

Sulfonated Alumina: A Suitable Catalyst for Furfural Biomass Building-Block Valorization Through Multicomponent Reactions

Alúmina sulfonada: un catalizador adecuado para la valorización de componentes básicos de biomasa del furfural a través de reacciones multicomponente

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Abstract

Sulfonated alumina was synthesized and tested for the first time in furfural valorization through a multicomponent reaction for the preparation of a nitrogenated heterocyclic compound containing the furan substructure. Ten polysubstituted heterocycles, belonging to the dihydropyrimidinones (thiones) and 1,4-dihydropyridines, were obtained with very good yields (70% - 85%) using the tandem methodology and green reaction conditions. The catalyst was easily separated from the reaction medium, giving a high yield in the reusability studies. Green metrics were analyzed in order to consider the reaction suitability.

Keywords: furfural valorization, sulfonated silica, multicomponent reaction, nitrogenated heterocyclic compounds, green metrics analysis

Resumen

La alúmina sulfonada se sintetizó y ensayó por primera vez en la valorización del furfural mediante una reacción multicomponente para la preparación de un compuesto heterocíclico nitrogenado que contiene la subestructura de furano. Se obtuvieron diez heterociclos polisustituídos, pertenecientes a las dihidropirimidinonas (tiones) y 1,4-dihidropiridinas, con muy buenos rendimientos (70% - 85%) utilizando la metodología tándem y las condiciones de reacción verde. El catalizador se separó fácilmente del medio de reacción, dando un alto rendimiento en los estudios de reutilización. Se analizaron las métricas verdes para considerar la idoneidad de la reacción.

Palabras clave: valorización de furfural, sílice sulfonada, reacción multicomponente, compuestos heterocíclicos nitrogenados, análisis de métricas verdes

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1 Introduction

The demand for a suitable approach to chemical processes has encouraged the use of recyclable solid acids as substitutes of unrecyclable mineral liquid acids, such as: H_2SO_4 , HCl or HF . The solid acid materials can be easily separated from the reaction mixture by means of centrifugation, decantation or filtration; as a result, the catalyst can be reused. The development of suitable heterogeneous catalysts to facilitate different organic transformations has been an interesting area of research in recent decades. In many cases the solid catalyst can be used and reused without appreciable loss of its catalytic activity [1].

H. Patel and *col./et al.* reviewed the utilization of several novel heterogeneous catalysts and their use in organic synthesis, for example, alumina sulfuric acid (ASA), tungstate sulfuric acid (TSA), molybdate sulfuric acid (MSA), and xanthan sulfuric acid (XSA) [2]. These materials are economical, efficient, and compatible with the environment. Particularly, they described the use of alumina sulfuric acid, obtained by the reaction between chlorosulfonic acid and activated neutral alumina in the synthesis of several organic compounds such as benzimidazoles, quinoxalines, nitration of aromatic compounds, synthesis of 2,5-disubstituted 1,3,4-oxadiazoles, dithioacetalization, ortho-silylation of alcohols, oximes and phenols, Biginelli-type condensation reaction, and Pechmann condensation [2].

On the other hand, due to the great demand for biorenewable resources as a different feedstock for the synthesis of bulk chemicals, furfural has gained considerable attention.

Biofuran aldehydes, especially furfural, which are derived from the dehydration of C_5 sugars, are a useful platform molecule used in the synthesis of chemical (furfuryl alcohol, tetrahydrofuran, *N*-alkyl pyrrolidones, biphenolic acid, and furoic acid), liquid fuels and additives (levulinic and valeric acid esters, γ -valerolactone, and 2-methyl tetrahydrofuran), and other suitable materials [3].

Another new challenge in the synthesis of biobased materials and intermediates is the transformation of monosaccharides or their derivatives

(furfural) into heterocycles via multicomponent reactions (MCR). These reactions are synthetic methodologies in which three or more reactants are put together in a simple vessel to form the product [4].

The remarkable characteristic of MCRs is that the unique reaction product contains almost all portions of substrates, generating almost no secondary products. Thus, MCRs have been widely studied in many fields such as the design of new drugs and combinatorial chemistry [4].

Two relevant families of compounds that can be obtained by multicomponent procedures are dihydropyrimidinones (thiones) and 1,4-dihydropyridines. They have a pyrimidine and pyridine core, respectively, which is a relevant pharmacophore used in the design of new drugs. Both compound families have a broad range of bioactivity that includes calcium channel inhibition, anticancer, anti-inflammatory, antimicrobial, antioxidant, neuroprotective, antidiabetic, antianginal, analgesic, antiviral, antifungal, and anti-ischemic effects [5-14].

Due to the relevance of these families of compounds, the literature reports on different methodologies for their synthesis. The most popular method for dihydropyrimidinone synthesis is the Biginelli reaction, a multicomponent methodology involving the condensation of aldehyde, β -ketoester, and urea (or thiourea) assisted by an acid catalyst [15].

A variety of new catalytic materials that include Lewis and Bronsted acids have been mentioned in the literature, for example, alumina-supported MoO_3 [16], antimony (III) chloride [17], iron (III) trifluoroacetate and trifluoromethanesulfonate [18], PSSA [19], silica sulfuric acid [20], $\text{H}_3\text{PW}_{12}\text{O}_{40}$ [21], zeolite-supported heteropolyacids (HPA) [22], among others.

The typical procedure leading to 1,4-dihydropyridines is the Hantzsch reaction. It is a one-pot condensation of β -dicarbonylic compounds with aldehydes and ammonia, which can also be assisted by different catalysts such as heteropolyacids [23], iodine [24], hydrotalcites [25], silica sulfuric acid [26], enzymes [27], H_2O -PEG [28], among others.

In this paper we report on the use of sulfonated alumina ($\text{Al}_2\text{O}_3\text{-SO}_3\text{H}$), a suitable catalyst for the synthesis of several dihydropyridines (thiones) and 1,4-dihydropyridines containing the furfural substructure. Figures 1 and 2 show two representative examples.

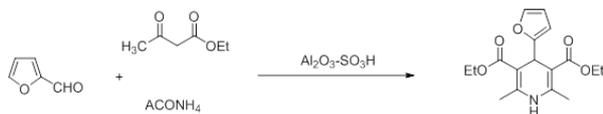


Figure 1. 1,4-Dihydropyridine synthesis using furfural as building block.

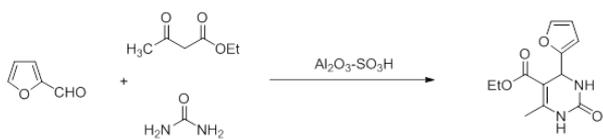


Figure 2. Dihydropyrimidinone synthesis using furfural as building block.

2 Experimental

2.1 General procedures

Melting points were measured in an open capillary using Buchi melting point apparatus and were uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer (400 and 100 MHz, respectively) using TMS as internal standard. Reactions were monitored by thin layer chromatography on 0.2 mm silica gel F-252 (Merck) plates and in some cases by gas chromatography using a Shimadzu GC 2010 instrument. All β -keto esters, aldehydes, amines, urea/thiourea and ammonium acetate derivatives were obtained from Aldrich Chemical Co. and used without further purification, with the exception of benzaldehyde, which was distilled in vacuo prior to use. All solid components were employed as grained powders. All synthesized compounds were known, and the melting point and NMR spectrum of selected molecules were added in the additional material sections.

2.2 Catalyst synthesis

For the synthesis of $\text{Al}_2\text{O}_3\text{-SO}_3\text{H}$, 5 g of alumina (Al_2O_3), 100 mL of dry toluene, and 1.15 mL of 3-mercaptopropyltrimethoxysilane (MPTMS) were

mixed and refluxed for 24 h, under constant stirring. Subsequently, mercaptopropyl groups were oxidized to sulfonic groups ($-\text{SO}_3\text{H}$) with the addition of excess hydrogen peroxide, which was kept under stirring for 24 h at room temperature. The final solid was washed several times with acetone and dried at 393 K [29].

2.3 Catalyst characterization

The material was characterized by acidity and surface measurements (SBET). The complete characterization of the material will be reported in a future work. The textural properties, which were determined from nitrogen adsorption-desorption at 77 K, were measured on Micromeritics ASAP 2020 equipment. Samples were previously evacuated at 623 K for 16 h. The surface area was calculated using a multipoint Brunauer-Emmett-Teller model.

The pore size distribution was obtained by the BJH model, and the total pore volume was estimated at a relative pressure of 0.99. The acid capacity was determined by titration with 0.01 M NaOH (aq.) [30]. In a typical experiment, 0.1 g of solid was added to 10 mL of deionized water. The resulting suspension was allowed to equilibrate and thereafter was titrated by dropwise addition of 0.01 M NaOH solution using phenolphthalein as pH indicator.

2.4 General procedure for synthesis of 1,4-dihydropyridine compounds using furfural, ethyl acetoacetate, and ammonium acetate as substrates

Ethyl acetoacetate (130 mg, 1 mmol), furfural (48 mg, 1 mmol), ammonium acetate (52 mg, 1.2 mmol), and the catalyst (35 mg) were thoroughly mixed and then heated at 80 °C for 2 h. The progress of the reaction was monitored by TLC. After completion of the reaction, acetone was added (3 x 1 mL), and the catalyst was filtered. The extracts were combined and dried with anhydrous sodium sulfate and concentrated in vacuum (40 °C). The crude product was recrystallized from methanol, ethanol or isopropanol to give pure 1,4-dihydropyridine.

2.5 General procedure for synthesis of 3,4-dihydropyrimidinone compounds using furfural, ethyl acetoacetate and urea as substrates

Ethyl acetoacetate (130 mg, 1 mmol), furfural (96 mg, 1 mmol), urea (90 mg, 1.5 mmol), and the catalyst (35 mg) were thoroughly mixed and then heated at 80 °C for 2.5 h. The progress of the reaction was monitored by TLC. After completion of the reaction, acetone was added (3 x 1 mL), and the catalyst was filtered. The extracts were combined and dried with anhydrous sodium sulfate and concentrated in vacuum (40 °C). The crude product was recrystallized from methanol, ethanol or isopropanol to give pure 3,4-dihydropyrimidinone.

2.6 Recycling of the catalyst in both synthesis

The reuse of the catalyst was checked in five consecutive batches after the first one; the catalysts showed almost constant activity. The catalyst was separated, washed in polar media such as acetone (3 x 1 mL), dried under vacuum (50 °C), and reused, repeating this procedure.

3 Results and discussion

3.1 Catalytic synthesis and characterization

Functionalized alumina (Al₂O₃-SO₃H) was synthesized, and the most relevant data are summarized in Table 1, which lists the textural properties obtained from the adsorption-desorption isotherms of N₂ at 77 K and the acid capacity of the synthesized material Al₂O₃-SO₃H. It can be seen that the surface area of Al₂O₃ ($S_{BET} = 186 \text{ m}^2/\text{g}$) decreases with the functionalization of sulfonic groups, because the textural properties of porous materials decrease when treated with organosilane compounds [30], which could be related to the distribution of sulfonic groups within the porous structure. In addition, this material has high acid capacity, which makes it a highly promising material for reactions that involve acid catalysis.

Table 1. Textural properties and acid capacity of Al₂O₃-SO₃H

Catalyst	S_{BET} (m^2g^{-1})	Pore volume (cm^3g^{-1})	Pore size (nm)	Acid capacity (mmol H ⁺ /g)
γ -Al ₂ O ₃	250	0.8	9	–
Al ₂ O ₃ -SO ₃ H	186	0.32	6.8	26.4

3.2 Catalytic tests

3.2.1 A-1,4-Dihydropyridine

Initially, the optimum reaction conditions for 1,4-dihydropyridine synthesis were evaluated employing furfural, ethyl acetoacetate, and ammonium (ratio 1:2:1.3, respectively) in solvent-free conditions at 80 °C for 2 h. to obtain the corresponding dihydropyridine (Scheme A).



Figure 3. Scheme A. Hantzsch reaction using furfural as building block.

In an experiment, without the presence of catalyst, a very poor yield (18%) of DHP was obtained (Table 2, entry 1). Similarly, a poor reaction yield was obtained when the support (Al₂O₃) (Table 2, entry 2) was used as catalyst, under the same reaction conditions (25%). After that the Al₂O₃-SO₃H catalyst was checked under the same reaction conditions (Table 2, entry 3) and a very good yield of DHP was obtained, 85%, indicating that the presence of one material with acidic properties was necessary to improve the reaction yields.

Another important issue to review in these tests, due to the material cost, is the amount of the Al₂O₃-SO₃H catalyst (Table 2, entries 3-6). It can be seen that 25 mg of Al₂O₃-SO₃H is the appropriate amount to give very good yields (Table 2, entry 3, 85%) and no relevant changes were found when the amount of catalyst doubled (50 mg) (Table 2, entry 6, 87%).

The temperature effect on the yield of DHP is shown in Table 2, entries 3, 7, 8, 9, and 10. Five tests were performed at 20, 40, 60, 80, and 100 °C by

using Al₂O₃-SO₃H as catalyst. The results showed the best yield at 80 °C (85%, Table 2, entry 3).

No reaction was detected when the test was performed at room temperature (20 °C) (Table 3, entry 7). The selectivity in all temperature conditions was 100%, and no secondary products were detected by GC and TLC analysis. However, at 100 °C the reaction mixture became considerably darker, the yield of the reaction dropped significantly, and TLC revealed the formation of numerous secondary products.

The reaction time was also tested at the selected optimal reaction temperature of 80 °C, using four different times of 30, 60, 120, and 180 min (Table 2, entries 3, 11, 12, and 13, respectively). A good yield (70%) was obtained at 60 min of reaction (Table 2, entry 12), reaching the optimal yields/yield at 120 h (85%, Table 2, entry 3), without any variation at longer reaction times such as 180 h (84%, Table 2, entry 13).

The catalyst reusability was also analyzed under the best reaction conditions (80 °C, 120 min, solvent-free conditions, using 25 mg of the catalyst, over six consecutive runs). The recovered catalyst was washed with ethanol (2 x 1.5 mL) and dried at 20 °C in vacuum. The results are listed in Table 2, entries 3, 14, 15, 16, 17, and 18. No appreciable variations of the yields were observed when the catalyst was reused five consecutive times. The loss of catalyst mass after the six runs was only 10%.

To test the possible catalyst solubilization, an additional experiment was performed. The catalyst sample (25 mg) was refluxed in ethanol (solvent used in the isolated reaction products (5 mL)) for 4 h, filtered at high temperature (60 °C), and dried in vacuum till constant weight. The activity of the treated catalyst was the same as that of the fresh catalyst (85% yield in 120 min).

3.2.2 B-1,3-Dihydropyrimidinones

In a similar way to the 1,4-dihydropyridine optimization synthesis, we studied the Biginelli reaction to obtain 1,3-dihydropyrimidinones. The optimum reaction conditions were evaluated using furfural, ethyl acetoacetate, and urea as test reaction substrates (ra-

Table 2. Effect of different reaction parameters on 1,4-DHP (%)^a

Entry	Catalyst	Amount of Al ₂ O ₃ -SO ₃ H (mg)	Temperature (°C)	Time (m)	Yield (%)
1	None	-	80	120	18
2	Al ₂ O ₃	-	80	120	25
3	Al ₂ O ₃ -SO ₃ H	25	80	120	85
4		5	80	120	32
5		10	80	120	58
6		50	80	120	87
7		25	20	120	-
8		25	40	120	34
9		25	60	120	67
10		25	100	120	70
11		25	80	30	41
12		25	80	60	70
13		25	80	180	84
14		25	80	120	85
15		25	80	120	85
16		25	80	120	84
17		25	80	120	82
18		25	80	120	82

Note: Reaction conditions: furfural (96 mg); ethyl acetoacetate (2 mmol); ammonium acetate (100 mg, 1.2 mmol); catalyst 25 mg; solvent-free; stirring. ^a Pure product. Catalyst reusability, entries 14-18.

tio 1:1:1.5, respectively) in solvent-free conditions (Scheme B).

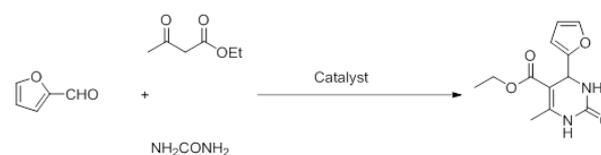


Figure 4. Scheme B. Biginelli reaction using furfural as building block

Table 3 lists the different reaction conditions including temperature, reaction time, and catalyst amount. As shown in Table 3, entry 3, the best reaction conditions were: catalyst: 50 mg, reaction time: 180 min, and temperature: 80 °C. It is important to note that at 100 °C several unidentified secondary products were detected by GC and TLC,

and at 120 °C urea decomposed to ammonia, and the Hantzsch 1,4-dihydropyridine product began to be detected. Similarly, to the 1,4-dihydropyridine synthesis, the catalyst was recycled and reused for five times. The results are listed in Table 3, entries 3, 14, 15, 16, 17, and 18. No appreciable variations of the yields were observed when the catalyst was reused five consecutive times. The loss of catalyst mass after the six runs was only 14%.

Table 3. Effect of different reaction parameters on 1,3-DHP (%)^a

Entry	Catalyst	Amount of Al ₂ O ₃ SO ₃ H (mg)	Temperature (° C)	Time (m)	Yield (%)
1	–	–	80	180	7
2	Al ₂ O ₃	–	80	180	18
3	Al ₂ O ₃ SO ₃ H	50	80	180	73
4		10	80	180	31
5		25	80	180	65
6		100	80	180	71
7		50	20	180	–
8		50	40	180	34
9		50	60	180	67
10		50	100	180	70
11		50	120	180	55
12		50	80	60	43
13		50	80	120	65
14		50	80	240	73
15		25	80	120	72
16		25	80	120	71
17		25	80	120	71
18		25	80	120	71
19		25	80	120	69

Note: Reaction conditions: furfural (96 mg, 1 mmol); ethyl acetoacetate (130 mg, 1 mmol); urea (90 mg, 1.5 mmol); catalyst 50 mg; solvent-free; stirring. ^a Pure product.

3.2.3 Synthesis of 1,4-dihydropyridines

Once the optimal reaction conditions for the synthesis of a 1,4-dihydropyridine were established, we explored the catalytic activity of Al₂O₃–SO₃H for different substrates to show the generality of the optimized procedure. In all cases furfural was used as

building block, and to obtain molecular diversity we employed different 1,3-dicarbonyl compounds and ammonia sources.

The 1,3-dicarbonyl compounds used were: ethyl acetoacetate, methyl acetoacetate, 2,4-pentanedione, cyclohexane 1,3-dione, 5,5 dimethyl cyclohexane 1,3-dione, and 3-oxobutanamide, and the ammonia sources were ammonium acetate and aniline. The results are listed in Table 4. The experiments were carried out under solvent-free conditions, in the presence of 25 mg of catalyst. The reactions were completed within 120 min at 80 °C. Five 1,4-dihydropyridines were obtained with very good yields. In all cases, the desired products were obtained with high selectivity, almost free of secondary products.

3.2.4 Synthesis of 1,3-dihydropyrimidinones

Similarly, the optimal reaction conditions for the synthesis of a 1,3-dihydropyrimidinone were applied to different substrates to show the generality of the optimized procedure, using Al₂O₃–SO₃H. In all cases furfural was used as building block, and we employed different 1,3-dicarbonyl compounds and urea or thiourea as nitrogen source. The results are listed in Table 5. The experiments were carried out under solvent-free conditions, in the presence of 50 mg of catalyst. The reactions were completed within 180 min at 80 °C. Five 1,3-dihydropyrimidinones were obtained with very good yields. In all cases, the desired products were obtained with high selectivity, almost free of secondary products. In entries 3 and 4 we used thiourea as nitrogen source, and in these cases the corresponding 1,3-dihydropyrimidinones were obtained. As in entries 7b and 8b, using 5-hydroxymethylfurfural, another building block obtained from biomass, the corresponding 1,3-dihydropyrimidinones were obtained with good yields.

Atom economy (AE), E-factor (E), reaction mass efficiency (RME), and material recovery parameter (MRP) were measured in order to quantify the “greenness” of the technology. Results are given in Tables 4 and 5. A comparison with modern classic synthetic methods for dihydropyrimidinones and dihydropyridines [31, 32] gives very good

Table 4. 1,4-Dihydropyridine synthesis using furfural as building block

Entry	N-source	Product	E Factor	Yield (%)	AE (%)	RME	MRP
1a	AcONH ₄		17.47	85	73.67	0.61	0.10
2a	AcONH ₄		19.88	82	71.85	0.57	0.09
3a	AcONH ₄		24.42	75	69.44	0.50	0.09
4a			15.22	79	77.60	0.67	0.11
5a			19.73	71	74.83	0.49	0.10

Note: Reaction conditions: furfural (1 mmol); 1,3-dicarbonyl compound (2 mmol); ammonia source (1.5 mmol); catalyst, 25 mg; temperature, 80 °C; time, 120 min; solvent-free; stirring.

parameters (Figures 4 and 5).

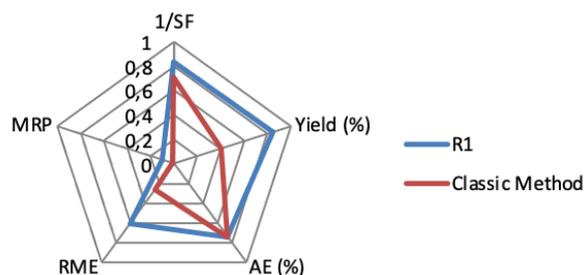


Figure 5. Comparison of green parameters of preparation of dihydropyridines with the classic synthesis method.

4 Conclusion

We prepared an Al₂O₃-SO₃H functionalized catalyst and examined its catalytic activity for the synthesis of several 3,4-dihydropyrimidinone and 1,4-dihydropyridine derivatives, using furfural (a building block present in vegetal biomass). The catalyst shows an environmentally friendly character, and its recyclability helps in the development of a greener methodology. Moreover, the different procedures

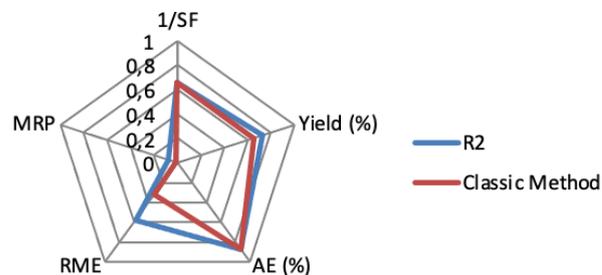


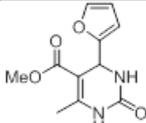
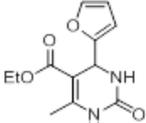
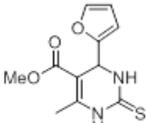
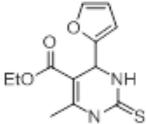
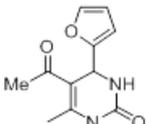
Figure 6. Comparison of green parameters of preparation of dihydropyrimidinones with the classic synthesis method.

offer several advantages including elevated yields, operational simplicity, environmentally friendly reaction conditions, and avoidance of toxic compounds.

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Table 5. 1,3-Dihydropyrimidinone synthesis using furfural as building block

Entry	Product	E factor	Yield (%)	AE (%)	RME	MRP
1b		28.81	70	86.76	0.55	0.08
2b		26.08	73	87.41	0.58	0.08
3b		29.10	65	87.50	0.50	0.08
4b		25.98	69	88.08	0.54	0.09
5b		30.47	71	85.94	0.55	0.07

Note: Reaction conditions: furfural (1 mmol); 1,3-dicarbonyl compound (1 mmol); ammonia source (urea or thiourea) (1.5 mmol); catalyst 50 mg; solvent-free; stirring.

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Additional information: Melting point and spectral data for representative synthesized compounds

Compound 1a [1]: m.p. 155-157 °C (methanol).

¹³C-NMR (CDCl₃, 100 MHz): δ = 167.5, 158.7, 145.3, 140.8, 110.0, 104.4, 100.5, 59.8, 33.4, 19.3, 14.3.

¹H-NMR (CDCl₃, 300 MHz): δ = 7.18 (1H, s), 6.18 (2H, s), 5.91 (1H, d, J = 4.8 Hz), 5.18 (1H, s), 4.17 (2H, q, J = 7.1 Hz), 4.12 (2H, q, J = 7.1 Hz), 2.29 (6H, s), 1.24 (6H, t, J = 7.1 Hz).

Compound 2a [2]: m.p. 150-151 °C (methanol).

¹³C-NMR (CDCl₃, 100 MHz): δ = 167.5, 154.8, 145.1, 140.7, 109.9, 102.6, 100.6, 39.7, 19.3, 13.3.

¹H-NMR (CDCl₃, 300 MHz): δ = 7.3-7.7 (5H, m), 6.20 (3H, m), 5.21 (4H, s), 4.12 (4H, q, J = 7.0 Hz), 2.11 (6H, s), 1.21 (6H, t, J = 7.0 Hz).

Compound 3a [3]: m.p. 185-187 °C (methanol).

¹³C-NMR (CDCl₃, 100 MHz): δ = 196.7, 159.8, 143.5, 140.6, 112.2, 104.2, 100.2, 57.9, 34.0, 19.4.

¹H-NMR (CDCl₃, 300 MHz): δ = 7.26 (1H, s), 6.40 (1H, s), 6.22 (1H, s), 5.90 (1H, s), 5.16 (1H, s), 2.33 (12H, m).

Compound 1b [4]: m.p. 208-209 °C (methanol).

¹³C-NMR (DMSO-d₆, 100 MHz): δ = 165.4, 155.8, 152.3, 149.6, 142.2, 110.3, 105.3, 96.5, 50.8, 47.5, 17.7.

¹H-NMR (DMSO-d₆, 300 MHz): δ = 9.25 (1H, s), 7.76 (1H, s), 7.54 (1H, s), 6.34 (1H, m), 6.08 (1H, d, J = 2.8 Hz), 5.18 (1H, d, J = 3.2 Hz), 3.55 (3H, s), 2.22 (3H, s)..

Compound 2b [5]: m.p. 209-211 °C (methanol).

¹³C-NMR (DMSO-d₆, 100 MHz): δ = 165.1, 155.8, 152.4, 149.1, 142.0, 110.3, 105.1, 96.8, 59.2, 47.8, 17.7, 14.2.

¹H-NMR (DMSO-d₆, 300 MHz): δ = 9.27 (1H, s), 7.74 (1H, s), 7.54 (1H, s), 6.34 (1H, s), 6.08 (1H, s), 5.20 (1H, s), 4.02 (2H, q, J = 7 Hz), 2.20 (3H, s), 1.11 (3H, t, J = 7 Hz).

Compound 3b [4]: m.p. 205-208 °C (methanol).

¹³C-NMR (DMSO-d₆, 100 MHz): δ = 183.4, 165.5, 154.5, 146.4, 142.8, 110.7, 106.4, 106.0, 51.4, 47.8, 17.3.

¹H-NMR (DMSO-d₆, 300 MHz): δ = 10.41 (1H, s), 8.94 (1H, s), 7.56 (1H, s), 6.35 (1H,

m), 6.14 (1H, d, J = 2.8 Hz), 5.20 (1H, d, J = 1.2 Hz), 3.76 (3H, s), 2.25 (3H, s).