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Efficient synthesis of bis(indolyl)methanes, bispyrazoles and biscoumarins using 4-sulfophthalic acid

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Abstract 4-Sulfophthalic acid (4-H_3SPA) solution 50 wt% in H_2O has been effectively catalyzed the synthesis of a series of biologically relevant bis(indolyl)methanes by the electrophilic substitution of indole derivatives on aldehyde compounds and 4,4′-(arylmethylene)-bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol)s by condensing 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one with various aldehydes under aqua conditions at room temperature. 3,3′-(Arylmethylene)-bis-4-hydroxycoumarins have also been synthesized in the presence of 0.1 mL (0.262 mmol) of 4-H_3SPA solution 50 wt% in H_2O at 80 °C. The procedure is simple and the expected bis-heterocyclic compounds were isolated in good to excellent yields. The present protocol provides the benefits of convenience, mild reaction conditions, eco-friendliness, and no use of hazardous organic solvents.

Keywords Bis(indolyl)methanes · Bispyrazoles · Biscoumarins · 4-Hydroxycoumarin · Indole derivatives · 5-Methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one · 4-Sulfophthalic acid

Introduction

Bis(indolyl)methanes (BIMs) are an important class of bis-heterocyclic compounds which have been studied owing to their applications in industry and pharmaceutics. They are present in numerous biologically important natural products and synthetic compounds [1, 2]. As previously reported, some of BIMs exhibited biological activities, including antibacterial [3], antifungal [4], anti-inflammatory [5], DNA damaging [6], antihyperlipidemic [7], anticancer [8], topoisomerase IIa inhibitory [9], tranquilizing [10], antileishmanial [11], and antibiotics [12]. Moreover,

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heterocycles having bis(indolyl)methane units act as dietary supplements [13], colorimetric chemosensors [14–17] and pH indicators [18].

Generally, BIMs were prepared using the three-component reaction (3CR) of indole derivatives and numerous aldehydes or ketones. So far, due to a variety of applications of BIMs, several synthetic methods have been developed for their construction. Resins [19], acidic organocatalysts [20–24], biocatalysts [25, 26], solid acid catalysts [27–34], Lewis acids [35–40], protic acids [41], ionic liquids [42, 43], supported Bronsted acids [8, 44], deep eutectic solvents [45], fruit juice natural catalysts [46, 47], and nanomaterials [48–56] have been utilized for the synthesis of these nitrogen-containing heterocyclic compounds. Furthermore, microwave heating [57–60] and ultrasonic waves [61, 62] are valuable tools to the synthesis of these bisheterocycles. BIMs have also been prepared in the presence of sulfonic acid-containing compounds [63–76], catalyst- and/or solvent-free [77–81] and aqua-mediated conditions [82–84]. Therefore, the synthesis of BIMs in an environmentally benign solvent is always attractive.

Besides, 4,4′-(arylmethylene)-bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol)s as an important class of pyrazolones, have been used as anti-inflammatory [85], antipyretic [86], gastric secretion stimulatory [87], antidepressant [88], antibacterial [89], antifilarial [90], antiviral [91], antioxidant [92], and hypoglycemic [93] agents. These molecules have also been investigated as fungicides [94], pesticides [95], insecticides [96], dyestuffs [97], chelating, as well as extracting reagents for different metal ions [98]. The synthesis of 4,4′-(Arylmethylene)-bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol)s have been carried out using several catalysts, including sulfuric acid ([3-(3-silicapropyl)sulfanyl]propyl)ester [99], 1,3,5-tris(hydrogen-sulfato) benzene (THSB) [100], $Ce(SO_4)_2.4H_2O$ [101], 2-hydroxy ethylammonium propionate (2-HEAP) [102], $CuCr_2O_4$ nanoparticles [103], $Fe(SO_4)_2.(NH_4)_2.6(H_2O)$ [104], CsF [105], $[HMIM]HSO_4$ under ultrasound irradiation [106], silica sulfuric acid (SSA) [107], $ZnAl_2O_4$ nanoparticles [108], diammonium hydrogen phosphate [109], 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$) [110], phosphomolybdic acid [111], nano *n*-propylsulphonated γ-Fe_2O_3 [112], and *N*-methylimidazolium perchlorate ($[MIm]ClO_4$) [113]. Catalyst-free in refluxing EtOH [114], catalyst- and solvent-free under heating [115] are the other methods for the preparation of 4,4′-(arylmethylene)-bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol) derivatives. More recently, a comprehensive survey of the various catalysts, reagents, and conditions/techniques for the synthesis of 4,4′-(arylmethylene)-bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol)s has been reported by Gouda [116].

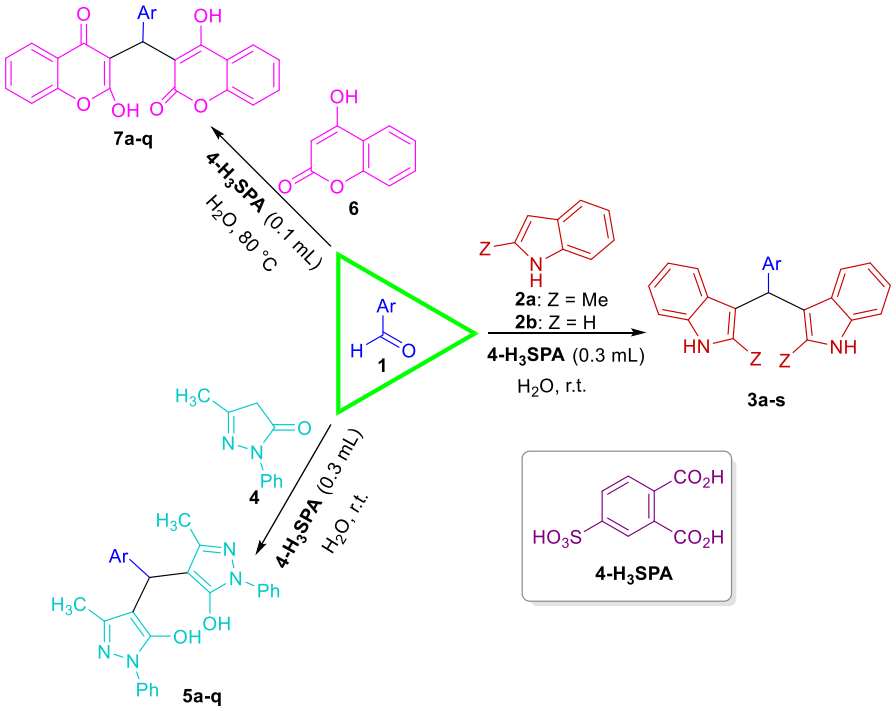
The 3,3′-(arylmethylene)-bis-(4-hydroxycoumarins), on the other hand, play a prominent role in organic chemistry due to a myriad of biological activities of their derivatives, including antibacterial [117], HIV-1 integrase inhibitory [118], anticoagulant [119], urease inhibitory [120], proliferation inhibition of K-562 [121] and α-glucosidase inhibitory [122]. They are also attractive heterocyclic molecules, which have been used for the development of fluorescent and colorimetric sensors [123], as well as photoluminescence probes [124] in recent years. Moreover, 3,3′-methylenebis-4-hydroxycoumarin (often known as dicoumarol), is a type of biscoumarins occurring naturally in moldy clover [125]. Biscoumarins also show optical properties since they are highly efficient laser dyes [126].

The synthesis of biscoumarins is based on the condensation two equivalents of 4-hydroxycoumarin with various (het)aryl and α,β-unsaturated aldehydes in the presence of a catalyst. So far, many catalysts have been used for the preparation of these compounds, for example triethylammonium bromide (TEAB) [117], sodium dodecyl sulfate (SDS) [127], poly(4-vinylpyridinium) perchlorate [128], $Bi(NO_3)_3$-$5H_2O$ [129], propane-1,2,3-triyltris(hydrogen sulfate) [130], tris(hydrogensulfato) boron $[B(HSO_4)_3]$ [131], sulfated titania $\left(TiO_2/SO_4^{2-}\right)$ [132], $NaHSO_4/SiO_2$/indion 190 resin [133], ionic liquids [134–136], silica sulforic acid nanoparticles [137], choline hydroxide [138], $Zn(Proline)_2$ [139], CuO–CeO_2 nanocomposite [140], nano-silica chloride [141], nano-MgO [142], trichloroacetic acid [143], tetrabutylammonium hexatungstate [144], titania sulfonic acid (TiO_2–SO_3H) [145], as well as $LiClO_4$ [146] have been reported to catalyze the aforementioned condensation reaction. Furthermore, microwave heating [147, 148], sonochemically mediated catalyst-free condensation [149, 150] and organic solid state reactions [151] were also reported for the preparation of biscoumarins.

Because of the role of biological and pharmacological related to the above mentioned bis-heterocyclic compounds, the development of convenient, efficient, inexpensive and eco-friendly new methodologies using readily available reagents to the synthesis of these types of heterocyclic dimers is of interest. Water is common solvent, which have the advantages of being green, clean and readily biodegradable. This solvent has been utilized as an environmentally attractive medium for some chemical transformations [152]. Because of the importance the potential of these drug-like heterocyclic compounds, we report a successful one-vessel reaction for synthesis of bis(indolyl)methanes, bispyrazoles and biscoumarins under eco-friendly reaction conditions (Scheme 1).

Experimental

All chemicals were purchased from Alfa Aesar and Aldrich as well as were used without further purification, with the exception of liquid aldehydes which were distilled before using. All solvents were distilled before using. The products were characterized by comparison of their physical data with those of known samples or by their spectral data. Melting points were measured on a Büchi 510 melting point apparatus and are uncorrected. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded at ambient temperature on a Bruker AVANCE DRX-400 MHz using deuterated chloroform ($CDCl_3$) or dimethyl sulfoxide (DMSO)-d_6 as solvent. Fourier-transform infrared (FT-IR) spectra were recorded on a PerkinElmer RXI spectrometer. Progress of reactions was monitored by thin layer chromatography (TLC) analysis on Merck pre-coated silica gel 60 F_{254} aluminum sheets, visualized by ultraviolet (UV) light.



Scheme 1 Synthesis of bis-heterocycles **3**, **5** and **7** catalyzed by 4-H_3SPA

General procedure for the synthesis of bis(indolyl)methanes (4a–r)

Aldehyde **1** (1 mmol), indole derivative **2** (2 mmol), and 4-H_3SPA solution 50 wt% in H_2O (0.3 mL, 0.787 mmol) and water (5 mL) was stirred at room temperature. After completion of the reaction, as confirmed by TLC analysis, the resulting precipitated product was filtered off, washed with distilled water (2 × 5 mL), and dried to afford the corresponding products in high purity. The filtrate containing the catalyst was used as such for exploring the reusability of the catalyst. The catalyst is soluble in water while the products are insoluble in water. Spectral data for **3a** and **3k** were as follows:

*3,3′-Benzylidenebis(2-methyl-1H-indole) (**3a**)* IR (KBr, cm^{-1}): 3398, 3051, 2921, 2860, 1615, 1461, 1305, 1218, 1016, 746, 594; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68 (s, 2H), 7.22-7.11 (m, 7H), 6.94 (t, *J* = 6.8 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.75 (t, *J* = 7.6 Hz, 2H), 5.91 (s, 1H), 1.98 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.5, 134.9, 131.6, 128.9, 128.7, 128.1, 126.0, 120.4, 119.2, 119.1, 113.2, 110.0, 39.6, 12.5.

*3,3′-(Phenylmethylene)bis(1H-indole) (**3 k**)* IR (KBr, cm^{-1}): 3392, 3056, 2922, 2347, 1603, 1454, 1328, 1218, 1093, 1014, 748, 702, 595; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (s, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.34-7.13 (m, 9H), 6.99 (t, *J* = 7.6 Hz, 2H), 6.63 (d, *J* = 1.6 Hz, 2H), 5.86 (s, 1H); ^{13}C NMR (100 MHz,

$CDCl_3$): δ = 144.1, 136.1, 128.7, 128.5, 127.2, 126.2, 124.1, 121.9, 119.8, 119.2, 118.9, 111.1, 40.2.

General procedure for the synthesis of 4,4′-(arylmethylene)-bis-(3-methyl-1-phenyl-1*H*-pyrazol-5-ol) derivatives (5a–q)

Aldehyde **1** (1 mmol), 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **4** (2 mmol), 4-H_3SPA solution 50 wt% in H_2O (0.3 mL, 0.787 mmol) and water (5 mL) was stirred at room temperature. After completion of the reaction, the resulting precipitated product was filtered off, washed with distilled water (2 × 5 mL), and dried to afford the corresponding products in high purity. The filtrate containing catalyst was used as such for exploring the reusability of the catalyst. Spectral data for **5e** and **5 h** were as follows:

*4,4′-[(4-Methylphenyl)methylene]bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (**5e**)* IR (KBr, cm^{-1}): 3432, 2921, 1600, 1501, 1408, 1294, 1026; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.38 (br, 2H), 7.69 (d, *J* = 7.7 Hz, 4H), 7.42 (t, *J* = 7.7 Hz, 4H), 7.20 (t, *J* = 7.7 Hz, 2H), 7.12 (d, *J* = 7.6 Hz, 2H), 7.07 (d, *J* = 8.3 Hz, 2H), 4.88 (s, 1H), 2.30 (s, 6H), 2.23 (s, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 154.5, 146.8, 139.7, 135.5, 129.5, 129.2, 128.0, 125.4, 124.7, 122.8, 120.5, 33.3, 21.1, 13.2.

*4,4′-[(4-Nitrophenyl)methylene]bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (**5 h**)* IR (KBr, cm^{-1}): 3422, 3056, 2972, 2920, 1604, 1580, 1504, 1348, 1108; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 13.52 (br, 2H), 8.28 (d, J = 8.5 Hz, 2H), 7.72 (d, *J* = 7.8, 4H), 7.65 (d, *J* = 8.3, 2H), 7.38 (d, *J* = 7.3, 4H), 7.20 (t, *J* = 7.1 Hz, 2H), 5.46 (s, 1H), 2.29 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 151.5, 148.6, 145.4, 145.1, 139.3, 131.1, 129.6, 128.1, 121.9, 121.6, 119.5, 31.9, 14.2.

General procedure for the synthesis of 3,3′-(arylmethylene)-bis-(4-hydroxycoumarins) (7a–q)

A mixture of aldehyde **1** (1 mmol), 4-hydroxycoumarin **6** (2 mmol), 4-H_3SPA solution 50 wt% in H_2O (0.1 mL, 0.262 mmol) and water (5 mL) in a round-bottomed flask was heated at 80 °C. Upon completion of the reaction, as confirmed by TLC analysis, the mixture was cooled to room temperature. After completion of the reaction, the mixture was cooled to room temperature and water was added. Then, the resulting precipitated product was filtered, washed with water (2 × 5 mL), and dried. The pure products were obtained by recrystallization from aqueous ethanol. The filtrate containing catalyst was used as such for exploring the reusability of the catalyst. Spectral data for **7c** and **7f** were as follows:

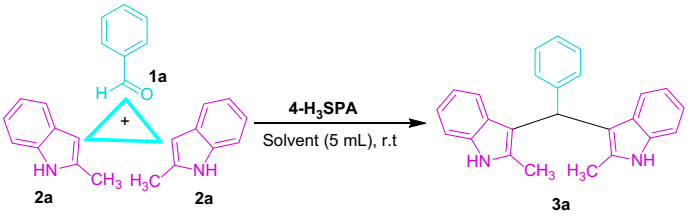
*3,3′-((4-Methoxyphenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (**7c**)* IR (KBr, cm^{-1}): 3440, 3072, 3002, 1668, 1604, 1565, 1510,1454, 1353, 1258, 1180, 1094, 907, 828, 768; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.53 (s, 1H), 11.31 (s, 1H), 8.02 (dd, 2H, *J* = 8.4 Hz), 7.65 (t, 2H, *J* = 8.2 Hz), 7.31-7.42 (m, 4H), 7.14 (d, 2H, *J* = 8.7 Hz), 6.89 (d, *J* = 8.7 Hz, 2H), 6.05 (s, 1H), 3.81 (s, 3H).

3,3′-((4-Chlorophenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) ***(7f)*** IR (KBr, cm^{-1}): 3069, 2680, 2610, 1669, 1619, 1600, 1491, 1455, 1353, 1310, 1267, 1185, 1096, 922, 910, 822, 790; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.59 (s, 1H), 11.37 (s, 1H), 8.11 (d, 1H, *J* = 7.74 Hz), 8.03 (d, 1H, *J* = 7.8 Hz), 7.66-7.69 (m, 2H), 7.41-7.46 (m, 4H), 7.32 (d, 2H, *J* = 1.9, 8.6 Hz), 7.19 (dd, 2H, *J* = 0.9, 8.5 Hz), 6.08 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.6, 167.3, 166.4, 165.1, 152.9, 152.7, 134.3, 133.5, 133.1, 129.2, 128.4, 125.4, 124.8, 117.2, 117.1, 117.0, 116.8, 105.7, 104.1, 36.2.

Results and discussion

In order to evaluate the optimization of the reaction conditions, a model reaction was performed using benzaldehyde (**1a**) and 2-methylindole (**2a**) at room temperature (r.t.) and the progress of the reaction was monitored by TLC analysis. The results are summarized in Table 1. It was found that when the reaction conducted in water without any catalyst the reaction did not proceed even until 24 h (Table 1, entry 1). Performing the same reaction in the presence of catalytic amounts of 4-sulfophthalic acid (4-H_3SPA, 50 wt% in H_2O) in water led to a 76 % yield of **3a** after 15 min (Table 1, entry 2). After obtaining the corresponding

Table 1 Optimization of reaction conditions for **3a** synthesis



Entry	Catalyst (mL)	Solvent	Time (min)[a]	Isolated yields (%)
1	–	H_2O	24 h	–
2	0.1	H_2O	15	76
3	0.2	H_2O	15	80
4[b]	**0.3**	**H_2O**	**15**	**89**
5	0.4	H_2O	15	70
6	0.3	EtOH	15	70
7	0.3	*n*-Hexane	15	50
8	0.3	EtOAc	15	30
9	0.3	CH_2Cl_2	15	30
10	0.3	None	15	60

Reaction were carried out with benzaldehyde **1a** (1 mmol), 2-methylindole **2a** (2 mmol), and catalyst at r.t.

[a] Reaction progress was monitored with TLC analysis

[b] Optimized reaction conditions shown in bold

product, the various volumes of 4-H_3SPA aimed at the completion of reaction was evaluated. The reaction was performed using 0.2 mL and 0.3 mL of the catalyst (Table 1, entries 3–4). It was observed that 0.3 mL of the 4-H_3SPA loading provided maximum yield (89 %) in 15 min. An additional increase of the volume catalyst loading to 0.4 mL did not improve the yield (Table 1, entry 5). A number of other common solvents, viz. ethanol, *n*-hexane, EtOAc and CH_2Cl_2 were tested (Table 1, entries 6–9). Solvent optimization studies indicated that water was the best solvent. It was observed that the product **3a** was formed in 60 % yield in the solvent-free conditions (Table 1, entry 10). Satisfactory results were not achieved from the reactions at other temperatures. For this reason we have not mentioned in Table 1.

The scope of the reaction was studied for indoles (**2a–b**) and various aldehydes under the optimal reaction conditions. Representative results are listed in Table 2. Substituted benzaldehydes with both electron-donating substituents (Table 2, entries 2–5 and 11–14) and electron-withdrawing groups (Table 2, entries 6–9, 16, 17 and 19) at the *ortho*, *meta*, and *para* positions on the phenyl ring contributed well in this 3CR toward the synthesis of BIMs. The aryl aldehydes containing electron-withdrawing substituents required longer reaction times compared its electron-donating counterparts. Furan-2-carbaldehyde (**1j**), as a heterocyclic

Table 2 Synthesis of BIMs (**3a–s**) by condensation of indoles (**2a–b**) and various aldehydes catalyzed by 4-H_3SPA at room temperature

Entry	Aldehyde	Indole	Product	Time (min)	Isolated yields (%)	Melting point (°C)	
						Observed	Reported [ref.]
1	C_6H_5CHO (**1a**)	**2a**	**3a**	15	89	241–244	246–248 [21]
2	4-HO-C_6H_4CHO (**1b**)	**2a**	**3b**	15	92	238–240	239–241 [46]
3	4-MeO-C_6H_4CHO (**1c**)	**2a**	**3c**	20	92	194–195	195–196 [77]
4	3-MeO-C_6H_4CHO (**1d**)	**2a**	**3d**	25	98	237–239	235–236 [77]
5	4-Me-C_6H_4CHO (**1e**)	**2a**	**3e**	30	92	176–177	173 [21]
6	4-Cl-C_6H_4CHO (**1f**)	**2a**	**3f**	50	90	235–237	238–239 [21]
7	2-Cl-C_6H_4CHO (**1 g**)	**2a**	**3g**	60	87	223–225	218–222 [77]
8	4-NO_2-C_6H_4CHO (**1 h**)	**2a**	**3h**	55	90	238–240	239–240 [77]
9	3-NO_2-C_6H_4CHO (**1i**)	**2a**	**3i**	60	98	262–264	262–266 [74]
10	Furan-2-carbaldehyde (**1j**)	**2a**	**3j**	70	89	207–209	208–212 [77]
11	C_6H_5CHO (**1a**)	**2b**	**3k**	15	88	146–147	89–91 [21]
12	4-HO-C_6H_4CHO (**1b**)	**2b**	**3l**	20	90	214–216	114–116 [57]
13	4-MeO-C_6H_4CHO (**1c**)	**2b**	**3m**	25	90	194–196	188 [21]
14	3-MeO-C_6H_4CHO (**1d**)	**2b**	**3n**	30	92	176–179	180 [77]
15	4-Me-C_6H_4CHO (**1e**)	**2b**	**3o**	30	88	94–96	93–95 [21]
16	4-NO_2-C_6H_4CHO (**1 h**)	**2b**	**3p**	30	94	241–243	215–217 [21]
17	3-NO_2-C_6H_4CHO (**1i**)	**2b**	**3q**	35	90	260–262	220 [21]
18	Furan-2-carbaldehyde (**1j**)	**2b**	**3r**	50	88	319–321	112–118 [21]
19	2-NO_2-C_6H_4CHO (**1 k**)	**2b**	**3s**	35	85	187–189	188–190 [77]

aldehyde, was also reacted with indoles (**2a**–**b**) and the desired product was isolated in good yields (Table 2, entries 10 and 18).

After the successful application of 4-H_3SPA catalyst in the synthesis of BIMs, we decided to use it in the condensation of 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (**4**) with a wide variety of aldehydes (**1a**–**q**) leading to 4,4′-(aryl-methylene)bis(1*H*-pyrazol-5-ol)s (**5a**–**q**). To obtain the best reaction conditions, the condensation of benzaldehyde (**1a**) with 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (**4**) as the model reaction, was explored using different amounts of 4-H_3SPA and various solvents such as water, ethanol, *n*-hexane, EtOAc and CH_2Cl_2 as well as solvent-free conditions. The best results were obtained in water using 0.3 mL of 4-H_3SPA at r.t. The scope of the catalyst was extended using catalyst with different aromatic aldehydes to prepare a series of 4,4′-(arylmethylene)bis(1*H*-pyrazol-5-ol) derivatives (Table 3). Various aromatic aldehydes containing electron-withdrawing substituents, electron-releasing substituents and halogens on their aromatic rings as well as heteroaromatic aldehydes were utilized successfully in this condensation reaction, and gave the corresponding products (**5a**–**q**) in good to high yields and relatively shorter reaction times.

In the next part of this contribution on the application of catalytic activity 4-H_3SPA in the synthesis of other bis-heterocyclic compounds, 4-hydroxycoumarin (**6**) as a suitable precursor was used in the condensation with aldehydes (**1a**-**q**). This reaction leads to the synthesis of 3,3′-(arylmethylene)-bis-(4-hydroxycoumarins).

Table 3 Synthesis of 4,4′-(arylmethylene)bis(1*H*-pyrazol-5-ols) (**5a**–**q**) by condensation of 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (**4**) and various aldehydes catalyzed by 4-H_3SPA at room temperature

Entry	Aldehyde	Product	Time (min)	Isolated yields (%)	Melting point (°C)	
					Observed	Reported [ref.]
1	C_6H_5CHO (**1a**)	**5a**	10	90	170–172	169–171 [100]
2	4-HO-C_6H_4CHO (**1b**)	**5b**	15	94	156–157	154–157 [100]
3	4-MeO-C_6H_4CHO (**1c**)	**5c**	15	94	179–181	176–179 [100]
4	3-MeO-C_6H_4CHO (**1d**)	**5d**	15	96	188–190	189–191 [110]
5	4-Me-C_6H_4CHO (**1e**)	**5e**	20	92	200–202	201–203 [100]
6	4-Cl-C_6H_4CHO (**1f**)	**5f**	15	95	216–217	215–216 [100]
7	2-Cl-C_6H_4CHO (**1g**)	**5g**	20	94	234–236	235–237 [100]
8	4-NO_2-C_6H_4CHO (**1h**)	**5h**	10	97	224–226	225 [100]
9	3-NO_2-C_6H_4CHO (**1i**)	**5i**	12	94	152–154	151–154 [100]
10	2-NO_2-C_6H_4CHO (**1k**)	**5j**	20	90	222–224	224–226 [111]
11	Furan-2-carbaldehyde (**1j**)	**5k**	15	91	189–191	188–191 [100]
12	2-HO-C_6H_4CHO (**1l**)	**5l**	15	93	225–226	227–229 [99]
13	Thiophen-2-carbaldehyde (**1m**)	**5m**	15	92	204–206	203–205 [110]
14	3-HO-C_6H_4CHO (**1n**)	**5n**	15	88	165–167	165–168 [107]
15	4-Br-C_6H_4CHO (**1o**)	**5o**	15	90	184–186	183–185 [100]
16	4-F-C_6H_4CHO (**1p**)	**5p**	15	92	182–183	181–182 [113]
17	Pyridine-2-carbaldehyde (**1q**)	**5q**	15	92	210–212	211–212 [110]

To accomplish this goal and to achieve the best reaction conditions, benzaldehyde (**1a**) was treated with 4-hydroxycoumarin (**6**), and various conditions including the amounts of catalyst, solvents, and reaction temperatures were investigated. The optimum conditions were obtained using a 0.1 mL catalyst loading, benzaldehyde (**1a**, 1 mmol), 4-hydroxycoumarin (**6**, 2 mmol) and at 80 °C under aqueous conditions. After the optimization of the reaction conditions, a variety of substituted benzaldehydes (Table 4, entries 2–10, 12 and 14–16) containing several functional groups and heterocyclic aldehydes (11, 13 and 17) have been successfully utilized and the corresponding 3,3′-(arylmethylene)-bis-(4-hydroxycoumarins) were obtained in good to excellent isolated yields.

The comparison of the catalytic performance of 4-H_3SPA with some of the reported catalysts is shown in Table 5. According to the data presented in Table 5, the synthesis of these bis-heterocycles using 4-H_3SPA catalyst is comparable in terms of yields and reaction times. It does not require the use of some hazardous organic solvents such as toluene, acetonitrile, and dichloromethane, and also avoids the preparation of the catalyst.

Reusability of the reaction media was conducted using the model reaction under the optimal conditions. After completion of the reaction, the resulting solid product was separated out by simple filtration. To the filtrate that contains the catalyst, benzaldehyde (**1a**) and 2-methylindole (**2a**) were added without additional catalyst

Table 4 Synthesis of 3,3′-(arylmethylene)-bis-(4-hydroxycoumarins) (**7a–q**) by condensation of 4-hydroxycoumarin (**6**) and various aldehydes (**1a–q**) catalyzed by 4-H_3SPA at 80 °C

Entry	Aldehyde	Product	Time (min)	Isolated yields (%)	Melting point (°C)	
					Observed	Reported [ref.]
1	C_6H_5CHO (**1a**)	**7a**	30	99	231–232	230–231 [140]
2	4-HO-C_6H_4CHO (**1b**)	**7b**	40	90	228–230	229–231 [140]
3	4-MeO-C_6H_4CHO (**1c**)	**7c**	25	100	252–254	251–253 [140]
4	3-MeO-C_6H_4CHO (**1d**)	**7d**	20	100	256–257	256–258 [126]
5	4-Me-C_6H_4CHO (**1e**)	**7e**	35	92	266–268	267–269 [140]
6	4-Cl-C_6H_4CHO (**1f**)	**7f**	20	93	261–263	259–261 [140]
7	2-Cl-C_6H_4CHO (**1g**)	**7g**	40	88	199–201	198–200 [139]
8	4-NO_2-C_6H_4CHO (**1h**)	**7h**	15	95	230–232	231–232 [140]
9	3-NO_2-C_6H_4CHO (**1i**)	**7i**	25	92	215–216	214–216 [140]
10	2-NO_2-C_6H_4CHO (**1k**)	**7j**	30	93	199–201	201–202 [140]
11	Furan-2-carbaldehyde (**1j**)	**7k**	30	88	204–205	203–205 [133]
12	2-HO-C_6H_4CHO (**1l**)	**7l**	30	95	254–256	254–257 [140]
13	Thiophen-2-carbaldehyde (**1m**)	**7m**	30	90	210–212	210–213 [139]
14	3-HO-C_6H_4CHO (**1n**)	**7n**	40	93	267–269	268–270 [140]
15	4-Br-C_6H_4CHO (**1o**)	**7o**	20	92	264–267	264–266 [131]
16	4-F-C_6H_4CHO (**1p**)	**7p**	18	92	215–216	214–216 [140]
17	Pyridine-2-carbaldehyde (**1q**)	**7q**	30	85	212–214	211–213 [119]

Table 5 Comparison of the catalytic performance of 4-H_3SPA with some of the literature results

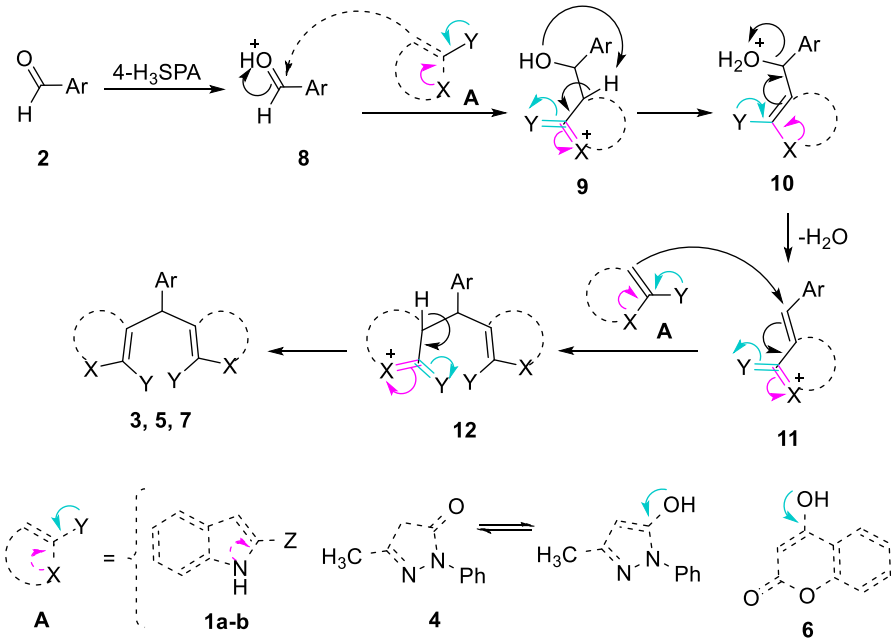
Compound	Catalyst (mol %)/conditions	Time (min)	Yield (%) [refence]
3p	Nafion-H (30 mg)/PEG-400: H_2O, 80 °C	40	92 [74]
	Indion Ina 225H resin (100 mg)/acetonitrile, 50 °C	126	95 [19]
	Catalyst-free, solvent-free, r.t.	6 day	58 [77]
	Oleic acid (12.5)/H_2O, 100 °C	120	99 [20]
	Tamarind fruit juice/H_2O, 80 °C	120	93 [46]
	4-H_3SPA (0.3 mL)/H_2O, r.t.	30	94 [current work]
5h	Sulfuric acid ([3-(3-silicapropyl)sulfanyl]propyl)ester (0.1 g)/EtOH, reflux	120	88 [99]
	Phosphomolybdic acid (10), EtOH, reflux/r.t.	210	96 [111]
	Silica sulfuric acid (0.08 g)/H_2O-EtOH, 70 °C	20	90 [107]
	N-Methylimidazolium perchlorate (5.4)/solvent-free, 50 °C	25	94 [113]
	4-H_3SPA (0.3 mL)/H_2O, r.t.	10	97 [current work]
7i	[P_4VPy-BuSO_3H]HSO_4 (10)/toluene, 90 °C	42	95 [134]
	Sodium dodecyl sulfate (20)/H_2O, 60 °C	147	95 [127]
	Poly(4-vinylpyridinium)perchlorate (30)/H_2O, 80 °C	15	87 [128]
	SiO_2Cl (75 mg)/CH_2Cl_2, 40 °C	210	90 [141]
	Nano-MgO (3)/solvent-free, 100 °C	21	88 [142]
	4-H_3SPA (0.1 mL)/H_2O, 80 °C	25	92 [current work]

Table 6 The recycling of 4-H_3SPA in the synthesis of **3a**

Run	Fresh	1	2	3	4
Time (min)	15	15	20	25	30
Isolated yields (%)	89	87	85	82	77

loading. The reaction mixture was stirred at r.t. for the required times (Table 6). The reaction media was reused as such for the subsequent reactions up to four runs.

Based on the proposed mechanisms in the literature, a plausible reaction mechanism for these reactions is shown in Scheme 2. It can be assumed that the reaction starts with the activation of an oxygen atom of the carbonyl group of the aldehydes, followed by the nucleophilic attack of heterocyclic compounds (**A**) on activated aldehydes (**8**) and departure of water which led to the formation of alkene intermediates **11**. The condensation of the second molecule of **A** with the alkene intermediates **11** and then elimination of proton from bis-heterocyclic intermediates **12** leads to the formation of the desired bis-heterocycles (**3**, **5** and **7**).



Scheme 2 Proposed mechanism for the formation of **3**, **5** and **7**

Conclusions

A series of bis-heterocycles such as bis(indolyl)methanes, 4,4′-(arylmethylene)-bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol)s, and 3,3′-(arylmethylene)-bis-4-hydroxy-coumarins were synthesized using 4-H_3SPA as an efficient catalyst. The experimental procedure is simple, convenient, and has the ability to a wide range of substrates, which affords a series of diversity bis-heterocycles. The use of 4-H_3SPA in these reactions is included notable features such as clean reaction profiles, minimization of waste, operational simplicity, non-toxicity, shorter reaction times, easy experimental work-up procedure, high yields of the products, and avoids usage of organic solvents. These advantages make the present protocol an interesting alternative to the previously reported methods for the synthesis of BIMs, 3,3′-(arylmethylene)-bis-(4-hydroxycoumarins), as well as 4,4′-(arylmethylene)-bispyrazoles.

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