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In water–ultrasound-promoted synthesis of tetraketones and 2-substituted-1H-benzimidazoles catalyzed by BiOCl nanoparticles

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Abstract A highly efficient, green protocol has been developed for the synthesis of various structurally diverse 2,2′-arylmethylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) and 2-substituted-1H-benzimidazole derivatives. The reaction was performed in water under ultrasound irradiation, using BiOCl nanoparticles as a catalyst. The nanocatalyst was found to be reusable for seven subsequent reactions without much loss in activity. Simple methodology with short reaction times and mild reaction conditions with easy work-up procedure are the salient features of this method.

Keywords Tetraketones · 2-Substituted-1-H-benzimidazoles · BiOCl nanoparticles · Ultrasound

Introduction

The development of rapid and selective synthetic routes for functionalized heterocyclic building blocks is of great importance to both human health and the environment. During the last few years, increasing environmental consciousness in chemical research and industry has meant that organic researchers are now directed to the finding of methods that largely take into account the criterion of sustainable chemistry [1]. Indeed, due to the demands of clean technology, many recyclable nano-catalysts have been reported [2–5].

Tetraketones, with four carbonyl functionalities, is an important intermediate in the preparation of xanthendione, acridinedione [6] and 4H-1-benzopyran derivatives

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[7]. 2,2′-aryl-methylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) or tetraketones exhibit a broad spectrum of biological activities, such as lipoxygenase inhibition, anti-oxidant [8] antibacterial and antiviral [9], and the prevention and treatment of thrombosis [10]. Because of their biological and chemical importance, synthesis of tetraketones is under considerable attention of many organic chemists. Tetraketones have been mainly synthesized through Knoevenagel condensations and Michael additions of aldehydes with cyclohexane-1,3-diones, dimedones or various 1,3-cyclic diketones [11]. Various synthetic methodologies have been developed, involving the use of pyridine [12], metal hydroxides [13, 14], L-proline [15], $HClO_4$-SiO_2 [16], choline chloride [17], and nano-Fe/NaY zeolite [18] as catalysts, cetyltrimethyl ammonium bromide as surfactant [19], or without any catalyst in water [11].

Benzimidazole is one of the important analogues generally found in drugs and agrochemicals. Hence, its derivatives are being targeted in medicinal chemistry research due to their pharmacological interest. Benzimidazole shows antibacterial [20], anti-inflammatory [21], antiviral [22], antiprotozoal [23], anticancer [24] and antimalarial activity [25].Various strategies employed in the synthesis of substituted benzimidazoles include the cyclo-condensation reaction of *o*-phenylenediamines with carboxylic acids, nitriles and orthoesters [26]. Another protocol is the direct condensation of 1,2-phenylenediamines with aryl aldehydes using a variety of catalysts, such as heteropoly acid containing ionic liquids [27], bismuth chloride [28], polyaniline-sulfate [29], Zn^{2+}-K10-clay [30], (bromodimethyl)sulfonium bromide [31], $TiCl_3OTf$ [32], NaY-zeolite [33], nano-In_2O_3 [34], $Fe(HSO_4)_3$ [35] and $MgCl_2$·$6H_2O$ [36]. However, these methods suffer from limitations such as longer reaction times (generally 2–24 h), and the use of expensive catalysts and organic solvents such as MeCN, CH_2Cl_2, $CHCl_3$, DMF, etc. Moreover, non-reusability of catalysts such as $MgCl_2$·$6H_2O$ and harsh reaction conditions decreasea the efficacy of the reported methods. Therefore, it is important to develop more efficient catalysts and alternate synthetic methodologies for the preparation of these compounds. Ultrasound-promoted organic synthesis [37, 38] has attracted considerable attention as it places emphasis on minimizing energy requirements, the avoidance of toxic reagents, the reduction of waste and increasing reaction efficiency. Bismuth oxychloride (BiOCl) nano-particles have been successfully employed as semiconductor photocatalysts [39–44]. The high reactivity of BiOCl nanoparticles is attributed to their large surface area which enables their use in the synthesis of organic compounds.

Materials and methods

All the chemicals were purchased from S.D. Fine Chemicals (India) and were used without further purification. All melting points were measured on a Gallenkamp melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker Avance-400 MHz spectrometer in $CDCl_3$ in the presence of tetramethyl-silane as an internal standard. IR spectra were recorded using a Perkin-Elmer 843 spectrometer with KBr plates. Sonochemical synthesis was performed with the help

of an ultrasonic instrument (ACE, USA Horn-type). Conditions: diameter of stainless steel tip of horn: 1.3×10^{-2} m, rated output power: 750 W, operating frequency: 22 kHz, surface area of ultrasound irradiating face: 1.32×10^{-4} m^2 and intensity: 3.4×10^5 W/m^2.

The temperature of the process was maintained at 35 ± 2 °C by means of a supply of water to the jacketed reactor used for the synthesis. The reactions were monitored by TLC on silicagel PolyGram SILG/UV 254 plates (Merck). All products are known compounds and were identified by comparison with those reported in the literature.

Synthesis and characterization of BiOCl nanoparticles

The BiOCl nanoparticles were prepared by the reported method using bismuth nitrate pentahydrate $Bi(NO_3)_3 \cdot 5H_2O$ as the precursor [45, 46]. Synthesized BiOCl nanoparticles were characterized by XRD and Fourier transform infrared (FT-IR).The crystal structure of BiOCl was determined by an X-ray diffractometer (Bruker D8 Advance Diffractometer) with CuKα radiations ($\lambda = 1.5416$ Å) in the range of 20°–80° as shown in Fig. 1a. Figure 1b represents the XRD patterns of reused BiOCl nanoparticles after seven cycles. The prepared BiOCl sample is in good agreement with the tetragonal structure and matched with the JCPDS data (01-075-1533). The crystallite size (D) was calculated from the XRD peak using the Debye–Scherrer formula.

$$D = \frac{K\lambda}{\beta cos\theta} \tag{1}$$

where K is the shape factor, which is a constant taken as 0.9, λ is the wavelength of the X-ray radiation ($\lambda = 1.5416$ Å), β is the full-width at half-maximum (FWHM) in radians, and θ is the Bragg's angle in degree. The crystallite size of the sample obtained from Eq. (1) has a grain size between 23 and 29 nm. The FT-IR spectrum in Fig. 2a shows the characteristic absorption peaks of the as-synthesized sample. The absorption band at 524 cm^{-1} is assigned to the stretching vibration of Fourier transform infrared Bi-O bond in BiOCl. [47] Figure 2b represents Fourier transform
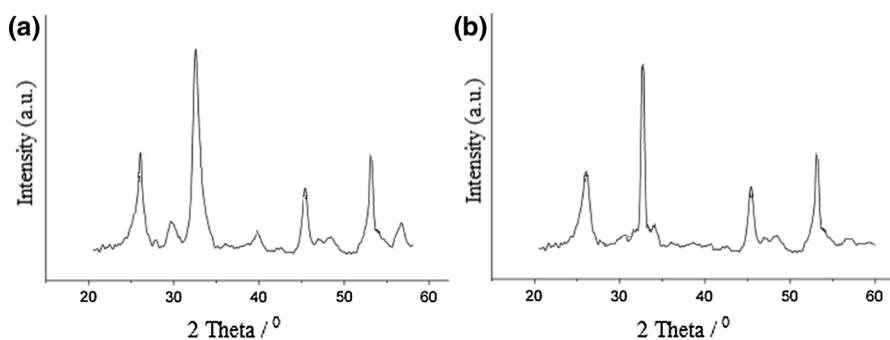

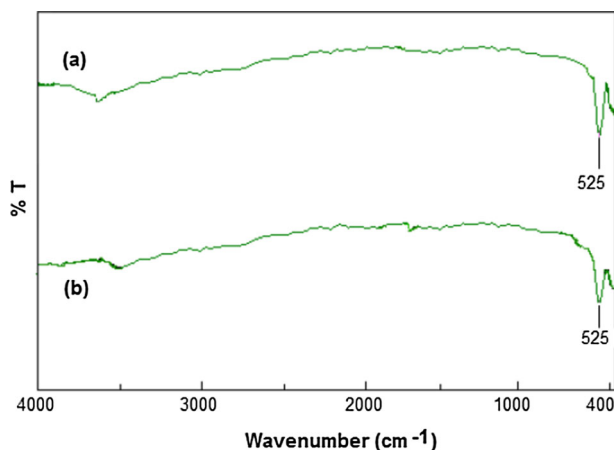Fig. 1 XRD patterns of BiOCl: (a) initial; (b) after seven cycles of reuse

Fig. 2 FT-IR of BiOCl: (*a*) initial; (*b*) after seven cycles of reuse

infrared IR spectra of recycled BiOCl nanoparticles after Fourier transform infrared seventh reuse.

Optimization of the reaction conditions

The reaction conditions were optimized for the synthesis of 2,2′-(4-methoxylphenyl)methylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) (3a) and 2-(4-nitrophenyl)-1H-benzo[d]imidazole (5b) under ultrasound irradiation (Table 1). The effects of various solvents on the model reactions were explored. Several organic solvents such as EtOH, CH_3CN, toluene, $CHCl_3$ and DMF were examined (Table 1, entries 1–5 and 16–20). It is exciting to find that water affords the product in good yield even better than other solvents for (3a) and (5b) synthesis (Table 1, entries 15 and 29). Water is highly polar, which possibly creates the necessary conditions for the formation of intermediates and their conversion to final products on the catalyst surface.

The catalytic activity of BiOCl was also studied. When the reaction was performed at room temperature in the presence of BiOCl nanoparticles and in the absence of ultrasonic irradiation, 3a was obtained in 45% yield after 150 min (Table 1, entry 6) and 5b was obtained in 50% yield after 120 min (Table 1, entry 21). In the presence of the catalyst (30 mg) and ultrasonic irradiation (400 W), the yield of 3a increased to 80% and the reaction time was reduced to 40 min (Table 1, entry 11) and in the presence of (Table 1, entry 6)catalyst (12 mg) and ultrasonic irradiation (400 W), the yield of 5b increased to 71% and the reaction time was reduced to 25 min (Table 1, entry 25). It was verified that the combination method (ultrasound irradiation and BiOCl nanoparticles) can be regarded as having an important role in the product yield and reaction time.

Table 1 Optimization condition for the synthesis of 3a and 5b

No.	Product	Catalyst	Solvent	Condition	Power (W)	Time (min)	Yield (%)
1	3a	BiOCl nano (30 mg)	EtOH	))))	750	25	70
2	3a	BiOCl nano (30 mg)	CH_3CN	))))	750	23	35
3	3a	BiOCl nano (30 mg)	Tolune	))))	750	30	65
4	3a	BiOCl nano (30 mg)	$CHCl_3$	))))	750	31	20
5	3a	BiOCl nano (30 mg)	DMF	))))	750	40	55
6	3a	No catalyst	H_2O	Silent	750	150	45
7	3a	BiOCl nano (30 mg)	H_2O	Silent	750	70	60
8	3a	BiOCl nano (10 mg)	H_2O	))))	750	45	60
9	3a	BiOCl nano (20 mg)	H_2O	))))	750	35	71
10	3a	BiOCl nano (25 mg)	H_2O	))))	750	20	83
11	3a	BiOCl nano (30 mg)	H_2O	))))	400	40	80
12	3a	BiOCl nano (30 mg)	H_2O	))))	550	35	60
13	3a	BiOCl nano (30 mg)	H_2O	))))	600	30	65
14	3a	BiOCl nano (30 mg)	H_2O	))))	650	25	84
15	**3a**	**BiOCl nano (30 mg)**	**H_2O**	**))))**	**750**	**15**	**93**
16	5b	BiOCl nano (12 mg)	EtOH	))))	750	20	79
17	5b	BiOCl nano (12 mg)	CH_3CN	))))	750	33	63
18	5b	BiOCl nano (12 mg)	Toluene	))))	750	80	50
19	5b	BiOCl nano (12 mg)	$CHCl_3$	))))	750	60	70
20	5b	BiOCl nano (12 mg)	DMF	))))	750	28	60
21	5b	No catalyst	H_2O	Silent	750	120	50
22	5b	BiOCl nano (12 mg)	H_2O	Silent	750	90	75
23	5b	BiOCl nano (05 mg)	H_2O	))))	750	50	59
24	5b	BiOCl nano (08 mg)	H_2O	))))	750	25	65
25	5b	BiOCl nano (12 mg)	H_2O	))))	400	25	71
26	5b	BiOCl nano (12 mg)	H_2O	))))	550	23	75
27	5b	BiOCl nano (12 mg)	H_2O	))))	600	20	82
28	5b	BiOCl nano (12 mg)	H_2O	))))	650	15	85
29	**5b**	**BiOCl nano (12 mg)**	**H_2O**	**))))**	**750**	**08**	**93**

The two best yields are shown in bold

General procedure for synthesis of 2, 2′-arylmethylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one)

A mixture of aldehyde (1 mmol) and dimedone (2 mmol) in the presence of BiOCl (30 mg) nanoparticles was added to water (5 mL) as solvent. The reaction mixture was then placed under sonication using an ultrasonic horn (22 kHz frequency) for the required time with a 5-s ON and 5-s OFF cycle from time $t = 0$ h. The progress of the reaction was monitored by TLC (eluent: 7:3 n-hexane–ethyl acetate) for the time period as indicated in Table 2. After completion of the reaction, the mixture was diluted by 1:1 H_2O: EtOAc (10 mL) stirred at ambient temperature (20 min) and centrifuged to separate the solid catalyst. The organic layer of the solution was

Table 2 BiOCl nanoparticles-catalyzed synthesis of 2, 2′-arylmethylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one)
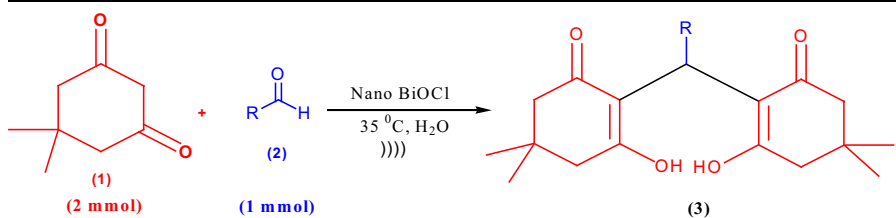
Entry	Product	R	Time (min)	Yield (%)[b]	M.P (°C)	
					Found	Reported
1	3a	4-CH$_3$OC$_6$H$_4$	15	93	141–143	(142–143)
2	3b	4-NO$_2$ C$_6$H$_4$	16	83	188–190	(188–190)
3	3c	3-NO$_2$ C$_6$H$_4$	12	95	191–193	(193–195)
4	3d	2-NO$_2$ C$_6$H$_4$	15	91	188–190	(188–189)
5	3e	4-Cl C$_6$H$_4$	15	90	141–143	(141–143)
6	3f	3-Cl C$_6$H$_4$	17	88	186–188	(188–190)
7	3g	2-Cl C$_6$H$_4$	15	90	200–201	(199–200)
8	3h	4-OH C$_6$H$_4$	12	92	187–189	(187–189)
9	3i	4-OH,3-CH$_3$O C$_6$H$_3$	17	95	193–195	(194–195)
10	3j	3,4-Cl$_2$ C$_6$H$_3$	17	91	164–165	(163–164)
11	3k	4-CH$_3$C$_6$H$_4$	16	91	141–143	(141–143)
12	3l	C$_6$H$_5$	15	95	188–190	(189–190)
13	3m	3-BrC$_6$H$_4$	12	83	201–203	(203–204)

The products were characterized by ^{1}H NMR spectroscopy

[b] Isolated yields

separated, dried over sodium sulfate, and the organic solvent and other residues were stripped in a vacuum evaporator. The residue obtained was purified by column chromatography (silica gel, 60–120 mesh; pet ether) to afford the desired products. All the products (3a–m) are known compounds and are confirmed by comparison of their spectroscopic data with literature data.

Spectral data for 2,2′-arylmethylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one)

2,2′-(4-Methoxylphenyl)methylenebis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) **(3a)** IR (KBr, cm^{-1}) υ_{max} = 3050, 2960, 2870, 1725, 1601. ^{1}H NMR (CDCl$_3$, 400 MHz) δ: 11.93 (s, 1H, OH), 11.56 (brs, 1H, OH), 7.02 (d, J = 8.3 Hz, 2H, Ph-H), 6.82 (d, J = 8.3 Hz, 2H, Ph-H), 5.50 (s, 1H, CH), 3.79 (s, 3H, CH$_3$O), 2.17–2.49 (m, 8H, CH$_2$), 1.24 (s, 6H, CH$_3$), 1.12 (s, 6H, CH$_3$). ^{13}C NMR (400 MHz, DMSO-d_6) δ: 27.3, 29.6, 31.4, 32.0, 46.4, 55.2, 113.6, 115.8, 127.8, 129.8, 157.6, 189.3, 190.0

2,2′-(4-Nitrophenyl)methylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) (3b) IR (KBr, cm^{-1}) v_{max} = 3062, 2955, 1590, 1510, 1384, 1345. ^{1}H NMR (CDCl$_3$, 400 MHz) δ: 11.80 (s, 1H, OH), 11.26 (brs, 1H, OH), 8.10 (d, J = 8.3 Hz, 2H, Ph-H), 7.22 (d, J = 8.3 Hz, 2H, Ph-H), 5.53 (s, 1H, CH), 2.30–2.49 (m, 8H, CH$_2$), 1.21 (s, 6H, CH$_3$), 1.09 (s, 6H, CH$_3$). ^{13}C NMR (400 MHz, DMSO-d_6) δ: 27.4, 29.4, 31.4, 33.2, 46.4, 114.8, 123.4, 127.6, 146.0, 146.6, 189.5, 191.0

2,2′-(3-Nitrophenyl)methylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) (3c) IR (KBr, cm^{-1}) v_{max} = 3055, 2961, 1592, 1514, 1391, 1340. ^{1}H NMR (CDCl$_3$, 400 MHz) δ: 11.83 (s, 1H, OH), 11.21(brs, 1H, OH), 8.26(m, 2H, Ph-H), 8.01 (s, 1H, Ph-H), 7.37(d, J = 8.6 Hz, 1H, Ph-H) 5.50 (s, 1H, CH), 2.37–2.47 (m, 8H, CH$_2$), 1.22 (s, 6H, CH$_3$), 1.14 (s, 6H, CH$_3$). ^{13}C NMR (400 MHz, DMSO-d_6) δ: 27.3, 29.6, 31.3, 32.8, 46.3, 46.9, 114.7, 120.9, 122.1, 129.0, 132.8, 140.6, 148.3, 189.5, 191.0

2,2′-(2-Nitrophenyl)methylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) (3d) IR (KBr, cm^{-1}) v_{max} = 3052, 2960, 1594, 1510, 1396, 1347. ^{1}H NMR (CDCl$_3$, 400 MHz) δ:11.80 (s, 1H, OH), 11.23(brs, 1H, OH), 7.57 (d, J = 7.9 Hz, 1H, Ph-H), 7.43 (t, J = 7.9 Hz, 1H, Ph-H), 7.31 (t, J = 7.9 Hz, 1H, Ph-H), 7.20 (d, J = 7.9 Hz, 1H, Ph-H), 5.82 (s, 1H, CH), 2.22–2.50 (m, 8H, CH$_2$), 1.14 (s, 6H, CH$_3$), 1.07 (s, 6H, CH$_3$).

2, 2′-(4-Chlorophenyl)methylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) (3e) IR (KBr, cm^{-1}) v_{max} = 3465, 3010, 2975, 1733, 1594. ^{1}H NMR (CDCl$_3$, 400 MHz) δ: 11.86 (s, 1H, OH), 11.47 (brs, 1H, OH), 7.21 (d, J = 8.1 Hz, 2H, Ph-H), 7.00 (d, J = 8.1 Hz, 2H, Ph-H), 5.46 (s, 1H, CH), 2.28–2.47 (m, 8H, CH$_2$), 1.21 (s, 6H, CH$_3$), 1.09 (s, 6H, CH$_3$). ^{13}C NMR (400 MHz, DMSO-d_6) δ: 27.4, 29.6, 31.4, 32.4, 46.4, 47.0, 47.04, 115.3, 128.2, 128.3, 131.5, 136.7, 189.4, 190.6

2, 2′-(3-Chlorophenyl)methylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) (3f) IR (KBr, cm^{-1}) v_{max} = 3469, 3017, 2970, 1735, 1591. ^{1}H NMR (CDCl$_3$, 400 MHz) δ: 11.91(s, 1H, OH), 11.50 (brs, 1H, OH), 7.19–7.31 (m, 2H, Ph-H), 7.04 (s, 1H, Ph-H), 6.95 (d, J = 7.8 Hz, 1H, Ph-H), 5.41 (s, 1H, CH), 2.21–2.36 (m, 8H, CH$_2$), 1.22 (s, 6H, CH$_3$), 1.10 (s, 6H, CH$_3$). ^{13}C NMR (400 MHz, DMSO-d_6) δ: 27.2, 29.4, 31.3, 32.5, 46.2, 47.1, 115.2, 124.8, 126.1, 127.0, 129.3, 134.0, 140.3, 189.3, 190.5.

2, 2′-(2-Chlorophenyl)methylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) (3g) IR (KBr, cm^{-1}) v_{max} = 3461, 3022, 2972, 1729, 1596. ^{1}H NMR (CDCl$_3$, 400 MHz) δ: 11.84(s, 1H, OH), 11.38 (brs, 1H, OH), 7.31 (d, J = 7.9 Hz, 1H, Ph-H), 7.27 (d, J = 7.9 Hz, 1H, Ph-H), 7.20 (t, J = 7.9 Hz, 1H, Ph-H), 7.13 (t, J = 7.9 Hz, 1H, Ph-H), 5.50 (s, 1H, CH), 2.23–2.43 (m, 8H, CH$_2$), 1.18 (s, 6H, CH$_3$), 1.09 (s, 6H, CH$_3$).

2,2′-(4-Hydroxyphenyl)methylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) (3h) ^{1}H NMR (CDCl$_3$, 400 MHz) δ: 11.81 (s, 1H, OH), 11.49 (brs, 1H, OH), 7.33 (d, J = 8.4 Hz, 2H, Ph-H), 7.24 (d, J = 8.4 Hz, 2H, Ph-H), 5.50 (s, 1H, OH), 5.42 (s, 1H, CH), 2.21–2.44 (m, 8H, CH$_2$), 1.22 (s, 6H, CH$_3$), 1.11 (s, 6H, CH$_3$).

2,2′-(4-Hydroxy-3-methoxyphenyl)methylenebis(3-hydroxy-5,5-dimethyl-2-cyclo-hexene-1-one) (3i) ¹H NMR (CDCl₃, 400 MHz) δ: 11.77 (s, 1H, OH), 11.26 (brs, 1H, OH), 6.98 (d, $J = 8.2$ Hz, 1H, Ph-H), 6.67 (s, 1H, Ph-H), 6.59 (d, $J = 8.2$ Hz, 1H, Ph-H), 5.47 (s, 1H, OH), 5.44 (s, 1H, CH), 3.81 (s, 3H, CH₃O), 2.31–2.44 (m, 8H, CH₂), 1.24 (s, 6H, CH₃), 1.12 (s, 6H, CH₃).

2,2′-(2,4-Dichlorophenyl)methylenebis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) (3j) ¹H NMR (CDCl₃, 400 MHz) δ: 11.81 (brs, 1H, OH), 10.67 (s, 1H, OH). 7.34–7.31(m, 2H, Ph-H), 7.20–7.18 (dd, J = 7.6 Hz, J = 2.5 Hz, 1H, Ph-H), 5.51 (s, 1H, CH), 2.24–2.41 (m, 8H, CH₂), 1.12 (s, 6H, CH₃), 1.08 (s, 6H, CH₃).

2,2′-(4-Methylphenyl)methylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) (3k) ¹H NMR (CDCl₃, 400 MHz) δ: 11.56 (brs, 1H, OH), 10.67 (s, 1H, OH). 7.11 (d, $J = 8.2$ Hz, 2H, Ph-H), 6.99 (d, $J = 8.2$ Hz, 2H, Ph-H), 5.49 (s, 1H, CH), 2.36–2.44 (m, 8H, CH₂), 2.31 (s, 3H, CH₃), 1.14 (s, 6H, CH₃), 1.07 (s, 6H, CH₃).

2,2′-Phenylmethylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) (3l) ¹H NMR (CDCl₃, 400 MHz) δ: 11.66 (brs, 1H, OH), 11.07 (s, 1H, OH) 7.27–7.45 (m, 5H, Ph-H), 5.44 (s, 1H, CH), 2.30–2.41 (m, 8H, CH₂), 1.15 (s, 6H, CH₃), 1.10 (s, 6H, CH₃).

2,2′-(3-Bromophenyl)methylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) (3m) ¹H NMR (CDCl₃, 400 MHz) δ: 11.87(s, 1H, OH), 11.22 (brs, 1H, OH), 7.17–7.30 (m, 2H, Ph-1.21 (s, 6H, CH₃), 1.16 (s, 6H, CH₃).

General procedure for synthesis of 2-substituted-1H-benzimidazoles

1, 2-phenylenediamine derivative (1 mmol), aryl aldehyde (1 mmol) and BiOCl nanoparticles (12 mg) were added to water (5 mL) as solvent. The reaction mixture was then placed under sonication using an ultrasonic horn (22 kHz frequency) for the required time with a 5-s ON and 5-s OFF cycle from time $t = 0$ h. The progress of the reaction was monitored by TLC (eluent: 7:3 *n*-hexane–ethyl acetate) for the time period as indicated in Table 3. After completion of the reaction, the mixture was diluted by 1:1 H₂O: EtOAc (10 mL) stirred at ambient temperature (20 min) and centrifuged to separate the solid catalyst. The organic layer of the solution was separated, dried over sodium sulfate, and the organic solvent and other residues were stripped in a vacuum evaporator. The residue obtained was recrystallized using the appropriate solvent. The products (5a–l) are known compounds and their ¹H NMR and melting points compared with those were reported in literature.

Spectral data for 2-substituted-1H-benzimidazoles

2-Phenyl-1H-benzimidazole (5a) ¹H NMR (DMSO-d_6, 400 MHz) δ: 13.01 (br, 1H, NH), 8.11–8.23 (m, 2H, Ph-H), 7.48–7.56 (m, 5H, Ph-H), 7.15–7.21 (m, 2H, Ph-H). ¹³C NMR (400 MHz, DMSO-d_6) δ: 111.84, 119.39, 122.1, 122.9, 126.8, 129.3, 130.2, 130.5, 135.4, 143.9, 151.6

Table 3 BiOCl nanoparticles catalyzed synthesis of 2-substituted-1H-benzimidazoles
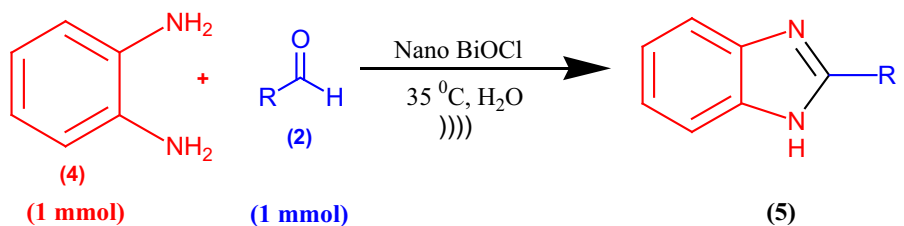
Entry	Product	R	Time (min)	Yield (%)[a]	M.P (°C) Found	Reported
1	5a	C_6H_5	12	88	288–290	(289–290)
2	5b	$4\text{-}NO_2C_6H_4$	08	93	296–298	(297–298)
3	5c	$3\text{-}NO_2\ C_6H_4$	05	91	203–204	(203)
4	5d	$2\text{-}NO_2\ C_6H_4$	10	93	205–207	–
5	5e	$4\text{-}CH_3OC_6H_4$	15	89	220–223	(223–226)
6	5f	$4\text{-}ClC_6H_4$	07	95	288–290	(289–290)
7	5g	$4\text{-}CN\ C_6H_4$	07	93	264–266	(265)
8	5h	$4\text{-}(Me_2N)C_6H_4$	15	94	233–234	(232)
9	5i	$4\text{-}CH_3C_6H_4$	12	70	176–177	(174–176)
10	5j	2-Pyridyl	15	67	217–219	(218)
11	5k	2-Furyl	17	60	287–289	(288)
12	5l	$4\text{-}F\ C_6H_4$	17	90	181–182	(180–183)

The products were characterized by ^{1}H NMR spectroscopy

[a] Isolated yields

2-(4-Nitrophenyl)-1H-benzo[d]imidazole (5b) ^{1}H NMR (CDCl₃, 400 MHz) δ: 13.04 (br, 1H, NH), 8.30 (d, $J = 8.6$ Hz, 2H, Ph-H), 8.03 (d, $J = 8.6$ Hz, 2H, Ph-H), 7.33–7.38 (m, 2H, Ph-H), 7.27–7.30 (m, 2H, Ph-H). ^{13}C NMR (400 MHz, DMSO-d_6) δ: 112.41, 120.07, 123.09, 124.90, 128.03, 136.71, 148.45, 149.66

2-(3-Nitrophenyl)-1H-benzo[d]imidazole (5c) ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 12.81 (br, 1H, NH), 8.22 (m, 2H, Ph-H), 8.10 (s, 1H, Ph-H), 7.34 (d, $J = 8.5$ Hz, 1H, Ph-H), 7.31–7.37 (m, 2H, Ph-H), 7.20–7.28 (m, 2H, Ph-H). ^{13}C NMR (400 MHz, DMSO-d_6) δ: 115.7, 116.9, 118.4, 123.0, 125.2, 128.8, 129.7, 134.0, 135.6, 138.2, 142.9, 148.7, 153.8

2-(2-Nitrophenyl)-1H-benzo[d]imidazole (5d) ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 12.89 (br, 1H, NH), 7.77 (d, $J = 8.1$ Hz, 1H, Ph-H), 7.40 (t, $J = 8.0$ Hz, 1H, Ph-H), 7.33 (t, $J = 8.0$ Hz, 1H, Ph-H), 7.21–7.27 (m, 2H, Ph-H), 7.11 (d, $J = 8.1$ Hz, 1H, Ph-H), 6.85–6.95 (m, 2H, Ph-H).

2-(4-Methoxyphenyl)-1H-benzo[d]imidazole (5e) ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 13.14 (br, 1H, NH), 8.26 (d, $J = 8.1$ Hz, 2H, Ph-H), 7.50–7.59 (m, 4H, Ph-H),

7.30 (d, $J = 8.1$ Hz, 2H, Ph-H), 3.82 (s, 3H, CH$_3$O). ^{13}C NMR (400 MHz, DMSO-d_6) δ: 55.84, 114.0, 121.9, 132.1, 128.4, 129.4, 151.7, 161.0.

2-(4-Chlorophenyl)-1H-benzo[d]imidazole (5f) ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 13.04 (br, 1H, NH), 8.19 (d, $J = 8.1$ Hz, 2H, Ph-H), 7.58–7.63 (m, 4H, Ph-H), 7.33 (d, $J = 8.1$ Hz, 2H, Ph-H). ^{13}C NMR (400 MHz, DMSO-d_6) δ: 111.0, 118.5, 121.8, 126.1, 128.5, 129.4, 129.1, 134.7, 143.4, 151.0

2-(4-Cyanophenyl)-1H-benzimidazole (5g) ^{1}H NMR (CDCl$_3$, 400 MHz) δ: 12.92 (br, 1H, NH), 8.36 (d, $J = 8.5$ Hz, 2H, Ph-H), 8.11 (d, $J = 8.5$ Hz, 2H, Ph-H), 7.35–7.37 (m, 2H, Ph-H), 7.21–7.27 (m, 2H, Ph-H).

2-(4-N,N-dimethylbenzenamine)-1H-benzimidazole (5h) ^{1}H NMR (CDCl$_3$, 400 MHz) δ: 11.89 (br, 1H, NH), 8.36 (d, $J = 8.4$ Hz, 2H, Ph-H), 8.23 (m, 2H, Ph-H), 7.30–7.35 (d, $J = 8.4$ Hz, 2H, Ph-H), 7.22–7.26(m, 2H, Ph-H), 2.13 (s, 6H, N(CH$_3$)$_2$. ^{13}C NMR (400 MHz, DMSO-d_6) δ: 21.40, 40.38, 111.79, 116.11, 170.02,119.41, 127.19, 130.43, 136.11, 136.58, 142.01, 152.53, 156.91

2-(4-Tolyl)-1H-benzimidazole (5i) ^{1}H NMR (CDCl$_3$, 400 MHz) δ: 11.91 (br, 1H, NH), 8.15 (d, 2H, $J = 8.0$ Hz, Ph-H), 7.56 (m, 2H, Ph-H), 7.30 (d, 2H, $J = 8.0$ Hz, Ph-H), 7.12 (m, 2H, Ph-H), 2.31 (s, 3H, CH$_3$).

2-(2-Pyridinyl)-1H-benzoimidazole (5j) ^{1}H NMR (CDCl$_3$, 400 MHz) δ: 12.33 (br, 1H, NH), 7.80–7.84(m, 2H, Ph-H), 7.53–7.57 (m, 2H, Ph-H), 7.12 (m, 2H, Ph-H), 6.92–6.96 (m, 2H, Ph-H).

2-(2-Furanyl)-1H-benzoimidazole (5k) ^{1}H NMR (CDCl$_3$, 400 MHz) δ: 12.18 (br, 1H, NH), 7.87(d, $J = 4.4$ Hz, 1H,Ph-H), 7.53–7.50 (m, 2H, Ph-H), 7.25 (dd, 1H, $J = 4.4$ Hz &$J = 2.0$ Hz, Ph-H), 6.63 (d, 1H, $J = 2.0$ Hz, Ph-H), 6.36–6.40 (m, 2H, Ph-H).

2-(2-Flurophenyl)-1H-benzo[d]imidazole (5l) ^{1}H NMR (CDCl$_3$, 400 MHz) δ: 12.41 (br, 1H, NH), 8.32 (d, $J = 8.2$ Hz, 2H, Ph-H), 8.21 (d, $J = 8.2$ Hz, Ph-H), 7.36–7.38 (m, 2H, Ph-H), 7.27–7.30 (m, 2H, Ph-H).

Results and discussion

To explore the scope and limitations of the protocol under optimized conditions (Table 1, entry 15), the reaction of dimedone (1) with various aromatic aldehydes 3(a–m) bearing electron-donating and electron-withdrawing groups gives rise to the corresponding 2,2′-arylmethylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) 3a–m in good to excellent yields (83–95%) at 35 °C within 12–17 min (Table 2). As is indicated in Table 2, both aromatic aldehydes bearing electron-donating and ithdrawing groups react at a faster rate with dimedone.

Encouraged by these excellent results, we then decided to test the generality and versatility of optimized reaction conditions (Table 1, entry 29) in the synthesis of substituted benzimidazoles, and several substituted aromatic aldehydes and
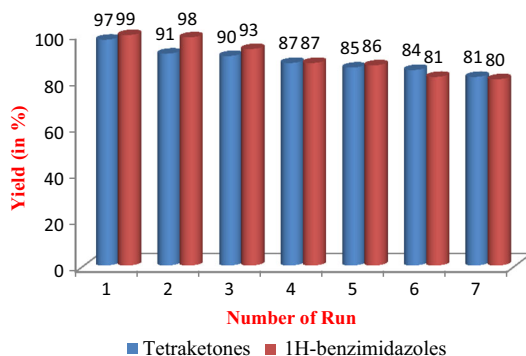
heteroaromatic aldehydes 5(a–l) were reacted with o-phenylenediamine (4). These results are shown in Table 3. Aromatic aldehydes bearing electron-donating and -withdrawing groups undergo smooth conversion to afford various benzimidazoles (5a–i, l) in good to excellent yields. When heteroaromatic aldehydes such as pyridine-2-aldehyde and 2-furfural (Table 3, entries 10, 11) were reacted with o-phenylenediamine under similar reaction conditions they gave corresponding benzimidazoles (5j, 5k) in lower yield compared to benzimidazole derivatives obtained from aromatic aldehydes.

Reusability of BiOCl nano-catalyst

Ther catalytic efficiency of the BiOCl nano-catalyst was estimated by a reusability study. We have conducted the experiments using the recycled BiOCl catalyst for the synthesis of 2,2′-arylmethylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) and 2-substituted-1H-benzimidazoles. The recovered catalyst was purified after each run by filtration, washed with acetone and dried at 100 °C for 2 h in an oven before use in the next catalytic cycle. The BiOCl catalyst was found to be reusable for seven times without any significant loss in activity (Fig. 3). After each subsequent run, more than 95% of the catalyst was easily recovered from the reaction mixture.

Conclusion

In summary, BiOCl nanoparticles (NPs) provide an alternative and efficient pathway for the production of heterocyclic intermediates. We have developed a practical and convenient synthetic method in aqueous media by using BiOCl NPs as the catalyst for the facile synthesis of 2,2′-arylmethylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) and 2-substituted-1H-benzimidazoles under ultrasound irradiation. Milder conditions, easy recovery and reusability of the BiOCl NPs catalyst make the method highly efficient.

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