Res Chem Intermed
DOI 10.1007/s11164-017-3011-7

Aqua one-pot, three-component synthesis of dihydropyrano[3,2-*c*]chromenes and amino-benzochromenes catalyzed by sodium malonate

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Received: 25 April 2017 / Accepted: 16 June 2017

Abstract The widespread biological properties of dihydropyrano[3,2-*c*]chromenes, 2-amino-4-aryl-4*H*-benzo[*h*]chromenes, and 3-amino-1-aryl-1*H*-benzo[*f*]chromenes have led to increasing efforts for the development of tremendously effective synthetic protocols aimed at their synthesis. In this contribution, sodium malonate was employed for the first time as an efficient catalyst for the one-pot, three-component tandem Knoevenagel–cyclocondensation reaction of 4-hydroxycoumarin (or naphthols), malononitrile/ethyl cyanoacetate, and various aldehydes. These compounds underwent Knoevenagel–Michael–Thorpe–Ziegler cyclization upon heating at 70 °C in water to give the respective medicinally relevant dihydropyrano[3,2-*c*]chromenes and amino-benzochromenes. The method is versatile and amenable to many substrates as it requires no specialized devices such as microwave, ultrasound and ball-milling. Also, the salient features of this high-yielding protocol are green reaction conditions, the use of commercially available catalyst, easy purification processes by a simple filtration, and relatively shorter reaction times.

Keywords Sodium malonate · Dihydropyrano[3,2-*c*]chromene · Green chemistry · Three-component reaction · Amino-benzochromene · Water

Introduction

The chromene skeleton is considered as one of the most important heterocyclic ring systems in organic synthetically chemistry and is implanted in many biologically active compounds. In recent years, densely functionalized chromenes and their derivatives have received considerable attention because of various applications in

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Published online: 27 June 2017

medicinal chemistry. Among functionalized chromenes known so far, dihydropyrano[3,2-*c*]chromenes and amino-benzochromenes as 'privileged medicinal scaffolds' possess a wide range of fascinating biological activities, such as antituberculosis [1], anti-oxidant [2], acetylcholinesterase (AChE) inhibitoy [3], antibacterial [4, 5], anti-anaphylactic [6], antimicrobial [7–9], antifungal [10], anti-inflammatory [11], anti-rheumatic [12], antitumor [13–16], and antiproliferative [17, 18]. Structures of some derivatives of these bioactive scaffolds can be seen in Fig. 1.

Up to now, keeping in view the importance of dihydropyrano[3,2-*c*]chromene frameworks and amino-benzochromene heterocyclic compounds, various synthetic methods have been reported for the synthesis of these heterocycles. A large number of homogeneous and heterogeneous catalysts have been used for this purpose, including starch [19], urea [20], thiourea dioxide (TUD) [21], hexamethylenetetramine (HMTA) [22], 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) [23], meglumine [24], *N*-propylpiperazine sodium *n*-propionate (SBPPSP) [25], poly(4-vinylpyridine) [26], Amberlyst A21 [27], borax [28], $BF_3{\cdot}SiO_2$ [29], CuO nanoparticles [30], 4-(dimethylamino)pyridine (DMAP) [31], silica gel [32], morpholine [33], ammonium or sodium formate [34], cetyltrimethylammonium bromide in water [35], I_2/K_2CO_3 [36], cetyltrimethylammonium bromide (CTABr) using ultrasound irradiation [37], $NaHCO_3$ [38], basic alumina [39], nano-sized MgO [40], nanostructured diphosphate $Na_2CaP_2O_7$ [41], triazinefunctionalised ordered mesoporous organosilica [42], potassium phosphate tribasic trihydrate [43], piperidine under microwave heating [44], Mg/Al hydrotalcite [45], Preyssler heteropolyacid [46], 1,4-diazabicyclo[2.2.2]octane (DABCO) entrapped in agar–agar [47], CeO_2/CaO nanocomposite oxide [48], nano-polypropylenimine dendrimer (DAB-PPI-G_1) Lewis base [49], VCaHAa [50], poly(4-vinylpyridine) [51], diammonium hydrogen phosphate [52], amino-functionalized MCM-41 [53], piperidine [14–16], imidazole [54], ionic liquids [55], nano-copper chromite (nano-$CuCr_2O_4$) [56], tetragonal

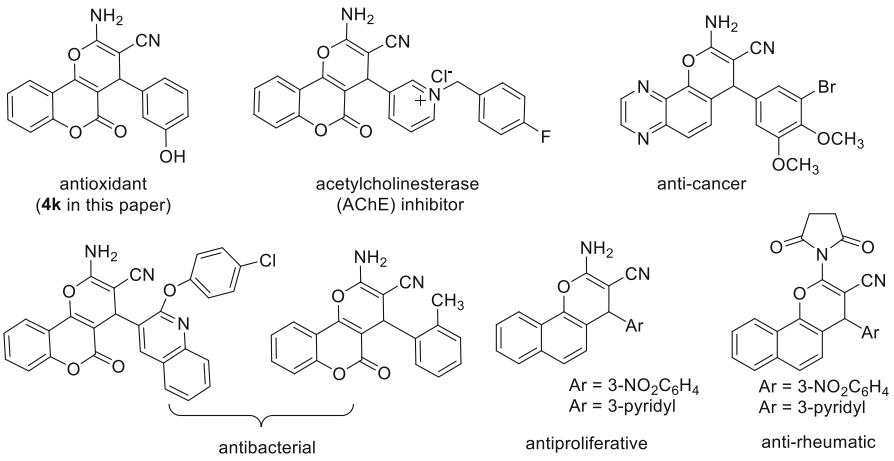


Fig. 1 Structures of some synthetically bioactive dihydropyrano[3,2-c]chromenes and amino-benzochromenes

ZrO_2 nanoparticle (*t*-ZrO_2 NP) [57], tetrabutylammonium chloride (TBAC) [58], (4-dimethylaminopyridine) functionalized polyacrylonitrile fiber catalyst ($PAN_{DMAP}F$) [59], piperazine-functionalized Fe_3O_4/SiO_2 magnetite nanoparticle [60], and Triton B [61]. Special apparatus such as ultrasound [62–64], microwave [65–67], and ball milling [68] have also been utilized for the synthesis of such biologically significant compounds. We have recently used potassium phthalimide (PPI) [69–71], potassium hydrogen phthalate (KHP) [72], and *N*,*N*-dimethylbenzylamine (DMBA) [73, 74] as catalysts for the synthesis of diversely 4*H*-pyran-annulated molecules.

In view of the aforementioned applications of densely functionalized chromenes, using an efficient catalyst toward the construction of dihydropyrano[3,2-*c*]chromene and amino-benzochromene scaffolds via simple multicomponent reaction (MCR) remains an issue of interest.

A MCR was recognized as an efficacious method for the construction of valuable organic compounds and pharmacologically active molecules from at least three reactants in a single vessel. Atomic and structural economy, mild reaction conditions, step economy, high convergence, high bond-forming index, substantial capacity to create molecular complexity and diversity, the product diversity, and the avoidance of complicated separation and purification processes are the chemical benefits of MCRs [75–81]. The development of environmentally friendly organic transformations without using any organic solvent is still a challenge. From an economical and green chemistry point of view, aqua-mediated chemical reactions have been considered as useful protocols in organic synthesis due to water being an easily available, clean, safe, non-toxic, noncombustible, non-explosive, the most environmentally benign, low-cost, and recyclable medium. Considering the above-mentioned benefits of water as the reaction medium, in recent years many chemists have been interested to use water in various organic transformations [82–88]. In the present study, the synthesis of functionalized chromenes from 4-hydroxycoumarin (or 1-naphthol and 2-naphthol), malononitrile/ethyl cyanoacetate, and diversified aldehydes in the presence of sodium malonate (SM) at 70 °C in water as an environmentally friendly solvent is reported.

Materials and methods

Instruments and characterization

Melting points were measured on a Büchi 510 melting point apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature on a Bruker Avance DRX-500 MHz spectrophotometer using DMSO-d_6 as the solvent. Elemental microanalyses were performed on an Elementar Vario EL III analyzer. The purity of the synthesized compounds as well as the progress of the reactions were monitored by thin layer chromatography (TLC) analysis on Merck pre-coated silica gel $60F_{254}$ aluminum sheets, visualized by UV light. All the targeted products are reported in the literature and are characterized by comparison of their spectral and physical data on the basis of literature descriptions.

General procedure for the synthesis of dihydropyrano[3,2-*c*]chromenes (4a–u), 2-amino-4-aryl-4*H*-benzo[*h*]chromenes (6a–h), and 3-amino-1-aryl-1*H*-benzo[*f*]chromenes (7a–i)

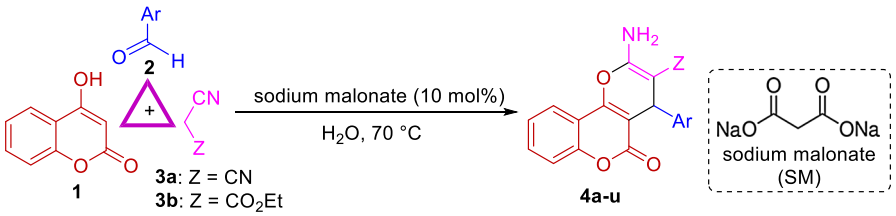
A mixture of 4-hydroxycoumarin/1-naphthol/2-naphthol (**1**, **6**, **7**, 1 mmol), aldehyde (**2**, 1 mmol), malononitrile/ethyl cyanoacetate (**3**, 1 mmol), water (5 mL) and SM (10 mol%) was heated with stirring at 70 °C for the required times. After completion of the reaction (monitored by TLC analysis), the reaction mixture was gradually cooled to room temperature and the resulting precipitates were collected by filtration, washed with cold water and air-dried to give the pure corresponding products. The solvent was removed from the filtrate to recover the catalyst and reused for subsequent runs. The identity of the known products was confirmed by comparison of their spectroscopic data and physical properties with those described in the respective literature.

*Data for 2-Amino-4-(3-nitrophenyl)-5-oxo-4H,5H-pyrano-[3,2-c]chromene-3-carbonitrile (**4c**)*

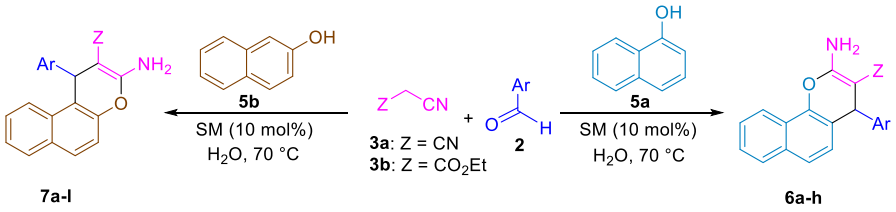
M.p. 259–261 °C (255–257 °C, Lit. [19]); IR (KBr): 3435, 3376, 3274, 2210, 1705, 1670, 1614, 1525, 1460, 1375, 1220, 1117, 1058, 783 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ 4.74 (s, 1H), 7.46–7.74 (m, 6H), 7.82 (d, $J = 7.8$ Hz, 1H), 7.93 (dd, $J = 1.4$, 7.9 Hz, 1H), 8.12–8.15 (m, 2H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 37.5, 57.8, 103.7, 113.8, 117.5, 119.8, 123.1, 123.3, 123.5, 125.6, 130.9, 135.6, 146.4, 148.7, 153.1, 154.7, 158.9, 159.0, 160.5. Anal. Calcd. for $C_{19}H_{11}N_3O_5$ (%): C, 63.15; H, 3.07; N,11.63. Found: C, 63.12; H, 3.05; N, 11.59.

*Data for 2-amino-4-(4-chlorophenyl)-4H-benzo[h]chromene-3-carbonitrile (**6d**)*

M.p. 231–233 °C (232–234 °C, Lit. [44]); IR (KBr): 3454, 3335, 2204, 1669, 1602, 1572, 1415, 1380,1105 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6), δ: 4.56 (s, 1H), 6.68 (s, 2H), 7.02 (d, $J = 8.7$ Hz, 1H), 7.19–7.34 (m, 4H), 7.43–7.48 (m, 3H), 7.79 (d, $J = 7.1$ Hz, 1H), 8.15 (d, $J = 8.2$ Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 42.4, 55.6, 119.9, 120.6, 122.2, 122.4, 123.7, 125.4, 125.9, 126.6, 127.5, 128.7, 130.2, 132.6, 133.8, 142.4, 146.8, 160.8. Anal. Calcd. for $C_{20}H_{13}ClN_2O$ (%): C, 72.18; H, 3.94; N, 8.42. Found: C, 72.17; H, 3.92; N, 8.46.

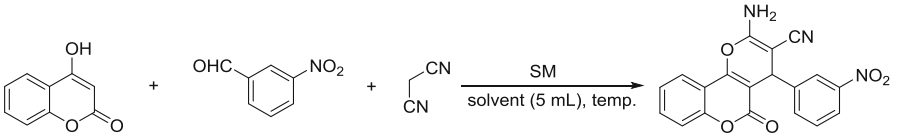


Scheme 1 Sodium malonate catalyzed one-pot, three-component reaction of 4-hydroxycoumarin (**1**), cyano compounds (**3a** and **3b**) and aldehydes (**2**) at 70 °C in H_2O



Scheme 2 Sodium malonate catalyzed one-pot, three-component synthesis of 2-amino-4-aryl-4*H*-benzo[*h*]chromenes (**6a–h**) and 3-amino-1-aryl-1*H*-benzo[*f*]chromenes (**7a–l**) at 70 °C in H_2O

Table 1 Optimization of the reaction conditions for the synthesis of 2-amino-4-(3-nitrophenyl)-5-oxo-4*H*,5*H*-pyrano[3,2-*c*]chromene-3-carbonitrile (**4c**)



Entry	Catalyst (mol%)	Solvent	Temp. (°C)	Time (min)	Isolated yields (%)
1	–	H_2O	rt	120	Trace
2	–	H_2O	Reflux	60	25
3	5	H_2O	rt	60	30
4	10	H_2O	rt	60	34
5	15	H_2O	rt	60	34
6	20	H_2O	rt	60	38
7	10	H_2O	45	45	65
8	10	H_2O	60	30	87
9	**10**	**H_2O**	**70**	**15**	**96**
10	10	EtOH	70	20	53
11	10	MeCN	70	20	Trace
12	10	1,4-dioxane	70	20	Trace
13	10	CH_2Cl_2	70	20	Trace
14	10	EtOAc	70	20	Trace
15	10	$CHCl_3$	70	20	Trace
16	10	H_2O/EtOH	70	20	67

Reaction conditions: a well ground mixture of 4-hydroxycoumarin (**1**, 1 mmol), 3-nitrobenzaldehyde (**2c**, 1 mmol), malononitrile (**3a**, 1 mmol), solvent (5 mL), catalyst and magnetic stirring at different temperatures *rt* room temperature

Optimized conditions shown in bold

Results and discussion

This work is the first report on the use of sodium malonate (SM) for the synthesis of dihydropyrano[3,2-*c*]chromenes (**4a–u**) (Scheme 1), 2-amino-4-aryl-4*H*-benzo[*h*]chromene and 3-amino-1-aryl-1*H*-benzo[*f*]chromene scaffolds (**6a–h** and **7a–l**) (Scheme 2).

Initially, 4-hydroxycoumarin (**1**), 3-nitrobenzaldehyde (**2c**) and malononitrile (**3a**) were chosen as the model substrates to optimize the reaction conditions including the effect of catalyst loading, the role of the solvents and reaction temperatures (Table 1). The result showed that 10 mol% sodium malonate (SM) was the most effective catalyst loading giving the product higher yields (96%) and lower reaction times (15 min). Among several solvents screened, water was found to be the best solvent. It was also found that the most suitable temperature is 70 °C. Consequently, the optimized reaction conditions were 10 mol% SM in water at 70 °C within 15 min (Table 1, entry 9).

After finding the proper reaction parameters, we studied the scope of this three-component reaction (3CR) by varying the structure of the aldehydes and active cynano-containing compounds. The reactions proceeded cleanly under green optimized reaction conditions.

Interestingly, almost all the substrates gave the desired dihydropyrano[3,2-*c*]chromene heterocycles (**4a–u**) in good to excellent yields of 88–96% within the

Table 2 Synthesis of the dihydropyrano[3,2-*c*]chromene derivatives (**4a–u**) catalyzed by sodium malonate

Entry	Aldehyde	Cyano compound/ Z	Product	Time (min)	Yield (mol%)[a]	Mp (°C)	
						Found	Reported references
1	C_6H_5CHO	CN (**3a**)	**4a**	20	94	260–261	258–260 [19]
2	2-NO_2–C_6H_4CHO	CN (**3a**)	**4b**	25	91	258–260	258–260 [25]
3	4-NO_2-C_6H_4CHO	CN (**3a**)	**4d**	12	97	258–260	260–262 [19]
4	4-Cl–C_6H_4CHO	CN (**3a**)	**4e**	15	94	264–266	263–265 [19]
5	2,4-di–ClC_6H_3CHO	CN (**3a**)	**4f**	15	95	255–257	258–260 [19]
6	2-Cl–C_6H_4CHO	CN (**3a**)	**4g**	20	92	272–274	275–277 [19]
7	4-Me–C_6H_4CHO	CN (**3a**)	**4h**	25	93	258–260	257–259 [20]
8	4-MeO–C_6H_4CHO	CN (**3a**)	**4i**	30	94	220–222	220–222 [29]
9	4-HO–C_6H_4CHO	CN (**3a**)	**4j**	22	95	259–261	260–263 [19]
10	3-HO–C_6H_4CHO	CN (**3a**)	**4k**	25	94	267–269	269–270 [25]
11	4-Me_2N–C_6H_4CHO	CN (**3a**)	**4l**	25	91	222–224	224–225 [23]
12	3-MeO-4-HO–C_6H_3CHO	CN (**3a**)	**4m**	20	96	252–254	253–254 [22]
13	3,4-di–MeO–C_6H_3CHO	CN (**3a**)	**4n**	37	90	226–228	225–228 [30]
14	Furan-2-carbaldehyde	CN (**3a**)	**4o**	25	90	251–253	250–252 [23]
15	Thiophen-2-carbaldehyde	CN (**3a**)	**4p**	25	89	225–227	228–229 [22]
16	C_6H_5CHO	CO_2Et (**3b**)	**4q**	30	89	210–211	208–210 [21]
17	4-NO_2–C_6H_4CHO	CO_2Et (**3b**)	**4r**	30	91	239–241	241–243 [23]
18	3-NO_2–C_6H_4CHO	CO_2Et (**3b**)	**4s**	35	90	241–242	242–245 [31]
19	4-Cl–C_6H_4CHO	CO_2Et (**3b**)	**4t**	25	90	192–194	192–194 [23]
20	4-Me–C_6H_4CHO	CO_2Et (**3b**)	**4u**	40	88	193–195	194–196 [21]

Reaction conditions: substrates 1 mmol; water (5 mL); SM (10 mol %); stirred at 70 °C

[a] Yields refer to the pure isolated products

specified reaction times (Table 2, entries 1–20). The 3CR of substituted benzaldehydes bearing electron-withdrawing groups occurred in higher yields and shorter reaction times than its electron-donating counterparts. The scope of the reaction was further extended with α- and β-naphthol (**5a** and **5b**) instead of 4-hydroxycoumaarin (**1**) (Scheme 2).

The experiments were performed under the optimized reaction conditions, and the corresponding 2-amino-4-aryl-4*H*-benzo[*h*]chromenes (**6a–h**) and 3-amino-1-aryl-1*H*-benzo[*f*]chromenes (**7a–j**) were obtained in high isolated yields (Table 3). From the results presented in Table 3, it is apparent that aldehydes containing both electron-deficient and electron-rich substituents in the aromatic ring give high yields of the desired amino-benzochromene products in reactions with malononitrile/ethyl cyanoacetoacetate (**3a** and **3b**) and nphthols (**5a** and **5b**) in 25–65 min (Table 3).

In all cases, the filtrate containing the residual solvent and the catalyst obtained upon filtration of the reaction mixture after completion of the reaction could be reused in the preparation of the model product (**4c**) under the above-mentioned optimized conditions. After each run, the resulting solid product was collected by

Table 3 Synthesis of 2-amino-4-aryl-4*H*-benzo[*h*]chromenes (**6a–h**) and 3-amino-1-aryl-1*H*-benzo[*f*]chromenes (**7a–l**) in the presence of SM

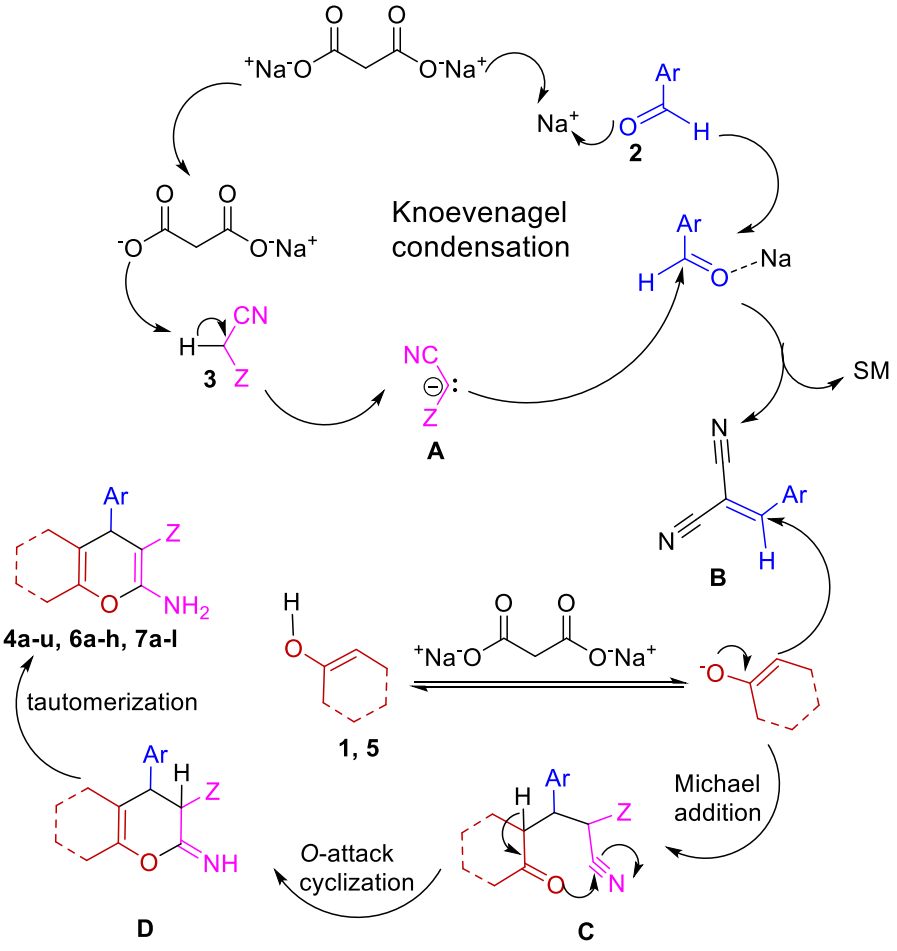
Entry	Aldehyde	Cyano compound/Z	Product	Time (min)	Yield (%)[a]	M.p. (°C)	
						Found	Reported references
1	C_6H_5CHO	CN (**3a**)	**6a**	50	92	205–207	210–211 [38]
2	$4\text{-}O_2NC_6H_4CHO$	CN (**3a**)	**6b**	30	94	241–243	242–243 [38]
3	$3\text{-}O_2NC_6H_4CHO$	CN (**3a**)	**6c**	45	91	211–213	210–212 [69]
4	$4\text{-}ClC_6H_4CHO$	CN (**3a**)	**6d**	25	94	231–233	232–234 [44]
5	$4\text{-}MeC_6H_4CHO$	CN (**3a**)	**6e**	50	92	197–198	202–204 [58]
6	$4\text{-}HOC_6H_4CHO$	CN (**3a**)	**6f**	40	93	245–247	247–249 [36]
7	$4\text{-}MeOC_6H_4CHO$	CN (**3a**)	**6g**	35	94	186–188	188–189 [38]
8	$3\text{-}O_2NC_6H_4CHO$	CO_2Et (**3b**)	**6h**	55	91	199–201	198–200 [61]
9	C_6H_5CHO	CN (**3a**)	**7a**	60	92	278–280	280–282 [62]
10	$4\text{-}O_2NC_6H_4CHO$	CN (**3a**)	**7b**	45	92	182–184	182–183 [38]
11	$3\text{-}O_2NC_6H_4CHO$	CN (**3a**)	**7c**	45	93	188–190	189–190 [58]
12	$4\text{-}ClC_6H_4CHO$	CN (**3a**)	**7d**	40	95	204–206	206–210 [63]
13	$4\text{-}BrC_6H_4CHO$	CN (**3a**)	**7e**	40	93	242–243	242–244 [51]
14	$4\text{-}MeC_6H_4CHO$	CN (**3a**)	**7f**	45	89	257–259	270–272 [51]
15	$4\text{-}OHC_6H_4CHO$	CN (**3a**)	**7g**	40	94	244–246	246–248 [51]
16	$4\text{-}MeOC_6H_4CHO$	CN (**3a**)	**7h**	50	92	184–186	184–187 [69]
17	$4\text{-}(Me)_2NC_6H_4CHO$	CN (**3a**)	**7i**	55	93	244–246	244–245 [58]
18	C_6H_5CHO	CO_2Et (**3b**)	**7j**	60	88	167–168	166–168 [61]
19	$3\text{-}O_2NC_6H_4CHO$	CO_2Et (**3b**)	**7k**	65	93	189–190	188–190 [61]
20	$3\text{-}ClC_6H_4CHO$	CO_2Et (**3b**)	**7l**	50	91	202–204	202–204 [61]

Reaction conditions: 1 mmol of each reactant, water (5 mL), SM (10 mol %), 70 °C

[a] Yields refer to the pure isolated products

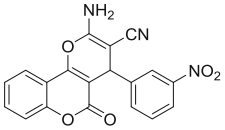
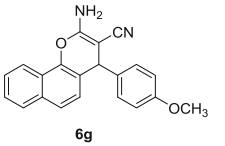
filtration. Substrates (**1**, **2c** and **3a**) were reacted together with the same molar ratios in the filtrate-containing catalyst. The result showed a slight decrease of yield in the first three runs (92, 89 and 86%), while in the fourth run the yield dropped to 79%, probably due to the possibility of a reduction in the amounts of catalyst in the recovery phase.

Mechanistically, we believe that this reaction goes via a Knoevenagel condensation of aldehydes with active cyano compounds (**3a** and **3b**) to provide the corresponding electron-deficient arylidene nitrile intermediates **D** (Knoevenagel adducts). On the other hand, the role of SM in aiding enol-keto tautomerism in hydroxyl-containing compounds (**1**, **5a** and **5b**) to **E** is also envisioned. Then, Michael-type addition of compounds **1**, **5a** and **5b** to arylidene nitriles (**D**) takes place to provide intermediates **B** and followed by intramolecular *O*-attack heterocyclization (Thorpe–Ziegler type reaction) to provide intermediates



Scheme 3 A plausible reaction mechanism for the synthesis of **4a–u**, **6a–h**, and **7a–l**

Table 4 Comparative study of SM for the one-pot three-component synthesis of **4c** and **6g**

Entry	Compounds	Catalyst/conditions	Time (min)	Yield (%)	References
1	 **4c**	Borax/EtOH, reflux	120	76	[28]
2		Urea/H_2O-EtOH, rt	180	97	[20]
3		PPI/H_2O, reflux	10	93	[70]
4		KHP/H_2O, 50 °C	180	88	[72]
5		Amberlyst A21/EtOH, rt	30	85	[27]
6		$BF_3{\cdot}SiO_2$/solvent-free, 50 °C	15–25	94	[29]
7		HMTA/EtOH, reflux	25	95	[22]
8		Morpholine/H_2O, reflux	240	80	[33]
9		Silica gel/absolute EtOH, rt	240	93	[32]
10		DMBA/EtOH, 60 °C	7	97	[73]
11		CTAB/H_2O, r.t.	60	95	[35]
12		Fe_3O_4@SiO_2–imid–PMA^n/H_2O, reflux, US	6	93	[64]
13		Sodium acetate/H_2O, US	7	85	[62]
14		Starch solution/50 °C	60	86	[19]
15		$HCOONH_4$/H_2O–EtOH, rt	60	92	[34]
16		SM/H_2O, 70 °C	15	96	This work
17	 **6g**	Basic alumina/H_2O, 100 °C	180	83	[39]
18		Mg/Al hydrotalcite/140 °C, MW, SF	16	76	[45]
19		I_2/K_2CO_3/H_2O, 100 °C	60	89	[36]
20		$H_{14}[NaP_5W_{30}O_{110}]$/$H_2O$, 100 °C	195	91	[46]
21		$NaHCO_3$/grinding	90	79	[38]
22		TBAC/H_2O, 100 °C	150	96	[58]
23		CeO_2–CaO/H_2O, 80 °C	75	81	[48]
24		Amberlyst A21/EtOH, rt	360	71	[27]
25		Nano-$Na_2CaP_2O_7$/H_2O, reflux	300	76	[41]
26		CTAB/H_2O, US	150	88	[37]
27		Imidazole/EtOH, reflux	30	92	[54]
28		Nano-MgO/(PEG–H_2O)	90	82	[40]
29		PPI/H_2O, reflux	35	93	[69]
30		KHP/H_2O, 50 °C	285	93	[72]
31		Na_2CO_3/H_2O, US	12	84	[63]
32		$PAN_{DMAP}F$/different solvents, reflux	60	96	[59]
33		$(NH_4)_2HPO_4$/H_2O–EtOH, reflux	150	84	[52]
34		Amino-functionalized MCM-41/H_2O, 70 °C	120	70	[53]
35		SM/H_2O, 70 °C	35	94	This work

rt room temperature, *PPI* potassium phthalimide, *KHP* potassium hydrogen phthalate *HMTA* hexamethylenetetramine, *DMBA* *N*,*N*-dimethylbenzylamine, *CTAB* cetyltrimethylammonium bromide, *US* ultrasound, *MW* microwave, *SF* solvent-free, *TBAC* tetrabutylammonium chloride, $PAN_{DMAP}F$ (4-dimethylaminopyridine) functionalized polyacrylonitrile fiber catalyst, *SM* sodium malonate

C which undergoes tautomerization and finally desired highly functionalized chromenes (**4a–u**, **6a–h** and **7a–j**) are formed (Scheme 3).

A comparative study on the catalytic performance of SM with other reported catalysts for the one-pot, three-component synthesis of **4c** and **6g** as typical examples are shown in Table 4. This comparison clearly indicates that the current work is better or comparable with others in terms of environmental safety, yields and reaction times. Furthermore, this method requires only sodium malonate as base and there is no need for the synthesis of the catalyst, ball-milling, microwave heating or ultrasound irradiation.

Conclusions

In conclusion, this study describes the first report on a one-pot, 3CR, sodium malonate-catalyzed synthesis of various dihydropyrano[3,2-*c*]chromenes, 2-amino-4-aryl-4*H*-benzo[*h*]chromenes and 3-amino-1-aryl-1*H*-benzo[*f*]chromenes. The present method provided an attractive alternative to the existing procedures for the synthesis of such significant heterocyclic compounds. The key advantages of the present method are high yields, no need for catalyst synthesis, operational simplicity, no column chromatography, the absence of tedious separation procedures, clean reaction profiles, the use of an inexpensive and environmentally benign solvent, and the reusability of the reaction medium.

Acknowledgement The authors would like to Damghan University for its partial financial support.

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