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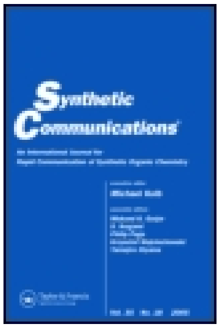

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Immobilization of 1,4-Diazabicyclo[2.2.2]Octane (DABCO) over Mesoporous Silica SBA-15: An Efficient Approach for the Synthesis of Functionalized Spirochromenes

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Accepted author version posted online: 15 Aug 2013.

To cite this article: Synthetic Communications (2013): Immobilization of 1,4-Diazabicyclo[2.2.2]Octane (DABCO) over Mesoporous Silica SBA-15: An Efficient Approach for the Synthesis of Functionalized Spirochromenes, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, DOI: 10.1080/00397911.2013.789527

To link to this article: http://dx.doi.org/10.1080/00397911.2013.789527

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Immobilization Of 1,4-Diazabicyclo[2.2.2]Octane (DABCO) Over Mesoporous Silica SBA-15: An Efficient Approach For The Synthesis Of Functionalized Spirochromenes

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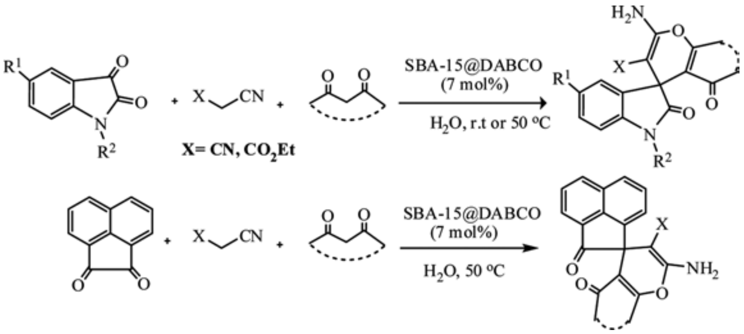
Abstract

Immobilization of 1,4-diazabicyclo[2.2.2]octane (DABCO) over mesoporous silica SBA-15 has been found to be an efficient heterogeneous base catalyst for the synthesis of biologically active functionalized spirochromene derivatives *via* three-component reaction of isatins/acenaphthoquinone, activated methylene reagents and 1,3-dicarbonyl compounds in the aqueous media. This eco-friendly protocol offers several advantages such as a cost-effective procedure with excellent yield, short reaction time, simple work-up, recovery, and reusability of catalyst, good functional group tolerance and broad scope of usable substrates. [Supplementary materials are available for this article. Go to the publisher's online edition of *Synthetic Communications*® for the following free supplemental resource(s): Full experimental and spectral details.]



KEYWORDS: Mesoporous SBA-15; multi component reaction; spirochromenes; heterogeneous catalyst

INTRODUCTION

Today, society with the new environment legislation demands more eco-friendly alternative catalytic processes, which makes the current homogeneous systems environmentally unacceptable.[1] The heterogenization of homogeneous catalysts has received much attention in recent years, where the active phase of homogeneous catalysts can be directly utilized and separation and recycling problems in the homogeneous systems can be avoided; obviously, the development of green and sustainable catalytic processes is achievable.[2] Normally this was afforded by supporting the active compounds on prefunctionalized solid materials such as carbon,[3] silicates,[4] alumina,[5] zeolites[6] and organic polymers.[7] Among them, SBA-15 as a mesoporous silica material is a promising candidate for the immobilization of organo-catalyst due to its high surface area, porosity, uniform pore size distributions and thermal stability.[8]

On the other hand, using water as a solvent offers many advantages, such as simplicity of reaction conditions, ease of work-up and product isolation, increasing the selectivity of a wide variety of organic reactions and accelerating reaction rates.[9] Therefore, the development of a catalyst that is not only stable toward water but also simply recyclable seems highly desirable.

The heterocyclic spirooxindoles are attractive targets in organic synthesis because of their highly pronounced biological activities as well as wide-ranging utility as synthetic intermediates for alkaloids, drug candidates, and clinical pharmaceuticals.[10] Among the spirooxindole compounds, those with fused 4H-chromenes have immense importance due to their diuretic, spasmolitic, anticoagulant, anticancer, and antinaphylactic activities.[11] In recent years, several improved protocols for the synthesis of spirooxindoles with fused chromenes have been reported by modification of three-component condensation of isatin derivatives, activated methylene reagents, and 1,3-dicarbonyl compounds using various catalysts such as $InCl_3$,[12] triethylbenzyl ammonium chloride (TEBA),[13] electro-generated base (NaBr/ROH),[14] NEt_3,[15] NH_4Cl,[16] β-cyclodextrin,[17]ethylenediaminediacetate,[18] surfactant metal carboxylates,[19] L-proline,[20] $[BMIm]BF_4$,[21] $HAuCl_4.3H_2O$,[22]MgO,[23] SBA-pr-NH_2,[24] and MSNs.[25]Although all of these methods are effective, but some of them have drawbacks such as, harsh reaction conditions,[12] long reaction times,[13,17] technical intricacy,[14] use of expensive,[21,22] unsafe,[15] and unreusablecatalysts.[13,15,16,18,19] Therefore, the development of a new and simple synthetic method for the preparation of spirooxindole derivatives has become an interesting challenge.

1,4-Diazabicyclo[2.2.2]octane (DABCO) has been applied as an inexpensive, eco-friendly, high reactive and non-toxic base catalyst for various organic transformations,[26] but in many of these cases it has not been recovered and eliminated as a residue. So converting homogenous DABCO into heterogeneous DABCO catalyst is a better option as it can be easily filtered as well as being recycled for several times.

Due to the current challenges for developing environmentally benign synthetic processes and in continuation of our investigations into the synthesis of biologically active heterocyclic compounds,[27] we report a green and simple procedure for the synthesis of some chromene derivatives using SBA-15@DABCO as a heterogeneous base catalyst in water. The synthesis of spirooxindoles**4a-y** was achieved by the three-component condensation of isatin derivatives **1a-h**, activated methylene reagents **2a, b** and 1,3-dicarbonyl compounds **3a-e** in the presence of SBA-15@DABCO (7 mol%) at 25 or 50 ^{o}C in water (Scheme 1).

RESULTS AND DISCUSSION

SBA-15@DABCO was synthesized according to the published procedure,[28] by silylation/condensation of SBA-15 with 3-chloro propyltrimethoxysilane, which was then reacted with DABCO to form DABCO-functionalized SBA-15 material (Scheme 2).

The catalyst structure was characterized by Fourier-transform infrared (FT-IR) spectroscopy, elemental analysis (CHN), thermo gravimetric analysis (TGA), X-ray diffraction and transmission electron microscopy (TEM). Potentiometric titration was also used to confirm TGA and elemental analysis. The amount of DABCO in SBA-15@DABCO was evaluated by the nitrogen content, 0.83 mmol/g, on the basis of nitrogen content by elemental analysis (C: 9.26%; H: 1.07%; N: 2.23%). We also determined the loading level of DAB-CO (0.82 mmol/g) based on the chlorine content by potentiometric titration method, with employing recent procedure,[29] which is shown to be in good agreement with results obtained from TGA and elemental analysis.

To illustrate the efficiency of our catalyst, the three-component reaction between isatin**1a**, malononitrile**2a** and dimedone**3a** in equimolar ratio as model substrates was investigated. Initially, the model reaction was examined in the presence of different amounts of SBA-15@DABCO in water at room temperature. The results are summarized in Table 1.

As it is observed, when the amount of SBA-15@DABCO increases from 3 to 6, 7 and 9 mol%, the yields increase from 68 to 85, 96 and 95%, respectively, in appropriate times (Table 1, entries 3-6). Using 7 mol% of SBA-15@DABCO in water at room temperature is sufficient to push this reaction forward (Table 1, entry 5). More amount of catalyst did not improve the product yields (Table 1, entry 6). Only a trace amount of the product was formed in the absence of catalyst (Table 1, entry 1). The model reaction was also checked in the presence of pure SBA-15, in which an increase in the reaction time and a decrease in the yield were observed (Table 1, entry 2). The effect of temperature was also studied. It was found that room temperature is appropriate for the SBA-15@DABCO-catalyzed reaction. The high temperature could improve the reaction rate and reduce the reaction time (Tabe 1, entry 9). The solvents also played an important role in the SBA-15@DABCO catalyzed reactions. Several solvents, such as $CHCl_3$, THF, CH_3CN, EtOAc, EtOH and CH_3OH were screened under similar reaction conditions (Table 1, entries 10–15). It is clear from Table 1, that water provided higher yield and shorter reaction time than other organic solvents. Therefore, water was selected as the reaction solvent in the following investigation.

To study the scope of the reaction, a series of substituted isatins (substitution in aromatic nucleus and at N1), different 1,3-dicarbonyl compounds (5,5-dimethyl-1,3-cyclohexanedione **3a**, 1,3-cyclohexane-dione **3b**, 2-thiobarbituric acid **3c,** 1,3-dimethyl-barbituric acid **3d**, and ethyl acetoacetate **3e**) and malononitrile**2a** or ethyl cyanoacetate**2b** were reacted using SBA-15@DABCO (7 mol%) in water at 25 or 50^{o}C. Under the optimized reaction conditions, a series of spiooxindoles**4a-y** were synthesized in high yields within short reaction times (Table 2). Additionally, the reaction of malononitrile or ethyl cyanoacetate proceeded smoothly, too.

In following further exploration of the potential of this protocol for spiro-heterocyclic synthesis, we also examined three-component reactions using another reactant, acenaphthoquinone instead of isatins under similar reaction conditions. Under these conditions, a variety of desired spiroacenaphthylenes were also produced in excellent yields within short reaction times (Table 3).

In order to compare the capability and efficiency of our catalyst with respect to the previously reported catalysts for the preparation of spirooxindole derivatives, the results for the synthesis of **4a** are collected in Table 4.

On the basis of the results shown in Table 4, the use of homogenous catalysts in water under heating conditions led to high product formation, while we designed a convenient and reusable heterogeneous-catalytic methodology for the synthesis of functionalized spirooxindoles at ambient temperature. Although the reaction proceeded more easily in [BMIm] BF_4, with its limitations in organic syntheses, naturally abundant water appeared to be a better option as an environmentally benign reaction medium, due to its inexpensive, non-toxic, non-corrosive, and non-inflammable nature.

In order to check the recyclability and stability of the catalyst, we designed a set of experiments by conducting successive condensation reaction of isatin**1a** with malononitrile**2a** and dimedone**3a** using SBA-15-DABCO catalyst (7 mol%) at 50 ^{o}C. After the completion of the first cycle, the reaction mixture was filtered, the residue was dissolved in acetone and then filtered to separate the catalyst. The catalyst was thoroughly washed with EtOH and finally dried at 80 °C for 3 h. It was found that the catalyst could be used directly for six cycles (Table 5). However, a little drop was observed in the product yield and catalytic activity after several cycles. It is obvious that the amount of recovered catalyst is reduced after each cycle, therefore, the reactants were taken with respect to the amount of the catalyst recovered after each reaction cycle.

A proposed mechanism for the synthesis of spirooxindole**4a** can be described as shown in Scheme 3.[4b,4d] The process represents a typical cascade reaction in which the isatin**1a** is firstly condensed with malononitrile**2a** in the presence of SBA-15@ DABCO to afford isatylidenemalononitrile**7**. Then, enolate**8** which is formed from dimedone**3a** usingSBA-15@ DABCO, is added to intermediate **7** *via* Michael addition to produce adduct **9**. Finally, enolate oxygen of intermediate **10** attacks nucleophilically to nitrile group and forms more stable product **4a**, after tautomeric proton shift.

CONCLUSION

In summary, a mild and efficient method for the synthesis of biologically active functionalized spiro-heterocyclic compounds *via* three-component reaction catalyzed by SBA-15@DABCO in the aqueous media is reported. The salient features of this atom economical procedure are its reusability, inexpensiveness, environmentally benign nature, high yield, short reaction times, tolerancy toward wide range of functional groups, operational simplicity, and easy separation**.**

EXPERIMENTAL

The chemical materials used in this work were obtained from Merck and Aldrich and used without purification. Mesoporous silica SBA-15 and DABCO functionalized SBA-15 were synthesized in according to the reported procedures.[31,28] IR spectra were determined on a Shimadzu instrument. Elemental analyses were carried out by Perkin-Elmer CHN 2400 instrument. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-400 AVANCE spectrometer at 400.13 and 100.61 MHz, respectively. ^{1}H and ^{13}C NMR spectra were obtained on solutions in DMSO-d_6 using TMS as internal standard. Chemical shifts are given in ppm (δ) relative to internal TMS, and coupling constants (*J*) are reported in Hertz (Hz). Thermo gravimetric analysis (TGA) were recorded on a Stanton Redcraft STA-780 (London, UK). Transmission electron microscopy (TEM) images were obtained using a Phlips CM10 microscope operated at 200 kV. X-ray powder diffraction (XRD) patterns of the PIs were recorded by an X-ray diffractometer (XRD, GBC MMA Instrument) with Be-filtered Cu Kα radiation. Melting points were determined on a thermo scientific IA9200 and are uncorrected.

General Procedure For The Synthesis Of Spirochromenes

A mixture of isatins or acenaphthoquinone (1 mmol), activated methylene reagents (1 mmol), 1,3-dicarbonyl compounds (1 mmol) and SBA-15@DABCO (0.085 g, 7 mol%) in water was stirred at 25 or 50 ^{o}C. Upon compilation, monitored by TLC (n-hexane/ethyl acetate: 2/1), the reaction mixture was allowed to cool to room temperature. The precipitate was filtered and dissolved in acetone. The catalyst was separated by filtration of this solution. The solution was concentrated under vaccum to afford the product, which was purified by recrystallization in the ethanol.

Compounds **4a-f**, **4h, 4i**, **4k**, **4p**, **4v**, **4w**, **4y**, **6a- 6c** and **6e** are known compounds and were characterized by comparison of their physical and spectroscopic data with those of reported ones. [12–25,30,32] Physical properties and spectral data of new compounds are reported in supplementary data.

SUPPLEMENTARY DATA AVAILABLE

Experimental procedure, characterization data for new compounds and catalyst. This material is available free of charge *via* the Internet in an online version.

ACKNOWLEDGMENTS

We are thankful to the Research Council of Mazandaran University for the partial support of this work.

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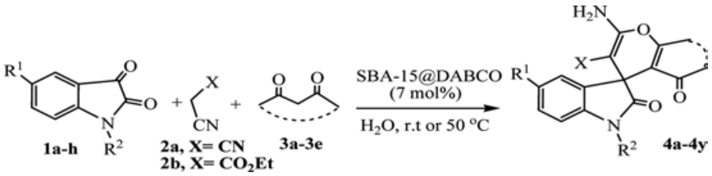
Table 1. Optimization of reaction conditions for the synthesis of **4a**.

Entry	**Catalyst (mol%)**	**Solvent (5ml)**	**Temp (^oC)**	**Time (min)**	**Yield(%)**[a]
1	-	H_2O	25	240	trace
2	SBA-15[b] (10)	H_2O	25	30	25
3	SBA-15@DABCO (3)	H_2O	25	30	68
4	6	H_2O	25	30	85
5	7	H_2O	25	10	96
6	9	H_2O	25	10	95
7	3	H_2O	50	15	80
8	6	H_2O	50	5	94
9	7	H_2O	50	2	98
10	7	$CHCl_3$	50	60	45
11	7	CH_3CN	50	60	64
12	7	THF	50	60	68
13	7	EtOAC	50	60	83
14	7	CH_3OH	50	30	72
15	7	EtOH	50	30	94

[a] Yields refer to isolated products.

[b] (10 wt% of isatin)

Table 2. SBA-15@DABCO catalyzed synthesis of spirooxindoles **4a-y** in queousmedium.



Entry	product	R^1	R^2	X	1,3-dicarbonyl compounds	Time (min)^a	Yield (%)^{a,c}	Time (min)^b	Yield (%)^{b,c}
1	4a	H	H	CN	3a	10	96	2	98[16]
2	4b	H	H	CN	3b	12	95	4	96[16]
3	4c	H	H	CN	3c	25	91	6	96[13]
4	4d	H	H	CN	3d	30	87	10	91[20b]
5	4e	H	H	CN	3e	90	91	30	95[20a]
6	4f	Br	H	CN	3a	7	93	3	97[20a]
7	4g	Br	H	CN	3c	20	90	4	92
8	4h	Br	H	CN	3e	70	88	20	93[21]
9	4i	Cl	H	CN	3a	6	92	2	94[20a]
10	4j	Cl	H	CN	3d	20	89	7	92
11	4k	NO_2	H	CN	3a	3	96	<1	98[17]
12	4l	NO_2	H	CN	3c	10	94	3	93

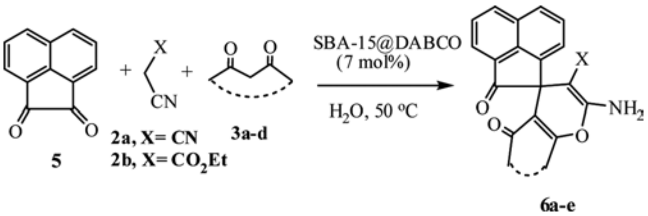
13	4m	H	Et	CN	3a	25	89	5	96
14	4n	H	Et	CN	3b	30	86	6	94
15	4o	H	Et	CN	3c	30	89	7	91
16	4p	H	Bn	CN	3a	30	88	5	94 [21]
17	4q	H	CH_2CO_2Et	CN	3a	17	93	4	97
18	4r	H	CH_2CO_2Et	CN	3b	20	91	5	96
19	4s	H	CH_2CO_2Et	CN	3c	30	90	5	93
20	4t	Cl	CH_2CO_2Et	CN	3a	13	94	3	97
21	4u	Cl	CH_2CO_2Et	CN	3b	15	92	4	95
22	4v	H	H	CO_2Et	3a	12	87	7	93 [21]
23	4w	H	H	CO_2Et	3e	95	83	35	90 [20a]
24	4x	H	CH_2CO_2Et	CO_2Et	3a	20	84	7	92
25	4y	Br	H	CO_2Et	3b	8	91	5	93 [20a]

[a] At r.t.

[b] At 50 °C

[c] Yields refer to isolated products.

Table 3. SBA-15@DABCO catalyzed multicomponent synthesis of spiroacenaphthylenes**6a-e** in aqueous medium.[a]



Entry	Product	X	1,3-dicarbonyl compounds	Time (min)	Yield (%)[b]
1	6a	CN	3a	3	95 [30b]
2	6b	CN	3b	4	93 [30b]
3	6c	CO_2Et	3a	15	84 [16]
4	6d	CN	3c	10	91
5	6e	CN	3d	20	83 [30b]

[a]Reaction conditions: acenaphthoquinone (1 mmol); activated methylene reagents (1 mmol); 1,3-dicarbonyl compounds (1 mmol); catalyst: SBA-15@DABCO (7 mol%); solvent: H_2O (5 mL); temperature: 50 °C. [b] Yields refer to isolated products.

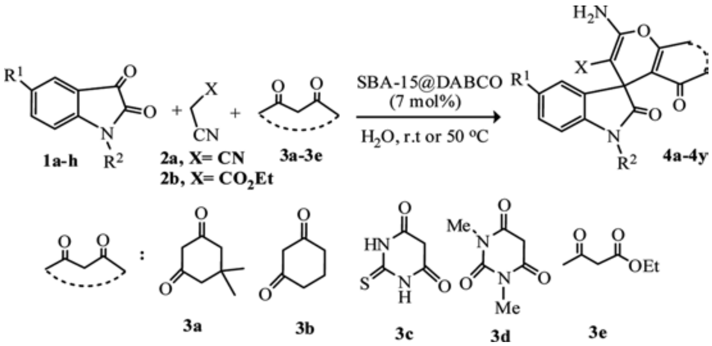
Table 4. Comparative the condensation of malononitrile with isatin and 5,5-dimethyl-cyclohexane-1,3-dione using the reported catalysts versus SBA-15@DABCO.

Reagents and conditions	**Time (min)**	**Yield(%)**	**Ref.**
$InCl_3$, 20 mol%, CH_3CN, reflux	90	75	12
TEBA, 20 mol%, H_2O, 60°C	120	94	13
NH_4Cl, 20 mol%, H_2O, 80°C	10	92	16
β-cyclodextrin, H_2O, 60 °C	300	90	17
EDDA, 10 mol%, H_2O, 60 °C	60	90	18
Sodium stearate, (10 mol %), H_2O, 60 °C	180	95	19
L-proline, 10 mol%, H_2O, 70 °C	20	94	20a
[BMIm] BF_4, r.t.	3	94	21
$HAuCl_4$, $3H_2O$, 5 mol%, PEG 400, 70 °C	30	96	22
Nano MgO, 15 mol%, H_2O, 80 °C	120	93	23
SBA-15@DABCO, 7 mol%, H_2O, r.t.	10	96	This work
SBA-15@DABCO, 7 mol%, H_2O, 50°C	2	98	This work

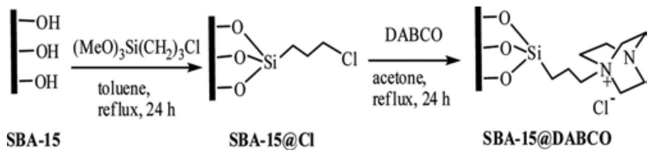
Table 5. Recyclability of SBA-15@DABCO

Cycle	1	2	3	4	5	6
Yield (%)	98	95	95	93	91	87

Scheme 1. Synthesis of spirooxindoles**4a-y** using SBA-15@DABCO in aqueous medium.



Scheme 2. Synhesis of SBA-15@DABCO.



Scheme 3. Plausible mechanism for the reaction of isatin and malononitrile with dimedone.