DE GRUYTER OPEN

ACTA CHEMICA IASI, **25_1**, 38 -50 (2017)

DOI: 10.1515/achi-2017-0005

THREE-COMPONENT SYNTHESIS OF MONO AND BIS 4,5-DIHYDROPYRANO[3,2-*C*]CHROMENES AND 4,5-DIHYDROPYRANO[4,3-*B*]PYRANS CATALYZED BY SODIUM BENZENESULFINATES AS A GREEN ORGANOCATALYST

Mehdi Abaszadeh[a*] and Mohammad Seifi[b]

[a]*Pharmaceutics Research Center, Institute of Neuropharmacology, Kerman University of Medical Sciences, Kerman 76175493, Iran.*

[b]*Department of Chemistry, Faculty of Sciences, Najafabad Branch, Islamic Azad University, Najafabad, Esfahan, Iran.*

Abstract: Mono and bis 4,5-dihydropyrano[3,2-*c*]chromene and 4,5-dihydropyrano[4,3-*b*]pyran derivatives were synthesized by three-component reaction of aromatic aldehydes, malononitrile and 4-hydroxycoumarin or 4-hydroxy-6-methylpyrone, in the presence of catalytic amounts of sodium benzenesulfinates, as a organocatalyst, in H_2O/EtOH, at reflux. High conversions, short reaction times, cleaner reaction profiles and usage of a stable and also inexpensive catalyst are some of the advantages of this method.

***Keywords*:** Sodium benzenesulfinates; Mono and bis 4,5-dihydropyrano[3,2-*c*]chromenes; Mono and bis 4,5-dihydropyrano[4,3-*b*]pyrans; Three-component reactions.

Introduction

Multi-component reactions (MCRs) have emerged as an attractive and powerful strategy for organic synthesis.[1,2] MCRs are highly flexible,

* Mehdi, Abaszadeh, *e-mail*: abaszadeh@kmu.ac.ir

supplying the opportunity of building up complex molecules with exceptional synthetic efficiency, frequently with high stereo selectivity, from simple and easily available substrates.[3-8] Hence, MCRs are considered a clean and practical protocol for the synthesis of polyfunctionalized heterocyclic compounds (PFHC).[9]

It is not surprising that the synthesis of these compounds has received considerable attention, because PFHC play important roles in the synthesis of a large number of biologically active molecules.[10,11] In the recent years, a great deal of research into PFHC has permitted the synthesis of bis-heterocyclic compounds that show various biological activities, such as antibacterial, fungicidal, tuberculostatic, and antiamoebic properties.[12-14]

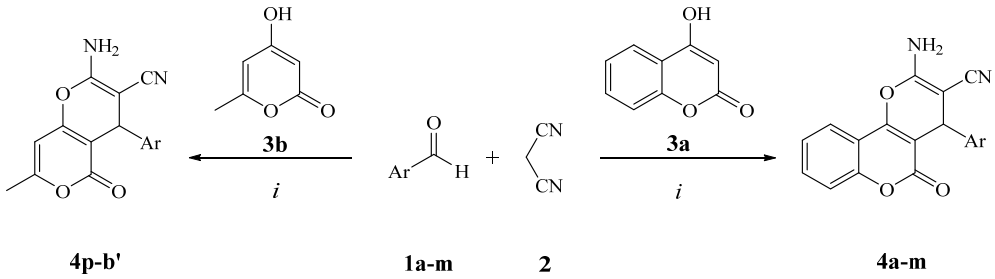
Among these aforementioned compounds, 4,5-dihydropyrano[3,2-*c*]chromene and 4,5-dihydropyrano[4,3-*b*]pyran derivatives have received much attention, due to their remarkable molecular structures and important biological[15] and pharmacological[16] applications. Therefore, considerable attention has been focused on the development of environmentally friendly procedures to synthesize dihydropyranochromene and dihydropyranopyran derivatives, by three-component reaction of aromatic aldehydes, malononitrile and 4-hydroxycoumarin or 4-hydroxy-6-methylpyrone. Various catalytic systems such as potassium phthalimide-*N*-oxyl (POPINO),[17] high surface area MgO,[18] 3-hydroxypropanaminium acetate (HPAA),[19] trisodium citrate,[20] hexamethylenetetramine (HMT),[21] ammonium acetate,[22] 1,4-diazabicyclo[2.2.2]octane (DABCO)[23] and KF/Al_2O_3[24] have been reported for synthesis these compounds. We previously reported synthesis these compounds in the presence of crown ether complex cation ionic liquids (CECILs) as catalyst.[25] Each of these methods has its own advantages, but there are also major drawbacks, as the use of toxic organic solvents, expensive catalysts, difficult work up, high reaction time, and low yields. The finding a simple and green synthesis of

dihydropyranochromene and dihydropyranopyran derivatives is therefore very necessary.

Sodium benzenesulfinates (SBSs) have been used in many organic reactions as traceless linker,[26] as nucleophile[27] and as catalyst.[28] According to our knowledge, SBSs have never used as catalyst in the synthesis of dihydropyranochromene and dihydropyranopyran derivatives. In this work, we expose a method to synthesize these compounds in H_2O/EtOH by using inexpensive and commercially available SBSs as catalyst, working under reflux.

Results and Discussion

SBSs was used as a green and effective organocatalyst in the synthesis of 4,5-dihydropyrano[3,2-*c*]chromene (**4a-m**) and 4,5-dihydropyrano[4,3-*b*]pyran derivatives (**4p-b'**) by using three-component reaction of aromatic aldehydes (**1a-m**), malononitrile (**2**) and 4-hydroxycoumarin (**3a**) or 4-hydroxy-6-methylpyrone (**3b**), in H_2O/EtOH and at reflux (Scheme 1).



i: H_2O/EtOH (7mL/3mL), 4-Chloro SBS (10 mol%), reflux

Scheme 1. Three-component reaction of aromatic aldehydes **(1a-m)**, malononitrile **(2)** and 4-hydroxycoumarin **(3a)** or 4-hydroxy-6-methylpyrone **(3b).**

The optimization of the reaction conditions was made by using a model, the reaction between benzaldehyde (**1a**), malononitrile (**2**) and 4-hydroxycoumarin (**3a**) (Table 1). When the three-component reaction was

carried out in the presence of 4-chloro SBS (10 mol%), in H_2O/EtOH, at reflux, the yield towards 2-amino-5-oxo-4-phenyl-4,5-dihydropyrano[3,2-*c*]chromene-3-carbonitrile **4a** was obtained in 91% yield after 12 minutes reaction time. Different solvents were also tested, such as H_2O, EtOH, AcOEt, MeCN and toluene; the best results in terms of reaction time and yield of the desired product **4a** was obtained in H_2O/EtOH (Table 1, entries 1-6). SBS and 4-methyl SBS were also tested as catalyst (Table 1, entries 7-8). Decreasing the catalyst loading from 10 to 4 mol% significantly lowered the yield of the reaction (Table 1, entries 9-11).

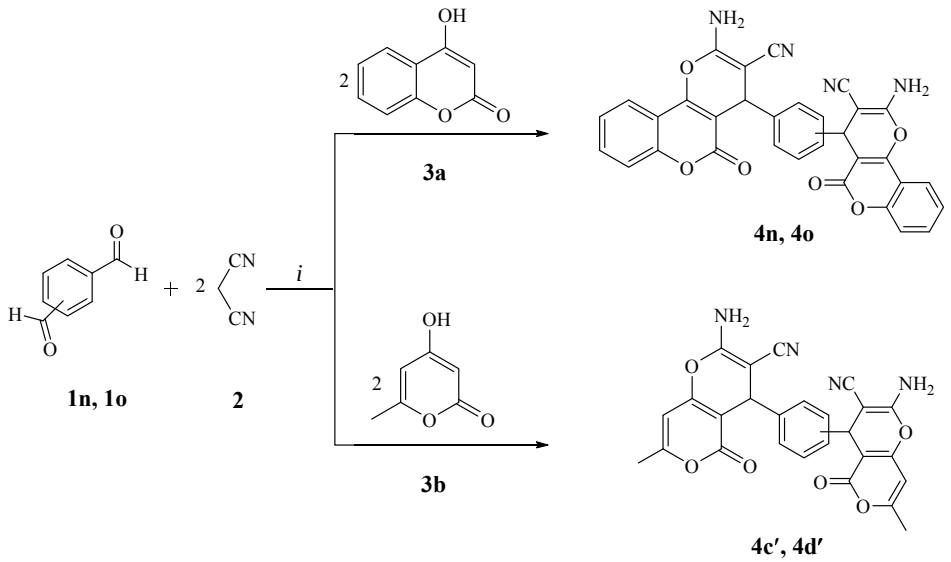
Table 1. Optimization of the model reaction between benzaldehyde **(1a)**, malononitrile **(2)** and 4-hydroxycoumarin **(3a).**

Entry	Solvent	Catalyst	Catalyst (mol %)	Time (min)	Yield (%)
1	H_2O/EtOH (7mL/3mL)	4-chloro SBS	10	12	91
2	Water (10 mL)	4-chloro SBS	10	18	85
3	Ethanol (10 mL)	4-chloro SBS	10	15	89
4	Ethyl acetate (10 mL)	4-chloro SBS	10	40	80
5	Acetonitrile (10mL)	4-chloro SBS	10	38	81
6	Toluene (10 mL)	4-chloro SBS	10	80	60
7	H_2O/EtOH (7mL/3mL)	SBS	10	23	89
8	H_2O/EtOH (7mL/3mL)	4-methyl SBS	10	30	85
9	H_2O/EtOH (7mL/3mL)	4-chloro SBS	8	20	85
10	H_2O/EtOH (7mL/3mL)	4-chloro SBS	6	26	81
11	H_2O/EtOH (7mL/3mL)	4-chloro SBS	4	35	78

According to the obtained data, we decided to apply this method for the synthesis of 4,5-dihydropyrano[3,2-*c*]chromene (**4a-m**) and 4,5-dihydropyrano[4,3-*b*]pyran derivatives (**4p-b'**) by three component reaction of aromatic aldehydes (**1a-m**), malononitrile (**2**) and 4-hydroxycoumarin

(**3a**) or 4-hydroxy-6-methylpyrone (**3b**), in H_2O/EtOH, at reflux, in the presence of 4-chloro SBS (Table 2).

The versatility of the reaction was explored further by extending the procedure to the synthesis of bis-4,5-dihydropyrano[3,2-*c*]chromene (**4n, 4o**) and bis-4,5-dihydropyrano[4,3-*b*]pyran derivatives (**4c', 4d'**). When para and meta phthalaldehyde (**1n, 1o**) was treated with two equiv. malononitrile and 4-hydroxycoumarin (**3a**) or 4-hydroxy-6-methylpyrone (**3b**) under similar conditions, the reaction proceeded quickly to give the corresponding bis-4,5-dihydropyrano[3,2-*c*]chromenes (**4n, 4o**) and bis-4,5-dihydropyrano[4,3-*b*]pyrans (**4c', 4d'**) in high yield (Table 2 and Scheme 2).



i: H_2O/EtOH (7mL/3mL), 4-Chloro SBS (10 mol%), reflux

Scheme 2. Synthesis of bis-4,5-dihydropyrano[3,2-*c*]chromene (**4n, 4o**) and bis-4,5-dihydropyrano[4,3-*b*]pyran derivatives (**4c', 4d'**).

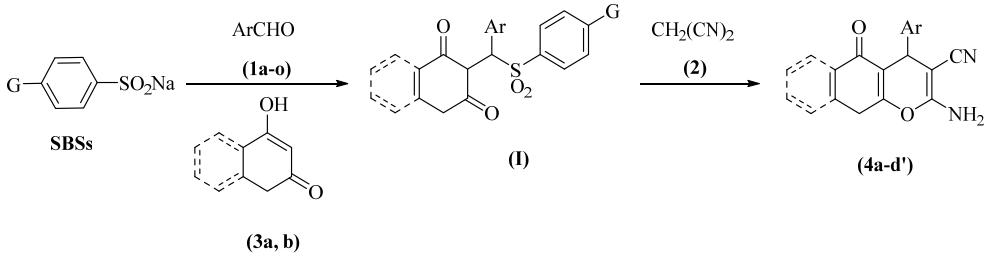
According to some authors[26,28] condensation of sodiumbenzenesulfinates, aromatic aldehydes (**1a-o**) and 4-hydroxycoumarin (**3a**) or 4-hydroxy-6-methylpyrone (**3b**), provided compound **I**. Subsequent coupling of **I** with malononitrile (**2**) gave the

expected products **4a-4d'** (mono and bis 4,5-dihydropyrano[3,2-*c*]chromene and 4,5-dihydropyrano[4,3-*b*]pyran derivatives) (Scheme 3).

Table 2. Three-component reaction of aromatic aldehydes (**1a-o**), malononitrile (**2**) and 4-hydroxycoumarin (**3a**) or 4-hydroxy-6-methylpyrone (**3b**).

M. P. reported (°C)	M. P. observed (°C)	Yield (%)	Time (min)	Ar	Activated C-H acid	Compd. No.
4a	3a	C_6H_5	12	91	259-261	261-263 [17]
4b	3a	4-Cl-C_6H_4	10	92	265-268	265-267 [17]
4c	3a	2,4-$(Cl)_2$-C_6H_3	8	93	253-255	256-258 [23]
4d	3a	4-Br-C_6H_4	10	91	246-248	247-250 [23]
4e	3a	2-Br-C_6H_4	11	91	293-296	295-297 [21]
4f	3a	4-NO_2-C_6H_4	8	92	250-251	250-252 [17]
4g	3a	3-NO_2-C_6H_4	11	91	264-266	263-265 [17]
4h	3a	4-CH_3-C_6H_4	15	90	258-260	257-259 [17]
4i	3a	4-CH_3O-C_6H_4	17	89	232-234	235-237 [17]
4j	3a	Furan-2-yl	17	89	250-253	253-255 [17]
4k	3a	Thiophen-2-yl	18	88	227-229	226-230 [23]
4l	3a	Pyridin-2-yl	13	90	257-259	——
4m	3a	Pyrrole-2-yl	15	90	278-280	——
4n	3a	p-Phthalaldehyde	20	91	>300	——
4o	3a	m-Phthalaldehyde	22	90	278-281	281-283 [21]
4p	3b	C_6H_5	13	90	233-235	234-236 [22]
4q	3b	4-Cl-C_6H_4	10	91	230-231	231-232 [24]
4r	3b	2,4-$(Cl)_2$-C_6H_3	8	92	233-234	234-235 [24]
4s	3b	4-Br-C_6H_4	10	90	220-222	223-225 [24]
4t	3b	2-Br-C_6H_4	10	91	271-273	271-273 [25]
4u	3b	4-NO_2-C_6H_4	8	92	215-217	215-218 [22]
4v	3b	3-NO_2-C_6H_4	10	91	229-232	232-233 [24]
4w	3b	4-CH_3-C_6H_4	17	90	222-223	224-225 [22]
4x	3b	4-CH_3O-C_6H_4	20	89	202-204	202-205 [22]
4y	3b	Furan-2-yl	17	89	220-222	223-224 [22]
4z	3b	Thiophen-2-yl	18	89	240-243	242-244 [22]

4a'	3b	Pyridin-2-yl	13	90	222-224	——
4b'	3b	Pyrrole-2-yl	15	90	221-224	——
4c'	3b	p-Phthalaldehyde	23	90	>300	——
4d'	3b	m-Phthalaldehyde	25	89	>300	——



Scheme 3. Proposed synthesis mechanism of mono and bis 4,5-dihydropyrano[3,2-*c*]chromene and 4,5-dihydropyrano[4,3-*b*]pyran derivatives

Experimental

General

All chemicals and reagents used were of analytical grade or were chemically pure, and were supplied by Merck and Sigma Aldrich Co. (Germany). Melting points were measured on an Electrothermal-9100 apparatus and are uncorrected. IR spectra were recorded on a Brucker FT-IR Tensor 27 infrared spectrophotometer. ^{1}H NMR spectra were recorded on a Brucker Avance III 400 MHz spectrometer. ^{13}C NMR spectra were recorded on the same instruments at 100 MHz using TMS as an internal standard. Elemental analyses were performed using a Heracus CHN-O-Rapid analyzer.

Typical procedure for the preparation of mono and bis 4,5-dihydropyrano[3,2-*c*]chromene (4a-o) and mono and bis 4,5-dihydropyrano[4,3-*b*]pyran derivatives (4p-d')

A mixture of aromatic aldehydes (**1a-m**) (2 mmol) or para and meta phthalaldehyde (**1n, 1o**) (1 mmol), malononitrile (**2**) (2 mmol) and 4-

hydroxycoumarin (**3a**) or 4-hydroxy-6-methylpyrone (**3b**) (2 mmol), and sodium 4-chloro benzenesulfinate (10 mol%) in H_2O/EtOH (7mL/3mL) was refluxed for in the reported time in Table 2 (the progress of the reaction being monitored by TLC and hexane/ethyl acetate was used as an eluent). After completion of the reaction, the reaction mixture was poured into ice-cold water; the crude product was filtered, dried and recrystallized from ethanol.

*2-Amino-5-oxo-4-(pyridin-2-yl)-4H,5H-pyrano[3,2-c]chromene-3-carbonitrile (**4l**):*

White powder; IR (KBr, ν_{max}/cm^{-1}): 3376, 3280 (NH_2), 2192 (CN), 1670 (C=O), 1603, 1571 (C=C); ^{1}H NMR (400 M*Hz*, DMSO-d_6) δ_H: 8.52-7.31 (m, 10H, CH-Ar, NH_2), 4.43 (s, 1H, CH); ^{13}C NMR (100 M*Hz*, DMSO-d_6) δ_C: 161.2 (C=O), 159.7, 155.3, 152.8, 150.5, 149.7, 140.2, 137.2, 133.5, 126.6, 125.4, 123.1, 120.5, 118.4, 114.2 (CN), 104.5, 57.6, 37.3; Anal. calcd. for $C_{18}H_{11}N_3O_3$: C, 68.14; H, 3.49; N, 13.24%. Found: C, 67.93; H, 3.30; N, 13.05%.

*2-Amino-5-oxo-4-(1H-pyrrol-2-yl)-4H,5H-pyrano[3,2-c]chromene-3-carbonitrile (**4m**):*

Yellow powder; IR (KBr, ν_{max}/cm^{-1}): 3457, 3387, 3312 (NH, NH_2), 2192 (CN), 1677 (C=O), 1600, 1577 (C=C); ^{1}H NMR (400 M*Hz*, DMSO-d_6) δ_H: 11.22 (s, 1H, NH), 7.86-7.42 (m, 7H, CH-Ar), 6.87 (s, 2H, NH_2), 5.23 (s, 1H, CH); ^{13}C NMR (100 M*Hz*, DMSO-d_6) δ_C: 162.2 (C=O), 160.1, 154.2, 153.2, 150.1, 137.3, 135.0, 133.6, 132.1, 130.6, 127.3, 125.2, 124.0, 113.3 (CN), 104.2, 58.7, 33.1; Anal. calcd. for $C_{17}H_{11}N_3O_3$: C, 66.88; H, 3.63; N, 13.76%. Found: C, 66.67; H, 3.45; N, 13.57%.

*4,4'-(1,4-Phenylene)bis(2-amino-5-oxo-4H,5H-pyrano[3,2-c]chromene-3-carbonitrile) (**4n**):*

White powder; IR (KBr, ν_{max}/cm^{-1}): 3472, 3327 (NH_2), 2192 (CN), 1677 (C=O), 1606, 1574 (C=C); ^1H NMR (400 M*Hz*, DMSO-d_6) δ_H: 7.83-7.48 (m, 12H, CH-Ar), 7.41 (s, 4H, NH_2), 4.45 (s, 2H, CH); ^{13}C NMR (100 M*Hz*, DMSO-d_6) δ_C: 162.0 (C=O), 159.3, 158.9, 151.6, 138.5, 135.0, 132.2, 129.1, 126.0, 122.7, 120.1, 114.0 (CN), 101.6, 57.5, 32.5; Anal. calcd. for $C_{32}H_{18}N_4O_6$: C, 69.31; H, 3.27; N, 10.10%. Found: C, 69.10; H, 3.09; N, 9.93%.

*2-Amino-7-methyl-5-oxo-4-(pyridin-2-yl)-4H,5H-pyrano[4,3-b]pyran-3-carbonitrile (**4a'**):*

Yellow powder; IR (KBr, ν_{max}/cm^{-1}): 3408, 3394 (NH_2), 2192 (CN), 1670 (C=O), 1587, 1523 (C=C); ^1H NMR (400 M*Hz*, DMSO-d_6) δ_{ppm}: 8.26 (s, 2H, NH_2), 7.54-7.22 (m, 4H, CH-Ar), 6.12 (s, 1H, CH), 4.37 (s, 1H, CH), 2.38 (s, 3H, CH_3); ^{13}C NMR (100 M*Hz*, DMSO-d_6) δ_{ppm}: 162.4 (C=O), 160.1, 158.8, 151.5, 150.1, 140.2, 136.5, 126.0, 121.0, 114.1 (CN), 101.2, 99.5, 57.8, 35.6, 20.8 (CH_3); Anal. calcd. for $C_{15}H_{11}N_3O_3$: C, 64.05; H, 3.94; N, 14.94%. Found: C, 63.87; H, 3.77; N, 14.76%.

*2-Amino-7-methyl-5-oxo-4-(1H-pyrrol-2-yl)-4H,5H-pyrano[4,3-b]pyran-3-carbonitrile (**4b'**):*

White powder; IR (KBr, ν_{max}/cm^{-1}): 3407, 3392, 3292 (NH, NH_2), 2192 (CN), 1670 (C=O), 1600, 1568 (C=C); ^1H NMR (400 M*Hz*, DMSO-d_6) δ_H: 11.63 (s, 1H, NH), 7.45 (d, $^3J_{HH}$=4 Hz, CH-Ar), 7.22 (s, 2H, NH_2), 6.88-6.56 (m, 2H, CH-Ar), 6.09 (s, 1H, CH), 4.44 (s, 1H, CH), 2.21 (s, 3H, CH_3); ^{13}C NMR (100 M*Hz*, DMSO-d_6) δ_C: 163.0 (C=O), 160.3, 153.3, 150.2, 137.0, 134.6, 133.2, 131.5, 126.2, 114.0 (CN), 105.2, 58.5, 34.2, 20.8 (CH_3); Anal. calcd. for $C_{14}H_{11}N_3O_3$: C, 62.45; H, 4.12; N, 15.61%. Found: C, 62.26; H, 3.95; N, 15.44%.

*4,4'-(1,4-Phenylene)bis(2-amino-7-methyl-5-oxo-4H,5H-pyrano[4,3-b]pyran-3-carbonitrile) (**4c'**):*

White powder; IR (KBr, ν_{max}/cm^{-1}): 3407, 3358 (NH_2), 2192 (CN), 1670 (C=O), 1593, 1523 (C=C); ^1H NMR (400 MHz, DMSO-d_6) δ_{ppm}: 8.49-7.09 (m, 8H, CH-Ar, NH_2), 6.27 (s, 2H, CH), 4.40 (s, 2H, CH), 2.19 (s, 6H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ_{ppm}: 162.9 (C=O), 160.6, 159.8, 150.5, 140.4, 132.4, 120.1, 114.8 (CN), 99.5, 58.0, 37.4, 20.9 (CH_3); Anal. calcd. for $C_{26}H_{18}N_4O_6$: C, 64.73; H, 3.76; N, 11.61%. Found: C, 64.54; H, 3.58; N, 11.44%.

*4,4'-(1,3-Phenylene)bis(2-amino-7-methyl-5-oxo-4H,5H-pyrano[4,3-b]pyran-3-carbonitrile) (**4d'**):*

White powder; IR (KBr, ν_{max}/cm^{-1}): 3360, 3312 (NH_2), 2192 (CN), 1664 (C=O), 1580, 1542 (C=C); ^1H NMR (400 MHz, DMSO-d_6) δ_{ppm}: 8.49-7.09 (m, 8H, CH-Ar, $2NH_2$), 6.29 (s, H, CH), 6.25 (s, H, CH), 4.40 (s, H, CH), 4.22 (s, H, CH), 2.20 (s, 3H, CH_3), 2.02 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ_{ppm}: 163.0 (C=O), 162.8 (C=O), 160.9, 160.5, 159.2, 158.3, 151.2, 150.8, 141.0, 140.6, 132.3, 130.9, 121.0, 120.7, 114.6 (CN), 113.8 (CN), 101.0, 99.5, 58.2, 57.6, 37.4, 36.9, 21.3 (CH_3), 20.9 (CH_3); Anal. calcd. for $C_{26}H_{18}N_4O_6$: C, 64.73; H, 3.76; N, 11.61%. Found: C, 64.53; H, 3.57; N, 11.42%.

Conclusions

In summary, we have reported the use of sodium benzenesulfinates as an effective organocatalyst, for obtaining mono and bis 4,5-dihydropyrano[3,2-*c*]chromene and 4,5-dihydropyrano[4,3-*b*]pyran derivatives by the three component reaction of aromatic aldehydes, malononitrile and 4-hydroxycoumarin or 4-hydroxy-6-methylpyrone. These reactions were carried out in H_2O/EtOH at reflux. High yields, operational simplicity, and clean reaction conditions are advantages of this procedure that make it a useful practical process for the synthesis of these compounds.

Acknowledgements

The authors express their great appreciation to Pharmaceutics Research Center, Institute of Neuropharmacology, Kerman University of Medical Sciences for supporting this investigation.

References

1. Zhu, J., In *Multicomponent Reactions*, Wiley-VCH, Weinheim, Germany, 2005.

2. Tietze, L. F. Domino Reactions in Organic Synthesis. *Chem. Rev*. **1996**, *96*, 115-136.

3. Abaszadeh, M.; Seifi, M.; Asadipour, A. Ultrasound Promotes One-pot Synthesis of 1,4-Dihydropyridine and Imidazo[1,2-*a*]quinolone Derivatives, Catalyzed by ZnO Nanoparticles. *Res. Chem. Intermed.* **2015**, *41*, 5229-5238.

4. Abaszadeh, M.; Seifi, M.; Ebrahimipour, S. Y. Two Ligand Oxidio-Vanadium (IV) Complexes as Novel Efficient Catalysts in Multicomponent Reactions for Synthesis of Tetrahydrobenzopyran Derivatives. *Bull. Chem. Soc. Ethiop.* **2016**, *30*, 253-262.

5. Zhanguo, C.; Manfei, D.; Wei, X.; Junli, H. One-pot Synthesis of α,β-Dehydroamino Derivatives from β,β-Dicyanostyrene with 1,3-Dibromo-5,5-dimethylhydantoin Promoted by Mild Base. *Chem. Res. Chin. Univ.* **2016**, *32*, 68-75.

6. Chengwei, L.; Yanhang, L.; Xiaoxia, L.; Jiajing, W. One-pot Three-component Reaction for Efficient and Facile Synthesis of γ-Nitrocarbonyl Compounds Under Solvent-free Conditions. *Chem. Res. Chin. Univ.* **2015**, *31*, 208-211.

7. Jin, L.; Lei, Y. One-pot Three-component Mannich Reaction Catalyzed by 2-Hydroxylpyridine. *Chem. Res. Chin. Univ.* **2013**, *29*, 710-713.

8. Xu-dong, J.; Song-yang, H.; Hai-feng, D.; Ying-jie, L.; Jun-gang, C.; Da-peng, L.; Mao-cheng, W. Efficient One-pot Synthesis of 12-Aryl-8, 9, 10, 12-tetrahydrobenzo[*a*]xanthen-11-ones Under Solvent-free Conditions. *Chem. Res. Chin. Univ.* **2013**, *29*, 82-86.

9. Shaker, R. M. Synthesis of 1,4-Phenylene Bridged Bis-heterocyclic Compounds. *Arkivoc*. **2012**, *i*, 1-44.

10. Bellina, F.; Rossi, R. Synthesis and Biological Activity of Pyrrole, Pyrroline and Pyrrolidine Derivatives with Two Aryl Groups on Adjacent Positions. *Tetrahedron*. **2006**, *62*, 7213-7256.

11. Abaszadeh, M.; Seifi, M. Ultrasound-assisted 1,3-Dipolar Cycloaddition and Cyclopropanation Reactions for the Synthesis of Bis-indolizine and Bis-cyclopropane Derivatives. *Org. Biomol. Chem.* **2014**, *12*, 7859-7863.

12. Niknam, K.; Hasaninejad, A.; Arman, M. Synthesis of Some New Bis-3,4-dihydropyrimidin-2(1*H*)-ones by Using Silica-supported Tin Chloride and Titanium Tetrachloride. *Chin. Chem. Lett*. **2010**, *21*, 399-402.

13. Bhat, A.R.; Athar, F.; Azam, A. Bis-pyrazolines: Synthesis, Characterization and Antiamoebic Activity as Inhibitors of Growth of Entamoeba Histolytica. *Eur. J. Med. Chem*. **2009**, *44*, 426-431.

14. Iqbal, P. F.; Parveen, H.; Bhat, A. R.; Hayat, F.; Azam, A. Synthesis, Characterization, Antiamoebic Activity and Toxicity of Novel Bisdioxazole Derivatives. *Eur. J. Med. Chem*. **2009**, *44*, 4747-4751.

15. Green, G. R.; Evans, J. M.; Vong, A. K. *Pyrans and Their Benzo Derivatives Synthesis*, *In Comprehensive Heterocyclic Chemistry II*, A. R. Katritzky, C. W. Rees, E. F. V. Scriven, Pergamon Press, Oxford, UK, 1995, pp 469-500.

16. Uher, M.; Konecny, V.; Rajniakove, O. Synthesis of 5-Hydroxy-2-hydroxymethyl-4*H*-pyran-4-one Derivatives with Pesticide Activity. *Chem. Pap.* **1994**, *48*, 282-284.

17. Dekamin, M. G.; Eslami, M.; Maleki, A. Potassium Phthalimide-*N*-oxyl: A Novel, Efficient and Simple Organocatalyst for the One-pot Three-component Synthesis of Various 2-Amino-4*H*-chromene Derivatives in Water. *Tetrahedron*. **2013**, *69*, 1074-1085.

18. Seifi, M.; Sheibani, H. High Surface Area MgO as a Highly Effective Heterogeneous Base Catalyst for Three-component Synthesis of Tetrahydrobenzopyran and 3,4-Dihydropyrano[*c*]chromene Derivatives in Aqueous Media. *Catal. Lett.* **2008**, *126*, 275-279.

19. Shaterian, H. R.; Oveisi, A. R. A Simple Green Approach to the Synthesis of 2-Amino-5-oxo-4,5-dihydropyrano[3,2-*c*]chromene-3-carbonitrile Derivatives Catalyzed by 3-Hydroxypropanaminium Acetate (HPAA) as a New Ionic Liquid. *J. Iran. Chem. Soc.* **2011**, *8*, 545-552.

20. Zheng, J.; Li, Y. Q. One-pot Synthesis of Tetrahydrobenzo[*b*]pyran and Dihydropyrano[*c*]chromene Derivatives in Aqueous Media by Using Trisodium Citrate as a Green Catalyst. *Arch. Appl. Sci. Res.* ***2011****, 3*, 381-388.

21. Wang, H. J.; Lu, J.; Zhang, Z. H. Highly Efficient Three-component, One-pot Synthesis of Dihydropyrano[3,2-*c*]chromene Derivatives. *Monatsh Chem*.

2010, *141*, 1107-1112.

22. Rajguru, D.; Keshwal, B. S.; Jain, S. Solvent-free, Green and Efficient Synthesis of Pyrano[4,3-*b*]pyrans by Grinding and Their Biological Evaluation as Antitumor and Antioxidant Agents. *Med. Chem. Res*. **2013**, *22*, 5934-5939.

23. Raj, T.; Bhatia, R. K.; Kapur, A.; Sharma, M.; Saxena, A. K.; Ishar, M. P. S. Cytotoxic Activity of 3-(5-Phenyl-3*H*-[1,2,4]dithiazol-3-yl)chromen-4-ones and 4-Oxo-4*H*-chromene-3-carbothioic Acid *N*-Phenylamides. *Eur. J. Med. Chem.* **2010**, *45*, 790-794.

24. Wang, X. S.; Zhou, J. X.; Zeng, Z. S.; Li, Y. L.; Shi, D. Q.; Tua, S. J. One-pot Synthesis of Pyrano[3,2-*c*]pyran Derivatives Catalyzed by KF/Al_2O_3. *Arkivoc*. **2006**, *xi*, 107-113.

25. Abaszadeh, M.; Seifi, M. Crown Ether Complex Cation Ionic Liquids (CECILs) as Environmentally Benign Catalysts for Three-component Synthesis of 4,5-Dihydropyrano[3,2-*c*]chromene and 4,5-Dihydropyrano[4,3-*b*]pyran Derivatives. *Res. Chem. Intermed*. **2015**, *41*, 7715-7723.

26. Chen, Y.; Lam, Y.; Lai, Y. H. Solid-phase Synthesis of Pyrazolines and Isoxazolines with Sodium Benzenesulfinate as a Traceless Linker. *Org. Lett.* **2003**, *5*, 1067-1069.

27. Ochiai, M.; Kitagawa, Y.; Toyonari, M.; Uemura, K.; Oshima, K.; Shiro, M. Nucleophilic Vinylic Substitutions of (Z)-(β-Haloalkenyl)phenyliodonium Salts with Sodium Benzenesulfinate: First Evidence of a Michael Addition of Nucleophiles to Alkenyliodonium Salts at the C_β Atom. *J. Org. Chem.* **1997**, *62*, 8001-8008.

28. Abaszadeh, M.; Seifi, M. Sodium Benzenesulfinates: Novel and Effective Organo Catalyst for Three Component Synthesis 5,6,7,8-Tetrahydro-4*H*-chromene Derivatives Under Ultrasound Irradiation. *Lett. Org. Chem*. **2015**, *12*, 271-276.