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$Mn(pbdo)_2Cl_2$/MCM-41 as a green catalyst in multi-component syntheses of some heterocycles

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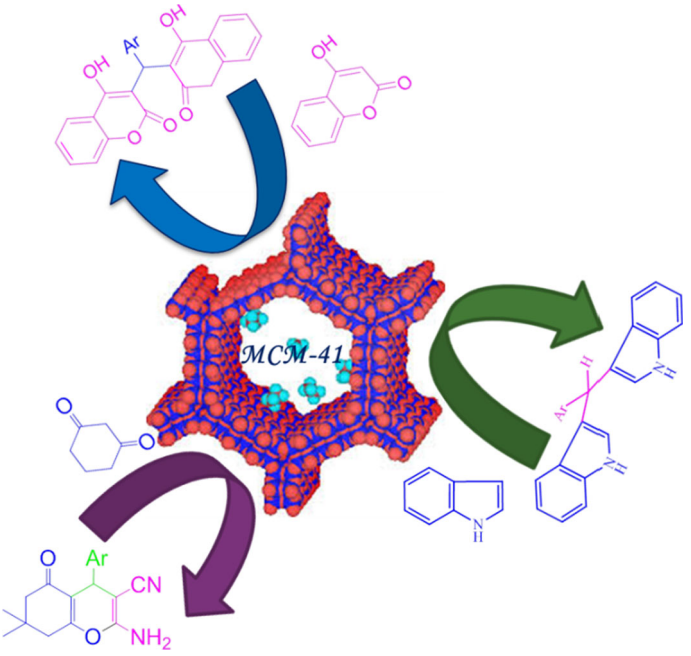
Abstract $Mn(pbdo)_2Cl_2$/MCM-41 as a solid acid catalyst was used as an efficient, green, reusable catalyst for an improved and rapid one-pot multi-component reaction in the synthesis of bis-(4-hydroxycoumarin), bis(indolyl)methane, and 4*H*-benzo[*b*]pyran derivatives.

Graphical Abstract



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Keywords $Mn(pbdo)_2Cl_2$/MCM-41 · Multi-component reactions · Solid acid catalysts · Bis-(4-hydroxycoumarin) derivatives · Bis(indolyl)methanes · 4*H*-benzo[*b*]pyrans

Introduction

Multi-component reactions (MCRs) have emerged as an important tool for building diverse and complex organic molecules through carbon–carbon and carbon–hetero atom bond formations taking place in a tandem manner [1]. In recent years in particular, MCRs have captured the attention and interest of synthetic organic chemists, and a number of one-pot three- and four-component reactions have been developed and introduced [2]. As a matter of fact, MCRs can go beyond four-component reactions [3]. Interestingly, multi-component reactions today have been expanded to the synthesis of peptides [4] and asymmetric synthesis [5]. The use of small heterocycles [6] and the synthesis of common heterocyclic compounds [7] in MCRs are other recent developments. Undoubtedly, the combination of MCRs and biology should be considered as the state of the art among organic chemists and biologists [8].

In the past decade, heterogeneous catalysis has been widely used in industrial chemical transformations because of its mild reaction conditions, easy separation from the reaction mixture by filtration, and good thermal stability. The replacement of homogeneous with heterogeneous catalysts could represent a more environmentally friendly substitute in acid-catalyzed organic reactions [9].

Since 1992, when MCM-41 (Mobil Composition of Matter No. 41) was discovered by Mobil Corporation laboratory scientists [10], silica-based materials have been employed as efficient catalysts and catalyst supports in various reactions [11–15]. MCM-41 possesses several unique properties, including high surface area, uniform and tunable pore sizes, excellent physicochemical stability, and modifiable surfaces. However, its direct use as a catalyst is difficult due to a lack of sufficient acidity. Therefore, many research groups have worked on introducing various kinds of metals, metal ions, and metal complexes into MCM-41 to improve its catalytic activity [16–21]. Functionalization of MCM-41 with transition metals, especially by manganese (Mn), leads to effective catalysts for a variety of organic reactions [22, 23].

Manganese complexes have been intensively studied as catalysts for epoxidation reactions [24]. In recent years, researchers have investigated the immobilization of Mn complexes onto silica mesoporous materials. The preparation of Mn-MCM-41 using a molecular organic chemical vapor deposition (MOCVD) method was reported by Caps and Tsang [25]. Surface-grafted manganese–oxo species on the walls of MCM-41 channels were obtained by Burch et al. [26], and a template ion-exchange (TIE) method used in another study for the synthesis of Mn-MCM-41 [27].

As a part of our ongoing program to develop new synthetic transformations using inexpensive and eco-friendly materials as catalysts [28–33], and given our interest in MCRs, we examined the possibility of using $Mn(pbdo)_2Cl_2$/MCM-41 in several

multi-component one-pot reactions, including the synthesis of bis-(4-hydroxycoumarin), bis(indolyl)methane, and 4*H*-benzo[*b*]pyran derivatives.

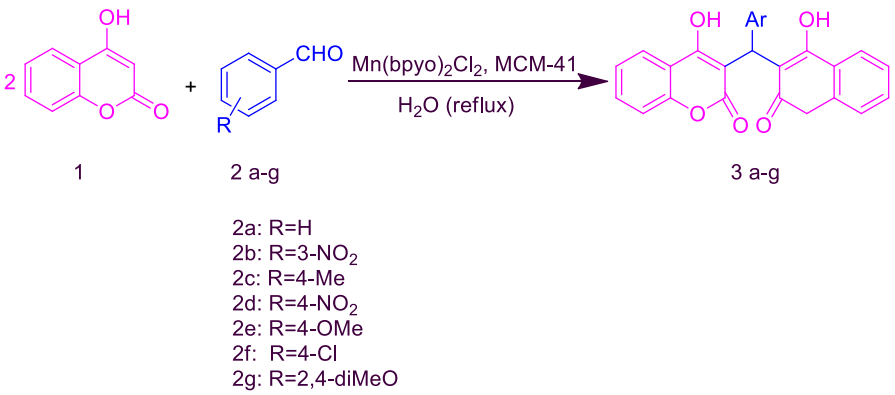
We previously reported the synthesis and catalytic activity of the Mn(II) complex with a 2,2′-bipyridine and 1,1′-dioxide ligand within nanoreactors of MCM-41 [34].

Catalytic reactions

Synthesis of bis-(4-hydroxycoumarin) derivatives

Coumarin derivatives exhibit a wide range of activities [35–38]. Studies have recently revealed novel biological activity with remarkable potential in therapeutic applications apart from their traditional employment [39–42]. However, the drugs of this group exhibit some side effects, including the warfarin-related purple toes syndrome. 4-Hydroxycoumarin derivatives are also of interest because of their anticoagulant [43], spasmolytic [44], and rodenticidal [45] properties. Through the synthesis of different 3,3′-arylidene-bis-4-hydroxycoumarins, it is possible to obtain compounds with biological activity similar to that of warfarin but with lower toxicity and fewer side effects. Synthesis of 3,3′-arylidene-bis-4-hydroxycoumarins from the condensation of benzaldehyde derivatives with 4-hydroxycoumarin has been reported in the literature [46] (Scheme 1).

To optimize the catalytic system, the synthesis of 3,3′-phenylmethylene-bis-(4-hydroxycoumarin) from the condensation of 4-hydroxycoumarin and benzaldehyde was used as a model reaction. We examined a variety of catalysts, solvents, and temperatures. $Mn(bpyo)_2Cl_2$/MCM-41 was found to be the best catalyst among tested catalysts, which included basic alumina, DABCO, $H_{14}[NaP_5W_{30}O_{110}]$, and sulfamic acid, in the model reaction (Table 1).



Scheme 1 Synthesis of bis-(4-hydroxycoumarine) derivatives

Table 1 Optimization of reaction conditions in the model reaction in reflux conditions

Entry	Catalyst	Solvent	Time (min)	Yield (%)[a]
1	Basic alumina	H_2O	85	70
2	DABCO	H_2O	90	70
3	$H_{14}[NaP_5W_{30}O_{110}]$	H_2O	70	80
4	Sulfamic acid	H_2O	80	85
5	MCM-41	H_2O	65	89
6	$Mn(bpyo)_2Cl_2$	H_2O	70	70
7	$Mn(bpyo)_2Cl_2$/MCM-41	H_2O	30	96

[a] Yields are related to isolated pure products

The best results are obtained in H_2O in the presence of $Mn(bpyo)_2Cl_2$/MCM-41 (0.04 g) under reflux conditions.

Using these optimized reaction conditions, we explored the scope and efficiency of this aqueous approach for the synthesis of a wide variety of substituted bis-(4-hydroxycoumarin) methanes, and the results obtained are summarized in Table 2. All reactions afforded the desired products in high yields and accommodated a wide range of aromatic aldehydes bearing both electron-donating and electron-withdrawing substituents. In all cases, the pure product was isolated by simple filtration and recrystallization in absolute ethanol.

It is worth noting that the catalyst is recyclable and can be reused without significant loss of activity. The catalyst was recycled and reused twice in the model reaction, and the results obtained are summarized in Table 3.

Synthesis of bis(indolyl)methanes

Indole fragments are important intermediates and exhibit various physiological and pharmaceutical properties [48]. Bis(indolyl)methanes are members of an important class of heterocyclic compounds that show a broad spectrum of biological activities [49, 50]. These compounds have demonstrated pharmaceutical potencies including

Table 2 Synthesis of 3,3′-phenylmethylene-bis-(4-hydroxy-2*H*-1-benzopyran-2-one) derivatives

Entry	Aromatic aldehyde	Time (min)	Yield (%)[a]	m.p. (°C)	
				Found	Rep. [47]
1	C_6H_5	35	96	232	228–30
2	3-NO_2–C_6H_4	30	98	242	240–2
3	4-Me–C_6H_4	30	98	269	265–7
4	4-NO_2–C_6H_4	35	95	236	232–4
5	4-MeO–C_6H_4	40	94	245	242–4
6	4-Cl–C_6H_4	30	96	253	252–4
7	2,4-di-MeO–C_6H_4	42	94	200	197–8

[a] Isolated yield

Table 3 Reusability of catalyst in the model reaction (35 min)

Entry	Number of uses	Yield (%)[a]
1	Fresh	96
2	1	95
3	2	91

[a] Isolated yield

anti-HIV, antiviral, antimicrobial, and antihyperglycemic properties, and are known as cytotoxic active compounds against human tumor cells [51]. Importantly, bis(indolyl)methanes are known to promote estrogen metabolism [52–54].

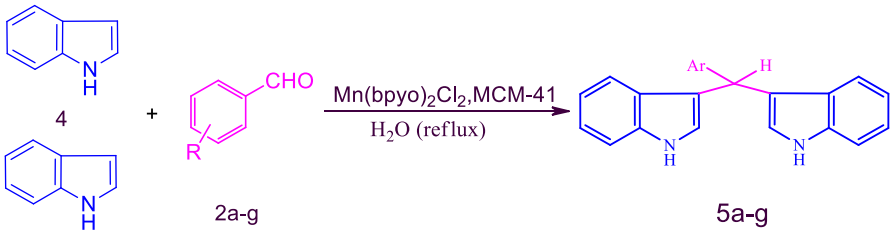
A simple and direct method for the synthesis of bis(indolyl)methanes is the reaction of indole with aldehydes (Scheme 2).

Our initial studies were focused on the optimization of the reaction conditions for the synthesis of bis(indolyl)methanes. 4-Nitrobenzaldehyde and indole were chosen as model substrates. The reaction in the presence of 0.04 g Mn(bpyo)$_2$-Cl$_2$/MCM-41 in refluxing water afforded the corresponding product at an 87 % yield. With the optimized reaction conditions in hand, we next studied the reaction of a series of aldehydes with indole derivatives. The results are shown in Table 4.

Synthesis of 4*H*-benzo[*b*]pyrans

4*H*-benzo[*b*]pyrans represent an important class of compounds, appearing as the main components of many naturally occurring products [59]. They have diverse pharmacological properties, including anticoagulant, anticancer, spasmolytic, diuretic, and anti-anaphylactic activity [60]. 4*H*-Pyrans also constitute the structural unit of a series of natural products [61] (Scheme 3).

To optimize the catalytic system, the condensation of benzaldehyde, dimedone and malononitrile under reflux conditions (Table 5) was used as a model reaction. A variety of solvents and catalysts were examined in the model reaction, and the best results were obtained using by Mn(bpyo)$_2$Cl$_2$/MCM-41 in refluxing water (Table 5).

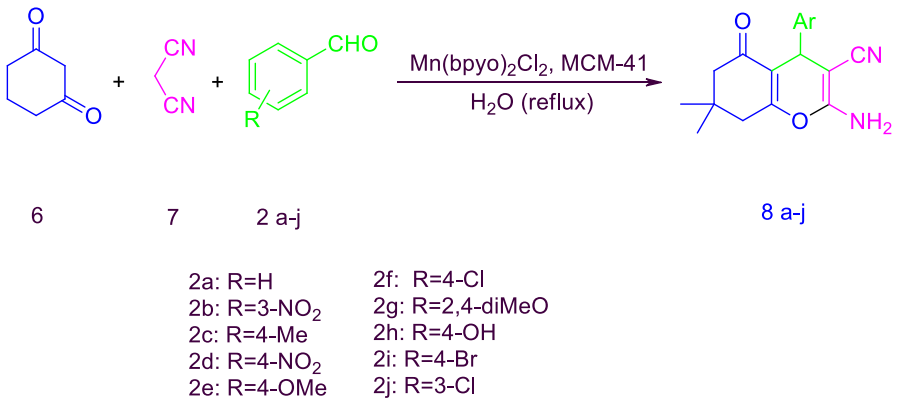


Scheme 2 Synthesis of bis(indolyl)methanes

Table 4 Synthesis of bis(indolyl)methane derivatives

Entry	Aldehyde	Time (min)	Yield (%)[a]	m.p. (°C)	
				Found	Rep.
1	C_6H_5	25	91	123	125–127 [55]
2	3-NO_2–C_6H_4	30	90	260–262	77–81 [56]
3	4-Me–C_6H_4	25	89	95–97	–
4	4-NO_2–C_6H_4	35	87	244–246	220–222 [57]
5	4-MeO–C_6H_4	35	86	264–266	265–266 [55]
6	4-Cl–C_6H_4	30	88	192	191–193 [55]
7	C_6H_4–CH=CHCHO	25	92	96–98	94–96 [58]

[a] Isolated yield



Scheme 3 Synthesis of 4H-benzo[b]pyranes

Table 5 Optimization of reaction conditions in the condensation of benzaldehyde, dimedone and malononitrile under reflux conditions for 20 min

Entry	Catalyst	Solvent	Yield (%)[a]
1	$Mn(bpyo)_2Cl_2$/MCM-41	CH_3CN	85
2	$Mn(bpyo)_2Cl_2$/MCM-41	CH_3COOEt	60
3	$Mn(bpyo)_2Cl_2$/MCM-41	DCM	78
4	$Mn(bpyo)_2Cl_2$/MCM-41	H_2O	96
5	$Mn(bpyo)_2Cl_2$/MCM-41	C_2H_5OH	90
6	MCM-41	H_2O	82
7	HMTA	H_2O	85

[a] Isolated yield

The optimized conditions were used to construct a variety of 4*H*-benzo[*b*]pyran derivatives. This method was found to be effective with a variety of substituted aromatic aldehydes independently of the nature of the substituents in the aromatic rings (Table 6).

Table 6 Synthesis of pyran derivatives using aromatic aldehydes

Entry	Aromatic aldehyde	Time (min)	Yield (%)[a]	m.p.	
				Found	Rep.
1	C_6H_5	20	96	227–230	227–229 [62]
2	3-NO_2–C_6H_4	18	92	209–211	208–210 [62]
3	4-Me–C_6H_4	25	90	212–214	208–210 [64]
4	4-NO_2–C_6H_4	20	91	177–179	177–178 [63]
5	4-OMe–C_6H_4	30	90	202–204	199–201 [63]
6	4-Cl–C_6H_4	25	90	207–209	207–209 [64]
7	2,4-DiCl–C_6H_4	28	92	184–186	186–188 [62]
8	4-OH–C_6H_4	32	91	205–207	208–210 [62]
9	4-Br–C_6H_4	30	96	197–200	201–203 [62]
10	3-Cl–C_6H_4	25	92	226–228	224–226 [63]

[a] Isolated yield

General procedure

*General procedure for the synthesis of bis-(4-hydroxycoumarin) derivatives (**3a–g**)*

A solution of an aromatic aldehyde (1 mmol), 4-hydroxycoumarin (2 mmol), and $Mn(bpyo)_2Cl_2$/MCM-41 (0.04 g) in H_2O (5 mL) was stirred under heating conditions for an appropriate time. After completion of the reaction, which was monitored by thin-layer chromatography (TLC), the mixture was cooled to room temperature. The resulting solid product was then removed by filtration, washed with water to separate the catalyst, and recrystallized from absolute ethanol to give the pure product.

*General procedure for the synthesis of bis(indolyl)methanes (**5a–g**)*

A mixture of an appropriate aromatic aldehyde (1 mmol), indole derivative (2 mmol), and $Mn(bpyo)_2Cl_2$/MCM-41 (0.04 g) in H_2O (5 mL) was heated under reflux conditions. The progress of the reaction was monitored by TLC. Upon completion of the reaction, the mixture was cooled to room temperature. The resulting solid product was then removed by filtration and pure product was obtained by recrystallization from the solvent.

*General procedure for the synthesis of 4H-benzo[b]pyran derivatives (**8a–j**)*

A solution of an aromatic aldehyde (1 mmol), dimedone (1 mmol), malononitrile (1 mmol) and $Mn(bpyo)_2Cl_2$/MCM-41 (0.04 g) in H_2O (5 mL) was stirred under heating conditions for an appropriate time. After completion of the reaction, which was monitored by TLC, the mixture was filtered off and the filtrate was washed with water and dissolved in boiling ethanol. The catalyst was filtered off and the mixture

was cooled to room temperature. The resulting solid product was then removed by filtration and washed with ethanol.

Selected spectroscopic data

(*3,3′-Phenylmethylene-bis-(4-hydroxycoumarin*) (**3a**) IR (KBr) $\upsilon_{max} = 3067$, 2889, 1659, 1608, 758 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 500 MHz) $\upsilon_H = 6.15$ (s, 1H, CH), 7.26–7.46 (m, 9H, ArH), 7.66–7.69 (t, 2H, J = 7.6, ArH), 8.05–8.11 (d, 2H, J = 27.8, ArH), 11.33 (s, 1H, OH), 11.56 (s, 1H, OH) ppm.

3,3-(3-Nitrophenylmethylene)bis-(4-hydroxycoumarin) (**3b**) IR (KBr) $\upsilon_{max} =$ 3069, 1654, 1613, 1528, 1311,761 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 500 MHz) $\delta_H = 6.17$ (s, 1H, CH), 7.44–7.49 (m, 4H, ArH), 7.54–7.57 (t, 1H, J = 7.99, ArH), 7.61–7.63 (m, 1H, ArH), 7.69-7.71 (t, 2H, J = 7.4), 8.11–8.20 (m, 4H, ArH), 11.41 (s,1H, OH), 11.61 (s,1H, OH) ppm.

3,3-(4-Methoxyphenylmethylene)bis-(4-hydroxycoumarin) (**3e**) IR (KBr) $\upsilon_{max} =$ 3379, 3068, 1670, 1606, 1259, 1050, 767 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 500 MHz) $\upsilon_H = 3.84$ (s, 3H, CH_3), 6.09 (s,1H, CH), 6.89–6.91 (d, 2H, J = 8.69, ArH), 7.16–7.18 (d, 2H, J = 8.51, ArH), 7.44–7.46 (d, 2H, J = 8.24, ArH), 7.65–7.68 (m, 2H, ArH), 8.05–8.10 (d, 2H, J = 26.93, ArH), 11.32 (s, 1H, OH), 11.54 (s, 1H, OH) ppm.

1H,1H′-3,3′-(4-Nitro-phenylmethanediyl)-bisindole (**5d**) m.p. = 244–246 °C; IR (KBr) $\nu_{Max} = 3454, 3420, 3100, 3050, 2925, 2850, 1593, 1454, 1339, 1037$ cm^{-1}; ^{1}H-NMR ($CDCl_3$, 500 MHz): $\delta_H = 6.03$ (s,1H, CH), 6.85–6.90 (m, 4H, Ar–H), 7.02–7.08 (m, 2H, Ar–H), 7.27–7.3 (d, 2H, J = 9.6, Ar–H), 7.35–7.38 (d, 2H, J = 9.6, Ar–H), 7.59–7.63 (d, 2H, J = 10.5), 8.13–8.17 (d, 2H, J = 10.9), 10.93 (s, 2H, 2NH) ppm.

1H,1H′-3,3′-(4-Methoxy-phenylmethanediyl)-bisindole (**5f**) m.p. = 264–266 °C; IR (KBr) $\nu_{Max} = 3444, 3403, 3100, 3052, 2924, 2842, 1544, 1454, 1337,$ 1037 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): $\delta_H = 3.50$ (s,3H, CH_3), 5.85 (s,1H, CH), 6.67–6.85 (m,2H, Ar–H), 6.99–7.04 (m, 2H, Ar–H), 7.15-–7.20 (t, 2H, J = 9.6, Ar–H), 7.25–7.28 (3, 2H, J = 9.6, Ar–H), 7.36–7.42 (m, 4H, J = 10.5), 7.92 (s, 2H, J = 10.9) ppm.

2-amino-3-cyano-4-phenyl-7,7-dimethyl-5-oxo-4H-5,6,7,8-tetrahydrobenzo[b]pyran (**8a**) m.p. = 227–230 °C; IR (KBr) $\nu_{Max} = 3395, 3212, 2960, 2199, 1680$. ^{1}H NMR (400 MHz, DMSO-d6) δ: 0.96 (s, 3H, Me), 1.05 (s, 3H, Me), 2.11 (d, J = 16.1 Hz, 1H, CH_2),2.26 (d, J = 16.1 Hz, 1H, CH_2), 2.53 (s, 2H, CH_2),4.18 (s, 1H, CH),7.02 (s, 2H, NH_2), 7.14–7.21 (m,3H, H–Ar) 7.29 (t, J = 7.5 Hz, 2H, H–Ar) ppm [65].

2-amino-3-cyano-4–(3-nitro-phenyl)-7,7-dimethyl-5-oxo-4H-5,6,7,8-tetrahydrobenzo [b]pyran (**8b**) m.p. = 209–211 °C; IR (KBr) $\nu_{Max} = 3438, 3328, 2961, 1686,$ 1525. ^{1}H NMR (300 MHz, CDCl3), δ: 1.03 (3H, s, Me), 1.16 (3H, s, Me), 1.19 (3H, t, J = 7.1 Hz, Me), 2.21 (1H, d, J = 16.0 Hz, H-6), 2.28 (1H, d, J = 16.0 Hz, H-6),

2.51 (2H, m, CH_2), 4.07 (2H, m, OCH_2), 4.85 (1H, s, H-4), 6.28 (2H, br, NH_2) 7.40 (1H, t, J = 7.9 Hz, H–Ar), 7.68 (1H, d, J = 7.90 Hz, H–Ar), 8.0 (1H, d, J = 7.90 Hz, H–Ar) ppm [66].

Conclusion

In summary, we report here a high-yielding, simple, convenient, straightforward, and practical one-pot procedure for the synthesis of bis-(4-hydroxycoumarin), bis(indolyl)methane and 4*H*-benzo[*b*]pyran derivatives. The conditions are mild, and a wide range of functional groups can be tolerated. The use of Mn(bpyo)$_2$Cl$_2$/MCM-41 as a catalyst affords advantages that include simplicity of operation, easy work-up, and high product yields.

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