

A novel and efficient synthesis of bisindolylmethanes by using silica-supported-3-(triethoxysilyl) propane-1-ammonium chloride as a reusable catalyst under solvent free conditions

Mohammad Reza Poor Heravi*, Aazam Monfared, Masoumeh Ahmadi

Department of Chemistry, Payame Noor University, P.O. BOX 19395-3697, Tehran, Iran

Received: 15 May 2015, Accepted: 29 February 2016, Published: 29 February 2016

Abstract

A facile and efficient synthesis of bis(indolyl)methanes derivatives (**3a-u**) was reported *via* a condensation reaction of aldehydes and indole in the presence of silica-supported-3-(triethoxysilyl) propane-1-ammonium chloride catalysis under solvent free conditions. We studied the model reaction in different conditions, temperature, and amount of optimized catalyst. The use of just 0.02 g of (silica gel-ammonium salt) is sufficient. The reaction was carried out at 110°C under thermal condition. This method includes some advantages such as mild reaction condition, easy work-up, and recoverable and reusable catalyst.

Keywords: Bis(indolyl)methanes; multicomponent reactions; silica-supported-3-(triethoxysilyl) propane-1-ammonium chloride; solvent-free conditions.

Introduction

Bis(indolyl)methane [1] and indole [2] are important derivatives of indole in organic synthesis and pharmaceutical chemistry and they exhibit various physiological properties.

Bis(indolyl)methane is the most active cruciferous substances for promoting

beneficial estrogen metabolism in human [3] and induce apoptosis in human cancer cells [4]. Consequently, numerous methods have been reported for the preparation of bis(indolyl)methanes [5].

Generally, bis(indolyl)methanes are prepared by the condensation of indoles with

*Corresponding author: Mohammad Reza Poor Heravi

Tel: +98 (24) 35240943, Fax: +98 (24) 35226932

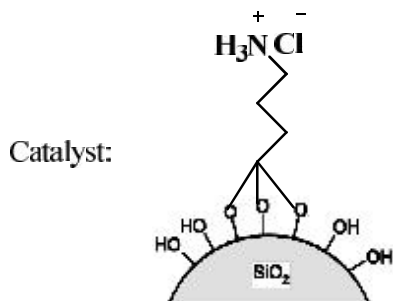
E-mail: heravimr@gmail.com, mrheravi@yahoo.com

various aldehyde or ketones in the presence of either protic [6], or Lewis acids [7] such as I_2 [8], $LiClO_4$ [9], a variety of reagents such as acetic acid [10], $InCl_3$ [11], $In(OTf)_3$ [7], InF_3 [12], $Dy(OTf)_3$ [13], $Ln(OTf)_3$ [14], $FeCl_3$ [15], NBS [16], $KHSO_4$ [17], $NaHSO_4$, SiO_2 [18], PPh_3 , $HClO_4$ (TPP) [19], CAN [20], zeolites [21], clay [22], $H_3PMo_{12}O_{40} \cdot xH_2O$ [23], and 1-butyl-3-methylimidazoliumtetrafluoroborate or 1-butyl-3-methylimidazoliumhexafluorophosphate ionic liquids [24] have been employed to accomplish this transformation. Recently, rare-earth perfluorooxanoates [$RE(PFO)_3$] [25], trichloro-1,3,5-triazine [26], hexamethylenetetraamine-bromine [27], ion-exchange resin [28], and ionic Lanthanide

triflates are also found to catalyze these reactions [29]. Herein, we investigated silica-supported-3-(triethoxysilyl)propane-1-ammonium chloride catalysis that could act as a catalyst (Scheme 1). The catalyst was prepared and characterized by FT-IR and identification with ninhydrine solution in ethyl acetate solvent. Therefore, the discovery of a new and an inexpensive catalyst for the preparation of bis(indolyl)methanes under neutral and mild conditions is of prime importance. For the increasing environmental and economic concerns in recent years, it is now essential for chemists to search environmentally benign catalytic reactions as much as possible.



R^1 : C_6H_5 , C_6H_5 , 4- ClC_6H_4 , 2- ClC_6H_4 , 4- $\text{CH}_3\text{C}_6\text{H}_4$, 4- $\text{CH}_3\text{OC}_6\text{H}_4$, 4- HOC_6H_4 , 3- $\text{CH}_3\text{O-4-OHC}_6\text{H}_3$,
 2-Naphthyl, 1-Naphthyl, 3- $\text{NO}_2\text{C}_6\text{H}_4$, 4- $\text{NO}_2\text{C}_6\text{H}_4$, 4- CNC_6H_4 , 4- FC_6H_4 , 4- $\text{CF}_3\text{C}_6\text{H}_4$, 2- $\text{Cl-6-FC}_6\text{H}_3$,
 2-Furyl, 4- $(\text{CH}_3)_2\text{N-C}_6\text{H}_4$, CH_3 , nC_5H_{11}
 R^2 : H
 R_1 and R_2 : Cyclohexanone, Isophthalaldehyde



Scheme 1. Preparation of bis(indolyl)methanes using of silica-supported-3-(triethoxysilyl) propane-1-ammonium chloride as a reusable catalyst under solvent free conditions

Experimental

Reagents and equipment

All reagents were purchased from Merck. Aldehydes were distilled before use. Melting points were determined on an Electrothermal X6 microscopy, digital instrument, uncorrected. IR spectra were recorded on a Bruker Equinox 55 spectrometer using KBr pellets. NMR spectra were recorded using either a Bruker DRX500 machine at room temperature. ^1H , ^{13}C NMR and ^{19}F NMR

spectra were measured using $\text{DMSO-}d_6$ as solvent. CHN analyses were performed on Exeter Analytical Inc. Model C-400 CHN Analyzer Mass spectra were obtained using a Micro Mass LCT machine in EI model HRMS machine in GC-QT mode. All the reactions were monitored by TLC using 0.25 mm silica gel plates (Merck 60F₂₅₄) UV indicator.

Preparation of the silica-supported-3-(triethoxysilyl) propane-1-ammonium chloride catalyst

A mixture of dry silica gel (10 gr 70-230 mesh) and 3-(triethoxy)propylamine (5 mL) in dry toluene (20 mL) was stirred and refluxed for 20 h. The precipitate was filtered by centrifuges. The obtained solid was washed with dry toluene and dried at 120 °C

for 10 h under reduced pressure, and then a mixture of 2 g of silica-supported, 3-(triethoxysilyl) propane-1-ammonium chloride and 10 mL of HCl (2 N) was stirred for 20 h at room temperature. The resulted suspension was filtered by centrifuges. The obtained solid was washed with water and dried at 80 °C under reduced pressure for 10 h [30] (Figure 1).

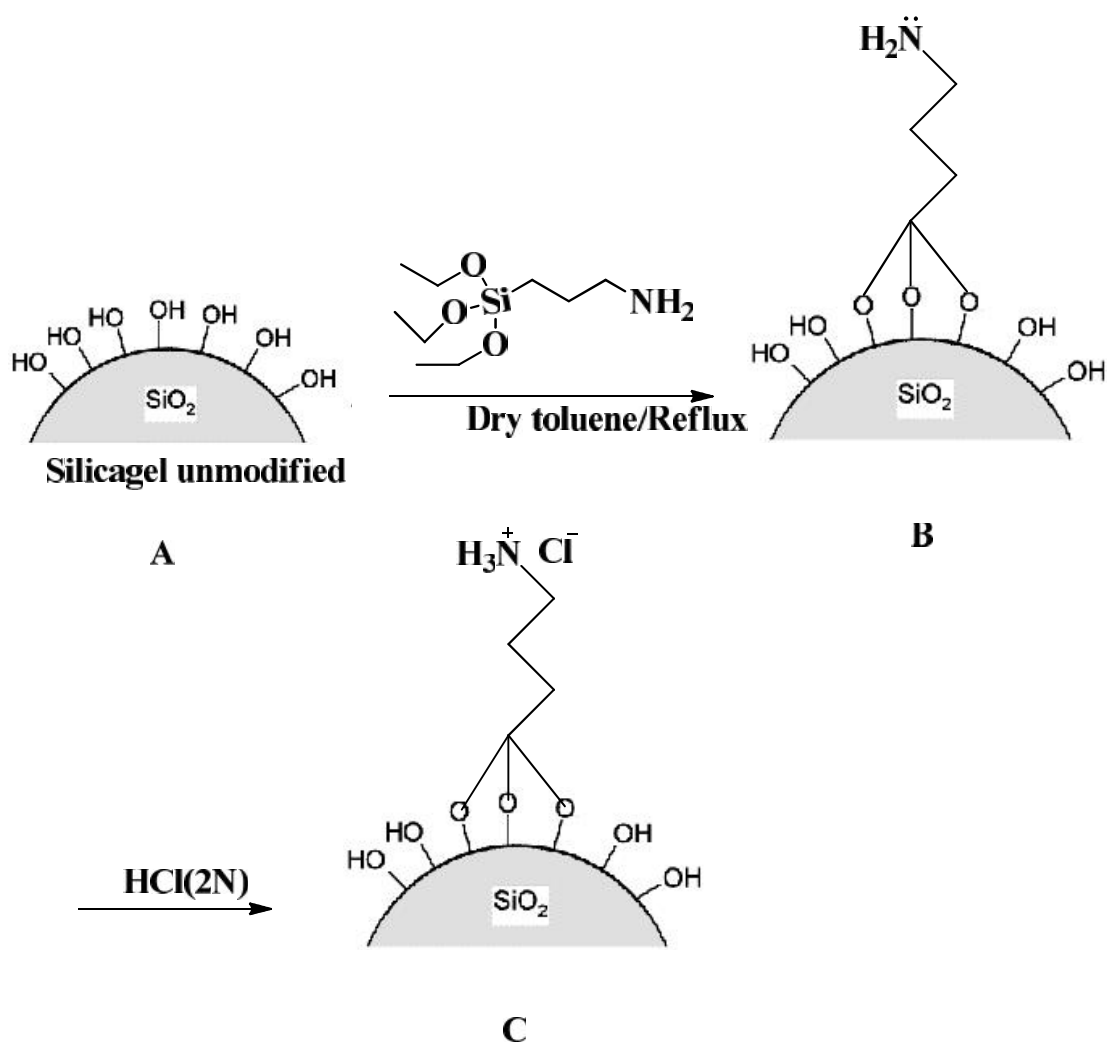


Figure 1. Mechanism of heterogeneous catalyst synthesis

General procedure for the synthesis of bis(indolyl)methanes under thermal solvent-free conditions in the presence of catalyst

Heterogeneous mixture of aromatic aldehyde (1 mmol), indole (2 mmol) and silica-supported-3-(triethoxysilyl) propane-1-ammonium chloride as catalyst (0.02 g) was heated with stirring for 1-3 h at 100 °C, in an oil bath. After completion of the reaction (indicated by TLC), the reaction was cooled to room temperature and ethanol or ethyl acetate (10 mL) was added to the reaction mixture and stirred for 5 min. The undisclosed solid separated was filtered, washed with cold water, the residue was recrystallized from hot absolute ethanol to afford a pure product and the solid on the filter was the catalyst (recover the catalyst).

Characterization data of some representative compounds

3,3'-(Naphthalen-2-ylmethylene)bis(1*H*-indole) (**3h**). 0.448g (90%); white solid; mp 198-202 °C. IR (KBr): 3456, 3043, 2943, 1632, 1522, 1465, 1143, 803 cm⁻¹. ¹H NMR (DMSO-*d*₆, 500 MHz): 5.75 (s, 1H), 6.87 (d, 1H, *J*=8.0 Hz), 7.43-7.56 (m, 4H, Ar-H), 7.62-7.98 (m, 10H, Ar-H), 8.04 (d, 1H, *J*=8.0 Hz), 8.21 (d, 1H, *J*=8.0 Hz), 10.82 (s, 2H, indole-NH). ¹³C NMR (DMSO-*d*₆, 125 MHz): 41.43, 113.34, 119.43, 119.98,

120.32, 121.34, 122.43, 122.58, 123.54, 125.34, 126.02, 128.54, 129.06, 130.35, 132.93, 133.09, 136.98, 137.44, 137.96, 141.65, 143.54, 147.34, 148.01, 148.79. MS (EI), *m/z* (%) =372 (M⁺, 15), 227 (75). HRMS (EI) Found: M⁺, 372.1604. C₂₇H₂₀N₂ requires M⁺, 372.1602. Anal Calcd for C₂₇H₂₀N₂: C, 87.07; H, 5.41; N, 7.52; Found: C, 87.03, H, 5.45; N, 7.53.

3,3'-(Naphthalen-1-ylmethylene)bis(1*H*-indole) (**3i**).0.448g (92%); white solid; mp 233-235 °C. IR (KBr): 3434, 3076, 2932, 1645, 1555, 1461, 1132, 802 cm⁻¹. ¹H NMR (DMSO-*d*₆, 500 MHz): 5.67 (s, 1H), 6.89 (d, 1H, *J*=8.0 Hz), 7.56-7.77 (m, 4H, Ar-H), 7.83-7.96 (m, 10H, Ar-H), 8.09 (d, 1H, *J*=8.0 Hz), 8.32 (d, 1H, *J*=8.0 Hz), 10.55 (s, 2H, indole-NH). ¹³C NMR (DMSO-*d*₆, 125 MHz): 43.65, 112.24, 118.23, 119.65, 120.04, 121.56, 122.03, 122.98, 123.04, 124.34, 125.92, 127.94, 128.16, 131.55, 132.73, 133.49, 135.08, 136.94, 137.96, 140.65, 142.84, 147.57, 148.31, 149.745. MS (EI), *m/z* (%) =372 (M⁺, 25), 227 (65). HRMS (EI) Found: M⁺, 372.1603. C₂₇H₂₀N₂requires M⁺, 372.1602. Anal Calcd for C₂₇H₂₀N₂: C, 87.07; H, 5.41; N, 7.52; Found: C, 87.03, H, 5.45; N, 7.53.

3,3'-((4-(Trifluoromethyl)phenyl)methylene)bis(1*H*-indole) (**3n**).0.351g (95%); yellow solid; mp

212-214 °C. IR (KBr): 3479, 3112, 2954, 1651, 1522, 1474, 1109, 802 cm⁻¹. ¹H NMR (DMSO-*d*₆, 500 MHz): 5.86 (s, 1H), 7.11 (t, 2H, *J*=8.3 Hz), 7.51 (d, 2H, *J*=8.3 Hz), 7.61-7.78 (m, 6H, Ar-H), 7.81 (d, 2H, *J*=7.9 Hz), 7.94 (d, 2H, *J*=8.0 Hz), 10.62 (s, 2H, indole-NH). ¹³C NMR (DMSO-*d*₆, 125 MHz): 48.87, 59.42, 121.43, 122.54, 123.21, 123.98, 124.54, 125.65, 126.32, 127.08, 128.21, 129.76, 130.54, 131.32, 133.83, 134.12, 135.65, 136.09, 137.96 (q, ¹*J*_{CF}=255.7 Hz), 147.34, 156.43. ¹⁹F NMR (DMSO-*d*₆, 470 MHz): -111.4. MS (EI), *m/z* (%) =390 (M⁺, 15), 227 (56). HRMS (EI) Found: M⁺, 390.1303. C₂₄H₁₇F₃N₂ requires M⁺, 390.1301. Anal Calcd for C₂₄H₁₇F₃N₂: C, 73.84; H, 4.39; N, 7.18. Found: C, 73.89, H, 4.36; N, 7.17.

1,3-Bis(di(1*H*-indol-3-yl)methyl)benzene(**3v**).0.481g (85%); yellow solid; mp 271-272 °C. IR (KBr): 3446, 3079, 2978, 1624, 1545, 1494, 1101, 801 cm⁻¹. ¹H NMR (DMSO-*d*₆, 500 MHz): 5.62 (s, 1H), 6.85 (s, 2H, Ar-H), 7.11-7.31 (m, 9H, Ar-H), 7.40-7.51 (m, 6H, Ar-H), 7.53-7.72 (m, 4H, Ar-H), 7.81-8.06 (m, 6H, Ar-H), 10.50 (s, 2H, indole-NH). ¹³C NMR (DMSO-*d*₆, 125 MHz): 65.98, 118.63, 120.87, 120.93, 122.09, 122.93, 125.02, 126.92, 128.54, 130.08, 131.98, 132.98, 133.76, 136.98, 137.16, 138.05, 139.38, 141.94, 142.80,

143.92,. MS (EI), *m/z* (%) =566 (M⁺, 15), 448 (56). HRMS (EI) Found: M⁺, 566.2519. C₄₀H₃₀N₄ requires M⁺, 566.2521. Anal Calcd for C₄₀H₃₀N₄: C, 84.78; H, 5.34; N, 9.89. Found: C, 84.75; H, 5.31; N, 9.83.

Results and discussion

Heterogeneous catalysts have gained attention in recent years due to economic and environmental consideration. These catalysts are inexpensive and easily available. They can conveniently be handled and removed from the reaction mixture, thus making the experimental procedure simple and eco-friendly. The activity and selectivity of a reagent dispersed on the surface of a support is improved as the effective surface area of the reagent can be increased up to one hundred-fold. Silica-supported-3-(triethoxysilyl)propan-1-ammonium chloride catalyst was prepared according to the method reported in the literature [30].

Figure 2 shows X-Ray diffraction patterns of the silica gel sample and silica-supported 3-(triethoxysilyl)propan-1-ammonium chloride sample synthesized. No peaks are observed in the silica gel sample except for the harrow like pattern at 2 degree between 15 °C and 24 °C attributed to amorphous silica gel. XRD patterns of silica-supported-3-(triethoxysilyl)propan-1-ammonium chloride showed a high intensity

peak at $2\theta = 20.7^\circ$ with a basal spacing of 4.3 Å and broad hump in the region of $2\theta = 8-11^\circ$. This spacing indicated that 3-

(triethoxysilyl) propan-1-ammonium chloride can enter the interlayer space and link with silica.

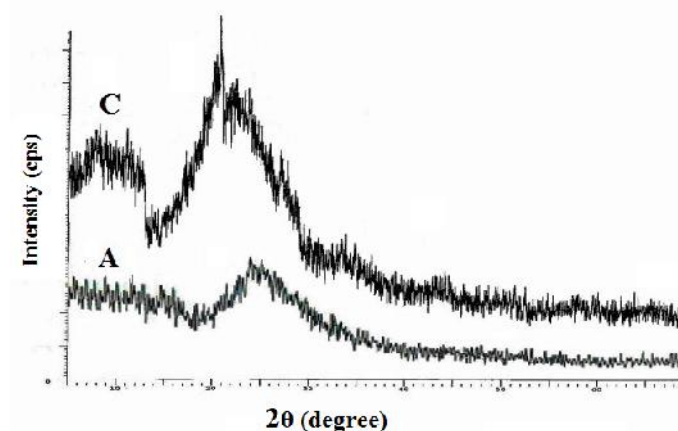


Figure 2. The powder XRD patterns of silica gel (A), silica-supported 3-(triethoxysilyl) propan-1-ammonium chloride (C)

In the IR spectra of dry silica gel (A), silica gel-supported propylamine (B), silica-supported-3-(triethoxysilyl)-propan-1-ammonium chloride (C) (Scheme 4), all samples showed the absorption bands for Si-OH and Si-O-Si in $\sim 800\text{ cm}^{-1}$ and $\sim 1100\text{ cm}^{-1}$, respectively. OH stretching band is

observed at $3300-3500\text{ cm}^{-1}$ and strong intermolecular hydrogen bonding occurs in the hydroxyl groups or NH group. Therefore, the resulting O-H absorption is very broad. IR spectrum of catalyst (C) showed absorption bands for Si-CH₂ at 2900 and 3000 cm^{-1} (Figure 3).

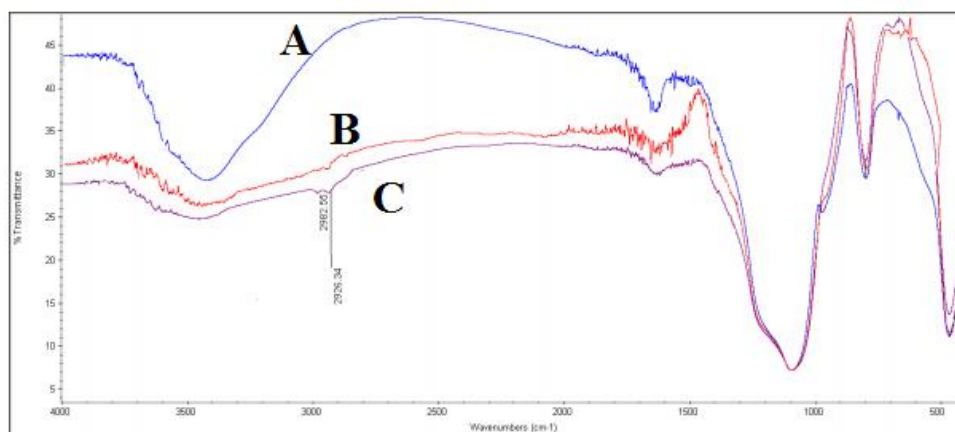


Figure 3. FT-IR spectrum of dry silica gel (A), silica gel-supported propylamine (B), silica-supported 3-(triethoxysilyl) propan-1-ammonium chloride (C)

The catalytic efficiency of silica-supported-3-(triethoxysilyl)propan-1-ammonium chloride catalyst was evaluated by conducting a model reaction of benzaldehyde (**2a**) with indole (**1**) under different catalytic conditions (Table 1).

Among these conditions, the reaction in the presence of silica-supported-3-(triethoxysilyl)propan-1-ammonium chloride catalyst was found to be rapid, more facile and high yielding under thermal and solvent-free conditions (Table 1, Entry 22).

Table 1. The results of reaction of indole (**1**) and benzaldehyde (**2a**) under different catalytic conditions

Entry	Catalyst	Time (h)	Yield (%) ^a [Ref]
1	None	10	null
2	BiCl ₃	5	87[31]
3	Bi(NO ₃) ₃ .5H ₂ O	4	86[31]
4	CuCl ₂	2	93[32]
5	InCl ₃	6	91[33]
6	InBr ₃	2	92[33]
7	In(OTf) ₃	0.8	78[33]
8	CoCl ₂ .6H ₂ O	24	37[32]
9	ZnCl ₂	24	11[32]
10	ZnBr ₂	24	20[32]
11	FeCl ₃	24	73[32]
12	Ga(ClO ₄) ₃	8	90[32]
13	LaCl ₃	15	8[34]
14	LiBr	24	18[33]
15	LiCl	24	16[35]
16	SrCl ₂ .6H ₂ O	15	25[35]
17	Ti(SO ₄) ₂	4	92[33]
18	AlCl ₃	15	89[33]
19	ZrSO ₄ .4H ₂ O	8	84[33]
20	ZrOCl ₂ .8H ₂ O	20	62[34]
21	SbCl ₃	1	92[36]
22	SiO ₂ -nPr-NH ₃ ⁺ Cl ⁻ /110 °C, Solvent-free	45	90-This work

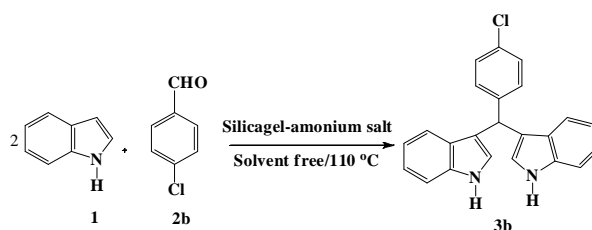
^aIsolated yield

Recently, solid-supported reagents, such as silica gel-supported acids, have gained considerable interest in organic synthesis. One of these solid-supported catalysts is silica-supported 3-(triethoxysilyl)propan-1-ammonium chloride which was prepared, as a reusable heterogeneous catalyst, from the reaction of silica with 3-(triethoxysilyl)propylamine, then stirred in HCl (2N) [30]. The catalyst is a highly efficient and economically viable catalyst for

the synthesis of bis(indolyl)methanes under thermal and solvent free conditions.

Moreover, when the reaction was carried out in solvent-free condition at 110 °C, good conversion was achieved and the results showed that, ‘no solvent’ is the ‘best solvent’ and complies with the green chemistry principles (Table 2, Entry 6).

Table 2. Screening of the temperature of the model reaction^a



Entry	T (°C)	Yield (%) ^b
1	25	None
2	40	25
3	60	40
4	80	55
5	100	90
6	110	95
7	120	85

^aReaction condition: 4-chloro benzaldehyde (1 mmol) and indole (2 mmol) using 0.02 g catalyst in solvent-free conditions and 110°C

^bIsolated yields

Optimization of the amount of silica-supported-3-(triethoxysilyl) propane-1-ammonium chloride on the condensation reaction of 4-chloro benzaldehyde (1mmol) and indole (2 mmol) under solvent-free conditions were investigated. After many studies on the above condensation, we found

that when less than 0.02 g was applied, lower yields of the corresponding product (Table 3, Entries 1-4) was resulted, whereas use of more than 0.02 g did not improve the yield (Table 1, Entry 6,7). So, 0.02 g catalyst is sufficient to carry out the reaction (Table 3, Entry 5).

Table 3. Effect of the amounts of catalyst on the model reaction^a

Entry	NH ₃ ⁺ .SiO ₂ (gr)	Yield (%) ^b
1	None	None
2	0.005	50
3	0.010	65
4	0.015	70
5	0.020	92
6	0.025	91
7	0.030	90

^aReaction condition: 4-chloro benzaldehyde (1 mmol) and indole (2 mmol) in solvent-free conditions and 110 °C

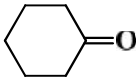
^bIsolated yields

With this result in hand, we went on to study the scope of the methodology. Under the optimized conditions, a variety of structurally diverse alkyl/aromatic aldehydes

were investigated. Various substituted aromatic aldehydes were reacted to obtain the corresponding bis(indolyl)methanes in high yields (Table 4). It was observed that the aldehydes containing electron-withdrawing substituents in the para position reacted faster and gave a high yield of the product as compared to those containing electron-donating substituents. Reactions of aliphatic carbonyl groups with indole were satisfactorily performed by the current method but they needed longer times and afforded lower yields of products than aromatic aldehydes (Table 4, Entries 15-17). The yields, time reaction and melting points of the products are reported in Table 4.

Table 4. Silica-supported-3-(triethoxysilyl) propane-1-ammonium chloride catalyzed of bis(indolyl)methnes from indole and carbonyl compounds

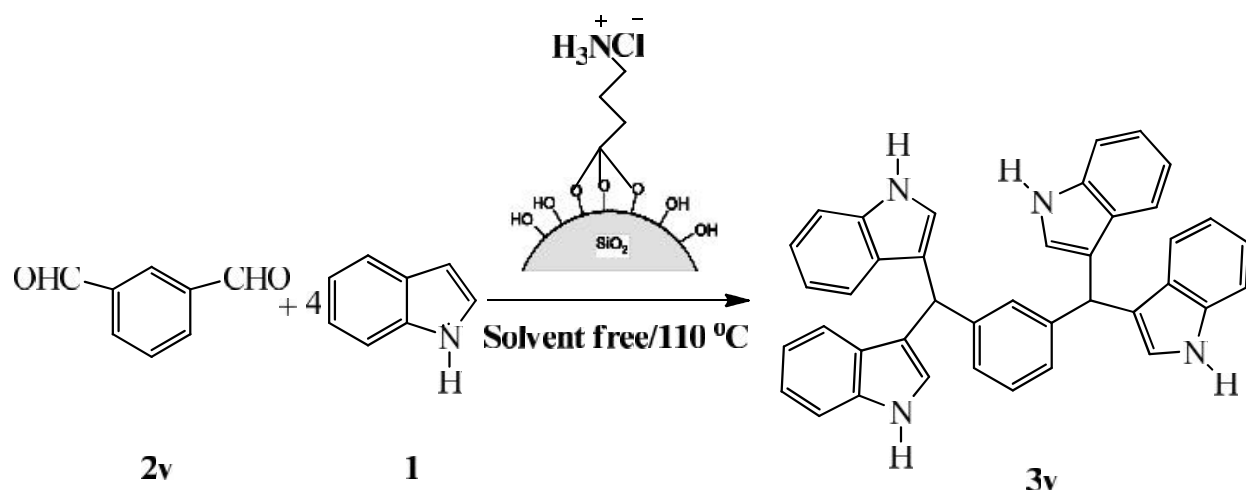
Entry	R ¹	R ²	Product	Time/min	Yields(%) ^a	Mp/°C	Lit. Mp/°C[Ref.]
1	C ₆ H ₅	H	3a	45	90	149–151	150–152 [37]
2	4-ClC ₆ H ₄	H	3b	100	90	78–79	79–80 [37]
3	2-ClC ₆ H ₄	H	3c	70	97	71–73	72–74 [37]
5	4-CH ₃ C ₆ H ₄	H	3d	100	85	93–95	94–96 [37]
6	4-CH ₃ OC ₆ H ₄	H	3e	110	85	184–186	186-188 [37]
7	4-HOC ₆ H ₄	H	3f	110	80	121–123	122-124 [38]
8	3-CH ₃ O-4-OHC ₆ H ₃	H	3g	110	85	125-127	126-127 [39]
9	2-Naphthyl	H	3h	90	90	199-201	198-202

10	1-Naphthyl	H	3i	95	90	233-235	New Comp.
10	3-NO ₂ C ₆ H ₄	H	3j	35	95	263–265	264–265 [37]
11	4-NO ₂ C ₆ H ₄	H	3k	20	98	219–221	220–222 [37]
12	4-CNC ₆ H ₄	H	3l	15	98	121–123	120–122 [38]
13	4-FC ₆ H ₄	H	3m	25	95	81-83	80-82 [38]
13	4-CF ₃ C ₆ H ₄	H	3n	25	95	212-214	New Comp.
14	2-Cl-6-FC ₆ H ₃	H	3o	65	83	209–210	93–95 [40]
15	2-Furyl	H	3p	25	85	320-322	321-322 [38]
16	4-(CH ₃) ₂ N-C ₆ H ₄	H	3q	20	90	171-173	170-172 [38]
15	CH ₃	H	3r	125	75	91-93	92-94 [37]
16	nC ₅ H ₁₁	H	3s	145	70	66-69	68-70 [37]
17		-	3t	120	70	162-164	163-165 [37]

^aIsolated yield

Furthermore, di[bis(indolyl)methyl]benzene can be achieved by this method. The reaction of isophthalaldehyde (**2v**) with 4 equiv. of indole (**1**) was performed in the presence of silica-supported-3-(triethoxysilyl) propane-1-

ammonium chloride catalyst (0.02 g) under optimized conditions and 1,3-bis(di(1H-indol-3-yl)methyl)benzene (**3v**) was produced in 85% yields after 55 min (Scheme 2).



Scheme 2. Reaction for the preparation of 1,3-bis(di(1H-indol-3-yl)methyl)benzene

The mechanism proposed for preparation of bis(indolyl)methanes from aryl/alkyl aldehydes (**2a-u**) and indole (**1**) using silica-supported-3-(triethoxysilyl) propane-1-ammonium chloride as catalyst under solvent-free conditions is depicted in Scheme 3. In the presence of catalyst, the electrophilicity of carbonyl carbon has been increased and it (**I**) readily reacts with

indole(**1**), affording the corresponding 3-(hydroxydiaryl/alkylmethyl)-3H-indol-1-ium (**II**), and H-transfer converts to ((1H-indol-3-yl)diaryl/alkylmethyl)oxonium (**III**). Intermediate (**III**) on reaction with second mole of indole converts to intermediate (**IV**) and followed by rearrangement affords the final product (**3a-u**) in good yield (Figure 4).

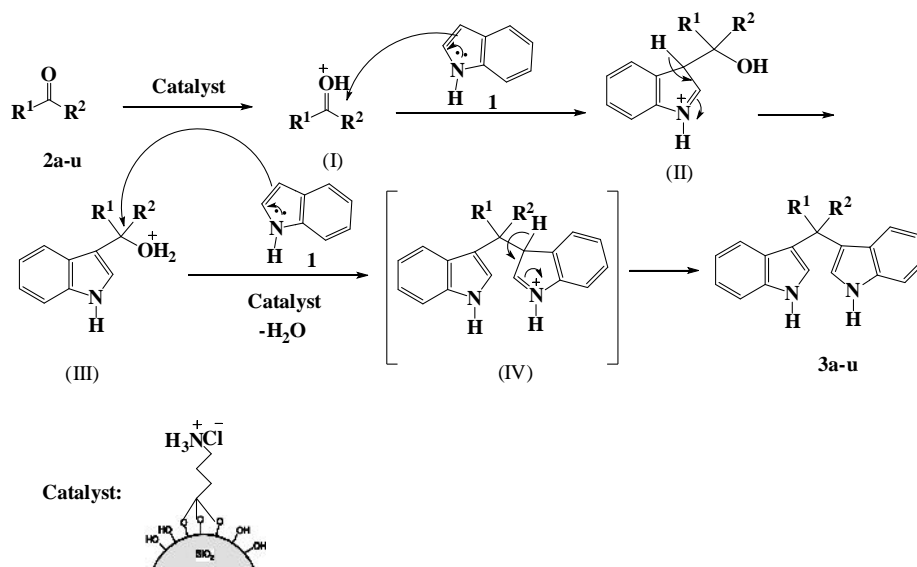


Figure 4. Proposed mechanisms for preparation of bis(indolyl)methanes using silica-supported-3-(triethoxysilyl) propane-1-ammonium chloride as a reusable catalyst under solvent free conditions

In view of the green chemistry, the catalyst was further explored for the reusability by a model reaction of 4-chlorobenzaldehyde and indole under similar conditions in the presence of 0.02 g catalyst. The catalyst was easily recovered by washing the reaction mixture with distilled water and directly

reused for the next turn after evaporation of water under reduced pressure. The recycled catalyst has been reused five times to catalyze the model reaction affording the corresponding chromene in 90, 90, 89, 89, and 87% yields, and without appreciable decreases of yield (Figure 5).

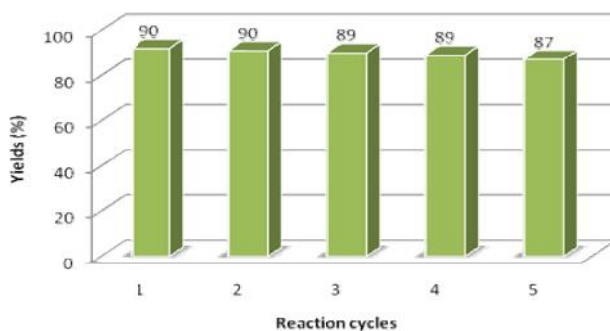


Figure 5. Reusability of gel-supported ammonium salt as a reusable catalyst under solvent free conditions. Reaction of 4-chlorobenzaldehyde and indole was used as model reaction

In summary, we describe a practical and efficient procedure for the preparation of bis(indolyl)methanes through the three-component reaction of aromatic aldehydes (**2a-v**) and indole (**1**) using silica-supported-3-(triethoxysilyl) propane-1-ammonium chloride as a reusable catalyst under solvent-free conditions. This procedure offers several advantages, including mild reaction conditions, cleaner reaction, and satisfactory yields of products, as well as a simple experiment and isolated procedure, which makes it a useful and attractive protocol for the synthesis of these compounds. The catalyst reused another cycle after evaporation of water. All of the products are known and the data are found to be identical with those that reported in the literature (Table 4).

Conclusion

In conclusion, we have developed a simple, convenient and effective method for the one-pot synthesis of bis(indolyl)methanes using silica-supported-3-(triethoxysilyl) propane-1-ammonium chloride which is not expensive and easily available as a recyclable heterogeneous catalyst under solvent-free conditions. The simplicity of the system, easy separation of

catalyst and products from the reaction mixture, high yields, purification of compound by crystallization method and shorter reaction times make this an improved protocol than existing methods. Further silica-supported-3-(triethoxysilyl) propane-1-ammonium chloride catalysts can be easily recovered and reused without loss in their activities. Therefore, the use of these catalysts not only makes the process economical viable but also help to reduce environmental pollution to achieve environmentally friendly processes.

Acknowledgments

We are grateful to the Payame Noor University for support of this study.

References

- [1] A. Domling, I. Ugi, *Angw. Chemie Inter. Ed.*, **2000**, 39(18), 3168-3210.
- [2] S.A. Morris, R.J. Andersen, *Tetrahedron*, **1990**, 46, 715-720.
- [3] G. Bifulco, I. Bruno, R. Riccio, J. Lavayre, G. Bourdy, *J. Nat. Prod.*, **1995**, 58, 1254-1260.
- [4] M.A. Zeligs, *J. Med. Food*, **1998**, 1 (2), 67-82.
- [5] X. Ge, S. Yannai, G. Rennert, N. Gruener, F.A. Gares, *Biochem. Biophys. Res. Commun.*, **1996**, 28, 153-157.

- [6] M. Chakrabarty, R. Basak, Y. A. Harigaya, *Heterocycles*, **2001**, *55*, 2431–2447.
- [7] M. Roomi, S. MacDonald, *Can. J. Chem.*, **1970**, *48*, 139–143.
- [8] R. Nagarajan, P. T. Perumal, *Tetrahedron*, **2002**, *58*, 1229–1232.
- [9] J.S. Yadav, B.V. S. Reddy, C.V.S. R. Murthy, G.M. Kumar, C. Madan, *Synthesis*, **2001**, 783–787.
- [10] G. Babu, N. Sridhar, P.T. Perumal, *Synth. Commun.*, **2000**, *30*, 1609–1614.
- [11] R. Nagarajan, P.T. Perumal, *Chem. Lett.*, **2004**, *33*, 288–289.
- [12] L.-P. Mo, Z.-C. Ma, and Z.-H. Zhang, *Synthetic Commun.*, **2004**, *35*, 1997–2005.
- [13] B.P. Bandgar, K.A. Shaikh, *J. Chem. Res. Synop.*, **2004**, 34–36.
- [14] X.-L. Mi, S.-Z. Luo, J.-Q. He, J.-P. Cheng, *Tetrahedron Lett.*, **2004**, *45*, 4567–4570.
- [15] D. Chen, L. Yu, P.G. Wang, *Tetrahedron Lett.*, **1996**, *37*, 4467–4470.
- [16] M. Xia, S.-B. Wang, W.-B. Yuan, *Synth. Commun.*, **2004**, *34*, 3175–3182.
- [17] (a) S.-J. Ji, S.-Y. Wang, Y. Zhang, T.-P. Loh, *Tetrahedron*, **2004**, *60*, 2051–2055; (b) B.P. Bandgar, K.A. Shaikh, *Tetrahedron Lett.*, **2003**, *44*, 1959–1961.
- [18] H. Koshima, W. Matsuoka, *J. Heterocycl. Chem.*, **2002**, *39*, 1089–1091.
- [19] R. Nagarajan, P.T. Perumal, *Chem. Lett.*, **2004**, *33*, 288–289.
- [20] C. Ramesh, J. Baneree, R. Pal, B. Das, *Adv. Synth. Catal.*, **2003**, *345*, 557–559.
- [21] R. Nagarajan, P.T. Perumal, *Synth. Commun.*, **2002**, *32*, 105–109.
- [22] C. Ramesh, N. Ravindranath, B. Das, *J. Chem. Res. Synop.*, **2003**, 72–74.
- [23] (a) M. Karthik, A.K. Tripathi, N.M. Gupta, M. Palanichamy, V. Murugesan, *Catal. Commun.*, **2004**, *5*, 371–375; (b) A.V. Reddy, K. Ravinder, V.L.N. Reddy, T.V. Goud, V. Ravikanth, Y. Venkateseswarlu, *Synth. Commun.*, **2003**, *33*, 3687–3694.
- [24] (a) M. Chakrabarty, N. Gosh, R. Basak, Y. Harigaya, *Tetrahedron Lett.*, **2002**, *43*, 4075–4078; (b) G. Penierres-Carrillo, J.G. Garcí'a-Estrada, J.L. Gutiérrez-Ramírez, C. Alvarez-Toledano, *Green Chem.*, **2003**, *5*, 337–339.
- [25] M.A. Zolfigol, P. Salehi, M. Shir, *Phosphorus, Sulfur Silicon Relat. Elem.*, **2004**, *179*, 2273–2277.

- [26] G.V.M. Sharma, J.J. Reddy, P.S. Lakshmi, P.R. Krishna, *Tetrahedron Lett.*, **2004**, *45*, 7729–7732.
- [27] J.S. Yadav, B.V.S. Reddy, S. Sunitha, *Adv. Synth. Catal.*, **2003**, *345*, 349–352.
- [28] X.-L. Feng, C.-J. Guan, C.-X. Zhao, *Synth. Commun.*, **2004**, *34*, 487–492.
- [29] S.-J. Ji, M.-F. Zhou, D.-G. Gu, S.-Y. Wang, T.-P. Loh, *Synlett*, **2003**, 2077_2079.
- [30] R. Ranjbar-Karimi, A. KhajehKhezri, M. Anary-Abbasinejad, *Het. Lett.*, **2014**, *4*, 2, 301-310.
- [31] R.R. Nagawade, D.B. Shinde, *Bull. Korean Chem. Soc.*, **2005**, *26*, 12, 1962-1964.
- [32] M. Xia, S.B. Wang, W.B. Yuan, *Synth. Commun.*, **2004**, *34*, 3175-3182.
- [33] S.X. Wang, J.T. Li, L.I. Geng, *J. Chem. Res. Synop.*, **2003**, 370-373.
- [34] A. Ahad, M. Farooqui, P.M. Arifkhan, M. Farooqui, *Int. J. Green Chem. Bioproc.*, **2012**, *2*, 4, 31-33.
- [35] R.R. Nagawade, D.B. Shinde, *ActaChemie, Slov.*, **2006**, *53*, 210-213.
- [36] Z. Ji-ming, X. Rui-ping, T. Yan, Z. Jian-hua, *Chem. Res. Chinese Uni.*, **2009**, *25*, 6, 941-944.
- [37] (a) A. Hasaninejad, A. Zare, H. Sharghi, K. Niknam, M. Shekouhy, *Arkivoc*, **2007**, *xiv*, 39-50; (b) A. Azizi, E. Gholibeghlo, Z. Manocheri, *ScientiaIranica*, **2012**, *19*, 574-578; (c) H. Firouzabadi, N. Iranpoor, H. Jafarpour, A. Ghaderi, *J. Mol. Catal. A: Chem.*, **2006**, *253*, 249-251.
- [38] B.P. Bandgar, A.V. Patil, V.T. Kamble, *Arkivoc*, **2007**, *xiv*, 252-258.
- [39] D.M. Pore, U.V. Desai, T.S. Thopate, P.P. Wadgaonkar, *Arkivoc*, **2006**, *12*, 75-80.
- [40] J. Banothv, R. Gali, R. Velpula, R. Bavantula, P.A. Grooms, *ISRN Org. Chem.* Article ID 616932, **2013**, 5 Pages.