Scientific paper

Solvent-free Synthesis of Dihydropyrano[3,2-c]chromene and Biscoumarin Derivatives Using Magnesium Oxide Nanoparticles as a Recyclable Catalyst

Javad Safaei-Ghomi,* Fahime Eshteghal and Mohammad Ali Ghasemzadeh

Department of Chemistry, Qom Branch, Islamic Azad University, Qom, I. R. Iran

** Corresponding author: E-mail: Safaei@kashanu.ac.ir, Telefax: +983615912385*

Received: 28-01-2014

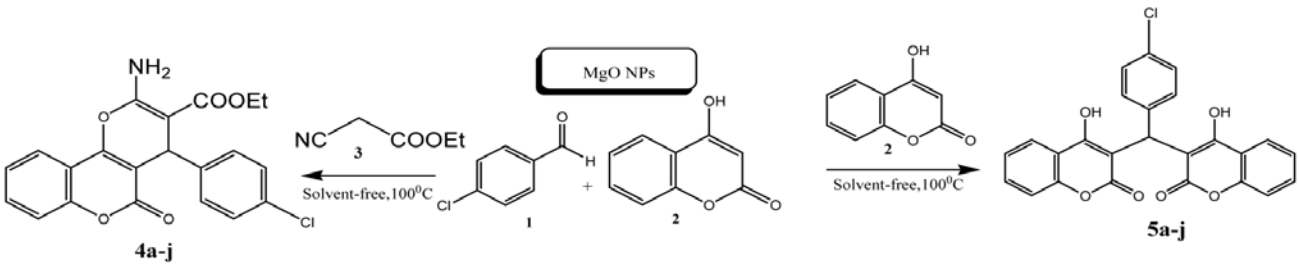
Abstract

In these research, an efficient one pot approach for the synthesis of dihydropyrano[3,2-c]chromenes and biscoumarins as important heterocyclic compounds with pharmacological and biological properties have been prepared using nanocrystalline magnesium oxide. Magnesium oxide nanoparticles were significantly catalyzed three-component reaction of aldehydes, ethyl cyanoacetate and 4-hydroxycoumarin in high yields and short reaction times under solvent-free conditions. Nano magnesium oxide as an efficient, available and cheap heterogeneous nanoparticles were used for several times in the synthesis of dihydropyrano [3,2-c]chromenes and biscoumarins.

Keywords: MgO nanoparticle, Multi-component reactions, Solvent-free, Chromene, Biscoumarins

1. Introduction

In recent years multi-component reactions (MCRs) have been developed to combine economic aspects for the synthesis of important medical and industrial compounds.[1] Multi-component reactions are convergent reactions, in which three or more preliminary materials react to form a product, where basically all or most of the atoms contribute to the lately created product.[2] Multi-component reactions have become an important device for the synthesis of structurally complex compounds in addition to drug like molecules.[3] Choromene and coumarin driveatives are an important group of heterocyclic compounds and have found much synthetic importance due to their biological activity that make them attractive targets for MCRs.[4–6] In addition, dihydropyrano[3,2-c]chromene and biscoumarin derivatives have various biological properties such as antimicrobial,[7] antibacterial,[8] anticoagulant,[9] anticancer.[10] Also they are used for the treatment of some diseases including Alzheimer,[11] Parkinson,[12] Huntington,[13] HIV,[14] Down's syndrome,[15] and Schizophrenia.[16] Recently, several methods have been reported for the synthesis of biscoumarin and dihydropyrano[3,2-c]chromene derivatives in the presence of diverse catalysts such as: ruthenium(III)chloride hydrate,[17] various heteropolyacid,[18] [BMIm]BF_4-LiCl,[19] silicagel,[20] $H_6P_2W_{18}O_{62}.18H_2O$,[21] tetrabutylammonium bromide (TBAB),[22] and DBU.[23] Many of these methods have some disadvantages and hardships including long reaction times, using toxic solvents and expensive catalysts. Recent progresses in nanoscience and nanotechnology have led to a new research interest in using nano-scale particles as an alternative matrix for supporting catalytic reactions.[24] The chemical synthesis efficiency can be increased by nano sized catalysts because of their low size and high surface area to volume ratios.[25] The use of environmentally benign nano catalysts represents extremely important green chemical technology procedures from both the economical and synthetic points of view.[26] Among the various nano catalysts MgO find out extensive application as heterogeneous catalysts in diverse organic reactions. Lately nanocrystalline magnesium oxide have been used in different organic reactions as catalyst such as synthesis of Bettibases,[27]polyhydroquinoline derivatives,[28] flavanones,[29] and 2,4,5-trisubstituted imidazole derivatives.[30] Considering the above mentioned topics and also in continuation of our research on the application of nanocatalysts in MCRs.[31–35] We decided to prepare some dihydropyrano[3,2-c]chromenes and biscou-



Scheme 1. Synthesis of dihydropyrano [3, 2-c]chromene (4a-j) and biscoumarin (5a-j) derivatives.

marins *via* reaction of aldehydes, ethyl cyanoacetate and 4-hydroxycoumarin in the presence MgO nanoparticles under solvent-free conditions (Scheme 1).

2. Results and Discussion

In this research we decided to optimize the reaction conditions *via* three-component reactions of 4-chlorobenzaldehyde **1**, 4-hydroxycoumarin **2** and ethyl cyanoacetate **3** (molar ratio: 1:1:1.1) as a model reaction (Scheme 1). We investigated various catalysts in this reaction for the synthesis of 2-Amino-4-aryl-3-carboethoxy-4H,5H-pyrano[3,2-c]chromene-5-ones (**4a-j**).

Nanocrystalline MgO showed the best catalytic activity in comparison with $FeCl_3$, NEt_3, HCl, CuI and bulk MgO catalysts (Table 1). Furthermore nano MgO was used in the model reaction to optimized different amounts of the catalyst, varying temperatures and different solvents and also under solvent-free conditions (Table 2). No yield was obtained in the nonattendance of the catalyst (Table 1, entry 1) and in the presence of the catalyst at room temperature (Table 1, entry 2), indicating that the reaction was occurred high efficient in the presence of catalyst and high temperature. The best results were obtained when the reaction was carried out at 100 °C and the optimum amount of catalyst was found to be 3 mol% of MgO NPs. Also under the same conditions the reaction was investigated with different ratio of starting materials. In the new model reaction 4-chlorobenzaldehyde **1**, 4-hydroxycoumarin **2** with molar ratio 1:2 were used for the synthesis 3,3-aryl-bis-(4-hydroxy-2H-1-benzopyran-2-ones) (Scheme 1). We used the optimized reaction conditions in the presence of MgO NPs to produce dihydropyrano[3,2-c]chromenes and biscoumarins (**5a-j**).

To study the scope of this procedure, we next used a diversity of aldehydes to investigate three-component

Table 1: Preparation of dihydropyranochromenes and biscoumarins by different catalysts at 100 °C.[a]

Entry	Catalyst	Time (min)	Yield[b] (%)
1	None	240	0
2	$FeCl_3$	80	50
3	Et_3N	120	45
4	HCl	140	40
5	CuI	80	45
6	MgO	60	62
7	MgO NPs	20	93

[a] The reaction was carried out under solvent-free conditions.
[b] Isolated yields.

Table 2: Optimization amount of MgO NPs for the synthesis of 4a-j and 5a-j

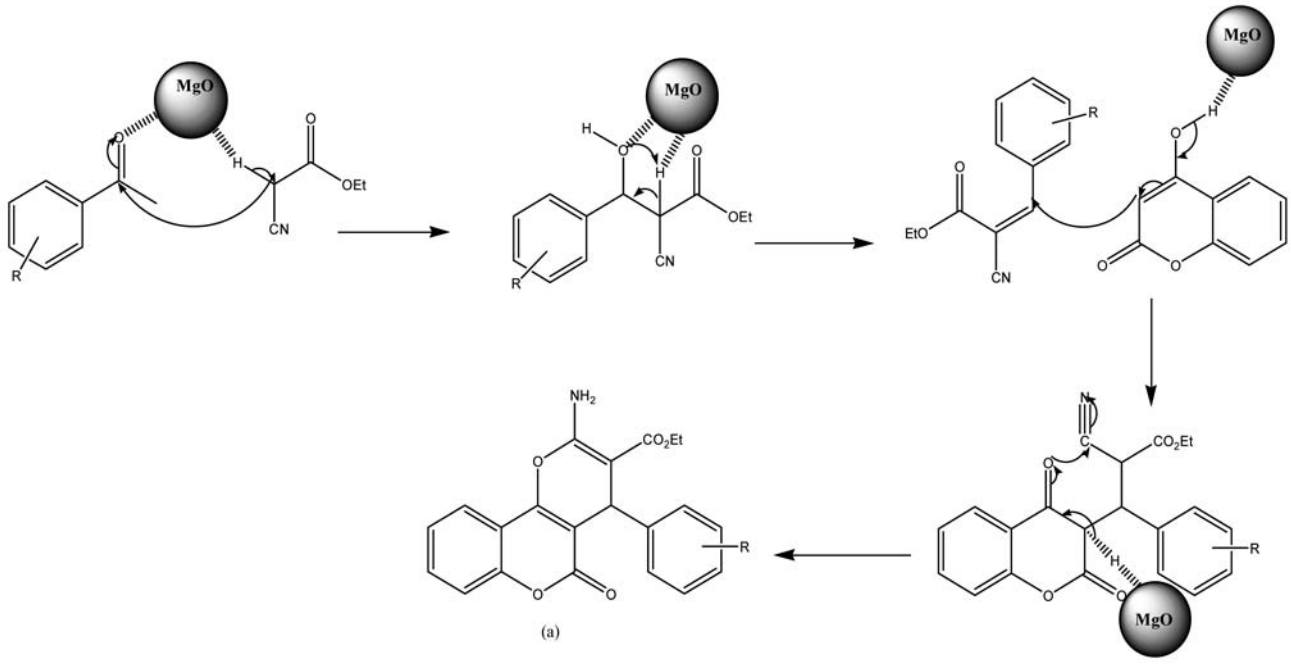
Entry	(Mol%)	T/°C	Time (min)	Yield[a](%)
1	None	100	300	0
2	3	r.t	300	15
3	1	100	35	45
4	2	100	30	65
5	3	100	20	93
6	4	100	20	93
7	5	120	20	92

[a] Isolated yields.

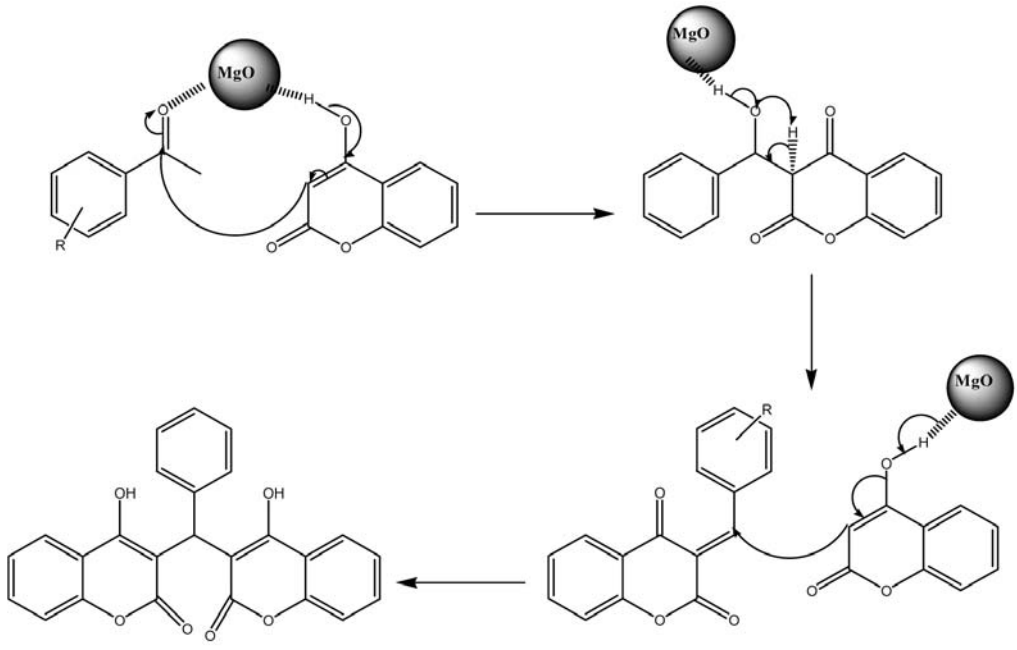
Table 3. One pot synthesis ofdihydropyrano[3,2-c]chromenes (4a-j) and biscoumarins (5a-j) by MgO NPs.

Product	Aldehydes	Time (min)	Yield (%)[a]	MP [Ref] °C
4a	4-Cl-C_6H_4	23	87	191–193[37]
4b	4-NO_2-C_6H_4	20	89	240–242[18]
4c	4-Me-C_6H_4	27	88	189–190[37]
4d	4-F-C_6H_4	28	90	223–225[37]
4e	4-OH-C_6H_4	35	70	259–260
4f	3- NO_2-C_6H_4	25	86	247–250[21]
4g	4-Br-C_6H_4	25	93	193–194[37]
4h	C_6H_5	27	91	197–199[37]
4i	4-OMe-C_6H_4	30	75	160–162[37]
4j	2,4-Cl-C_6H_4	25	88	200–201[37]
5a	4-Cl-C_6H_4	20	93	254–256[36]
5b	4-NO_2-C_6H_4	20	92	236–237[36]
5c	4-Me-C_6H_4	25	75	268–270[20]
5d	4-F-C_6H_4	22	80	267–269[20]
5e	4-OH-C_6H_4	27	75	220–224[36]
5f	3- NO_2-C_6H_4	21	88	247–250[21]
5g	4-Br-C_6H_4	23	90	265–267[20]
5h	C_6H_5	22	88	229–231[20]
5i	4-OMe-C_6H_4	28	76	244–246[36]
5j	2,4-Cl-C_6H_4	25	90	254–256

[a] Isolated yields.



Scheme 2. The proposed mechanism for the synthesis of dihydropyrano[3,2-c]chromenes catalyzed by MgO NPs



Scheme 3. The proposed mechanism for the synthesis of biscoumarins (5a-j) catalyzed by MgO NPs

reactions under the optimized conditions (Table 3). A plausible mechanism for the syntheses of dihydropyrano[3,2-c]chromenes (4a-j) and biscoumarins (5a-j) using MgO NPs have been shown in (Scheme 2,3). We suppose that magnesium oxide nanoparticles behave as coordinate with carbonyl and hydroxyl groups to promote cyclization reaction, so interaction of nanocatalyst with reactants leading to speed up the rate of reaction.

3. Experimental

3. 1. General

Chemicals were purchased from the Sigma-Aldrich and Merck and were used without further purification. All of the materials were of commercial reagent grade and were used without further purification. All melting points

are uncorrected and were determined in capillary tubes on Boetius melting point microscope. ^{1}H NMR and ^{13}C NMR spectra were obtained on Bruker 400 MHz spectrometer with DMSO-d_6 and $CDCl_3$ as solvent using tetramethylsilane (TMS) as an internal standard; the chemical shift values are in δ. FT-IR spectrum was recorded on Magna-IR, spectrometer 550 Nicolet in KBr pellets in the range of 400–4000 cm^{-1}. The elemental analyses (C, H, N) were obtained from a Carlo ERBA Model EA 1108 analyzer. Powder X-ray diffraction (XRD) was carried out on a Philips diffractometer of X'pert Company with mono chromatized Cu Kα radiation (λ = 1.5406 Å). Microscopic morphology of products was visualized by SEM (LEO 1455VP).The mass spectra were recorded on a Joel D-30 instrument at an ionization potential of 70 eV.

3. 2. Preparation of MgO Nanoparticles

We prepared Magnesium oxide nanoparticles (NPs) in this study using ultrasound technique. A solution of **1** mol/L sodium hydroxide was added drop-wise to a solution prepared from dissolving 2 g of Mg $(NO_3)_2.6H_2O$ and 0.5 g polyvinyl pyrolydon (PVP) as surfactant. Then the reaction mixture was sonicated for 30 min ultrasonic power 90W. The prepared gel was centrifuged and washed several times with deionized water and ethanol, and finally calcined in a furnace at 600 °C for 2 h.

In order to study the morphology and particle size of MgO nanoparticles, scanning electron microscopy (SEM) image of MgO NPs was presented in Fig. 1. As shown in Fig. 2. The crystalline nature of the synthesized MgO NPs sample was further verified by X-ray diffraction pattern (XRD). The crystallite size diameter (D) of the MgO NPs has been calculated by Debye–Scherrer equation (D = Kλ/βcosθ). The results show that hexagonal MgO NPs[27] were gained with an average diameter of 18 nm.

Nano-crystals of magnesium oxide catalyst has a multidimensional structure in three dimensions with a high level of edge and corner that caused by the inherent high reactivity. Moreover, nano-magnesium oxide has a network crystalline structure contain of Lewis basic and Lewis acid. All these factors cause that nano-magnesium oxide employs as an efficient catalyst.

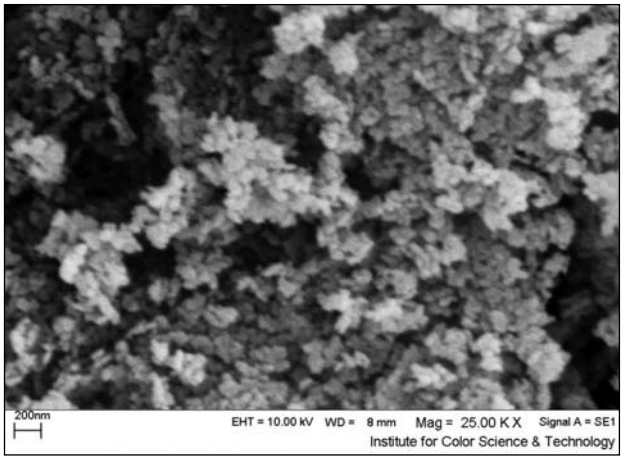


Figure 1. SEM image of MgO NPs;

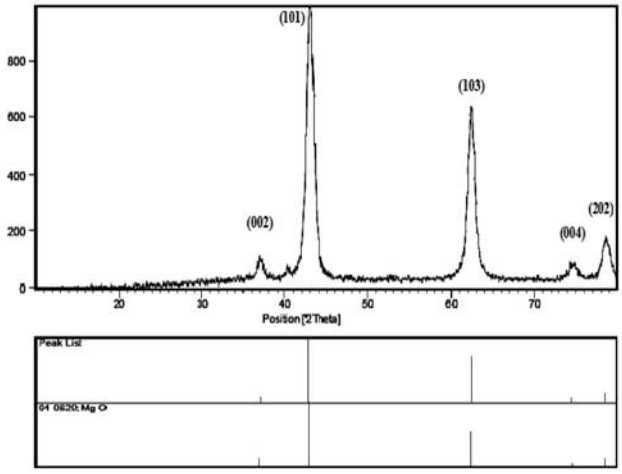


Figure 2. The XRD pattern of MgO NPs

3. 3. Preparation of Dihydropyrano[3,2-c] chromene and Biscoumarin Derivatives

A mixture of an aromatic aldehyde (1 mmol), ethyl cyanoacetate (1.2 mmol), 4-hydroxycoumarin (1 mmol) and nano MgO (3mol%) were heated at 100 °C for 20–40 min. During the procedure, the reaction was monitored by TLC. Upon completion, the reaction mixture was cooled to room temperature and ethyl acetate was added. The catalyst was insoluble in ethylacetate and it could therefore be recycled by a simple filtration. The solvent was evaporated and the solid obtained recrystallized from ethanol to afford the pure dihydropyrano[3,2-c]chromene. Meanwhile we prepared biscoumarins *via* reaction of aldehyde (1 mmol) and 4-hydroxycoumarin (2 mmol) at the same as above conditions (Table 1).

2-Amino-4-(4-chlorophenyl)3-carboethoxy-4H,5H-pyrano[3,2-c]chromene-5-one (4a). White powder; mp 191–193 °C, IR (KBr, cm^{-1}): ν_{max} 3415, 3334, 3215, 1685, 1650, 1601, 1247, 1003; ^{1}H NMR (400 MHz, DMSO-d_6):δ 1.10 (3H, t, *J*= 7.3Hz, CH_3), 3.98 (2H, m, CH_2), 4.64 (1H, s, CH), 7.29 –7.95 (8H, m, Ar), 7.12 (2H, s, NH_2); ^{13}C NMR (100 MHz, DMSO-d_6): δ 14.2, 39.2, 61.7, 74.9, 105.3, 117.5, 121.5, 125.5, 126.8, 128.4, 130.7, 131.3, 140.3, 150.2, 160.2, 162.2, 168.2, Anal. Calcd. for $C_{21}H_{16}ClNO_5$: C 63.40, H 4.05, N 3.52, Found: C 63.38, H 3.95, N 3.63, MS (EI) (*m/z*): 397.

2-amino-4-(4-nitrophenyl)3-carboethoxy-4H,5H-pyrano[3,2-c]chromene-5-one (4b). Yellow powder; mp 240–242 °C, IR (KBr, cm^{-1}): ν_{max} 3430, 3312, 1714, 1690,

1660, 1611, 1500; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.16 (3H, t, *J*=7.1, CH_3), 4.08 (2H, m, CH_2), 5.03 (1H, s, CH), 7.33 –8.13 (8H, m, Ar), 6.59 (2H, s, NH_2); ^{13}C NMR (100 MHz, DMSO-d_6): δ 14.2, 42.3, 61.7, 75.6, 105.3, 117.5, 121.5, 125.5, 126.8, 128.4, 130.0, 145.4, 148.3, 150.2, 160.2, 162.2, 168.4, Anal. Calcd. for $C_{21}H_{16}N_2O_7$: C 61.77, H 3.95, N 6.86 Found: C 61.89, H 4.05, N 6.76 MS (EI) (*m/z*): 408.

2-Amino-4-(4-Fluorophenyl)-3-carboethoxy-4H,5H-pyrano[3,2-c]chromene-5-one (4d). White powder; mp 223–225 °C, IR (KBr, cm^{-1}): ν_{max}3433, 3315, 1710, 1687, 1657, 1609, 1579; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.09 (3H, t, *J*= 7.4 Hz, CH_3), 4.19 (2H, m, OCH_2), 4.83 (1H, s, CH), 7.46–8.06 (8H, m, Ar), 7.96 (2H, s, NH_2); ^{13}C NMR (100MHz, DMSO-d_6): δ14.2, 40.9 61.7, 75.2, 105.3, 117.5, 121.5, 125.5, 126.8, 128.4, 132.7, 135.8, 150.2, 159.9, 160.2, 162.2, 168.6, Anal. Calcd. for $C_{21}H_{16}FNO_5$: C 66.14, H 4.23, N 3.67, Found: C 66.09, H 4.18, N 3.71, MS (EI) (*m/z*): 381.

2-Amino-4-(2,4-dicholorophenyl)-3-carboethoxy-4H,5H-pyrano[3,2-c]chromene-5-one (4j). White powder; mp 200–202 °C, IR (KBr, cm^{-1}): ν_{max}3482, 3432, 3371, 3335, 1718, 1673, 1607, 1506, 1374, 1306; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.09 (3H, t, *J*= 7.4 Hz, CH_3), 3.98 (2H, m, OCH_2), 5.06 (1H, s, CH), 7.47–8.18 (7H, m, Ar), 7.57 (2H, s, NH_2); ^{13}C NMR (100MHz, DMSO-d_6): δ14.2, 41.0, 61.7, 74.9, 105.3, 117.5, 121.5, 125.5, 126.9, 128.4, 128.8, 128, 9, 131.9, 132.7, 135.8, 141.7, 150.2, 160.2, 162.2, 167.2, Anal. Calcd. for $C_{21}H_{15}Cl_2NO_5$: C 58.35, H 3.50, N 3.24, Found: C 58.25, H 3.40,N 3.34 MS (EI) (*m/z*): 431.

2-Amino-4-(4-hydroxyphenyl)-3-carboethoxy-4H,5H-pyrano[3,2-c]chromene-5-one (4e). White powder; mp 259–260°C, IR (KBr, cm^{-1}): ν_{max} 3445, 3372, 3190, 1710, 1672, 1608; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.09 (3H, t, *J*= 7.2 Hz, CH_3), 3.94 (2H, m, OCH_2), 4.46 (1H, s, CH), 6.87–7.89 (8H, m, Ar), 7.46 (2H, br s, NH_2), 9.53 (1H, s, OH);^{13}C NMR (100MHz, DMSO-d_6): δ 55.90, 59.10, 105.13, 113.84, 114.71, 117.37, 120.18, 123.29, 125.47, 129.64, 133.66, 136.26, 152.94, 153.94, 158.79, 159.20, 160.38, Anal. Calcd. for $C_{21}H_{17}NO_6$: C 66.59, H 4.62, N 3.59, Found: C 66.49, H 4.55, N 3.68 MS (EI) (*m/z*): 379.11.

3,3-(4-Chlorophenyl)bis-(4-hydroxy-2H-1-benzopyran-2-one) (5a). White powder; mp 254–256 °C, IR (KBr, cm^{-1}): ν_{max} 3432, 3311, 3070, 3001, 1668, 1604, 1466, 1510, 1452, 1352, 1309, 1259, 769; ^{1}H NMR (400MHz, DMSO-d_6): δ 6.05 (1H, s, CH), 6.87–8.05 (12H, m, Ar): 11.29 (2H, s, OH, br s), ^{13}C NMR (100MHz, DMSO-d_6): δ 36.04, 90.02, 103.58, 115.89, 116.20, 118.26, 123.58, 123.60, 123.97, 125.62, 129.80, 130.20, 131.10, 132.81, 132.90, 143.51, 152.32, 164.56, 165.85 Anal. Calcd. for $C_{25}H_{15}ClO_6$: C 67.20, H 3.38, Found: C 67.12, H 3.18 MS (EI) (*m/z*): 446.

3,3-(4-nitro-phenyl)bis-(4-hydroxy-2H-1-benzopyran-2-one) (5b). Yellow powder; mp 236–237 °C, IR (KBr, cm^{-1}): ν_{max} 3482, 3412, 3080, 1660, 1616, 1600, 1566, 1518, 1450, 1348, 765; ^{1}H NMR (400MHz, DMSO-d_6): δ 6.13 (1H, s, CH), 7.26–8.22 (12H, m, Ar), 11.37 (2H, s, OH, br s), ^{13}C NMR (100MHz, DMSO-d_6): δ 35.68, 105.49, 115,41, 115.52, 116.39, 116.68, 116.72, 116.89, 124.41, 128.14, 130.84, 130.90, 133.01, 145.10, 152.29, 152.60, 160.30, 164.63, 165.03; Anal. Calcd. for $C_{25}H_{15}NO_8$: C 65.65, H 3.31, N 3.06 Found: C 65.89, H 3.24, N 3.17 MS (EI) (*m/z*): 457.

3,3-(2,4-dicholorophenyl)bis-(4-hydroxy-2H-1-benzopyran-2-one) (5j). White powder; mp 254–256 °C, IR (KBr, cm^{-1}): ν_{max} 3462, 3351, 3072, 1668, 1604, 1466, 1510, 1452, 1352, 1309, 1259, 769; ^{1}H NMR (400MHz, DMSO-d_6): δ 6.09 (1H, s, CH), 6.98–8.22 (11H, m, Ar): 11.45 (2H, br s, OH); ^{13}C NMR (100MHz, DMSO-d_6): δ 36.08, 90.02, 103.96, 116.22, 116.40, 117.17, 122.93, 123.60, 124.88, 125.52, 129.80, 130.20, 131.10, 132.81, 133.58, 143.57 144.03, 152.87, 154.23, 165.10, 167.22; Anal. Calcd. for $C_{25}H_{14}Cl_2O_6$: C 63.03, H 3.03, Found: C 62.93, H 5.09 MS (EI) (*m/z*): 480.02.

4. Conclusions

In conclusion, we have synthesized dihydropyrano [3,2-c]chromenes (**4a-j**) and biscoumarins (**5a-j**) using magnesium oxide nanoparticles with high yields and short reaction times. The reactions could be carried out in solvent free condition. This reaction conditions are environmentally friendly which makes proposed pathway a green synthetic method. The simplicity, easy workup, as well as safety and reusability of catalyst are advantages of this procedure over the previous reported ones.

5. Acknowledgements

The authors thank the Research Affairs Office of the Islamic Azad University, Qom Branch, Qom, I. R. Iran for financial support to carry out this work.

6. References

1. T. Masquelin, H. Bui, G. Stephenson, J. Schwerkoske, C. Hulme, *Tetrahedron Lett*. **2006**, *47*, 2989–2991.
2. A. Mobinkhaledi, M. A. BodaghiFard, *Acta Chim. Slov.* **2010,** *57,* 931–935.
3. R. P. Jain, J. C. Vederas, *Bioorg. Med. Chem. Lett*. **2004**, *14*, 3655–3658.

4. M. A. Domling, I. Ugi, *Angew. Chem. Int. Ed*. **2000**, *39*, 3168–3210.
5. A. Kumar, M. K. Gupta, M. Kumar, *Green Chem*. **2012**, *14*, 290–295.
6. I. Ugi, A. Dömling, W. Hörl, *Endeavour*. **1994**, *18*, 115–122.
7. C. C. Chiang, L. Y. HsuH, H. J. Tsai, C. W. Yao, T. C. Chang, Synthesis and Antimicrobial evaluation of coumarin derivatives, *J. C.C.I.T*. **2008**, *37*.
8. S. Kanakaraju, B. Prasanna, S. Basavoju, G. V. P. Chandramouli, *J. Mol. Struct.* **2012**, *1017*, 60–64.
9. W. O. Foye, Principi di chimica farmaceutica, *Piccin: Padova. Italy*. **1991**.
10. L. R. Morgan, B. S. Jursic, C. L. Hooper, D. M. Neumann, K. Thangaraj, B. Leblance, *Bioorg. Med. Chem. Lett.* **2002**, *12*, 3407–3411.
11. T. A. Bayer, S. Schafer, H. Breyh, O. Breyhan, C. Wirths, G. A. Treiber, *Clin Neuropathol*. **2006**, *25*, 163–171.
12. I. Kostava, I. Manolov, I. Nicolova, S. Konstantonov, M. Karaivanova, *Eur. J. Med. Chem*. **2001**, *36*, 339–347.
13. E. A. A. Hafez, M. H. Elnagdi, A. G. A. Elagamey, F. M. A. A. EL-Taweel, *J. Heterocyclic. Chem*. **1987**, *26*, 903–907.
14. B. Jian Lia, C. Chia Chiang, L. Yih HsuH, *J. Chin. Chem. Soc*. **2010**, *57*, 742–749.
15. A. Bolognese, G. Correale, M. Manfra, A. Lavecchia, O. Mazzoni, E. Novellino, P. La colla, G. Sanna, R. Loddo, *J. Med. Chem*. **2004**, *47*, 849–858.
16. C. S. Konkoy, D. B. Fick, S. X. Cai, N. C. Lan, J. F. Keana, WO patent application, 7A 61K 31/352 B; 7A 61P 25/28 B; 7C 07D 311/04. **2000**.
17. A. K. Tabatabaeian, H. Heidari, A. R. Khorshidi, M. Mamaghani, N. Mahmoodi, *J. Serb. Chem. Soc.* **2012**, *77*, 407–413.
18. M. M. Heravi, S. Sadjadi, N. Mokhtari Haj, H. A. Oskooie, F. F. Bamoharram, *C. Catalysis*. **2009**, *10*, 1643–1646.
19. E. Abbaspour-Gilandeh, S. C. Azimia, K. Rad-Moghadama, A. Mohammadi-Barkchai, *Iran. J. Catal.* **2013**, *3*, 91–97.
20. S. Khodabakhshi, M. Baghernejad, *Iran. J. Catal*. **2013**, 3, 67–71.
21. M. M. Heravi, B. Alimadadi Jani, F. Derikvand, F. F. Bamoharram, H. A. Oskooie, *C. Catalysis*. **2008**, *10*, 272–275.
22. J. M. Khurana, S. Kumar, *Tetrahedron Lett*. **2009**, *50*, 4125–4127.
23. J. M. Khurana, B. Nand, P. Saluja, *Tetrahedron*. **2010**, *66*, 5637–5641.
24. A. K. Edward, L. M. Anton, S. K. Yulia, A. S. Vitaliy, V. K. Sergey, V. P. Viktoriya, Y. T. Marta, L. L. Elena, A. S. Jeffrey, L. C. Scott, *Appl. Catal. A:Gen*. **2010**, *385*, 62–72.
25. L. Lu, M. L. Sui, K. Lu, *Science*. **2000**, *287*, 1463–1466.
26. Y. Jiang, S. Y. Gao, Z. D. Li, X. X. Jia, Y. L. *Chen, Mat. Sci. Eng. B*. **2011**, *176*, 1021–1027.
27. B. Karmakar, J. Banerji, *Tetrahedron Lett*. **2011**, *52*, 4957–4960.
28. R. Ranjbar-Karimi, S. Hashemi-Uderji, A. Bazmandegan-Shamili, *Chin. J. Chem*. **2011**, *29*, 1624–1628.
29. B. M. Choudary, K. V. S. Ranganath, Jagajit Yadav, M. Lakshmi Kantam, *Tetrahedron Lett*. **2005**, *46*, 1369–1371.
30. J. Safari , S. Dehghan Khalili, M. Rezaei, S. H. Banitaba, F. Meshkani, *Monatsh Chem*. **2010**, *141*, 1339–1345.
31. J. Safaei-Ghomi, M. A. Ghasemzadeh, *Acta Chim. Slov*. **2012**, *59*, 697–702.
32. J. Safaei-Ghomi, M. A. Ghasemzadeh, *J. Sulfur. Chem*. **2013**, *34*, 233–241.
33. J. Safaei-Ghomi, M. A. Ghasemzadeh, *J. Chem. Sci*. **2013**, *125*, 1003–1008.
34. J. Safaei-Ghomi, A. Ziarati, M. Tamimi, *Acta Chim. Slov.* **2013**, *60*, 403–410.
35. J. Safaei-Ghomi, M. A. Ghasemzadeh, *Chin. Chem. Lett*. **2012**, *23*, 1225–1229.
36. M. A. Abdulkarim, A. L. Kadasi, G. M. Nazeruddin, *Int. J. Chem. Sci*. **2012**, *10*, 324–330.
37. D. Q. Shi, N. Wu, Q. Y. Zhuang, *J. Chem. Res*. **2008**, *54*, 542–545.

Povzetek

Raziskali smo učinkovit »one-pot« pristop k sintezi dihidropirano[3,2-*c*]kromenov in biskumarinov, kataliziran s pomočjo nanokristaliničnega magnezijevega oksida. Pripravljene spojine predstavljajo pomembne heterocikle, ki izkazujejo farmakološko in biološko zanimive lastnosti. Nanodelci magnezijevega oksida so imeli izrazit katalitski učinek na to trokomponentno reakcijo, ki poteka med aldehidi, etil cianoacetatom in 4-hidroksikumarinom, ter so omogočili visoke izkoristke, kratke reakcijske čase in uporabo pogojev brez prisotnosti topil. Nano magnezijev oksid, kot učinkovit, lahko dosegljiv in cenovno ugoden heterogeni katalizator, sestavljen iz nanodelcev, smo za sintezo dihidropirano[3,2-*c*] kromenov in biskumarinov uporabili večkrat.