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CAN-catalyzed synthesis of 10-arylpyrano[3,2-*b*] chromene-4,9-diones under solvent-free conditions

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Abstract A novel and efficient one-pot synthesis of 10-aryl-7,8-dihydropyrano[3,2-*b*]chromene-4,9(6*H*,10*H*)-diones by three-component reaction of aromatic aldehydes, 5-hydroxy-2-methylpyran-4-one, and cyclic 1,3-dicarbonyl compounds in the presence of a catalytic amount of ceric ammonium nitrate under solvent-free conditions is described. The advantages of this method include operational simplicity, short reaction time, recyclable catalyst, and high yields.

Keywords MCRs · CAN · Pyrano[3,2-*b*]chromene · Synthesis · Solvent-free

Introduction

Pyrans and fused pyran derivatives are an important structural groups in many natural and synthetic compounds with a wide range of biological activity, for example anticancer [1], anti-tuberculosis [2], anti-HIV [3], calcium channel antagonist activity [4], anti-fungal agents [5], antimicrobial [6], antiproliferative [7], antidiabetic [8], anti-inflammatory, and antiviral [9]. Pyranochromenes, also, are known for their biological properties including antioxidant and cytotoxic activity [10]. Because of the importance of pyranochromene derivatives, different synthetic methods have been developed for synthesis of this group of compounds. Miyazaki et al. [11] prepared tricyclic compounds containing the pyranochromene skeleton in very good yields from salicylaldehyde dimethyl acetal and unsaturated alcohols in benzene in the presence of *p*-toluenesulfonic acid (*p*-TsOH). Yadav et al. [12] reported the reaction of glycals, *o*-hydroxybenzaldehydes, and trimethyl orthoformate in the presence of a catalytic amount of scandium triflate under mild

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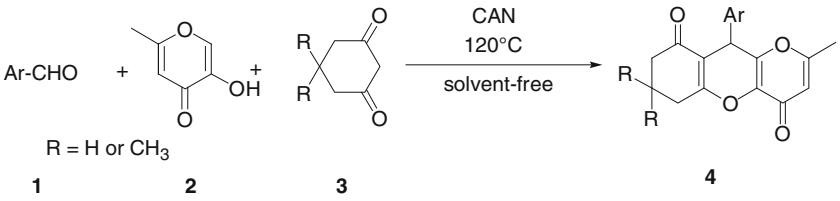
reaction conditions to afford the corresponding *cis*-annelated pyranochromenes in good yields with high diastereoselectivity. Reddy et al. [13] reported the synthesis of dihydropyrano[3,2-*b*]chromenediones via three-component coupling of kojic acid, aldehydes, and 1,3-diones, with $InCl_3$ as catalyst, under solvent-free conditions. Li et al. [14, 15] synthesized dihydropyrano[3,2-*b*]chromenediones from kojic acid, aldehydes, and active methylene carbonyl compounds, with alum as catalyst or $FeCl_3$–SiO_2 as solid acid catalyst. However, these methods suffer from such disadvantages as use of toxic organic solvents, expensive catalysts, and long reaction times. Development of a synthetic procedure free from these problems yet environmentally benign, simple, efficient, and cost-effective for the synthesis of pyranopyranones remains an important task.

Multicomponent reactions (MCRs), in which multiple reactions are combined in a one-pot synthetic operation, have been widely used to prepare bioactive heterocyclic compounds [16]. MCRs with environmentally benign methods have been one of most important topics of green chemistry. One approach used to reduce the environmental impact of a reaction is to conduct it under solvent-free conditions [17]. Advantages of solvent-free reactions include low cost, ease of work-up, and clean and efficient processes. The solvent-free reaction has became a useful strategy for formation of heterocycles.

In recent years, cerium ammonium nitrate (CAN) has attracted special attention and has been extensively used as a useful catalyst in synthetic organic chemistry, because it is eco-friendly, easy to handle, highly reactive, and economically viable [18]. However, most examples require stoichiometric quantities of CAN. In continuation of our studies in developing environmentally benign methods for synthesis of heterocyclic compounds [19–21], here we report on a highly atom-economic synthesis of 10-aryl-pyrano [3,2-*b*]chromene-4,9(6*H*,10*H*)-diones by one-pot reaction of aromatic aldehydes, 5-hydroxy-2-methylpyran-4-one, and cyclic 1,3-dicarbonyl compounds under solvent-free conditions at 120 °C requiring CAN at only 10 mol% (Scheme 1). To the best of our knowledge, this method has not been reported in the literature.

Results and discussion

Initially, we investigated the condensation reaction of 4-chlorobenzaldehyde, 5-hydroxy-2-methylpyran-4-one, and 1,3-cyclohexanedione using 10 mol% of CAN in different solvents. The results are listed in Table 1. Under these conditions product **4a** was formed in low yields (Table 1, entries 1–3), even after 9 h, whereas



Scheme 1 Synthesis of compound **4**

the same reaction under solvent-free conditions provided 52 % **4a** in only 0.5 h at 60 °C (Table 1, entry 5).

To further optimize the reaction conditions, we investigated the effect of temperature on reaction rate and on product yields. The work showed that no product could be detected at room temperature (Table 1, entry 4) even after 5 h. The yield of product **4a** was improved and the reaction time was shortened as the temperature was increased from 60 to 120 °C (Table 1, entries 5–7). The yield reached a plateau when temperature was further increased to 130 °C (Table 1, entry 8). So the most suitable reaction temperature was 120 °C.

We also examined this reaction using different catalysts under solvent-free conditions; again the results are listed in Table 1. It was found that CAN had better catalytic activity than *p*-TSA, $FeCl_3$, $ZnCl_2$, and $AlCl_3$ (Table 1, entries 9–12). Moreover, we found that yields were obviously affected by the amount of CAN used. Increasing the quantity of CAN from 2 to 10 mol% increased product yield from 63 to 95 % (Table 1, entries 14–16). The yield levelled off when 15 mol% CAN was used in the reaction (Table 1, entry 17). The catalytic activity of recycled CAN was also examined. CAN was reused four times without apparent loss of activity (Table 1, entry 16). In addition, no desired product was detected in the absence of the catalyst (Table 1, entry 13). These results showed that CAN was essential for the reaction, and the best results were obtained when the reaction was performed with 10 mol% of CAN under solvent-free conditions at 120 °C.

With these optimized conditions, to investigate the generality of the reaction we extended our study to different aromatic aldehydes to prepare a series of

Table 1 Optimization of the reaction conditions for synthesis of **4a**

Entry	Solvent	Catalyst (mol%)	Temp. (°C)	Time (min)	Yield (%)[a]
1	EtOH	CAN (10)	Reflux	540	Trace
2	DMF	CAN (10)	120	540	32
3	MeCN	CAN (10)	Reflux	540	Trace
4	None	CAN (10)	r.t.	300	0
5	None	CAN (10)	60	120	52
6	None	CAN (10)	90	60	72
7	None	CAN (10)	120	30	95
8	None	CAN (10)	130	30	94
9	None	*p*-TSA (10)	120	30	34
10	None	$ZnCl_2$ (10)	120	30	42
11	None	$AlCl_3$ (10)	120	30	45
12	None	$FeCl_3$ (10)	120	30	41
13	None	None	120	120	0
14	None	CAN (2)	120	30	63
15	None	CAN (5)	120	30	72
16	None	CAN (10)	120	30	95 (94, 95, 93)[b]
17	None	CAN (15)	120	30	95

Reaction conditions: 1 mmol 4-chlorobenzaldehyde, 1 mmol 5-hydroxy-2-methylpyran-4-one, 1 mmol 1,3-cyclohexanedione

[a] Isolated yields

[b] Catalyst was reused four times after drying

10-aryl-7,8-dihydropyrano[3,2-*b*]chromene-4,9(6*H*,10*H*)-diones. The results, summarized in Table 2, showed that aromatic aldehydes with electron-withdrawing or electron-releasing substituents were converted to their corresponding 10-aryl-7,8-dihydropyrano[3,2-*b*]chromene-4,9(6*H*,10*H*)-dione derivatives in good yields under the optimum conditions described above. All the products were characterized by their melting points, ^{1}H NMR, IR, and HRMS. Furthermore, the structure of **4g** was established by an X-ray crystallographic analysis (Fig. 1) [22].

On the basis of the literature [13], we propose a plausible mechanism for formation of **4** (Scheme 2). In first step, the Knoevenagel condensation between aromatic aldehyde **1** and cyclic 1,3-dicarbonyl compounds **3** in the presence of a catalytic amount of CAN gives an intermediate heterodiene **5**, benzylidenecyclohexane-1,3-dione. Hetero Diels–Alder reaction of 5-hydroxy-2-methylpyran-4-one **2** with **5** followed by dehydration then furnishes the corresponding products **4a**–**4t**.

Experimental

General

Melting points were determined in open capillaries without further correction. IR spectra were recorded on a Tensor 27 spectrometer in KBr. ^{1}H NMR spectra were

Table 2 Synthesis of **4** under solvent-free conditions

Entry	Ar	R	Product	Time (min)	Yield (%)[a]
1	4-ClC_6H_4	H	**4a**	30	95
2	4-BrC_6H_4	H	**4b**	30	90
3	4-FC_6H_4	H	**4c**	30	90
4	3-$CH_3OC_6H_4$	H	**4d**	35	93
5	3-FC_6H_4	H	**4e**	30	92
6	3,4-$Cl_2C_6H_3$	H	**4f**	30	85
7	2,4-$Cl_2C_6H_3$	H	**4g**	30	87
8	4-$CH_3C_6H_4$	H	**4h**	30	91
9	2,3-$Cl_2C_6H_3$	H	**4i**	30	86
10	3,4-$OCH_2OC_6H_3$	H	**4j**	30	84
11	3-HOC_6H_4	H	**4k**	40	82
12	4-HOC_6H_4	H	**4l**	35	84
13	3-$CF_3C_6H_4$	H	**4m**	35	89
14	2-ClC_6H_4	H	**4n**	30	91
15	2-BrC_6H_4	H	**4o**	30	88
16	4-BrC_6H_4	CH_3	**4p**	30	92
17	4-HOC_6H_4	CH_3	**4q**	35	84
18	3,4-$(CH_3)_2C_6H_3$	CH_3	**4r**	30	86
19	4-ClC_6H_4	CH_3	**4s**	30	94
20	3,4-$OCH_2OC_6H_3$	CH_3	**4t**	30	88

Reaction conditions: 1 mmol 5-hydroxy-2-methylpyran-4-one, 1 mmol aromatic aldehyde, 1 mmol cyclic 1,3-dicarbonyl compound, solvent free, 120 °C

[a] Isolated yield

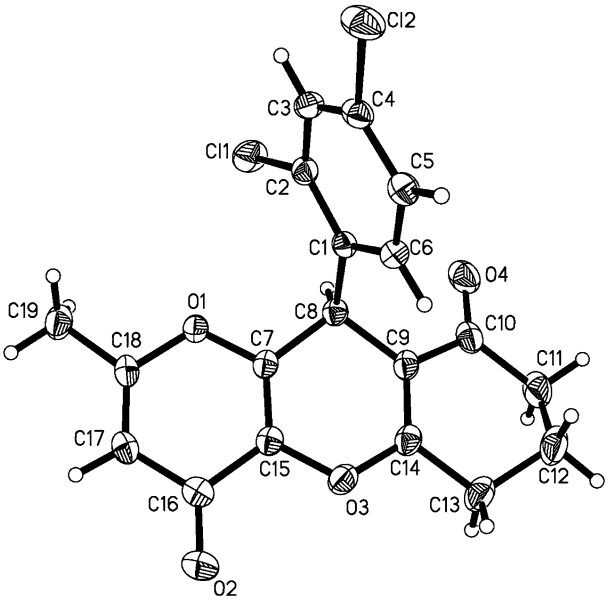
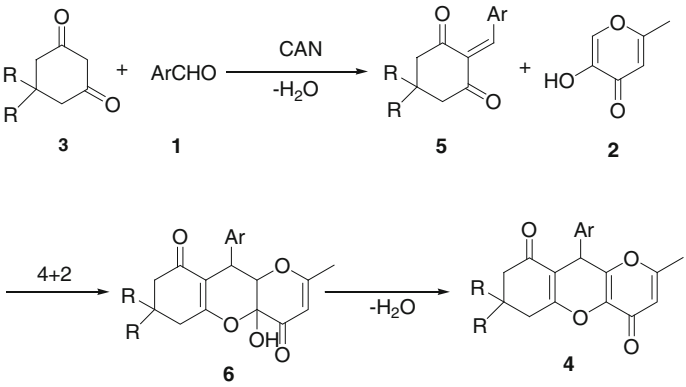


Fig. 1 The crystal structure of **4g**



Scheme 2 Mechanism of the reaction

obtained from solution in $CDCl_3$, with Me_4Si as internal standard, using a Bruker-400 spectrometer. HRMS data were obtained by use of a MicroTOF-QII instrument.

General procedure for preparation of **4**

A mixture of aromatic aldehyde **1** (1 mmol), 5-hydroxy-2-methylpyran-4-one **2** (1 mmol), cyclic 1,3-dicarbonyl compounds **3** (1 mmol), and CAN (10 mol%) was stirred at 120 °C under solvent-free conditions for the given time (Table 2). On completion of the reaction (monitored by TLC), the reaction mixture was cooled to

room temperature, and ethyl acetate was added. The mixture was shaken well to dissolve all organic components, then filtered to remove CAN. The filtrate was concentrated and purified by silica gel column chromatography to give **4**.

Characterization data

*10-(4-Chlorophenyl)-7,8-dihydro-2-methylpyrano[3,2-b]chromene-4,9(6H,10H)-dione (**4a**)*

White powder, m.p. 213–215 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.95–2.12 (m, 2H, CH_2), 2.20 (s, 3H, CH_3), 2.32–2.46 (m, 2H, CH_2), 2.66–2.87 (m, 2H, CH_2), 4.88 (s, 1H, CH), 6.18 (s, 1H, =CH), 7.18–7.29 (m, 4H, ArH); IR (KBr) *v*: 2954, 2891, 1671, 1655, 1640, 1627, 1600, 1490, 1377, 848 cm^{-1}; HRMS calcd for $C_{19}H_{15}ClO_4$ $(M + Na)^+$: requires 365.0557, found: 365.0550.

*10-(4-Bromophenyl)-7,8-dihydro-2-methylpyrano[3,2-b]chromene-4,9(6H,10H)-dione (**4b**)*

White powder, m.p. 236–238 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.97–2.13 (m, 2H, CH_2), 2.20 (s, 3H, CH_3), 2.32–2.46 (m, 2H, CH_2), 2.67–2.87 (m, 2H, CH_2), 4.87 (s, 1H, CH), 6.18 (s, 1H, =CH), 7.16 (d, 2H, ArH, $J = 8.4$ Hz), 7.44 (d, 2H, ArH, $J = 8.4$ Hz); IR (KBr) *v*: 2960, 2923, 2870, 2850, 2850, 1673, 1642, 1629, 1600, 1487, 1375, 816 cm^{-1}; HRMS calcd for $C_{19}H_{15}BrO_4$ $(M + Na)^+$: requires 409.0051, found: 409.0023.

*10-(4-Fluorophenyl)-7,8-dihydro-2-methylpyrano[3,2-b]chromene-4,9(6H,10H)-dione (**4c**)*

Yellow powder, m.p. 218–220 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.95–2.12 (m, 2H, CH_2), 2.20 (s, 3H, CH_3), 2.32–2.43 (m, 2H, CH_2), 2.67–2.88 (m, 2H, CH_2), 4.90 (s, 1H, CH), 6.19 (s, 1H, =CH), 6.88–6.92 (m, 2H, ArH), 6.97–7.02 (m, 1H, ArH), 7.23–7.24 (m, 1H, ArH); IR (KBr) *v*: 2924, 2852, 1674, 1641, 1628, 1603, 1509, 1383, 848 cm^{-1}; HRMS calcd for $C_{19}H_{15}FO_4$ $(M + H)^+$: requires 327.1033, found: 327.1026.

*10-(3-Methoxyphenyl)-7,8-dihydro-2-methylpyrano[3,2-b]chromene-4,9(6H,10H)-dione (**4d**)*

Yellow powder, m.p. 193–194 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.97–2.12 (m, 2H, CH_2), 2.20 (s, 3H, CH_3), 2.31–2.47 (m, 2H, CH_2), 2.67–2.89 (m, 2H, CH_2), 3.79 (s, 3H, OCH_3), 4.88 (s, 1H, CH), 6.18 (s, 1H, =CH), 6.78 (dd, 1H, ArH, $J_1 = 2.0$ Hz, $J_2 = 8.0$ Hz), 6.81 (s, 1H, ArH), 6.86 (d, 1H, ArH, $J = 8.0$ Hz), 7.23 (t, 1H, ArH, $J = 8.0$ Hz); IR (KBr) *v*: 3051, 2960, 2924, 2852, 1673, 1657, 1636, 1599, 1491, 1374, 771, 720 cm^{-1}; HRMS calcd for $C_{20}H_{18}O_5$ $(M + Na)^+$: requires 361.1052, found: 361.1025.

*10-(3-Fluorophenyl)-7,8-dihydro-2-methylpyrano[3,2-b]chromene-4,9(6H,10H)-dione (**4e**)*

Yellow powder, m.p. 207–209 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.98–2.13 (m, 2H, CH_2), 2.20 (s, 3H, CH_3), 2.32–2.47 (m, 2H, CH_2), 2.67–2.88 (m, 2H, CH_2), 4.90 (s, 1H, CH), 6.19 (s, 1H, =CH), 6.93–6.99 (m, 2H, ArH), 7.07 (d, 1H, ArH, $J = 7.6$ Hz), 7.29 (d, 1H, ArH, $J = 8.0$ Hz); IR (KBr) *v*: 3048, 2960, 2920, 2850, 1673, 1642, 1629, 1604, 1488, 1377, 775, 724 cm^{-1}; HRMS calcd for $C_{19}H_{15}FO_4$ $(M + H)^+$: requires 327.1033, found: 327.1056.

*10-(3,4-Dichlorophenyl)-7,8-dihydro-2-methylpyrano[3,2-b]chromene-4,9(6H,10H)-dione (**4f**)*

Yellow powder, m.p. 198–200 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.97–2.13 (m, 2H, CH_2), 2.21 (s, 3H, CH_3), 2.32–2.46 (m, 2H, CH_2), 2.68–2.89 (m, 2H, CH_2), 4.87 (s, 1H, CH), 6.20 (s, 1H, =CH), 7.14 (dd, 1H, ArH, $J_1 = 2.0$ Hz, $J_2 = 8.0$ Hz), 7.34 (d, 1H, ArH, $J = 2.0$ Hz), 7.38 (d, 1H, ArH, $J = 8.4$ Hz); IR (KBr) *v*: 2960, 2920, 1672, 1656, 1641, 1628, 1371, 877, 821 cm^{-1}; HRMS calcd for $C_{19}H_{14}Cl_2O_4$ $(M + Na)^+$: requires 399.0167, found: 399.0188.

*10-(2,4-Dichlorophenyl)-7,8-dihydro-2-methylpyrano[3,2-b]chromene-4,9(6H,10H)-dione (**4g**)*

White powder, m.p. 200–201 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.96–2.13 (m, 2H, CH_2), 2.19 (s, 3H, CH_3), 2.32–2.45 (m, 2H, CH_2), 2.69–2.88 (m, 2H, CH_2), 5.39 (s, 1H, CH), 6.17 (s, 1H, =CH), 7.14 (d, 1H, ArH, $J = 8.4$ Hz), 7.19 (dd, 1H, ArH, $J_1 = 2.0$ Hz, $J_2 = 8.4$ Hz), 7.39 (d, 1H, ArH, $J = 2.0$ Hz); IR (KBr) *v*: 3059, 2923, 1651, 1606, 1373, 888 cm^{-1}; HRMS calcd for $C_{19}H_{14}Cl_2O_4$ $(M + Na)^+$: requires 399.0167, found: 399.0149.

*10-(4-Methylphenyl)-7,8-dihydro-2-methylpyrano[3,2-b]chromene-4,9(6H,10H)-dione (**4h**)*

Yellow powder, m.p. 201–202 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.96–2.12 (m, 2H, CH_2), 2.19 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.34–2.44 (m, 2H, CH_2), 2.66–2.87 (m, 2H, CH_2), 4.87 (s, 1H, CH), 6.17 (s, 1H, =CH), 7.11 (d, 2H, ArH, $J = 7.6$ Hz), 7.17 (d, 2H, ArH, $J = 8.0$ Hz); IR (KBr) *v*: 3034, 2959, 2917, 1672, 1656, 1641, 1627, 1603, 1513, 1373, 859 cm^{-1}; HRMS calcd for $C_{20}H_{18}O_4$ $(M + Na)^+$: requires 345.1103, found: 345.1099.

*10-(2,3-Dichlorophenyl)-7,8-dihydro-2-methylpyrano[3,2-b]chromene-4,9(6H,10H)-dione (**4i**)*

Yellow powder, m.p. 226–227 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.96–2.13 (m, 2H, CH_2), 2.20 (s, 3H, CH_3), 2.34–2.45 (m, 2H, CH_2), 2.69–2.90 (m, 2H, CH_2), 5.50 (s, 1H, CH), 6.17 (s, 1H, =CH), 7.11–7.18 (m, 2H, ArH), 7.37 (dd, 1H, ArH,

$J_1 = 1.6$ Hz, $J_2 = 7.6$ Hz); IR (KBr) *v*: 3079, 2960, 2921, 2850, 1679, 1643, 1630, 1602, 1452, 1375, 772, 734 cm^{-1}; HRMS calcd for $C_{19}H_{14}Cl_2O_4$ $(M + Na)^+$: requires 399.0167, found: 399.0157.

*10-(3,4-Methylenedioxyphenyl)-7,8-dihydro-2-methylpyrano[3,2-b]chromene-4,9(6H,10H)-dione (**4j**)*

Yellow powder, m.p. 210–212 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ: 1.98–2.12 (m, 2H, CH_2), 2.21 (s, 3H, CH_3), 2.31–2.46 (m, 2H, CH_2), 2.69–2.90 (m, 2H, CH_2), 4.82 (s, 1H, CH), 5.93 (s, 2H, CH_2), 6.18 (s, 1H, =CH), 6.74 (s, 3H, ArH); IR (KBr) *v*: 2960, 2886, 1673, 1651, 1636, 1609, 1500, 1380, 790, 815, 886 cm^{-1}; HRMS calcd for $C_{20}H_{16}O_6$ $(M + H)^+$: requires 353.1025, found: 353.1030.

*10-(3-Hydroxyphenyl)-7,8-dihydro-2-methylpyrano[3,2-b]chromene-4,9(6H,10H)-dione (**4k**)*

Yellow powder, m.p. 213–215 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ: 1.96–2.09 (m, 2H, CH_2), 2.21 (s, 3H, CH_3), 2.30–2.46 (m, 2H, CH_2), 2.63–2.81 (m, 2H, CH_2), 4.86 (s, 1H, CH), 6.07 (s, 1H, OH), 6.19 (s, 1H, =CH), 6.73 (dd, 1H, ArH, $J_1 = 2.4$ Hz, $J_2 = 8.0$ Hz), 6.76 (s, 1H, ArH), 6.84 (d, 1H, ArH, $J = 8.0$ Hz), 7.17 (t, 1H, ArH, $J = 8.0$ Hz); IR (KBr) *v*: 3193, 2947, 2920, 1670, 1633, 1620, 1603, 1488, 1380, 798, 727 cm^{-1}; HRMS calcd for $C_{19}H_{16}O_5$ $(M + Na)^+$: requires 347.0895, found: 347.0875.

*10-(4-Hydroxyphenyl)-7,8-dihydro-2-methylpyrano[3,2-b]chromene-4,9(6H,10H)-dione (**4l**)*

Yellow powder, m.p. 207–209 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ: 1.98–2.11 (m, 2H, CH_2), 2.20 (s, 3H, CH_3), 2.30–2.46 (m, 2H, CH_2), 2.66–2.85 (m, 2H, CH_2), 4.84 (s, 1H, CH), 5.52 (s, 1H, OH), 6.18 (s, 1H, =CH), 6.75 (d, 2H, ArH, $J = 8.4$ Hz), 7.13 (d, 2H, ArH, $J = 8.4$ Hz); IR (KBr) *v*: 3234, 2960, 2923, 2852, 1673, 1658, 1634, 1611, 1592, 1515, 1377, 830 cm^{-1}; HRMS calcd for $C_{19}H_{16}O_5$ $(M + Na)^+$: requires 347.0895, found: 347.0889.

*10-(3-Trifluoromethylphenyl)-7,8-dihydro-2-methylpyrano[3,2-b]chromene-4,9(6H,10H)-dione (**4m**)*

White powder, m.p. 211–213 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ: 1.98–2.13 (m, 2H, CH_2), 2.20 (s, 3H, CH_3), 2.32–2.47 (m, 2H, CH_2), 2.69–2.90 (m, 2H, CH_2), 4.98 (s, 1H, CH), 6.19 (s, 1H, =CH), 7.39–7.53 (m, 4H, ArH); IR (KBr) *v*: 3080, 2963, 2926, 1668, 1646,1632, 1375, 794, 699 cm^{-1}; HRMS calcd for $C_{20}H_{15}F_3O_4$ $(M + Na)^+$: requires 399.0820, found: 399.0794.

*10-(2-Chlorophenyl)-7,8-dihydro-2-methylpyrano[3,2-b]chromene-4,9(6H,10H)-dione (**4n**)*

Yellow powder, m.p. 234–236 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.98–2.13 (m, 2H, CH_2), 2.19 (s, 3H, CH_3), 2.31–2.44 (m, 2H, CH_2), 2.69–2.90 (m, 2H, CH_2), 5.45 (s, 1H, CH), 6.17 (s, 1H, =CH), 7.16–7.21 (m, 3H, ArH), 7.37 (d, 1H, ArH, $J = 8.0$ Hz); IR (KBr) v: 3061, 2952, 2924, 1678, 1664, 1642, 1628, 1606, 1374, 745 cm^{-1}; HRMS calcd for $C_{19}H_{15}ClO_4$ $(M + Na)^+$: requires 365.0557, found: 365.0535.

*10-(2-Bromophenyl)-7,8-dihydro-2-methylpyrano[3,2-b]chromene-4,9(6H,10H)-dione (**4o**)*

Yellow powder, m.p. 238–240 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.98–2.13 (m, 2H, CH_2), 2.19 (s, 3H, CH_3), 2.31–2.43 (m, 2H, CH_2), 2.70–2.90 (m, 2H, CH_2), 5.48 (s, 1H, CH), 6.17 (s, 1H, =CH), 7.08–7.16 (m, 2H, ArH), 7.24 (d, 1H, ArH, $J = 7.6$ Hz), 7.57 (d, 1H, ArH, $J = 8.0$ Hz); IR (KBr) v: 3057, 2959, 2925, 2873, 1675, 1642, 1629, 1600, 1488, 1373, 765 cm^{-1}; HRMS calcd for $C_{19}H_{15}BrO_4$ $(M + Na)^+$: requires 409.0051, found: 409.0037.

*10-(4-Bromophenyl)-7,8-dihydro-2,7,7-trimethylpyrano[3,2-b]chromene-4,9(6H,10H)-dione (**4p**)*

White powder, m.p. 213–214 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.03 (s, 3H, CH_3), 1.11 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 2.23–2.28 (m, 2H, CH_2), 2.58–2.70 (m, 2H, CH_2), 4.84 (s, 1H, CH), 6.18 (s, 1H, =CH), 7.15 (d, 2H, ArH, $J = 8.4$ Hz), 7.43 (d, 2H, ArH, $J = 8.4$ Hz); IR (KBr) v: 3056, 2959, 2923, 2873, 1675, 1642, 1629, 1602, 1488, 1372, 845 cm^{-1}; HRMS calcd for $C_{21}H_{19}BrO_4$ $(M + Na)^+$: requires 437.0364, found: 437.0346.

*10-(4-Hydroxyphenyl)-7,8-dihydro-2,7,7-trimethylpyrano[3,2-b]chromene-4,9(6H,10H)-dione (**4q**)*

Yellow powder, m.p. 298–300 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.04 (s, 3H, CH_3), 1.11 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 2.18–2.29 (m, 2H, CH_2), 2.57–2.69 (m, 2H, CH_2), 4.81 (s, 1H, CH), 5.78 (s, 1H, OH), 6.18 (s, 1H, =CH), 6.72 (d, 2H, ArH, $J = 8.4$ Hz), 7.11 (d. 2H, ArH, $J = 8.4$ Hz); IR (KBr) v: 3649, 3170, 3023, 2950, 2924, 1672, 1635, 1622, 1591, 1513, 1382, 843 cm^{-1}; HRMS calcd for $C_{21}H_{20}O_5$ $(M + Na)^+$: requires 375.1208, found: 375.1216.

*10-(3,4-Dimethylphenyl)-7,8-dihydro-2,7,7-trimethylpyrano[3,2-b]chromene-4,9(6H,10H)-dione (**4r**)*

Yellow powder, m.p. 185–186 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.05 (s, 3H, CH_3), 1.11 (s, 3H, CH_3), 2.14–2.24 (m, 11H, $CH_2 + 3 \times CH_3$), 2.58–2.71 (m, 2H, CH_2), 4.80 (s, 1H, CH), 6.16 (s, 1H, =CH), 6.95–7.07 (m, 3H, ArH); IR (KBr) v:

3069, 2956, 2923, 1674, 1658, 1633 1602, 1502, 1374, 881, 828, 670, 652 cm^{-1}; HRMS calcd for $C_{23}H_{24}O_4$ $(M + Na)^+$: requires 387.1572, found: 387.1600.

*10-(4-Chlorophenyl)-7,8-dihydro-2,7,7-trimethylpyrano[3,2-b]chromene-4,9(6H,10H)-dione (**4s**)*

Yellow powder, m.p. 203–205 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ: 1.04 (s, 3H, CH_3), 1.11 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 2.23–2.29 (m, 2H, CH_2), 2.58–2.70 (m, 2H, CH_2), 4.86 (s, 1H, CH), 6.18 (s, 1H, =CH), 7.21 (d, 2H, ArH, $J = 8.0$ Hz), 7.28 (d, 2H, ArH, $J = 8.4$ Hz); IR (KBr) v: 3058, 2960, 2924, 2874, 1678, 1644, 1630, 1603, 1491, 1373, 847 cm^{-1}; HRMS calcd for $C_{21}H_{19}ClO_4$ $(M + Na)^+$: requires 393.0870, found: 393.0900.

*10-(3,4-Methylenedioxyphenyl)-7,8-dihydro-2,7,7-trimethylpyrano[3,2-b]chromene-4,9(6H,10H)-dione (**4t**)*

Yellow powder, m.p. 236–237 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ: 1.06 (s, 3H, CH_3), 1.10 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 2.20–2.24 (m, 2H, CH_2), 2.57–2.70 (m, 2H, CH_2), 4.78 (s, 1H, CH), 5.92 (s, 2H, CH_2), 6.17 (s, 1H, =CH), 6.72–6.74 (m, 3H, ArH); IR (KBr) v: 2961, 2932, 1680, 1665, 1635, 1600, 1503, 1378, 854, 824, 797, 659 cm^{-1}; HRMS calcd for $C_{22}H_{20}O_6$ $(M + Na)^+$: requires 403.1158, found: 403.1180.

Conclusion

In conclusion, we have efficiently synthesized 10-aryl-7,8-dihydropyrano[3,2-*b*]chromene-4,9(6*H*,10*H*)-diones via CAN-catalyzed three-component reactions under solvent-free conditions. Low cost, operational simplicity, higher yields (82–95 %), ready availability of catalyst, an environmentally benign procedure, and recyclable catalyst make this methodology a useful contribution to existing procedures available for synthesis of dihydropyrano[3,2-*b*]chromene-4,9(6*H*,10*H*)-dione derivatives.

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22. Crystallographic data for the structures of **4g** reported in this paper have been deposited at the Cambridge Crystallographic Data Centre with No. CCDC-891132