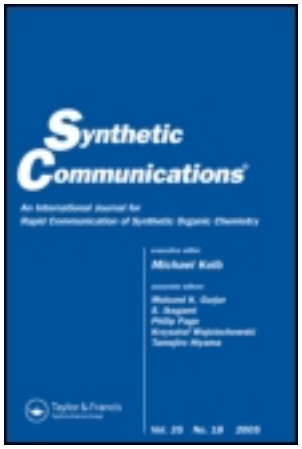

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Catalytic Method for Synthesis of Benzopyrano[3,2-c]chromene-6,8-dione Derivatives by Heteropoly Acids

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CATALYTIC METHOD FOR SYNTHESIS OF BENZOPYRANO[3,2-c]CHROMENE-6,8-DIONE DERIVATIVES BY HETEROPOLY ACIDS

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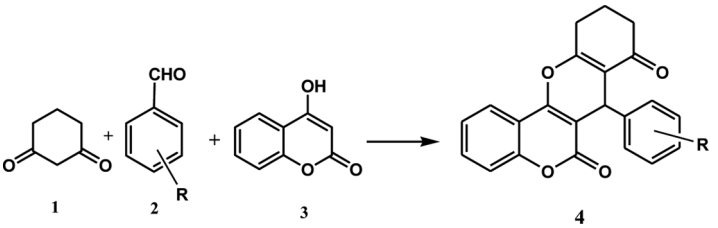
GRAPHICAL ABSTRACT



Abstract *Benzopyrano[3,2-c]chromene-6,8-dione derivatives were prepared by a three-component one-pot cyclocondensation of 4-hyroxycoumarin, aldehydes, and 1,3,cyclohexadione using a catalytic amount of heteropolyacids in boiling ethanol in very good yields and rates.*

Keywords Benzopyrano[3,2-c]chromene; catalytic cyclocondensation; catalytic reaction; heteropolyacid

INTRODUCTION

4-Hydroxycoumarin **3** constitutes the structural nucleus of many natural products, drugs and pesticides.[1–3] It is the key intermediate for various widely used oral anticoagulants and rodenticides.[4] Similarly, several derivatives of pyran or fused pyran ring systems have been shown to possess different types of biological activities[5] such as antidiabetic[6] and anti-Alzheimer[7] activities. Various other medical activities have been exhibited by pyran derivatives, including antimicrobial,[8] anti tumor,[9] anti fungal, antidepressant,[10] and platelet antiaggregating[11] activities. They have also been developed as photosensitive drugs,[12] potent and

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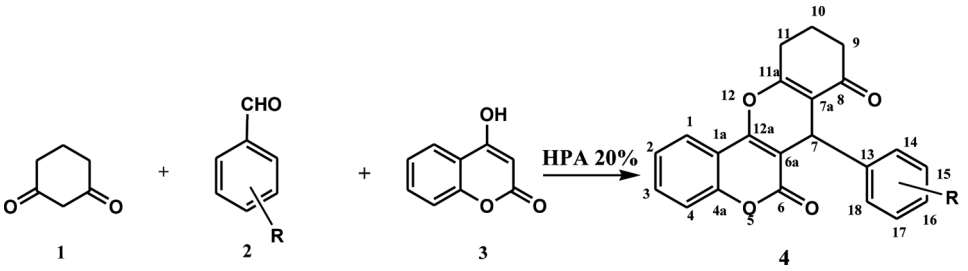


Scheme 1. General synthetic pathway for the preparation of benzopyrano[2,3-c]chromene-6,8-dione derivatives.

selective human dopamine D4 antagonists,[13] nonpentidic HIV protease inhibitors,[14] and antibiotic agents such as novebiocin.[15]

We have recently reported design, synthesis and toxicity effect of novel benzopyrano[3,2-c]chromene-6,8-diones **4** derivatives (Scheme 1).[16] In continuation of our attempts to develop selective and preoperatively useful methodology, using heteropolyacids as green catalysts in various organic reactions,[17] we report a rapid and convenient method for synthesis of these compounds, catalyzed by heteropolyacids (HPAs).

(HPAs) are considered to be environmentally benign catalysts because of their unique properties such as high thermal stability, low cost, ease of preparation, and ease of recyclability.[18,19] Many organic reactions, including oxygenation, estrification, and polymerization[20–23] can be catalyzed effectively by HPAs because of their high oxidation capatibility, strong acidity, and unique pseudo-liquid-phase behavior.[24]

RESULTS AND DISCUSSION

We have previously described synthesis of novel 7-aryl benzopyrano[3,2-c] chromene-6,8-dione **4** derivatives by one-pot, three-component cyclocondensation of 4-hydroxy coumarin, 1,3-cyclohexadione, and aryl aldehyde after 5 h refluxing in acetic acid in yields of 60–78% (Scheme 1).[16]

The structures of compounds **4** were deduced from their infrared (IR)[16] Armed with our experiences using various HPAs as green catalysts in acidic catalytic reactions,[17] we were persuaded to study the use of these catalysts for synthesis of compounds **4**. Initially the coupling reaction of 4-hydroxy coumarine **3**, 4-nitrobenzaldehyde **2a**, and 1,3-cyclohexadione **1** in ethanol with different catalytic amounts of $H_6P_2Mo_{18}O_{62}$ and at room temperature and refluxing condition was investigated to optimize the reaction conditions. The best yield was obtained in presence of 10% molar ratio of the catalyst in boiling ethanol. Then using the optimized reaction conditions, the coupling reaction was examined in different solvents such as methanol, ethanol and acetic acid to find the best solvent. The yields in all cases were the same. Therefore, ethanol was selected as a suitable solvent.

In the next step, using the optimized conditions, the one-pot coupling reactionof a series of aryl aldehyde in the presence of $H_6P_2Mo_{18}O_{62}$(10%) was investigated,

Table 1. Catalytic synthesis of 7-aryl-benzopyrano[3,2-c]chromene-6,8-dione derivatives in ethanol was refluxed by $H_6P_2Mo_{18}O_{62}$ (10%)

Compound	R	Yield (%)	Time (min)	Mp
4a	4-Nitro	90	4	196 (195–197)
4b	3-Nitro	90	4	219 (218–220)
4c	2-Nitro	90	4	222 (222–223)
4d	4-Bromo	80	4	170 (170–171)
4e	3-Bromo	79	4	265 (265–264)
4f	2-Bromo	80	4	238 (238–239)
4g	4-Chloro	85	4	244 (244–245)
4h	3-Chloro	84	4	247 (247–248)
4i	2-Chloro	85	4	294 (294–295)
4j	4-Methoxy	86	4	196 (196–197)
4k	3-Methoxy	87	4	188 (188–189)
4l	2-Methoxy	88	4	246 (245–246)

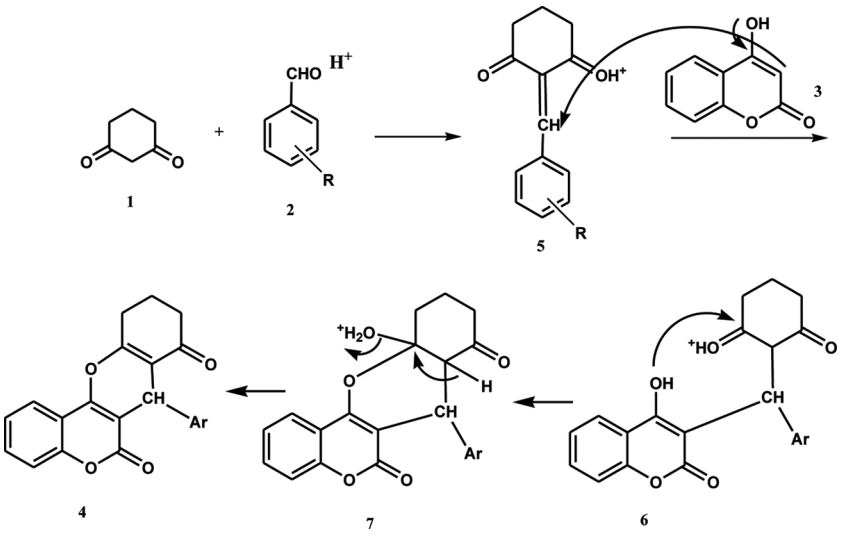
and the obtained results are summarized in Table 1. All the aforementioned catalyzed reactions delivered excellent product yields and reaction times compared to those without catalyst. All products were identified by comparison with authentic samples.[16]

These results demonstrate that both the yields and the reaction time are relatively independent of the position of the substituent in aryl aldehyde. However, nitrobenzaldehyde had relatively better yields. To show the effect of the different catalysts, the one-pot coupling reaction of 4-hydroxylcoumarine **3**, 4-nitrobenzaldehyde **2a,** and 1,3-cyclohexadione **1** was examined in presence of 10% molar ratio of different HPA catalysts such as $H_6P_2Mo_{18}O_{62}$, $H_6P_2W_{18}O_{62}$, $K_7PWMo_{11}O_{39}$, $H_{14}[NaP_5W_{29}MoO_{110}]$, and $K_3PW_{12}O_{40}$. The results are presented in Table 2. As shown in Table 2, however, both $H_{14}[NaP_5W_{29}MoO_{110}]$ and $H_6P_2W_{18}O_{62}$ showed the best yield. The rates of reactions were two to 10 times faster in the presence of Preyssler-type HPA $H_{14}[NaP_5W_{29}MoO_{110}]$. Among HPA and Preyssler structures used in the present study, $H_{14}[NaP_5W_{29}MoO_{110}]$ showed more activity and yields because of the it has more acidic protons, which is in a good agreement with the findings of earlier work.[17]

HPA were separated by filtration, and the products were purified by recrystalizing from ethyl acetate. The reactions were monitored by thin-layer chromatography (TLC), and subsequent workup afforded a single compound (by TLC) in

Table 2. Catalytic synthesis of 4-nitro-benzopyrano[3,2-c]chromene-6,8-dione derivatives in ethanol was refluxed by heteropolyacids

	Yield (%)	Time (min)
$H_6P_2Mo_{18}O_{62}$	90	4
$H_6P_2W_{18}O_{62}$	98	30
$K_7PWMo_{11}O_{39}$	80	7
$H_{14}[NaP_5W_{29}MoO_{110}]$	98	2
$K_3PW_{12}O_{40}$	85	5



Scheme 2. Possible mechanism of formation of **4** in reaction pathway.

each case. The product was identified by its ^{1}H NMR, mass, and IR spectra, which were compared to those reported previously.[16]

Generally, reactions catalyzed by HPAs may be represented by the conventional mechanisms of Brønsted acid catalysis. A plausible mechanism for the formation of compounds **4** is given in Scheme 2. It is reasonable to assume that in the first step aldol condensation between arylaldehydes and 1,3-cyclohexadione affords compound **5**. In the second step Michael addition of 4-hydroxycoumarine to compound **5** led to the formation of the intermediates **6,** which undergo cyclization followed by dehydration to give the desired compounds **4** (Scheme 2). The proton can catalyze all three steps.

Catalysts based on HPAs have many advantages over acid catalyzsts. They are not corrosive, are environmetally benign, present fewer disposals problem, and separates easily and have thermal stability. These catalysts are not soluble in ethanol, which enables easy separation and recovery by filtering for immediate reuse without any important decrease of the catalyst reactivity.

EXPERIMENTAL

General Procedure for the Synthesis of 7-Aryl-9,10-dihydro-7h,11h-benzopyrano[3,2-c]chromene-6,8-dione Derivatives

4-Hydroxyl coumarin **3** (0.162 g, 1 mmol), 1,3 cyclohexadione **1** (0.112 g, 1 mmol) and arylaldehydes (1 mmol), and the appropriate HPA (0.04 mmol) were refluxed in ethanol (50 ml) for the indicated time (Table 1).

The catalyst was removed by filtration and washed with warm ethanol (the catalyst is not soluble in ethanol). The catalyst was further washed with diethyl ether after filtration. It could be reused for a second run of the reaction. The yields of

product were almost identical to those obtained using fresh catalyst. The filtrate was cooled, and the precipitated solid was collected by filtration, washed with cold ethyl acetate, dried, and recrystallized from ethyl acetate to give the pure product **4** (Table 1). All products were identified by their mass and ^{1}H NMR spectra by comparison with authentic samples.[16]

9,10-Dihydro-7-(4-nitrophenyl)-7h,11 h-benzopyrano[3,2c]chromene-6, 8-dione 4a. IR (KBr) ν: 3068 (C-H aromatic), 2914 (C-H aliphatic), 1721 (C=O), 1526, 1362 (NO_2) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 2.08–2.21 (m, 2H, H_{10}), 2.44–2.47 (m, 2H, H_{11}), 2.79–2.84 (m, 1H, H_9), 2.89–2.90 (m, 1H, H_9), 5.08 (s, 1H, H_7), 7.36 (dd, 1H, $J = 8.0$, 1.0 Hz, H_4), 7.40 (td, 1H, $J = 8.0$, 1.0 Hz, H_2), 7.57 (d, 2H, $J = 8.5$ Hz, H_{14}, H_{18}), 7.62 (td, 1H, $J = 8.0$, 1.5 Hz, H_3), 7.91 (dd, 1H, $J = 8.0$, 1.5 Hz, H_1), 8.13 (d, 2H, $J = 8.5$ Hz, H_{15}, H_{17}). MS: m/z (%), 389 (M^+, 11), 372 (47), 342 (22), 267 (100), 149 (17), 122 (13), 83 (23), 55 (40). Anal. calcd. for $C_{22}H_{15}NO_6$: C, 67.86; H, 3.88; N, 3.60. Found: C, 67.69; H, 3.70; N, 3.82.

9,10-Dihydro-7-(3-nitrophenyl)-7h,11h-benzopyrano[3,2-c]chromene-6, 8-dione (4b). IR (KBr) ν: 3100 (C-H aromatic), 2934 (C-H aliphatic), 1731 (C=O), 1526, 1362 (NO_2) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 2.08–2.21 (m, 2H, H_{10}), 2.40–2.50 (m, 2H, H_{11}), 2.77–2.85 (m, 1H, H_9), 2.92–2.99 (m, 1H, H_9), 5.09 (s, 1H, H_7), 7.36 (d, 1H, $J = 8.0$ Hz, H_4), 7.41 (t, 1H, $J = 8.0$ Hz, H_2), 7.48 (t, 1H, $J = 8.0$ Hz, H_{17}), 7.62 (t, 1H, $J = 8.0$ Hz, H_3), 7.94 (m, 2H, H_{18}, H_1), 8.05–8.08 (m, 2H, H_{14}, H_{16}). MS: m/z (%), 390 ($M^+ + 1$, 29), 389 (M^+, 8), 373 (86), 343 (16), 267 (100). Anal. calcd. for $C_{22}H_{15}NO_6$: C, 67.86; H, 3.88; N, 3.60. Found: C, 68.15; H, 3.65; N, 3.85.

9,10-Dihydro-7-(2-nitrophenyl)-7h,11h-benzopyrano[3,2-c]chromene-6, 8-dione (4c). IR (KBr) ν: 3078 (C-H aromatic), 2950 (C-H aliphatic), 1731 (C=O), 1526, 1357 (NO_2) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 2.05–2.14 (m, 2H, H_{10}), 2.40–2.42 (m, 2H, H_{11}), 2.72–2.79 (m, 1H, H_9), 2.83–2.89 (m, 1H, H_9), 5.75 (s, 1H, H_7), 7.31 (t, 1H, $J = 7.5$ Hz, H_{16}), 7.34 (d, 1H, $J = 8.0$ Hz, H_4), 7.38 (t, 1H, $J = 8.0$ Hz H_2), 7.47 (t, 1H, $J = 7.5$ Hz, H_{17}), 7.54 (d, 1H, $J = 7.5$ Hz, H_{18}), 7.59 (t, 1H, $J = 8.0$ Hz, H_3), 7.78 (d, 1H, $J = 7.5$ Hz, H_{15}), 7.91 (d, 1H, $J = 8.0$ Hz H_1). MS: m/z (%), 389 (M^+, 33), 342 (40), 267 (100), 149 (23), 122 (57), 83 (31), 55 (91). Anal. calcd. for $C_{22}H_{15}NO_6$: C, 67.86; H, 3.88; N, 3.60. Found: C, 67.63; H, 4.15; N, 3.89.

7-(4-Bromophenyl)-9,10-dihydro-7h,11h-benzopyrano[3,2-c]chromene-6, 8-dione (4d). IR (KBr) ν: 3080 (C-H aromatic), 2939 (C-H aliphatic), 1716 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 2.07–2.18 (m, 2H, H_{10}), 2.42–2.46 (m, 2H, H_{11}), 2.78–2.80 (m, 1H, H_9), 2.85–2.90 (m, 1H, H_9), 4.94 (s, 1H, H_7), 7.25 (d, 2H, $J = 8.5$ Hz, H_{14}, H_{18}), 7.34 (dd, 1H, $J = 8.0$, 1.0 Hz, H_4), 7.36 (td, 1H, $J = 8.0$, 1.0 Hz, H_2), 7.37 (d, 2H, $J = 8.5$ Hz, H_{15}, H_{17}),7.59 (td, 1H, $J = 8.0$, 1.5 Hz, H_3), 7.88 (dd, 1H, $J = 8.0$, 1.5 Hz, H_1). MS: m/z (%), 424 ($M^+ + 2$, 18), 422 (M^+, 16), 342 (40), 267 (100), 154 (25), 122 (18), 93 (38), 74 (42). Anal. calcd. for $C_{22}H_{15}BrO_4$: C, 62.43; H, 3.57. Found: C, 62.67; H, 3.81.

7-(3-Bromophenyl)-9,10-dihydro-7h,11h-benzopyrano[3,2-c]chromene-6, 8-dione (4e). IR (KBr) ν: 3050 (C-H aromatic), 2950 (C-H aliphatic), 1731 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 2.18–2.09 (m, 2H, H_{10}), 2.50–2.30 (m, 2H, H_{11}), 2.74–2.80 (m, 1H, H_9), 2.88–2.93 (m, 1H, H_9), 4.95 (s, 1H, H_7), 7.15 (t, 1H,

$J = 8.0$ Hz, H_{17}), 7.29 (dt, 1H, $J = 8.0$, 1.0 Hz,H_{18}), 7.34 (d, 1H, $J = 8.0$ Hz, H_4), 7.38 (t, 1H, $J = 8.0$ Hz, H_2),7.39 (t, 1H, $J = 1.0$ Hz,H_{14}), 7.41 (dt, 1H, $J = 8.0$, 1.0 Hz, H_{16}), 7.58 (td, 1H, $J = 8.0$, 1.0 Hz H_3), 7.90 (dd, 1H, $J = 8.0$, 1.0 Hz, H_1). MS: m/z (%), 424 ($M^+ + 2$, 10), 422 (M^+, 10), 343 (50), 267 (41), 249 (100), 122 (23), 93 (10). Anal. calcd. for $C_{22}H_{15}BrO_4$: C, 62.43; H, 3.57. Found: C, 62.68; H, 3.82.

7-(2-Bromophenyl)-9,10-dihydro-7h,11h-benzopyrano[3,2-c]chromene-6, 8-dione (4f). IR (KBr) ν: 3052 (C-H aromatic), 2919 (C-H aliphatic), 1726 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 2.05–2.157 (m, 2H, H_{10}), 2.36–2.45 (m, 2H, H_{11}), 2.72–2.78 (m, 1H, H_9), 2.82–2.88 (m, 1H, H_9), 5.25 (s, 1H, H_7), 7.06 (t, 1H, $J = 7.5$ Hz, H_{16}), 7.24 (t, 1H, $J = 7.5$ Hz, H_{17}), 7.33 (d, 1H, $J = 8.0$ Hz, H_4), 7.35 (t, 1H, $J = 8.0$ Hz, H_2),7.49-7.46 (m, 2H, H_{15}, H_{18}), 7.57 (td, 1H, $J = 8.0$, 1.0 Hz, H_3), 7.90 (dd, 1H, $J = 8.0$, 1.0 Hz, H_1). MS: m/z (%), 424 ($M^+ + 2$, 10), 422 (M^+, 10), 343 (100), 267 (22). Anal. calcd. for $C_{22}H_{15}BrO_4$: C, 62.43; H, 3.57. Found: C, 62.71; H, 3.38.

7-(4-Chlorophenyl)-9,10-dihydro-7h,11h-benzopyrano[3,2-c]chromene-6, 8-dione (4g). IR (KBr) ν: 3100 (C-H aromatic), 2939 (C-H aliphatic), 1716 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 2.05–2.16 (m, 2H, H_{10}), 2.42–2.46 (m, 2H, H_{11}), 2.74–2.80 (m, 1H, H_9), 2.85–2.91 (m, 1H, H_9), 4.96 (s, 1H, H_7), 7.23 (d, 2H, $J = 8.5$ Hz, H_{14}, H_{18}), 7.33 (d, 2H, $J = 8.5$ Hz, H_{15}, H_{17}), 7.34–7.39 (m, 2H, H_2, H_4), 7.61 (td, 1H, $J = 8.0$, 1.5 Hz, H_3), 7.88 (dd, 1H, $J = 8.0$, 1.5 Hz, H_1), MS: m/z (%), 380 ($M^+ + 2$, 8), 378 (M^+, 25), 344 (15), 327 (85), 266 (80), 216 (100), 111 (65), 54 (95). Anal. calcd. for $C_{22}H_{15}ClO_4$: C, 69.75; H, 3.99. Found: C, 69.97; H, 3.76.

7-(3-Chlorophenyl)-9,10-dihydro-7h,11h-benzopyrano[3,2-c]chromene-6, 8-dione (4h). IR (KBr) ν: (C-H aromatic), 2965 (C-H aliphatic), 1726 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$)δ: 2.09–2.17 (m, 2H, H_{10}), 2.38–2.50 (m, 2H, H_{11}), 2.74–2.80 (m, 1H, H_9), 2.88–2.92 (m, 1H, H_9), 4.96(s, 1H, H_7), 7.15 (dt, 1H, $J = 7.5$, 1.5 Hz, H_{18}), 7.20 (t, 1H, $J = 7.5$ Hz, H_{17}), 7.26 (t, 1H, $J = 1.5$, H_{14}), 7.33 (dd, 1H, $J = 8.0$, 1.0 Hz,H_4), 7.36–7.39 (m, 2H, H_{16}, H_2), 7.59 (td, 1H, $J = 8.0$, 1.5 Hz, H_3), 7.89 (dd, 1H, $J = 8.0$, 1.5 Hz, H_1), MS: m/z (%), 380 ($M^+ + 2$, 3.5), 378 (M^+, 10), 344 (100), 268 (38), 111(10). Anal. calcd. for $C_{22}H_{15}ClO_4$: C, 69.75; H, 3.99. Found: C, 69.47; H, 4.28.

7-(2-Chlorophenyl)-9,10-dihydro-7h,11h-benzopyrano[3,2-c]chromene-6, 8-dione (4i). IR (KBr) ν: 3062 (C-H aromatic), 2955 (C-H aliphatic), 1726 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.93 (m, 2H, H_{10}), 2.29–2.33 (m, 2H, H_{11}), 2.82–2.85 (m, 2H, H_9), 5.06 (s, 1H, H_7), 7.16 (t, 1H, $J = 7.6$ Hz, H_{16}), 7.24 (t, 1H, $J = 7.6$ Hz, H_{17}), 7.29 (d, 1H, $J = 7.6$, H_{18}), 7.34 (d, 1H, $J = 8.0$ Hz, H_4), 7.46 (t, 1H, $J = 8.0$ Hz, H_2), 7.50 (d, 1H, $J = 7.6$ Hz, H_{15}), 7.7 (td, 1H, $J = 8.0$, 1.0 Hz, H_3), 7.98 (dd, 1H, $J = 8.0$, 1.0 Hz, H_1). MS: m/z (%), 380 ($M^+ + 2$, 3), 378 (M^+, 10), 344 (100), 343 (55), 268 (25). Anal. calcd. for $C_{22}H_{15}ClO_4$: C, 69.75; H, 3.99. Found: C, 69.46; H, 3.70.

9,10-Dihydro-7-(4-methoxyphenyl)-7h,11h-benzopyrano[3,2-c]chromene-6,8-dione (4j). IR (KBr) ν: 3080 (C-H aromatic), 2939 (C-H aliphatic), 1726 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 2.07–2.16 (m, 2H, H_{10}), 2.41–2.46 (m, 2H, H_{11}), 2.73–2.79 (m, 1H, H_9), 2.85-2.90 (m, 1H, H_9), 3.74 (s, 3H, CH_3), 4.94 (s, 1H, H_7), 6.79 (d, 2H,

$J = 9.0$ Hz, H_{15}, H_{17}), 7.30 (d, 2H, $J = 9.0$ Hz, H_{14}, H_{18}) 7.32 (dd, 1H, $J = 8.0$, 1.0 Hz,H_4), 7.36 (td, 1H, $J = 8.0$, 1.0 Hz, H_2), 7.57 (td, 1H, $J = 8.0$, 1.5 Hz, H_3), 7.87 (dd, 1H, $J = 8.0$, 1.5 Hz, H_1). MS: m/z (%), 374 (M^+, 18), 343 (10), 300 (10), 267 (100). Anal. calcd. for $C_{23}H_{18}O_5$: C, 73.79; H, 4.05. Found: C, 73.48; H, 3.83.

9,10-Dihydro-7-(3-methoxyphenyl)-7h,11h-benzopyrano[3,2-c]chromene-6,8-dione (4k). IR (KBr) ν: 3080 (C-H aromatic), 2939 (C-H aliphatic), 1736 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 2.08–2.16 (m, 2H, H_{10}), 2.41–2.49 (m, 2H, H_{11}), 2.73–2.79 (m, 1H, H_9), 2.85-2.90 (m, 1H, H_9), 3.78 (s, 3H, CH_3), 4.99 (s, 1H, H_7), 6.72 (dd, 1H, $J = 8.0$, 1.5 Hz, H_{18}), 6.94 (t, 1H, $J = 1.5$ Hz, H_{14}), 6.99 (dd, 1H, $J = 8.0$, 1.5 Hz H_{16}), 7.17 (t, 1H, $J = 8.0$ Hz, H_{17}), 7.32 (d, 1H, $J = 8.0$ Hz, H_4), 7.36 (t, 1H, $J = 8.0$ Hz H_2), 7.57 (td, 1H, $J = 8.0$, 1.0 Hz, H_3), 7.88 (dd, 1H, $J = 8.0$, 1.0 Hz, H_1). MS: m/z (%), 374 (M^+, 70), 343 (65), 267 (100), 93 (90), 76 (95). Anal. calcd. for $C_{23}H_{18}O_5$: C, 73.79; H, 4.05. Found: C, 73.95; H, 3.82.

9,10-Dihydro-7-(2-methoxyphenyl)-7h,11h-benzopyrano[3,2-c]chromene-6,8-dione (4 l). IR (KBr) ν: 3067 (C-H aromatic), 2945 (C-H aliphatic), 1721 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 2.02–2.13 (m, 2H, H_{10}), 2.34–2.43 (m, 2H, H_{11}), 2.70–2.78 (m, 2H, H_9), 3.70 (s, 3H, CH_3), 5.06 (s, 1H, H_7), 6.79 (dd, 1H, $J = 8.0$, 1.0 Hz, H_{15}), 6.94 (td, 1H, $J = 8.0$, 1.0 Hz, H_{17}), 7.17 (td, 1H, $J = 8.0$, 1.5 Hz, H_{16}), 7.32 (dd, 1H, $J = 8.0$, 1.0 Hz, H_4), 7.35 (td, 1H, $J = 8.0$, 1.0 Hz H_2), 7.52 (dd, 1H, $J = 8.0$, 1.5 Hz, H_{18}), 7.55 (td, 1H, $J = 8.0$, 1.5 Hz, H_3, 7.94 (dd, 1H, $J = 8.0$, 1.5 Hz, H_1), MS: m/z (%), 374 (M^+, 55), 344 (30), 319 (18), 268 (100), 122 (25), 56 (12). Anal. calcd. for $C_{23}H_{18}O_5$: C, 73.79; H, 4.05. Found: C, 73.98; H, 4.33.

CONCLUSION

We have developed a method using an ecofriendly and reusable heterogeneous inorganic catalyst for synthesis of 7-aryl-benzopyrano[3,2-c]chromene-6,8-dione derivatives 4 using heteropolyacids catalysts. Among the heteropolyacids, $H_{14}[NaP_5W_{30}O_{110}]$ have exhibited high activities for the synthesis of these compounds. The reasonable reaction times, good yields, simple workup procedure, and environmentally friendly conditions are the main advantages of this method.

All catalysts are not soluble in ethanol, which enabled easy separation and recovery by filtering for their immediate reuse without any important decrease of the catalyst reactivity.

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