# BiCl<sub>3</sub>-loaded montmorillonite K10: a new solid acid catalyst for solvent-free synthesis of bis(indolyl)methanes

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**Abstract** We report an efficient green process for synthesis of bis(indolyl)methane derivatives under solvent-free conditions by use of a new solid acid catalyst, BiCl<sub>3</sub>-loaded montmorillonite K10. The catalyst was characterized by SEM, BET surface area measurement, and determination of its surface acidity by temperature-programmed desorption measurements. The salient features of the procedure are its simplicity, ease of preparation of the catalyst, cost effectiveness, excellent yield with short reaction time, reusability of the catalyst, and enhancement of the acidity of montmorillonite K10 catalyst by BiCl<sub>3</sub> loading.

**Keywords** BiCl<sub>3</sub>–MK10  $\cdot$  Bis(indolyl)methanes  $\cdot$  Simple grinding  $\cdot$  Solid acid catalyst  $\cdot$  Green synthesis  $\cdot$  Reusability

### Introduction

The indole ring system is an extremely important constituent in many natural products, pharmaceuticals, agrochemicals, and other compounds of importance [1, 2]. Many bis(indolyl) and tris(indolyl) methanes have been isolated from a variety of terrestrial and marine natural sources and they have a range of important biological activity [3–6]. 3,3'-Bis(indolyl)methane and its derivatives are used as dietary supplements for humans [7, 8]. The activity of bis(3-indolyl)methanes in cancer chemotherapy [9], inhibition of bladder growth [10], and in lung cancer cells [11] has been studied in detail. They also have antibiotic [12], antibacterial [13], antimetastatic [14], radical-scavenging [15] antimicrobial and antifungal [16], and analgesic and anti-inflammatory [17] activity. Because of this vast range of

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Scheme 1 BiCl<sub>3</sub>-MK10 catalyzed synthesis of bis(indolyl)methanes

biological activity and associated medicinal applications, a variety of methods for synthesis of bis(indolyl)methanes have been reported in the literature; many of these methods use protic and Lewis acid catalysts in electrophilic substitution of indoles with aldehydes [18–29]. However, many Lewis acids can be deactivated, and some decompose nitrogen-containing reactants. Even when the reactions proceed as expected, more than a stoichiometric amount of the Lewis acid is required, because the acids are trapped by nitrogen [30].

Commercially available montmorillonite clay K10 (MK10) is an environmentally benign, economically feasible, stable, mild, and easily reusable solid acid catalyst which has been used for many organic transformations [31-34]. Commercially available BiCl<sub>3</sub> has been widely used as a Lewis acid catalyst in the aldol [35] and hetero Diels-Alder [36] reactions, for ring opening of epoxides with aromatic amines [37], for deoxygenative allylation of substituted benzylic alcohols with allyltrimethylsilane [38], and for three-component synthesis of  $\beta$ -amino carbonyl compounds [39]. Owing to its highly hygroscopic nature, BiCl<sub>3</sub> cannot be easily handled and reused; it is, therefore, loaded on suitable support materials for easy handling and reuse. Because MK10 clay is one such material that can fulfill this requirement, in continuation of our work on green chemical synthesis of heterocyclic compounds [40, 41] we report herein a simple, rapid and efficient method for synthesis of bis(indolyl)methanes by use of a newly developed catalyst, BiCl<sub>3</sub>-loaded montmorillonite K10 (BiCl<sub>3</sub>-MK10), as a solid acid catalyst under ambient and solvent free conditions (Scheme 1). To the best of our knowledge, this is the first report of the preparation of bis(indolyl)methanes using this solid acid catalyst.

#### Experimental

Materials and methods

Bismuth chloride, 2-propanol (Spectrochem,  $\geq$ 99.50 %), montmorillonite K10 (Aldrich, composition (wt%) SiO<sub>2</sub>: 67.6; Al<sub>2</sub>O<sub>3</sub>: 14.6; Fe<sub>2</sub>O<sub>3</sub>: 2.9; MgO: 1.8) were used as received. All other chemicals were of AnalaR grade and used as received. IR spectra were recorded by use of an Avatar-330 FT-IR spectrophotometer. Product analysis was performed by GC–MS by use of a GC–MS QP2010 plus with DB-5-MS capillary column. Proton and carbon NMR spectra were recorded on a Bruker AVIII FT-NMR spectrometer operating at 400 MHz.

# Preparation of BiCl<sub>3</sub>-MK10

BiCl<sub>3</sub>–MK10 catalyst was prepared by a simple solid dispersion method. MK10 (2.7 g) was dispersed in 50 mL 2-propanol and  $2.5 \times 10^{-4}$  mol BiCl<sub>3</sub> (0.081 g) in 10 mL 2-propanol was added to the MK10–2-propanol mixture. The mixed suspension was stirred for 4 h at room temperature, then the solvent was evaporated to furnish the product. The solid obtained was dried at 110 °C for 3 h. The BiCl<sub>3</sub>–MK10 catalyst was obtained as a fine powder. This catalyst contained 3 wt% BiCl<sub>3</sub>.

Characterization of BiCl<sub>3</sub>-MK10

BiCl<sub>3</sub>-loaded montmorillonite K10 catalyst was characterized by SEM–EDS, BET surface area measurement, and determination of surface acidity by ammonia TPD measurements. SEM images of bare MK10 and BiCl<sub>3</sub>–MK10, and the SEM–EDS spectrum of BiCl<sub>3</sub>–MK10 are shown in Fig. 1. Agglomeration of BiCl<sub>3</sub> on the MK10 catalyst is apparent from SEM images recorded at three different magnifications (Fig. 1b–d), and the EDS spectrum confirms the presence of Bi in the BiCl<sub>3</sub>–MK10 catalyst (Fig. 1e). In BET surface area measurements, the BiCl<sub>3</sub>–MK10 catalyst had a lower surface area than MK10, because of impregnation of the MK10 surface with BiCl<sub>3</sub>; BiCl<sub>3</sub> loading leads to reduced pore volume and an increase in median pore width (Table 1).The efficiency of solid acid catalysts depends on their surface acidity. The surface acidity of BiCl<sub>3</sub>–MK10 (Table 2) was determined by temperature-programmed desorption (TPD), using ammonia as probe molecule, in the temperature range 120–600 °C. The results indicated that the acidity of BiCl<sub>3</sub>–MK10 was approximately 18 times larger than that of MK10 [42]; this large increase is because of loading of the MK10 with BiCl<sub>3</sub>.

General procedure for synthesis of 3,3'-bis(indolyl)methane

BiCl<sub>3</sub>–MK10 catalyst (0.1 g) was added to a mixture of indole (2 mmol) and aldehyde (1 mmol), and the mixture was ground in a mortar with a pestle at room temperature. After completion of the reaction (tested by thin-layer chromatography, TLC), ethyl acetate was added and the insoluble catalyst was removed by filtration. The filtrate was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated under vacuum to furnish the product. All the products were characterized by GC–MS, and selected compounds were characterized by <sup>1</sup>H and <sup>13</sup>C NMR. NMR data for three representative compounds are given below.

## 3,3'-(Phenylmethylene)bis(1H-indole) (3a)

Pink solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  5.87 (1H, s, Ar–CH), 6.60 (2H, s), 6.98–7.01 (2H, t), 7.24–7.26 (3H, m), 7.28–7.39 (8H, m), 7.85 (2H, bs, NH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 40.20, 111.08, 119.25, 119.69, 120.76, 121.95, 123.68, 124.20, 126.18, 127.07, 128.27, 136.68, 144.02; GC–MS (*m*/*z*) = 322(M<sup>+</sup>);



Fig. 1 SEM images of a MK10 ( $\times$ 50,000), b MK10 ( $\times$ 100,000), c BiCl<sub>3</sub>-MK10 ( $\times$ 50,000), d BiCl<sub>3</sub>-MK10 ( $\times$ 100,000), and e EDS spectrum of BiCl<sub>3</sub>-MK10

Table1	Surface area and	pore size	of MK10 and	BiCl <sub>3</sub> -MK10	catalysts
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Measurement	MK10 catalyst	BiCl <sub>3</sub> –MK10 catalys	
BET surface area $(m^2 g^{-1})$	241	170.27	
Maximum pore volume (cm <sup><math>3</math></sup> g <sup><math>-1</math></sup> )	0.36	0.286	
Median pore width (Å)	57.52	77.15	

Temperature (°C)	MK10 catalyst (mmol g <sup>-1</sup> )	BiCl <sub>3</sub> -MK10 catalyst (mmol g <sup>-1</sup> )
120–200	0.55	9.48
200-600	0.37	6.90
Total	0.92	16.38

Table2 Surface acidity of MK10 and BiCl<sub>3</sub>-MK10 catalysts

### 3,3'-(3-Bromophenylmethylene)bis(1H-indole)(3e)

Pink solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  5.838 (1H, s, Ar–CH), 6.611 (2H, s), 6.99–7.03 (2H, t), 7.10–7.19 (4H, m), 7.24–7.27 (2H, m), 7.33–7.38 (3H, m), 7.49 (1H,s), 7.89 (2H, bs, NH) <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 39.96, 111.16, 118.95, 119.42, 119.79, 122.13, 122.44, 123.71, 126.88, 127.42, 129.41, 129.89, 131.73, 136.69, 146.52; GC–MS (*m*/*z*) = 402(M<sup>+</sup>);

## 3,3'-(3-Methoxyphenylmethylene)bis(1H-indole) (3l)

Pink solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  3.717 (3H, s, OCH<sub>3</sub>), 5.83 (1H, s), 6.70–6.74 (3H, m), 6.91–6.96 (4H, m), 7.08–7.12 (2H,t), 7.15–7.19 (2H, t), 7.35–7.37 (3H, m), 7.39 (2H, s, NH) <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 40.64, 54.99, 111.21, 114.64, 118.77, 119.55, 121.27, 123.84, 126.96, 128.92, 136.78, 146.19, 159.37; GC–MS (*m*/*z*) = 352(M<sup>+</sup>).

#### **Results and discussion**

To determine the optimum conditions and amount of catalyst, 3,3'-(phenylmethylene)bis(1*H*-indole) was synthesized by reaction of indole and benzaldehyde under different conditions. No reaction occurred when 2 mmol indole and 1 mmol benzaldehyde were ground without catalyst. The yield of product with 0.1 g bare MK10 catalyst after simple grinding for 10 min was only 55 %. When the reactants were ground with 0.1 g 3 wt% BiCl<sub>3</sub>–MK10 catalyst for 3 min, the product yield was 99 %. Reaction of 2 mmol indole and 1 mmol benzaldehyde with 0.05 g of BiCl<sub>3</sub>–MK10 catalyst under simple grinding resulted in 60 % product yield in 3 min. Increasing the amount of catalyst beyond 0.1 g/mmol did not result in any significant improvement in reaction yield and time. These results clearly indicate that simple grinding is efficient and 0.1 g BiCl<sub>3</sub>–MK10 is the optimum amount of catalyst for the reaction to proceed with high yield (Fig. 2).

To assess the scope of the method, this reaction was performed with a variety of substituted aromatic aldehydes **1a–1r**, indole **2**, and BiCl<sub>3</sub>–MK10 catalyst under the optimized conditions by simple grinding, and the corresponding bis(indolyl)methanes **3a–3r** were obtained (Table 3). There was no significant change in yield with the electronic nature of the substituents (yields were more than 90 % with p-NO<sub>2</sub>



**Fig. 2** Effect of catalyst loading. Catalyst =  $BiCl_3$ -MK10, benzaldehyde = 1 mmol, indole = 2 mmol, time = 3 min (grinding under solvent-free conditions at room temperature)

and p-OCH<sub>3</sub> benzaldehyde; Table 3, entries i and k) but the size of the substituent had some effect on reaction time and yield. Thus, chloro benzaldehydes gave higher yields than bromo and iodo benzaldehydes (Table 3, entries b–h). For 4-fluoro-3-phenoxybenzaldehyde (Table 3, entry m) the yield was 82 % after grinding for 40 min. The longer reaction time is due to the steric effect of the phenoxy group. Naphthaldehydes react more slowly than benzaldehydes; this could be because of a steric effect. Furan-2-aldehydes and thiophene-2-aldehyde gave good yields.

The efficiency of BiCl<sub>3</sub>–MK10 was compared with that of other catalysts reported [43–47] for synthesis of 3,3'-(phenylmethylene)bis(1*H*-indole) (Table 4). BiCl<sub>3</sub>–MK10 was found to be more efficient than other catalysts. The greater activity can be attributed to the high surface acidity of the catalyst. As is apparent from Table 2, the surface acidity of BiCl<sub>3</sub>–MK10 is approximately 18 times that of bare MK10 and it catalyzes the reaction more efficiently. Based on the Lewis acidity of the catalyst, an acid catalyzed mechanism was proposed (Scheme 2). This mechanism involves:

- 1 attack at the carbonyl group of the aldehyde by BiCl<sub>3</sub>-MK10 producing intermediate **a**;
- 2 nucleophilic addition of one molecule of indole to the intermediate **a**, giving intermediate **b** which, after aromatization, forms the azafulvene intermediate **c**; and

Entry	Aldehyde (1)	Product (3)	Grinding time in min	Yield <sup>a</sup> %	Observed mass $M^+$ M + 1/M - 1
a	Ś		3	99	322
b	H y O		4	92	356
с	a fo		4	92	356
d	H O Br		4	84	400
e	F <sup>0</sup> Br		4	80	402
f	H O Br		4	80	400
g			4	60	448
h			4	60	448
i	H O NO <sub>2</sub>		5	90	367

Table 3 Percentage yields of bis(indolyl)methanes from different aldehydes

Entry	Aldehyde (1)	Product (3)	Grinding time in min	Yield <sup>a</sup> %	Observed mass $M^+$ M + 1/M - 1
j	H Me		4	99	336
k	H OMe		4	99	352
1	H O OMe	OMe CHARACTER H	4	99	352
m	H J O F J		40	82	432
n	OH OH	OH OH H H H	5	90	338
0			8	83	372
р			8	60	372
q			5	99	312

#### Table 3 continued

Table 3	continued
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Entry	Aldehyde (1)	Product (3)	Grinding time in min	Yield <sup>a</sup> %	Observed mass $M^+$ M + 1/M - 1
r	S S		5	99	328

Reaction conditions: benzaldehyde 1 mmol, indole 2 mmol, catalyst BiCl<sub>3</sub>-MK10, 0.10 g simple physical grinding

<sup>a</sup> Yields based on aldehyde

Table 4 Comparison of the efficiency of BiCl<sub>3</sub>–MK10 and other catalysts used for synthesis of bis(indolyl)methanes from benzaldehyde and indole

Entry	Reaction conditions	Reaction time (min)	Catalyst qty	Yield <sup>a</sup> (%)
1	Bare MK10, RT physical grinding	10	0.1 g	55 <sup>b</sup>
2	BiCl <sub>3</sub> -MK10, RT, physical grinding	3	0.1 g	99 <sup>b</sup>
3	AlPW12O40/CH3CN	15	2–7 mol %	92 [ <mark>43</mark> ]
4	La(PFO) <sub>3</sub> /EtOH	30	5 mol %	90 [ <mark>44</mark> ]
5	LiClO <sub>4</sub> /CH <sub>3</sub> CN	300	10 mol %	90 [ <mark>20</mark> ]
6	HFIP <sup>c</sup> , RT	60	_	90 [ <mark>45</mark> ]
7	ZrOCl <sub>2</sub> /CH <sub>3</sub> CN	35	10 mol %	89 [ <mark>46</mark> ]
8	HY-Zeolite/CH <sub>2</sub> Cl <sub>2</sub>	60	0.20 g	85 [47]

<sup>a</sup> Yield based on benzaldehyde

<sup>b</sup> This work

<sup>c</sup> HFIP: 1,1,1,3,3,3-Hexafluoro-2-propanol

3 addition of another molecule of indole to intermediate **c** then aromatization to give the corresponding condensed product **d**.

The solid acid catalyst BiCl<sub>3</sub>-MK10 promotes deprotonation and dehydration.

The reusability of the catalyst was tested for five runs. The catalyst was separated from the reaction mixture by filtration and dried at 100 °C for 1 h. This recovered catalyst was used again. The results revealed that the catalyst can be used continuously for the reaction. The yield of the products is >95 % even in the 5th run. Percentage yields of the product for five runs are given in Table 5.

We tested the stability of the catalyst by checking for desorption of BiCl<sub>3</sub> by use of atomic absorption spectroscopy (AAS). The concentration of bismuth in the fresh catalyst was 1.95 % (equivalent to 2.95 % as BiCl<sub>3</sub>); that in the catalyst recovered after the 5th run was 1.82 % (equivalent to 2.75 % as BiCl<sub>3</sub>). This shows that no significant desorption of BiCl<sub>3</sub> occurred.



Scheme 2 Plausible reaction mechanism for synthesis of bis(indolyl)methane catalyzed by BiCl<sub>3</sub>-MK10

Table 5 BiCl<sub>3</sub>-MK10 Catalyst Reusability

Run	1	2	3	4	5
Yield (%)	99.0	98.0	96.0	94.0	94.0

Reaction conditions: indole = 2 mmol, benzaldehyde = 1 mmol,  $BiCl_3-MK10 = 0.1$  g, room temperature, grinding. Yield based on benzaldehyde

## Conclusion

A new solid acid catalyst, BiCl<sub>3</sub>-loaded MK10, was prepared by simple solid dispersion method and characterized by SEM, EDS, BET surface area, and surface acidity measurements. SEM EDS confirmed the presence of Bi<sup>3+</sup> in the catalyst. The surface acidity of the BiCl<sub>3</sub>–MK10 catalyst was approximately 18 times more than that of bare MK10, and BiCl<sub>3</sub>–MK10 catalyzes the reaction more efficiently. BiCl<sub>3</sub>–MK10 is introduced as an excellent catalyst for synthesis of bis(indolyl)methane derivatives from a variety of substituted aldehydes by simple grinding at room temperature. BiCl<sub>3</sub>–MK10 promotes both dehydration and deprotonation in the reaction. This novel and practical method has the advantages of mild conditions, excellent yield of products, and short reaction time. Recovery and reusability of the catalyst make this a green process. This method can easily scaled up for large-scale

production of bis(indolyl)methanes using commercially available grinding equipment. We believe this novel catalyst will have wide applications in organic synthesis.

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