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Original Research article

Sulfonylbis(1,4-phenylene)bissulfamic acid (SPSA): Introduction of an efficient and reusable catalyst for the synthesis of bis(indolyl)methanes

Masoud Mohammadi Zeydi*, Nosrat O Allah Mahmoodi, Ghorban Ardeshiri Terogeni

Department of Organic Chemistry, Faculty of Sciences, University of Guilan, Rasht, Iran

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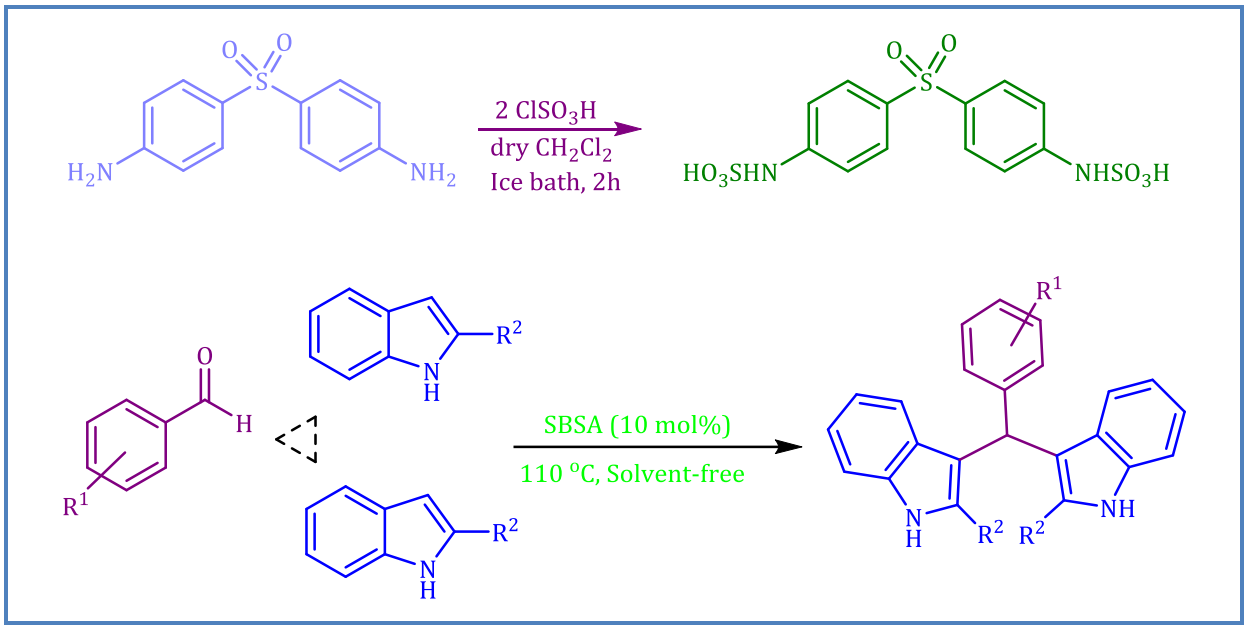
ABSTRACT

A simple, efficient and convenient route is described for the synthesis of *bis*-indolyl methanes by using recyclable catalyst sulfonylbis(1,4phenylene)bissulfamic acid (SPSA). In this procedure, we synthesize a *bis*-indolyl methane derivative *via* the three component reactions of two equivalent indoles with one equivalent of various aromatic aldehydes in the presence of 10 mol% SBSA as a heterogeneous catalyst under solvent-free conditions at 110 °C for the convinced reaction times (30–60 min). The advantages of this protocol towards the synthesis of *bis*-indolyl methane derivatives are: I) use of solvent-free conditions, II) inexpensive catalyst, III) using commercially available precursors, d) reusability of SBSA up to several cycles without much loss in reactivity, IV) simple work-up, V) high yields of pure products, VI) short reaction times. The structure of all bis(indolyl)methane derivatives were confirmed by melting point, FT-IR, ^{1}H NMR spectra and were compared with reliable references.

Corresponding author, email: zedi.65@gmail.com (M. Mohammadi Zeydi).
Tel.: +98939 5145655; Fax: +9813 3336706.

Graphical Abstract



Introduction

Recently, multi-component reactions (MCRs) have been widely paid attention by synthetic organic chemist from all over the world due to their efficacy for the building of heterocyclic complex molecules with diverse ranges of complexity in a single synthetic step from available starting molecules. These reactions represent very strong chemical method from both synthetic and economical points of view and time-efficient reactions are one of the most influential methods in industrial chemistry, green chemistry and the novel drug discovery process. Hence, the discovery of novel multicomponent is an interesting subject for organic chemistry researchers [1, 2].

The most important goals in the designing of catalysts, in terms of green chemistry, is to expand environmentally benign, economical, clean, practical, and efficient methods for catalyst separation and recycling. A convenient way of achieving these goals is the use of heterogeneous catalyst system for various organic reactions [3-6]. A heterogeneous catalyst system provides more filtration as it avoids catalyst loss. We have recently reported sulfonylbis(1,4-phenylene)bissulfamic acid (SPSA) [7], as an effective heterogeneous acidic catalyst for the preparation of chromene derivatives. simple work-up procedures, ease of preparation, and improved product yields, facile purification, shorter reaction times, mild reaction conditions, more stability, reusability, low toxicity and ease of handling of the catalyst are the main superiorities of SPSA.

Bis(indolyl)methanes, indole and its derivatives are a valuable group of nitrogen heterocyclic compound, which known as an kind of natural and synthetic intermediates in pharmaceutical

industry [8]. *Bis*(indolyl)methanes possessing diverse pharmacological activities such as anticancer [9], antimicrobial [10], anti-oxidant [11], and anti-inflammatory [12] activities; also, these types of compounds can aid the inhibition cancer cell growth via the induction of metastasis and apoptosis [13]. The main approach for the direct synthesis of this class of molecules is based on the electrophilic substitution of indole with carbonyl compounds in the presence of acidic catalysts such as silica sulfuric acid (SSA) [14], tetrabutylammo-nium tribromide [15], metal hydrogen sulfates [16], sulfated zirconia [17], montmorillonite clay K-10 [18], sodium dodecyl sulfate [19], trichloro-1,3,5-triazine [20], Zeolites [21], $AlPW_{12}O_{40}$ [22], $InCl_3$ [23], $H_3PW_{12}O_{40}$ [24], TiO_2 [25], $LiClO_4$ [26], $ZrOCl_2/SiO_2$ [27], $NaBF_4$ [28], $HClO_4–SiO_2$ [29], NBS [30], and $Bi(NO_3)_3.5H_2O$ [31]. Of course, most of the reported methods involve toxic solvent and metal ions, cumbersome work-up procedures and high cost.

In this research we wish to report the applicability of sulfonylbis(1,4-phenylene)bissulfamic acid (SPSA) in the promotion of the preparation of *bis*(indolyl)methanes through the electrophilic substitution of indole derivatives with various aldehydes.

Experimental

Matreials and methodes

All chemicals were purchased from Fluka and Merck chemical companies. Melting points were recorded by using capillary tubes on an electrothermal 9100 apparatus and are uncorrected. The IR and FT-IR spectra were obtained using a 4300 Shimadzu spectrophotometer as KBr disks. ^1H NMR spectra were recorded on a DPX 400 MHz spectrometer in $CDCl_3$ as the solvent relative to TMS. All yields refer to the isolated products and the known products were characterized by their physical constants and comparison with valid samples.

General procedure for the preparation of sulfonylbis(1,4-phenylene)bissulfamic acid (SPSA)

A 15 mL suction flask charged with a solution of 4,4'-sulfonyldianiline (10 mmol, 2.843 g) in dry CH_2Cl_2 (5 mL) was equipped with a constant pressure-dropping funnel containing 1.165 g chlorosulfonic acid (10 mmol) and a gas inlet tube for conducting HCl gas over an adsorbing solution, i.e., water. Chlorosulfonic acid was added drop wise over a period of 10 min while the reaction mixture was stirred slowly in an ice bath. Let the mixture reach to room temperature and stir in an additional 2 h. The mixture was filtered and the solid residue was washed with ether (3x5 mL) and dried under vacuum. SPSA was obtained as a withe-colored solid, 3.119 g (95% yields) (Scheme 1) [7]. White-colored solid, M.p. 244–248 °C, IR (KBr) (ν_{max}/ cm^{-1}): 3424, 3378, 3123,

2412, 1632, 1589, 1277, and 1143 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 6.85 (d, J = 8.8 Hz, 4H), 7.61 (d, J = 8.8 Hz, 4H), 7.95 (s, 2H, 2OH), 10.92 (s, 2H, 2NH). ^{1}3C NMR (100 MHz, $CDCl_3$): δ 146.9, 133.7, 129.6, 118.6.

General procedure for the preparation of 3,3'-((4-chlorophenyl)methylene)bis(1H-indole)

A mixture of 4-chlorobenzaldehede (1 mmol, 0.141 g), and indole (2.0 mmol, 0.234 g) and SBSA (10 mol%, 0.040 g) was heated at 110 °C. The progress of the reaction was monitored by TLC (*n*-hexane-ethyl acetate (3:1)). After completion of the reaction, the mixture was solved in hot and dry ethanol and insoluble catalyst was removed by filtration with a filter paper. The resulting crude material was purified by recrystallization from EtOH to afford pure products.

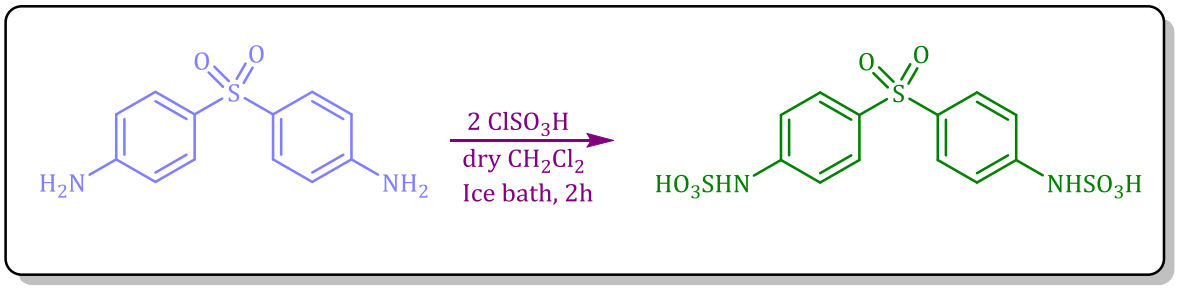
The selected spectral data

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

FT-IR (KBr) (ν_{max}/ cm^{-1}): 3482, 3012, 1598, 1532, 1465, 1465, 1427, 1218, and 1091. ^1H NMR (400 MHz, $CDCl_3$): δ 5.86 (s, 1H), 6.66 (s, 2H), 7.11 (t, J = 6.9 Hz, 2H), 7.14-7.22 (m, 3H), 7.28-7.31 (m, 2H), 7.35-7.42 (m, 6H), 7.93 (br, 2H, NH).

3,3'-((4-Chlorophenyl)methylene)bis(1H-indole) (3b)

FT-IR (KBr) (ν_{max}/ cm^{-1}): 3417, 1637, 1486, 1455, 1416, 1338, and 1092. ^1H NMR (400 MHz, $CDCl_3$): δ 5.87 (s, 1H), 6.83 (s, 2H), 6.87 (t, J = 7.5 Hz, 2H), 7.04 (t, J = 7.5 Hz, 2H), 7.27 (d, J = 7.9 Hz, 2H), 7.31 (d, J = 8.5 Hz, 2H), 7.39–7.33 (m, 4H), 10.86 (s, 2H) ppm.



Scheme 1. Preparation of sulfonylbis(4,1-phenylene)bis(sulfamic acid)

3,3′-((2-Chlorophenyl)methylene)bis(1H-indole) (3c)

FT-IR (KBr) (ν_{max}/ cm^{-1}): 3414, 1627, 1458, 1417, 1338, and 1093. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.34 (s, 1H), 6.62 (s, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 7.14–7.10 (m, 1H), 7.17 (s, 2H), 7.21 (s, 1H), 7.23 (s, 1H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 7.9 Hz, 2H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.93 (s, 2H).

3,3′-((2-Hydroxyphenyl)methylene)bis(1H-indole) (3d)

FT-IR (KBr) (ν_{max}/ cm^{-1}): 3419, 2924, 1620, 1516, 1483, 1455, 1420, 1195, and 1096; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.93 (s, 1H), 6.70 (s, 2H), 6.78 (d, *J* = 6.2 Hz, 1H), 6.80 (d, *J* = 3.8 Hz, 1H), 6.95 (t, *J* = 7.5 Hz, 2H), 7.09 (d, *J* = 7.0 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 7.29 (s, 1H), 7.19 (s, 2H), 7.31 (d, *J* = 3.4 Hz, 2H), 7.34 (s, 1H), 7.96 (s, 2H).

3,3′-((4-Hydroxylphenyl)methylene)bis(1H-indole) (3e)

FT-IR (KBr) (ν_{max}/ cm^{-1}): 3416, 1617, 1509, 1454, 1416, 1338, 1218, 1166, and 1095. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.70 (s, 1H), 6.65 (d, *J* = 8.4 Hz, 2H), 6.77 (s, 2H), 6.85 (t, *J* = 7.4 Hz, 2H), 7.02 (t, *J* = 7.5 Hz, 2H), 7.13 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 7.9 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 9.14 (s, 1H), 10.77 (s, 2H).

3,3′-((3-Nitrophenyl)methylene)bis(1H-indole) (3F)

FT-IR (KBr) (ν_{max}/ cm^{-1}): 3411, 1637, 1508, 1456, 1417, 1339, and 1094. ^{1}H NMR (400 MHz, DMSO-d_6): δ 6.07 (s, 1H), 6.88 (m, 4H), 7.06 (t, *J* = 7.2 Hz, 2H), 7.30 (d, *J* = 8 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.58 (t, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 8.17 (s, 1H), 10.94 (s, 2H) ppm.

3,3′-((4-Nitrophenyl)methylene)bis(1H-indole) (3g)

FT-IR (KBr) (ν_{max}/ cm^{-1}): 3455, 1637, 1506, 1456, 1414, 1341, and 1101. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.04 (s, 1H), 6.96–6.78 (m, 4H), 7.06 (t, *J* = 7.5 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.61 (d, *J* = 8.7 Hz, 2H), 8.15 (d, *J* = 8.7 Hz, 2H), 10.95 (s, 2H).

3,3′-((4-Bromophenyl)methylene)bis(1H-indole) (3h)

FT-IR (KBr) (ν_{max}/ cm^{-1}): 3402, 3058, 2924, 2854, 1617, 1457, and 1010. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.91 (s, 1H), 6.79 (d, *J* = 7.2 Hz, 2H), 6.87 (t, *J* = 7.5 Hz, 2H), 7.07 (t, *J* = 7.4 Hz, 2H), 7.28 (d, *J* = 8 Hz, 2H), 7.36 -7.40 (m, 6H), 10.93 (s, 2H).

3,3'-((3-Methoxyphenyl)methylene)bis(1H-indole) (3i)

FT-IR (KBr) (ν_{max}/ cm^{-1}): 3400, 3047, 2964, 1591, and 1253. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.73 (s,3H), 5.86 (s, 1H), 6.67-6.75 (d, *J* = 8.7 Hz, 2H), 6.93-7.37 (m, 12H), 7.90 (s, 2H, NH).

3,3'-((4-Methoxyphenyl)methylene)bis(1H-indole) (3j)

FT-IR (KBr) (ν_{max}/ cm^{-1}): 3412, 1636, 1564, 1509, 1455, 1417, 1340, 1250, 1175, 1095, and 1027. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.77 (s, 3H), 5.83 (s, 1H), 6.63 (s, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 7.00 (t, *J* = 7.3 Hz, 2H), 7.16 (t, *J* = 7.4 Hz, 2H), 7.24 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.90 (s, 2H).

3,3'-((4-Methylphenyl)methylene)bis(1H-indole) (3k)

FT-IR (KBr) (ν_{max}/ cm^{-1}): 3421, 1635, 1512, 1454, 1416, 1339, and 1095. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.31 (s, 3H), 5.85 (s, 1H), 6.66 (s, 2H), 7.00 (t, *J* = 7.5 Hz, 2H), 7.08 (d, *J* = 7.7 Hz, 2H), 7.16 (t, *J* = 7.5 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.91 (s, 2H).

3,3'-((4-Nitrophenyl)methylene)bis(2-methyl-1H-indole) (3l)

FT-IR (KBr) (ν_{max}/ cm^{-1}): 3418, 1647, 1512, 1449, 1410, and 1335. ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.75 (s, 6H), 6.05 (s, 1H), 6.62 (s, 2H), 7.08 (t, *J* = 7.3 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 2H), 7.39 (t, *J* = 8.6 Hz, 4H), 7.56 (d, *J* = 8.6 Hz, 2H), 8.18 (d, *J* = 8.6 Hz, 2H).

4-(Bis(2-methyl-1H-indol-3-yl)methyl)phenol (3m)

FT-IR (KBr) (ν_{max}/ cm^{-1}): 3423, 1611, 1516, 1438, 1421, 1341, and 1082. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.85 (s, 6H), 5.64 (s, 1H), 6.50 (m, 4H), 6.71 (m, 4H), 7.01 (d, *J* = 7.5 Hz, 2H), 7.17 (d, *J* = 7.5 Hz, 2H), 8.62 (s, H), 9.65 (s, 2H).

4-(Bis(2-methyl-1H-indol-3-yl)methyl)-N,N-dimethylaniline (3n)

FT-IR (KBr) (ν_{max}/ cm^{-1}): 3410, 3050, 1510, 1455, 1245, 1135, and 1020. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.08 (s, 6H), 3.71 (s, 3H), 3.85 (s, 3H), 5.96 (s, 1H), 6.75 (s, 2H), 6.85 (m, 3H), 7.03 (t, *J* = 6.4 Hz, 4H), 7.24 (t, *J* = 7.6 Hz, 2H), 7.77 (s, 2H).

Results and discussion

In order to optimize the reaction conditions, we have used of SPSA as a catalyst for the condensation of indole with 4-chlorobenzaldehede at various conditions such as different amounts

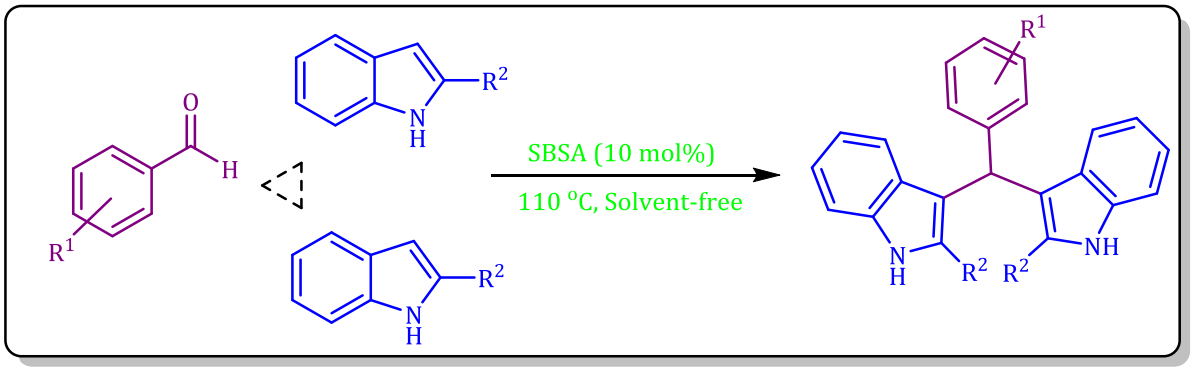
of catalyst, temperature, solvent and solvent-free conditions (Table 1). A highly dense orange mixture was prepared with down yield after a long time. Hence, we investigated the catalytic effect of SPSA for the same reactions. We noticed that when the reaction is carried out in the presence of SPSA catalyst, in addition to a significant reduction in reaction time, the product yield became more. These studies showed that the best result was obtained by carrying out the reaction of 4-chlorobenaldehyde (1 mmol) with indole (2 mmol) in the presence of 10 mol% of SBSA at 110 °C for 30 min under solvent-free conditions (Table 1, Entry 9).

After optimization of the reaction conditions (Table 1, Entry 9) and in order to show the extent of the application of the method, various types of aldehydes and indoles were subjected to the similar reaction under the determined conditions (Scheme 2). As shown in Table 2, the corresponding compounds were obtained during relatively short reaction times in high yields.

Table 1. Optimization of the amount of the catalyst, temperature and solvent in the synthesis of bis(indolyl) methane derivative of 4-chlorobenzaldehyde

Entry	Amount of catalyst (mol%)	Solvent	Temp. (°C)	Time (min)	Yield (%)[a]
1	-	Solvent-free	100	120	Trace
2	-	EtOH	Reflux	120	Trace
3	5	Solvent-free	100	60	72
4	5	EtOH	Reflux	100	65
5	5	H_2O	Reflux	100	40
6	5	CH_3CN	Reflux	100	Trace
7	10	Solvent-free	80	50	85
8	10	Solvent-free	100	45	93
9	10	Solvent-free	110	30	97
10	10	Solvent-free	120	30	95

[a] Isolated yield



Scheme 2. Synthesis of bis(indolyl)methane derivatives

Table 2. Synthesis of *bis*(indolyl)methanes in the absence of solvent [a]

Entry	Aldehyde	R^2	Product	Time (min)	Yield (%)[a] [ref.]
1	C_6H_4CHO	H	3a	40	92 [32]
2	4-ClC_6H_4CHO	H	3b	30	97 [33]
3	2-ClC_6H_4CHO	H	3c	35	95 [32]
4	2-OHC_6H_4CHO	H	3d	50	88 [34]
5	4-OHC_6H_4CHO	H	3e	50	87 [33]
6	3-$NO_2C_6H_4CHO$	H	3f	35	95 [33]
7	4-$NO_2C_6H_4CHO$	H	3g	40	93 [35]
8	4-BrC_6H_4CHO	H	3h	45	90 [32]
9	3-$OCH_3C_6H_4CHO$	H	3i	50	88 [36]
10	4-$OCH_3C_6H_4CHO$	H	3j	55	97 [32]
11	4-$CH_3C_6H_4CHO$	H	3k	50	90 [37]
12	4-$NO_2C_6H_4CHO$	Me	3l	45	91 [37]
13	4-HOC_6H_4CHO	Me	3m	60	88 [37]
14	3,4-$(MeO)_2C_6H_3CHO$	Me	3n	50	89 [37]

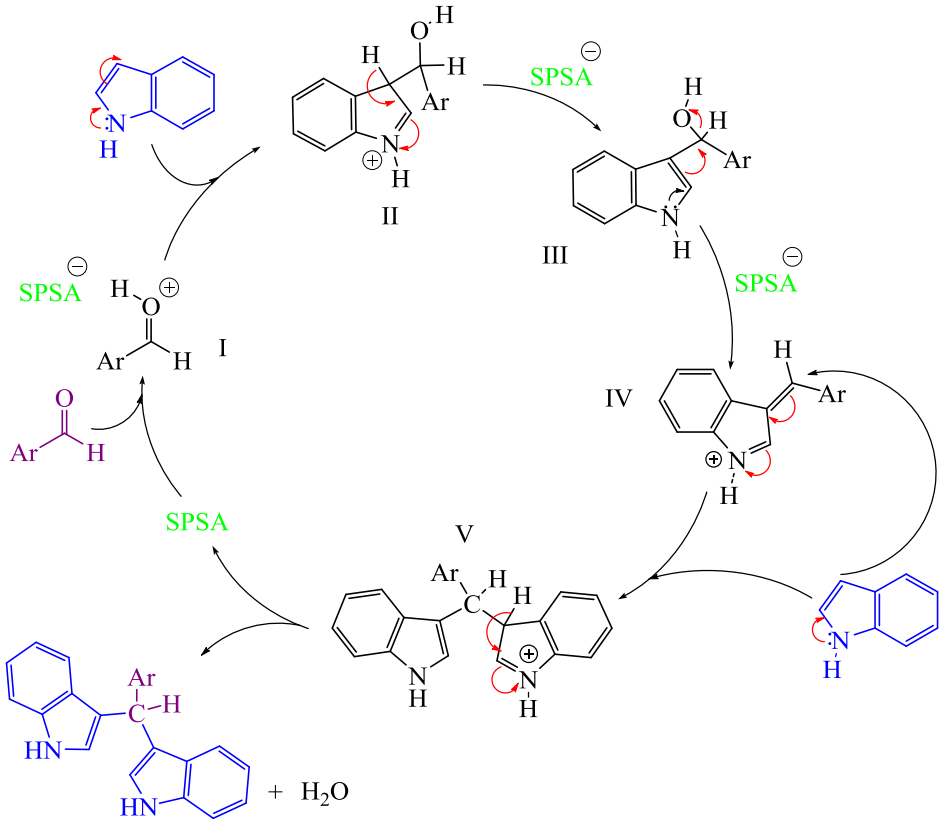
[a] Isolated yield

A reasonable mechanism for the preparation of *bis*(indole)methanes is shown in Scheme 3. in the first stage, the aldehyde is activated by using H^+ catalyst. Reaction of intermediate **I** with indole led to the formation of intermediate **II** and loss of H_2O from **II** to afford **IV**. In the following step, the desired *bis*-indole was obtained from the reaction of **IV** and other indole in the presence of catalyst.

The ability of the current method is shown through comparison with the results of other catalysts in the literature (Table 3). The reaction of the preparation of *bis*(indole)methane was accelerated in the presence of sulfonylbis(1,4-phenylene)bissulfamic acid (SPSA) and the reaction was completed in short time. Our discussed catalyst (SPSA) can with of the release two acidic hydrogen from both of the active positions, causes the more increase in yield and reduce the reaction times.

Table 3. Compared efficiency of various catalysts in preparation of *bis*(indolyl) methane of 4-ClC_6H_4CHO

Entry	Catalyst	Conditions	Time (h)	Yield (%)[Ref.]
1	TBATB	MeOH, r.t.	1.5	85 [15]
2	$M(HSO_4)x$	EtOH, r.t.	2.5-7.5	91 [16]
3	$V(HSO_4)_3$	Solvent-free, 80 °C	0.66	85 [33]
4	BTPTB	Solvent-free, 90 °C	0.13	80 [37]
5	P_2O_5/SiO_2	Solvent-free, r.t.	0.5	92 [38]
6	[hmim][HSO4]	EtOH, r.t.	1	93 [39]
7	ILIS-SO_2Cl	MeCN, r.t.	5.5	93 [40]
8	Zeokarb-225	CH_3CN, r.t.	8.5	70 [41]
9	SQ	H_2O/r.t.	2-4	82 [35]
10	SPSA	Solvent-free, 110 °C	0.5	97 [this work]



Scheme 3. The reasonable mechanism in preparation of *bis*(indolyl)methane

Conclusion

In conclusion, we have described a simple and efficient method for the preparation of *bis*(indole)methane derivatives catalyzed using SPSA under solvent-free conditions. The procedure offers several advantages such as relatively short reaction times, high yields of the products, simple experimental procedure, easy and clean work-up methode, solvent-free conditions and as ease of the preparation and simple recyclability of the SPSA, Which makes this method as a suitable route compared with available methods for the synthesis of *bis*(indole)methanes.

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