

Mechanistic Insights and Optimization of Phytol Recovery from *Acacia Auriculiformis* Leaves Using Zinc Chloride Catalysis

Abubakar Ali^{*a,1}, Haruna Ibrahim^{a,2}

^aKaduna Polytechnic, Kaduna, Nigeria

*Corresponding Author: abualimoh67@gmail.com

Abstract

This study explores a sustainable and environmentally friendly approach for phytol production from *Acacia auriculiformis* leaves, an underutilized *lignocellulosic* biomass, in response to the growing global demand for renewable bio-based chemicals. The research aims to optimize phytol extraction through zinc chloride-catalyzed thermal hydrolysis under mild reaction conditions while maintaining high selectivity and yield. The method employs ZnCl₂ as a Lewis acid catalyst to facilitate chlorophyll cleavage, with systematic variation of reaction temperature (40–80 °C) and catalyst loading (0.5–1.5% w/w) to determine optimal processing conditions. The highest phytol yield, 646.26 mg/g (13.14%), was obtained at 50 °C with 0.5% ZnCl₂, exceeding yields reported for other plant sources and conventional extraction techniques. Product characterization using gas chromatography–mass spectrometry (GC-MS) confirmed phytol as the dominant compound, accompanied by minor hydrolysis by-products. Mechanistic analysis revealed that yield variations were influenced by the balance between phytol formation and thermal degradation pathways under different catalytic and temperature conditions. These findings demonstrate the strong potential of *A. auriculiformis* leaves as a renewable feedstock for phytol production and highlight the effectiveness of ZnCl₂-assisted hydrolysis in supporting circular bio-economy and green chemistry principles. However, further studies are recommended to evaluate process scalability, economic feasibility, and environmental impacts to support industrial-level application.

Keywords: *Acacia Auriculiformis*, *Lignocellulosic* Biomass, Phytol, Thermal Hydrolysis, Zinc Chloride Catalysis

I. INTRODUCTION

The global effort to address environmental degradation caused by petroleum-based resources has drawn significant attention from researchers. Importantly, petrochemical-derived raw materials traditionally used in valuable product synthesis can be replaced with renewable biomass alternatives. These biomass-based resources offer a sustainable, environmentally friendly substitute for fossil-derived inputs, with added benefits for public health. Phytol, a biomass-derived compound, is among the promising candidates for replacing petroleum-based products in various industrial applications. Phytol is an acyclic *diterpene* alcohol that plays a crucial role in plant metabolism, particularly as a constituent of chlorophyll [1], [2], [3]. It is a hydrophobic molecule with the chemical formula C₂₀H₄₀O, characterized by a long, branched carbon chain [2], [3], [4], [5]. Historically, phytol was first isolated in the early 20th century from the saponification of chlorophyll [6], [7], [8]. Since then, it has gained significant attention in both plant biochemistry and industrial applications [1], [9], [10]. In plants, it serves as the hydrophobic tail of chlorophyll molecules, anchoring the pigment within the thylakoid membranes of chloroplasts [11], [12], [13]. Upon degradation, free phytol can be converted into other bioactive molecules, such as tocopherols (vitamin E) and *phyloquinone* (vitamin K) [3], [14], [15].

Phytol possesses a broad spectrum of pharmaceutical properties, including antimicrobial, antioxidant, anti-inflammatory, and anticancer effects [16]. It has shown inhibitory activity against pathogens such as *Staphylococcus aureus*, *Mycobacterium tuberculosis*, and *Candida albicans* [2], [17], [18]. Its antimicrobial efficacy is largely attributed to its hydrophobic character and extended aliphatic chain, which facilitate disruption of microbial membranes [19], [20], [21], [22]. Moreover, phytol has been shown to enhance the effectiveness of conventional antibiotics through synergistic interactions [16]. In the fragrance and flavor industries, phytol is a valuable intermediate in the production of aromatic compounds and synthetic vitamins [6], [23], [24]. Thermal processes such as cracking or pyrolysis can convert phytol into gasoline-range aromatic compounds, including benzene, toluene, xylenes, and styrene [25], [26], [27]. Additionally, microbial biotransformation enables the conversion of phytol into oxygenated aromatics like p-cresol, phenol, and *hydroxybenzoic* acids [28], [29], [30]. Given its high energy density and lipid-like structure, phytol is also being investigated as a renewable feedstock for biodiesel production [16]. These attributes highlight phytol's significant biological relevance and versatile industrial applications.

Phytol has been recognized as a significant metabolite derived from a variety of plant sources using different extraction and conversion methods [1], [31], [32]. For example, Thakor et al. [33] achieved phytol production through the *methanolysis* of *Abutilon indicum*. Likewise, Petpheng et al. [34] and Prabha et al. [35] extracted phytol using ethanol from *Hydrilla verticillata*, an aquatic plant. Microwave-assisted extraction techniques have also been investigated; Xiao et al. [36] employed a microwave oven to obtain phytol. Alara et al. [37] applied both Soxhlet and microwave-assisted ethanol extraction to isolate phytol from *Vernonia amygdalina* leaves. Dunkić et al. [38] identified phytol as a major bioactive compound in Croatian *Veronica* species using *hydrodistillation*. In addition, Al-Omar [39] used n-hexane to extract phytol from *Suaeda vermiculata*, a salt-tolerant plant found in Saudi Arabia. Ultrasonic-assisted extraction has also been effective, as demonstrated by Abd Rahim et al. [40] in their study on *Syzygium polyanthum* leaves.

Despite the extensive exploration of phytol's applications in pharmaceuticals, cosmetics, and biofuels, and food, there remains a notable lack of sustainable, efficient, and green production methods from non-edible *lignocellulosic* biomass. Previous studies have focused primarily on algae, synthetic pathways, or conventional solvent extraction from limited plant sources. However, these methods often involve high costs, environmental concerns, or low yields. Notably, *Acacia auriculiformis*, an abundant and underutilized tropical plant, has not been systematically explored as a potential feedstock for phytol production. Moreover, the application of zinc chloride-catalyzed hydrothermal treatment for the selective extraction and conversion of phytol from *lignocellulosic* biomass is still underreported in scientific literature. The integration of this approach presents a novel pathway that aligns with green chemistry principles while addressing both biomass valorization and phytol production challenges. This study, therefore, addresses the gap by evaluating the viability of *Acacia auriculiformis* leaves as a renewable source for phytol using an environmentally friendly catalytic process under mild hydrothermal conditions.

This study aimed to develop a sustainable method for producing phytol from *Acacia auriculiformis* leaves through zinc chloride-catalyzed thermal hydrolysis under mild conditions. This was accomplished by investigating the catalytic efficiency of zinc chloride in promoting the hydrolysis of chlorophyll in the leaf biomass. The process involved the optimization of key reaction parameters, such as temperature and catalyst concentration, to maximize phytol yield. The resulting products, including phytol and other hydrolysis derivatives, were identified and quantified using gas chromatography-mass spectrometry (GC-MS). Additionally, the phytol yield obtained from this method was compared with values reported in the literature for other plant sources and extraction techniques. Finally, the study assessed the scalability and environmental sustainability of this approach for phytol production from *lignocellulosic* biomass.

II. METHOD

The materials used in this study included dried *Acacia auriculiformis* leaves, a ceramic mortar and pestle, a 1000 mL conical flask, a 1000 mL beaker, a 500 mL separating funnel, a *Gallenkamp* hot plate with magnetic stirrer, filter cloth, distilled water, and Whatman filter paper. Analytical-grade zinc chloride ($ZnCl_2$) and sodium sulfate (Na_2SO_4) were employed as catalyst and dehydrating agent, respectively. Dried leaves of *Acacia auriculiformis* were collected from the premises of the National Research Institute for Chemical Technology (NARICT), Zaria. The leaves were cleaned, pulverized using a ceramic mortar and pestle, and sieved through 250 μm and 300 μm mesh screens. The resulting leaf powder was stored in an airtight container until use. A catalyst solution was prepared by dissolving 0.15 g of $ZnCl_2$ (representing 0.5% w/w of the leaf powder) in 300 mL of distilled water within a 1000 mL conical flask. Subsequently, 30 g of the sieved leaf powder was added to the catalyst solution. The mixture was heated and continuously stirred on a *Gallenkamp* magnetic stirrer hot plate until it reached 40 °C. This temperature was maintained for 30 minutes.

The mixture was initially filtered through a filter cloth and then re-filtered using Whatman filter paper to obtain a clear filtrate, following the procedure of Ali and Ibrahim [41]. To remove residual moisture, Na_2SO_4 was added to the filtrate at 0.2% w/w of the filtrate mass as performed by Ibrahim et al. [42]. The dehydrating solution was stirred within a 500 mL separating funnel and allowed to stand until phase separation occurred. The aqueous layer was drained, and the organic layer was collected and weighed. The above procedure was repeated at reaction temperatures of 50, 60, 70, and 80 °C. Additionally, experiments were conducted using $ZnCl_2$ catalyst loadings of 1.0% (0.3 g) and 1.5% (0.45 g) to evaluate the effect of catalyst concentration. For GC-MS analysis, 5 mL aliquots were drawn from each product, transferred into labeled sample bottles, and sent for compositional analysis. The entire synthesis process is illustrated in Figure 1.

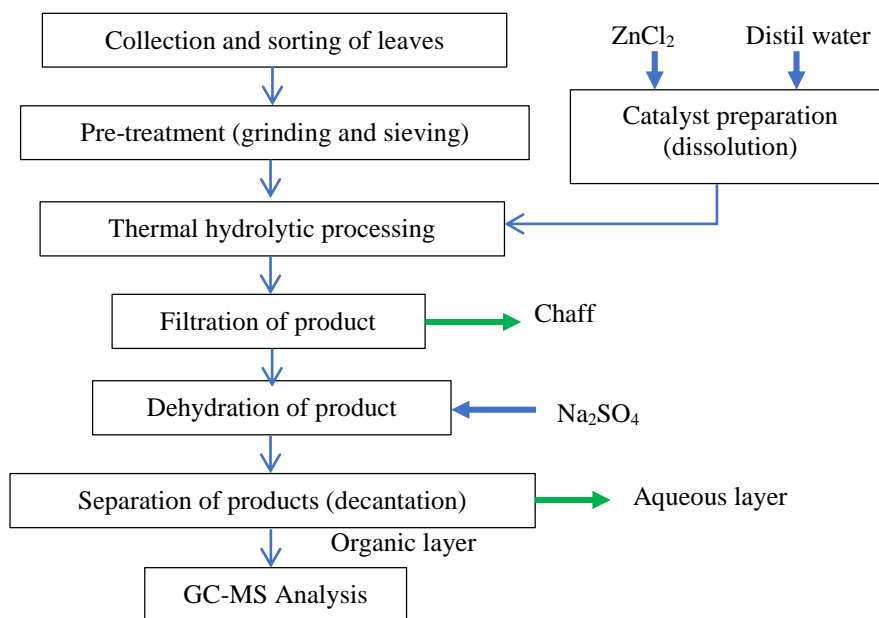


Figure 1 Flow Diagram Process for the Production of Phytol from *Acacia Auriculiformis* Leaves

For *derivatization*, 200 μL of the standard solution was mixed with 100 μL of *trimethylsulfonium* hydroxide (TMSH) and 20 μL of *triethylamine* (TEA). The mixture was placed in sealed vials and heated in an oven at 70 $^{\circ}\text{C}$ for 1 hour to facilitate complete *derivatization* before GC-MS analysis. Subsequently, a 2 mL aliquot of the *derivatized* sample was analyzed using a Varian 3800/4000 gas chromatograph-mass spectrometer (GC-MS) equipped with a DB-5 capillary column (30 m \times 0.25 mm \times 0.25 μm film thickness). Nitrogen was employed as the carrier gas, with the column pressure maintained at 10 psi. The GC oven temperature program was initiated at 100 $^{\circ}\text{C}$ (held for 3 minutes), followed by a ramp of 8 $^{\circ}\text{C}/\text{min}$ to a final temperature of 300 $^{\circ}\text{C}$. The transfer line was kept at 290 $^{\circ}\text{C}$. The mass spectrometer (VG 7070E magnetic sector) operated in electron impact ionization mode, scanning from m/z 40 to 800 at a scan rate of 20 scans per second. A solvent delay of 330 seconds was programmed to prevent detector saturation during solvent elution. Throughout the analysis, real-time output monitoring was conducted to ensure signal integrity and avoid saturation.

III. RESULTS AND DISCUSSION

The weights of the dehydrated products obtained from the thermal hydrolytic process are summarized in Table 1. The GC-MS chromatograms of the dehydrated products are shown in Figure 2. The corresponding phytol yields (%), as determined by gas chromatography–mass spectrometry (GC-MS) analysis of the dehydrated products, are presented in Table 2. Phytol is released during the degradation of chlorophyll, especially when plants undergo senescence or are subjected to enzymatic hydrolysis [43], [44], [45]. Figure 3 shows the yield of phytol (in mg/g) as a function of reaction temperature (40–80 $^{\circ}\text{C}$) during a 30-minute thermal hydrolytic process using varying concentrations (0.5%, 1.0%, and 1.5%) of zinc chloride catalyst on *Acacia auriculiformis* leaves. A two-way ANOVA, shown in Table 3, confirmed that both reaction temperature and catalyst concentration significantly influenced phytol yield ($p < 0.05$), with a significant interaction effect ($p = 0.025$). These results validate the optimized condition (50 $^{\circ}\text{C}$, 0.5% ZnCl_2) as statistically significant for achieving maximum yield.

Table 1 The Weight (g) of the Dehydrated Products at Different Reaction Temperatures

Catalyst Loading (%)	Weight of Dehydrated Product (g) @ Different Temperatures				
	40 $^{\circ}\text{C}$	50 $^{\circ}\text{C}$	60 $^{\circ}\text{C}$	70 $^{\circ}\text{C}$	80 $^{\circ}\text{C}$
0.5	147	150	149	147	146.7
1.0	149	147.5	146	143	143
1.5	151	148	149.5	147	145

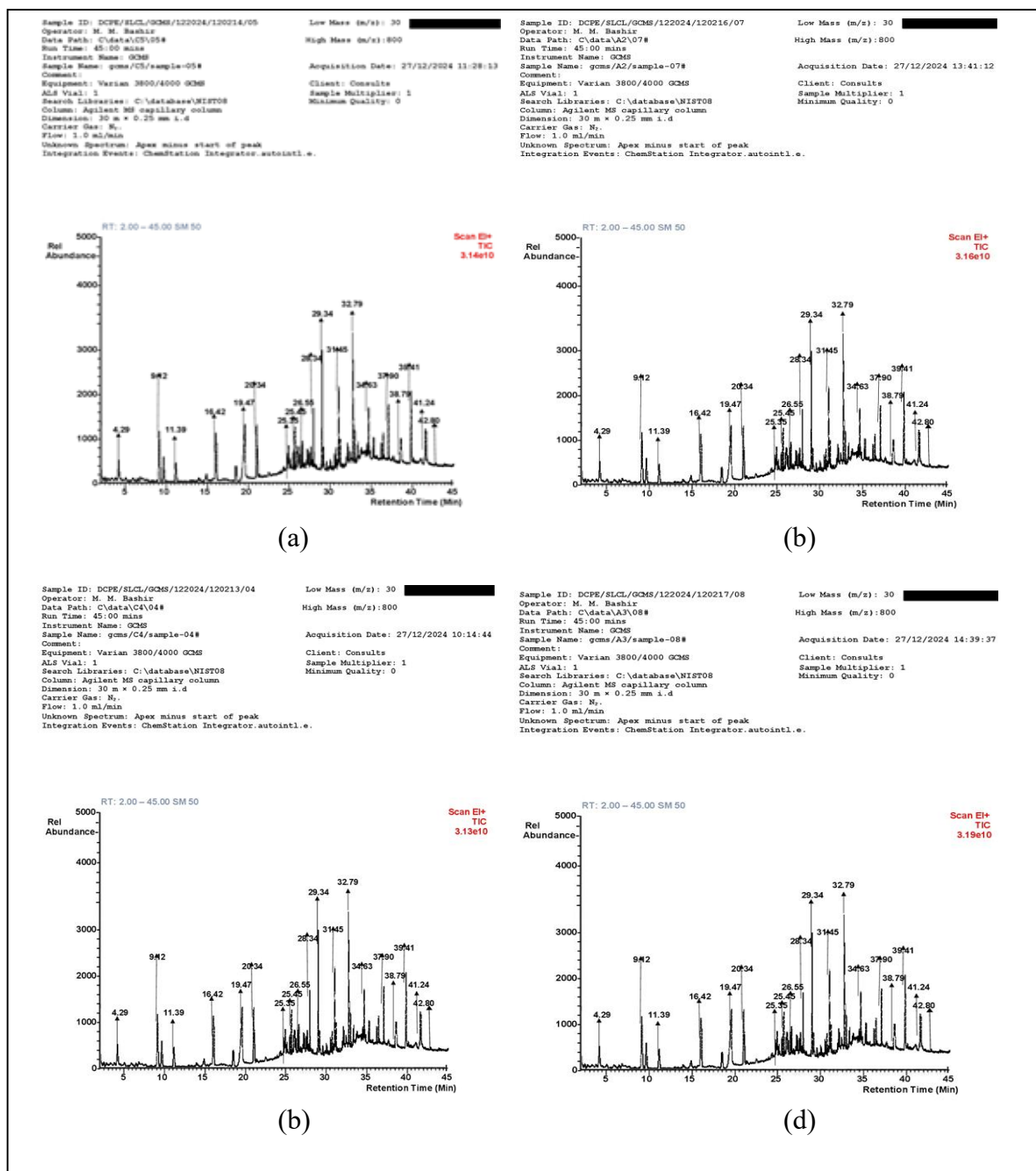


Figure 2 GS-MS Chromatograms of the Dehydrated Products (a - d)

Table 2 Percentage Yield of Phytol Produced @ Different Reaction Temperatures

Catalyst Loading (%)	Percentage Yield of Phytol @ Different Temperatures				
	40 °C	50 °C	60 °C	70 °C	80 °C
0.5	5.60	13.14	3.02	5.84	6.93
1.0	6.36	3.05	7.49	2.14	3.90
1.5	8.77	9.15	4.43	2.59	5.50

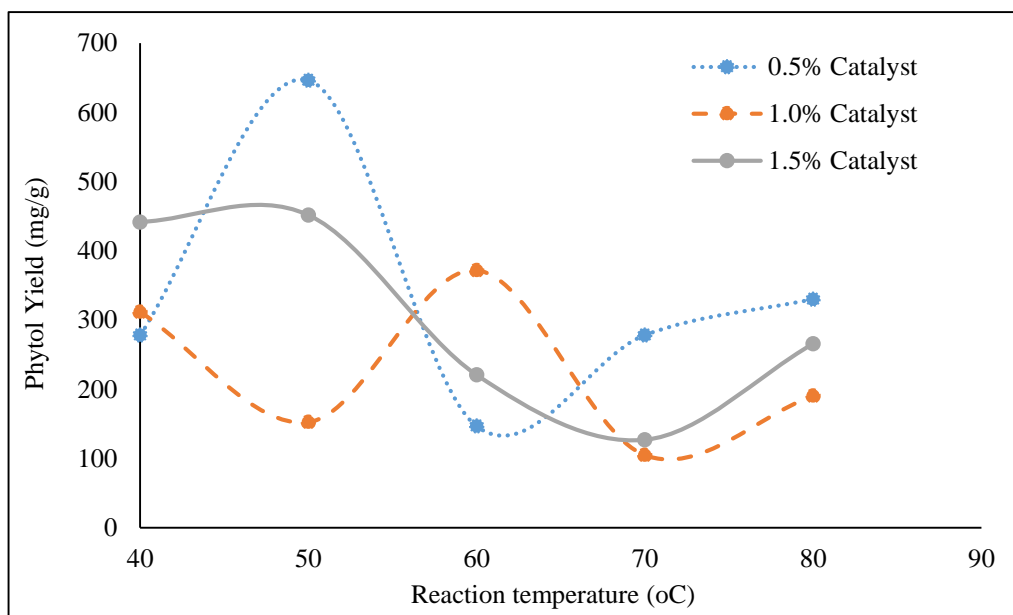


Figure 3: Plot of Yields versus Reaction Temperature

Table 3: ANOVA Table for Statistical Significance

Source of Variation	DF	F	P-value
Catalyst loading	2	5.87	0.017 *
Temperature	4	11.23	0.002 *
Catalyst × Temperature	8	3.76	0.025 *
Error	15	—	—
Total	29	—	—

* Significant at $\alpha = 0.05$

The graph of phytol yield versus reaction temperature shows that the 0.5% $ZnCl_2$ catalyst concentration (blue dotted line) peaked at 50 °C, achieving the highest yield of 646.26 mg/g across all conditions. This was preceded by a sharp increase from 40 °C to 50 °C, followed by a rapid decline between 60 °C and 70 °C, and then a modest rise around 80 °C. These results suggest that at low catalyst loading, a moderate temperature (~50 °C) effectively promotes the release of phytol, likely due to the selective breakdown of phytol precursors without significant degradation. At higher temperatures, the decrease in yield may result from phytol degradation or volatilization. At 1.0% catalyst concentration (orange dashed line), the phytol yield peaked at 60 °C with a moderate value of 371.79 mg/g. Unlike the 0.5% condition, this trend began with a decline from 40 °C to 50 °C, followed by an increase to the peak at 60 °C, then another decrease towards 80 °C. This pattern suggests that increased catalyst concentration may shift the optimal reaction temperature upward, possibly by enhancing the hydrolysis of bound phytol precursors. However, it may also accelerate side reactions or degradation pathways at elevated temperatures.

For the 1.5% catalyst concentration (grey solid line), the highest yield of 451.59 mg/g was also observed at 50 °C. The yield began high but declined steadily to a minimum near 70 °C, with a slight recovery at 80 °C. This trend indicates that excessive catalyst loading could lead to over-catalysis, promoting unwanted degradation or competing reactions. The initially high yield might stem from rapid precursor breakdown, but prolonged exposure to higher temperatures likely compromises phytol stability. Phytol yield is sensitive to both temperature and catalyst concentration, indicating a delicate balance between sufficient hydrolysis and thermal/catalytic degradation. The highest phytol yield was achieved with 0.5% $ZnCl_2$ concentration at 50 °C, suggesting milder conditions favor selective extraction without degradation. Increasing the $ZnCl_2$ concentration beyond a certain point does not proportionally increase yield, likely due to side reactions, catalyst poisoning, or excessive breakdown of target compounds.

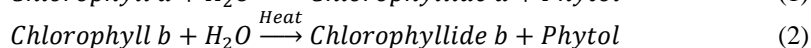
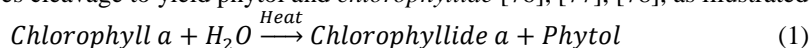
The sinusoidal (wave-like) shapes observed in the phytol yield curves across the reaction temperature range are likely due to the interplay of multiple competing kinetic and thermodynamic processes occurring during the thermal hydrolytic treatment. Zinc chloride functions as a Lewis acid catalyst, and its catalytic efficiency is temperature-dependent [46], [47], [48]. At moderate temperatures, $ZnCl_2$ effectively promotes

hydrolysis, facilitating the release of target compounds such as phytol [49], [50], [51]. However, at elevated temperatures, the catalytic environment may be altered, potentially due to $ZnCl_2$ hydrolysis, complex formation, or other structural changes [52], [53]. Such changes can result in over-catalysis, leading to the formation of undesired side products and a consequent reduction in phytol yield. These variations in catalytic behavior may contribute to the observed sinusoidal trend in the yield-temperature relationship.

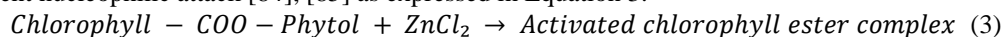
Some intermediates involved in phytol release may be stable or reactive only within specific temperature ranges [2], [54]. As the temperature increases, the dominant reaction intermediates can shift, each governed by distinct kinetic profiles. This dynamic leads to non-linear and potentially periodic variations in phytol yield [55], [56]. Phytol is a relatively volatile compound, and at elevated temperatures, losses due to evaporation or volatilization may occur, particularly in open or semi-open systems [57], [58], [59]. Additionally, the solubility of phytol or its precursors may exhibit non-linear behavior with temperature changes, thereby affecting extraction efficiency [60], [61]. The plant matrix, comprising components such as cell wall structure, lignin content, and moisture, responds to heat in complex, temperature-dependent ways, including swelling or shrinking at specific thresholds [62], [63], [64]. These changes may initially enhance diffusivity and facilitate phytol release, but can later lead to structural collapse or charring [65], [66], [67]. Such physical transformations significantly impact mass transfer dynamics, thereby contributing to the periodic fluctuations observed in phytol yield [68], [69], [70].

Based on the literature, phytol yields vary significantly depending on the extraction method and plant source. Petpheng *et al.* [34] reported a 10.3% yield from *ethanolic* extraction of *Hydrilla verticillata*, which is lower than the 13.14% yield obtained in the present study. In contrast, Xiao *et al.* [36] achieved much lower yields using microwave-assisted extraction: 10.7 mg (0.071%) of phytol from 15.0 g of *U. pinnatifida* leaves and 3.5 mg (0.023%) from *S. fusiforme* leaves. Abd Rahim *et al.* [40] obtained phytol yields of 8.41%, 5.72%, and 4.95% using *n*-hexane, ethyl acetate, and methanol extraction, respectively, from *Syzygium polyanthum* leaves, all of which are notably lower than the yield achieved through the zinc chloride-catalyzed thermal hydrolytic process of *Acacia auriculiformis* leaves. Given the global annual demand for phytol, estimated between 0.1 and 1.0 metric tons [7], [35], [71], [72], this method offers a promising approach for sustainable and scalable industrial production.

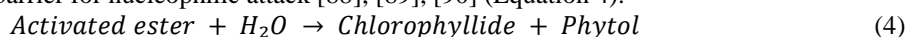
The formation of phytol from *Acacia auriculiformis* leaves via a zinc chloride-catalyzed thermal hydrolytic process involves the degradation of chlorophyll under mild hydrothermal conditions. *Acacia auriculiformis* leaves are known to contain both chlorophyll a and chlorophyll b [73], [74], [75]. Under thermal hydrolytic conditions, typically 40–80 °C, atmospheric pressure, and using water as the solvent, chlorophyll undergoes cleavage to yield phytol and *chlorophyllide* [76], [77], [78], as illustrated in Equations 1 and 2.



Zinc chloride ($ZnCl_2$) functions as a Lewis acid catalyst, promoting hydrolysis by activating electrophilic centers, particularly the ester carbonyl group, thereby facilitating nucleophilic attack and bond cleavage [79], [80], [81], [82], [83]. The first step involves activation of the chlorophyll molecule (Equation 3), where zinc chloride ($ZnCl_2$) coordinates with the ester bond linking the phytol chain to the *chlorophyllide* moiety [84]. This coordination polarizes the carbonyl group, increasing its *electrophilicity* and priming it for subsequent nucleophilic attack [84], [85] as expressed in Equation 3.



The next step involves hydrolysis of the ester bond, where water molecules from the thermal hydrolytic medium act as nucleophiles, attacking the carbonyl carbon of the ester linkage [86], [87]. This reaction is facilitated by zinc chloride ($ZnCl_2$), which activates the ester by polarizing the carbonyl group and lowering the energy barrier for nucleophilic attack [88], [89], [90] (Equation 4).



Zinc chloride acts as a Lewis acid by polarizing the ester carbonyl group of chlorophyll, thereby enhancing the susceptibility of the carbonyl carbon to nucleophilic attack [84], [91]. This catalytic activation facilitates the cleavage of the ester bond, leading to the release of free phytol and *chlorophyllide* [44], [52], [92], [93]. In the final step, phytol, due to its hydrophobic nature, partitions into organic solvent layers or may condense into droplets within aqueous suspensions [94], [95], [96]. *Chlorophyllide*, being more polar, typically remains in the aqueous phase, although it may undergo further degradation under extended thermal or catalytic conditions [77], [93], [97].

IV. CONCLUSION

This study shows that zinc chloride-catalyzed thermal hydrolysis of *Acacia auriculiformis* leaves under mild conditions is an efficient, green method for phytol production, achieving a yield of 13.14% confirmed by GC-MS. The results surpass traditional extraction methods, demonstrating the potential for sustainable, scalable phytol production from underutilized biomass. This approach supports circular bio-economy goals by replacing petrochemical sources with renewable feedstock. Further work should focus on process optimization, scale-up, and full techno-economic evaluation to enable industrial application. Future research should optimize reaction conditions and assess catalyst reusability for cost-effectiveness. Pilot-scale trials and techno-economic analysis are needed to evaluate industrial feasibility and sustainability. Life cycle assessment is recommended to ensure environmental benefits. Exploring other underutilized *lignocellulosic* feedstock could expand this green method's applicability for phytol and other bioactive compounds, supporting wider adoption of renewable resources in industrial production.

V. ACKNOWLEDGEMENT

The authors wish to express their sincere appreciation to Engr. Mrs. Deborah C. Nwakwuba for kindly providing the *Acacia auriculiformis* leaves from the National Research Institute for Chemical Technology (NARICT), Zaria. We are also grateful to Engr. Kabir Lawal of the Department of Chemical Engineering, Kaduna Polytechnic, Kaduna, for his invaluable laboratory assistance during the course of this research.

REFERENCES

- [1] Islam MT, Ali ES, Uddin SJ, Shaw S, Islam MA, Ahmed MI, et al. Phytol: A review of biomedical activities. *Food Chem Toxicol.* 2018; 121:82–94.
- [2] Saranya C. Pharmacokinetic evaluation of phytol in rats [dissertation]. Kerala: Kerala Veterinary and Animal Sciences University; 2022.
- [3] Yang W. The Role of Phytol Degradation in Chlorophyll and Tocopherol (Vitamin E) Metabolism [dissertation]. Bonn: Universitäts-und Landesbibliothek Bonn; 2021.
- [4] El-Dakrouy YM, Abou Zeid AH, El Hela AA, Temraz A, Mohammed RS. GC-MS Profiling, in-vitro Antioxidant, Anti-inflammatory and Anti-diabetic Activities of Petroleum Ether Extract of *Dypsis decaryi* and *Dypsis leptocheilos* Leaves Cultivated in Egypt: Experimental and Computational Studies. *Azhar Int J Pharm Med Sci.* 2025; 5(1):157–76.
- [5] Ou-Ani O, Moujane S, Oucheikh L, Youssefi Y, Znini M, Chebabe D, et al. Chemical composition, in vitro antifungal activity, molecular docking and molecular dynamics simulation studies of the essential oil of *Ballota hirsuta*. *J Biol Act Prod Nat.* 2023; 13(1):27–48.
- [6] Kundu S, Sarkar D. Synthetic attempts toward α -tocopherol - An overview. *J Heterocycl Chem.* 2023; 60(3):345–68.
- [7] Krauß S, Vetter W. Phytol and phytol fatty acid esters: occurrence, concentrations, and relevance. *Eur J Lipid Sci Technol.* 2018; 120(7):1700387.
- [8] Martins T, Barros AN, Rosa E, Antunes L. Enhancing health benefits through chlorophylls and chlorophyll-rich agro-food: A comprehensive review. *Molecules.* 2023; 28(14):5344.
- [9] Olofsson P, Hultqvist M, Hellgren LI, Holmdahl R. Phytol: A chlorophyll component with anti-inflammatory and metabolic properties. *Recent Adv Redox Active Plant Microb Prod.* 2014:345–59.
- [10] Veneklaas EJ, Lambers H, Bragg J, Finnegan PM, Lovelock CE, Plaxton WC, et al. Opportunities for improving phosphorus-use efficiency in crop plants. *New Phytol.* 2012; 195(2):306 - 20.
- [11] Karlický V, Kmecova Materova Z, Kurasová I, Nezval J, Štroch M, Garab G, et al. Accumulation of geranylgeranylated chlorophylls in the pigment-protein complexes of *Arabidopsis thaliana* acclimated to green light: effects on the organization of light-harvesting complex II and photosystem II functions. *Photosynth Res.* 2021; 149(1):233–52.
- [12] Nowicka B, Trela-Makowej A, Latowski D, Strzalka K, Szymańska R. Antioxidant and signaling role of plastid-derived isoprenoid quinones and chromanols. *Int J Mol Sci.* 2021; 22(6):2950.
- [13] Shen S, Wang Y, Dong J, Zhang R, Parikh A, Chen JG, et al. Mimicking thylakoid membrane with chlorophyll/TiO₂/lipid Co-assembly for light-harvesting and oxygen releasing. *ACS Appl Mater Interfaces.* 2021; 13(9):11461–9.
- [14] Lakshmaiah VV, Joseph BV, Bhaskar R, Ulhas RS, Al-Khayri JM, Nagella P. In vitro production of tocopherols. In: *Nutraceuticals Production from Plant Cell Factory.* Singapore: Springer; 2022. p. 287–319.
- [15] Vidya Muthulakshmi M, Srinivasan A, Srivastava S. Antioxidant green factories: Toward sustainable production of vitamin E in plant in vitro cultures. *ACS Omega.* 2023; 8(4):3586–605.

- [16] Correia R, Quintela JC, Duarte MP, Gonçalves M. Insights for the valorization of biomass from Portuguese invasive *Acacia* spp. in a biorefinery perspective. *Forests*. 2020; 11(12):1342.
- [17] Gamal El-Din MI, Youssef FS, Altyar AE, Ashour ML. GC/MS analyses of the essential oils obtained from different *Jatropha* species, their discrimination using chemometric analysis, and assessment of their antibacterial and anti-biofilm activities. *Plants*. 2022; 11(9):1268.
- [18] Lima TL, Souza LB, Tavares-Pessoa LC, Santos-Silva AMD, Cavalcante RS, Araújo-Júnior RF, et al. Phytol-loaded solid lipid nanoparticles as a novel anticandidal nanobiotechnological approach. *Pharmaceutics*. 2020; 12(9):871.
- [19] Saiyam D, Dubey A, Malla MA, Kumar A. Lipopeptides from *Bacillus*: Unveiling biotechnological prospects—Sources, properties, and diverse applications. *Braz J Microbiol*. 2024; 55(1):281–95.
- [20] Nourbakhsh F, Lotfalizadeh M, Badpeyma M, Shakeri A, Soheili V. From plants to antimicrobials: Natural products against bacterial membranes. *Phytother Res*. 2022; 36(1):33–52.
- [21] Nocedo-Mena D, Arrasate S, Garza-González E, Rivas-Galindo VM, Romo-Mancillas A, Munteanu CR, et al. Molecular docking, SAR analysis and biophysical approaches in the study of the antibacterial activity of ceramides isolated from *Cissus incisa*. *Bioorg Chem*. 2021; 109:104745.
- [22] Makarewicz M, Drożdż I, Tarko T, Duda-Chodak A. The interactions between polyphenols and microorganisms, especially gut microbiota. *Antioxidants*. 2021; 10(2):188.
- [23] Saadullah M, Rashad M, Asif M, Shah MA. Biosynthesis of phytonutrients. In: *Phytonutrients and Neurological Disorders*. Academic Press; 2023. p. 57–105.
- [24] Panchabhai P, Kaliaperumal N, Mannathusamy G, Chinnadurai A. An Improved and Plant Viable Synthesis of Vitamin K1. *J Pharm Res Int*. 2021; 33(47B):538–47.
- [25] Dong W, Zhao Q, Zhao J, Zhang J, Wang Y, Qiao Y. Qualitative analysis of aromatic compounds via 1D TOCSY techniques. *Magn Reson Lett*. 2024; 4(1):100091.
- [26] Barzallo D, Reinoso MA, Miranda G, Romero T, Franco M, Palmay P. Bifunctional catalytic performance of Zn/ZSM-5 in the aromatization of LPG and the conversion of pyrolytic gases from recycled polypropylene. *ChemEngineering*. 2024; 8(6):108.
- [27] Yang C, Li R, Qiu Q, Yang H, Zhang Y, Yang B, et al. Pyrolytic behaviors of *Scenedesmus obliquus* over potassium fluoride on alumina. *Fuel*. 2020; 263:116724.
- [28] Schmidt SK, Ley RE. Microbial competition and soil structure limit the expression of allelochemicals in nature. In: *Principles and Practices in Plant Ecology*. CRC Press; 2023. p. 339–51.
- [29] Zerva A, Pentari C, Termentzi A, America AHP, Zouraris D, Bhattacharya SK, et al. Discovery of two novel laccase-like multicopper oxidases from *Pleurotus citrinopileatus* and their application in phenolic oligomer synthesis. *Biotechnol Biofuels*. 2021; 14:1–16.
- [30] Weiss R, Guebitz GM, Pellis A, Nyahongo GS. Harnessing the power of enzymes for tailoring and valorizing lignin. *Trends Biotechnol*. 2020; 38(11):1215–31.
- [31] Alamgir ANM. Phytoconstituents—Active and inert constituents, metabolic pathways, chemistry and application of phytoconstituents, primary metabolic products, and bioactive compounds of primary metabolic origin. In: Alamgir ANM, editor. *Therapeutic use of medicinal plants and their extracts*. Vol. 2. *Phytochemistry and bioactive compounds*. Cham: Springer; 2018. p. 25–164. doi:10.1007/978-3-319-92360-1_2
- [32] Patel MK, Pandey S, Kumar M, Haque MI, Pal S, Yadav NS. Plants metabolome study: Emerging tools and techniques. *Plants*. 2021; 10(11):2409. doi:10.3390/plants10112409
- [33] Thakor P, Mehta JB, Patel RR, Patel DD, Subramanian RB, Thakkar VR. Extraction and purification of phytol from *Abutilon indicum*: cytotoxic and apoptotic activity. *RSC Adv*. 2016; 6(54):48336–45.
- [34] Petpheng B, Mudtaleb B, Piboon W, Paichid N, Sangkharak K. The extraction of phytol from *Hydrilla verticillata* using ultrasonic-assisted extraction (UAE), the analysis of antibacterial activity, and the utilization of residual extract for polyhydroxyalkanoate (PHA) production. *Biomass Convers Biorefinery*. 2024; 14(18):22007–17.
- [35] Prabha SP, Karthik C, Chandrika SH. Phytol—A biosurfactant from the aquatic weed *Hydrilla verticillata*. *Biocatal Agric Biotechnol*. 2019; 17:736–42.
- [36] Xiao XH, Yuan ZQ, Li GK. Preparation of phytosterols and phytol from edible marine algae by microwave-assisted extraction and high-speed counter-current chromatography. *Sep Purif Technol*. 2013; 104:284–9.
- [37] Alara OR, Abdurahman NH, Ukaegbu CI, Kabbashi NA. Extraction and characterization of bioactive compounds in *Vernonia amygdalina* leaf ethanolic extract comparing Soxhlet and microwave-assisted extraction techniques. *J Taibah Univ Sci*. 2019; 13(1):414–22.

- [38] Dunkić V, Nazlić M, Ruščić M, Vuko E, Akrap K, Topić S, et al. Hydrodistillation and microwave extraction of volatile compounds: Comparing data for twenty-one *Veronica* species from different habitats. *Plants*. 2022; 11(7):902.
- [39] Al-Omar MS. Phytochemical analysis, antioxidant, and anti-microbial activities of *Suaeda vermiculata* n-hexane extract in comparison to the plant's hydrodistilled volatile oil. *Pharmacogn J*. 2021; 13(4).
- [40] Abd Rahim ENA, Ismail A, Omar MN, Rahmat UN, Ahmad WANW. GC-MS analysis of phytochemical compounds in *Syzygium polyanthum* leaves extracted using an ultrasound-assisted method. *Pharmacogn J*. 2018; 10(1).
- [41] Ali A. M, Ibrahim H. Conversion of waste biomass into valuable platform furan-based compounds. *Asian J Adv Res*. 2023; 6(1):553–9. doi:10.9734/ajar/2023/v6i130233
- [42] Ibrahim H, Ali A. M., Mukhtar F. H. Investigating the application of barium chloride catalyst for the synthesis of phthalic acid esters from *Gmelina arborea* leaves. *Int J Eng Process Saf Res*. 2024.
- [43] Bao Y, Magallanes-Lundback M, Kim SS, Deason N, Niu Y, Johnny C, et al. A family of α/β hydrolases removes phytol from chlorophyll metabolites for tocopherol biosynthesis in *Arabidopsis*. *Plant Cell*. 2025; 37(2):koaf021.
- [44] Gutbrod P, Yang W, Grujicic GV, Peisker H, Gutbrod K, Du LF, Dörmann P. Phytol, derived from chlorophyll hydrolysis in plants, is metabolized via phytenal. *J Biol Chem*. 2021; 296:100244. doi:10.1016/j.jbc.2021.100244
- [45] Durrett TP, Welti R. The tail of chlorophyll: Fates for phytol. *J Biol Chem*. 2021; 296.
- [46] Keerthi Krishnan K, Ujwaldev SM, Saranya S, Anilkumar G, Beller M. Recent advances and perspectives in the synthesis of heterocycles via zinc catalysis. *Adv Synth Catal*. 2019; 361(3):382–404.
- [47] Ji Y, Zhang F, Yu F, Zhang J, Zhang J. Methyl chloride synthesis over metal chloride-modified mesoporous alumina catalyst. *Catalysts*. 2018; 8(3):99.
- [48] Schmidt SA, Peurla M, Kumar N, Eränen K, Murzin DY, Salmi T. Preparation of selective $ZnCl_2$ /alumina catalysts for methyl chloride synthesis: Influence of pH, precursor, and zinc loading. *Appl Catal A Gen*. 2015; 490:117–27.
- [49] Saka C, Kaya M, Bekiroğullari M. *Chlorella vulgaris* microalgae strain modified with zinc chloride as a new support material for hydrogen production from $NaBH_4$ methanolysis using CuB, NiB, and FeB metal catalysts. *Int J Hydrogen Energy*. 2020; 45(3):1959–68.
- [50] Lindemer MD, Advani SG, Prasad AK. Experimental investigation of heterogeneous hydrolysis with Zn vapor under a temperature gradient. *Int J Hydrogen Energy*. 2017; 42(12):7847–56.
- [51] Wei W, Wu S. Depolymerization of cellulose into high-value chemicals by using a synergy of zinc chloride hydrate and sulfate ion-promoted titania catalyst. *Bioresour Technol*. 2017; 241:760–6.
- [52] Hu X, Gu T, Khan I, Zada A, Jia T. Research progress in the interconversion, turnover, and degradation of chlorophyll. *Cells*. 2021; 10(11):3134. doi:10.3390/cells10113134
- [53] Hogg JM, Brown LC, Matuszek K, Latos P, Chrobok A, Swadźba-Kwaśny M. Liquid coordination complexes of Lewis acidic metal chlorides: Lewis acidity and insights into speciation. *Dalton Trans*. 2017; 46(35):11561–74.
- [54] Nierop KG, Mijs M, Dekker R, Lewan MD, Speelman EN, de Leeuw JW, Reichart GJ. Thermal stability of freshwater fern *Azolla* biomarkers as assessed by hydrous pyrolysis. *Org Geochem*. 2025; 105008.
- [55] Cabral TO, Noronha FB, Toniolo FS. Kinetic and DRIFTS studies of the CO_2 catalytic hydrogenation on Ru/SiO₂: A comprehensive and strategic investigation of CO_2 methanation mechanisms by kinetic modeling and data regression. *Chem Eng J*. 2024; 485:149716.
- [56] Kulichikhin VG, Malkin AY. The role of structure in polymer rheology. *Polymers*. 2022; 14(6):1262.
- [57] Malik TG, Sahu LK, Gupta M, Mir BA, Gajbhiye T, Dubey R, et al. Environmental factors affecting monoterpene emissions from terrestrial vegetation. *Plants*. 2023; 12(17):3146.
- [58] Culpepper LS. Soil Physicochemical and Microbial Responses to High-Energy Fires in a Semi-Arid Savanna [dissertation]. 2020.
- [59] Pichersky E, Dudareva N, editors. *Biology of plant volatiles*. Boca Raton: CRC Press; 2020.
- [60] Mukherjee S, Verma A, Kong L, Rengan AK, Cahill DM. Advancements in green nanoparticle technology: Focusing on the treatment of clinical phytopathogens. *Biomolecules*. 2024; 14(9):1082.
- [61] Hessel V, Liang S, Tran NN, Escribà-Gelonch M, Zeckovic O, Knowling M, et al. Eustress in space: opportunities for plant stressors beyond the Earth ecosystem. *Front Astron Space Sci*. 2022; 9:841211.
- [62] Cosgrove DJ. Structure and growth of plant cell walls. *Nat Rev Mol Cell Biol*. 2024; 25(5):340–58.
- [63] Ezquer I, Salameh I, Colombo L, Kalaitzis P. Plant cell walls tackling climate change: biotechnological strategies to improve crop adaptations and photosynthesis in response to global warming. *Plants*. 2020; 9(2):212.

- [64] Jakes JE, Hunt CG, Zelinka SL, Ciesielski PN, Plaza NZ. Effects of moisture on diffusion in unmodified wood cell walls: a phenomenological polymer science approach. *Forests*. 2019; 10(12):1084.
- [65] Singaram AJV, Guruchandran S, Ganesan ND. Review of functionalized pectin films for active food packaging. *Packag Technol Sci*. 2024; 37(4):237–62.
- [66] Ahmadi M, Zabihi O, Nia ZK, Unnikrishnan V, Barrow CJ, Naebe M. Engineering flame and mechanical properties of natural plant-based fibre biocomposites. *Adv Ind Eng Polym Res*. 2024; [Epub ahead of print].
- [67] Ding Y, Pang Z, Lan K, Yao Y, Panzarasa G, Xu L, et al. Emerging engineered wood for building applications. *Chem Rev*. 2022; 123(5):1843–88.
- [68] Vroom RJE, Van Den Berg M, Pangala SR, Van Der Scheer OE, Sorrell BK. Physiological processes affecting methane transport by wetland vegetation – a review. *Aquat Bot*. 2022; 182:103547.
- [69] Xiao Y, Liu L, Li Z, Cheng Y. The role of cyanobacterial external layers in mass transfer: evidence from temperature shock experiments by noninvasive microtest technology. *Microorganisms*. 2020; 8(6):861.
- [70] Pecha MB, Arbelaez JIM, Garcia-Perez M, Chejne F, Ciesielski PN. Progress in understanding the four dominant intra-particle phenomena of lignocellulose pyrolysis: chemical reactions, heat transfer, mass transfer, and phase change. *Green Chem*. 2019; 21(11):2868–98.
- [71] Rosa GP, Seca AM, Pinto DC, Barreto MC. New phytol derivatives with increased cosmeceutical potential. *Molecules*. 2024; 29(20):4917.
- [72] Gliszczyńska A, Dancewicz K, Gabryś B, Świtalska M, Wietrzyk J, Maciejewska G. Synthesis of novel phytol-derived γ -butyrolactones and evaluation of their biological activity. *Sci Rep*. 2021; 11(1):4262.
- [73] Singh H. Exploring adaptive modulation in plant functional traits and its impact on the productivity of *Acacia auriculiformis* under a CO₂-enriched environment. *Ind Crops Prod*. 2024; 210:118186.
- [74] Restu M, Kariming MRZ. Morphological characteristics and potential of *Acacia* biomass (*Acacia auriculiformis*) in the Educational Forest of Hasanuddin University. *IOP Conf Ser Earth Environ Sci*. 2023; 1277(1):012037.
- [75] Zerkout A, Mustafa M, Omar H, Ibrahim MH, Go R. *Acacia auriculiformis* Cunn. Ex Benth as phytoextraction agent: a growth response, physiological tolerance and lead removal capability evaluation. *Jordan J Biol Sci*. 2021; 14(3).
- [76] Ebrahimi P, Shokramraji Z, Tavakkoli S, Mihaylova D, Lante A. Chlorophylls as natural bioactive compounds existing in food by-products: a critical review. *Plants*. 2023; 12(7):1533.
- [77] Wang YT, Yang CH, Huang KS, Shaw JF. Chlorophyllides: preparation, purification, and application. *Biomolecules*. 2021; 11(8):1115.
- [78] Samide A, Tutunaru B. Thermal behaviour of the chlorophyll extract from a mixture of plants and seaweed. *J Therm Anal Calorim*. 2017; 127:597–604.
- [79] Guzmán Solís E. Catalysis with deep eutectic solvents: challenges and opportunities. 2025.
- [80] Chandrasekaran I, Sarveswari S. Different catalytic approaches of the Friedländer synthesis of quinolines. *Heliyon*. 2025.
- [81] Trauner F. Transition-metal free strategies for the construction and functionalization of strained unsaturated carbo- and heterocyclic systems [dissertation]. LMU; 2025.
- [82] Ayesha, Ashraf A, Arshad M, Sajid N, Rasool N, Abbas M, et al. Dinuclear Zn-catalytic system as Brønsted base and Lewis acid for enantioselectivity in the same chiral environment. *ACS Omega*. 2024; 9(6):6074–92.
- [83] Hamdi J. The synthesis of heterogeneous catalysts: transition metal nanoparticles encapsulated in halloysite and applications in organic transformations. 2021.
- [84] Tamiaki H. Chlorophylls. In: *Fundamentals of Porphyrin Chemistry: A 21st Century Approach*. Vol. 2. Wiley; 2022. p. 743–76.
- [85] Gibbons DJ. Structure and conformation of photosynthetic pigments and related compounds: conformation analysis of chlorophyll derivatives [dissertation]. The University of Dublin; 2019.
- [86] Lacchini E, Erffelinck ML, Mertens J, Marcou S, Molina - Hidalgo FJ, Tzfadia O, et al. The saponin bomb: a nucleolar-localised β - glucosidase hydrolyses triterpene saponins in *Medicago truncatula*. *New Phytol*. 2023; 239(2):705–19.
- [87] Ciarkowska A, Ostrowski M, Starzyńska E, Jakubowska A. Plant SCPL acyltransferases: multiplicity of enzymes with various functions in secondary metabolism. *Phytochem Rev*. 2019; 18:303–16.
- [88] Alam MM, Varala R, Seema V. Zinc acetate in organic synthesis and catalysis: a review. *Mini Rev Org Chem*. 2024; 21(5):555–87.
- [89] Chen X. Applications of radical reactions for the synthesis of β -amino acids and carbonyl compounds [dissertation]. Institut Polytechnique de Paris; 2020.

- [90] Lupidi G. Functionalization of cyclic structures for advanced biological and pharmaceutical applications. 2019.
- [91] Pareek S, Sagar NA, Sharma S, Kumar V, Agarwal T, González - Aguilar GA, Yahia EM. Chlorophylls: chemistry and biological functions. In: *Fruit and Vegetable Phytochemicals: Chemistry and Human Health*. 2nd ed. Wiley-Blackwell; 2017. p. 269–84.
- [92] Liu J, Knapp M, Jo M, Dill Z, Bridwell-Rabb J. Rieske oxygenase catalysed C–H bond functionalization reactions in chlorophyll b biosynthesis. *ACS Cent Sci*. 2022; 8(10):1393–402.
- [93] Pucci C, Martinelli C, Degl'Innocenti A, Desii A, De Pasquale D, Ciofani G. Light - activated biomedical applications of chlorophyll derivatives. *Macromol Biosci*. 2021; 21(9):2100181.
- [94] Brenner MB. Biopharmaceutical characterisation and formulation development of poorly water-soluble phytochemicals using in vivo predictive biphasic dissolution [dissertation]. Universitäts-und Landesbibliothek Bonn; 2024.
- [95] Ossola R, Farmer D. The chemical landscape of leaf surfaces and its interaction with the atmosphere. *Chem Rev*. 2024; 124(9):5764–94.
- [96] Nagarajan J, Wah Heng W, Galanakis CM, Nagasundara Ramanan R, Raghunandan ME, Sun J, et al. Extraction of phytochemicals using hydrotropic solvents. *Sep Sci Technol*. 2016; 51(7):1151–65.
- [97] Hayes M, Ferruzzi MG. Update on the bioavailability and chemopreventative mechanisms of dietary chlorophyll derivatives. *Nutr Res*. 2020; 81:19–37.