C. R. Chimie 19 (2016) 551–555

Contents lists available at ScienceDirect

Comptes Rendus Chimie

www.sciencedirect.com

Preliminary communication/Communication

A very simple solvent-free method for the synthesis of 2-arylchromones using $KHSO_4$ as a recyclable catalyst

María Pérez [a], Diego Ruiz [a], Juan Autino [a], Angel Sathicq [b], Gustavo Romanelli [a, b, *]

[a] Centro de Investigación en Sanidad Vegetal (CISaV), Facultad de Ciencias Agrarias y Forestales, Universidad Nacional de La Plata, Calles 60 y 119 s/n, B1904AAN La Plata, Argentina

[b] Centro de Investigación y Desarrollo en Ciencias Aplicadas 'Dr. J. J. Ronco' (CINDECA), Departamento de Química, Facultad de Ciencias Exactas, UNLP-CCT – La Plata-CONICET, Calle 47 No 257, B1900AJK La Plata, Argentina

ARTICLE INFO

Article history:
Received 21 November 2015
Accepted 25 February 2016
Available online 1 April 2016

Keywords:
Flavones
Chromones
$KHSO_4$
Solvent-free reaction
Catalytic procedure

ABSTRACT

An efficient and solvent-free procedure for the synthesis of flavones using $KHSO_4$ as a recyclable catalyst is described. The methodology represents an environmentally friendly process in comprehensive consideration compared with other catalytic systems listed in publications. This method provides a clean, simple, solvent-free reaction and useful alternatives to prepare flavones and chromones. The use of $KHSO_4$ catalyst provides excellent yields, also leading to an easy separation and recovery of the catalysts, which allows both low environmental impact and low cost. Other green advantages of the method are the low formation of wastes and the replacement of corrosive, soluble mineral acids.

1. Introduction

Compounds containing the chromone skeleton (*4H*-benzopyran-4-one) as the substructure are widely distributed in nature; they constitute a group of compounds in the flavonoid family [1]. Because of their broad range of bioactivities, these types of molecules have been widely investigated, and more than 10,000 chemically unique flavonoids have been isolated from the plant kingdom.

These compounds have multiple biological and pharmacological properties, for example, anti-inflammatory [2], antibacterial [2], antifungal [3], antioxidant [4], anti-HIV [5], vasodilator, antiviral, antiallergic [6], and gastroprotective [7]. Furthermore, it has been reported that flavones have a repelling property against some phytophagous insects and a *Coptotermes* sp. subterranean termite [8,9].

The great importance of flavones and related compounds has led to the development of various methods for their synthesis; for example, the Kostanecki-Robinson strategy [10], from chalcones [11], and the Wittig strategy [12].

The most common methods for the synthesis of flavones and chromones involve the acylation of an *o*-hydroxyacetophenone with an aromatic acid chloride yielding an aryl ester. The ester is then rearranged, in the presence of one base (the Baker–Venkataraman rearrangement), to a 1,3-diaryl 1,3-diketone, and finally the compound gives a 2-arylchromone for cyclodehydration [13].

This cyclodehydration is usually a catalytic reaction, and it has been performed in different reaction media. Some reaction conditions employed are the use of sulfuric acid [14], sulfuric acid in glacial acetic acid [15], Co^{III}(salpr)(OH) under neutral conditions [16], copper (II) chloride in ethanol and microwaves [2], P_2O_5 under gridding conditions [17], cationic exchange resins in isopropanol [18], and Preyssler and Wells-Dawson heteropolyacids in bulk and supported on silica [19,20].

On the other hand, the search of eco-friendly processes to replace the existing task is absolutely necessary, and the use of an inexpensive, versatile, robust and reusable

* Corresponding author.
E-mail address: gpr@quimica.unlp.edu.ar (G. Romanelli).

http://dx.doi.org/10.1016/j.crci.2016.02.014
1631-0748/

catalyst is crucial in the development of new processes aimed at reducing waste at the source. In this way, the use of $KHSO_4$ as an inexpensive, stable, easily recoverable and reusable catalyst began to be studied. Some catalytic applications of this material include the synthesis of bis-(4-hydroxycoumarin-3-yl) methanes [21], 1-aryl-1*H*,3*H*-thiazolo[3,4-*a*]benzimidazoles [22], alkylation of *tert*-enamides with indoles or amines [23], transesterification of methyl acetate with isobutanol [24], triarylmethanes via bisarylation of aryl aldehydes with arenes [25] and N1-alkylated 3,4-dihydropyrimidine-2(1*H*)-ones [26].

Recently, we reported a simple procedure for the synthesis of flavone using $KHSO_4$ as a catalyst. In this paper, we extend the reaction to the synthesis of several flavones and chromones. The procedure is simple, clean and environmentally friendly and includes the cyclodehydration of 1-(2-hydroxypenyl) 3-aryl-1,3-propanodiones using $KHSO_4$ as a catalyst, under solvent-free conditions (Scheme 1). Also, the advantages of this methodology are evaluated in terms of a Green Metrics analysis.

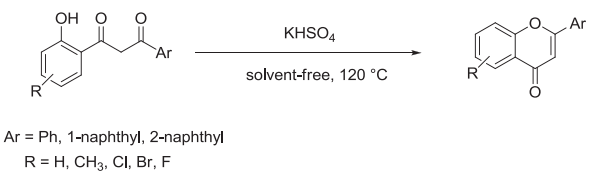
In this paper, we report a simple, clean and environmentally friendly procedure for the solvent-free preparation of 2-arylchromones from 1-(2-hydroxyphenyl)-3-aryl-1,3 propanodiones using $KHSO_4$ as a recyclable catalyst (Scheme 1).

1.1. General

Chemicals were purchased from Aldrich, Fluka and Merck chemical companies and were freshly used after purification by standard procedures (distillation and recrystallization). The catalyst was dried overnight prior to its use. All the reactions were monitored by TLC on precoated silica gel plates (254 mm). Flash column chromatography was performed with 230–400 mesh silica gel. All the yields were calculated from pure products. All the products were identified by comparison of physical data (mp, TLC and NMR) with those reported or with those of authentic samples prepared by the respective conventional methods using sulfuric acid as a catalyst. The melting points of the compounds were determined in sealed capillary tubes and are uncorrected. The ^1H NMR and ^{13}C NMR spectra were obtained on a Bruker instrument 400 MHz model as $CDCl_3$ solutions, and the chemical shifts were expressed in d units with Me_4Si (TMS) as the internal standard. All the starting 1,3-diketones were prepared following a method described elsewhere [28]. Potassium bisulfate was dried in vacuum for 1 h at 100 °C.

1.2. Representative procedure for the synthesis of flavone using $KHSO_4$ as a catalyst

A mixture of 120 mg (0.5 mmol) 1-2(2-hydroxyphenyl)-3-phenyl-1,3-propanedione and 200 mg potassium bisulfate was heated with stirring for 120 min at 120 °C. When the reaction time was over, 3 mL ethyl acetate was added in portions (3 × 1 mL), and the catalyst was filtered. The extracts were combined and the organic solution was concentrated in the vacuum, giving the pure product. The solid products were recrystallized from methanol.



Scheme 1. Solvent-free synthesis of 2-arylchromone derivatives.

1.3. Catalyst reuse

Stability tests of the catalysts were carried out running four consecutive experiments, under the same reaction conditions. After each test, the catalyst was separated from the reaction mixture by filtration, washed with ethyl acetate (2 × 1 mL), and then it was dried under vacuum and reused.

1.4. Melting point, ^{13}C NMR and ^1H NMR spectra of synthesized 2-arylchromones

Flavone (**1**). Mp: 96–97 °C (methanol) (lit. mp: 96–99 °C) [15]; ^1H NMR (400 MHz, $CDCl_3$), δ: 6.80 (s, 1H), 7.41 (ddd, 1H, J = 8.2, 7.1, 1.0 Hz), 7.46–7.55 (m, 4H), 7.68 (ddd, 1H, J = 8.2, 7.1, 1.7 Hz), 7.91–7.95 (m, 2H), 8.22 (dd, 1H, J = 8.2, 1.7 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 107.2, 117.5, 123.5, 124.6, 125.3, 125.8, 128.8, 131.3, 131.6, 133.1, 155.5, 163.0, 177.6.

6-Methylflavone (**2**). Mp: 122–123 °C (methanol) (lit. mp: 122–123 °C) [27]; ^1H NMR (400 MHz, $CDCl_3$), δ: 2.48 (s, 3H), 6.83 (s, 1H), 7.48–7.56 (m, 5H), 7.94–7.96 (m, 2H), 8.03 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.7, 107.1, 117.5, 123.3, 124.7, 126.0, 128.6, 131.2, 131.6, 134.7, 135.0, 154.3, 163.0, 178.3.

7-Methylflavone (**3**). Mp: 121–122 °C (methanol) (lit. mp: 120 °C) [28]; ^1H NMR (250 MHz, $CDCl_3$), δ: 2.47 (s, 3H), 6.77 (s, 1H), 7.22 (d, 1H, J = 9.7 Hz), 7.33 (s, 1H), 7.42–7.57 (m, 3H), 7.93–7.99 (m, 2H), 8.11 (d, 1H, J = 9.7 Hz). ^{13}C NMR (62.5 MHz, $CDCl_3$), δ: 22.3, 107.8, 118.3, 122.3, 126.3, 127.0, 127.5, 129.3, 131.9, 132.3, 145.4, 156.5, 163.5, 178.4.

6-Chloroflavone (**4**). Mp: 184–185 °C (methanol) (lit. mp: 184–185 °C) [29]; ^1H NMR (400 MHz, $CDCl_3$), δ: 6.82 (s, 1H), 7.50–7.55 (m, 4H), 7.62 (dd, 1H, J = 8.9, 2.5 Hz), 7.88–7.92 (m, 2H), 8.20 (d, 1H, J = 2.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 107.3, 119.8, 125.0, 125.1, 126.3, 129.1, 131.2, 131.4, 131.7, 133.9, 154.2, 163.5, 177.0.

7-Chloroflavone (**5**). Mp: 156–157 °C (methanol) (lit. mp: 156–157 °C) [30]; ^1H NMR (250 MHz, $CDCl_3$), δ: 6.81 (s, 1H), 7.40 (dd, 1H, J = 8.5, 1.8 Hz), 7.49–7.54 (m, 3H), 7.60 (d, 1H, J = 1.9 Hz), 7.90–7.92 (m, 2H), 8.23 (d, 1H, J = 8.5 Hz). ^{13}C NMR (62.5 MHz, $CDCl_3$), δ: 106.9, 117.9, 122.2, 125.8, 126.1, 126.6, 129.0, 131.2, 131.5, 139.4, 155.8, 163.1, 177.6.

6-Bromoflavone (**6**). Mp: 190–191 °C (methanol) (lit. mp: 189–190 °C) [31]; ^1H NMR (400 MHz, $CDCl_3$), δ: 6.86 (s, 1H), 7.54–7.57 (m, 4H), 7.87 (dd, 1H, J = 8.2, 2.4 Hz), 7.94–7.97 (m, 2H), 8.39 (d, 1H, J = 2.4 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz), δ: 107.2, 119.2, 119.6, 124.9, 125.9, 127.8, 128.9, 130.8, 131.6, 136.0, 154.3, 163.5, 177.9.

7-Bromoflavone (**7**). Mp: 163–165 °C (methanol) (lit. mp: 164–165 °C) [31]; ^1H NMR (400 MHz, $CDCl_3$), δ: 6.83 (s, 1H), 7.51–7.55 (m, 3H), 7.60 (dd, 1H, J = 8.2, 1.6 Hz), 7.78(d, 1H, J = 1.5 Hz), 7.89–7.92 (m, 2H), 8.16 (d, 1H, J = 8.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 107.2, 121.0, 122.1, 125.8, 126.2, 128.0, 128.3, 128.7, 131.2, 131.3, 155.1, 163.2, 176.8.

2-Furylchromone (**8**). Mp: 134–135 °C (methanol) (lit. mp: 135 °C) [32]; ^{1}H NMR ($CDCl_3$, 250 MHz), δ: 6.61–6.63 (1H, m), 6.75 (1H, s), 7.14 (1H, d, J = 3.3 Hz), 7.41 (1H, m), 7.50 (1H, d, J = 8.2 Hz), 7.65–7.72 (2H, m), 8.22 (1H, dd, J = 7.4, 1.2 Hz). ^{13}C NMR ($CDCl_3$, 62.5 MHz); δ: 105.2, 112.1, 112.6, 117.6, 124.0, 124.8, 125.4, 133.3, 145.5, 146.1, 154.9, 155.5, 177.3.

2-(2-Naphthyl)chromone (**9**). Mp: 162–163 °C (methanol) (lit. mp: 164–165 °C) [33]; ^{1}H NMR (400 MHz, $CDCl_3$), δ: 6.96 (s, 1H), 7.43 (ddd, 1H, J = 8.0, 6.5, 1.5 Hz), 7.55–7.62 (m, 2H), 7.62 (d, 1H, J = 8.0 Hz), 7.71 (ddd, 1H, J = 8.0, 6.5, 1.5 Hz), 7.85–8.02 (m, 4H), 8.24 (dd, 1H, J = 7.9, 1.4 Hz), 8.47 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 108.0, 118.3, 122.6, 124.2, 125.5, 125.9, 127.1, 127.2, 128.0, 128.2, 129.0, 129.1, 130.1, 133.0, 134.0, 134.8, 156.5, 163.5, 178.6.

2-(1-Naphthyl)chromone (**10**). Mp: 142–143 °C (methanol) (lit. mp: 138–139 °C) [33]; ^{1}H NMR (400 MHz, $CDCl_3$), δ: 6.69 (s, 1H), 7.42 (dt, 1H, J = 7.8, 1.3 Hz), 7.49–7.59 (m, 4H), 7.71 (dt, 1H, J = 7.8, 1.8 Hz), 7.77 (dd, 1H, J = 7.6, 1.2 Hz), 7.91–7.94 (m, 1H), 8.03 (d, 1H, J = 8.1 Hz), 8.10–8.13 (m, 1H), 8.32 (dd, 1H, J = 7.8, 1.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 113.0, 118.2, 123.9, 125.0, 125.3, 125.4, 125.7, 126.5, 127.4, 127.5, 128.7, 130.3, 130.6, 131.5, 133.7, 133.8, 156.6, 165.2, 177.9.

7-Chloro-2-(2-naphthyl)chromone (**11**). Mp: 219–220 °C (methanol) (lit. mp: 219–220 °C) [34]; ^{1}H NMR (250 MHz, $CDCl_3$), δ: 6.96 (s, 1H), 7.42 (dd, 1H, J = 8.6, 2.0 Hz), 7.57–7.65 (m, 2H), 7.68 (d, 1H, J = 2.0 Hz), 7.89–8.01 (m, 4H), 8.21 (d, 1H, J = 8.6 Hz), 8.47 (s, 1H) ^{13}C NMR (62.5 MHz, $CDCl_3$), δ: 108.4, 118.5, 122.7, 122.9, 126.4, 127.2, 127.3, 127.4, 128.1, 128.5, 128.9, 129.3, 129.4, 133.6, 135.1, 140.1, 156.7, 163.7, 177.6.

7-Chloro-2-(1-naphthyl)chromone (**12**). Mp: 198–199 °C (methanol) (lit. mp: 198–199 °C) [35]; ^{1}H NMR (400 MHz, $CDCl_3$), δ: 6.72 (s, 1H), 7.48 (dd, 1H, J = 1.9, 8.5 Hz), 7.61–7.66 (m, 4H), 7.81 (dd, 1H, J = 7.2, 1.1 Hz), 7.99–8.01 (m, 1H), 8.08 (d, 1H, J = 8.2 Hz), 8.15–8.17 (m, 1H), 8.29 (d, 1H, J = 8.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 113.6, 118.7, 122.8, 124.9, 125.4, 126.5, 127.0, 127.4, 127.9, 128.3, 129.1, 130.4, 130.6, 131.9, 134.1, 140.2, 157.1, 165.9, 177.7.

2. Results and discussion

In this work we report on the use of a solvent-free system for the preparation of 2-arylchromones in the presence of $KHSO_4$ as a cheap and reusable catalyst. The flavone and chromone synthesis involves the cyclodehydration of 1-(2-hydroxyphenyl)-3-aryl-1,3-propanodiones under solvent-free conditions (Scheme 1).

Initially, a noncatalytic experiment using 1-(2-hydroxyphenyl)-3-phenyl-1,3-propanodione (120 mg, 0.5 mmol) was tested, and it was observed that, under the experimental conditions (120 °C, 120 min and solvent-free), only traces of flavone were detected, indicating that from a practical point of view the reaction is not taking place in the absence of a catalyst.

Then, the $KHSO_4$ catalyst was tested with very good results. First, the influence of the reaction temperature on 1-(2-hydroxyphenyl)-3-phenyl-1,3-propanodione was analyzed using 200 mg of $KHSO_4$. In order to obtain the optimal temperature, five temperatures were studied (25, 60, 80, 100, 120 and 140 °C). The experimental reaction conditions were: 1-(2-hydroxyphenyl)-3-phenyl-1,3-propanodione (0.5 mmol), 200 mg of $KHSO_4$, and the mixture reaction was stirred for 120 min. No reaction was observed at 25, 60 and 80 °C. A further temperature increase leads to a higher flavone yield. For example, the yield of flavone for a reaction time of 120 min at 100 °C was 80%. At 120 °C, at the same reaction time, yield was 98%. Finally, at 140 °C the reaction yields were considerably lower (67%), due to the several unidentified side products that were detected by TLC. For this reason, 120 °C was employed as the ideal temperature to continue with the analysis of other reaction variables.

Results for the reaction time for flavone synthesis under the same reaction conditions (flavone, 0.5 mmol; catalyst, 400 mg; temperature, 120 °C, and reaction time, 120 min) shows that yields of flavone increased when the reaction time increased to approx. 120 min and then remained at a constant level.

The effects of the amount of catalyst ($KHSO_4$) on the yield of flavone under the experimental conditions were tested from 1-(2-hydroxyphenyl)-3-phenyl-1,3-propanodione, 0.5 mmol; 120 °C, 120 min, using a variable amount of the $KHSO_4$ catalyst (50, 100, 150, 200 and 250 mg). The yields increased from 88% to 98% when the amount of $KHSO_4$ increased from 150 to 200 mg. No relevant changes of reaction yields were observed with further increase in the amount of $KHSO_4$. Thus, 200 mg of $KHSO_4$ results in the suitable amount for this reaction.

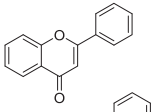
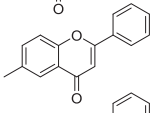
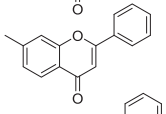
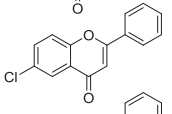
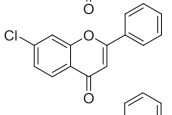
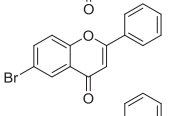
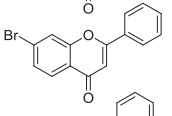
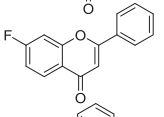
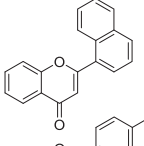
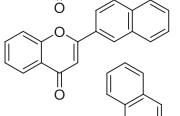
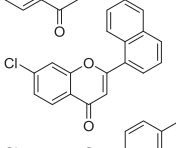
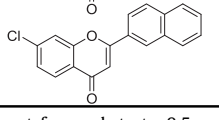
The scale-up in chemical engineering is the migration of a process from the lab scale to the pilot plant scale or commercial scale. We performed the reaction at different scales from 1 mmol to 0.1 mol. This topic is very important in solvent-free reactions because it is difficult to achieve uniformity between the substrates and the catalyst in the system. However no significant changes in the reaction yields were observed.

The reusability of the catalysts was investigated in the sequential reaction of cyclodehydration of 1-(2-hydroxyphenyl)-3-phenyl-1,3-propanodione. At the end of each run the catalyst was removed, washed with toluene, dried in the vacuum at 40 °C and reused. The results showed that the reuse of the catalyst in four consecutive runs results in no appreciable loss of its catalytic activity (98%, 96%, 96%, and 95% of flavone yields, respectively).

Under the optimized conditions: substituted 1-(2-hydroxyphenyl)-3-aryl-1,3-propanodione, 0.5 mmol; $KHSO_4$, 200 mg; 120 °C; and 120–150 min, twelve flavones and chromones were prepared. Results are given in Table 1. In all the cases, the desired products were obtained with high selectivity, almost free of secondary products. The unchanged starting materials were recovered nearly quantitatively. No relevant stereoelectronic effects on the yields due to the substituent were observed.

Finally, in order to quantify how much 'greener' the methodology is, the Atom Economy (AE), Atomic efficiency factor (E), Process Mass Intensity (PMI) and Eco-Scale were calculated for each reaction product and the results are presented in Table 1 for each compound. We compared these values with the ones previously reported in the literature, and it is important to note that this

Table 1
Solvent-free synthesis of 2-arylchromones.

Entry	Product	Time (min)	EA (%)	*E* factor	PMI	Eco-scale	Yield (%)[a]
1		120	92.5	32.75	33.99	86	98
2		120	92.9	33.01	34.05	84.5	95
3		120	92.9	30.87	32.64	85	96
4		150	93.4	30.30	32.03	82	90
5		150	93.4	30.64	32.39	84.5	89
6		150	94.4	26.40	27.91	81	88
7		150	94.4	27.02	28.56	80	86
8		150	93.0	32.74	34.62	81.5	89
9		120	93.8	29.22	30.89	81	88
10		120	93.8	28.57	30.20	82	90
11		120	94.5	27.83	29.42	78	82
12		120	94.5	27.17	28.72	79	84

Reaction conditions: Solvent-free; substrate, 0.5 mmol; catalyst, $KHSO_4$; 400 mg; temperature, 110 °C; stirring.
[a] Isolated yield.

methodology is the most suitable method to prepare flavones [36].

It can be observed in Table 1 that the proposed methodology gives excellent yields (82%–98%). Green metrics parameters also showed a very environmentally friendly methodology for the synthesis for 2-arylchromones.

3. Conclusion

The present catalytic strategy represents an environmentally friendly process in comprehensive consideration compared with other systems listed in publications. The method provides a simple, clean, solvent-free reaction and useful alternative for preparing 2-arylchromones. The utilization of the $KHSO_4$ catalyst gives excellent yields and easy separation and recovery of the catalyst for further use. The catalytic activity was constant in consecutive batches, and the high recovery of the catalyst allows for both low environmental impact and low cost. Other green advantages are the low formation of wastes and the replacement of corrosive, soluble mineral acids such as sulfuric, hydrochloric acids.

Acknowledgments

We thank Universidad Nacional de La Plata, CONICET (PIP 003) and ANPCyT (PICT 0406) for financial support. GPR is a member of CONICET.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.crci.2016.02.014.

References

[1] S. Martens, A. Mithöfer, Phythochem 66 (20) (2005) 2399–2407.
[2] G.W. Kabalka, A.R. Mereddy, Tetrahedron Lett. 46 (37) (2005) 6315–6317 and references cited therein.
[3] H. Goker, D.W. Boykin, S. Yildiz, Biorg. Med. Chem. 13 (5) (2005) 1707–1714.
[4] J. Grassmann, S. Hippeli, E. Eltsner, Plant Physiol. Biochem. 40 (6) (2002) 471–478.
[5] J. Wu, X. Wang, Y. Yi, K. Lee, Bioorg. Med. Chem. Lett. 13 (10) (2003) 1813–1815.
[6] J.A. Seijas, M.P. Vázquez-Tato, R. Carballido-Reboredo, J. Org. Chem. 70 (2005) 2855–2858 and references cited therein.
[7] J. Ares, P. Outt, J. Randall, P. Murray, P. Weisshaar, L. Obrien, B. Ems, S. Kakodkar, G. Kelm, W. Kershaw, K. Werchowski, A. Parkinson, J. Med. Chem. 38 (25) (1995) 4937–4943.
[8] M. Morimoto, K. Tanimoto, S. Nakano, T. Ozaki, A. Nakano, K. Komai, J. Agric. Food Chem. 51 (2) (2003) 389–393.
[9] W. Ohmura, S. Doi, M. Aoyama, S. Ohara, J. Wood Sci. 46 (2) (2000) 149–153.
[10] J. Staunton, Gamma-Pyrones and Chromones, in: D. Barton, W.D. Ollis (Eds.), Comprehensive Organic Chemistry, The Synthesis and Reactions of Organic Compounds, Vol. 4, Pergamon Press, Oxford, 1979, pp. 678–679.
[11] J. Staunton, Gamma-Pyrones and Chromones, in: D. Barton, W.D. Ollis (Eds.), Comprehensive Organic Chemistry, The Synthesis and Reactions of Organic Compounds, Vol. 4, Pergamon Press, Oxford, 1979 (b) pp. 687–688.(c) pp. 678.
[12] A. Ganguly, S. Kaur, P. Mahata, D. Biswas, B. Pramanik, T. Chan, Tetrahedron Lett. 46 (23) (2005) 4119–4121 and references cited therein.
[13] R. Varma, R. Saini, D. Kumar, J. Chem. Res. (S) 1998 (6) (1998) 348–349 and references cited therein.
[14] A. Banerji, N.C. Goomer, Synthesis 1980 (11) (1980) 874–875.
[15] B.S. Furniss, A.J. Hannaford, V. Rogers, P.W.G. Smith, A.R. Tatchell, Vogel's Textbook of Practical Organic Chemistry, 4th ed., Longman, New York, 1978, pp. 925–926.
[16] A. Nishinaga, H. Ando, K. Maruyama, T. Machino, Synthesis 1992 (9) (1992) 839–841.
[17] D. Sharma, J.K. Makrandi, Green Chem. Lett. Rev. 2 (3) (2009) 157–159.
[18] Y. Hoshino, N. Takeno, Bull. Chem. Soc. Jpn. 60 (5) (1987) 1919–1920.
[19] G.P. Romanelli, E.G. Virla, P.R. Duchowicz, A.L. Gaddi, D.M. Ruiz, D.O. Bennardi, E.V. Ortiz, J.C. Autino, J. Agr. Food Chem. 58 (2010) 6290–6295.
[20] D.O. Bennardi, G.P. Romanelli, A.G. Sathicq, J.C. Autino, G.T. Baronetti, H.J. Thomas, Appl. Catal. A 404 (1–2) (2011) 68–73.
[21] V. Padalkar, K. Phatangare, S. Takale, R. Pisal, A. Chaskar, J. Saudi Chem. Soc. 19 (1) (2015) 42–45.
[22] A. Chaskar, V. Padalkar, K. Phatangare, S. Takale, K. Murugan, Green Chem. Lett. Rev 6 (3) (2013) 217–221.
[23] X.Q. Chu, S.Y. Wang, S.J. Ji, Royal Soc. Chem. Adv. 3 (22) (2013) 8380–8387.
[24] A. Vega Rodriguez, V. Pleşu, A. Calvet Tarragona, J. Bonet Ruiz, A.E. Bonet Ruiz, J. Llorens Llacuna, Chem. Eng. Trans. 35 (2013) 1093–1098.
[25] Y. Leng, F. Chen, L. Zuo, W. Duan, Tetrahedron Lett. 51 (17) (2010) 2370–2373.
[26] K. Singh, D. Arora, E. Poremsky, J. Lowery, R.S. Moreland, Eur. J. Med. Chem. 44 (5) (2009) 1997–2001.
[27] Beilstein's Handbuch der Organischen Chemie, XVII, I 206, II 400.
[28] A. Robertson, R.B. Waters, E.T. Jones, J. Chem. Soc. 1932 (1932) 1681–1688.
[29] S. Ruhemann, Ber. Dtsch. Chem. Ges. 54 (1921) 912.
[30] F.C. Chen, C.T. Chang, J. Chem. Soc. 1958 (1958) 146–150.
[31] C.T. Chang, F.C. Chen, T.S. Chen, K.K. Hsu, T. Ueng, M. Hun, J. Chem. Soc. 1961 (1961) 3414–3417.
[32] W.D. Ollis, D. Weight, J. Chem. Soc. 1952 (1952) 3826–3830.
[33] V.V. Virkar, R.C. Shah, J. Univ. Bombay 11 (3) (1942) 140–143.
[34] D. Bennardi, D. Ruiz, G.P. Romanelli, G. Baronetti, H. Thomas, J. Autino, Lett. Org. Chem. 5 (8) (2008) 607–615.
[35] D.O. Bennardi, G.P. Romanelli, J.L. Jios, P.G. Vázquez, C.V. Cáceres, J.C. Autino, Heterocycl. Commun. 13 (2007) 77–81.
[36] A.G. Sathicq, D.M. Ruiz, G.P. Romanelli, Solvent-free Flavone Synthesis Reaction Using KHSO4 as Recyclable Catalyst, in: P. Tundo, J. Andraos (Eds.), Green Syntheses, Vol. 1, Taylor & Francis, 2014, pp. 101–110.