

RESEARCH PAPER

CdO Nanoparticles: A Highly Effective Catalyst in Cyclocondensation Reaction of 3,4-Methylenedioxyphenol, Aromatic Aldehydes, and Active Methylene Compounds under Ultrasonic Irradiation

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ABSTRACT

In the last decades, metal oxide nanoparticles (NPs) have been used as inexpensive efficient heterogeneous catalysts in different chemical reactions, due to their favorable properties such as high available surface area, small loading of catalyst, convenient catalyst recycling, and degradation of environmental pollutants. An efficient synthesis of xanthenones and [1] benzopyrano[d]pyrimidinediones are achieved by cyclocondensation reaction of 3,4-methylenedioxyphenol, aromatic aldehydes, and active methylene compound including dimedone or 1,3-dimethylbarbituric acid using CdO NPs as a robust catalyst under ultrasonic irradiation in water at room temperature. The described catalyst was prepared successfully by a simple precipitation method and characterized by the Fourier transformed infrared absorption (FT-IR) spectroscopy, X-Ray diffraction (XRD) analytical technique, and scanning electron microscopy (SEM). All synthesized compounds were well characterized by IR, ¹H and ¹³C NMR spectroscopy, and also by elemental analyses. The remarkable advantages of this protocol are high yields of products, short reaction times, use of simple and readily available starting materials, experimental simplicity, and applying the sonochemical method as an efficient method and innocuous tool for the synthesis of heterocycles.

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INTRODUCTION

Benzopyranopyrimidines represent an important class of heterocyclic compounds with an array of biological and pharmacological properties such as antithrombotics [1], anticoagulant [2], antagonists as potential antipsychotic agents [3], and estrogenic activity on MCF-7 breast carcinoma cells [4]. Xanthenes are also heterocyclic organic compounds that have been proved to be active as antibacterial [5], antiviral [6], anti-inflammatory [7], antinociceptive [8], and CCR1 antagonist [9].

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Green chemistry is a scientific approach which has basically concentrated on the use of safer compounds, solvents and reaction conditions [10]. In comparison with the traditional methods for organic transformations, ultra sonication method as an alternate greener approach allows assembly of complex molecules in one-pot and exhibits several pronounced features such as enhancement of reaction rates, formation of pure products in high yields and easier operation [11-16].

Furthermore, metal oxide nanoparticles

(NPs) have been used as inexpensive efficient heterogeneous catalysts in different chemical reactions. These catalysts possessed promising advantageous such as high available surface area, small loading of catalyst, convenient catalyst recycling, and degradation of environmental pollutants [17-20]. Cadmium oxide is an interesting multifunctional material for its extensive applications in the field of optoelectronic devices such semiconductor [21], phototransistors [22], photodiodes [23], solar cells [24], and gas sensors [25]. The cadmium oxide nanoparticles (CdO NPs) is also considered to display such economically and environmentally friendly benefits as Lewis acid/base catalyst [26,27].

Though several methods for the synthesis of xanthenones and [1]benzopyrano[*d*]pyrimidinediones have been reported [28-32], but due to their particular importance, the improvement of new synthetic approaches by mild reaction conditions remains enough scope for an efficient and reusable catalyst with high catalytic activity for the preparation of those. In the course of our studies for exploration of catalytic activity of nanomaterial in heterocyclic synthesis [33], we herein report the use of CdO NPs as catalyst for the preparation of a series of 7,7-dimethyl-10-aryl-6,7,8,10-tetrahydro-9*H*-[1,3]dioxolo[4,5-*b*]xanthen-9-ones **4** and 6,8-dimethyl-10-aryl-6,10-dihydro-7*H*-[1,3]dioxolo[4',5':6,7] [1]benzopyrano[2,3-*d*]pyrimidine-7,9(8*H*)-diones **6** by the cyclocondensation reaction of 3,4-methylenedioxyphenol **1**, aromatic aldehydes **2**, and active methylene compound including dimedone **3** or 1,3-dimethylbarbituric acid **5** under ultrasonic irradiation at room temperature in water (Fig. 1).

MATERIALS AND METHODS

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 9100 apparatus. IR spectra were obtained on an ABB FT-IR (FTLA 2000) spectrometer. ¹H NMR and ¹³C 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 K α radiation ($\lambda = 1.54 \text{ \AA}$). The microscopic morphology of the catalyst was revealed using scanning electron microscope (SEM, Philips, XL-30). Ultrasonication was performed using on a multiwave ultrasonic generator (Sonicator 3200; Bandelin, MS 73), equipped with a converter/transducer and titanium oscillator (horn), 12.5 mm in diameter, with an operation frequency of 20 KHz with a maximum power output of 200 W.

General procedure for the synthesis of CdO NPs

A simple precipitation procedure was applied to synthesis of the catalyst. Firstly, cetyltrimethylammonium bromide (CTAB, 0.50 gr) as surfactant was added into the stock solution obtained from dissolving of cadmium nitrate tetrahydrate (Cd(NO₃)₂·4H₂O) (0.31 gr, 1 mmol) in 20 mL water, under strong magnetic stirring. Then a solution of NaOH 2 M (5 mL) was added into the above mixture and stirred for another 20 min. The obtained white solid Cd(OH)₂ was collected by centrifugation and then dried in a vacuum oven at 70 °C for about 5 h. After 2 h heating at 400 °C, and then washing multiple times with distilled water and ethanol a dark brown powder of CdO nanoparticles was produced.

General procedure for the preparation of compounds 4a-g and 6a-g

A mixture of 3,4-methylenedioxyphenol **1** (1 mmol), an aromatic aldehyde **2** (1 mmol), active methylene compound including dimedone **3** or 1,3-dimethylbarbituric acid **5** (1 mmol), and CdO NPs (13 mgr, 10 mol %) in H₂O (5 mL) was equipped with ultrasonic probe under the power of 70 W at room temperature. After completion of the reaction, as monitored by TLC (ethyl acetate/n-hexane 3:2), the reaction mixture was cooled to ambient temperature, filtered and then poured in to hot ethanol (2 mL), and the heterogeneous catalyst was removed by simple filtration, washed with EtOH, and reused after dried in a vacuum oven at 50 °C for several hours. The ethanol solution was cooled to room temperature and the pure product was grown from this solution.

Spectroscopic and physical data

7,7-Dimethyl-10-phenyl-6,7,8,10-tetrahydro-9*H*-[1,3]dioxolo[4,5-*b*]xanthen-9-one (**4a**): White powder, yield: 331 mgr (95%). M.p. 189-190°C (lit: 190-192°C [30]). IR (KBr): $\nu_{\text{max}} = 2963, 2905, 2839,$

2634, 1581, 1492, 1448, 1369, 1299 cm^{-1} . ^1H NMR (500 MHz, $\text{DMSO-}d_6$): δ = 1.05 (s, 3 H, CH_3), 1.16 (s, 3 H, CH_3), 2.24 (d, J = 16.3 Hz, 1 H, H-6), 2.30 (d, J = 16.3 Hz, 1 H, H-6'), 2.57 (s, 2 H, H-8, H-8'), 4.94 (s, 1 H, H-10), 5.90 (d, J = 1.3 Hz, 1 H, H-2), 5.96 (d, J = 1.3 Hz, 1 H, H-2'), 6.68 (m, 2 H, H_{Ar}), 7.24 (m, 5 H, H_{Ar}) ppm. ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$): δ = 27.5, 28.7, 33.4, 37.6, 39.9, 50.5, 98.6, 101.9, 108.4, 113.3, 119.4, 126.7, 128.6, 144.2, 145.7, 147.4, 148.7, 164.8, 196.2 ppm. Anal. for $\text{C}_{22}\text{H}_{20}\text{O}_4$ (348.40): calcd. C 75.85, H 5.79; found C 75.62, H 5.61%.

10-(4-Bromophenyl)-7,7-dimethyl-6,7,8,10-tetrahydro-9H-[1,3]dioxolo[4,5-b]xanthen-9-one (4b): White powder, yield: 419 mgr (98%). M.p. 221-223°C (lit: 223-224°C [30]). IR (KBr, cm^{-1}): ν_{max} 2889, 2697, 2642, 2616, 1574, 1483, 1458, 1365, 1300 cm^{-1} . ^1H NMR (500 MHz, $\text{DMSO-}d_6$): δ = 1.09 (s, 3 H, CH_3), 1.13 (s, 3 H, CH_3), 2.24 (d, J = 16.0 Hz, 1 H, H-6), 2.376 (d, J = 16.0 Hz, 1 H, H-6'), 2.61 (s, 2 H, H-8, H-8'), 5.13 (s, 1 H, H-10), 5.84 (d, J = 1.2 Hz, 1 H, H-2), 5.96 (d, J = 1.2 Hz, 1 H, H-2'), 6.88 (m, 2 H, H_{Ar}), 7.32 (d, J = 8.1 Hz, 2 H, H_{Ar}), 7.46 (d, J = 8.1 Hz, 2 H, H_{Ar}). ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$): δ = 27.7, 28.6, 32.2, 37.5, 40.4, 51.6, 98.9, 101.8, 108.0, 112.8, 123.8, 125.7, 136.7, 139.0, 145.5, 146.3, 146.7, 165.4, 195.6 ppm. Anal. for $\text{C}_{22}\text{H}_{19}\text{BrO}_4$ (427.29): calcd. C 61.84, H 4.48; found C 62.01, H 4.62%.

10-(4-Chlorophenyl)-7,7-dimethyl-6,7,8,10-tetrahydro-9H-[1,3]dioxolo[4,5-b]xanthen-9-one (4c): White powder, yield: 371 mgr (97%). M.p. 202-204 °C (lit: 203-204°C [30]). IR (KBr): ν_{max} = 2959, 2897, 2844, 2593, 1580, 1486, 1462, 1368, 1302 cm^{-1} . ^1H NMR (500 MHz, $\text{DMSO-}d_6$): δ = 1.07 (s, 3 H, CH_3), 1.14 (s, 3 H, CH_3), 2.20 (d, J = 16.1 Hz, 1 H, H-6), 2.29 (d, J = 16.1 Hz, 1 H, H-6'), 2.59 (s, 2 H, H-8, H-8'), 5.32 (s, 1 H, H-10), 5.90 (d, J = 1.0 Hz, 1 H, H-2), 5.93 (d, J = 1.0 Hz, 1 H, H-2'), 6.97 (m, 2 H, H_{Ar}), 7.20 (d, J = 8.4 Hz, 2 H, H_{Ar}), 7.26 (d, J = 8.4 Hz, 2 H, H_{Ar}) ppm. ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$): δ = 27.4, 29.2, 33.0, 38.3, 42.5, 51.8, 98.9, 102.2, 108.6, 113.5, 128.6, 129.9, 132.7, 135.2, 145.1, 145.7, 146.9, 164.4, 194.5 ppm. Anal. for $\text{C}_{22}\text{H}_{19}\text{ClO}_4$ (382.84): calcd. C 69.02, H 5.00; found C 69.33, H 4.96%.

7,7-Dimethyl-10-(4-methylphenyl)-6,7,8,10-tetrahydro-9H-[1,3]dioxolo[4,5-b]xanthen-9-one (4f): White powder, yield: 355 mgr (98%). M.p. 211-212°C (lit: 213-215°C [30]). IR (KBr): ν_{max} = IR (KBr, cm^{-1}): ν_{max} 2959, 2893, 2870, 2636, 1580, 1526, 1453, 1373, 1345 cm^{-1} . ^1H NMR (500 MHz,

$\text{DMSO-}d_6$): δ = 1.07 (s, 3 H, CH_3), 1.16 (s, 3 H, CH_3), 2.19 (s, 3 H, CH_3), 2.22 (d, J = 16.1 Hz, 1 H, H-6), 2.30 (d, J = 16.1 Hz, 1 H, H-6'), 2.56 (s, 2 H, H-8, H-8'), 5.12 (s, 1 H, H-10), 5.84 (d, J = 1.1 Hz, 1 H, H-2), 5.90 (d, J = 1.1 Hz, 1 H, H-2'), 6.40 (s, 1 H, H_{Ar}), 6.64 (s, 1 H, H_{Ar}), 7.98 (d, J = 7.6 Hz, 2 H, H_{Ar}), 8.14 (d, J = 7.6 Hz, 2 H, H_{Ar}) ppm. ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$): δ = 20.9, 28.3, 29.9, 32.8, 39.1, 43.4, 51.9, 98.8, 102.7, 109.4, 113.3, 127.8, 128.9, 136.5, 137.1, 144.7, 145.2, 146.6, 166.1, 196.0 ppm. Anal. for $\text{C}_{23}\text{H}_{22}\text{O}_4$ (362.42): calcd. C 76.22, H 6.12; found C 76.09, H 5.85%.

6,8-Dimethyl-10-phenyl-6,10-dihydro-7H-[1,3]dioxolo[4',5':6,7][1]benzopyrano[2,3-d]pyrimidine-7,9(8H)-dione (6a): White powder, yield 350 mgr (96%). M.p. 241-242 °C (lit: 242-244°C [32]). IR (KBr, cm^{-1}): ν_{max} 3077, 2967, 2874, 1708, 1686, 1653, 1590, 1487, 1434, 1378, 1295 cm^{-1} . ^1H NMR (500 MHz, $\text{DMSO-}d_6$): δ = 3.26 (s, 3H, CH_3), 3.57 (s, 3H, CH_3), 5.02 (s, 1H, H-10), 5.89 (d, J = 1.3 Hz, 1H, H-2), 5.94 (d, J = 1.3 Hz, 1H, H-2'), 6.52 (s, 1H, H_{Ar}), 6.66 (s, 1H, H_{Ar}), 7.21 (m, 5H, H_{Ar}) ppm. ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$): δ = δ 28.0, 29.2, 40.1, 90.1, 97.7, 101.6, 109.7, 116.8, 127.9, 129.2, 129.3, 140.2, 145.0, 146.7, 146.9, 150.8, 152.4, 161.8 ppm. Anal. for $\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}_5$ (364.36): calcd. C 65.93, H 4.43, N 7.69; found: C 66.04, H 4.59, N 7.57%.

10-(4-Bromophenyl)-6,8-dimethyl-6,10-dihydro-7H-[1,3]dioxolo[4',5':6,7][1]benzopyrano[2,3-d]pyrimidine-7,9(8H)-dione (6b): White powder, yield 434 mgr (98%). M.p. 266-268 °C (lit: 268-270 °C [32]). IR (KBr, cm^{-1}): ν_{max} 3041, 2965, 2887, 1710, 1670, 1656, 1601, 1488, 1431, 1381, 1301 cm^{-1} . ^1H NMR (500 MHz, $\text{DMSO-}d_6$): δ = 3.28 (s, 3H, CH_3), 3.55 (s, 3H, CH_3), 5.01 (s, 1H, H-10), 5.91 (d, J = 0.9 Hz, 1H, H-2), 5.95 (d, J = 0.9 Hz, 1H, H-2'), 6.50 (s, 1H, H_{Ar}), 6.65 (s, 1H, H_{Ar}), 7.37 (d, J = 8.0 Hz, 2H, H_{Ar}), 7.47 (d, J = 8.0 Hz, 2H, H_{Ar}) ppm. ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$): δ = 28.2, 29.6, 38.2, 89.7, 98.1, 101.5, 109.7, 117.7, 122.5, 124.2, 136.4, 140.2, 146.5, 147.3, 148.6, 150.3, 152.4, 162.6 ppm. Anal. for $\text{C}_{20}\text{H}_{15}\text{BrN}_2\text{O}_5$ (443.25): calcd. C 54.20, H 3.41, N 6.32; found: C 54.03, H 3.53, N 6.46%.

6,8-Dimethyl-10-(3-hydroxyphenyl)-6,10-dihydro-7H-[1,3]dioxolo[4',5':6,7][1]benzopyrano[2,3-d]pyrimidine-7,9(8H)-dione (6d): Yellow powder, yield 365 mgr (96%). M.p. 262-264 °C (lit: 265-267 °C [32]). IR (KBr, cm^{-1}): ν_{max} 3181, 3064, 2925, 2851, 1709, 1688, 1651, 1600, 1532, 1362, 1292 cm^{-1} . ^1H NMR (500 MHz,

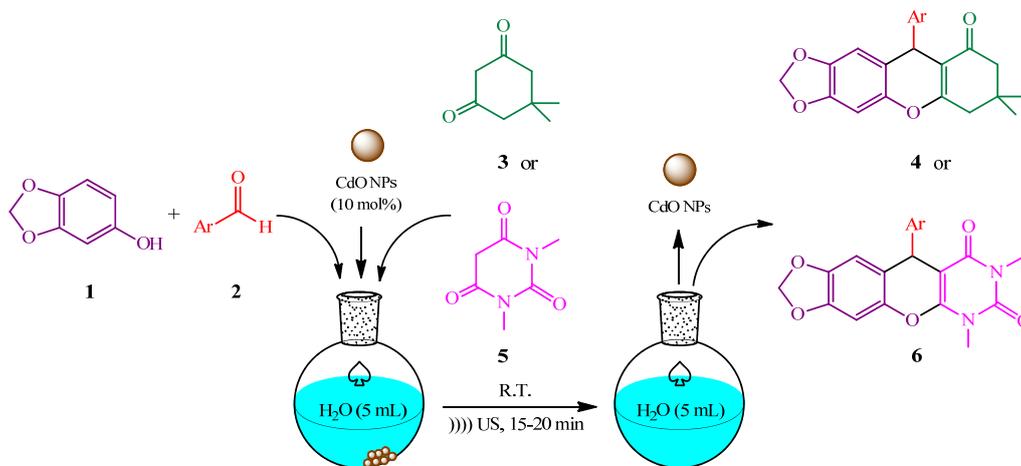


Fig. 1. Cyclocondensation reaction of 3,4-methylenedioxyphenol, aromatic aldehydes, and active methylene compounds using CdO NPs under ultrasonic irradiation.

DMSO- d_6): δ = 3.27 (s, 3H, CH₃), 3.53 (s, 3H, CH₃), 4.99 (s, 1H, H-10), 5.92 (d, J = 1.2 Hz, 1H, H-2), 5.97 (d, J = 1.2 Hz, 1H, H-2'), 6.49 (s, 1H, H_{Ar}), 6.67 (s, 1H, H_{Ar}), 7.14 (m, 1H, H_{Ar}), 7.40 (m, 3H, H_{Ar}), 9.41 (s, 1H, OH) ppm. ¹³C NMR (125 MHz, DMSO- d_6): δ = 28.7, 30.0, 39.6, 90.2, 97.7, 101.5, 109.0, 114.6, 116.4, 116.9, 119.3, 120.1, 140.2, 145.5, 146.9, 147.2, 150.0, 152.3, 158.1, 163.2 ppm. Anal. for C₂₀H₁₆N₂O₆ (380.35): calcd. C 63.16, H 4.24, N 7.36; found: C 63.04, H 4.33, N 7.57%.

6,8-Dimethyl-10-(4-hydroxyphenyl)-6,10-dihydro-7H-[1,3]dioxolo[4',5':6,7][1]benzopyrano[2,3-d]pyrimidine-7,9(8H)-dione (6e): White powder, yield 369 mgr (97%). M.p. 270-272 °C (lit: 272-274 °C [32]). IR (KBr, cm⁻¹): ν_{\max} 3188, 3085, 2931, 2866, 1711, 1689, 1636, 1570, 1475, 1430, 1386, 1297 cm⁻¹. ¹H NMR (500 MHz, DMSO- d_6): δ = 3.25 (s, 3H, CH₃), 3.54 (s, 3H, CH₃), 4.97 (s, 1H, H-10), 5.88 (d, J = 1.0 Hz, 1H, H-2), 5.95 (d, J = 1.0 Hz, 1H, H-2'), 6.50 (s, 1H, H_{Ar}), 6.66 (s, 1H, H_{Ar}), 7.54 (d, J = 8.4 Hz, 2H, H_{Ar}), 7.88 (d, J = 8.4 Hz, 2H, H_{Ar}), 9.38 (s, 1H, OH) ppm. ¹³C NMR (125 MHz, DMSO- d_6): δ = 28.8, 29.4, 38.9, 90.0, 98.4, 101.4, 109.0, 114.5, 116.3, 124.6, 139.2, 146.5, 147.0, 148.0, 151.8, 153.1, 157.3, 163.5 ppm. Anal. for C₂₀H₁₆N₂O₆ (380.35): calcd. C 63.16, H 4.24, N 7.36; found: C 63.28, H 4.34, N 7.29%.

RESULTS AND DISCUSSION

In the present work as illustrated in Fig. 1, synthesis of xanthenones **4** and [1]benzopyrano[*d*]pyrimidinediones **6** were occurred using highly efficient CdO NPs as catalyst under ultrasonic irradiation. The procedure that was employed

for the preparation of CdO NPs was a simple chemical precipitation technique described in general procedure. The synthesized CdO NPs were characterized using scanning electron microscopy (SEM), X-Ray diffraction (XRD) analysis, and Fourier transformed infrared absorption (FT-IR) spectroscopy. The SEM image of the synthesized CdO NPs is depicted in Fig. 2a. The polycrystalline nanoparticles of the CdO exhibited an agglomerated shape with an average size of about 24.8 nm.

The crystal structure and phase composition of the synthesized CdO NPs were determined by XRD pattern (Fig. 3a). The cubic phase of CdO (JCPDS No. 03-065-2908) was confirmed and the diffraction peaks corresponding to the planes (111), (200), (220), (311), and (222) are obtained at 2θ = 32.99°, 38.27°, 55.25°, 65.86°, and 69.21° respectively.

The synthesized CdO NPs was also characterized by FT-IR spectrum (Fig. 4a). The broad peak with low intensity in the region of 3200-3400 cm⁻¹ can be assigned to the stretching vibration of the hydroxyl group (OH) of the adsorbed water. The peak at around 1251 cm⁻¹ can be detected the residual organic compounds. The peak appearing at 456 cm⁻¹ is also attributed to the Cd-O stretching mode in the lattice.

With a desire to achieve suitable conditions for the synthesis mentioned above, a reaction of 3,4-methylenedioxyphenol **1**, 4-chlorobenzaldehyde **2c**, and dimedone **3** was therefore conducted under different reaction conditions (Fig. 5 and Table 1). In order to explore

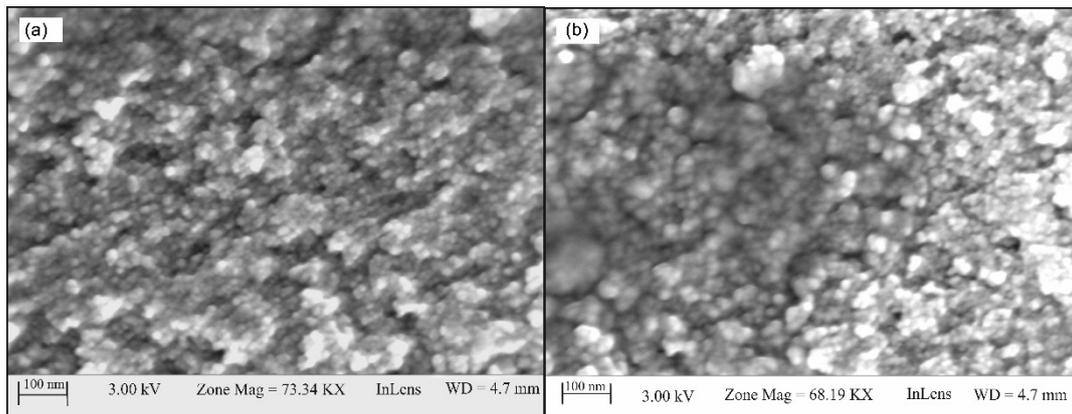


Fig. 2. SEM images of a) original CdO NPs catalyst, and b) 3rd recycled catalyst use.

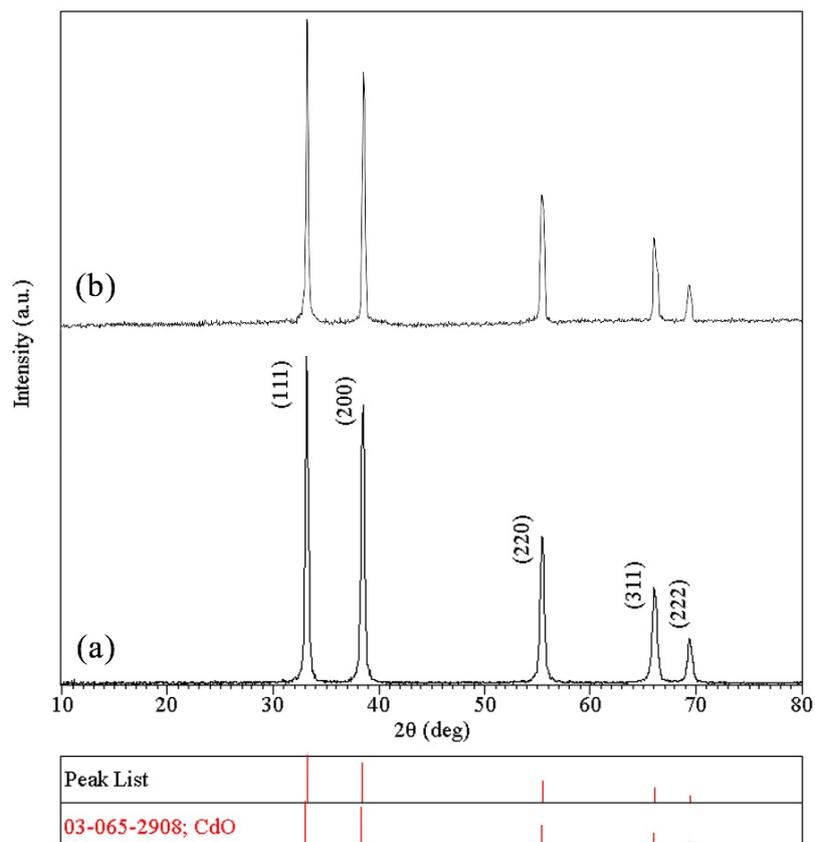


Fig. 3. XRD pattern of a) original CdO NPs catalyst, and b) 3rd recycled catalyst use.

the effect of ultrasonic irradiation, firstly, the model reaction was examined using 15 mol% of CdO NPs, in refluxing various solvents or under solvent-free conditions, almost moderate yields (63-81%) with prolonged reaction times (30-40 min) were found (Table 1, entries 1-6). When

the reaction was carried out under ultrasonic irradiation at power of 70 W, using 10 mol% of CdO NPs in water at room temperature, excellent yield of corresponding product (**2c**, 97%) was obtained with short reaction time (15 min) (Table 1, entry 7). Meanwhile, no by-product was observed

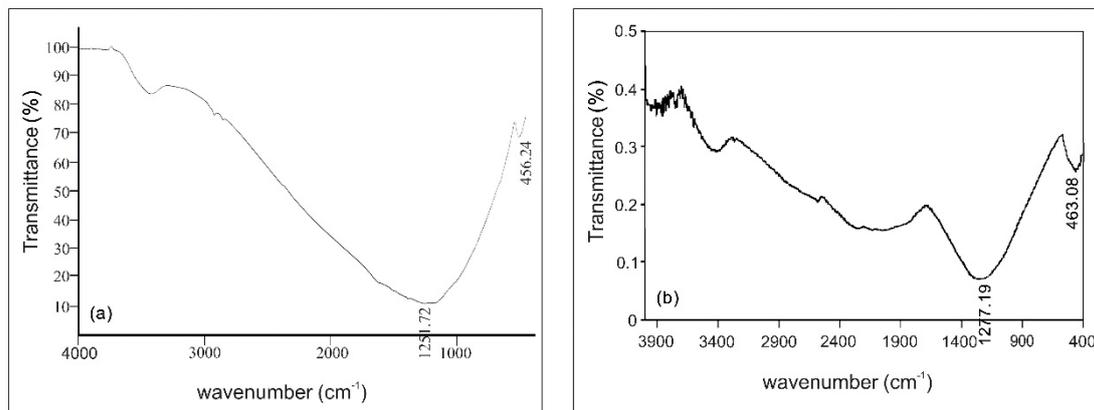


Fig. 4. FT-IR spectra of a) original CdO NPs catalyst, and b) 3rd recycled catalyst use.

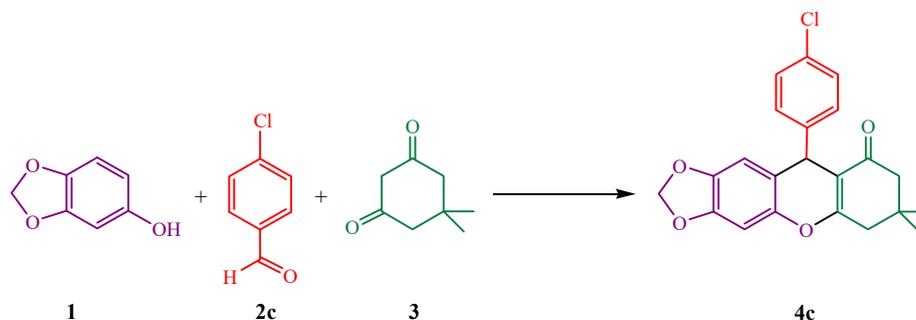


Fig. 5. Synthesis of 10-(4-chlorophenyl)-7,7-dimethyl-6,7,8,10-tetrahydro-9H-[1,3]dioxolo[4,5-b]xanthen-9-one (4c) under various conditions.

Table 1. Optimization of reaction conditions for preparation of 10-(4-chlorophenyl)-7,7-dimethyl-6,7,8,10-tetrahydro-9H-[1,3]dioxolo[4,5-b]xanthen-9-one (4c).

Entry	Conditions	Catalyst (mol%)	Time (min)	Yield (%) ^d
1	H ₂ O (Reflux)	CdO NPs (15 mol%)	30	81
2	EtOH (Reflux)	CdO NPs (15 mol%)	40	75
3	CH ₂ Cl ₂ (Reflux)	CdO NPs (15 mol%)	40	63
4	CH ₃ CN (Reflux)	CdO NPs (15 mol%)	40	70
5	DMF ^a (Reflux)	CdO NPs (15 mol%)	30	72
6	Solvent-free (100 °C)	CdO NPs (15 mol%)	30	68
7	H ₂ O (US, 70 W, R.T.)	CdO NPs (10 mol%)	15	97
8	H ₂ O (US, 65 W, R.T.)	CdO NPs (10 mol%)	15	90
9	H ₂ O (US, 80 W, R.T.)	CdO NPs (10 mol%)	15	93
10	H ₂ O (US, 70 W, R.T.)	CdO NPs (5 mol%)	15	63
11	H ₂ O (US, 70 W, R.T.)	CdO NPs (15 mol%)	10	97
12	H ₂ O (US, 70 W, R.T.)	HCl (10 mol%)	15	90
13	H ₂ O (US, 70 W, R.T.)	<i>p</i> -TsOH ^b (15 mol%)	15	86
14	H ₂ O (US, 70 W, R.T.)	DAHP ^c (15 mol%)	15	78

^aDMF: Dimethyl formamide.

^b*p*-TsOH: *p*-Toluenesulfonic acid.

^cDAHP: Diammonium hydrogen phosphate.

^dIsolated yield.

Table 2. CdO NPs catalyzed syntheses of 7,7-dimethyl-10-aryl-6,7,8,10-tetrahydro-9H-[1,3]dioxolo[4,5-*b*]xanthen-9-ones 4a-g and 6,8-dimethyl-10-aryl-6,10-dihydro-7H-[1,3]dioxolo[4',5':6,7][1]benzopyrano[2,3-*d*]pyrimidine-7,9(8H)-diones 6a-g.

Product	Ar	Compound 3 or 5	Time (min)	Yield (%) ^{a,b}	M.p (°C)	
					Obsd.	Lit.
4a	C ₆ H ₅	3	20	95	189-190	193-194 [30]
4b	4-Br-C ₆ H ₄	3	20	98	221-223	223-224 [30]
4c	4-Cl-C ₆ H ₄	3	20	97	202-204	203-204 [30]
4d	3-OH-C ₆ H ₄	3	20	96	228-229	227-229 [30]
4e	4-OH-C ₆ H ₄	3	20	98	220-222	218-220 [30]
4f	4-CH ₃ -C ₆ H ₄	3	20	98	211-212	213-215 [30]
4g	3-NO ₂ -C ₆ H ₄	3	20	97	159-161	158-160 [30]
6a	C ₆ H ₅	5	15	96	241-242	242-244 [32]
6b	4-Br-C ₆ H ₄	5	15	98	266-268	268-270 [32]
6c	4-Cl-C ₆ H ₄	5	15	98	257-259	255-257 [32]
6d	3-OH-C ₆ H ₄	5	15	96	262-264	265-267 [32]
6e	4-OH-C ₆ H ₄	5	15	97	270-272	272-274 [32]
6f	4-CH ₃ -C ₆ H ₄	5	15	95	249-250	248-250 [32]
6g	3-NO ₂ -C ₆ H ₄	5	15	96	261-263	260-262 [32]

^aYields refer to those of pure isolated products characterized by IR, ¹H NMR and ¹³C NMR spectral data and by elemental analyses.

^bReaction conditions: A mixture of 3,4-methylenedioxyphenol **1** (1 mmol), an aromatic aldehyde **2** (1 mmol), active methylene compound **3** or **5** (1 mmol), CdO NPs (13 mgr, 10 mol%) in H₂O (5 mL) was kept under ultrasonic irradiation at power of 70 W at room temperature.

when the reaction was occurred using ultrasound irradiation. Next, the power of ultrasonic irradiation was also investigated. It was found that the power of 70 W is desirable for this reaction (Table 1, entries 7-9). Finally, endeavor on the catalytic potential of the CdO NPs in comparison to other acid or base catalysts, indicated that CdO NPs in optimal quantity of 10 mol% gives the best results under ultrasonic irradiation at power of 70 W in water at room temperature (Table 1, entries 7 and 10-14).

Under optimized conditions, we then have extended the reaction of active methylene compound including dimedone or 1,3-dimethylbarbituric acid with a range of aromatic aldehydes and 3,4-methylenedioxyphenol to furnish the respective xanthenones **4** and [1]benzopyrano[*d*]pyrimidinediones **6** in high yields (Table 2).

Next, the recyclability of the catalyst was examined by separation of the catalyst from the reaction mixture, washed with ethanol and

dried. The recovered catalyst was reused four additional times in subsequent reaction to afford the corresponding product **4c** with a congruous catalytic activity (product yields: 97%, 97%, 96%, and 94%, respectively). The SEM, XRD, and FT-IR images of the fresh and third recycled catalyst reuse, as expected showed no change in the catalyst structure after catalysis (Figs. 2-4).

In general, the plausible mechanism for the preparation of corresponding products **4** or **6** in the presence of CdO NPs as a heterogeneous catalyst is presented in Fig. 6. As can be observed, at the first time, CdO NPs activated the carbonyl group of aromatic aldehyde **2** for Knoevenagel condensation with dimedone **3** or 1,3-dimethylbarbituric acid **5** to produce alkene **9**. The catalyst can also be considered as a base in Michael addition of 3,4-methylenedioxyphenol **1** to alkene **9** to generate products **4** or **6** after cyclization and dehydration *via* intermediates **10** and **11**.

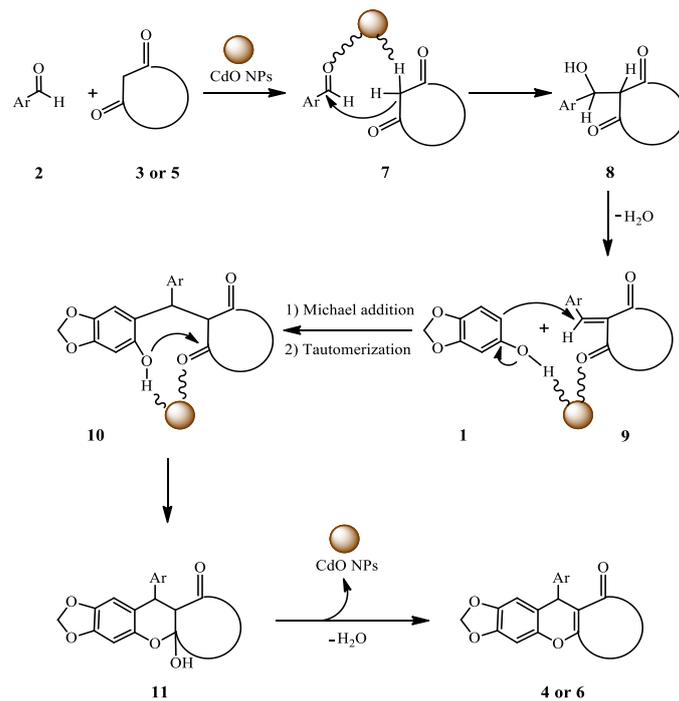


Fig. 6. Proposed mechanism for the synthesis of compounds 4 or 6.

CONCLUSION

CdO NPs were employed as a heterogeneous catalyst for cyclocondensation reaction of 3,4-methylenedioxyphenol, aromatic aldehydes, and active methylene compound including dimedone or 1,3-dimethylbarbituric acid at room temperature in water and under ultrasonic irradiation. The Operational simplicity, high yields, short reaction times, reusability of catalyst, and easy work-up procedure makes this procedure more attractive for the synthesis of xanthenones and [1]benzopyrano[d]pyrimidinediones.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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