄ COCH=CHC ₆ H ₄ F	308	82		308M+, 289, 310M2+, 225, 213, 200, 187, 159, 149, 121, 108, 95, 83, 77, 21, 19
44	4-Cyclohexylphenyl	4-OHC ₆ H ₄	4-C ₆ H ₁₁ C ₆ H ₄ COCH=CHC ₆ H ₄ OH	306	84		306M+, 289, 223, 213, 200, 187, 159, 149, 147, 119, 106, 93, 83, 67
45	4-Cyclohexylphenyl	2-OCH ₃ C ₆ H ₄	4-C ₆ H ₁₁ C ₆ H ₄ COCH=CHC ₆ H ₄ OCH ₃	320	85		320M+, 289, 237, 213, 200,

							187, 161, 159, 107, 83, 77
46	4-Cyclohexylphenyl	4-OCH ₃ C ₆ H ₄	4-C ₆ H ₁₁ C ₆ H ₄ CO CH=CHC ₆ H ₄ OCH ₃	320	85		320M+, 289, 237, 213, 200, 187, 161, 159, 107, 83
47	4-Cyclohexylphenyl	4-CH ₃ C ₆ H ₄	4-C ₆ H ₁₁ C ₆ H ₄ CO CH=CHC ₆ H ₄ CH ₃	304	84		304M+, 289, 221, 213, 200, 187, 159, 154, 145, 117, 104, 91, 83
48	4-Cyclohexylphenyl	3-NO ₂ C ₆ H ₄	4-C ₆ H ₁₁ C ₆ H ₄ CO CH=CHC ₆ H ₄ NO ₂	335	83		335M+, 289, 252, 213, 200, 187, 159, 148, 135, 83, 45
49	4-Cyclohexylphenyl	3-NO ₂ C ₆ H ₄	4-C ₆ H ₁₁ C ₆ H ₄ CO CH=CHC ₆ H ₄ NO ₂	335	85		335M+, 289, 271, 252, 213, 200, 187, 159, 148, 135, 83, 77, 45
50	4-Cyclohexylphenyl	3-OPhC ₆ H ₄	4-C ₆ H ₁₁ C ₆ H ₄ CO CH=CHC ₆ H ₄ OPh	382	83		382M+, 380, 297, 289, 221, 213, 200, 193, 187, 167, 159, 91, 83, 77, 71

Table 2: Reusability of catalyst on condensation of 4-cyclohexylphenyl methyl ketone (2 mmol) and benzaldehydes (2 mmol) under microwave irradiation (Entry 39).

Run	1	2	3	4	5
Yield	87	87	86.8	86.7	86.5

Table 3: Uv-Vis λ_{max} (nm) and infrared spectral data (ν , cm⁻¹) of substituted styryl 4-cyclohexylphenyl ketones (Entries 39-50).

Entry X	λ_{max}	ν CO _(s-cis)	ν CO _(s-trans)	ν CH _{ip}	ν CH _{op}	ν CH=CH _{op}	ν	C=C _{op}
39	H	308.80	1656.37	1599.75	1178.07	764.60	1025.99	566.98
40	3-Br	299.80	1659.68	1602.66	1178.41	782.47	1025.47	575.08
41	3-Cl	302.60	1660.58	1601.64	1181.22	788.61	1025.40	553.42
42	4-Cl	308.40	1656.28	1600.24	1180.31	783.56	1018.15	517.91
43	4-F	309.80	1656.67	1601.42	1160.08	818.57	1022.07	527.74
44	4-OH	337.20	1653.64	1594.59	1173.72	822.64	1033.43	549.82
45	4-OCH ₃	352.80	1660.27	1579.40	1170.68	824.13	1023.46	540.83
46	4-OCH ₃	316.40	1653.84	1595.47	1172.37	822.26	1029.74	546.90
47	4-CH ₃	280.00	1654.97	1598.26	1161.64	810.96	465.43	1022.63
48	3-NO ₂	294.80	1657.13	1603.91	1177.27	808.12	1021.27	577.86
49	4-NO ₂	316.40	1658.72	1603.81	1177.21	822.51	1019.11	531.18
50	3-OPh	303.60	1649.32	1602.06	1150.68	876.71	1022.07	539.38

Table 4: Results of statistical analysis of Uv-vis and infrared spectral frequencies of substituted styryl 4-cyclohexyl phenyl ketones (Entries 39-50) with Hammett substituent constants, F and R parameters.

Frequency	Constants	r	l	p	s	n	Correlated derivatives
Uv λ_{max}	σ	0.954	316.99	-29.035	18.59	10	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 3-NO ₂ ,
	σ^+	0.953	312.06	-20.026	18.76	10	4 H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 3-NO ₂ , 4-NO ₂ , -NO ₂
	σ^l	0.801	313.61	-1.402	22.18	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	σ^R	0.858	301.98	-48.871	18.01	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	F	0.800	313.27	-0.462	22.18	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	R	0.860	305.22	-37.193	17.72	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
ν CO _{s-cis} (cm ⁻¹)	σ	0.926	1656.16	2.173	3.27	10	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.960	1656.63	3.452	2.71	10	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂

	σ I	0.928	1654.93	4.127	3.25	11	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ R	0.731	1657.36	4.015	3.22	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	F	0.823	1655.17	3.327	3.30	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	R	0.720	1656.04	1.937	3.32	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
$\nu\text{CO}_{s\text{-trans}}(\text{cm}^{-1})$	σ	0.974	1596.90	12.666	4.70	11	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	$\sigma+$	0.958	1598.96	7.003	5.73	11	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	σ I	0.937	1594.43	11.291	6.56	11	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	σ R	0.916	1602.34	16.460	5.56	11	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	F	0.936	1594.51	10.614	6.58	11	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	R	0.957	1601.01	11.390	5.76	11	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
$\nu\text{CH}_p(\text{cm}^{-1})$	σ	0.948	1170.91	6.649	9.58	10	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	$\sigma+$	0.718	1172.22	8.162	8.73	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	σ I	0.852	1168.83	8.052	9.79	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	σ R	0.805	1176.30	19.771	8.48	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	F	0.811	1170.85	2.467	9.95	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	R	0.953	1171.13	-3.153	9.91	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
$\nu\text{CH}_{op}(\text{cm}^{-1})$	σ	0.810	811.44	-7.577	30.11	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	$\sigma+$	0.942	809.30	21.760	27.41	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	σ I	0.817	802.05	22.676	29.81	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	σ R	0.849	797.53	-56.655	26.29	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	F	0.820	800.32	26.250	29.60	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	R	0.814	812.95	11.938	29.97	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
$\nu\text{CH}=\text{CH}_{op}(\text{cm}^{-1})$	σ	0.860	1024.94	-6.524	3.62	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	$\sigma+$	0.862	1023.81	-4.775	3.54	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	σ I	0.841	1027.07	-8.156	4.11	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	σ R	0.738	1022.56	-6.580	4.17	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	F	0.736	1026.70	-6.858	4.21	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	R	0.756	1022.55	-7.137	3.73	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
$\nu\text{C}=\text{C}_{op}(\text{cm}^{-1})$	σ	0.729	538.03	22.378	30.18	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	$\sigma+$	0.725	541.75	13.728	30.53	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	σ I	0.737	522.25	50.908	29.28	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	σ R	0.812	544.34	14.499	31.35	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	F	0.728	526.76	37.084	30.29	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	R	0.680	542.63	7.528	31.47	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh

r= correlation coefficient; I= intercept; p=slope; s= standard deviation; n= number of derivatives

Table 5: The NMR spectral data of substituted styryl 4-cyclohexylphenyl ketones (Entries 39-50)

Entry	X	H _a	H _b	CO	C _a	C _β
39	H	7.573	7.837	190.09	122.18	144.35
40	<i>m</i> -Br	7.347	7.736	197.94	127.05	153.79
41	<i>m</i> -Cl	7.559	7.752	189.64	123.35	142.58
42	<i>p</i> -Cl	7.533	7.771	189.75	122.6	153.72
43	<i>p</i> -F	7.492	7.793	189.83	121.88	153.63
44	<i>p</i> -OH	7.451	7.808	190.1	119.89	144.18
45	<i>o</i> -OCH ₃	7.447	7.805	190.13	119.91	144.18
46	<i>p</i> -OCH ₃	7.451	7.808	190.11	119.89	144.18
47	<i>p</i> -CH ₃	7.526	7.814	197.2	121.21	144.34
48	<i>m</i> -NO ₂	7.682	7.844	197.17	122.05	148.75
49	<i>p</i> -NO ₂	7.67	7.83	189.16	124.2	148.5
50	<i>m</i> -OPh	7.3	7.764	189.94	120.65	143.56

Table 6: Results of statistical analysis of NMR spectral frequencies δ (ppm) of substituted styryl 4-cyclohexyl phenyl ketones(Entries 39-50) with Hammett substituent constants, F and R parameters

Frequency	Constants	r	l	ρ	s	n	Correlated derivatives
δ_{H_a} (ppm)	σ	0.946	7.485	0.132	0.1	10	H, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.961	7.509	0.124	0.09	10	H, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_l	0.821	7.461	0.111	0.11	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	σ_R	0.974	7.579	0.744	0.08	10	H, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.821	7.462	0.105	0.11	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	R	0.918	7.516	0.062	0.11	10	H, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂
δ_{H_b} (ppm)	σ	0.804	7.797	-0.004	0.03	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	σ^+	0.704	7.797	0.001	0.03	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	σ_l	0.701	7.808	-0.03	0.03	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	σ_R	0.719	7.808	0.05	0.03	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	F	0.736	7.804	-0.018	0.03	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	R	0.812	7.798	0.003	0.03	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
δ_{CO} (ppm)	σ	0.941	190.75	3.123	2.86	10	H, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 4-NO ₂ , 3-OPh
	σ^+	0.943	191.29	2.312	2.83	10	H, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 4-NO ₂ , 3-OPh
	σ_l	0.932	189.58	4.322	2.97	10	H, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 4-NO ₂ , 3-OPh
	σ_R	0.935	192.14	4.249	2.93	10	H, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 4-NO ₂ , 3-OPh
	F	0.925	189.87	3.384	3.03	10	H, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 4-NO ₂ , 3-OPh
	R	0.917	191.5	1.553	3.09	10	H, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 4-NO ₂ , 3-OPh
δ_{C_a} (ppm)	σ	0.968	121.59	3.586	1.6	11	H, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	σ^+	0.976	122.22	2.856	1.4	11	H, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	σ_l	0.94	120.66	3.823	2	11	H, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	σ_R	0.956	123.13	4.652	1.81	11	H, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	F	0.832	120.94	2.934	2.07	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	R	0.831	122.48	1.938	2.08	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
δ_{C_β} (ppm)	σ	0.739	146.57	4.378	4.19	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	σ^+	0.846	147.34	3.569	4.05	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	σ_l	0.752	143.34	10.342	3.88	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	σ_R	0.719	147.91	3.305	4.48	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	F	0.858	142.89	11.071	3.7	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh
	R	0.805	147.01	-0.676	4.56	12	H, 3-Br, 3-Cl, 4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4-CH ₃ , 3-NO ₂ , 4-NO ₂ , 3-OPh

r= correlation coefficient; l= intercept; ρ =slope; s= standard deviation; n= number of derivatives

Table 7: Antibacterial activities of substituted styryl 4-cyclohexenyl ketones(Entries 39-50)

Entry	X	<i>E.coli</i>	<i>S.aures</i>	<i>Pseudomonas</i>	<i>Klebsiella</i>	<i>P.vulgaris</i>	<i>Entrococcus faecalis</i>
39	H	±	+	±	±	±	---
40	3-Br	++	++	+	++	+	++
41	3-Cl	++	++	+	++	+	++
42	4-Cl	+	+	+	+	+	---
43	4-F	+	+	+	+	+	---
44	4-OH	+	+	+	+	+	---
45	2-OCH ₃	++	++	++	+	+	+
46	4-OCH ₃	+	+	+	+	+	---
47	4-CH ₃	++	++	++	++	++	++
48	3-NO ₂	±	+	±	±	±	+
49	4-NO ₂	+	+	+	+	+	---
50	3-OPh	+	+	+	+	+	---

Disc size: 6.35 mm; Duration: 24-45 h; Standard: Ampicillin (30-33 mm) and Streptomycin(20-25 mm); Control: Methanol; -- -: No activities; ±: Active(8-12 mm); +: Moderately active(13-19 mm); ++: Active(20-24 mm).

Table 8: Antifungal activities of substituted styryl 4-cyclohexenyl ketones(Entries 39-50)

Entry	X	Disc diffusion technique (250µg/mL) <i>Candida albicans</i>	Drug dilution method (50µg/mL)	
			<i>Penicillium</i>	<i>Aspergillus niger</i>
39	H	+	---	---
40	3-Br	+	+	+
41	3-Cl	++	++	++
42	4-Cl	++	++	++
43	4-F	---	±	+
44	4-OH	±	---	---
45	2-OCH ₃	±	++	++
46	4-OCH ₃	+	+	+
47	4-CH ₃	++	++	++
48	3-NO ₂	+	+	---
49	4-NO ₂	+	---	---
50	3-OPh	+	±	±

Standard: Griseofulvin and Gentamycin; Duration : 72 h; Control: Methanol; Medium: Potato dextrose agar; ++: No fungal colony; +: One fungal colony; ±: Two-three fungal colonies; ---: Heavyfungalcolony.

Table 9: Insect antifeedant activities of substituted styryl 4-cyclohexenyl ketones(Entries 39-50)

Entry	X	4-6 pm	6-8 pm	8-10 pm	10-12 pm	12-6 am	6-8 am	8am-12Nn	12Nn-2 pm	2-4 pm	Total leaf disc consumed in 24 hrs
39	H	1	1	0.5	0.5	0.5	1	1	1	1	8
40	3-Br	0.5	0.25	0.25	0.5	0.1	0	1	1	0.5	2
41	3-Cl	0.5	0.25	0.25	0.5	0.5	0.5	1	1	0.5	0.5
42	4-Cl	0.5	0.5	0.25	1	0.5	0.5	0.25	0.25	0.25	0.4
43	4-F	0.5	0.5	0.25	1	0.5	0.5	0.25	0.25	0.25	0.4
44	4-OH	0.5	0.5	0.25	1	0.5	0.5	0.25	0.25	0.25	0.4
45	2-OCH ₃	1	2	2	1	0	0	1	1	1	9
46	4-OCH ₃	1	1	1	0.5	0.5	1	2	1	1	10
47	4-CH ₃	1	0.5	0.5	1	1	0	1	1	1	9
48	3-NO ₂	0.5	1	0.5	2	2	0.5	0.5	1	1	7
49	4-NO ₂	2	3	3	1	1	1	0.5	1	0	12
40	3-OPh	2	3	3	1	0	0	0.5	1	0	7

Number of leaf discs consumed by the insect (Values are mean + SE of five).

Table 10: Insect antifeedant activity of compound 40 3-bromo styryl 4-cyclohexylphenyl ketone at the concentration of 50, 100 and 150 ppm

ppm	4-6 pm	6-8 pm	8-10 pm	10-12 pm	12am-6 am	6-8 am	8am-12Nn	12Nn-2 pm	2-4 pm	Total leaf disc consumed in 24 hrs
50	0.5	0.5	0	0	0	0	0	0	0	0.1
100	0	0.25	0.25	0	0	0	0	0	0	0.05
150	0	0.5	0.25	0	0.25	0	0	0	0	0.1

Number of leaf discs consumed by the insect (Values are mean + SE of five).

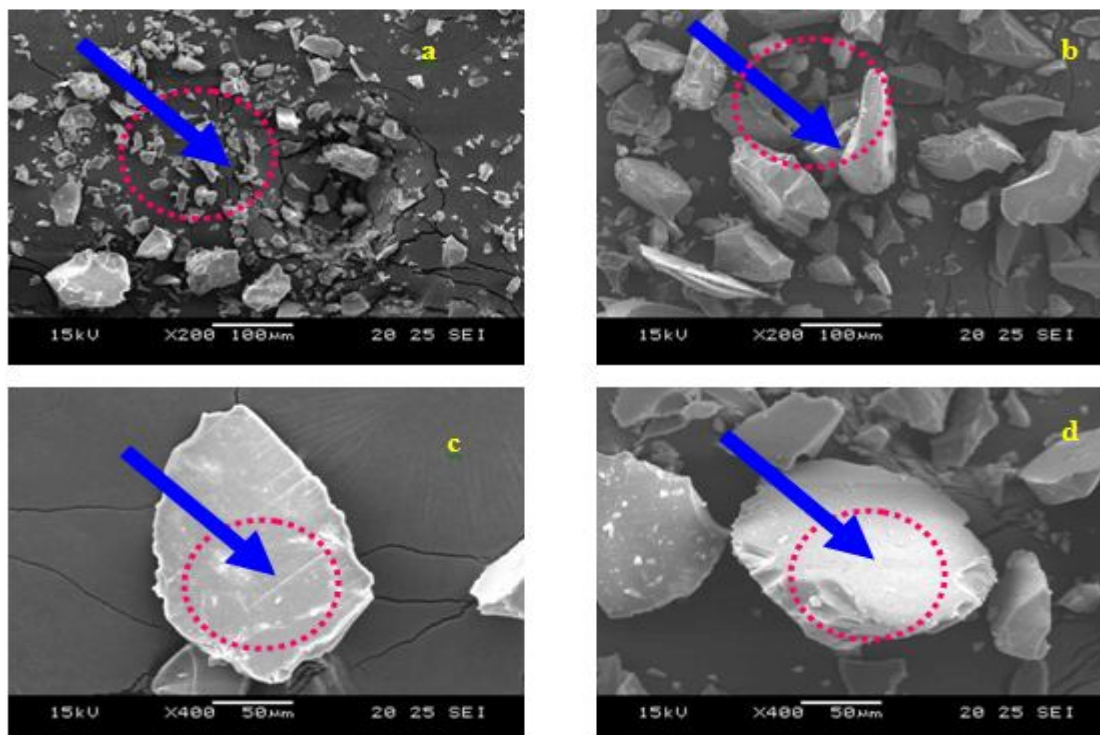
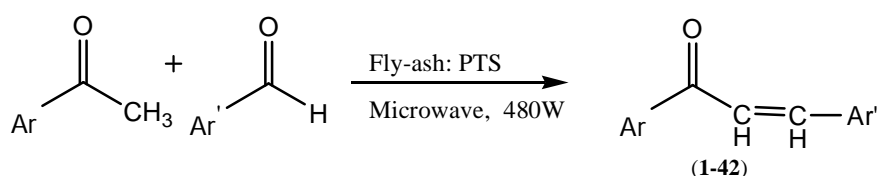


Fig. 1: SEM images of pure fly ash and PTSA-fly ash ; a) pure fly ash (1 μ m), b) pure fly ash (50 μ m), c) PTSA- fly ash (1 μ m) (\Rightarrow – corroded), d) PTSA- fly ash (50 μ m) (\Rightarrow – corroded)



Scheme 1

Synthesis of aryl chalcones by fly-ash:PTS catalyzed aryl methyl ketones and benzaldehydes in microwave irradiation.

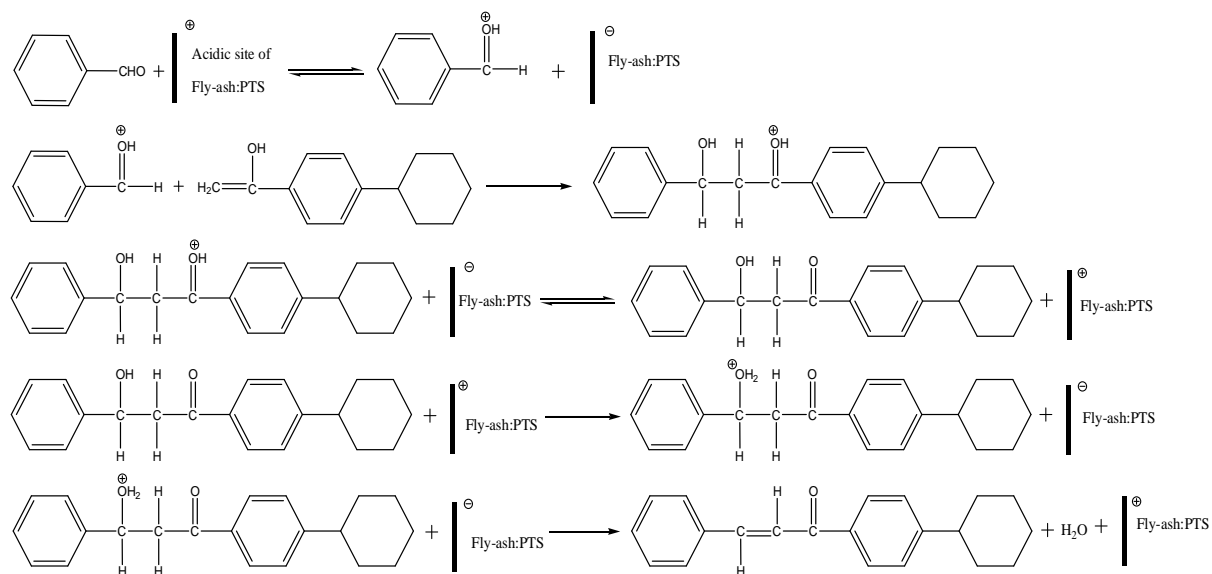


Fig. 2: The proposed mechanism for the fly-ash:PTS catalyzed aldol condensation of 4-cyclohexylphenyl methyl ketone and benzaldehyde

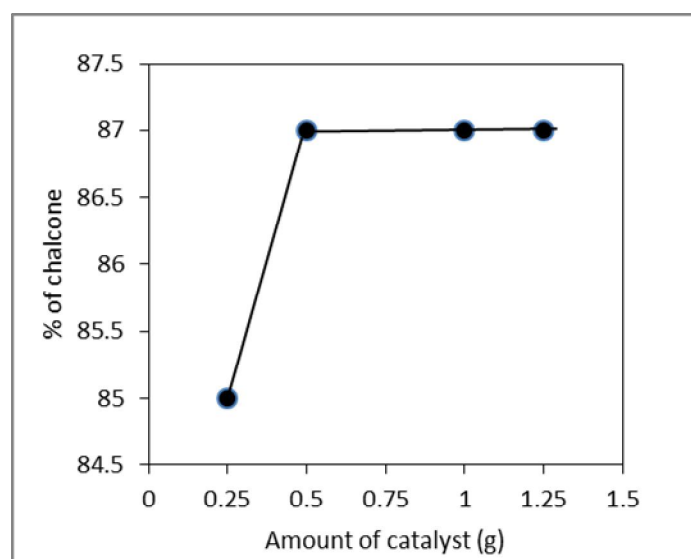


Fig. 3: Effect of catalyst loading

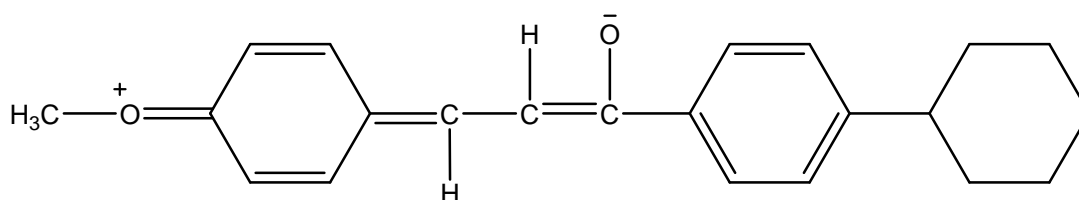


Fig. 4: The resonance conjugative structure

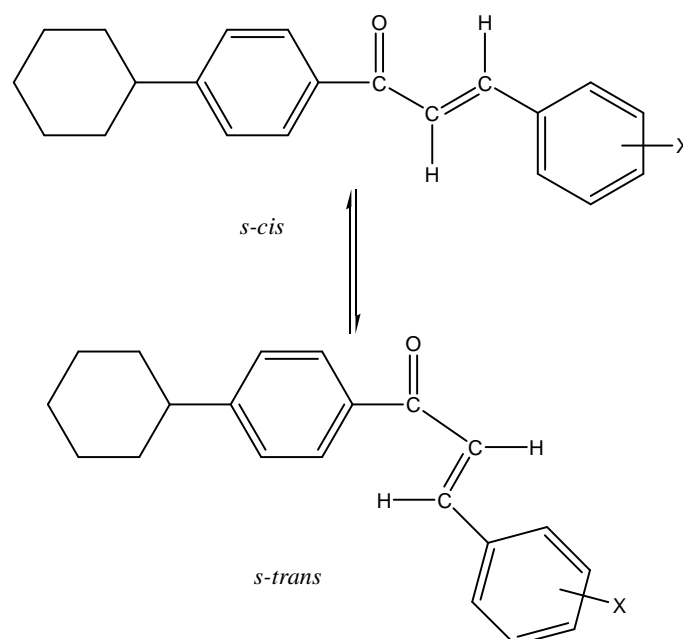


Fig. 5: The *s-cis* and *s-trans* conformers of substituted styryl 4-cyclohexenyl phenyl ketones

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