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ARTICLE

Application of biological-based nano and nano magnetic catalysts in the preparation of arylbispyranylmethanes

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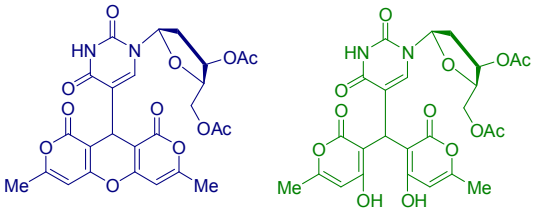
Herein, the utilization of 2-carbamoylhydrazine-1-sulfonic acid, carbamoylsulfamic acid and their related nano magnetic core-shell catalysts were described as biological-based nano catalysts with urea moiety in the synthesis of arylbispyranylmethane derivatives under mild and eco-friendly reaction conditions. A good range of aromatic aldehydes were treated with 4-hydroxy-6-methyl-2-pyrone to give arylbispyranylmethane derivatives through a tandem Knoevenagel condensation and Michael addition procedure in relatively short reaction times with high yields. The presented protocols have merits like the eco-friendly nature, high efficiency, simple operational procedures and benign reaction conditions.

Introduction

In the modern era in the field of organic chemistry, the enhancement of the reaction efficacy, improvement of the atom and step economy, construction of the complex molecules in a simple manner, the reduction of waste production and avoidance of utilization of a large amount of unsafe organic solvents have become crucial objectives [1]. The aforementioned concerns can be resolved in the case of using one-pot multi component reactions as a premium strategy compared to the conventional step wise organic reactions [2-5]. Therefore, by keeping these merits in mind, the designing and applying a one-pot multi component reaction strategy for the preparation of the biologically active compounds is desired.

Among the heterocyclic compounds, the arylbispyranylmethane derivatives present a wide variety of therapeutic and pharmaceutical properties as they can be utilized as anticoagulant agents, similar to the structurally related anticoagulant agent 3,3'-methylenebis (4-hydroxycoumarin) [6]. Also, these compounds are related to similar structural motifs that exhibit anti-inflammatory activities and can be used as an inhibitor for mPGES-1 and 5-LO [7]. In addition, 5-substituted pyrimidine nucleoside derivatives of the arylbispyranylmethanes have potential antiviral activities (**Scheme 1**) [6b].

Despite of above mentioned biological merits of this versatile heterocyclic scaffold, only a few methods, including under the



Scheme 1: 5-Substituted pyrimidine nucleosides with potential antiviral activities

catalysis of organic bases [8-9], Ionic liquid mediated [6b] and using AcOH and piperidine [9], have been investigated for the synthesis of arylbispyranylmethane derivatives. By the way, all of the presented protocols suffer from one or more serious drawbacks like employing hazardous and unsafe solvents, acidic or basic media, lengthen reaction times, harsh reaction conditions and tedious work up. Therefore, due to the high importance role of the green chemistry in the domain of organic synthesis, the development of more eco-friendly and environmentally benign procedures for the synthesis of arylbispyranylmethanes is desirable.

The catalytic active species with small metal-free organic molecules entitled "organocatalysts" found their key roles as promoter and established highly dynamic area in the academic and also industrial sectors in the past few years and the organocatalysis has grown dramatically [10]. A striking advantage of organocatalysts is their high surface to volume ratio which can intensify the possibility of the interaction between reactants and catalyst and lead to multiplying the catalytic performance of the applied organocatalysts [11-13]. Nowadays, the applications of magnetic nano-sized particles as versatile inorganic support for organic and inorganic species have appeared as a potent branch in the field of green chemistry. Utilizing of the magnetic nano particles as supports for immobilization of organocatalysts can add varied

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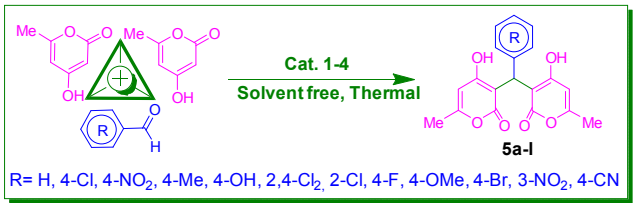
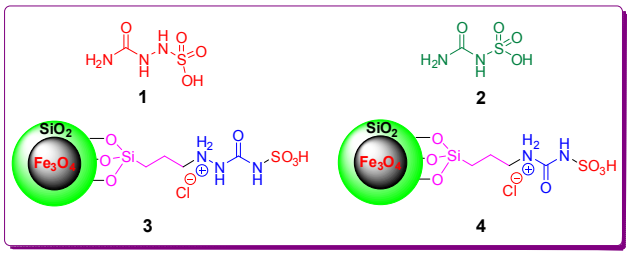
merits to homogeneous nature of them and make them powerful and easy recoverable heterogeneous active catalysts [14].

In continuation of our previously research interest related to the maturation of the design, construction, applications and knowledge-based development of solid acids [15] and inorganic acidic salts [16] for the organic functional group interconversion and also in order to find the new synthetic organic methods in competence with principles of green chemistry, we wish to report the more applications of our previously reported nano organo solid acid catalysts namely, 2-carbamoylhydrazine-1-sulfonic acid **1**, carbamoylsulfamic acid **2** and their related nano magnetic core-shell catalysts **3** and **4**, as biological-based, efficient and mild nanocatalysts for the preparation of the arylbispyranylmethane derivatives under benign and solvent free reaction conditions as portrayed in **Scheme 2**.



Scheme 2: The preparation of the arylbispyranylmethanes in the presence of biological-based nano solid acid catalysts



Scheme 3: The structure of applied biological-based nano solid acid catalysts with urea moiety for the synthesis of arylbispyranylmethanes

Results and discussion

The 2-carbamoylhydrazine-1-sulfonic acid **1** and carbamoylsulfamic acid **2** and their related nano magnetic core-shell catalysts $\{Fe_3O_4@SiO_2@(CH_2)_3$Semicarbazide-$SO_3H/HCl\}$ **3** and $\{Fe_3O_4@SiO_2@(CH_2)_3$-Urea-$SO_3H/HCl\}$ **4**, as biological-based nano solid acid catalysts with urea moiety were prepared according to our previously reported methods (**Scheme 3)** [11, 17, 18].

In order to study the morphology and particles size of our previously reported biological based catalysts **1**-**4**, the transmission electron microscopy (TEM) images of the catalysts were prepared and portrayed in Figure 1. The TEM micrographs confirmed that the all presented catalysts are in nano meter scale as reported in the literatures [11, 17, 18].

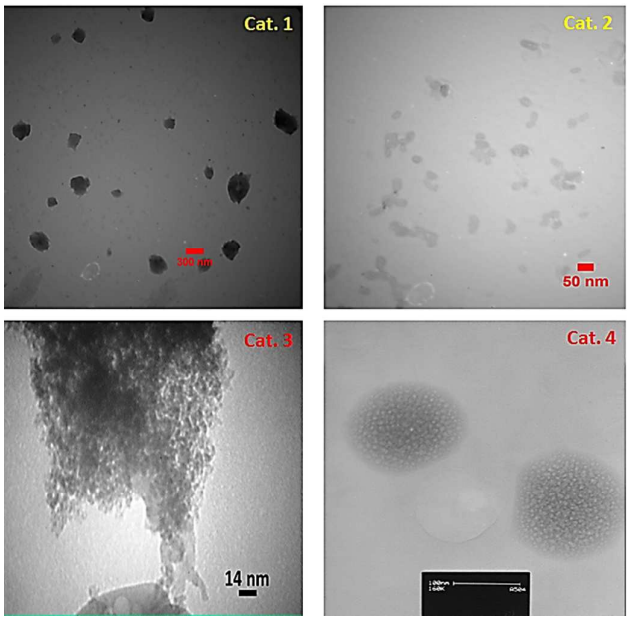


Figure 1: Recorded TEM images of four biological based nano and nanomagnetic catalysts **1-4**

Before all else, in order to find the best promoter for the synthesis of arylbispyranylmethane derivatives, due to the structural similarity, the catalytic activity of the two biological-based nano organo solid acid catalysts and their nano magnetic core-shell equivalents of them (**Scheme 3**), were investigated at the synthesis of target molecule **5a**. The obtained data were embedded in Table 1.

Table 1: Screening of different catalysts at the synthesis of compound **5a**[*]

Catalyst	Load of catalyst	Temperature (^{o}C)	Time (min)	Yield (%)[**]
Catalyst **1**	15 mol%	80	25	92
Catalyst **2**	10 mol%	100	20	90
Catalyst **3**	7 mg	100	20	93
Catalyst **4**	5 mg	100	16	95

[*]Reaction condition: benzaldehyde (1 mmol, 0.106 g), 4-hydroxy-6-methyl-2-pyrone (2 mmol, 0.252 g), [**]Isolated yields

From the achieved data in the screening of the catalysts (Table 1), it can be inferred that the all tested catalysts can act as excellent promoter for the synthesis of compound **5a**. Therefore, the catalytic application of four biological-based nano catalysts were explored at the synthesis of a good range of arylbispyranylmethane under mild and solvent free conditions (**Scheme 2**).

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In continue, to find the best experimental conditions for the preparation of the 3,3'-(phenylmethylene)bis(4-hydroxy-6-methyl-2*H*-pyran-2-one) in the presence of 2-carbamoylhydrazine-1-sulfonic acid **1**, the optimal reaction temperature, amount of the catalyst and different solvents were scrutinized upon the reaction of benzaldehyde and 4-hydroxy-6-methyl-2-pyrone. The attained data have revealed that the best results were obtained in the presence of a catalytic amount of catalyst **1** under solvent free conditions at 80 °C (Table 2, Entry 3).

Table 2: Optimization of reaction conditions for the synthesis of arylbispyranylmethanes in the presence of 2-carbamoylhydrazine-1-sulfonic acid **1** *

Entry	Solvent	Load of catalyst (mol%)	Temperature (^{o}C)	Time (min)	Yield (%)**
1	-	15	r.t.	60	Trace
2	-	15	54	85	42
3	**-**	**15**	**80**	**25**	**92**
4	-	15	100	25	90
5	-	5	80	30	89
6	-	10	80	23	78
7	-	20	80	20	88
8	-	-	80	110	Trace
9	H_2O	15	Reflux	130	85
10	EtOH	15	Reflux	120	89
11	CH_3CN	15	Reflux	30	86
12	*n*-Hexan	15	Reflux	50	63

*Reaction conditions: benzaldehyde (1 mmol, 0.106 g), 4-hydroxy-6-methyl-2-pyrone (2 mmol, 0.252 g), **Isolated yields.

In another study, the application of the carbamoylsulfamic acid **2** as an effective biological-based nano organocatalysts with urea moiety was inspected in the synthesis of 3,3'-(phenylmethylene)bis(4-hydroxy-6-methyl-2*H*-pyran-2-one). At the beginning, to exploration of the best experimental conditions, the reaction of benzaldehyde and 4-hydroxy-6-methyl-2-pyrone was picked up as a test reaction. The achieved data for the investigation of different loads of the catalyst **2**, operational temperatures and solvents are indexed in Table 4. The attained results show that the best condition for the model reaction, were attain when the reaction was performed using catalytic load of the catalyst **2** under solvent free conditions at 100 ^{o}C (Table 3, Entry 7).

It is worthy to mention that in the case of nano organocatalysts **1** and **2**, increasing in the load of catalysts or temperatures did not effect in the yields or reaction times for the synthesis of target compounds. Also, the resulting from solvents screening, did not show more positive effect over solvent free condition.

Table 3: Optimization of reaction conditions for the synthesis of arylbispyranylmethanes in the presence of 2- carbamoylsulfamic acid **2** *

Entry	Solvent	Load of catalyst (mol%)	Temperature (^{o}C)	Time (min)	Yield (%)**
1	-	15	r.t.	100	Trace
2	-	15	54	67	69
3	-	15	80	30	68
4	-	15	100	26	93
5	-	15	113	26	75
6	-	5	100	26	87
7	**-**	**10**	**100**	**20**	**90**
8	-	20	100	15	78
9		-	100	227	53
10	EtOH	10	Reflux	30	82
11	CH_3CN	10	Reflux	125	93
12	*n*-Hexan	10	Reflux	85	72
13	EtOAc	10	Reflux	55	91

*Reaction conditions: benzaldehyde (1 mmol, 0.106 g), 4-hydroxy-6-methyl-2-pyrone (2 mmol, 0.252 g), **Isolated yields.

As in the case of two biologically-based organocatalysts, the optimal reaction conditions for the synthesis of arylbispyranylmethanes were inspected in the presence of their nano magnetic core-shell equivalents **3** and **4** of them. In the case of nano catalyst **3**, the reaction between 4-chlorobenzaldehyde and 4-hydroxy-6-methyl-2-pyrone was selected as a model reaction to afford 3,3'-((4-chlorophenyl)methylene)bis(4-hydroxy-6-methyl-2H-pyran-2-one) and the attained data for the study of different amount of the catalyst, temperatures and solvents were embedded in Table 4. The best reaction conditions are in the presence of 7 mg nano magnetic core-shell catalyst at 100 ^{o}C under solvent free conditions (Table 4, Entry 3).

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Table 4: Optimization of reaction conditions for the synthesis of arylbispyranylmethanes in the presence of Cat. **3**

Entry	Solvent	Load of catalyst (mg)	Temperature (^{o}C)	Time (min)	Yield (%)**
1	-	7	r.t.	360	60
2	-	7	80	30	85
3	**-**	**7**	**100**	**20**	**93**
4	-	7	110	17	92
5	-	5	100	30	85
6	-	10	100	25	90
7	-	-	100	227	53
9	H_2O	7	Reflux	20	77
10	EtOH	7	Reflux	100	72
11	CH_3CN	7	Reflux	60	47
12	EtOAc	7	Reflux	85	50
13	*n*-Hexan	7	Reflux	120	7

*Reaction conditions: 4-Chlorobenzaldehyde (1 mmol, 0.140 g), 4-hydroxy-6-methyl-2-pyrone (2 mmol, 0.252 g), **Isolated yields.

Table 5: Optimization of reaction conditions for the synthesis of arylbispyranylmethanes in the presence of Cat. 4

Entry	Solvent	Load of catalyst (mg)	Temperature (^{o}C)	Time (min)	Yield (%)**
1	-	10	80	45	85
2	-	10	100	15	90
3	-	10	110	12	66
4	-	15	80	30	53
5	-	7	100	16	77
6	**-**	**5**	**100**	**16**	**95**
7	-	3	100	23	94
8	H_2O	5	Reflux	20	93
9	EtOH	5	Reflux	102	79
10	CH_3CN	5	Reflux	40	78
11	EtOAc	5	Reflux	190	38
12	*n*-Hexan	5	Reflux	160	42

*Reaction conditions: benzaldehyde (1 mmol, 0.106 g), 4-hydroxy-6-methyl-2-pyrone (2 mmol, 0.252 g), **Isolated yields.

In the case of nano magnetic core-shell catalyst **4**, the reaction of benzaldehyde and 4-hydroxy-6-methyl-2-pyrone was picked up for optimizing of the reaction conditions to yield 3,3'-(phenylmethylene)bis(4-hydroxy-6-methyl-2*H*-pyran-2-one). The resulting data inserted in Table 5, indicate that the optimized reaction conditions obtained when the reaction carried out under solvent free conditions in the presence of 5 mg of nano magnetic catalyst **4** at 100 ^{o}C (Table 5, Entry 6). The obtained data were collected in Table 5.

Similar to nano organocatalysts **1** and **2**, as indicated in Tables 4 and 5, in the case of nano magnetic core-shell catalysts **3** and **4**, performing the reactions in various solvents or increasing the amount of catalyst and elevated temperature did not present any progress in the yield or reaction time**.**

In attempting to confirm the applicability and efficacy of the presented protocols for the arylbispyranylmethanes synthesis, a good range of aromatic aldehydes (containing those bearing electron-withdrawing, electron-releasing groups and halogens) were reacted with 4-hydroxy-6-methyl-2-pyrone in the presence of 2-carbamoylhydrazine-1-sulfonic acid **1**, carbamoylsulfamic acid **2** and their related nano magnetic core-shell catalysts **3** and **4** as biological-based nano catalysts with urea moiety at their optimal reaction conditions as embedded in Table 2-5. The obtained data have illustrated that the starting materials were reacted with each other to afford the desired products in good to excellent yields in short reaction times (Table 6).

Table 6: Synthesis of the arylbispyranylmethane derivatives in the presence of four nano solic acid catalysts[a]

Product	R	**Cat. 1**		**Cat. 2**		**Cat. 3**		**Cat. 4**		M. p (^{o}C) found [Lit][ref]
		Time (min)	Yield (%)[b]	Time (min)	Yield (%)[b]	Time (min)	Yield (%)[b]	Time (min)	Yield (%)[b]	
5a	**H**	25	92	20	90	18	90	16	95	213-216 [214-215][9]

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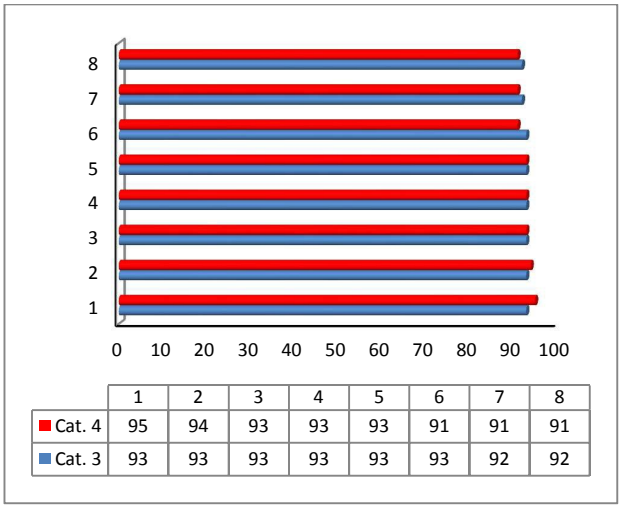
5b	**4-Cl**	40	75	62	86	20	93	30	95	202-206 [205-207][9]
5c	**4-NO_2**	90	93	85	95	20	92	25	96	232-234 [214-217][9]
5d	**4-F**	62	94	70	91	28	96	35	88	219-221 [202-204][7b]
5e	**4-OH**	38	98	42	98	47	90	45	88	202 [new]
5f	**4-Me**	33	90	48	84	13	89	37	76	183-185 [186-187][7b]
5g	**3-NO_2**	33	95	50	94	40	98	43	94	200-204 [193-194][10]
5h	**2,4-Cl_2**	46	93	70	90	45	91	30	91	244-246 [226-229][20]
5i	**2-Cl**	30	87	40	95	37	96	35	91	155-158 [155-156][10]
5j	**4-OMe**	35	89	57	84	38	92	60	96	174-176 [174-176][9]
5k	**4-Br**	65	77	28	95	38	73	23	72	212-215 [207-208][20]
5l	**4-CN**	30	94	90	95	55	92	43	98	223-225 [201-203][7b]

[a]Reaction condition: arylaldehydes (1 mmol), 4-hydroxy-6-methyl-2-pyrone (2 mmol, 0.252 g), [b]Refers to isolated yields

To the best of our knowledge, recyclability and reusability can be considered as one of the major factors which should be considered for applying of catalysts in the chemical processes. A comparison between the catalysts **1-4** on the basis of their recyclability and reusability, have shown that nano magnetic catalysts **3**-**4** are more better than the described catalysts **1**-**2**. Therefore, the recyclability and reusability of the two nano magnetic core-shell catalysts **3** and **4**, for the preparation of arylbispyranylmethane derivatives were successfully explored for eight times. After performance of each run, hot ethanol was added to the reaction mixture to dissolve the desired target molecules and unreacted starting materials (the examined catalysts were not dissolved in hot ethanol). Then, the used nano magnetic catalysts were separated from the reaction mixture by applying a simple external magnet and washed repetitively with ethanol and preserved for next attempt. The reusability test and recycling possibility of the{Fe_3O_4@SiO_2@$(CH_2)_3$Semicarbazide-SO_3H/HCl} **3** and {Fe_3O_4@SiO_2@$(CH_2)_3$-Urea-SO_3H/HCl} **4**, as biological-based nano magnetic solid acid catalysts were probed at the reaction of 4-chlorobenzaldehyde and 4-hydroxy-6-methyl-2-pyrone under optimal reaction conditions in constant times 20 and 30 minutes, respectively. The attained data as indicated in Figure 2, demonstrate that the catalytic activity of the two nano magnetic solid acidic catalysts were conserved after eight times without any considerable amount of loss in their initial catalytic performance.



	1	2	3	4	5	6	7	8
Cat. 4	95	94	93	93	93	91	91	91
Cat. 3	93	93	93	93	93	93	92	92

Figure 2: The recycling possibility and reusability of the two nano magnetic core-shell catalysts **3** and **4** at the synthesis of desired target molecules **5b**.

The manner of the catalytic performance of the biological-based nano catalysts **1-4** with urea moiety and the formation of the various arylbispyranylmethanes could be rationalized as follows (**Scheme 4**). Initially, the activated aromatic aldehydes were subjected in to the reaction with 4-hydroxy-6-methyl-2-pyrone and the related Knovengel adduct **A** was generated through dehydration. Subsequently, in the presence of the nano catalysts, the intermediate **A** acts as a Michael acceptor and by the reaction with the second molecule of the 4-hydroxy-6-methyl-2-pyrone, the intermediate **B** is formed. Eventually, the tautomerization of the intermediate **B** offers the full conjugated corresponding target product **5a-l**.

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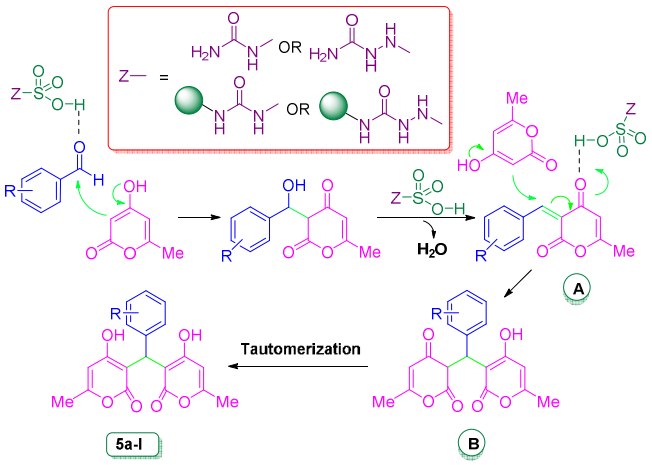

Scheme 4: The plausible mechanism for the preparation of the arylbispyranylmethanes in the presence of the described biological-based nano catalysts **1**-**4**.

Conclusion

In conclusion, in this investigation, we have explored the catalytic applicability of the biological-based nano catalysts with urea moiety in the synthesis of arylbispyranylmethane derivatives. The benefits of these procedures are the reducing of the reaction times, improving of the yields, benign and eco-friendly reaction conditions, step and atom viability, easy work-up and purification of the desired products. Since that the recyclability and reusability is a major factor for influencing the suitability of any catalyst, we observed that the nano magnetic catalysts **3**-**4** are more recyclable than the described organocatalysts **1**-**2**. Finally, on the basis of our observations and the above mentioned advantages, herein, we thought that all of the described biological-based nano solid acids and/or catalysts have potential for industrial production.

Experimental

General

All reagents and starting materials were obtained from Merck chemical company and employed without further purification. The known target molecules were identified by comparison of their physical properties and spectral data with their reported authentic samples in the literatures. The reaction progress and the purity of the compounds were verified using TLC skill performed with silica gel SIL G/UV 254 plates. NMR spectra were recorded on a Bruker Ultrashield 400 spectrometer, ^{1}H NMR (400.13) and ^{13}C NMR (100.62). The data for ^{1}H NMR are reported as follows: chemical shift (ppm), integration, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; and br, broad) and coupling constant (Hz). Melting points were recorded on Buchi B-545 apparatus in open capillary tubes. A neodymium block magnet (1.18 T) was used for separation of the catalyst from the reaction mixture.

Synthesis of arylbispyranylmethane derivatives in the presence of biological-based nano solid acid catalysts 1 and 2: A typical procedure

To a round bottom flask containing a mixture of aromatic aldehydes (1 mmol) and 4-hydroxy-6-methyl-2-pyrone (2 mmol, 0.252 g), and 2-carbamoylhydrazine-1-sulfonic acid **1** (0.0184 g, 15 mol%), 2- carbamoylsulfamic acid **2** (0.0108 g, 10 mol%), as catalysts was added. Afterwards, the obtained reaction mixture was placed in an oil bath at 80 ^{o}C (in the case of organo catalyst **1**) or 100 ^{o}C (in the case of organo catalyst **2**) and was vigorously stirred for appropriated times as indicated in their related Table 6. The reaction progress was checked using TLC technical skill with a mixture of *n*-hexane and ethyl acetate as the eluent. After performance of the reaction, the mixture was cooled to ambient temperature. Then, in the case of organo catalyst **1** and **2** in order to removing of the used catalyst, 5 mL of distillated water were added and the mixture was stirred for addition 5 minutes and decanted. Finally, the crude products were recrystallized from ethanol which to afford pure target molecules in good to high yields as depicted in Table 6.

Synthesis of arylbispyranylmethane derivatives in the presence of biological-based nano magnetic solid acid catalysts 3 and 4: A typical procedure

To a round bottom flask containing a mixture of aromatic aldehydes (1 mmol) and 4-hydroxy-6-methyl-2-pyrone (2 mmol, 0.252 g), and {Fe_3O_4@SiO_2@$(CH_2)_3$Semicarbazide-SO_3H/HCl} **3** (7 mg) and {Fe_3O_4@SiO_2@$(CH_2)_3$-Urea-SO_3H/HCl} **4** (5 mg) as catalysts were added. Afterwards, the obtained reaction mixture was placed in an oil bath at 100 ^{o}C and was vigorously stirred for appropriated times as indicated in their related Table 6. The reaction progress was checked using TLC technical skill with a mixture of *n*-hexane and ethyl acetate as the eluent. After performance of the reaction, the mixture was cooled to ambient temperature. Then, in the case of nano magnetic solid acid catalyst **3** and **4**, hot EtOH, was added to the mixture and the catalyst were separated using an external magnet. Finally, the crude products were recrystallized from ethanol which to afford pure target molecules in good to high yields as depicted in Table 6.

Selected spectral data

As it can be seen in ESI, for example in the case of compound 3,3'-((2,4-dichlorophenyl)methylene)bis(4-hydroxy-6-methyl-2H-pyran-2-one) (5h), the FT-IR spectrum shows a broad peak at 3423 cm^{-1} which can be attributed to the OH functional groups in the structure. Also, the vibration mode of C=O functional groups appear at 1678 cm^{-1}. In addition C=C stretching mode observed at 1633 cm^{-1}. In ^{1}H NMR spectrum, a signal appears as a broad singlet at 11.22 ppm is related to -OH functional groups. The three aromatic protons can be found in the aromatic region

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as three separated coupled peaks. Also, due to the structural symmetry, the two olefinic protons resonate at 5.94 ppm as a singlet. A singlet peak at 5.56 ppm can be ascribed to the tertiary proton in the structure and finally, a singlet peak appears at 2.15 ppm is related to the 6 protons of two methyl groups in the structure of the target compound 5h. In ^{13}C NMR spectrum, all predicted carbon atoms are appeared in the related regions. For example the carbon and methyl groups are resonated at 34.7 and 19.2 ppm respectively. Also, the carbons of carbonyl functional groups are appeared at 166.2 ppm. It is worthy to mention that, the used FT-IR, ^{1}H NMR and ^{13}C NMR spectrums confirmed the formation of the target molecules 5a-l.

3,3'-((4-hydroxyphenyl)methylene)bis(4-hydroxy-6-methyl-2H-pyran-2-one) (5e)

Melting point = 202 ^{o}C
FT-IR (KBr): ν (cm^{-1})= 3423, 1680, 1603, 1591, 1385, 833.
^{1}H NMR (400 MHz, DMSO) δ (ppm) = 11.62 (brs, 2H, OH), 6.78 (d, *J* = 8.6 Hz, 2H), 6.63 (d, *J* = 8.6 Hz, 2H), 6.09 (s, 2H), 5.89(s, 1H), 2.20 (s, 6H).
^{13}C NMR (101 MHz, DMSO) δ (ppm) = 167.9, 166.4, 161.1, 155.3, 129.0, 127.4, 114.9, 102.0, 101.3, 100.1, 88.1, 32.9, 19.1.

3,3'-((2,4-dichlorophenyl)methylene)bis(4-hydroxy-6-methyl-2H-pyran-2-one) (5h)

Melting point = 244-246 ^{o}C
FT-IR (KBr): ν (cm^{-1})= 3423, 1678, 1633, 1575, 1385, 866.
^{1}H NMR (400 MHz, DMSO) δ (ppm) = 11.22 (brs, 2H, OH), 7.42 (d, *J* = 2.2 Hz, 1H), 7.27 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.12 (d, *J* = 8.5 Hz, 1H), 5.94 (s, 2H), 5.56 (s, 1H), 2.15 (s, 6H).
^{13}C NMR (101 MHz, DMSO) δ (ppm) = 166.2, 164.0, 160.5, 138.8, 133.4, 131.5, 130.7, 127.8, 126.3, 100.3, 100.2, 34.7, 19.2.

3,3'-((2-chlorophenyl)methylene)bis(4-hydroxy-6-methyl-2H-pyran-2-one) (5i)

Melting point = 155-158 ^{o}C
FT-IR (KBr): ν (cm^{-1})= 3440, 1683, 1617, 1571, 1407, 745.
^{1}H NMR (400 MHz, DMSO) δ (ppm) = 11.40 (brs, 2H, OH), 7.50-7.48 (m, 1H), 7.40-7.32 (m, 3H), 6.16 (s, 2H) 5.86 (s, 2H), 2.36 (s, 6H).
^{13}C NMR (101 MHz, DMSO) δ (ppm) =166.5, 164.4, 160.4, 139.2, 132.7, 130.1, 128.6, 127.2, 126.2, 100.5, 34.9, 19.1.

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Application of biological-based nano and nano magnetic catalysts in the preparation of arylbispyranylmethanes

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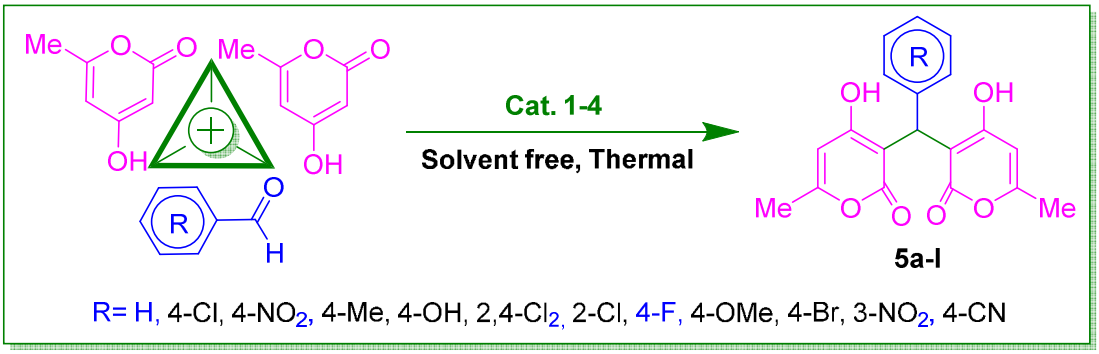

Nano 2-carbamoylhydrazine-1-sulfonic acid, carbamoylsulfamic acid and their related nano magnetic core-shell catalysts as biological-based nano catalysts with urea moiety were used in the synthesis of arylbispyranylmethanes.