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ARTICLE

$Ag_2Cr_2O_7$ nanoparticles: An eco-friendly and reusable catalyst for synthesis of pyrano[*c*]chromenediones and [1,3]dioxolo[*g*]chromeneones in aqueous media at ambient temperature

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Abstract

An efficient and green protocol for the synthesis of 4-aryl-3,4-dihydro-2*H*,5*H*-pyrano[3,2-*c*]chromene-2,5-diones and 8-aryl-7,8-dihydro-6*H*-[1,3]dioxolo[4,5-*g*]chromene-6-ones through the $Ag_2Cr_2O_7$ nanoparticles catalyzed cyclocondensation reaction of active methylene compounds including 4-hydroxycoumarin or 3,4-methylenedioxyphenol, aromatic aldehydes, and meldrum's acid in water at ambient temperature was described. This method demonstrates several advantages compared with methods that are currently employed such as a mild reaction conditions, simple work-up, good to excellent yields, avoiding toxic catalyst and hazardous solvent, and recovery and reuse of the catalyst.

KEYWORDS

[1,3]dioxolo[*g*]chromeneones, aqueous media, environmentally benign procedure, pyrano[*c*]chromenediones, recyclability of catalyst, silver(I) *dichromate* ($Ag_2Cr_2O_7$ NPs)

1 | INTRODUCTION

The chromene ring system is presumably the most well-known heterocycle, a common and significant core structure in a variety of natural and nonnatural pharmacological agents.[1] Interest on the discover of new procedures for the synthesis of chromene derivatives has been continously increasing as they possess important biological properties such as antioxidant,[2,3] antibacterial,[4–6] antimicrobial,[7–9] antiviral,[10] antifungal,[11] anti-inflammatory,[12] anticancer,[13–17] hypotensive,[18] local anesthetic, antiarrhythmic,[19] and cognitive enhancing activity.[20] Several examples which exhibit anticancer activity and are mainly found in natural products (isolated from plants) include tephrosin (lung cancer),[21] calanone (leukemia and cervical carcinoma)[22,23] acronycine (lung, colon and ovary cancer),[24] and seselin (skin cancer)[25] (Figure 1).

Recently, considerable attention has been paid to develop the utilities of nanoscale metal salts as catalysts in organic reactions because they have been found to influence the chemical and physical properties of the bulk material.[26–33] The diverse silver nanostructure salts are extensively applied in different fields.[34] However, there is no report on the application of silver(I) dichromate ($Ag_2Cr_2O_7$ NPs) as catalyst in any organic synthesis. These facts encouraged us to investigate and evaluate the catalytic ability of $Ag_2Cr_2O_7$ NPs as a new efficient heterogeneous catalyst for either exclusive synthesis of the pyrano[*c*]chromenedione and [1,3]dioxolo[*g*]chromeneone derivatives. According to the literature survey, several procedures have been reported to catalyze the

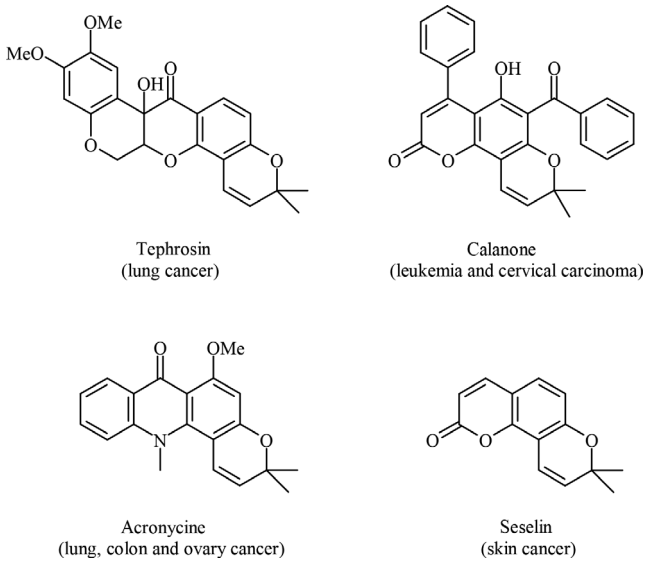


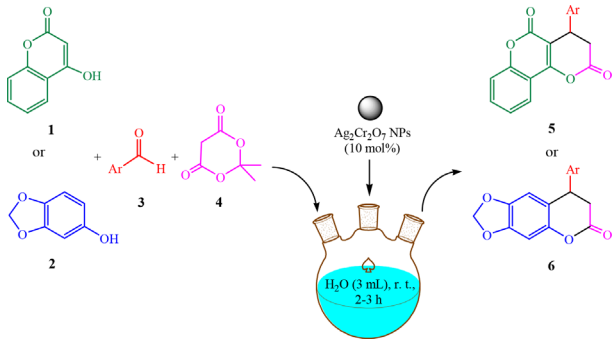
FIGURE 1 Representative of naturally chromene-containing compounds with anticancer activity

formation of these compounds, some of them include the use of catalysts such as proline,[35] $CeCl_3.7H_2O$,[36] basic alumina,[37] CuI NPs.[38] While most of these catalysts are helpful to construct the products in good yields, but these methods, unfortunately, have certain limitations such as long reaction times, harsh reaction conditions, and utilization of hazardous chemicals.

With this background in mind, and in continuation of our earlier efforts to develop new facile and efficient routes in heterocyclic synthesis,[39] herein we would like to report an efficient and simple approach to synthesize 4-aryl-3,4-dihydro-2*H*,5*H*-pyrano[3,2-*c*]chromene-2,5-diones **5** and 8-aryl-7,8-dihydro-6*H*-[1,3]dioxolo[4,5-*g*]chromene-6-ones **6** *via* an environmentally benign cyclocondensation reaction of active methylene compounds including 4-hydroxycoumarin **1** or 3,4-methylenedioxyphenol **2**, aromatic aldehydes **3**, and meldrum's acid **4** using $Ag_2Cr_2O_7$ NPs as a new, efficient, and recyclable heterogeneous catalyst in water at ambient temperature (Scheme 1).

2 | RESULTS AND DISCUSSION

The preliminary effort has been made to prepare the $Ag_2Cr_2O_7$ NPs catalyst according to a simple precipitation route reported by Salavati-Niasari et al.[40] The nanostructures of the synthesized $Ag_2Cr_2O_7$ NPs were characterized by scanning electron microscopy (SEM), energy-dispersive X-Ray spectroscopy (EDS), Fourier transform infrared (FT-IR) spectroscopy, and X-Ray diffraction (XRD) analysis.



SCHEME 1 Synthesis of pyrano[*c*]chromenedione and [1,3]dioxolo[*g*]chromeneone derivatives

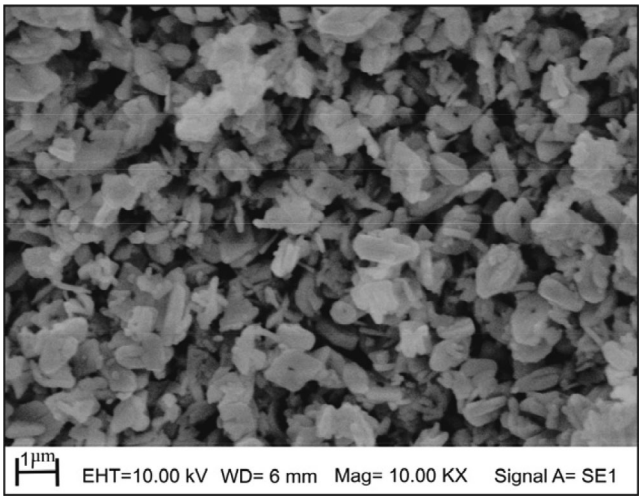


FIGURE 2 SEM images of the $Ag_2Cr_2O_7$ NPs

As revealed in Figure 2, the SEM image of the synthesized $Ag_2Cr_2O_7$ NPs confirmed the formation of bundles nanorod-shaped nanoparticles with the average particle size of about 40 nm.

The EDS spectra of the synthesized $Ag_2Cr_2O_7$ NPs, is given in Figure 3. As shown in Figure, the presence of Ag, Cr, and S as the main elemental components is observed. The appearance of sulfur element in this spectrum is due to the SDS adsorbed on the nanoparticles.

Figure 4 shows the FTIR spectrum of the synthesized $Ag_2Cr_2O_7$ NPs. The characterization peak at 886 cm^{-1} can be attributed to the Cr—O stretching vibrations. The broad peak at 3,436 cm^{-1} is also corresponded to the O—H stretching vibrations of water molecules adsorbed on the surface of $Ag_2Cr_2O_7$ NPs. The very weak peaks at 2,928, 2,853, and 1,092 cm^{-1} are due to the C—H and S—O stretching bonds of SDS.

As can be seen in the XRD pattern of the synthesized $Ag_2Cr_2O_7$ NPs (Figure 5), all the obtained diffraction peaks corresponded to the $Ag_2Cr_2O_7$ NPs, which can be readily supported by JCPDS file No. 01-0963.

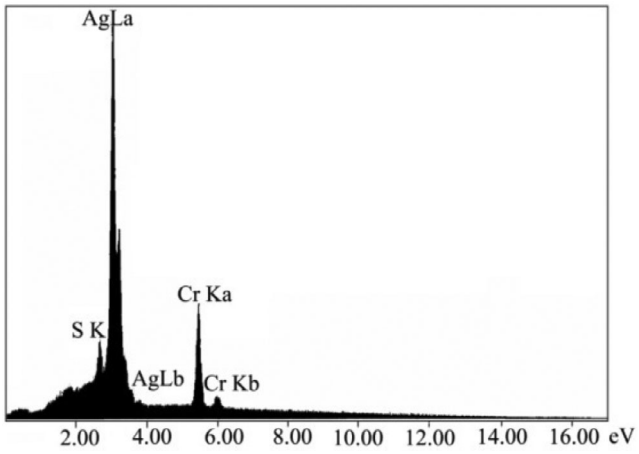


FIGURE 3 EDS analysis of the $Ag_2Cr_2O_7$ NPs

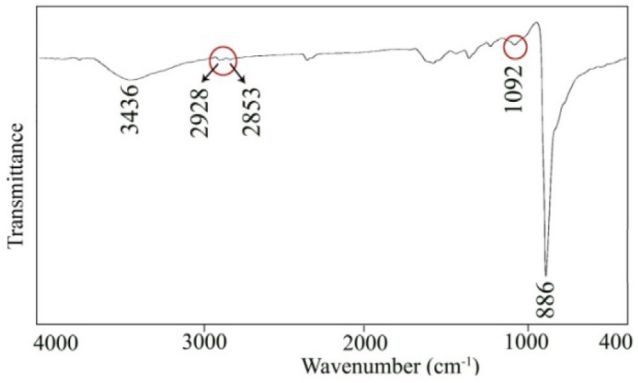


FIGURE 4 FTIR spectrum of the $Ag_2Cr_2O_7$ NPs

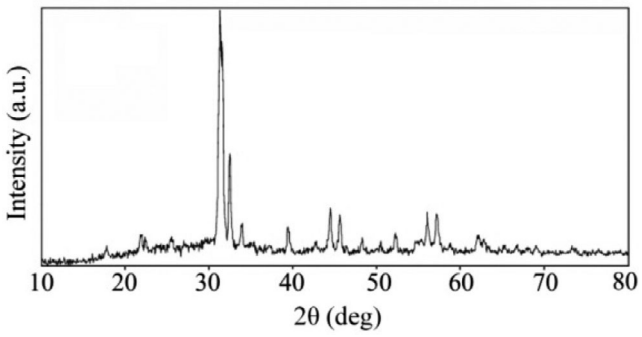
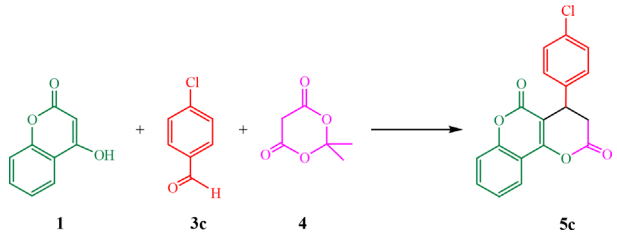


FIGURE 5 XRD spectra of the $Ag_2Cr_2O_7$ NPs

To select the optimization reaction conditions, a typical reaction of 4-hydroxycoumarin (1), 4-chlorobenzaldehyde (**3c**), and meldrum's acid (4) was examined for the synthesis of compound **5c** under various reaction conditions (Scheme 2 and Table 1). Performing the reaction without any catalyst under refluxing in water, gave only 67% of product **5c** after 5 hr (Table 1, entry 1). Then, different



SCHEME 2 Synthesis of **5c** from the reaction of 4-hydroxycoumarin, 4-chlorobenzaldehyde, and meldrum's acid under various reaction conditions

amounts of the $Ag_2Cr_2O_7$ NPs as catalyst were tried in water at ambient temperature. It was observed that 10 mol % of catalyst is sufficient for this conversion (Table 1, entries 2–4). Next, the influence of the temperature was tested, and it was apparent that using 10 mol% of catalyst and under refluxing gave the same yield of the desired product in shorter reaction time (Table 1, entries 3 and 5). The replacement of water with other organic solvents such as EtOH, CH_3CN, CH_2Cl_2, and DMF in the model reaction led to moderate conversions of the particular reactants (Table 1, entries 3 and 6–9).

In order to determine the scope and limitation of this reaction, various substituted aromatic aldehydes were conducted with meldrum's acid and 4-hydroxycoumarin or 3,4-methylenedioxyphenol, to obtain the corresponding products **4a–g** and **6a–g** in high yields under optimized conditions (Table 2). Because of the volatile nature of many aliphatic aldehydes and also lower activity of those compared to aromatic ones, we used only aromatic aldehydes for mentioned reaction. However, aliphatic aldehydes gave only trace yields of products on TLC.

The reusability of the $Ag_2Cr_2O_7$ NPs as catalyst was then investigated for the synthesis of **5c** under the optimized reaction conditions. The recovered catalyst was able to recycle five times without significant loss of activity (Figure 6). It should be noted that a slight weight loss of catalyst was also detected during recycling process. Although the reaction occurred at ambient temperature, it may be related to the slow decomposition of $Ag_2Cr_2O_7$ in water.

A proposed reaction mechanism for the formation of pyrano[*c*]chromenediones 5 through $Ag_2Cr_2O_7$ NP-catalyzed cyclocondensation reaction of 4-hydroxycoumarin, aromatic aldehydes, and meldrum's acid is illustrated in Scheme 3. $Ag_2Cr_2O_7$ NPs play the role of bifunctional Lewis acid-Lewis base catalyst for the formation of alkene 8, readily prepared in situ from Knoevenagel condensation of Meldrum's acid 4 and aromatic aldehyde 3, which proceed via intermediate 7. Then, 4-hydroxycoumarin adds to

TABLE 1 Synthesis of 4-(4-chlorophenyl)-3,4-dihydro-2*H*,5*H*-pyrano[3,2-*c*]chromene-2,5-dione **5c** under different conditions

Entry	Nanocatalyst (mol%)	Solvent	Temp. (°C)	Time (hr)	Yield (%)[a]
1	None	H_2O	Reflux	5	67
2	$Ag_2Cr_2O_7$ (5 mol%)	H_2O	r.t.	3	88
3	$Ag_2Cr_2O_7$ (10 mol%)	H_2O	r.t.	2	95
4	$Ag_2Cr_2O_7$ (15 mol%)	H_2O	r.t.	2	94
5	$Ag_2Cr_2O_7$ (10 mol%)	H_2O	Reflux	1	95
6	$Ag_2Cr_2O_7$ (10 mol%)	EtOH	r.t.	2.5	73
7	$Ag_2Cr_2O_7$ (10 mol%)	CH_3CN	r.t.	3	66
8	$Ag_2Cr_2O_7$ (10 mol%)	CH_2Cl_2	r.t.	3	48
9	$Ag_2Cr_2O_7$ (10 mol%)	DMF	r.t.	2	78

[a]Isolated yield.

TABLE 2 $Ag_2Cr_2O_7$ NPs catalyzed synthesis of pyrano[*c*]chromenedione and [1,3]dioxolo[*g*]chromeneone derivatives in water at ambient temperature

Product	Ar	Active methylene compounds	Time (hr)	Yield (%)[a,b]	M.p (°C)	
					Obsd.	Lit.
5a	C_6H_5	1	2	98	168–170	169–171[35]
5b	2-Cl-C_6H_4	1	2	97	210–212	212–214[35]
5c	4-Cl-C_6H_4	1	2	95	196–197	197–199[35]
5d	4-OH-C_6H_4	1	2	98	207–209	—
5e	4-OCH_3-C_6H_4	1	2	95	146–147	143–145[35]
5f	2-CH_3-C_6H_4	1	2	95	193–194	192–195[35]
5g	3-NO_2-C_6H_4	1	2	96	181–183	180–182[35]
6a	C_6H_5	2	2	96	130–132	133–134[36]
6b	2-Cl-C_6H_4	2	3	96	162–164	160–161[36]
6c	4-Cl-C_6H_4	2	3	97	200–202	205–2,061[36]
6d	4-OH-C_6H_4	2	3	97	208–210	—
6e	4-OCH_3-C_6H_4	2	3	93	128–129	129–130[36]
6f	2-CH_3-C_6H_4	2	3	94	155–157	—
6g	3-NO_2-C_6H_4	2	3	95	139–141	142–143[36]

[a]Isolated yield.
[b]Reaction conditions: A mixture of 4-hydroxycoumarin (**1**) or 3,4-methylenedioxyphenol (**2**) (1 mmol), an aromatic aldehyde **3** (1 mmol), meldrum's acid (**4**, 1 mmol), and $Ag_2Cr_2O_7$ NPs (43.2 mgr, 10 mol%) in H_2O (3 ml) was sttring at room temperature for appropriate times.

alkene 8 in a Michael-type addition to give intermediate 9. The cyclization of 9 followed by elimination of acetone generates product 5 after decarboxylation of intermediate 10. The formation of [1,3]dioxolo[*g*]chromeneones 6 can be explained similarly.

Confirmation of the structures of compounds **5**(**a–g**) and **6**(**a–g**) were established with IR, ^{1}H NMR and ^{13}C NMR spectroscopic data and also by elemental analyses. Spectroscopic data have been given in general procedure section. The synthesized catalyst was fully characterized by SEM, EDS, FTIR, and XRD techniques.

3 | CONCLUSION

In this research, an efficient and green method for the synthesis of pyrano[*c*]chromenediones and [1,3]dioxolo[*g*]chromeneones using $Ag_2Cr_2O_7$ NPs as an new efficient and recyclable heterogeneous catalyst was developed. Compared with previous methods,[35–38] this new approach provides several advantages like higher yields, avoiding toxic catalyst and hazardous solvent, recovery and reuse of the catalyst, simple work-up, and treatment under milder reaction conditions.

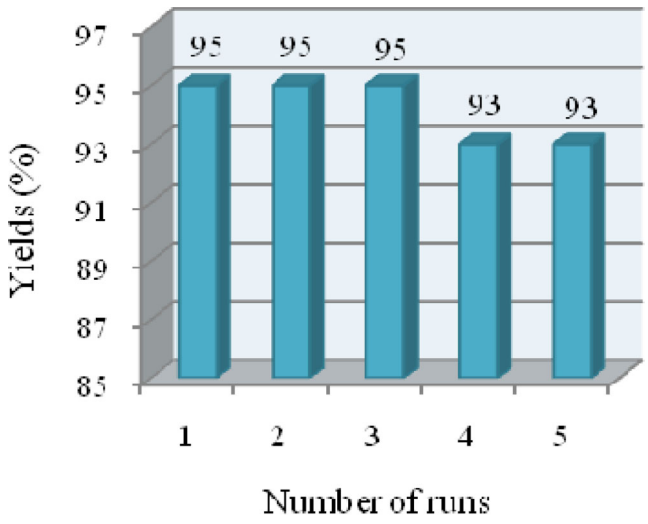
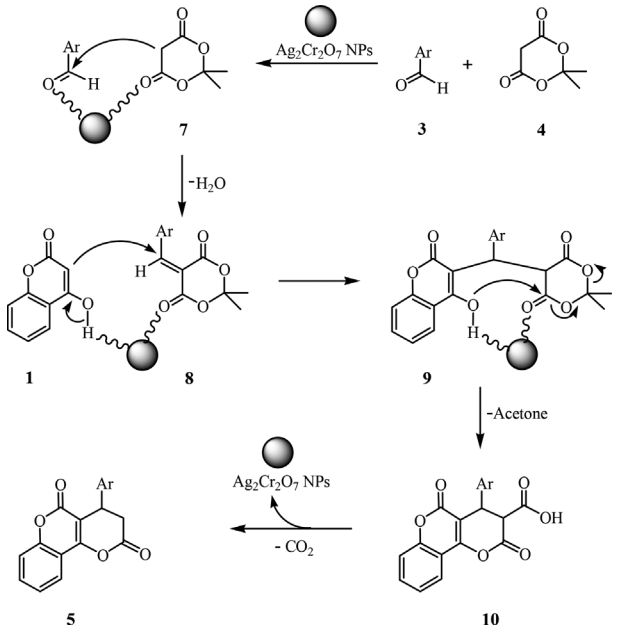


FIGURE 6 Reusability of the $Ag_2Cr_2O_7$ NPs as catalyst toward synthesis of **5c**



SCHEME 3 The proposed mechanism

4 | EXPERIMENTAL

All of the chemical materials used in this work were purchased from Merck and Fluka and used without further purification. Melting points were determined on an Electrothermal 9,100 apparatus. IR spectra were obtained on a Bruker, Equinox 55 FT-IR spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX-500 AVANCE at 500 and 125 MHz, respectively, using TMS as internal standard and DMSO-d_6 as solvent. Elemental analyses were carried out on Foss-Heraeus *CHN*-O-rapid analyzer instruments. Powder X-ray diffraction data were determined on a Rigaku D-max C III, X-ray Diffractometer using Cu Kα radiation (λ = 1.54 Å).The microscopic morphology of the catalyst was revealed using scanning electron microscope (SEM, Philips, *XL-30*) equipped with energy-dispersive X-ray analysis system (EDS).

4.1 | General procedure for the preparation of $Ag_2Cr_2O_7$ NPs catalyst

The catalyst was prepared according to the literature method.[40] To a magnetically stirred mixture of $AgNO_3$ (2 mmol) in 40 ml of distilled water, a solution of sodium salicylate (2 mmol) in an equal volume of distilled water was added dropwise and the resulted mixture was continued to be stirred at 80°C for about 30 min. Afterward, the produced precursor silver(I) salicylate, [Ag(HSal)] as a white precipitate was filtered and washed with distilled water and ethanol several times to remove impurities. In the next step, precursor silver(I) salicylate, [Ag(HSal)] (4 mmol) and sodium dodecyl sulfate (SDS) (0.05 g) as shape controller were dissolved in 50 ml of distilled water and then, a previously prepared solution of $(NH_4)_2Cr_2O_7$ (2 mmol) in 20 ml of distilled water, was added dropwise into the above mixture under strong magnetic stirring for 20 min. Subsequently, the obtained precipitate of $Ag_2Cr_2O_7$ NPs was vacuum-filtered, washed in ethanol, and dried in a vacuum oven at 50°C for about 20 hr.

4.2 | General method for the preparation of compounds 5a–g and 6a–g

A mixture of 4-hydroxycoumarin 1 or 3,4-methylenedioxyphenol 2 (1 mmol), arylaldehyde 3 (1 mmol), meldrum's acid (4, 1 mmol), and $Ag_2Cr_2O_7$ NPs (43.2 mgr, 10 mol%) in H_2O (3 ml) was magnetically stirred at room temperature. After completion of the reaction (monitored by TLC), the reaction mixture was filtered and the residue was dissolved in hot ethanol (3 ml) and then centrifuged for 5 min at 2,000–3,000 rpm to recover the catalyst. The recovered catalyst was washed three times with EtOH and then dried in a vacuum oven at 50°C for reuse. The pure product was obtained by cooling the ethanol solution to room temperature, diluted with 1 ml H_2O, and allowed to crystallize.

4.3 | Selected spectroscopic data

4.3.1 | 4-Phenyl-3,4-dihydro-*2H*,*5H*-pyrano[3,2-c]chromene-2,5-dione (5a)

White powder, yield 0.293 g (98%), m. p. 168–170°C (lit: 169–171°C[35]). IR (KBr): ν_{max} = 1,784, 1,702, 1,659,

1,087 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 3.13 (1 H, d, J = 16.1 Hz, H-3), 3.20 (1 H, d, J = 16.1 Hz, H-3′), 4.52 (1 H, s, H-4), 7.28 (3 H, m, HAr), 7.29 (1 H, d, J = 7.0 Hz, HAr), 7.34 (1 H, d, J = 7.0 Hz, HAr), 7.39 (2 H, m, HAr), 7.61 (1 H, t, J = 7.2 Hz, HAr), 7.91 (1 H, d, J = 7.4 Hz, HAr) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 36.8, 37.1, 105.6, 113.2, 116.9, 122.8, 126.3, 128.1, 128.8, 130.3, 133.2, 141.2, 154.1, 156.7, 160.1, 163.9 ppm. Anal. calcd. for $C_{18}H_{12}O_4$ (299.29): C 72.24, H 4.04; found: C 72.19, H 4.12%.

4.3.2 | 4-(2-Chlorophenyl)-3,4-dihydro-*2H*,*5H*-pyrano[3,2-c]chromene-2,5-dione (5b)

White powder, yield 0.317 g (97%), m. p. 210–212°C (lit: 212–214°C[35]). IR (KBr): ν_{max} = 1,792, 1,701, 1,623, 1,100 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 3.12 (1 H, d, J = 15.0 Hz, H-3), 3.18 (1 H, d, J = 15.0 Hz, H-3′), 4.59 (1 H, s, H-4), 6.95 (1 H, d, HAr, J = 8.5), 7.15 (1 H, t, J = 7.2, Hz HAr), 7.23 (1 H, t, J = 7.2 Hz, HAr), 7.43 (3 H, m, HAr), 7.66 (1 H, t, J = 7.9, Hz HAr), 7.95 (1H, d, J = 7.9, Hz HAr) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 33.5, 35.0, 104.8, 113.4, 117.1, 122.9, 124.7, 126.9, 127.6, 129.5, 130.7, 133.2, 133.5, 135.9, 153.5, 158.7, 160.3, 163.6 ppm. Anal. calcd. for $C_{18}H_{11}ClO_4$ (326.73): C 66.17, H 3.39; found: C 65.90, H, 3.31%.

4.3.3 | 4-(4-Hydroxyphenyl)-3,4-dihydro-*2H*,*5H*-pyrano[3,2-c]chromene-2,5-dione (5d)

White powder, yield 0.302 g (98%), m. p. 207–209°C. IR (KBr): ν_{max} = 3,499, 1,768, 1,716, 1,644, 1,115 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 2.96 (1 H, d, J = 15.6 Hz, H-3), 3.48 (1 H, d, J = 15.6, Hz H-3′), 4.36 (1 H, s, H-4), 6.75 (2 H, d, J = 6.8 Hz, HAr), 7.05 (2 H, d, J = 7.0 Hz, HAr), 7.46 (2 H, m, HAr), 7.70 (1 H, d, J = 6.6 Hz, HAr), 7.84 (1 H, d, HAr, J = 6.8 Hz), 9.45 (s, 1 H, OH) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 35.4, 37.3, 107.5, 114.2, 116.5, 116.6, 117.5, 123.3, 125.6, 131.0, 133.8, 153.4, 157.6, 157.7, 161.1, 166.1 ppm. Anal. calcd. for $C_{18}H_{12}O_5$ (308.29): calcd. C 70.13, H 3.92; found: C 70.27, H 4.08%.

4.3.4 | 4-(4-Methoxyphenyl)-3,4-dihydro-*2H*,*5H*-pyrano[3,2-c]chromene-2,5-dione (5e)

White powder, yield 0.306 g (95%), m. p. 146–147°C (lit: 143–145°C[35]). IR (KBr): ν_{max} = 1,774, 1,705, 1,668, 1,102 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 3.10 (1 H, d, J = 16.0 Hz, H-3), 3.19 (1 H, d, J = 16.0, Hz H-3′), 3.71 (3 H, s, OCH_3), 4.50 (1 H, s, H-4), 6.79 (2 H, d, J = 8.4 Hz, HAr), 7.17 (2 H, d, J = 8.4 Hz, HAr), 7.37 (2 H, m, HAr), 7.69 (1 H, t, J = 8.0 Hz, HAr), 7.88 (1 H, d, J = 8.1 Hz, HAr) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 34.8, 36.7, 56.1, 105.9, 114.1, 116.6, 117.5, 125.8, 127.8, 130.7, 132.8, 152.3, 156.2, 158.5, 159.1, 160.9, 164.1 ppm. Anal. calcd. for $C_{19}H_{14}O_5$ (322.32): C 70.80, H 4.38; found: C 70.65, H 4.16%.

4.3.5 | 4-(3-Nitrophenyl)-3,4-dihydro-*2H*,*5H*-pyrano[3,2-c]chromene-2,5-dione (5g)

White powder, yield 0.324 g (96%), m. p. 181–183°C (lit: 180–182°C[35]). IR (KBr): ν_{max} = 1,781, 1,719, 1,645, 1,506, 1,491, 1,119 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 2.86 (1 H, d, H-3, J = 15.9 Hz), 3.44 (1 H, d, H-3′, J = 15.9 Hz), 4.27 (1 H, s, H-4), 6.52 (4 H, m, HAr), 7.04 (1 H, t, J = 7.5 Hz, HAr), 7.39 (2 H, m, HAr), 7.77 (1 H, d, J = 7.4 Hz, HAr) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 36.1, 37.0, 107.1, 114.1, 115.4, 120.6, 121.0, 123.3, 125.8, 130.4, 131.1, 134.0, 142.3, 145.9, 153.5, 158.7, 161.0, 166.0 ppm. Anal. calcd. for $C_{18}H_{11}NO_6$ (337.29): C 64.01, H 3.29, N 4.15; found: C 63.89, H 3.14, N 4.23%.

4.3.6 | 8-Phenyl-7,8-dihydro-*6H*-[1,3]dioxolo[4,5-g]chromene-6-one (6a)

White powder, yield 0.258 g (96%), m. p. 130–132 ° C (lit: 133–134°C[36]). IR (KBr): ν_{max} = 2,995, 2,904, 2,856, 1,716, 1,668, 1,554, 1,512, 1,370, 1,149 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): 2.90 (1 H, d, J = 15.9 Hz, H-7,), 3.05 (1 H, d, J = 15.9 Hz, H-7′), 4.25 (1 H, s, H-8), 5.93 (1 H, d, J = 1.2 Hz, H-2), 5.95 (1 H, d, J = 1.2 Hz, H-2′), 6.40 (1H, s, HAr), 6.68 (1 H, s, HAr), 7.10–7.13 (2 H, m, HAr), 7.23–7.30 (3 H, m, HAr) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 37.0, 40.1, 99.3, 101.6, 107.4, 117.5, 119.9, 128.4, 129.6, 140.4, 144.4, 145.6, 146.5, 167.3 ppm. Anal. calcd. for $C_{16}H_{12}O_4$ (268.27): C 71.64, H 4.51; found: C 71.59, H 4.32%.

4.3.7 | 8-(4-Chlorophenyl)-7,8-dihydro-*6H*-[1,3]dioxolo[4,5-g]chromene-6-one (6c)

White powder, yield 0.294 g (97%), m. p. 200–202°C (lit: 205–206°C[36]). IR (KBr): ν_{max} = 3,046, 2,916, 2,882, 1,720, 1,673, 1,574, 1,519, 1,361, 1,152 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 2.88 (1 H, d,

J = 16.0 Hz, H-7,), 3.04 (1 H, d, J = 16.0 Hz, H-7′), 4.23 (1 H, s, H-8), 5.99 (1 H, d, J = 1.0 Hz, H-2), 5.97 (1 H, d, J = 1.0 Hz, H-2′), 6.41 (s, 1H, HAr), 6.66 (1 H, s, HAr), 7.11 (2 H, d, J = 8.3 Hz, HAr), 7.36 (2 H, d, J = 8.3 Hz, HAr) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 36.5, 39.8, 99.4, 101.2, 107.3, 116.5, 128.2, 129.0, 132.3, 139.4, 144.0, 146.1, 147.8, 167.7 ppm. Anal. calcd. for $C_{16}H_{11}ClO_4$ (302.72): C 63.48, H 3.66; found: C 63.30, H 3.78%.

4.3.8 | 8-(4-Hydroxyphenyl)-7,8-dihydro-6*H*-[1,3]dioxolo[4,5-g]chromene-6-one (6d)

White powder, yield 0.276 g (97%), m. p. 208–210°C. IR (KBr): ν_{max} = 3,189, 3,084, 2,930, 2,865, 1,725, 1,670, 1,580, 1,516, 1,372, 1,152 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.92 (1 H, d, J = 16.1 Hz, H-7), 500 (1 H, d, J = 16.1 Hz, H-7′), 4.91 (1 H, s, H-8), 5.95 (1 H, d, J = 1.1 Hz, H-2), 5.96 (1 H, d, J = 1.1 Hz, H-2′), 6.42 (1 H, s, HAr), 6.70 (1 H, s, HAr), 6.96 (2 H, d, J = 7.5 Hz, HAr), 7.03 (2 H, d, J = 7.5 Hz, HAr), 9.37 (1 H, s, OH) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 36.4, 39.5, 98.7, 101.6, 107.0, 116.3, 117.1, 128.9, 142.4, 144.2, 145.8, 146.9, 155.6, 166.5 ppm. Anal. calcd. for $C_{16}H_{12}O_5$ (284.27): C 67.60, H 4.25; found: C 67.78, H 4.12%.

4.3.9 | 8-(2-Methylphenyl)-7,8-dihydro-6*H*-[1,3]dioxolo[4,5-g]chromene-6-one (6f)

White powder, yield 0.265 g (94%), m. p. 155–157°C. IR (KBr): ν_{max} = 2,961, 2,654, 1,721, 1,665, 1,580, 1,486, 1,368, 1,160 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.39 (3 H, s, CH_3), 2.95 (1 H, d, H-7, J = 16.0 Hz), 3.05 (1 H, d, H-7′, J = 16.0 Hz), 4.76 (1 H, s, H-8), 5.93 (1H, d, H-2, J = 1.3 Hz), 5.95 (1 H, d, H-2′, J = 1.3 Hz), 6.40 (1 H, s, HAr), 6.69 (1 H, s, HAr), 7.22 (4 H, m, HAr) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 20.5, 35.4, 38.7, 98.8, 102.0, 108.6, 116.9, 125.4, 126.6, 128.6, 131.1, 135.7, 138.4, 145.1, 145.6, 147.3, 165.8 ppm. Anal. calcd. for $C_{17}H_{14}O_4$ (282.29): C 72.33, H 5.00; found: C 72.18, H 4.89%.

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