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$ZrCl_4$@Arabic Gum: An effective and environmentally friendly catalyst for the preparation of 14-aryl-14H-dibenzo[a,j]xanthene derivatives at ambient temperature without solvent

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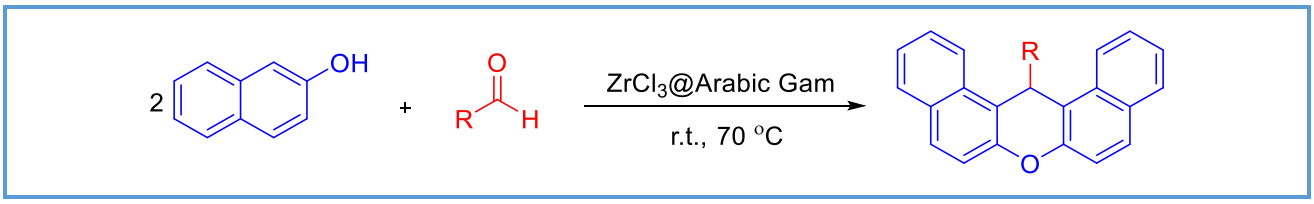
Heterogeneous catalyst
Green chemistry

ABSTRACT

In this research, zirconium fixed on the Arabic Gum ($ZrCl_4$@Arabi Gum) was used as a heterogeneous and recyclable Lewis acid catalyst for the one-pot synthesis of 14-aryl-14H-dibenzo[a,j]xanthene derivatives from the reaction of 2-naphthol, and various aldehydes under solvent-free conditions and at 70 °C. The present method has many advantages such as catalyst reusability, high yields, non-toxic, easy of operation, short reaction time, environmentally friendly and high efficiency.

Graphical Abstract



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Introduction

Xanthenes and benzoxanthene are heterocyclics and are used as important biological intermediates. These compounds have important applications in the dye industry [1], fluorescent materials for the visualization of biomolecules [2] and laser technologies [3]. Recently, due to the numerous biological and therapeutic properties of these compounds such as antibacterial [4], anti-inflammatory [5], antiviral activities [6], to eliminate the activity of zoxozolamine [7] and deft dynamic therapy [8], much attention has been paid to the synthesis of these compounds. Therefore, the wide range of applications of xanthenes has only introduced them as the main synthetic candidates, thus emphasizing the need to develop newer artificial paths for manipulating xanthan derivatives scaffolding. Protocols for the synthesis of xanthene from the mixing of 2-naphthol with aldehydes in the presence of catalysts previously.

It has been reported, such as the preparation of this compound with dowex-50PW [9], silica sulfuric acid [10, 11], γ-Fe_2O_3–HAp-Fe^{2+} NPs [12], I_2 [13, 14], sulfamic acid [15], $HClO_4$–SiO_2 [16], PW acid [17] cyanuric chloride [18], $Yb(OTf)_3$ [19], alum [20], $Sb(OAc)_3$ [21], AgNPs [22].

Many homogeneous and heterogeneous acid catalysts are used for the synthesis of xanthenes. However, the above catalysts such as H_2SO_4, HCl, and BF_3 have many disadvantages because they are corrosive, toxic or volatile and produce a lot of waste. Following our research on the applications of heterogeneous acid catalysts in organic synthesis, we report a new method for synthesis xanthenes derivatives in the presence of $ZrCl_4$@Arabic Gum under solvent-free conditions at 70 °C.

Multicomponent reactions (MCRs) are convergent reactions, in which three or more starting materials react to form a product, where basically all or most of the atoms contribute to the newly formed product. In MCR, the product is assembled according to the cascade of primary chemical reactions and is widely utilized in the synthesis of organic compounds [24-26].

Experimental

Matrials and methods

All chemicals were purchased from commercial suppliers and were used as received. All products were identified by their spectra and physical data. Melting points were measured by using the capillary tube method with an electrothermal 9100 apparatus. The IR spectra were recorded on a Shimadzu spectrometer 883 (KBr pellets, Nujol mulls, 4000–400 cm^{-1}). ^1H NMR spectra were recorded on a Bruker-Avance DRX 400 spectrometer using TMS as an external standard. The morphologies of the samples were investigated by scanning electron microscopy (SEM) and the elemental analysis was performed by Energy-dispersive X-ray spectroscopy (EDAX) using FESEM model MIRA II (TESCAN, Check republic), The Thermal behavior was observed by thermogravimetry (TG) and differential scanning calorimetry (DSC) on a TA Instruments, model SDT Q600 V20.9 Build 20 (USA), at a heating rate of 10 °C/min in air atmosphere, from 25 to 400 °C.

Synthesis of $ZrCl_4$@Arabic Gum

Weigh one gram of Arabic step, add 13.4 g of zirconium tetrachloride, add some dichloromethane solvent to the mixture, mix the ingredients together in a mortar for about an hour and stir. Add a little dichloromethane to the mixture each time and the amount of

dichloromethane consumed should be about 2 mL.

Prepration of 14-aryl-14H-dibenzo[a,j]xanthene catalyzed by $ZrCl_4$@Arabic Gum

A mixture of 2-naphthol (2 mmol), aldehyde (1 mmol) and catalyst (0.03 g) $ZrCl_4$@Arabic Gum was spun for 10 min in a test tube at 70- °C. Reaction progress was monitored by TLC. After completion of the reaction, the mixture was dissolved in ethanol, filtered, and washed with ethanol (5 mL) to separate the catalyst. The solvent was evaporated under reduced pressure to give a pure product.

Result and Discussion

Characterization by SEM-EDAX

To verify the elemental analysis and particle morphology and texture elucidation, SEM-EDX analysis was performed for the ZrCl4@Arabic Gum (Figure 1).

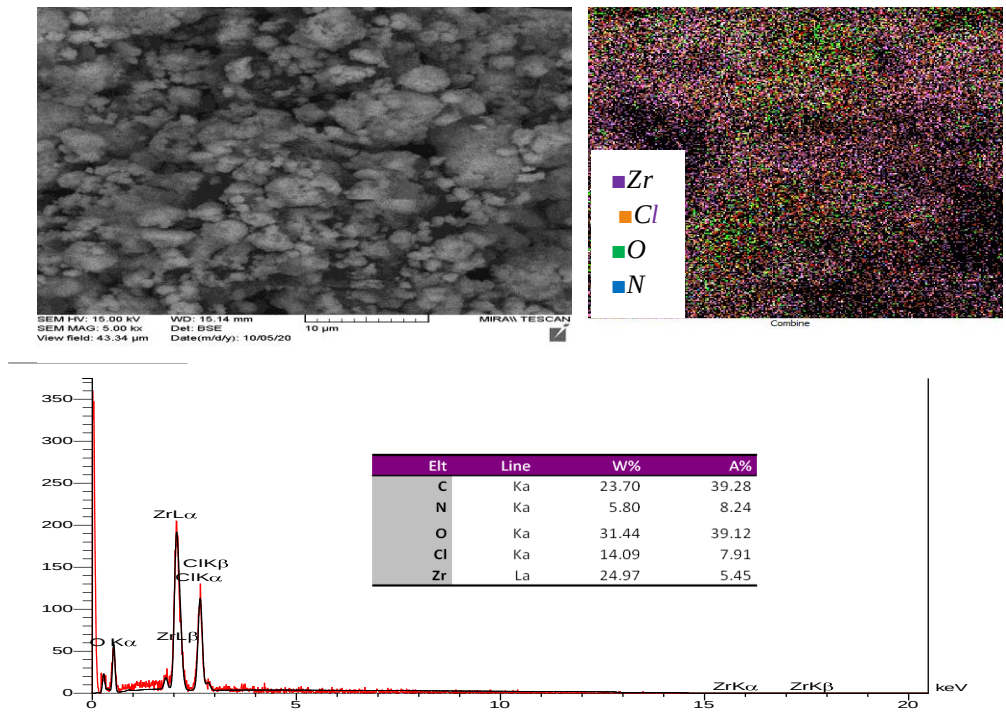


Figure 1. SEM-EDX analysis of the $ZrCl_4$@Arabic Gum

The surface was sound to be porous with irregular arrangement of particles with uneven particles distribution (bigger and smaller particles). The surface morphology of the composite shows smaller particles on a bed of larger particles. The EDAX spectrum of $ZrCl_4$@Arabic Gum illustrated the high intense peak of elemental Zr at 2 keV, also presence of other elemental carbon, oxygen, and chloride (2.7 keV) were observed that confirmed the capping of Arabic Gum. The elemental distribution map of this analysis shows the zirconium-chloride-carbon signals in the ratio of 25: 14: 23.7 wt%, respectively. As shown in Figure 1, the EDAX spectrum is free of impurities that confirm the purity of $ZrCl_4$@Arabic Gum.

TG and DSC analysis

Figure 2 shows the combination of TG curve and DSC curve for 5.6760 mg of $ZrCl_4$@Arabic Gum.The TG curve of $ZrCl_4$@Arabic Gum shows it has onset degradation temperature about 50 °C. Moisture and other impurity loss are

observed until 150 °C with a mass loss of 25%. This degradation continues with a gentler slope up to 400 °C with a mass reduction of 50% in total mass, that can be attributed to the formation of CO_2, CH_4 and H_2O because of dehydration, and decomposition and of carboxylic functional groups of Arabic Gum at high temperature. The DSC thermogram of $ZrCl_4$@Arabic Gum revealed two exothermic events, crystallite melting during heating, about 50 °C and 100 °C, which reflect the water and heat induced disorganization of crystallites due to presence of $ZrCl_4$.

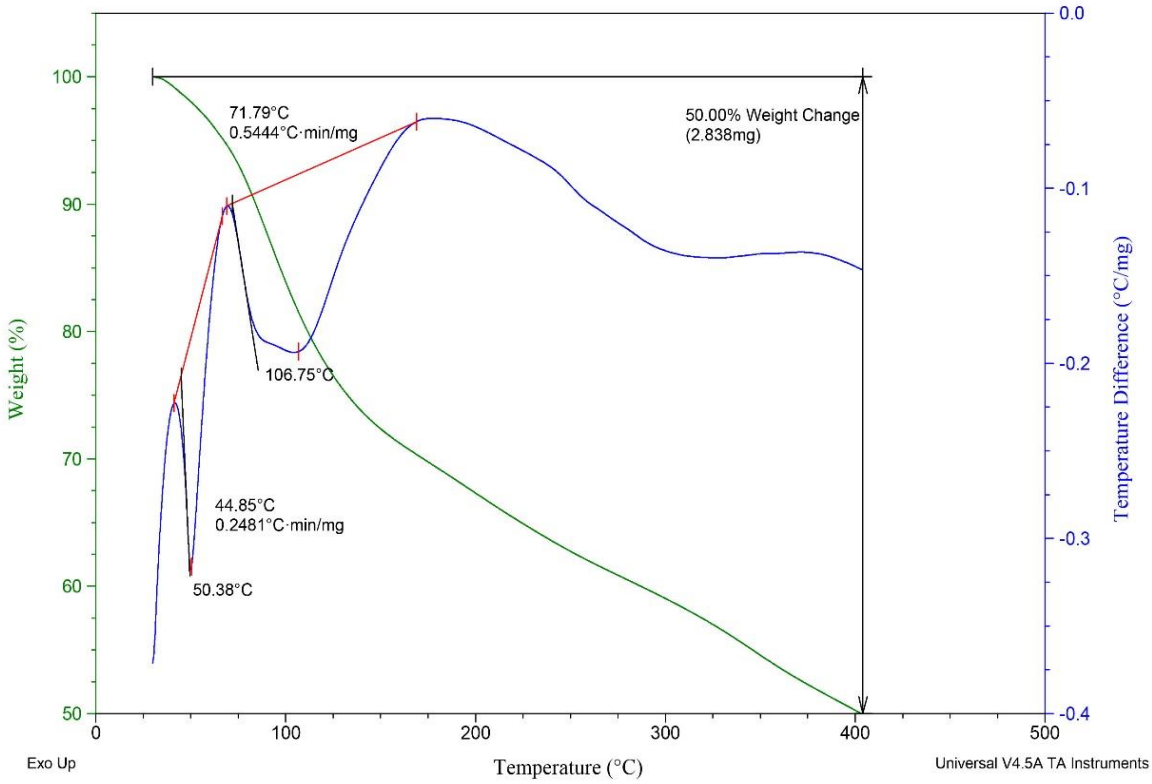


Figure 2. TG and DSC analysis by $ZrCl_4$@Arabic Gum

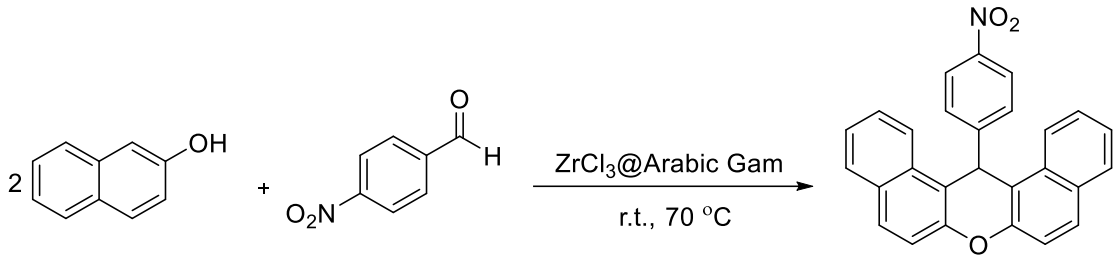
Prepration of 14-aryl-14H-dibenzo[a,j]xanthene catalyzed by $ZrCl_4$@Arabic Gum

In this study of the applications of heterogeneous acid catalysts in organic synthesis, we investigated the synthesis of 14-aryl-14H-dibenzo[a,j]xanthene in the presence of $ZrCl_4$@Arabic Gum. The reaction of 4-nitrobenzaldehyde (1 mmol) with 2-naphthol (2 mmol) was investigated to optimize the reaction conditions.

Reaction at different temperatures and different molar ratios of the substrates in the presence of $ZrCl_4$@Arabic Gum showed that the best conditions for solvent-free conditions in paraffin bath, temperature 70 °C and molar ratio of 2-naphthol: benzaldehyde: is 2:1 and 0.03 g) $ZrCl_4$@Arabic Gum catalyst (Scheme 1 and Table 1).

The reusability of the $ZrCl_4$@Arabic Gum catalyst was also examined. After each run, the product was filtered, the solvent was evaporated, and the catalyst residue was washed with EtOH and reused. 2-Naphthol and various aldehyde were used as substrates for the synthesis of xanthenes under solvent-free at room temperature (Scheme 2 and Table 2).

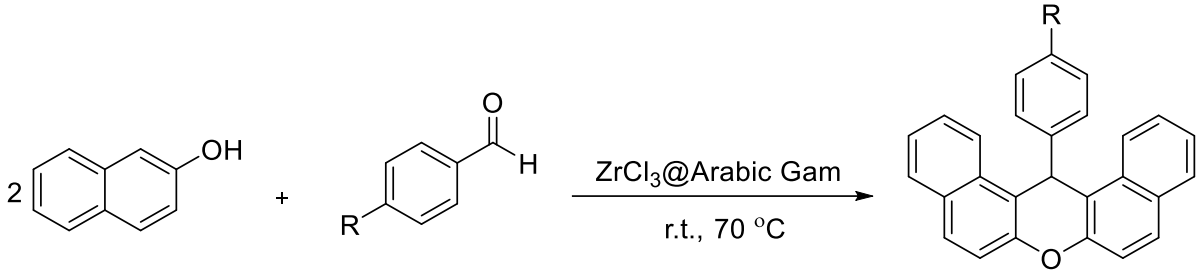
The proposed mechanism for this reaction is shown in Scheme 3, in which the $ZrCl_4$@Arabic Gum catalyst activates the aldehyde by protonating the carbonyl group. By attacking 2-naphthol to this interface, the product is formed. In the next step, by increasing 2-naphthol as Michel to the intermediate 4 and following ring formation, the desired product is formed.



Scheme 1. The $ZrCl_4$@Arabic Gum catalyst for the synthesis of the 14-aryl-14H-dibenzo[a,j]xanthene

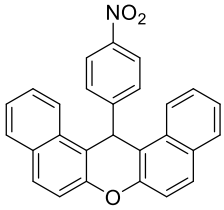
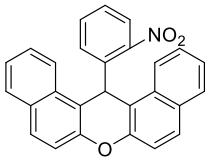
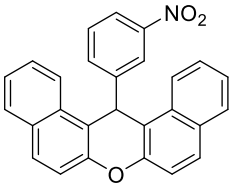
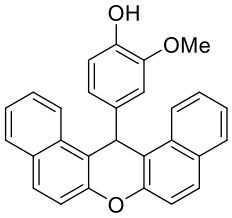
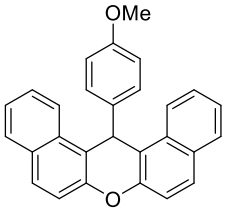
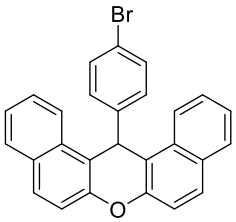
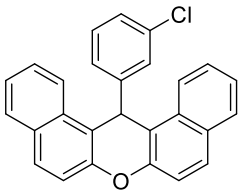
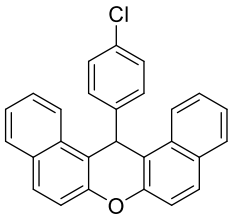
Table 1. Comparison of the results obtained from the reaction of β-naphthol with different aldehydes in the present method with the methods reported in the sources

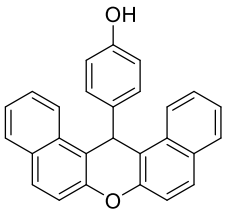
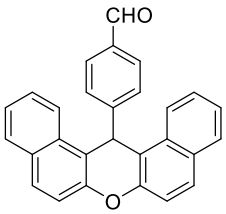
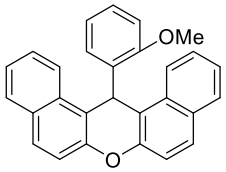
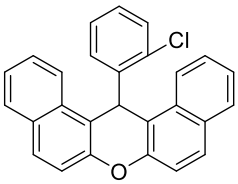
Entry	Catalyst (g)	Solvent	Conditions	Time (min)	Yield (%)	Reference
1	$ZrCl_4$@Arabic Gum (0.01)	Chloroform	rt	60	-	-
2	$ZrCl_4$@Arabic Gum (0.01)	Ethanol	rt	60	5	-
3	$ZrCl_4$@Arabic Gum (0.01)	Chloroform	Reflux	30	10	-
4	$ZrCl_4$@Arabic Gum (0.01)	Ethanol	Reflux	30	70	-
5	$ZrCl_4$@Arabic Gum (0.01)	Chloroform	60 °C	60	30	-
6	$ZrCl_4$@Arabic Gum (0.01)	Ethanol	60 °C	60	50	-
7	$ZrCl_4$@Arabic Gum (0.01)	Solvent-free	25 °C	20	92	-
8	$ZrCl_4$@Arabic Gum (0.02)	Solvent-free	25 °C	15	92	-
9	$ZrCl_4$@Arabic Gum (0.03)	Solvent-free	70 °C	3	98	-
10	$Sb(OAc)_3$ (0.04)	Solvent-free	25 °C	5	96	[21]
11	Ag Nanoparticles	Solvent-free	25 °C	5	95	[22]
12	$BF_3.SiO_2$ (0.10)	Solvent-free	60 °C	15	94	[23]
13	$BF_3.SiO_2$ (0.06)	Solvent-free	60 °C	15	42	[23]
14	$BF_3.SiO_2$ (0.04)	Solvent-free	60 °C	15	73	[23]

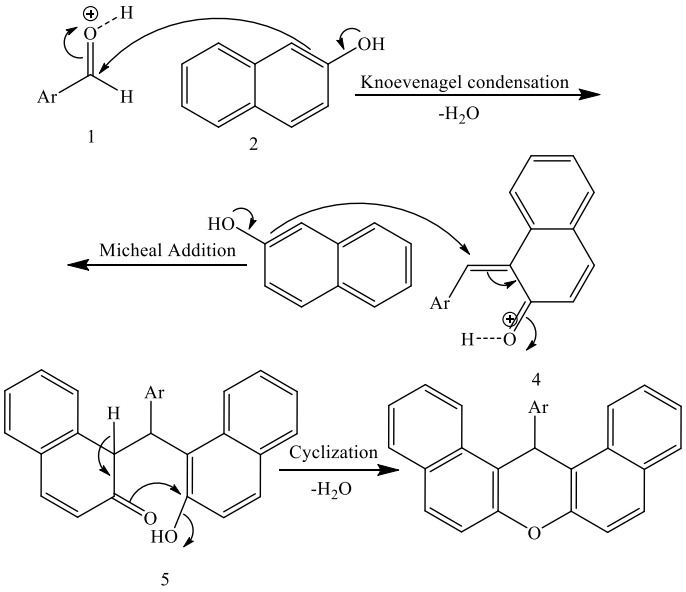


Scheme 2.

Table 2. The synthesis of 14-aryl-14H-dibenzo[a,j]xanthene using $ZrCl_4$@Arabic Gum as catalyst

Entry	R	Product	Time (min)/ Yield (%)	m.p.(°C)
1	4-NO_2Ph		10/98	311-312 [10]
2	2-NO_2Ph		12/97	215-217 [10]
3	3-NO_2Ph		12/98	210-211 [10]
4	4-OH-3-OCH3Ph		15/95	206-207 [11]
5	4-MeOPh		15/96	203-205 [10]
6	4-BrPh		15/92	297-298 [10]
7	3-ClPh		20/90	210-212 [10]
8	4-ClPh		20/90	289-290 [10]

9	4-OHPh		20/90	135-136 [10]
10	4-CHOPh		20/97	252-267 [10]
11	2-MeOPh		20/99	258-259 [9]
12	2-ClPh		20/98	214-216 [9]



Scheme 3.

Conclusions

In this research study, we successfully synthesized carbon tetrachloride zirconium stabilized on the Arabic Gum ($ZrCl_4$@Arabic Gum) as a highly efficient catalyst. The activity of this catalyst in the synthesis of the 14-aryl-14H-dibenzo[a,j]xanthene derivatives was

explored under solvent-free conditions at 70 °C. Easy, cheap, readily available catalysts make this method an attractive option for the existing methods for xanthenes synthesis.

Disclosure Statement

No potential conflict of interest was reported by the authors

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