

Carboxymethyl Cellulose (CMC) as a Recyclable Green Catalyst Promoted Eco-Friendly Protocol for the Solvent-Free Synthesis of 1*H*-Pyrazolo[1,2-*b*]Phthalazine-5,10-Dione Derivatives

Farzaneh Mohamadpour

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Carboxymethyl Cellulose (CMC) as a Recyclable Green Catalyst Promoted Eco-Friendly Protocol for the Solvent-Free Synthesis of 1*H*-Pyrazolo[1,2-*b*]Phthalazine-5,10-Dione Derivatives

Farzaneh Mohamadpour

School of Engineering, Apadana Institute of Higher Education, Shiraz, Iran

ABSTRACT

An eco-safe synthetic route for convenient one-pot synthesizing 1*H*-pyrazolo[1,2-*b*] phthalazine-5,10-dione derivatives through Knoevenagel-Michael cyclocondensation is reported in carboxymethyl cellulose (CMC) based on green chemistry principles. The prominent benefits include use of recyclable green catalyst, commercially accessible inexpensive starting materials, operational simplicity, non-hazardous reaction circumstances, high atom-economy, solvent-free, short reaction times and high yields.

ARTICLE HISTORY

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KEYWORDS

1*H*-pyrazolo[1,2-*b*]phthalazine-5,10-dione derivatives; carboxymethyl cellulose (CMC); green procedure; recyclable and biodegradable catalyst

Introduction

Pyrazolophthalazines with various pharmacological features^{1,2} like anticancer,³ anti-inflammatory,⁴ anti-microbial⁵ and they have been reported to possess vasorelaxant,⁶ cardiotoxic,⁷ anticonvulsant⁸ and antifungal.⁹ There are numerous approaches for synthesizing these compounds using various catalysts such as Ce(SO₄)₂·4H₂O,¹⁰ SBA-Pr-SO₃H,¹¹ InCl₃,¹² NiCl₂·6H₂O,¹³ [Bmim] OH,¹⁴ Ultrasound-assisted,¹⁵ *P*-TSA,¹⁶ STA,¹⁷ CuI nanoparticles,¹⁸ PTSA/[Bmim]Br,¹⁹ TBBAD,²⁰ Cu(OAc)₂·H₂O,²¹ K₂CO₃,²² β-Cyclodextrin,²³ [Bu₃NH][HSO₄],²⁴ CuO nanoparticles,²⁵ NZF@HAP-Cs,²⁶ theophylline²⁷ and STA-Amine-Si-Magnetite.²⁸ Each of these methods has its own merits but some of these methods are limited in terms of the use of expensive catalysts, long reaction periods, low yields, harsh reaction conditions, tedious work-up and needing additional quantities of catalysts or reagents and hazardous or toxic catalysts with column chromatographic separation. Hence, finding the environmentally friendly and appropriate approaches for synthesizing this kind of compounds is vital. Since we partly aimed to develop green synthetic processes^{29–33} and due to the above considerations, the search for eco-safe, simple and effective strategies capable of promoting organic reactions under green circumstances has attracted a huge deal of interest in producing 1*H*-pyrazolo[1,2-*b*]phthalazine-5,10-dione derivatives. Hence, here solvent-free environmentally friendly synthesis of 1*H*-pyrazolo[1,2-*b*]phthalazine-5,10-dione derivatives are reported via carboxymethyl cellulose (CMC) (Figure 1) as a green, recyclable, and biodegradable catalyst³⁴ via tandem Knoevenagel-Michael cyclocondensation provided the anticipated products in outstanding yields and short reaction times which might solve some cost problems in industry. Subsequently, we studied the recyclability of the green CMC for the above reaction. However, the CMC can be recycled at least five times with no considerable reduction in activity making it greatly advantageous in addressing the industrial requirements and environmental worries.

CONTACT Farzaneh Mohamadpour ✉ mohamadpour.f.7@gmail.com 📧 School of Engineering, Apadana Institute of Higher Education, Shiraz, Iran.

📄 Supplemental data for this article is available online at <https://doi.org/10.1080/10406638.2020.1768412>.

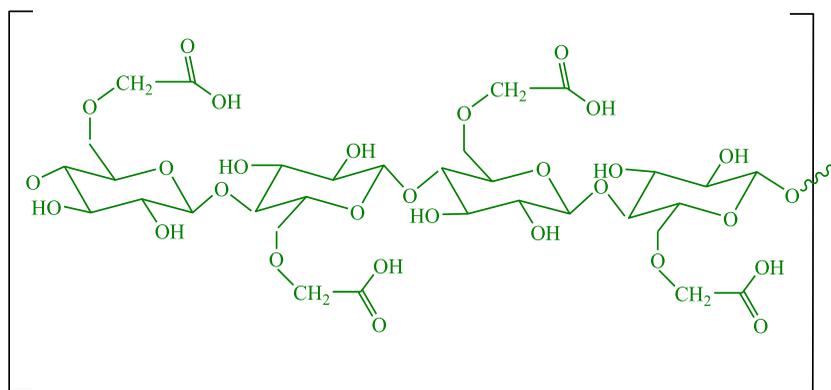


Figure 1. Chemical structure of CMC.

Experimental

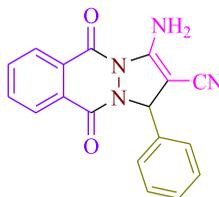
General

Utilizing an Electro thermal 9100 device, all compounds' melting points were found. Moreover, recording nuclear magnetic resonance, ¹H NMR spectra was carried out on a Bruker DRX-400 and Bruker DRX-300 Avance tool with DMSO-d₆ as solvent. All solvents and reagents were bought from Acros, Merck, and Fluka chemical companies and were utilized with no additional purification.

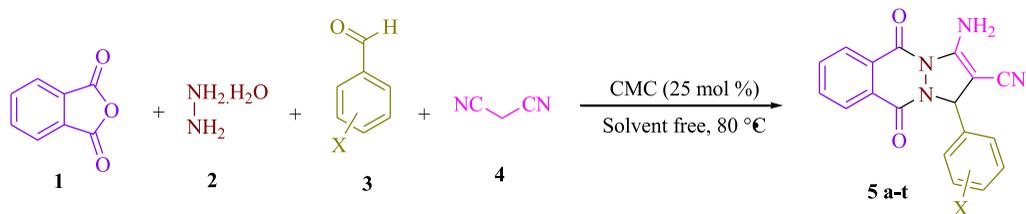
Overall process of preparing (5a-t)

A combination of phthalic anhydride (**1**, 1.0 mmol), hydrazine monohydrate (**2**, 1.0 mmol) and CMC (25 mol%) was heated for 2 h at 80 °C. Then, adding aromatic aldehyde (**3**, 1.0 mmol) and malononitrile (**4**, 1.0 mmol), the reaction was heated for apposite period (Scheme 1). The reaction progress was monitored by TLC utilizing *n*-hexane/EtOAc (4:1) as an eluent. The reaction mass was chilled to room temperature after completing the reaction and then poured on hot water. The achieved solid was filtered, rinsed with water and the crude solid was recrystallized from ethanol to provide the pure material without requiring more purification. The aqueous filtrate was refined at 100 °C to eliminate water to give CMC as white powder. Then powder washed with ethyl acetate and filtered, air dried and reused which was used for the next run under similar reaction conditions. The CMC was improved and reused with no activity loss. Comparing the spectroscopic information, the products were categorized (¹H NMR). Supporting Information associated with this article can be found, in the online version.

3-Amino-1-(phenyl)-5,10-dihydro-5,10-dioxo-1H-pyrazolo[1,2-b]phthalazine-2-carbonitrile (5d)



Yield: 91%; M.p. 271-273 °C; ¹H NMR (300 MHz, DMSO-d₆): 6.14 (1H, s, CHAr), 7.33-7.48 (3H, m, ArH), 7.46 (2H, d, *J* = 8.4 Hz, ArH), 7.97-8.29 (6H, m, NH₂ and ArH).

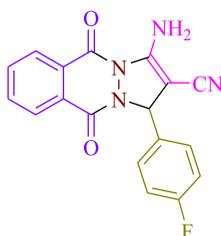


Scheme 1. Synthesis of 1*H*-pyrazolo[1,2-*b*]phthalazine-5,10-dione derivatives.

Table 1. Optimizing the reaction circumstance in the existence of various quantities of CMC.

| Isolated yields (%) | Time (min) | Temperature (°C) | CMC (mol%) | Entry |
|---------------------|------------|------------------|---------------|----------|
| No product | 420 | 80 | Catalyst free | 1 |
| 23 | 240 | 80 | 5 | 2 |
| 37 | 180 | 80 | 10 | 3 |
| 54 | 115 | 80 | 15 | 4 |
| 76 | 85 | 80 | 20 | 5 |
| 91 | 75 | 80 | 25 | 6 |
| No product | 420 | rt | 25 | 7 |
| 29 | 210 | 40 | 25 | 8 |
| 47 | 155 | 50 | 25 | 9 |
| 62 | 120 | 60 | 25 | 10 |
| 73 | 90 | 70 | 25 | 11 |
| 91 | 75 | 90 | 25 | 12 |
| 92 | 75 | 80 | 30 | 13 |

3-Amino-1-(4-fluorophenyl)-5,10-dihydro-5,10-dioxo-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carbonitrile (**5o**)



Yield: 94%; M.p. 261-263 °C; ¹H NMR (400 MHz, DMSO-*d*₆): 6.17 (1H, s, CHAr), 7.20 (2H, t, *J* = 8.8 Hz, ArH), 7.53-7.57 (2H, m, ArH), 7.96-8.26 (6H, m, NH₂ and ArH).

3-Amino-1-(4-methylphenyl)-5,10-dihydro-5,10-dioxo-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carbonitrile (**5q**)

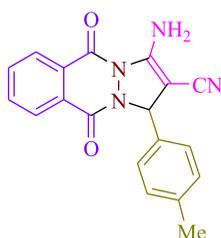
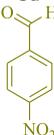
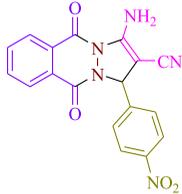
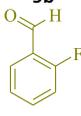
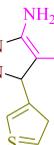
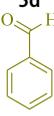
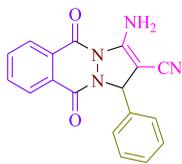
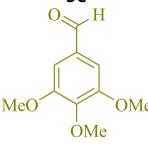
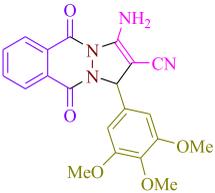
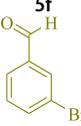
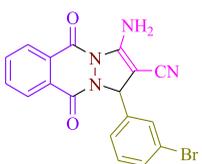
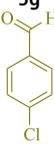
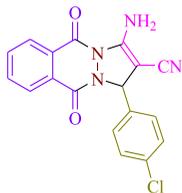
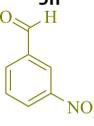
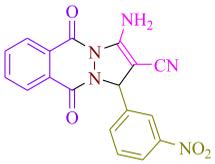
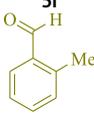
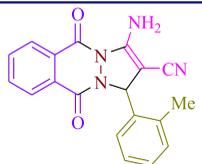
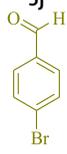
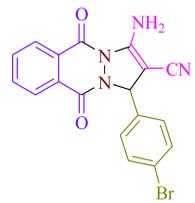
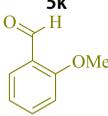
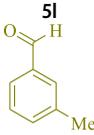
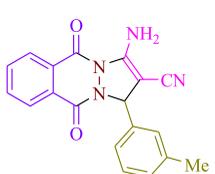
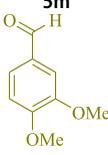
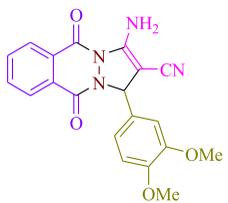
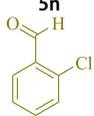
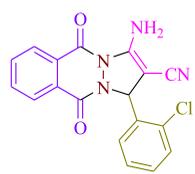
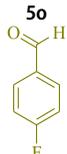
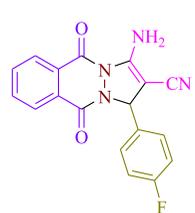
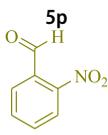
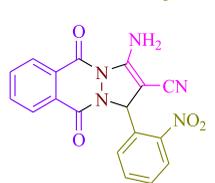


Table 2. CMC catalyzed synthesizing 1*H*-pyrazolo[1,2-*b*]phthalazine-5,10-dione derivatives.

| Lit. M.p. °C | M.p. °C | Isolated yields (%) | Time (min) | Product | Ar | Entry |
|-----------------------|---------|---------------------|------------|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|-------|
| 228–229 ¹⁷ | 227–229 | 89 | 70 |  |  | 1 |
| 268–270 ¹² | 270–272 | 93 | 60 |  |  | 2 |
| 244–246 ¹⁸ | 245–247 | 87 | 75 |  |  | 3 |
| 270–272 ¹⁸ | 271–273 | 91 | 75 |  |  | 4 |
| 253–255 ¹² | 253–255 | 86 | 90 |  |  | 5 |
| 270–272 ¹¹ | 268–270 | 82 | 95 |  |  | 6 |
| 270–272 ¹⁹ | 272–274 | 81 | 85 |  |  | 7 |
| 269–271 ¹⁹ | 267–269 | 86 | 70 |  |  | 8 |

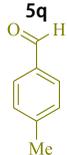
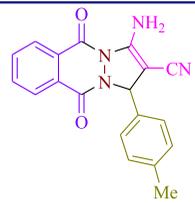
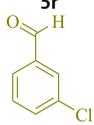
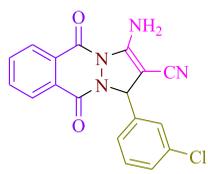
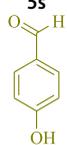
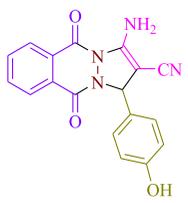
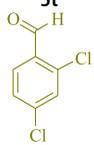
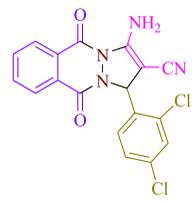
(continued)

Table 2. Continued.

| Lit. M.p. °C | M.p. °C | Isolated yields (%) | Time (min) | Product | Ar | Entry |
|-----------------------|---------|---------------------|------------|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|-------|
| 248–250 ¹⁸ | 249–251 | 94 | 65 |  |  | 9 |
| 265–267 ¹¹ | 267–269 | 85 | 95 |  |  | 10 |
| 153–155 ²⁶ | 154–156 | 89 | 75 |  |  | 11 |
| 250–252 ¹⁸ | 249–251 | 92 | 65 |  |  | 12 |
| 150–152 ²⁰ | 151–153 | 88 | 85 |  |  | 13 |
| 257–259 ¹⁷ | 256–258 | 84 | 75 |  |  | 14 |
| 263–265 ¹¹ | 261–263 | 94 | 65 |  |  | 15 |
| 265–266 ¹¹ | 264–266 | 91 | 65 |  |  | 16 |

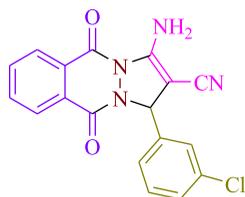
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Table 2. Continued.

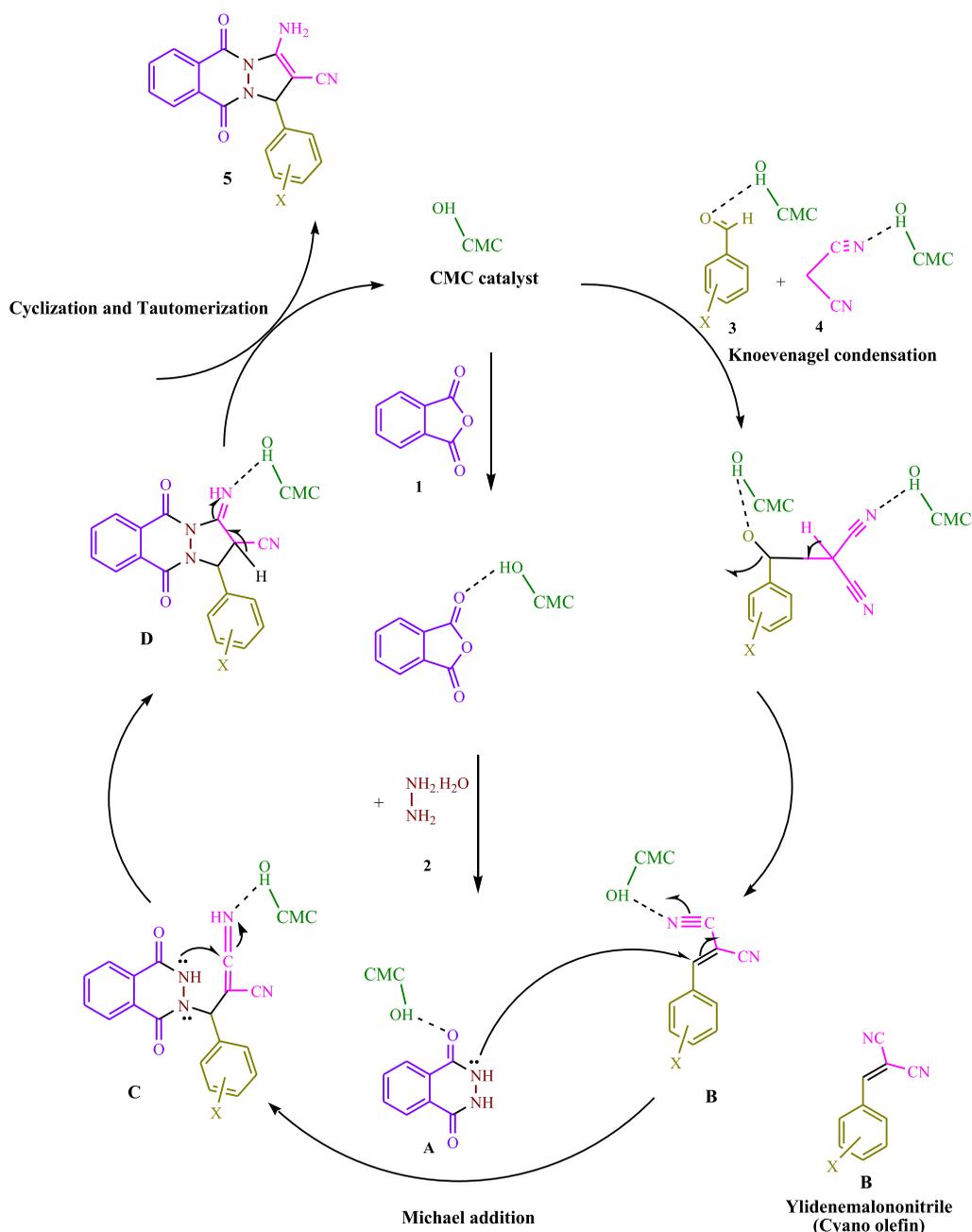
| Lit. M.p. °C | M.p. °C | Isolated yields (%) | Time (min) | Product | Ar | Entry |
|-----------------------|---------|---------------------|------------|-----------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|-------|
| 253–255 ¹⁸ | 255–257 | 89 | 70 |  |  | 17 |
| 266–267 ¹¹ | 264–266 | 78 | 85 |  |  | 18 |
| 270–272 ¹² | 272–274 | 80 | 95 |  |  | 19 |
| 230–232 ²⁵ | 231–233 | 77 | 90 |  |  | 20 |

Yield: 89%; M.p. 255–257 °C; ¹H NMR (400 MHz, DMSO-d₆): 2.30 (3H, s, CH₃), 6.10 (1H, s, CHAr), 7.18 (2H, d, *J* = 8.0 Hz, ArH), 7.34 (2H, d, *J* = 8.0 Hz, ArH), 7.97–8.28 (6H, m, NH₂ and ArH).

3-Amino-1-(3-chlorophenyl)-5,10-dihydro-5,10-dioxo-1H-pyrazolo[1,2-b]phthalazine-2-carbonitrile (5r)



Yield: 78%; M.p. 264–266 °C; ¹H NMR (300 MHz, DMSO-d₆): 6.15 (1H, s, CHAr), 7.39–7.41 (2H, m, ArH), 7.44–7.48 (1H, m, ArH), 7.65 (1H, s, ArH), 7.88–8.29 (6H, m, NH₂ and ArH).



Scheme 2. Recommended mechanistic path for synthesizing 1H-pyrazolo[1,2-b]phthalazine-5,10-dione derivatives.

Results and discussion

The primarily, carboxymethyl cellulose's catalytic activity was examined in a model system in the four-element reaction between a combination of phthalic anhydride (1.0 mmol), hydrazine monohydrate (1.0 mmol), benzaldehyde (1.0 mmol) and malononitrile (1.0 mmol) under solvent-free conditions. The enhanced circumstances were defined by changing the number of the catalyst equivalents and different temperature factors. Lack of a catalyst, a product was not found at

Table 3. Comparing catalytic capability.^a

| References | Time/yield (%) | Conditions | Catalyst | Entry |
|------------------|----------------|-------------------------------|----------------------------------------|-------|
| 12 | 1.5 h/85 | Water, Reflux | InCl ₃ | 1 |
| 13 | 3 h/87 | EtOH, Reflux | NiCl ₂ .6H ₂ O | 2 |
| 16 | 3 h/94 | [Bmim]Br, 100 °C | <i>p</i> -TSA | 3 |
| 17 | 20 min/94 | Solvent-free, 70 °C | STA | 4 |
| 18 | 27 min/91 | MeCN, Reflux | CuI nanoparticles | 5 |
| 20 | 15 min/89 | Solvent-free, 80-100 °C | TBBAD | 6 |
| 21 | 3 h/83 | Solvent-free, 80 °C | Cu(OAc) ₂ .H ₂ O | 7 |
| 22 | 50 min/95 | EtOH, Reflux | K ₂ CO ₃ | 8 |
| 23 | 2.5 h/86 | H ₂ O/EtOH, 100 °C | β -Cyclodextrin | 9 |
| This work | 75 min/91 | Solvent-free, 80 °C | CMC | 10 |

^aBased on synthesizing 3-Amino-1-(phenyl)-5,10-dihydro-5,10-dioxo-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carbonitrile.

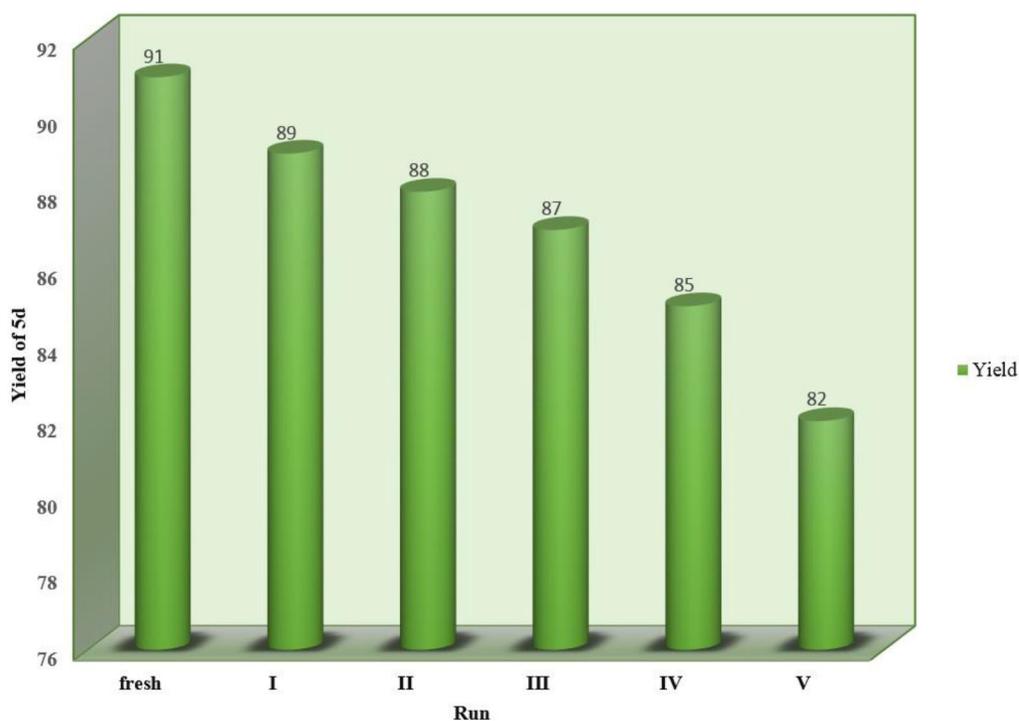


Figure 2. The recyclability of the CMC in the preparation of 5d.

80 °C within 420 min reaction period (Table 1, entry 1). Inserting 5 mol% of the catalyst, a considerable progress was found by the reaction completing in around 240 min (Table 1, entry 2). Using 25 mol% of catalyst, the competent advance and completion were found in the reaction in less reaction period (75 min) (Table 1, entry 6). No considerable enhancement in the product yield and reaction period was found by additional incrementing catalyst quantity (Table 1, entry 13). Further studies determined the effect of different temperature factors on the reaction rate and yields (Table 1). We studied temperature changes from rt to 90 °C. The results show that increasing the temperature to 80 °C results in an increase in reaction rate and product yield. It was also found that increasing the temperature to more than 80 °C had no effect on product yield (Table 1, entry 12). Finally, from the environmental and economic aspects, CMC (25 mol%) was chosen as catalyst at 80 °C under solvent-free conditions for all additional reactions (Table 1, entry 6). As observed in Table 2 and Scheme 1, it was indicated that this technique can work

with various substrates. It should be noted that for purifying the products (**5a-t**), a modest filtration, washed and recrystallizing with ethanol is needed.

Scheme 2 shows the suggested mechanism for synthesizing 1*H*-pyrazolo[1,2-*b*]phthalazine-5,10-dione derivatives. Table 3 represents the comparison of the catalytic capability of some catalysts reported in the literature for synthesis of 1*H*-pyrazolo[1,2-*b*]phthalazine-5,10-dione derivatives. Within this work, it is revealed that CMC possesses its amazing potential as a substitute green, recyclable, biodegradable and inexpensive catalyst for the one-pot synthesizing these naturally active heterocyclic compounds, along with outstanding yields and short reaction periods are the remarkable benefits of this current procedure.

Reusability of CMC

Recovery and reusability is very significant from both environmental and economic perspectives, the recovery and reusability of CMC was investigated in several subsequent runs. For this appeal, the reaction of phthalic anhydride (1.0 mmol), hydrazine monohydrate (1.0 mmol), benzaldehyde (1.0 mmol) and malononitrile (1.0 mmol) for synthesizing (**5d**) was examined in the existence of CMC (25 mol%) was heated at 80 °C for 75 min. After completing, the mixture was chilled to room temperature and poured on hot water. The created precipitate was filtered, rinsed with water and the crude product was purified by recrystallizing from ethanol to obtain the pure product **5d**. To eliminate water, the aqueous filtrate was distilled at 100 °C to give CMC as white powder. Then powder washed with ethyl acetate and filtered, air dried and reused which was used for the next run under similar reaction conditions. The recovered CMC was effectively utilized in consecutive runs (five runs) including the use of fresh medium with no further efficiency loss and with insignificant CMC loss (Figure 2). Slight decrease in the product yield was found in the first, second, third, fourth and fifth reaction runs (89%, 88%, 87%, 85% and 82%, respectively).

Conclusions

In conclusion, in the present work, it was demonstrated that a recyclable green and biodegradable catalyst, carboxymethyl cellulose (CMC), can be used as a greatly efficient and availability catalyst for solvent-free one-pot 4-component synthesizing 1*H*-pyrazolo[1,2-*b*]phthalazine-5,10-dione derivatives. Use of inexpensive initiating substances, solvent-free, time-saving aspects of the reaction, excellent yields, the application of non-hazardous reaction circumstances, direct work-up without column chromatographic separation, convenient and expedient procedure are the notable advantages of this green and simple protocol. However, the CMC can be recycled at least five times with no considerable reduction in activity making it greatly advantageous in addressing the industrial requirements and environmental worries.

Disclosure statement

There are no conflicts of interest.

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References

1. M. J. Genin, C. Biles, B. J. Keiser, S. M. Poppe, S. M. Swaney, W. G. Tarpley, Y. Yagi, and D. L. Romero, "Novel 1,5-Diphenylpyrazole Nonnucleoside HIV-1 Reverse Transcriptase Inhibitors with Enhanced Activity Versus the Delavirdine-Resistant P236L Mutant: Lead Identification and SAR of 3- and 4-Substituted derivatives," *Journal of Medicinal Chemistry* 43, no. 5 (2000): 1034–40.
2. S. K. Singh, P. G. Reddy, K. S. Rao, B. B. Lohray, P. Misra, S. A. Rajjak, Y. K. Rao, and A. Venkateswarlu, "Polar Substitutions in the Benzenesulfonamide Ring of Celecoxib Afford a Potent 1,5-Diarylpyrazole Class of COX-2 Inhibitors," *Bioorganic & Medicinal Chemistry Letters* 14, no. 2 (2004): 499–504.
3. J. Li, Y.-F. Zhao, X.-Y. Yuan, J.-X. Xu, and P. Gong, "Synthesis and Anticancer Activities of Novel 1,4-Disubstituted Phthalazines," *Molecules (Basel, Switzerland)* 11, no. 7 (2006): 574–82.
4. C.-K. Ryu, R.-E. Park, M.-Y. Ma, and J.-H. Nho, "Synthesis and Antifungal Activity of 6-Arylamino-Phthalazine-5,8-Diones and 6,7-Bis(Arylthio)-Phthalazine-5,8-Diones," *Bioorganic & Medicinal Chemistry Letters* 17, no. 9 (2007): 2577–80.
5. J. N. Liu, J. Li, L. Zhang, L. P. Song, M. Zhang, W. J. Cao, S. Z. Zhu, H. G. Deng, and M. Shao, "Facile One-Pot Three-Component Reaction to Synthesize Trifluoromethylated Cyclopenta[b]Pyran Derivatives and Their Further Transformation," *Tetrahedron Letters* 53, no. 19 (2012): 2469–72.
6. N. Watanabe, Y. Kabasawa, Y. Takase, M. Matsukura, K. Miyazaki, H. Ishihara, K. Kodama, and H. Adachi, "4-Benzylamino-1-Chloro-6-Substituted Phthalazines: Synthesis and Inhibitory Activity Toward Phosphodiesterase 5," *Journal of Medicinal Chemistry* 41, no. 18 (1998): 3367–77.
7. Y. Nomoto, H. Obase, H. Takai, M. Teranishi, J. Nakamura, and K. Kubo, "Studies on Cardiotoxic Agents. II. Synthesis of Novel Phthalazine and 1,2,3-Benzotriazine Derivatives," *Chemical & Pharmaceutical Bulletin* 38, no. 8 (1990): 2179–83.
8. S. Grasso, G. De Sarro, A. De Sarro, N. Micale, M. Zappalà, G. Puja, M. Baraldi, and C. De Micheli, "Synthesis and Anticonvulsant Activity of Novel and Potent 6,7-Methylenedioxyphthalazin-1(2H)-Ones," *Journal of Medicinal Chemistry* 43, no. 15 (2000): 2851–9.
9. J. S. Kim, H. K. Rhee, H. J. Park, S. K. Lee, C. O. Lee, and H. Y. Park Choo, "Synthesis of 1-/2-Substituted-[1,2,3]Triazolo[4,5-g]Phthalazine-4,9-Diones and Evaluation of Their Cytotoxicity and Topoisomerase II Inhibition," *Bioorganic & Medicinal Chemistry* 16, no. 8 (2008): 4545–50.
10. E. Mosaddegh, and A. Hassankhani, "A Rapid, One-Pot, Four-Component Route to 2H-Indazolo[2,1-b]Phthalazine-Triones," *Tetrahedron Letters* 52, no. 4 (2011): 488–90.
11. G. M. Ziarani, N. H. Mohtasham, A. Badiei, and N. Lashgari, "Efficient One-Pot Solvent-Free Synthesis of 1H-Pyrazolo[1,2-b]Phthalazine-5,10-Diones Catalyzed by Sulfonic Acid Functionalized Nanoporous Silica (SBA-Pr-SO₃H)," *Journal of the Chinese Chemical Society* 61, no. 9 (2014): 990–4.
12. M. V. Reddy, and Y. T. Jeong, "InCl₃-Catalyzed Green Synthesis of 1H-Pyrazolo[1,2-b]Phthalazine-5,10-Diones under Solvent-Free Conditions," *Tetrahedron Letters* 54, no. 27 (2013): 3546–9.
13. S. H. Song, J. Zhong, Y. H. He, and Z. Guan, "One-Pot Four-Component Synthesis of 1H-Pyrazolo[1,2-b]Phthalazine-5,10-Dione Derivatives," *Tetrahedron Letters* 53, no. 52 (2012): 7075–7.
14. D. S. Raghuvanshi, and K. N. Singh, "A Highly Efficient Green Synthesis of 1H-Pyrazolo[1,2-b]Phthalazine-5,10-Dione Derivatives and Their Photophysical Studies," *Tetrahedron Letters* 52, no. 43 (2011): 5702–5.
15. M. R. Nabid, S. J. T. Rezaei, R. Ghahremanzadeh, and A. Bazgir, "Ultrasound-Assisted One-Pot, Three-Component Synthesis of 1H-Pyrazolo[1,2-b]Phthalazine-5,10-Diones," *Ultrasonics Sonochemistry* 17, no. 1 (2010): 159–61.
16. M. Sayyafi, M. Seyyedhamze, H. R. Khavasi, and A. Bazgir, "One-Pot, Three-Component Route to 2H-Indazolo[2,1-b]Phthalazine-Triones," *Tetrahedron* 64, no. 10 (2008): 2375–8.
17. M. V. Reddy, P. C. R. Kumar, G. C. S. Reddy, and C. S. Reddy, "Silica Gel-Supported Tungstic Acid (STA): a New, Highly Efficient and Recyclable Catalyst for the Synthesis of 1H-Pyrazolo[1,2-b]Phthalazine-5,10-Dione Carbonitriles and Carboxylates under Neat Conditions," *Comptes Rendus Chimie* 17, no. 12 (2014): 1250–6.
18. J. Safaei-Ghomi, H. Shahbazi-Alavi, A. Ziarati, R. Teymuri, and M. R. Saberi, "A Highly Flexible Green Synthesis of 1H-Pyrazolo[1,2-b]Phthalazine-5,10-Dione Derivatives with CuI Nanoparticles as Catalyst under Solvent-Free Conditions," *Chinese Chemical Letters* 25, no. 3 (2014): 401–5.
19. R. Ghahremanzadeh, G. I. Shakibaei, and A. Bazgir, "An Efficient One-Pot Synthesis of 1H-Pyrazolo[1,2-b]Phthalazine-5,10-Dione Derivatives," *Synlett* 2008, no. 8 (2008): 1129–32.
20. R. Ghorbani-Vaghei, S. Noori, Z. Toghracai-Semiromi, and Z. Salimi, "One-Pot Synthesis of 1H-Pyrazolo[1,2-b]Phthalazine-5,10-Dione Derivatives under Solvent-Free Conditions," *RSC Advances* 4, no. 89 (2014): 47925–8.
21. F. Mohamadpour, M. T. Maghsoodlou, R. Heydari, and M. Lashkari, "Copper(II) Acetate Monohydrate: An Efficient and Eco-Friendly Catalyst for the One-Pot Multi-Component Synthesis of Biologically Active

- Spiropyrans and 1*H*-Pyrazolo[1,2-*b*]Phthalazine-5,10-Dione Derivatives under Solvent-Free Conditions,” *Research on Chemical Intermediates* 42, no. 12 (2016): 7841–53.
22. M. Abdesheikhi, and Z. Karimi-Jaberi, “Four-Component Synthesis of 3-Amino-1-Aryl-5,10-Dioxo-1*H*-Pyrazolo[1,2-*b*] Phthalazine-2-Carbonitrile Derivatives Promoted by Potassium Carbonate,” *Journal of Chemical Research* 39, no. 8 (2015): 482–3.
 23. Y. A. Tayade, and D. S. Dalal, “ β -Cyclodextrin as a Supramolecular Catalyst for the Synthesis of 1*H*-Pyrazolo[1,2-*b*]Phthalazine-5,10-Dione Derivatives in Water,” *Catalysis Letters* 147, no. 6 (2017): 1411–21.
 24. M. Akmal Shaikh, M. Farooqui, and S. Abed, “[Bu₃NH][HSO₄] Catalyzed: An Eco-Efficient Synthesis of 1*H*-Pyrazolo[1,2-*b*]Phthalazine-5,10-Diones and 2*H*-Indazolo[2,1-*b*]Phthalazine-Triones under Solvent-Free Conditions,” *Research on Chemical Intermediates* 44, no. 9 (2018): 5483–500.
 25. S. Patil, A. Mane, and S. Dhongade-Desai, “CuO Nanoparticles as a Reusable Catalyst for the Synthesis of 1*H*-Pyrazolo[1,2-*b*]Phthalazine-5,10-Dione Derivatives under Solvent-Free Conditions,” *Journal of the Iranian Chemical Society* 16, no. 8 (2019): 1665–75.
 26. B. Maleki, S. Barat Nam Chalaki, S. Sedigh Ashrafi, E. Rezaee Seresht, F. Moeinpour, A. Khojastehnezhad, and R. Tayebee, “Caesium Carbonate Supported on Hydroxyapatite-Encapsulated Ni_{0.5}Zn_{0.5}Fe₂O₄ Nanocrystallites as a Novel Magnetically Basic Catalyst for the One-Pot Synthesis of Pyrazolo[1,2-*b*]Phthalazine-5,10-Diones,” *Applied Organometallic Chemistry* 29, no. 5 (2015): 290–5.
 27. F. Mohamadpour, “Theophylline as a Green Catalyst for the Synthesis of 1*H*-Pyrazolo[1,2-*b*]Phthalazine-5,10-Diones,” *Organic Preparations and Procedures International* 52, no. 1 (2020): 64–8.
 28. P. Arora, and J. Kaur Rajput, “Amelioration of H₄[W₁₂SiO₄₀] by Nanomagnetic Heterogenization: For the Synthesis of 1*H*-Pyrazolo[1,2-*b*]Phthalazinedione Derivatives,” *Applied Organometallic Chemistry* 32, no. 2 (2018): e4001–18.
 29. F. Mohamadpour, “Green and Convenient One-Pot Access to Polyfunctionalized Piperidine Scaffolds via Glutamic Acid Catalyzed Knoevenagel- Intramolecular [4 + 2] aza-Diels-Alder Imin-Based Multi-Component Reaction under Ambient Temperature,” *Polycyclic Aromatic Compounds* (2018): 1–12.
 30. F. Mohamadpour, “Synthesis of Pyran-Annulated Heterocyclic Systems Catalyzed by Theophylline as a Green and Bio-Based Catalyst,” *Polycyclic Aromatic Compounds* (2019): 1–13.
 31. F. Mohamadpour, “Glutamic Acid as Green and Bio-Based α -Amino Acid Catalyst Promoted One-Pot Access to Polyfunctionalized Dihydro-2-Oxypyrrroles,” *Journal of the Serbian Chemical Society* 84, no. 10 (2019): 1083–92.
 32. F. Mohamadpour, “Imin-Based Synthesis of Polyfunctionalized Dihydro-2-Oxypyrrroles Catalyzed by Glycine Amino Acid via Tandem Michael–Mannich Cyclocondensation Reaction under Ambient Temperature,” *Research on Chemical Intermediates* 46, no. 3 (2020): 1931–40.
 33. F. Mohamadpour, and M. Lashkari, “Three-Component Reaction of β -Keto Esters, Aromatic Aldehydes and Urea/Thiourea Promoted by Caffeine, a Green and Natural, Biodegradable Catalyst for Eco-Safe Biginelli Synthesis of 3,4-Dihydropyrimidin-2(1*H*)-Ones/Thiones Derivatives under Solvent-Free Conditions,” *Journal of the Serbian Chemical Society* 83, no. 6 (2018): 673–84.
 34. M. Karimi, and M. R. Naimi-Jamal, “Carboxymethyl Cellulose as a Green and Biodegradable Catalyst for the Solvent-Free Synthesis of Benzimidazoloquinazolinone Derivatives,” *Journal of Saudi Chemical Society* 23, no. 2 (2019): 182–7.