J IRAN CHEM SOC
DOI 10.1007/s13738-014-0514-7

ORIGINAL PAPER

Bismuth triflate, $Bi(OTf)_3$, as an efficient and reusable catalyst for synthesis of dihydropyrano[3,2-*b*]chromenediones

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Received: 1 May 2014 / Accepted: 18 July 2014

Abstract $Bi(OTf)_3$ was found to be an efficient, reusable and high yielding catalyst for the synthesis of dihydropyrano[3,2-*b*]chromenediones via the three-component reaction of aromatic aldehydes, kojic acid and 1,3-diones. The catalyst could be separated and recovered easily, and was reused for several runs without significant loss of its activity.

Keywords Chromenediones · Kojic acid · Bismuth triflate · Multi-component reaction · 1,3-Diones

Introduction

Chromenes are an important class of fused oxygenated heterocycles which have attracted significant attention due to their pharmacological and therapeutic properties such as antibacterial [1], anticancer [2], anti-anaphylactic [3], and anticonvulsant activities [4]. These heterocyclic compounds have been also used as cognitive enhancers as well as for the treatment of Alzheimer's, Parkinson's, and Huntington's diseases [5, 6]. Recently, kojic acid (a derivative of 4-pyrone and as a source of OH-acid) has been used as a useful component for the synthesis of chromenes. The compounds containing this inexpensive component have attracted much synthetic interest, owing to their wide variety of biological activities [7–10]. In spite of a broad range of application of chromene derivatives, little attention has been paid to the synthesis of dihydropyrano[3,2-*b*]chromenediones using kojic acid and only a few reports are available dealing with the synthesis of these imperative heterocycles [11–13]. Consequently, the development of an efficient and convenient synthetic method of chromene derivatives using a recyclable and environmentally benign catalyst is highly desirable.

In recent years, multi-component reactions (MCRs) have attracted a great deal of interest in organic and medicinal chemistry due to the construction of biologically active compounds with significant structural diversity [14–17]. In fact, these reactions have been recognized as efficient, fast, economically and environmentally favorable processes over the complicated stepwise methods [18–20]. Therefore, the synthesis of heterocyclic compounds of biological significance via MCRs has been the spotlight of many researchers.

During the past years, Bi(III) salts have concerned the attention of synthetic organic chemists as effective catalysts because of their low toxicity, ease of handling, low cost and relative insensitivity to air and moisture [21–26]. Among the Bi(III) salts, $Bi(OTf)_3$ is the most efficient catalyst, and particularly pretty because it is commercially available or can be easily prepared from commercially available starting materials [27–39].

As a part of our continuing efforts in developing efficient synthetic methodologies for the preparation of fine chemicals [40–44], we report herein a convenient and highly efficient protocol for the synthesis of dihydropyrano[3,2-*b*]chromenediones via a one-pot, three-component reaction of aldehydes, kojic acid and dimedone or 1,3-cyclohexanedione catalyzed by $Bi(OTf)_3$ under solvent-free conditions (Scheme 1).

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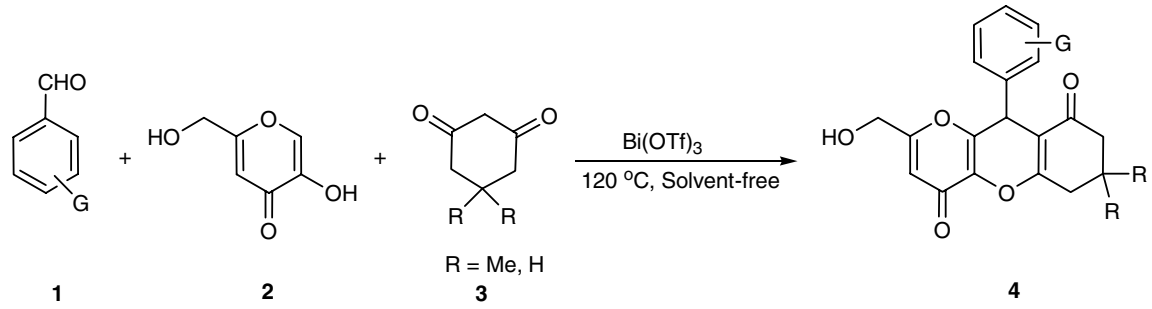
Published online: 13 August 2014



Scheme 1 Synthesis of dihydropyrano[3,2-*b*]chromenediones in the presence of $Bi(OTf)_3$ catalyst

Experimental section

Melting points were determined with a Stuart Scientific SMP2 apparatus. FT-IR spectra were recorded on a Jasco 6300D spectrophotometer. ^{1}H and ^{13}C NMR spectra (400 and 100 MHz) were recorded on a Bruker Avance 400 MHz spectrometer using $CDCl_3$ solvent. Mass spectra were recorded on a Platform II spectrometer from Micromass; EI mode at 70 eV.

General procedure for the synthesis of dihydropyrano[3,2-*b*]chromenediones

A mixture of aromatic aldehyde (1 mmol), kojic acid (1 mmol), 1,3-diones (1 mmol) and $Bi(OTf)_3$ (0.05 mmol) was stirred at 120 °C for the appropriate time according to Table 2. The progress of the reaction was monitored by TLC (eluent: *n*-hexane–EtOAc, 1:2). After completion of the reaction, the mixture was cooled to room temperature, chloroform (10 mL) was added and the catalyst was separated by simple filtration. The solvent was evaporated and the resulting crude product was purified by chromatography on silica gel to afford the pure product (Table 2).

Characterization data of some representative compounds

10-(3,4-Dimethoxyphenyl)-2-(hydroxymethyl)-7,7-dimethyl-7,8-dihydropyrano[3,2-b]chromene-4,9-(6H,10H)-dione (**4h**): Mp: 182–184 °C. FT-IR (KBr): ν_{max} = 3,385, 2,959, 1,671, 1,636, 1,613, 1,444, 1,372, 1,213, 1,189, 1,076 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.08 (s, 3H),1.14 (s, 3H), 1.54 (bs, 1H), 2.27 (AB-q, 2H, J = 16.8 Hz), 2.66 (AB-q, 2H, J = 18.0 Hz), 3.85 (s, 3H), 3.86 (s, 3H), 4.42 (AB-q, 2H, J = 15.6 Hz), 4.85 (s, 1H), 6.52 (s, 1H), 6.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.26, 29.16, 32.23, 37.93, 40.89, 50.42, 55.87, 55.95, 60.67, 111.31, 112.19, 112.43, 120.28, 133.17, 137.41, 148.54, 149.09, 151.80, 163.72, 167.42, 171.33, 196.30. MS: *m/z* (%): 412.15 ([M]$^+$, 4.58), 303.41 (2.80), 274.00 (3.18), 243.21 (3.18), 165.43 (5.06), 97.14 (7.18), 55.14 (33.19), 43.30 (71.55).

2-(Hydroxymethyl)-7,7-dimethyl-10-(naphthalen-2-yl)-7,8-dihydropyrano[3,2-b]chromene-4,9-(6H,10H)-dione (**4j**): Mp: 237–239 °C. FT-IR (KBr): ν_{max} = 3,300, 2,955, 1,671, 1,639, 1,377, 1,216, 1,195, 1,078, 862 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.06 (s, 3H),1.14 (s, 3H), 1.76 (bs, 1H), 2.25 (AB-q, 2H, J = 16.8 Hz), 2.48 (AB-q, 2H, J = 17.6 Hz), 4.37 (AB-q, 2H, J = 15.6 Hz), 5.08 (s, 1H), 6.53 (s, 1H),7.41 (dd, 1H, J = 8.8, 2.0 Hz), 7.46–7.49 (m, 2H), 7.75–7.82 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.42, 29.03, 32.30, 38.58, 40.93, 50.42, 60.69, 112.36, 112.43, 125.82, 126.22, 126.40, 127.32, 127.65, 127.94, 128.68, 132.82, 133.32, 137.68, 138.01, 151.56, 163.79, 167.03, 171.21, 196.14. MS: *m/z* (%): 402.08 ([M]$^+$, 5.15), 384.20 (9.93), 271.78 (6.43), 164.69 (8.82), 127.40 (18.87), 57.05 (91.18), 43.10 (100.00).

2-(Hydroxymethyl)-7,7-dimethyl-10-(thiophen-2-yl)-7,8-dihydropyrano[3,2-b]chromene-4,9-(6H,10H)-dione (**4k**): Mp: 195–197 °C. FT-IR (KBr): ν_{max} = 3,370, 3,099, 2,955, 1,666, 1,633, 1,376, 1,220, 1,191, 1,073 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.13 (s, 3H), 1.15 (s, 3H), 2.14 (bs, 1H), 2.32 (s, 2H), 2.66 (AB-q, 2H, J = 18.0 Hz),4.48 (AB-q, 2H, J = 16.0 Hz), 5.25 (s, 1H), 6.55 (s, 1H), 6.93 (dd, 1H, J = 4.8, 3.6 Hz), 6.97 (dd, 1H, J = 3.6, 0.8 Hz), 7.19 (dd, 1H, J = 5.6, 0.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.43, 29.13, 32.21, 33.12, 40.90, 50.40, 60.70, 111.98, 112.42, 125.26, 125.89, 127.12, 137.37, 143.87, 150.40, 164.10, 167.04, 171.12, 196.05. MS: *m/z* (%): 358.04 ([M]$^+$, 5.35), 340.05 (5.92), 83.19 (33.88), 57.23 (76.64), 55.21 (100.00).

2-(Hydroxymethyl-10-phenyl-7,8-dihydropyrano[3,2-b]chromene-4,9-(6H,10H)-dione (**4l**): Mp: 182–184 °C. FT-IR (KBr): ν_{max} = 3,418, 2,927, 1,671, 1,632, 1,377, 1,220, 1,077, 703, 640 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.06–2.11 (m, 2H), 2.25 (bs, 1H), 2.34–2.49 (m, 2H), 2.72–2.90 (m, 2H), 4.43 (AB-q, 2H, J = 15.6 Hz), 4.97 (s, 1H), 6.61 (s, 1H), 7.24 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.24, 27.37, 36.58, 38.35, 60.79, 112.17, 113.52, 127.85, 128.09, 128.88, 137.40, 140.39, 152.37,

165.50, 167.93, 196.17. MS: *m/z* (%): 324.05 ($[M]^+$, 3.28), 247.10 (4.31), 128.17 (4.87), 97.22 (10.13), 77.18 (100.00), 55.21 (89.24).

2-(Hydroxymethyl)-10-(3-nitrophenyl)-7,8-dihydroxypyrano[3,2-b]chromene-4,9-(6H,10H)-dione (**4m**): Mp: 210–212 °C. FT-IR (KBr): ν_{max} = 3,352, 3,060, 2,944, 1,671, 1,626, 1,595, 1,528, 1,441, 1,378, 1,349, 1,223, 1,062 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.01–2.19 (m, 2H), 2.36–2.48 (m, 2H), 2.63 (t, 1H, J = 6 Hz), 2.73–2.95 (m, 2H), 4.38 (dd, 1H, J = 15.6, 5.6 Hz), 4.45 (dd, 1H, J = 18.0, 6.0 Hz), 5.08 (s, 1H), 6.54 (s, 1H), 7.50–7.55 (m, 1H), 7.65–7.68 (m, 1H), 8.12–8.15 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.21, 27.39, 36.47, 38.24, 60.68, 112.53, 112.70, 122.95, 123.07, 129.79, 134.32, 142.49, 148.58, 149.93, 166.29, 166.88, 170.98, 196.16. MS: *m/z* (%): 369.08 ($[M]^+$, 65.49), 351.07 (50.20), 323.08 (56.86), 247.06 (86.67), 152.08 (58.04), 77.05 (90.98), 54.85 (100.00).

10-(4-Chlorophenyl)-2-(hydroxymethyl-7,8-dihydropyrano[3,2-b]chromene-4,9-(6H,10H)-dione (**4n**): Mp: 183–185 °C. FT-IR (KBr): ν_{max} = 3,525, 3,085, 2,949, 1,669, 1,636, 1,602, 1,488, 1,215, 1,174, 864 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.59 (bs, 1H), 1.91–2.05 (m, 2H), 2.23–2.38 (m, 2H), 2.60–2.80 (m, 2H), 4.31 (AB-q, 2H, J = 15.6 Hz), 4.82 (s, 1H), 6.43 (s, 1H), 7.13 (d, 2H, J = 8.4 Hz), 7.20 (d, 2H, J = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.72, 26.83, 36.03, 37.27, 60.12, 111.83, 112.69, 128.51, 128.94, 133.21, 137.04, 138.51, 150.60, 165.25, 166.89, 170.65, 195.80. MS: *m/z* (%): 358.26 ($[M]^+$, 12.20), 322.60 (13.78), 247.16 (18.17), 110.72 (100.00), 54.89 (95.12).

2-(Hydroxymethyl)-10-(4-methoxyphenyl)-7,8-dihydropyrano[3,2-b]chromene-4,9-(6H,10H)-dione (**4o**): Mp: 180–182 °C. FT-IR (KBr): ν_{max} = 3,299, 2,896, 1,671, 1,637, 1,602, 1,439, 1,367, 1,203, 1,069, 834 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.73 (bs, 1H), 1.97–2.13 (m, 2H), 2.31–2.45 (m, 2H), 2.67–2.88 (m, 2H), 3.80 (s, 3H), 4.41 (AB-q, 2H, J = 16.0 Hz), 4.87 (s, 1H), 6.51 (s, 1H), 6.83 (d, 2H, J = 8.8 Hz), 7.18 (d, 2H, J = 8.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.26, 27.32, 36.60, 37.41, 55.27, 60.65, 112.18, 113.67, 114.19, 129.10, 132.75, 137.37, 151.96, 159.07, 165.45, 167.45, 171.32, 196.46. MS: *m/z* (%): 354.64 ($[M]^+$, 13.43), 335.01 (27.84), 307.16 (27.84), 246.68 (100.00), 127.04 (20.98), 76.98 (56.08), 55.03 (59.61).

4-(2-(Hydroxymethyl)-7,7-dimethyl-4,9-dioxo-4,6,7,8,9,10-hexahydropyrano[3,2-b]chromen-10-yl) benzaldehyde(**4p**): Mp: 218–220 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.97 (s, 3H), 1.06 (s, 3H), 2.18 (AB-q, 2H, J = 16.0 Hz), 2.57 (AB-q, 2H, J = 15.6 Hz), 4.32 (AB-q, 2H, J = 16.0 Hz), 4.92 (s, 1H), 6.45 (s, 1H), 7.39 (d, 2H, J = 8.0 Hz), 7.76 (d, 2H, J = 8.0 Hz), 9.90 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.95, 28.45, 31.82, 38.20, 40.41, 49.84, 60.11, 111.24, 111.88, 127.32, 128.40, 135.31, 137.30, 146.54, 149.99, 163.73, 166.68, 170.49, 191.15, 195.54.

Table 1 Optimization of the conditions for the synthesis of **4b**

Entry	Catalyst (mol %)	Temp (°C)	Time (min)	Yield (%)[a]
1	No catalyst	120	120	10
2	$H_3PW_{12}O_{40}$ (5)	120	20	55
3	$ZnCl_2$ (5)	120	20	35
4	$ZrOCl_2{\cdot}8H_2O$ (5)	120	20	30
5	$BiCl_3$ (5)	120	20	45
6	$Bi(NO_3)_3{\cdot}5H_2O$ (5)	120	20	60
7	$Bi(OTf)_3$ (5)	120	20	91
8	$Bi(OTf)_3$ (4)	120	20	80
9	$Bi(OTf)_3$ (6)	120	20	91
10	$Bi(OTf)_3$ (5)	80	20	45
11	$Bi(OTf)_3$ (5)	100	20	60
12	$Bi(OTf)_3$ (5)	110	20	78

[a] Isolated yield

Results and discussion

To optimize the reaction conditions, the reaction of 4-chlorobenzaldehyde, kojic acid and dimedone was first examined in the absence of the catalyst at 120 °C under solvent-free conditions and the product was obtained in only 10 % yield after 120 min (Table 1, entry 1). Then, the catalytic activity of some protic and Lewis acid catalysts such as $H_3PW_{12}O_{40}$, $ZnCl_2$, $ZrOCl_2{\cdot}8H_2O$, $BiCl_3$, $Bi(NO_3)_3{\cdot}5H_2O$, and $Bi(OTf)_3$ (5 mol %) (Table 1, entries 2–7) was investigated and the results showed that $Bi(OTf)_3$ is the most effective catalyst for the synthesis of desired dihydropyrano[3,2-*b*]chromenedione **4b** (Table 1, entry 7). The effect of amount of the catalyst on the yield of the product was subsequently examined using 4–6 mol % of $Bi(OTf)_3$ (Table 1, entries 7–9) and it was found that 5 mol % of the catalyst is optimal to carry out the reaction efficiently (Table 1, entry 7). The effect of temperature on this transformation was also studied, and the results demonstrated that 120 °C is the optimum temperature (Table 1, entries 7, 10–12). Thus, the best yield was achieved on employing 5 mol % of $Bi(OTf)_3$ at 120 °C under solvent-free conditions.

To substantiate the synthetic scope and the generality of the present protocol, a variety of aldehydes were used in this reaction and the results are shown in Table 2. Aromatic aldehydes carrying either electron donating or electron withdrawing groups reacted efficiently with kojic acid and dimedone, affording high yields of the corresponding dihydropyrano[3,2-*b*]chromenediones (Table 2, entries 1–10).

Table 2 Synthesis of dihydropyrano[3,2-*b*]chromenediones catalyzed by $Bi(OTf)_3$ under solvent-free conditions

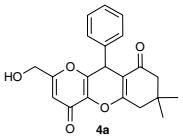
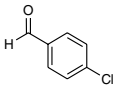
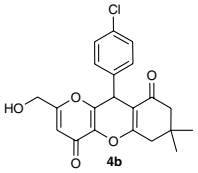
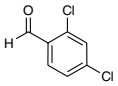
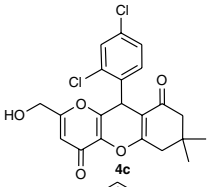
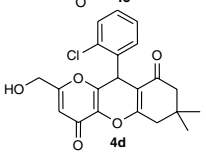
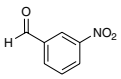
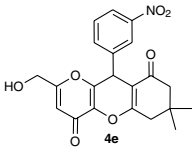
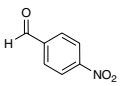
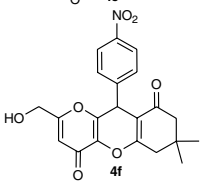
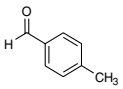
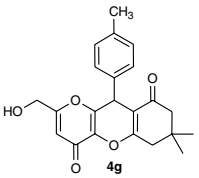
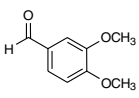
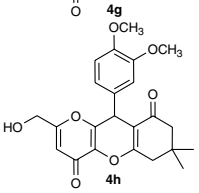
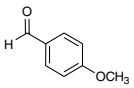
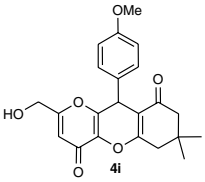
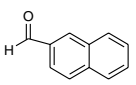
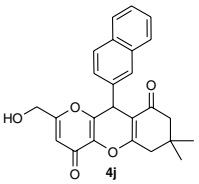
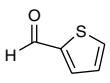
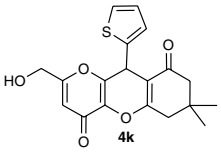
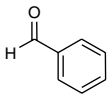
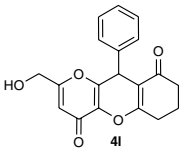
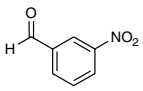
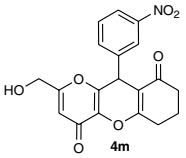
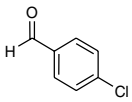
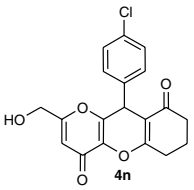
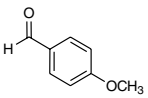
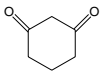
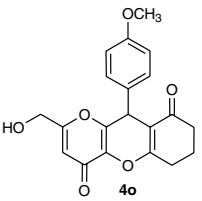
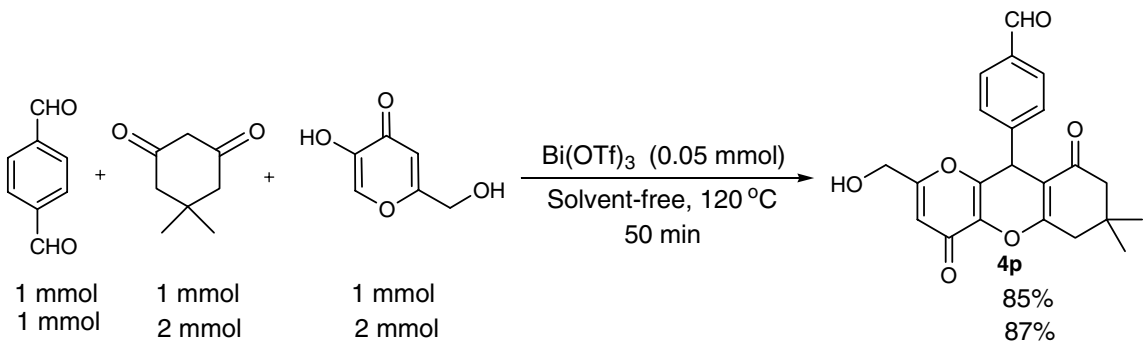
Entry	Aldehyde	Diketone	Product	Time (min)	Yield (%)[a]	Mp/°C (Lit)
1			 **4a**	20	90	187-189 (186-188 [11])
2			 **4b**	20	91	203-205 (205-206 [12])
3			 **4c**	20	94	168-170 (166-167 [12])
4			 **4d**	20	90	214-216 (216-217 [12])
5			 **4e**	20	95	213-215 (212-213 [13])
6			 **4f**	20	92	227-229 (229-230 [13])
7			 **4g**	25	88	214-216 (214-215 [12])
8			 **4h**	25	90	182-184
9			 **4i**	30	87	177-179 (178-179 [12])
10			 **4j**	45	85	237-239

Table 2 continued

Entry	Aldehyde	Diketone	Product	Time (min)	Yield (%)[a]	Mp/°C (Lit)
11				40	92	195-197
12				20	90	182-184
13				20	94	210-212
14				20	92	183-185
15				30	85	180-182

[a] Isolated yield

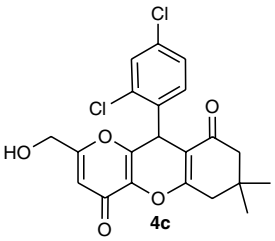
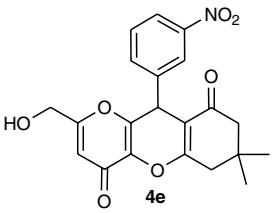
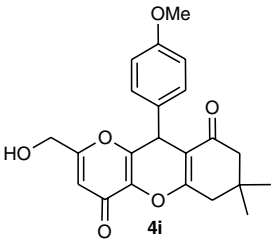


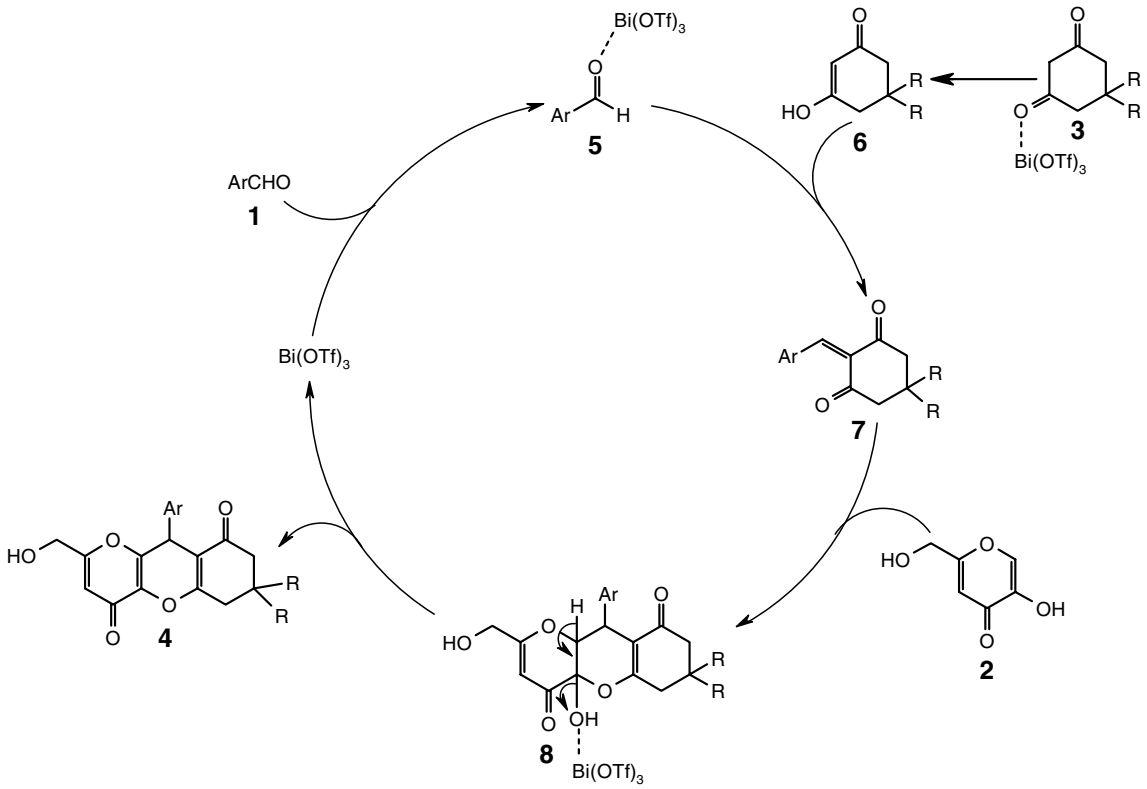
Scheme 2 Selective synthesis of mono-dihydropyrano[3,2-*b*]chromenedione by the reaction of terephthalaldehyde with kojic acid and dimedone catalyzed by $Bi(OTf)_3$

Acid-sensitive aldehyde such as thiophene-2-carbaldehyde also displayed good reactivity and gave the desired product in 92 % yield (Table 2, entry 11). Furthermore, the present methodology has been used successfully with cyclohexane-1,3-dione in place of dimedone, provided the corresponding dihydropyrano[3,2-*b*]chromenediones in high yields under the same conditions (Table 2, entries 12–15).

It is interesting to note that excellent selectivity was observed in the reaction of terephthalaldehyde with kojic acid and dimedone, the results of which are shown in Scheme 2. As it is seen, only one formyl group participated and the corresponding mono-dihydropyrano[3,2-*b*]chromenedione **4p** was obtained in high yield with excellent selectivity. It is also noteworthy that no bis-dihydropyrano[3,2-*b*]chromenedione was observed even

Table 3 Comparison of the results obtained by $Bi(OTf)_3$ with some of those reported by other reagents

Entry	Product	Catalyst (mmol)	Time (min)	Yield (%)	TOF (h^{-1})
1	 **4c**	$CeCl_3{\cdot}7H_2O/SiO_2$ (0.05 mmol) [12]	40	90	27.0
2		$KAl(SO_4)_2{\cdot}12H_2O$ (0.1 mmol) [13]	50	91	10.9
3		$Bi(OTf)_3$ (0.05 mmol)	20	94	56.4
4	 **4e**	$CeCl_3{\cdot}7H_2O/SiO_2$ (0.05 mmol) [12]	30	96	38.4
5		$KAl(SO_4)_2{\cdot}12H_2O$ (0.1 mmol) [13]	45	95	12.7
6		$Bi(OTf)_3$ (0.05 mmol)	20	95	57.0
7	 **4i**	$InCl_3$ (0.1 mmol) [11]	95	85	5.4
8		$CeCl_3{\cdot}7H_2O/SiO_2$ (0.05 mmol) [12]	45	88	23.5
9		$KAl(SO_4)_2{\cdot}12H_2O$ (0.1 mmol) [13]	70	87	7.5
10		$Bi(OTf)_3$ (0.05 mmol)	30	87	34.8



Scheme 3 Plausible mechanism for the $Bi(OTf)_3$-catalyzed synthesis of dihydropyrano[3,2-*b*]chromenediones

Table 4 Recycling results of $Bi(OTf)_3$ catalyst

Run	Cycle	Yield (%)[a]
1	0	91
2	1	90
3	2	89
4	3	86
5	4	82

Reaction conditions: 4-chlorobenzaldehyde (1 mmol), kojic acid (1 mmol), dimedone (1 mmol), $Bi(OTf)_3$, (0.05 mmol) at 120 °C for 20 min

[a] Isolated yield

with 2 mmol kojic acid and 2 mmol dimedone. Such selectivity has not been reported so far, and can be considered as a useful practical achievement in the synthesis of chromenediones, since the remaining formyl group can be renovated to some other important functional groups.

In Table 3, some of the results of our experiments are compared with those reported by other methods [11–13]. As seen in most cases, the yields are higher or comparable with the reported ones, and the amount of the catalyst is lower using this method. Moreover, the reaction times are shorter and the turnover frequencies (TOFs) are higher, indicating the efficiency of the present method.

A plausible mechanism for the formation of dihydropyrano[3,2-*b*]chromenedione derivatives is outlined in Scheme 3. At first, $Bi(OTf)_3$ activates the aldehyde **1** and also catalyzes the keto–enol tautomerization of 1,3-dione **3** to give **5** and **6**, respectively. Then, the reaction of **5** with **6** affords the heterodyne **7**. The Diels–Alder reaction of kojic acid **2** with **7** gives intermediate **8**, which upon dehydration in the presence of $Bi(OTf)_3$ furnishes the desired dihydropyrano[3,2-*b*]chromenedione **4** and releases the catalyst for the next catalytic cycle.

Finally, the recyclability of the catalyst was performed in the three-component reaction of 4-chlorobenzaldehyde, kojic acid and dimedone. After completion of the reaction, the mixture was allowed to cool to room temperature and chloroform (10 mL) was added. The catalyst was separated by simple filtration, dried at 80 °C and reused. The results indicate that the catalytic activity of $Bi(OTf)_3$ did not decrease significantly even after four catalytic cycles (Table 4).

Conclusion

In conclusion, we have demonstrated a convenient, highly efficient, and environmentally benign procedure for the synthesis of structurally diverse dihydropyrano[3,2-*b*]chromenedione derivatives by the one-pot three-component reaction of aromatic aldehydes, kojic acid and 1,3-diones catalyzed by $Bi(OTf)_3$ under solvent-free conditions. High yields, short reaction times, simple experimental procedure, high atom-economy, and the use of eco-friendly and recyclable catalyst are the important features of this new method in the synthesis of these important heterocyclic compounds.

Acknowledgments The authors are grateful to the Research Council of the University of Isfahan for financial support of this work.

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