

Synthesis, Characterization of Chalcone moiety

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Abstract: In this study two chalcone diols namely DBHB, DBHE were synthesised by base catalysed Claisen-Schmidt condensation method comprising 1-3 diacetyl benzene and varying benzaldehyde. The UV-Visible spectroscopy, Fourier Transform Infrared spectroscopy was done to prove the formation of chalcone diols. Nuclear Magnetic Resonance spectroscopy was applied to confirm the structural orientation. The optical band gap energy of DBHB, DBHE were done by UV-Visible spectroscopy found to be 4.27 and 4.18 eV respectively. Thus the synthesised chalcone diols behave like a semiconductor material.

Keywords: Claisen-Schmidt, Condensation, Resonance, Optical, Bandgap energy, Semiconductor.

I. INTRODUCTION

Recently, many researchers provoke a multifunctional behaviour of chalcones, due to their bioactivity and optoelectronic applications. Chalcones are α,β unsaturated ketones consisting of three aromatic rings and are chemically known as chalconoids[1]. It is used as a key precursor for organic synthesis[2]. Chalcones are widely used as biomedical applications[3,4] like anti-inflammatory, anti-HIV, anticancer, antifungal, anti-obesity[5] and chemopreventive activity. Some of the natural occurring chalcones are Ashitaba stem and leaves, edible fruits etc., The Ashitaba stem contains chalcone content that acts as a detoxifying agent[6].



Image Courtesy: [https://blog.strictlymedicalseeds.com/ashitaba-stem\(a\), \(b\) leaves](https://blog.strictlymedicalseeds.com/ashitaba-stem(a), (b) leaves).

Reported biomedical applications of chalcones are as follows. Reuben Jonathan *et al.*, (2007) studied the antibacterial activity of synthesised polyesteramides[7]. Chitra *et al.*, (2010) examined the antimicrobial activity of synthesised polyesters containing chalcone[8]. Kothai *et al.*, (2018) reported the cytotoxic activity of chalcone based copolyesters by MTT assay[9] (Human Breast Cancer). Choi *et al.*, (2018) evaluated the chalcone derivative for a therapeutic agent[10]. Mahapatra *et al.*, (2019) reported on the biomedical applications of chalcone based on the metal coordination compounds[11]. Kandaswamy *et al.*, (2019) studied the antimicrobial activity of the copolyesters with chalcone and biscoumarin moiety[12]. Tang *et al.*, (2020) synthesised a novel chalcone based bispiperazine linker and screened for the *in vivo* anti-inflammatory, cytotoxic activity[13].

Apart from the biomedical applications of chalcones, it is also fascinated in the field of optoelectronics[14] like Non-linear optics[15], Langmuir films[16], Electrochemical sensing[17], Photosensitization[18], Ultrasonication[19], Solvent-free solid-phase reaction[20]. Perundevi *et al.*, (2015) synthesised random copolyesters with bischalcone moiety and examined their photocrosslinking property[21]. Marioara Nechifor *et al.*, (2016) studied the photosensitivity of chalcone chromophore into the polymer backbone[22] and explained the dimerization of chalcone moiety. Sidharthan *et al.*, (2017) reported the photocrosslinking behaviour of the chalcone incorporated in the polyester and they found a nematic phase[23]. Kavitha *et al.*, (2018) reported[24] the liquid crystalline property of the synthesised poly (ester amides). Chen *et al.*, (2020) reported on the new perspectives for the design of chalcone and efficient photo initiating property[25]. Hassen *et al.*, (2020) synthesised chalcone diols and studied their spectral properties[26].

In this study, we report the synthesis of two chalcone diols namely DBHB, DBHE by base catalysed Claisen Schmidt Condensation method. The spectral behaviour of the chalcone diols is an important key factor to understand the formation of chalcones. The chalcones were analysed by UV-Visible, FTIR and NMR spectroscopy. The Bandgap energy of the chalcone diols was also studied.

II. MATERIALS AND METHODS

1,3 diacetyl benzene, 3-ethoxy-4-hydroxy benzaldehyde, 4-hydroxybenzaldehyde, Ethanol of analytical grade were purchased from Sigma Aldrich, Alfa Aesar.

2.1 Preparation of Chalcone Diols (DBHB)

The Chalcone diols were synthesised as follows by adopting the experimental Kohler and Chadwell[27]. 4 g of sodium hydroxide pellets are dissolved in 36 mL of distilled water. 0.4189 mL of 1,3 diacetyl benzene is dissolved in 20 mL of ethanol. The above two mixture is taken in a 250 mL RB flask and kept in a water bath. And then added 4-hydroxy benzaldehyde dissolved in 20 mL of ethanol. The mixture is continuously stirred for 5 hours. After the reaction time, the above mixture is kept in a refrigerator for one day. It is then filtered, washed with ethanol and dried at room temperature.

2.2 Preparation of Chalcone Diols (DBHE):

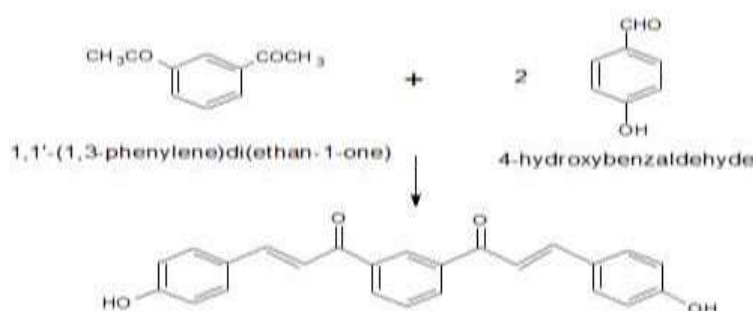
4 g of sodium hydroxide pellets are dissolved in 36 mL of distilled water. 0.4189 mL of 1,3 diacetyl benzene is dissolved in 20 mL of ethanol. The above two mixture is taken in a 250 mL RB flask and kept in a water bath. And then added 3-ethoxy-4-hydroxy benzaldehyde dissolved in 20 mL of ethanol. The mixture is continuously stirred for 5 hours. After the reaction time, the above mixture is kept in a refrigerator for one day. It is then filtered, washed with ethanol and dried at room temperature.

III. CHARACTERISATION

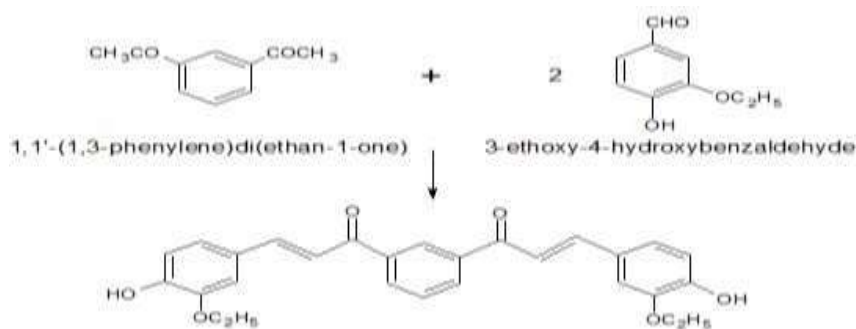
- **UV-Visible Spectroscopy:** The UV-Visible Spectroscopy is an important tool to analyse their absorption maxima either it's a bathochromic shift or hypsochromic shift. The chalcone diols were examined by Shimadzu UV-Visible Spectrometer. The UV-Visible spectrum was recorded in the range of 200 to 600 nm using ethanol as a reference.
- **Tauc Plot:** A Tauc Plot is used to determine the optical bandgap energy. Using the UV-Visible spectral data enables to characterise their optical properties of the chalcone diols.
- **Fourier Transform Infrared Spectroscopy:** FTIR Spectroscopy is a technique used to identify the functional group of a compound by producing an infrared spectrum. The samples were analysed by FTIR Spectrometer (Shimadzu). KBr (Spectroscopic Grade) is typically used as the window material because it is transparent in the IR region between 4000 to 400 cm^{-1} .
- **Nuclear Magnetic Resonance Spectroscopy:** It is used to examine their local magnetic field around the atomic nuclei. And also provide information about the chemical structure of a compound. The NMR Spectroscopy of the chalcone diols by using (Bruker) NMR spectrometer instruments.

IV. RESULTS AND DISCUSSION

The Chalcones were synthesized by the base-catalyzed Claisen Schmidt Condensation method.



Scheme: 1 Structure of Chalcone DBHB



Scheme: 2 Structure of Chalcone DBHE

4.1 UV-Visible Spectroscopy

Usually, the Chalcone derivatives have two main absorption maxima namely $\pi-\pi^*$ transition (bathochromic shift) and $n-\pi^*$ transition (hypsochromic shift). The UV-Visible spectroscopy of the DBHB, DBHE are shown in Fig 1 & 2 respectively. The UV-Visible spectrum of the chalcone diol DBHB the absorption maxima at 239 nm is due to the $\pi-\pi^*$ transition and the absorption band at 365 nm which corresponds to the $n-\pi^*$ transition[28]. The two absorption band observed for the Chalcone confirms the formation of DBHB.

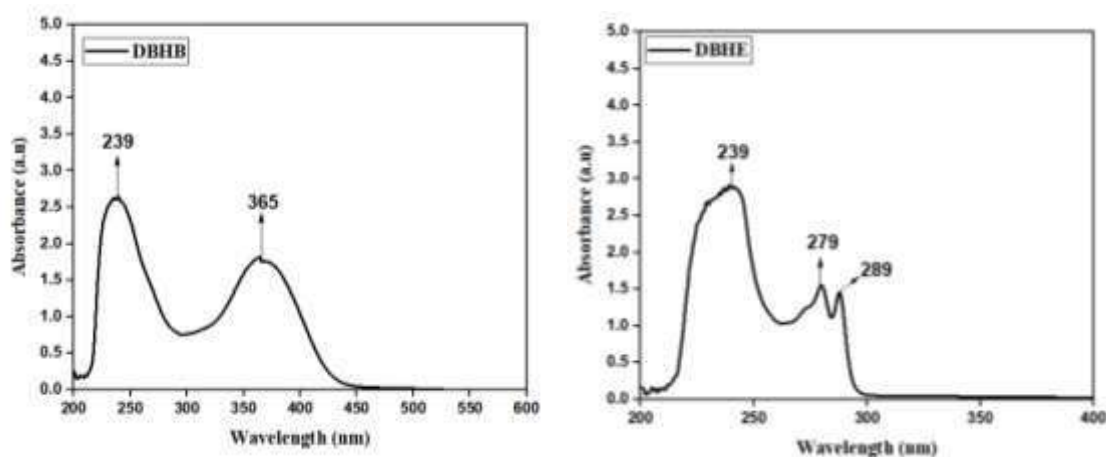


Fig 1&2 UV-Visible Spectrum of Chalcone diol DBHB, DBHE

But in the case of chalcone diol (DBHE) shows $\pi-\pi^*$ transition in three different wavelengths of 239, 279 and 289 nm. This may be attributed to the increased oxygenation of the ethoxy group which results in the bathochromic shift only[29].

4.2 Tauc Plot

Using the UV-Visible spectral data, assigning the tauc plot of chalcones for calculating the bandgap energies[30,31]. The bandgap energy is calculated by the formula[14]

$$E = \frac{hc}{\lambda}$$

Where, h – Planck's Constant, c –Speed of light, λ – Wavelength. Tauc Plot for the Chalcone diols DBHB and DBHE are shown in Fig 3 & 4. The bandgap energy is observed in the range of 4.27 and 4.18 eV for DBHB, DBHE. Thus the band edge is fitted with the UV-Visible spectral data revealing the semiconducting behaviour of the chalcone diols[32].

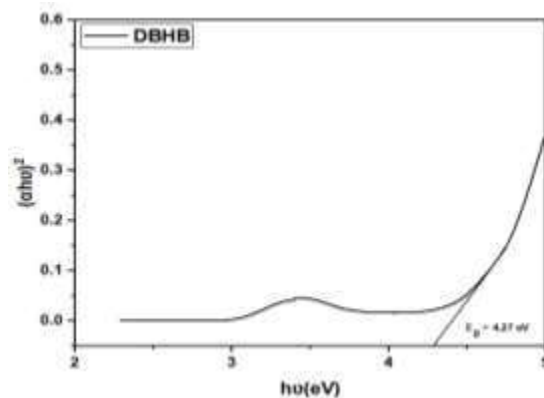


Fig 3 Tauc Plot of Chalcone DBHB

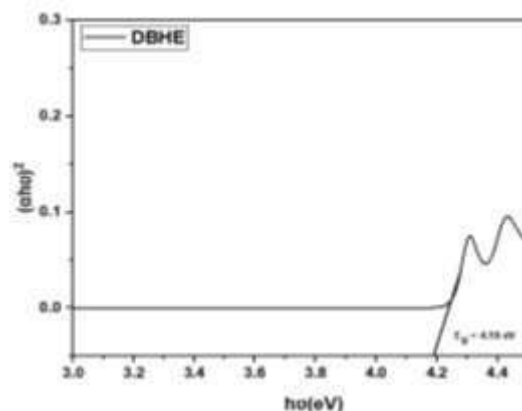


Fig 4 Tauc Plot of Chalcone DBHE

4.3 Fourier Transform Infrared Spectroscopy

The stretching vibrational frequency of the aromatic chalcones was analysed by FTIR spectroscopy [28]. The Fourier Transform Infrared Spectroscopy of the chalcone diols DBHB, DBHE are shown in Fig 5 & 6 respectively. The FTIR Spectrum of DBHB shows a characteristic absorption peak at 3248 cm^{-1} corresponds to the OH stretching frequency. The FTIR peak at 1670 cm^{-1} and 1606 cm^{-1} is due to the presence of conjugated ketone.

The FTIR Spectrum of DBHE exhibit the absorption peak at 1627 cm^{-1} indicates the presence of α,β unsaturated ketone which confirms the formation of chalcone diols[33]. The OH stretching frequency was observed at 3427 cm^{-1} .

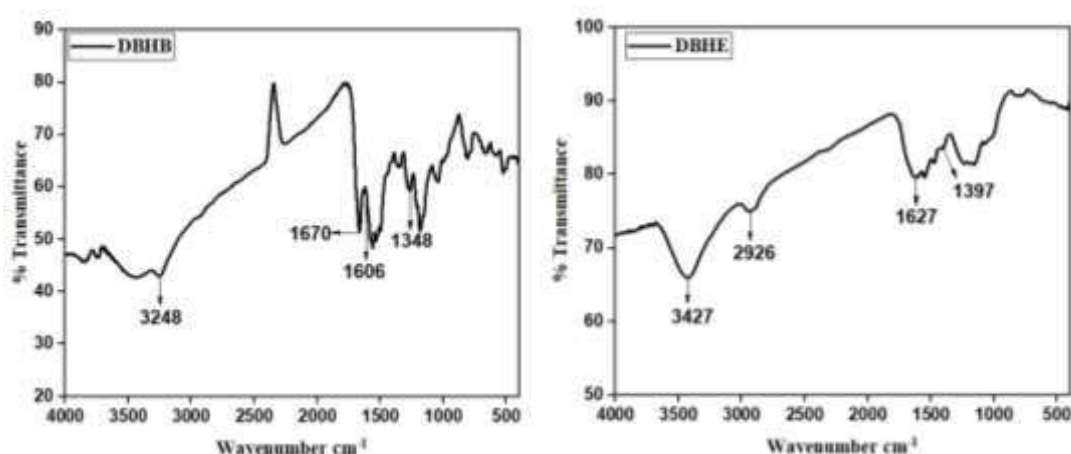


Fig 5 & 6 FTIR Spectrum of DBHB, DBHE

4.4 NMR Spectroscopy

The ^1H & ^{13}C NMR spectrum of chalcone diol DBHB was shown in Fig 7. The hydroxyl proton at 9.78 ppm is due to the intramolecular interaction between the carbonyl group. The methoxy proton in the chalcone moiety was observed in the ranges of 3.38 to 3.47 ppm[28]. The aromatic protons were observed at 6.94 ppm and the vinylic protons attached to the carbonyl group were observed at 7.65 ppm[33,34]. In the ^{13}C NMR spectrum, the carbonyl carbon was observed at 198 ppm and

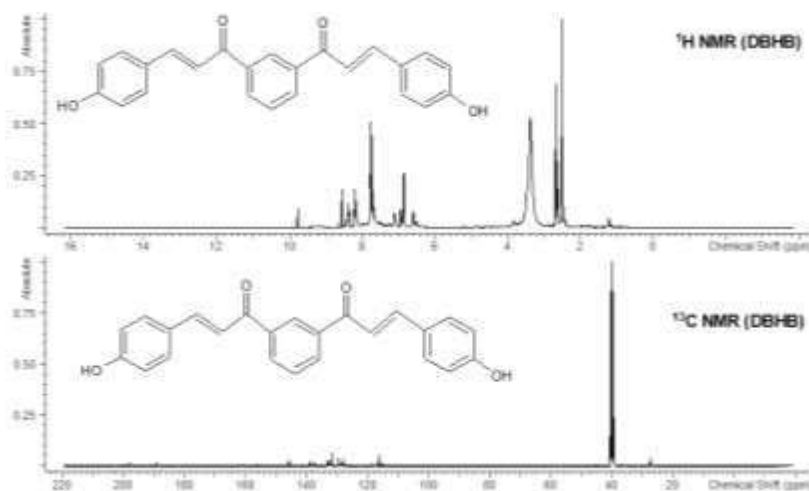


Fig 7 ^1H and ^{13}C NMR spectrum of chalcone DBHB

The ^1H and ^{13}C NMR spectrum of chalcone diol DBHE were shown in Fig 8. The aromatic protons were observed at 6.88 ppm. The vinylic protons attached to the carbonyl group were observed at 7.54 ppm and the hydroxyl proton at 9.76 ppm due to the intramolecular interaction between the carbonyl group[33,34]. The methoxy proton in the chalcone moiety in the ranges of 3.35 to 3.46 ppm.

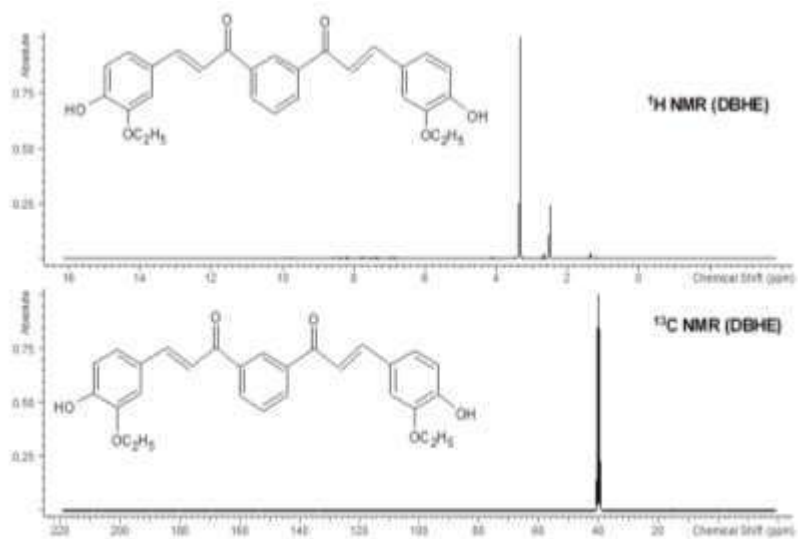


Fig 8 ^1H and ^{13}C NMR spectrum of chalcone DBHE

In the ^{13}C NMR spectrum, the carbonyl carbon was observed at 196.57 ppm. The aromatic carbons were observed in the range of 127 to 135 ppm.

V. CONCLUSION

The two chalcone diols namely DBHB, DBHE are synthesised by the base catalysed Claisen-Schmidt condensation method. It is then characterised by UV-Visible, FTIR and NMR Spectroscopy. The optical properties of the chalcones were examined by using UV-Visible spectral data, to find out the bandgap energy. Thus the bandgap energy of chalcone DBHB, DBHE are found to be 4.27 and 4.18 eV respectively. The FTIR spectrum of DBHB, DBHE shows a characteristic peak at 1670, 1627 cm^{-1} corresponds to the $\text{C}=\text{O}$ group of the stretching frequency which confirms the formation of chalcones. To predict the chemical structure, the two chalcones diols were analysed by ^1H and ^{13}C NMR spectroscopy. Thus, the synthesised chalcones can be an excellent candidate in the field of optoelectronic applications.

VI. ACKNOWLEDGEMENT

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REFERENCES

- [1] Chavan, B.B. Gadekar, A. S. Mehta, P. P. Vawhal, P. K. Kolsure, A. K. Chabukswar, A. R. 2016. Synthesis and Medicinal Significance of Chalcones-A Review. Asian Journal of Biomedical and Pharmaceutical Sciences, 6(56), 01-07.

- [2] Vidhya, T. Sidharthan, J. 2017. A study on photoactive bischalcone based liquid crystalline polyesters. *International Journal of Science, Engineering and Management*, 2(12), 200-205.
- [3] Dong, F. Jian, C. Zhenghao, F. Kai, G. Zuliang, L. 2008. Synthesis of chalcones via Claisen Schmidt condensation reaction catalyzed by acyclic acidic ionic liquids. *Catalysis Communications*, 9, 1924–1927.
- [4] Durairaj, M. Sivakumar, S. Gnanendra Shanmugam. 2018. Chemical Synthesis of Chalcones by Claisen-Schmidt Condensation Reaction and Its Characterization. *International Journal for Research in Applied Science & Engineering Technology*, 6(5), 2311-2315.
- [5] Birari, RB. Gupta, S. Mohan, CG. Bhutani, KK. 2011. Phytomedicine Antiobesity and lipid lowering effects of Glycyrrhiza chalcones : Experimental and computational studies. *Phytomedicine*, 18(8-9), 795–801.
- [6] Review ACS. Ashitaba Chalcone Powder. :1–18.
- [7] Kannappan, V. Reuben Jonathan, D. 2013. A study on the synthesis and bactericidal efficacy of certain poly (ester- amides) containing 2, 5-(benzylidene) cyclopentanone moiety in the main chain containing 2, 5-bis (benzylidene) cyclopentanone moiety in the main chain. *Journal of Chemical and Pharmaceutical Research*, 5(4), 382-386.
- [8] Chitra, M. Rajendran, TV. Duraipandian, V. Rajan, YC. Reuben Jonathan, D. 2010. A study on the synthesis and bactericidal activity of certain copolyesters containing bischalcone moiety in the main chain. *Indian Journal of Science and Technology*, 3(8), 890-893.
- [9] Kothai, S. Venkatesh, S. Lakshmi Devi, D. 2018. Design, Synthesis, Characterization of Chalcone Derivatives PTSH and PITI and Their Potential Anticancer Properties against MDA-MB-231 Cell Lines. *Journal of Chemistry and Chemical Sciences*, 8(4), 737–750.
- [10] Choi, D. Park, JC. Lee, HN. Moon, J. Ahn, H. Park, K. 2018. In vitro osteogenic differentiation and antibacterial potentials of chalcone derivatives. *Molecular Pharmaceutics*, 2(6), 1-26.
- [11] Debarshi Kar Mahapatra, Sanjay Kumar Bharti, Vivek Asati, Sushil Kumar Singh. 2019. Perspectives of medicinally privileged chalcone based metal coordination compounds for biomedical applications. *European Journal of Medicinal Chemistry*, 174, 145-159.
- [12] Kandaswamy, N. 2019. Synthesis, Characterisation and Antimicrobial Evaluation of Chalcone Coupled Biscoumarin Copolyesters. *Macromolecular Research*, 27, 593-600.
- [13] Tang, Y. Zheng, X. Qi, Y. Pu, X. Liu, B. Zhang, X. 2020. Bioorganic Chemistry Synthesis and anti-inflammatory evaluation of new chalcone derivatives bearing bispiperazine linker as IL-1 β inhibitors. *Bioorganic Chemistry*, 98(3), 103748.
- [14] Ali, MKM. Elzupir, AO. Ibrahim, MA. Suliman, II. Modwi, A. Idriss, H. 2017. Characterization of optical and morphological properties of chalcone thin films for optoelectronic applications. *Optik*, 145, 529–533.
- [15] Poornesh, P. Shettigar, S. Umesh, G. Manjunatha, KB. Kamath, KP. Sarojini, BK. 2009. Nonlinear optical studies on 1, 3-disubstituent chalcones doped polymer films. *Optical Material*. 31(6), 854–859.
- [16] Gu, C. Liu, L. Sui, Y. Zhao, J. Chen, Y. 2007. Highly enantioselective Michael additions of α -cyano acetate with chalcones catalyzed by bifunctional cinchona-derived thiourea organocatalyst. *Tetrahedron: Asymmetry*, 18, 455–463.
- [17] Sarojini, BK. Narayana, B. Ashalatha, BV. Indira, J. Lobo, KG. 2006. Synthesis, crystal growth and studies on non-linear optical property of new chalcones. *Journal of Crystal Growth*, 295, 54–59.
- [18] Li, J. Yang, W. Wang, S. Li, S. Li, T. 2002. Improved synthesis of chalcones under ultrasound irradiation. *Ultrasonics Sonochemistry*, 9, 237–239.
- [19] Parveen, H. Hayat, F. Salahuddin, A. Azam, A. 2010. Synthesis, characterization and biological evaluation of novel 6-ferrocenyl-4-aryl-2-substituted pyrimidine derivatives. *European Journal of Medicinal Chemistry*, 45(8), 3497–3503.
- [20] Asiri, AM. Khan, SA. Mussa, H. 2015. Single X-ray crystal and spectroscopic investigation of novel biologically active donor-acceptor chalcones as specific application for optoelectronics and photonics. *Journal of the Taiwan Institute of Chemical Engineers*, 1–8.
- [21] Perundevi, TS. Reuben Jonathan, D. Kothai, S. 2015. Synthesis and Characterization of Certain Photocrosslinkable Random Copolyesters with Bischalcone Moiety. *International Journal of Advanced Research*, 3(3), 1147-1154.
- [22] Nechifor, M. 2016. Novel chalcone-based aromatic polyamides: synthesis, characterization, and properties. *Designed*

- [23] Sidharthan, J. Amaladhas, TP. 2017. Synthesis and characterization of photo-crosslinkable liquid crystalline copolyesters containing arylidene-keto and chalcone moieties. Springer, 1–12.
- [24] Kalappa, KE. Antony, SA. Ramalakshmi, N. 2018. Synthesis, Characterisation and Photocrosslinkable studies of Certain Thermotropic Liquid Crystalline Poly (ester-amides). Journal of Advanced Chemical Sciences, 4(2), 562–566.
- [25] Chen, H. Lalevée, J. Noirbent, G. Zhang, Y. Brunel, D. Gigmes, D. Morlet-Savary, F. Graff, B. Xiao, P. Dumur, F. 2020. Novel D- π -A and A- π -D- π -A Three-Component Photoinitiating Systems Based on Carbazole/Triphenylamino based Chalcones and Application in 3D and 4D Printing, Polymer Chemistry, 1-36.
- [26] Hassen, HS. Majeed, NS. Mohsein, HF. Hassan, ES. 2020. Synthesis and Characterization of Monomer and Three Types of Polymers Containing Chalcone Groups in Main Chain. Egyptian Journal of Chemistry, 63(11), 4195- 4203.
- [27] Kohler, EP. Chadwell, HM. 1941. Preparation by the action of NaOH on an alcoholic solution of benzaldehyde and acetophenone: Org. Synth. coll. vol. I, 78 .
- [28] Evranos, B. Ertan, R. 2012. Spectral Properties of Chalcones II. FABAD Journal of Pharmaceutical Sciences, 205-216.
- [29] Harborne, JB. Mabry, TJ. Mabry, H. 1975. The Flavanoids. London: Chapman and Hall.
- [30] Prabhash, PG. Nair, SS. 2016. Synthesis of copper quantum dots by chemical reduction method and tailoring of its bandgap Synthesis of copper quantum dots by chemical reduction method and tailoring of its bandgap. AIP Advances, 6, 055003.
- [31] Tauc, R. Grigorovici. Vancu, A. 1966. Optical Properties and Electronic Structure of Amorphous Germanium. Physica status solidi (b) 15, 627.
- [32] Vanangamudi, G. Subramanian, M. Jayanthi, P. Arulkumaran, R. Kamalakkannan, D. Thirunarayanan, G. 2011. IR, NMR spectral studies of some 2-hydroxy-1-naphthyl chalcones: Assessment of substituent effects. Arab J Chem.
- [33] Lakshmi Devi, D. Aswini, R. Kothai, S. 2018. Synthesis and characterisation of chalcone based copolyesters and their anticancer activity. IJPSR, 9(4), 1589-1593.
- [34] Amakshi, R. Reddy, BSR. 2008. Synthesis of chalcone based fluorescent polymers: Diels Alder reaction of chalcones and their polymerization through ROMP. Journal of Polymer Science. Part A, 46, 1521-153.