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$B(C_6F_5)_3$ catalyzed synthesis of dihydropyrano[3,2-b] chromenediones under solvent-free conditions

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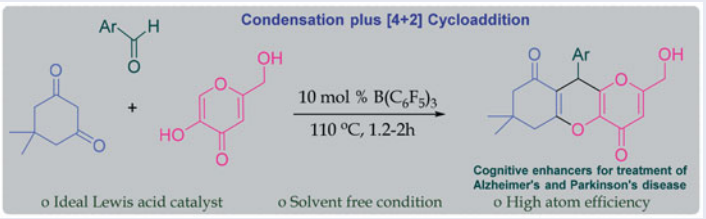
ABSTRACT

A simple, efficient, solventless, and one step, $B(C_6F_5)_3$ catalyzed, synthesis of dihydropyrano[3,2-b]chromenediones from dimedone, aldehyde and kojic acid is described. This protocol proceeds smoothly, accommodates aromatic as well as heteroaromatic aldehydes and gives dihydropyrano[3,2-b]chromenediones in excellent yield.

GRAPHICAL ABSTRACT



ARTICLE HISTORY
Received 16 August 2018

KEYWORDS
Aldehyde; chromenedione; dimedone; kojic acid; tris(pentafluoro-phenyl)borane

Introduction

Diversity-oriented, one-pot multi-component synthesis, especially of compounds having molecular skeleta found in both natural products and drug-like molecules, have attracted the attention of both academic and industrial researchers.[1] Being efficient and highly convergent, multi-component reactions (MCRs) produces structurally and stereochemically complex molecules in a single step.[2] Chromenes are known for their several biological activities such as anticonvulsant,[3] anti-anaphylactic,[4] anticancer,[5] antibacterial[6] and are used for the treatment of Huntington's, Parkinson's and Alzheimer's diseases.[7,8] kojic acid and its derivatives also exhibit many therapeutic applications. It inhibits melanin formation by suppressing tyrosinase and acts as a good skin lightener.[9] Moreover, it also acts as an antioxidant[10] in foodstuff, insecticide,[11] pesticide, herbicide,[12] antimicrobial agent[13] and bidentate ligand to form biologically

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potent metal complexes.[14] Heterocyclic compounds harboring chromene and kojic acid nucleus exhibit even more biological activities involving antifungal,[15] antineoplastic,[16] antiproliferative,[17] anti-HIV,[18] antiviral,[19] anticonvulsant,[20] anti-inflammatory,[21] anti-oxidative,[22] antibacterial,[23] antimicrobial agent,[24] tyrosinsae inhibitor[9] or skin whitening agent[9] and antimelanogenic.[25] Chromenes[26] and kojic acid derivatives[25] exhibit diverse biological potencies.

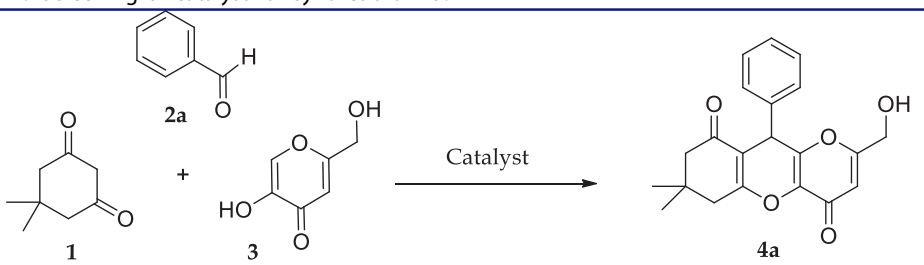
Because of easy availability, lability and biological potency of inexpensive kojic acid, several kojic acid derivatives have been synthesized.[27] In spite of the applications of chromene analogs, little attention has been paid to the synthesis of dihydropyrano[3,2-b] chromenediones and only a few methods are accessible, which deal with the synthesis of the essential heterocycles. In recent years, $InCl_3$, Alum, $CeCl_3{\cdot}7H_2O/SiO_2$, $FeCl_3/SiO_2$, $Bi(OTf)_3$, β-cyclodextrin, $Yb(PFO)_3$ and chloroaluminate ionic liquid-modified silica-coated magnetic nanoparticles have been used as a catalyst for the synthesis of dihydropyrano[3,2-b]chromenediones.[28–35] However, many of these reported synthetic methods suffer either from high temperature, longer reaction times, low yield, use of toxic solvents and a significant amount of moisture sensitivity and expensive catalysts. Although the reported methods are useful, the development of additional efficient synthetic methods with efficient catalysts is still in demand. Therefore, owing to the pharmaceutical and synthetic importance of dihydropyrano[3,2-b] chromenediones, development of a direct and efficient synthetic method is highly desirable.

Moderate Lewis acidic nature of BCF facilitates its usage in organic synthesis. In recent times, Tris(pentafluorophenyl)Borane (BCF) has evolved as a mild, non-toxic, environmentally benign, moisture-tolerant, air-stable, heat-stable, inherently electrophilic, moderate and versatile Lewis acid imparting high chemo-, region- and stereoselectivity in many organic transformations.[36] Low catalytic loading and moisture-tolerance, makes BCF a superior acid catalyst than traditional Lewis acids. In this paper, we report one step and convenient synthetic method for the synthesis of a series of dihydropyrano[3,2-b]chromenedione derivatives from Dimedone, aldehydes and kojic acid under solvent-free conditions in the presence of $B(C_6F_5)_3$ as an efficient solid Lewis acid catalyst.

Results and discussion

To demonstrate our methodology, we purchased kojic acid, substituted benzenoid as well as non benzenoid aromatic/heteroaromatic aldehydes and dimedone commercially and used without any purification. Synthesis of dihydropyrano[3,2-b]chromenediones (**4a–l**) has been achieved from dimedone (**1**), aldehyde (**2a–l**), and kojic acid (**3**) in the presence of $B(C_6F_5)_3$ as a solid acid catalyst at 110 °C. The structure of products (**4a–l**) was confirmed by comparing spectroscopic data with literature values. To optimize reaction conditions, we initially examined the role of catalyst and screened several solid acid catalysts. Dimedone (**1**), benzaldehyde (**2a**) and kojic acid (**3**) were selected as model starting materials and the reaction was carried out under solvent-free condition at 110 °C using 10 mol% of $B(C_6F_5)_3$ as a catalyst. The progress of the reaction was checked by TLC and after 2 h the product **4a** was obtained in 55% yield (Table 1, entry

Table 1. Screening of catalyst for synthesis of **4a**.



Entry	Catalyst (mol%)	Temp (°C)	Time (min)	Yield[a] (%)
1	–	110	200	00
2	$B(C_6F_5)_3$ (1)	110	120	55
3	$B(C_6F_5)_3$ (2)	110	120	67
4	$B(C_6F_5)_3$ (5)	110	90	75
5	$B(C_6F_5)_3$ (10)	110	90	83
6	$B(C_6F_5)_3$ (15)	110	90	84
7	p-TsOH (10)	110	90	32
8	Fe_3O_4 (10)	110	90	41
9	$ZnCl_2$ (10)	110	90	47
10	$BiCl_3$ (10)	110	90	54
11	$FeCl_3$ (10)	110	90	69
12	DABCO	110	90	30

[a]Yield refers to an isolated yield after column chromatography.

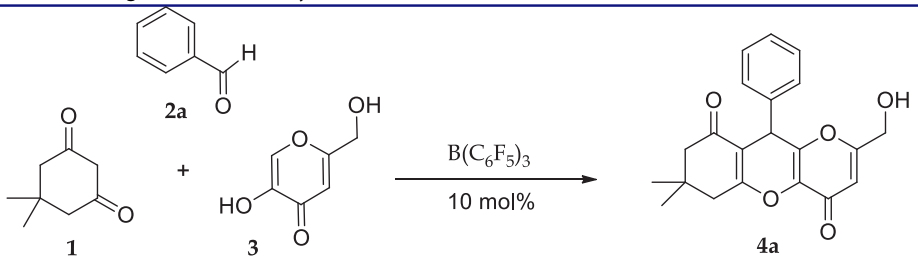
1). The formation of compound **4a** was confirmed by comparing ^1H, ^{13}C-NMR and mass spectroscopic data with literature data.

In order to enhance the yield of compound **4a**, we repeated the same reaction with 2, 5, 10 and 15 mol% of $B(C_6F_5)_3$ and we got product **4a** in 83% yield within 1.5 h when 10 mol% of BCF was used as catalyst (Table 1, entry 5). To realize the efficiency of $B(C_6F_5)_3$, same reaction was repeated with different solid acid catalysts such as p-TsOH, Fe_3O_4, $ZnCl_2$, $FeCl_3$, $BiCl_3$, $B(C_6F_5)_3$ and basic catalyst DABCO. Among these tested solid acid catalysts, BCF was found as excellent catalysts in terms of reaction time and chemical yield (Table 1, entry 5). To know the effect of solvent on chemical yield of this reaction, we performed same reaction with different solvents such as tetrahydrofuran, toluene[28], dichloromethane,[28] diethyl ether, acetonitrile[28], ethanol[28] and water and found that solvent-free condition provides the best results (Table 2, entry 1). Therefore, the use of 10 mol% of $B(C_6F_5)_3$ under the neat condition is superior for this conversion.

Under the optimized reaction conditions, we synthesized several dihydropyrano[3,2-b]chromenediones (**4a–l**) using aromatic/heteroaromatic aldehydes in 72–90% yield. All mentioned reactions proceeded well to give the corresponding product in excellent yields and accommodated multifunctional aldehydes also. However, sterically unhindered and more electrophilic aldehydes (Table 3, entries **4g–j**) gave excellent yields in shorter reaction times than those of hindered and less electrophilic aldehydes (Table 3, entry **4d** and **4e**).

Based on the above results and literature reports,[24] a plausible mechanism for the synthesis of dihydropyrano[3,2-b]chromenediones is illustrated in Scheme 1. $B(C_6F_5)_3$ coordinates with the carbonyl oxygen of aldehyde and makes it more susceptible towards the nucleophilic attack by enol form of dimedone giving enone. Enone cyclises

Table 2. Screening of solvent for synthesis of **4a**.



Entry	Solvent	Temp (°C)	Time (min)	Yield[a] (%)
1	–	110	90	83
2	THF	66	180	42
3	Toluene	110	180	24
4	DCM	40	180	26
5	CH_3CN	82	180	45
6	Et_2O	35	180	32
7	$CHCl_3$	50	180	35
8	EtOH	80	180	22
9	H_2O	100	180	n.d.

[a]Yield refers to an isolated yield after column chromatography.

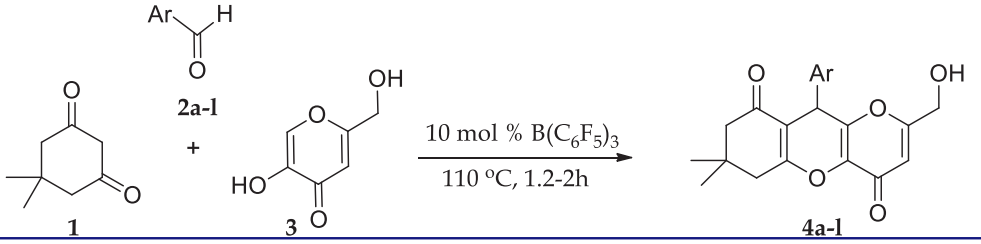
with kojic acid by [4 + 2] cycloaddition pericyclic reaction to give the final adduct (**4a–l**).

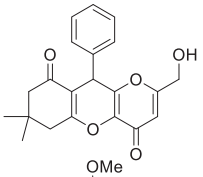
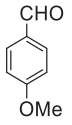
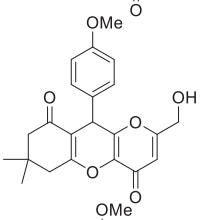
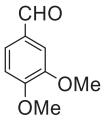
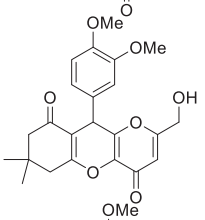
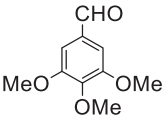
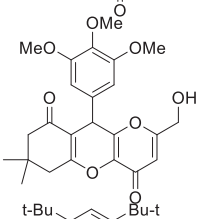
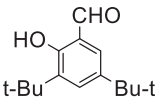
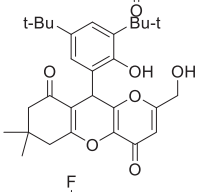
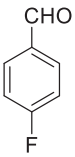
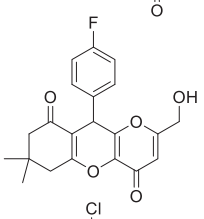
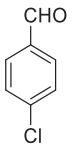
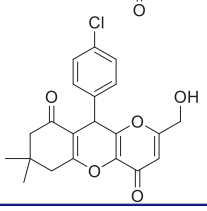
Experimental

General procedure for the synthesis of 2-(hydroxymethyl)-7,7-dimethyl-10-phenyl-6,7,8,10-tetrahydropyrano[3,2-b]chromene-4,9-dione (4a)

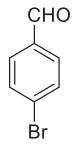
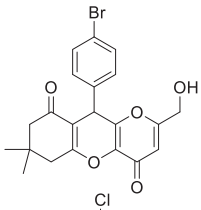
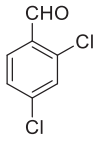
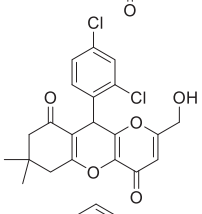
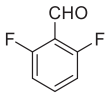
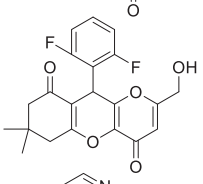
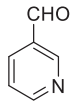
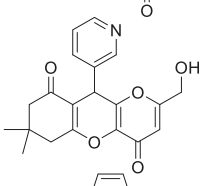
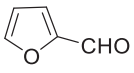
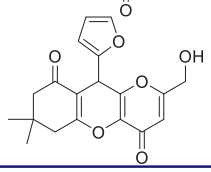
Dimedone 1 (50 mg, 0.357 mmol), Benzaldehyde 2a (38 mg, 0.358 mmol), kojic acid 3 (50 mg, 0.352 mmol) and Tris(pentafluorophenyl)Borane (10 mol%) was charged in a round bottom flask. The resulting reaction mass was stirred at 110 °C for 1.5 h. After complete conversion, as indicated by TLC, the reaction was quenched with water (5 ml) and extracted with ethyl acetate (3 × 5 mL). Organic layer was washed with brine and dried over anhydrous Na_2SO_4, filtered and concentrated in vacuum. The crude product was purified by column chromatography over silica gel using ethyl acetate–hexane (6:4) as eluent to afford the pure product **4a** in 83% yield. White solid (104 mg (83%) yield), mp 184–186 °C (lit.[1] mp: 186–188 °C); TLC R_f = 0.49 (EtOAc: Hexane = 6:4); IR ν_{max} (KBr, cm^{-1}): 3364, 3076, 2948, 1664, 1619, 1521, 1374, 1210, 1191, 1073, 993, 952, 716; ^{1}H NMR (400 MHz, $CDCl_3$ & DMSO-d_6): δ 1.04 (s, 3H), 1.13 (s, 3H), 2.28–2.20 (m, 2H), 2.70–2.60 (m, 2H), 4.45–4.38 (m, 2H), 4.88 (s, 1H), 6.54 (s, 1H), 7.38–7.21 (m, 5H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 27.4, 28.9, 32.2, 38.3, 40.8, 50.3, 60.4, 112.0, 112.2, 127.7, 128.0, 128.7, 137.4, 140.4, 151.7, 163.9, 167.9, 171.4, 196.3; HRMS (ESI) m/z $[M + H]^+$ Calculated for $C_{21}H_{21}O_5$: 353.1311, found: 353.1383.

Table 3. Synthesis of dihydropyrano[3,2-b]chromenediones (**4a–l**) under $B(C_6F_5)_3$ catalysis.

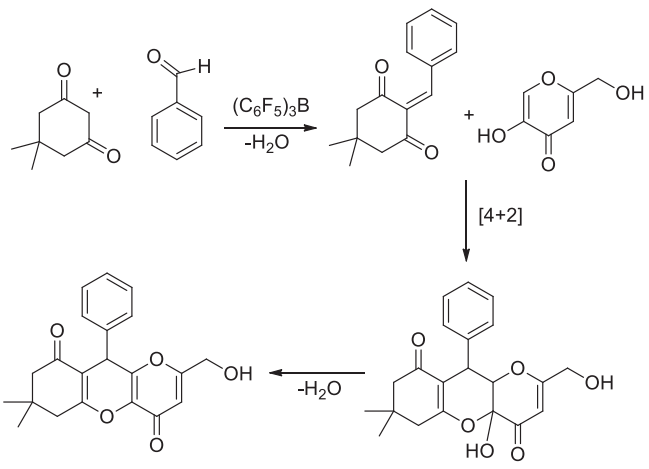


Entry	Aldehyde	Product	Time (min)	Yield[a] (%)
4a			90	83
4b			95	80
4c			95	78
4d			95	75
4e			100	72
4f			80	88
4g			85	84

(*continued*)

4h			85	82
4i			75	87
4j			70	90
4k			80	85
4l			90	78

[a]Yield refers to an isolated yield after column chromatography.



Scheme 1. Plausible mechanism for formation of **4a–l.**

10 -(2,6-difluorophenyl)-2-(hydroxymethyl)-7,7-dimethyl-6,7,8,10-tetrahydropyrano[3,2-b]chromene-4,9-dione (4j)

White solid (122 mg (90%) yield), mp 153–155 °C; TLC R_f = 0.37 (EtOAc: Hexane = 6:4); IR ν_{max} (KBr, cm^{-1}): 3388, 2959, 1728, 1635, 1586, 1467, 1377, 1228, 1148, 1003, 790; ^{1}H NMR (400 MHz, $CDCl_3$ & DMSO-d_6): δ 1.07 (s, 3H), 1.14 (s, 3H), 2.29–2.17 (m, 2H), 2.60–2.55 (m, 2H), 4.13 (s, 1H), 4.49–4.44 (m, 2H), 5.26 (s, 1H), 6.46 (s, 1H), 7.27–7.21 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 27.4, 29.0, 32.3, 37.9, 40.8, 50.4, 60.4, 66.4, 112.0, 129.0, 129.5, 133.7, 137.5, 139.0, 151.2, 164.2, 168.4, 171.4, 196.4; HRMS (ESI) m/z $[M+H]^+$ Calculated for $C_{21}H_{19}F_2O_5$: 389.1201, found: 389.1174.

Conclusion

In conclusion, we have developed a BCF catalyzed direct one pot, simple, efficient, solvent-free synthetic protocol for the exclusive synthesis of dihydropyrano[3,2-b]chromenediones from dimedone, aldehyde and kojic acid in good to excellent yields. High yields, shorter reaction times, easy workup, high atom-economy, solvent-free conditions, low cost and easy handling of the catalyst are important highlights of this protocol.

Acknowledgments

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