SYNTHESIS OF CHALCONES VIA CLAISEN–SCHMIDT CONDENSATION REACTION CATALYZED BY SILICA-H$_2$SO$_4$ UNDER ULTRASOUND IRRADIATION

Achraf Lahyani[1], Manef Chtourou[1], Mohamed Hédi Frikha[1], Mahmoud Trabelsi[1*]

1/Laboratory of Applied Chemistry: Heterocyclics, Fats and Polymers

Faculty of Sciences, University of Sfax, Route de Soukra Km 3,5 -3038- Sfax. Tunisia

E-mail: achraf.lahyani84@gmail.com

*Corresponding author: Mah.Trabelsi@fss.rnu.tn

ABSTRACT

The synthesis of 1,3-diaryl-2-propenones was carried out by using ultrasonic irradiation in the presence of silica-H$_2$SO$_4$, which was used as a catalyst in solvent-free conditions. The advantages of this process are the high yields (82–98%) it produces, the cost effectiveness of the catalyst, and the simple work-up and purification of products achieved via a non-chromatographic method.

Keywords

Trans-chalcones; Silica-H$_2$SO$_4$; Solvent-free; Ultrasound irradiation; Claisen-Schmidt condensation

Council for Innovative Research

1. INTRODUCTION

Trans-chalcones are a family of aromatic ketones with two aromatic groups bridged by an enone linkage (Ar–COCH=CH–Ar').

These compounds exhibit a broad spectrum of biological activities, including antimicrobial [1], anti-inflammatory, antifungal, antioxidant, cytotoxic, antitumor [2], anti- cancer [3], analgesic, antiplatele, antiulcerative, antiviral [4], antihyperglycemic, immunomodulatory, antiangeogenic [5], antileishmanial [6], and antimalarial [7] properties. In addition, chalcones are capable of inducing apoptosis [8]. These compounds are usually synthesized using the Claisen–Schmidt condensation reaction of aryl methyl ketones with aromatic aldehydes.

Traditionally, the synthesis of chalcones via Claisen–Schmidt condensation is carried out either in basic or acidic media under homogenous conditions [9]. For example, common methods for synthesizing 1,3-diaryl-2-propenones involve the use of strong bases such as sodium hydroxide, potassium hydroxide, telluroxide (bis (p-methoxyphenyl)), $Ba(OH)_2$, hydrotalcites, LiHMDS, calcined $NaNO_3$/natural phosphate [6].The following acids have also been used to catalysechalcone synthesis: $AlCl_3$, anhydrous HCl, $TiCl_4$, $RuCl_3$, BF_3 [10], B_2O_3, and p-toluenesulfonic acid [11]. Chalcone synthesis has also been achieved employing the Suzuki reaction [12]. All these reactions are performed in the presence of organic solvents.

The reported procedures have a number of disadvantages, such as long reaction times (14 h-5 days), special efforts needed to prepare the catalysts, high temperatures, use of costly reagents [10] and side reactions, such as a Cannizarro reaction and aldol condensation [13].

Recently, solvent-free conditions and heterogeneous catalysts have grown in importance in organic synthesis as their use reduces environmental pollution and lowers handling costs due to simplification of the work-up technique [14].

Different heterogeneous acid or basic catalysts have been employed to synthesize trans-chalcones, such as acid–clays [15], Bambo char sulfonic acid [9], potassium hydroxide impregnated silica gel [15], amino grafted zeolites [16], Amberlyst-15 and Amberlite-200C [17]. Silica-H_2SO_4 is a versatile, selective, and powerful catalyst that has been explored for various organic transformations, such as the synthesis of heterocyclic compounds [18], cross-aldol condensations [19], Michael additions [20], and oxidation reactions [21].

Our purpose in this work was to synthesize trans-chalcones using silica-H_2SO_4 as a catalyst under ultrasound irradiation and in solvent free conditions. This method has several advantages as compared to conventional methods, including a shorter reaction time, increased yield, moderate reaction temperatures, purity of the products, and an environmentally benign and safe protocol. Herein we obtained a highly effective and easily separable silica-H_2SO_4 catalyst under eco-friendly conditions.

2. EXPERIMENTAL

2.1 Materials

Silica-H_2SO_4 was used as a catalyst for the preliminary reaction between benzaldehyde and acetophenone. Silica gel 60 (with fluorescent indicator F254), aryl-benzaldehydes (98–99%), and aryl-acetophenones (98–99%) were purchased from commercial suppliers and used as received.

2.2 Catalyst Preparation

The silica-H_2SO_4 catalyst was prepared as prescribed by Andreas Kogelbauer et al. [22]. Silica gel 60 (Fluka) was used. The silica supports were calcined in static air at 400°C for 18 h and cooled in a desiccator. The silica was then added to an excess of 70% H_2SO_4 based on the total pore volume of the silica (2.33 g H_2SO_4 solution/g silica). This mixture was vigorously shaken for 5 min and allowed to rest for 7 days in a closed glass flask without maintaining incipient wetness. The resulting catalyst was filtered using a glass fritt and dried at 120°C in static air for 18 h. Subsequently, the catalyst was stored in a desiccator under vacuum and recalcined at 120°C prior to reaction.

2.3 General Procedure for the Synthesis of trans-Chalcones

The silica-H_2SO_4 (0.02 g) was added to a mixture of aryl-benzaldehyde (7.91 mmol, 1.05 eq.) and methyl aryl-ketone (7.53 mmol, 1 eq.) in a 10 mL glass reactor. The reaction mixture was then heated in an oil bath at 65±2°C. The ultrasound probe was immersed directly in the reactor. An ultrasonic generator (Bioblock Scientific 750 W) emitted sound vibration into the reaction mixture. Sonification was achieved at low frequencies of 20 kHz (amplitude of 30%). The reaction time was fixed at 1 h. The reaction mixture was then cooled to room temperature and partitioned between brine (25 mL) and dichloromethane (3 × 15 mL). Solid silica-H_2SO_4 was washed with acetone (15 mL) to ensure the desorption of product on the silica-H_2SO_4 surface. The combined organic extract was washed with brine (3 × 25 mL) and the organic extract was dried over anhydrous Na_2SO_4, filtered, and evaporated. The dried crude products where crystallised from 95% ethanol, except for the nitro-chalcones, which were crystallized from acetone, filtrated, and finally dried under vacuum for 48 h. The melting points of the isolated products were measured using a Reichert-Heizbank apparatus. The yields of the reactions were determined by gas chromatography on a Shimadzu 2014-GC apparatus using chloroform as solvent. The capillary column was DB-5 and the carrier gas was nitrogen.

2.4 Spectroscopic Analysis

The IR analysis was performed using a Perkin Elmer Spectrum version 10 spectrometer.

The NMR spectra of the isolated products were recorded in solution in CDCl$_3$ on a spectrometer type AC Bruker (^{1}H at 600 MHz and ^{13}C at 150 MHz). The internal reference was CDCl$_3$.

The spectral data of some isolated compounds, taken as representative examples, are summarized below.

2.4.1. 1,3-Diphenyl-propenone (3ab)

IR [v, cm^{-1}] 3060.2 (C=C-H, Ar-H), 1662.6 (C=O), 1602.5 (C=C, Ar), 1575.3; ^{1}H NMR [δ, ppm] 8.16 (2H, d, J$_{H-H}$ = 7.2 Hz), 7.93 (1H, d, J$_{Hα-Hβ}$ = 15.6 Hz), 7.65 (1H, d, J$_{Hα-Hβ}$ = 15.6 Hz), 7.59 (2H, t, J$_{H-H}$ = 7.2 Hz et J$_{H-H}$ =8.4 Hz) , and 6H between 7.51 and 7.67 ppm; ^{13}C NMR [δ,ppm] 190.6, 144.9 , 138.3 , 134.9 , 133.1 , 132.8, 130.6, 129.0 , 128.7 (2C) , 128.5 , 128.5, 128.2, 127.5, 122.2.

2.4.2. 3-(2-chlorophenyl)-1-(4-nitrophenyl)-propenone (3ec)

IR[v, cm^{-1}] 3085.04 (C=C-H, Ar-H), 1661.45 (C=O), 1589.62 (C=C, Ar), 1344.12 (NO$_2$); ^{1}H NMR [δ, ppm] 8.28 (2H, d, J$_{H-H}$ = 8.4 Hz), 8.06 (2H, d, J$_{H-H}$ = 8.4 Hz), 8.13 (1H, d, J$_{Hα-Hβ}$ = 15.6 Hz), 7.69 (1H, dd, J$_{H-H}$ = 7.2 Hz), 7.36 (1H, d, J$_{Hα-Hβ}$ 15.6 Hz), 7.39 (1H, dd, J$_{H-H}$ = 7.8 Hz), 7.30 (1H, m, J$_{H-H}$ = 7.8 Hz), 7.28 (1H, m, J$_{H-H}$ =7.2 Hz); ^{13}C NMR [δ,ppm] 191.7, 152.8, 145.4, 145.2, 138.4 , 135.3, 134,5, 133.12, 132.2 (2C), 130.5, 129.9, 126.7, 126,5 (2C).

### 2.4.3. 1-(4-chlorophenyl)-3-(2-methoxyphenyl)-propenone (3fd)

IR [v, cm^{-1}] 2933.21 (C=C-H, Ar-H), 2863.15, 2845.62, 1661.00 (C=O), 1572.04 (C=C, Ar); ^{1}H NMR [δ, ppm] 3.90 (3H, s), 8.06(1H, d, J$_{Hα-Hβ}$ =15,6 Hz), 7.94 (2H, d, J$_{H-H}$ =9 Hz), 7.61(1H, d, J$_{H-H}$ =7.8 Hz), 7.56(1H, d, J$_{Hα-Hβ}$ =15,6 Hz), 7.45 (2H, d, J$_{H-H}$ =9 Hz) and 3H between 6.93 and 7.39 ppm; ^{13}C NMR [δ,ppm] 192.5, 161.8, 143.6, 141.55, 139.7, 134.6 , 132.6 (2C) , 132.0, 131.5 (2C), 126.4, 125.0, 123.4, 113.9, 58.2.

2.4.4. 3-(4-methoxyphenyl)-1-(4-nitrophenyl)-propenone (3hc)

IR [v, cm^{-1}] 3077.07 (C=C-H, Ar-H), 2967.87, 2840.16, 1656.20 (C=O), 1591.15 (C=C, Ar), 1336.16 (NO$_2$); ^{1}H NMR [δ, ppm] 3.8 (3H, s), 8.26 (2H, d, J$_{H-H}$ =9 Hz), 8.05 (2H, d, J$_{H-H}$ =7.8 Hz), 7.74 (1H, d, J$_{Hα-Hβ}$ =15 Hz), 7.54 (2H,d, J$_{H-H}$ =9 Hz), 7.28 (1H, d, J$_{Hα-Hβ}$ =15 Hz), 6.88 (2H, d, J$_{H-H}$ =7.8 Hz); ^{13}C NMR [δ,ppm] 191.6, 164.9 , 152.2, 149.3 , 146.2, 133.3 (2C), 131.9 (2C), 129.7, 126.4 (2C), 121.6, 117.2 (2C) , 58.1.

3. RESULTS AND DISCUSSION

The preliminary reactions of aldol condensation of benzaldehyde (7.91 mmol) with acetophenone (7.53 mmol) were achieved using catalytic amounts of silica-H2SO4 under ultrasound irradiation lasting 90 min (see Scheme 1). The reactor was immersed in an oil bath to maintain a temperature of 65°C. We chose this system in order to optimize the catalytic amount of silica sulphuric acid in the synthesis of trans-chalcone.
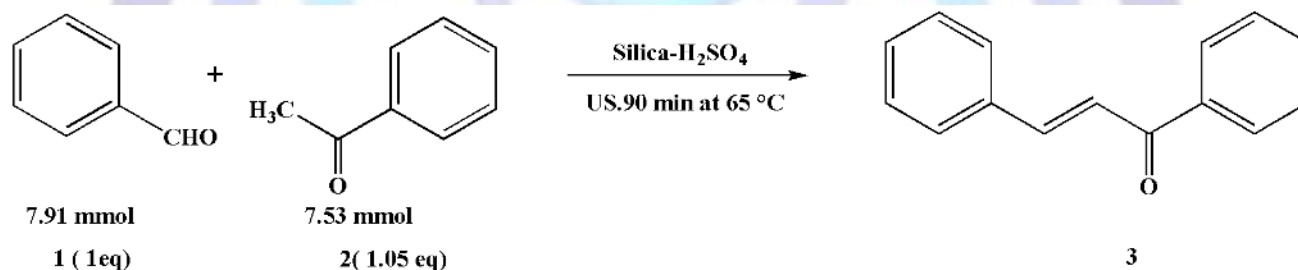
**Scheme 1.** *trans*-Chalcone synthesis catalyzed by silica-H$_2$SO$_4$

As is shown in Table 1, the reaction did not proceed in the absence of silica-H$_2$SO$_4$ after 90 min; the yield of trans-chalcone (3) increased with increasing catalyst amounts. The maximum yield (97%) was obtained by adding 0.02g of the catalyst. At amounts higher than 0.02g, the reaction yield remains almost constant. This result was expected. Indeed, the increased amount of catalyst increased the number of acid sites in the reaction mixture. 0.02g of catalyst appeared to be sufficient in these reaction conditions.

Table 1. Effect of the catalyst weight on the yield of *trans*-chalcone

Catalyst weight(g)	0.00	0.01	0.02	0.03	0.04
Yield (%)	0.0	84.0	97.0	97.4	97.5

Figure 1 shows that a fast kinetics reaction was obtained at 65°C. The reaction achieved a yield of 94% after only 30 min and reached its maximum (98%) after 60 min of ultrasound irradiation. This short reaction time was sufficient under solvent-free reaction conditions. Fig.1 also shows the high selectivity of the aldol condensation between benzaldehyde and acetophenone. Indeed, no secondary products or cis-isomer were detected by GC.
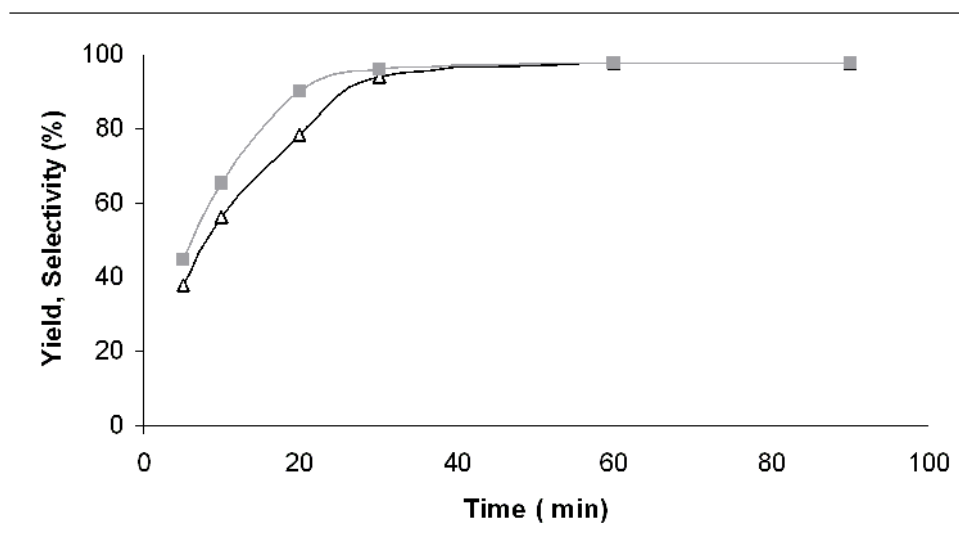
Figure 1. Yields (△) and selectivity's (■) of the aldol condensation between benzaldehyde and acetophenone at T = 65°C and 0.02 g of silica-H$_2$SO$_4$

The yield obtained after 60 min was higher than those mentioned in several previous works. For example, J.T.Li et al. obtained a chalcone yield of 86% after 240 min of ultrasonic irradiation [23]. Aeysha Sultan et al. obtained a chalcone yield of 91% after 90 minutes using silica sulphuric acid as catalyst at 65°C under stirring reaction conditions [18]. The present synthesis achieved a 94% yield after only 30 min of ultrasonification.

In order to identify the best temperature reaction, we carried out the aldol condensation at different temperatures for 60 min using 0.02 g of silica-H$_2$SO$_4$. Table 2 shows the evolution of the chalcone yield vs. the various reaction temperatures we used.

Table 2. Effect of temperature on the yield of *trans*-chalcone over silica-H$_2$SO$_4$

| Temperature (°C)	25-30	40	65	80
Yield (%)	63.0	94.0	98.0	96.6

It was observed that lower reaction temperatures produced lower yields. As shown in Table 2, we found that high temperatures could improve the reaction yield. Indeed, the reaction yield reaches its maximum (98%) at a temperature of 65°C. Slightly lower yields were obtained at 80°C.

Several variables may affect the efficiency of ultrasonication, in particular the viscosity and the presence of a solid catalyst. The increase in the viscosity of the reaction medium decreases the efficiency of the ultrasound. Indeed, the ultrasonic waves became unable to overcome the cohesive forces of very strong mix. Indeed, the size of the micro spheres becomes very small, which significantly influence the reaction yield [24].

The decrease of the reaction mixture's viscosity led to a higher chalcone yield at 65°C due to the acceleration of the molecular diffusion of the reagents and the increased number of ultrasonic cavitation bubbles per unit volume [25]. Cavitation is the formation, growth, and sudden collapse of bubbles in liquids.

Thus, ultrasound irradiation activates the reaction mixture by inducing high local temperatures and pressure generated inside the cavitation bubble and its interfaces when it collapses. Ultrasound irradiation also accelerates the reaction rate and shortens the reaction time. Indeed, sonochemistry has been found effective in activating organic reactants and improving their selectivity and yields for many chemical reaction systems, including Claisen-Schmidt condensation [24].

To explore the general validity of this process, a series of chalcones derivatives were prepared under optimized conditions (Scheme 2): specifically, a temperature of 65°C, catalyst weight of 0.02g, and ultrasound irradiation lasting 60 min.
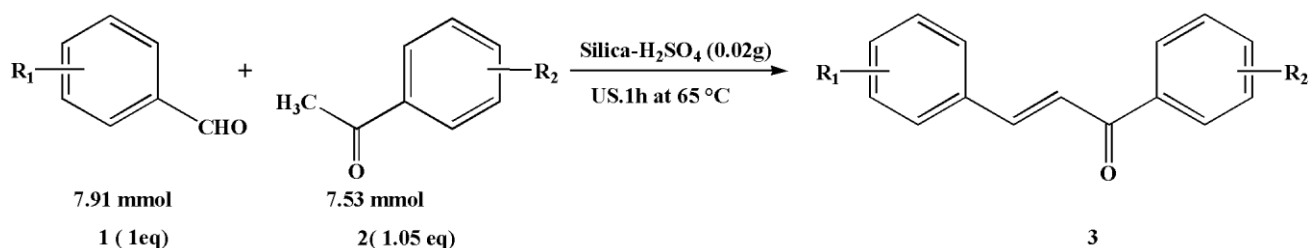
Scheme 2. Schematic representation of the synthesis and chemical structures of chalcones

The results of the yields of substituted chalcones obtained are summarized in Table 3. In all cases, these reactions afforded, after crystallisation, corresponding product 3 in good yields and pure form (IR, NMR and GC). There was no need to use a column chromatographer to obtain pure products. The trans-chalcones formation took place with excellent selectivity. No competitive side reactions, such as product decomposition, self-condensation, Michael addition, etc. were observed (GC).

Table 3. Yields of the synthesised 1,3-diaryl-2-propenones

Entry no.	Compound (3)	(1) R_1	(2) R_2	Yield (%)	mp (°C)
1	3ab	H	H	98.0	56-57
2	3ac	H	4-NO_2	94.3	150-151
3	3ad	H	4-Cl	85.2	99-101
4	3eb	2-Cl	H	96.8	50-51
5	3eca	2-Cl	4-NO_2	95.5	169-171
6	3ed	2-Cl	4-Cl	89.0	78-80
7	3fb	2-OCH_3	H	92.7	58-59
8	3fc	2-OCH_3	4-NO_2	89.1	153-155
9	3fd	2-OCH_3	4-Cl	95.3	79-81
10	3gb	4-Cl	H	90.7	113-114
11	3gc	4-Cl	4-NO_2	93.6	164-166
12	3gd	4-Cl	4-Cl	70.6	158-160
13	3hb	4-OCH_3	H	92.5	74-75
14	3hca	4-OCH_3	4-NO_2	90.0	188-190
15	3hd	4-OCH_3	4-Cl	82.6	119-120

[a]Reaction was achieved after 20 minutes

It is noted that the presence of electron donor groups (such as –OCH_3) in the aromatic ring of benzaldehyde slightly decreased the yields (compare entries 1 and 7, entries 2 and 8, and entries 3 and 15). The presence of an electronic withdrawing group in the aryl methyl ketone (Cl and NO_2) yielded comparable rates of condensation, even when the aldehyde contained an electronic withdrawing group such as Cl, presumably because of the ease of formation of the corresponding enolate anion (compare entries 1 and 2 and entries 4, 5, and 6).

The following representative examples provide a comparison of the efficiency of the present method with that of the reported procedures. Condensation of benzaldehyde and 4-methoxybenzaldehyde with acetophenone afforded 81% and 96% yields, respectively, after 18 h at 80°C in DMF in the presence of Zn(bpy)(OAc)$_2$ [15]; 90% and 94% yields, respectively, after 72 h under heating at 120°C in sealed glass tubes using RuCl$_3$ as catalyst [10]; and 75% and 69.7% yields, respectively, after 24 h using bamboo char sulfonic acid (heterogeneous acid system) as a catalyst [9]. The present method afforded 97% and 92.5% yields, respectively, after 60 min in solvent-free conditions. The condensation of benzaldehyde with 4-chloroacetophenone and 4-nitroacetophenone was found to afford 90% and 80% yields, respectively, at ambient temperature in ethanol in the presence of LiOH.H$_2$O as a catalyst [10]. The present method afforded 85.2% and 94.3% yields, respectively, under solvent free reaction conditions. The condensation of 2-chlorobenzaldehyde with 4-chloroacetophenone afforded 90% yield after 18 h of heating, in an autoclave, at 130 °C in presence of KSF montmorillonite as catalyst [26]. The present synthesis afforded 89.0% yield after only 1 h of ultrasonification at 65°C.

The obtained results demonstrate the efficiency of silica-H_2SO_4 for the synthesis of various substituted trans-chalcones under ultrasound irradiation. The major advantages of silica-H_2SO_4 include that it is economical and environmentally friendly, relatively easy to remove from reaction mixtures. This method is fast and environmentally friendly, as the synthesis is carried out under solvent-free conditions. In addition, the products obtained by our method were synthesized in good yields and excellent selectivity.

The physical properties were determined and structures were confirmed by IR and NMR spectra. Inspection of 1H NMR spectral data clearly indicated that the compounds were geometrically pure and suggested that the ethylene moiety in the enone linkage was in the trans-conformation ($J_{H\alpha-H\beta}$ = 14.9–17.4 Hz) [26]. The stereochemistry of chalcones followed unequivocally from the coupling constant between the α and β protons. In (E)-isomer $J_{H\alpha-H\beta} \approx 16$ Hz and in (Z)- isomer $J_{H\alpha-H\beta} \approx 12$ Hz, as confirmed by Makham and Geiger [27].

4. CONCLUSION

In summary, this paper presents an improved synthesis of trans-chalcones in good yields from aromatic aldehydes and ketones using silica-H_2SO_4 as a catalyst under ultrasound irradiation in solvent free conditions. This method has many advantages over existing methods such as high yields, a simple work-up, short reaction times, and no side reactions and is environmentally friendly, as the synthesis was carried out under solvent-free conditions.

REFERENCES

[1] N. Raghav, S. Jangra, M.Singh, R. Kaur, A. Rohilla, In-vitro studies of some chalcones on acid phosphatase, Int.J.Chem. Sci. 2 (2004) 96-100.

[2] Z. Nowakowska, A review of anti-infective and anti-inflammatory chalcones, Int.J.Chem. Sci. 42 (2007) 125-137.

[3] M. Wan, L. Xu, L. Hua, A. Li, S. Li, W. Lu, Y. Pang, C. Cao, X. Liu, P. Jiao, Synthesis and evaluation of novel isoxazolylchalcones as potential anticancer agents, Bioorg.Chem. 54 (2014) 38–43.

[4] N. Raghav, P. Malik, Spectrophotometric analysis of bovine serum albumin in presence of synthesized 1-(2'-thienyl) 3(substitutedphenyl)-2-propen-1-ones, Int.J.Chem. Sci. 2 (2011) 218-223.

[5] A. Boumendjel, X. Ronot, J. Boutonnat, A novel chalcone derivative which acts as a microtubule depolymerisation agent and an inhibitor of P-gp and BCRP in in-vitro and in-vivo glioblastoma models, Curr. Drug. Targets. 10 (2009) 363–371.

[6] Kumar, Akanksha, Zirconium chloride catalyzed efficient synthesis of 1,3-diaryl-2-propenones in solvent free conditions via aldol condensation, J. Mol. Catal. A Chem. 274 (2007) 212–216.

[7] A. Agarwal, K. Srivastava, S.K. Puri, P.M.S. Chauhan, Synthesis of substituted indole derivatives as a new class of antimalarial agents, Bioorg. Med. Chem. Lett. 15 (2005) 3133–3136.

[8] T. Sakai, R.N. Eskander, Y. Guo, K.J. Kim, J. Mefford, J. Hopkins, N.N. Bhatia, X. Zi, B.H. Hoang ,Flavokawain B, a Kava Chalcone, Induces Apoptosis in Synovial Sarcoma Cell Lines, J. Orthop. Res. 30 (2012) 1045–1050.

[9] Q. Xu, Z. Yang, D. Yin, F. Zhang, Synthesis of chalcones catalyzed by a novel solid sulfonic acid from bamboo, Catal.Commun. 9 (2008) 1579–1582.

[10] S. Bhagat, R. Sharma, D.M. Sawant, L. Sharma, A.K. Chakraborti, LiOH·H_2O as a novel dual activation catalyst for highly efficient and easy synthesis of 1,3-diaryl-2-propenones by Claisen–Schmidt condensation under mild conditions, J. Mol. Catal., A Chem. 244 (2006) 20-24.

[11] O. Petrov, Y. Ivanova, M. Gerova, $SOCl_2$/EtOH: Catalytic system for synthesis of chalcones, Catal.Commun. 9 (2008) 315–316.

[12] S. Eddarir, N. Cotelle, Y. Bakkour, C. Rolando. An efficient synthesis of chalcones based on the Suzuki reaction, Tetrahedron Lett. 44 (2003) 5359-5363.

[13] T. Narender, K.P. Reddy, A simple and highly efficient method for the synthesis of chalcones by using borontrifluoride-etherate, Tetrahedron Lett. 48 (2007) 3177–3180.

[14] G. Nagendrappa, Organic synthesis under solvent-free condition: an environmentally benign procedure- II, Resonance. 7 (2002) 59-68.

[15] M. Chtourou, R. Abdelhédi, M.H. Frikha, M. Trabelsi, Solvent free synthesis of 1,3-diaryl-2-propenones catalyzed by commercial acid-clays under ultrasound irradiation, Ultrason. Sonochem. 17 (2010) 246–249.

[16] E. Perozo-Rondon, R.M. Martın-Aranda, B. Casal, C. J.Duran –Valle, W.N. Lau, X.F. Zhang, King L, Yeung, Sonocatalysis in solvent free conditions: An efficient eco-friendly methodology to prepare chalcones using a new type of amino grafted zeolites, Catal. Today. 114 (2006) 183–187.

[17] A. Lahyani, M. Chtourou, M.H. Frikha, M. Trabelsi, Amberlyst-15 and Amberlite-200C: Efficient catalysts for aldol and cross-aldol condensation under ultrasound irradiation, Ultrason. Sonochem. 20 (2013) 1296-1301.

[18] A. Sultan, A. R. Raza, M. Abbas, K. M. Khan, M. N. Tahir, N. Saari, Evaluation of silica-H_2SO_4 as an efficient heterogeneous catalyst for the synthesis of chalcones, Molecules.18 (2013) 10081-10094.

[19] P. Salehi, M. Dabiri, M.A. Zolfigol, M.A.B. Fard, Silica sulfuric acid as an efficient and reusable reagent for crossed-aldol condensation of ketones with aromatic aldehydes under solvent-free conditions, J. Braz. Chem. Soc. 15 (2004) 773-776.

[20] Y. Wang, Y.Q. Yuan, S.R. Guo, Silica sulfuric acid promotes Aza-Michael addition reactions under solvent-free condition as a heterogeneous and reusable catalyst, Molecules. 14 (2009) 4779-4789.

[21] A. Ghorbani-Choghamarani, P. Zamani, Ammonium bromide as an effective and viable catalyst in the oxidation of sulfides using nitro urea and silica sulfuric acid, J. Iran. Chem. Soc. 8 (2011) 142–148.

[22] A. Kogelbauer, D. Vassena, R. Prins, J. N. Armor, Solid acids as substitutes for sulfuric acid in the liquid phase nitration of toluene to nitrotoluene and dinitrotoluene, Catal.Today. 55 (2000) 151–160.

[23] J.T. Li, W.Z. Yang, S.X. Wang, S.H. Li, T.S. Li, Improved synthesis of chalcones under ultrasound irradiation, Ultrason. Sonochem. 9 (2002) 237–239.

[24] N. Yuanmei, Y. Xingdong, L. Fuhou,Sonochemical, synthesis of maleated rosin, Chinese J. Chem.Engin. 16 (2008) 365-368.

[25] J. Raso, P. Manas, R.Pagan, F.J. Sala, Influence of different factors on the output power transferred into medium by ultrasound, Ultrason. Sonochem. 5 (1999) 157–162.

[26] R.M. Silverstein, G.C. Bassler, T.C. Morrill, Spectroscopicidentificationoforganiccompounds, fifthed, John Wiley, Singapore, 1991.

[27] K.R. Markham, H. Geiger, in: J.B. Harborne (Ed.), The Flavonoids, Advances in Research Since 1986, Chapman and Hall/CRC, London, 1993, p. 447.