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## FULL PAPER



# Phosphomolybdic acid supported on Schiff base functionalized graphene oxide nanosheets: Preparation, characterization, and first catalytic application in the multicomponent synthesis of tetrahydrobenzo[*a*]xanthene-11-ones

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Abolghasem Davoodnia, Department of Chemistry, Mashhad Branch, Islamic Azad University, Mashhad, Iran. Email: adavoodnia@mshdiau.ac.ir; adavoodnia@yahoo.com New Schiff base (SB) functionalized graphene oxide (GO) nanosheets containing phosphomolybdic counter-anion H<sub>2</sub>PMo<sub>12</sub>O<sub>40</sub> (H<sub>2</sub>PMo) were successfully prepared by grafting of 3-aminopropyltriethoxysilane (APTS) on GO nanosheets followed by condensation with benzil and finally reaction with phosphomolybdic acid (H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>, denoted as H<sub>3</sub>PMo) and characterized using Fourier transform infrared (FT-IR) spectroscopy, field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), particle size distribution, energy-dispersive X-ray (EDX) analysis, EDX elemental mapping, and inductively coupled plasma optical emission spectrometry (ICP-OES). The prepared new nanomaterial, denoted as GO-SB-H<sub>2</sub>PMo, was shown to be an efficient heterogeneous catalyst in one-pot, three-component reaction of  $\beta$ -naphthol, aldehydes, and dimedone, giving high yields of tetrahydrobenzo[a]xanthene-11-ones within short reaction times. The catalyst is readily recovered by simple filtration and can be recycled and reused several times with no significant loss of catalytic activity.

### KEYWORDS

functionalized graphene oxide, phosphomolybdic acid, Schiff base, tetrahydrobenzo[a]xanthene-11-ones

# **1** | INTRODUCTION

Graphene, one of the allotropes of carbon, is twodimensional monolayers of carbon atoms arranged in a honeycomb lattice that can be functionalized easily with acidic moieties to give new materials that can be used in acid-catalyzed processes.<sup>[1]</sup> It possesses unique physical properties, such as high thermal and electronic conductivity, high thermal stability, and high structural strength,<sup>[2-4]</sup> and therefore has diverse applications in various fields such as electrochemical sensors,<sup>[5]</sup> composite materials,<sup>[6]</sup> and energy technology.<sup>[7]</sup> Graphene is easily produced from graphene oxide (GO) by reduction using reducing agents such as NaBH<sub>4</sub><sup>[8]</sup> or hydrazine.<sup>[9]</sup> In recent years, GO which can be prepared from graphite powder using Hummers method,<sup>[10]</sup> has attracted great

interest as a promising ideal support for a number of metals, nanoparticles and organic compounds due to its extremely high specific surface area, high hydrophilic nature, high adsorption capacity, high chemical stability and good accessibility.<sup>[11-13]</sup> The presence of hydrophilic oxygen containing groups on the surface of GO nanosheets such as hydroxyl, epoxy, and carboxyl groups makes surface modification of GO further efficiently and allow construction of various novel functional groups attached at the GO surface.[13-15] Functionalized GObased materials are attractive for various application areas such as solar cells,<sup>[16]</sup> adsorption of organic dye,<sup>[17]</sup> and also serve as efficient heterogeneous catalysts in various chemical transformations such as oxidation of olefins,<sup>[18]</sup> synthesis of N-aryl-2-amino-1,6-naphthyridines,<sup>[19]</sup> and synthesis of indazolophthalazinetriones.<sup>[20]</sup> There are a number of methods developed for functionalization of GO including amidation reaction between the carboxylic acid group of GO and amine,<sup>[21]</sup> esterification reaction between the carboxylic acid group of GO and alcohols,<sup>[22]</sup> reaction between the hydroxyl and carboxyl groups of GO and isocyanates,<sup>[23]</sup> and many others. Silvlation of the hydroxyl groups of GO using 3-aminopropyltriethoxysilane (APTS), as a silane coupling agent, is another method to covalently modify the surface of GO.<sup>[14,15]</sup>

Condensation of an aldehyde or ketone with a primary amine that was introduced for the first time by Hugo Schiff<sup>[24]</sup> give a compound with an imine group (-C=N-) that is known as a Schiff base (SB). These compounds, either alone or in a metal chelated form, are widely applied as antioxidant,<sup>[25]</sup> anticonvulsant,<sup>[26]</sup> antihypertensive  $\alpha$ -blocking agent,<sup>[27]</sup> and in cancer diagnosis.<sup>[28]</sup> In recent years, SBs derived from aromatic (benzene) rings containing carbonyl groups such as benzil or benzil like compounds, salicyaldehyde, and benzoin are widely used in functionalization of nanomaterials.<sup>[18,29-33]</sup> These SB functionalized nanomaterials are used for different kinds of applications in catalysis,<sup>[18,29,30]</sup> CO<sub>2</sub> capture for environmental clean-up,<sup>[31]</sup> antibacterial agents,<sup>[32]</sup> fabrication of polymer nanocomposites,<sup>[33]</sup> and electromagnetic studies.<sup>[34]</sup>

The synthesis of xanthenes has received significant attention because of their wide range of biological and pharmaceutical properties.<sup>[35–37]</sup> They are also known as laser dyes.<sup>[38]</sup> Among xanthene based compounds, tetrahydrobenzo[*a*]xanthene-11-ones are generally synthesized by one-pot, three-component reaction of  $\beta$ -naphthol, aldehydes, and dimedone in the presence of a variety of catalysts.<sup>[39–49]</sup> Nevertheless, development of new efficient recyclable catalysts for the synthesis of these compounds was of certain demand.

Taking all these facts into consideration, and in line with our interest in catalysis,<sup>[50–57]</sup> in this paper, for the first time, a new SB functionalized GO containing a phosphomolybdic counter-anion H<sub>2</sub>PMo<sub>12</sub>O<sub>40</sub> (H<sub>2</sub>PMo) was prepared by grafting of APTS on GO nanosheets followed by condensation with benzil and finally reaction with phosphomolybdic acid (H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>, denoted as H<sub>3</sub>PMo) and fully characterized (Scheme 1). The catalytic activity of this new material which was denoted as GO-SB-H<sub>2</sub>PMo was also investigated in one-pot synthesis of tetrahydrobenzo[*a*]xanthene-11-ones by reaction of  $\beta$ naphthol, aldehydes, and dimedone (Scheme 2).

### 2 | RESULTS AND DISCUSSION

# 2.1 | Preparation and characterization of the catalyst GO-SB-H<sub>2</sub>PMo

At first, GO nanosheets were prepared from natural graphite powder by modified Hummers method.<sup>[10]</sup> Grafting of APTS on GO nanosheets gave GO-NH<sub>2</sub> to provide amino moieties for further functionalization. These amino moieties undergo condensation reaction with carbonyl groups in benzil to form GO-SB. Finally, interaction of obtained GO-SB with H<sub>3</sub>PMo gave GO-SB-H<sub>2</sub>PMo as a new SB functionalized GO containing a phosphomolybdic counter-anion. The latter was characterized using Fourier transform infrared (FT-IR) spectroscopy, field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), particle size distribution,



**SCHEME 1** Preparation of GO-SB-H<sub>2</sub>PMo nanosheets



**SCHEME 2** GO-SB-H<sub>2</sub>PMo nanosheets catalyzed synthesis of tetrahydrobenzo[*a*] xanthene-11-ones

energy-dispersive X-ray (EDX) analysis, EDX elemental mapping, and inductively coupled plasma optical emission spectroscopy (ICP-OES).

Figure 1 shows the FT-IR spectra of GO, GO-NH<sub>2</sub>, GO-SB and GO-SB-H<sub>2</sub>PMo. For GO (Figure 1(a)), the intense and broad peak at 3437 cm<sup>-1</sup> is attributed to the stretching vibration of OH groups at the surface of GO, which is major binding site for trialkoxysilane materials. The adsorption band at 1720 cm<sup>-1</sup> is assigned to the carbonyl group (C=O) of carboxylic acid. Other characteristic bands at 1639 and 1061 cm<sup>-1</sup> are related to C=C and C-O stretching vibrations, respectively. Subsequent, grafting of APTS with hydroxyl groups of GO was confirmed by the appearance of many vibrational peaks in



**FIGURE 1** FT-IR spectra of (a) GO, (b) GO-NH<sub>2</sub>, (c) GO-SB, (d) H<sub>3</sub>PMo, and (e) GO-SB-H<sub>2</sub>PMo

the FT-IR spectrum of GO-NH<sub>2</sub> (Figure 1(b)). The vibrational bands at 2927 and 2854  $\text{cm}^{-1}$  are attributed to the symmetric and asymmetric CH<sub>2</sub> of the alkyl chains and the bands located at around 3428 and 1572  $cm^{-1}$  are assigned to the vibrations of the amino groups in aminosilane moieties. Moreover, the appearance of bands at 1120 and 1040 cm<sup>-1</sup> which are attributed to characteristic absorption of Si-O bonds acquired during the silvlation process, provided more evidence for the successful grafting of APTS onto GO through chemical bonding. The loading of benzil on GO-NH<sub>2</sub> leads to GO-SB formation, which is corroborated by a sharp band at  $1658 \text{ cm}^{-1}$  attributed to the C=N (imine) stretching mode (Figure 1(c)). Finally, the successful preparation of GO-SB-H<sub>2</sub>PMo is confirmed by the appearance of the new bands at 797, 914, and 1056–1104  $\text{cm}^{-1}$  (overlapped with Si-O stretching vibration bands) (Figure 1(e)) which originates from the H<sub>2</sub>PMo stretching vibration bands similar to H<sub>3</sub>PMo (Figure 1(d)). Other bands in the FT-IR spectrum of GO-SB-H<sub>2</sub>PMo are similar to those of GO-SB with a slight shift for some of them.

The surface morphology of the GO-SB-H<sub>2</sub>PMo was characterized using FESEM image. As seen in Figure 2, the FESEM image exhibits a nanosheet-like structure in disordered phase with crumpled and wrinkled edges. These folded edges owing to  $sp^3$ -carbon in GO-SB-H<sub>2</sub>PMo, carry SB-H<sub>2</sub>PMo on both sides of the GO nanosheets. These sites may serve as reactive catalytic sites to provide the desired chemical transformation. On the other hand, the granular-like particles on the surfaces of GO nanosheets, confirm efficient grafting of new SB functionalized GO containing H<sub>2</sub>PMo anion on the GO nanosheets.

In the TEM image of the  $GO-SB-H_2PMo$  shown in Figure 3, some recognizable nanoparticles supported on the surface of the GO nanosheets can be seen.

Furthermore, the AFM topography images (twodimentional (2D), Figure 4a, and three-dimentional (3D), Figure 4b) were employed to observe the morphology of the GO-SB-H<sub>2</sub>PMo catalyst and measure its thickness. In these images, there is some prominence which confirm successful immobilization of organic and inorganic ligands onto the surface of GO. Moreover, according to 3D image, the thickness of the functionalized GO layer is about 4.5 nanometers which approve the nanosheetlike structure of the catalyst. 4 of 11 WILEY Organometallic Chemistry



FIGURE 2 FESEM image of GO-SB-H<sub>2</sub>PMo



FIGURE 3 TEM image of GO-SB-H<sub>2</sub>PMo

To determine the size of the nanoparticles, the particle size distribution of the GO-SB- $H_2$ PMo catalyst was measured and the results are shown in Figure 5. As depicted,



FIGURE 5 Particle size distribution of GO-SB-H<sub>2</sub>PMo

the catalyst has a size between 40 to 600 nm which probably the small parts are related to the organic and inorganic ligands attached to the GO nanosheets and the big ones are correspond to the GO nanosheets support.

In order to get more evidences about the chemical structure of GO-SB-H<sub>2</sub>PMo catalyst, EDX analysis was provided. As depicted in Figure 6, the EDX spectrum clearly shows the presence of oxygen, carbon, silicon, nitrogen, phosphorus and molybdenum elements in the catalyst, confirming the successful functionalization of GO.

In addition, EDX elemental mapping was used to investigate the elements distribution in GO-SB-H<sub>2</sub>PMo. As can be seen in Figure 7, the uniform distribution of Si, P, and Mo, indicates that the SB-H<sub>2</sub>PMo is uniformly immobilized on GO, which is very important to perform efficient catalytic organic transformations.

Based on ICP-OES, the amounts of P and Mo incorporated into the GO-SB-H<sub>2</sub>PMo are 2.076% and 7.131%, respectively, which is another conformation for immobilization of SB-H<sub>2</sub>PMo over the surfaces of GO nanosheets.

# 2.2 | Evaluation of catalytic activity of GO-SB-H<sub>2</sub>PMo in the synthesis of tetrahydrobenzo[*a*]xanthene-11-ones

The catalytic efficiency of GO-SB-H<sub>2</sub>PMo was tested in the three component coupling of  $\beta$ -naphthol, aldehydes, and



FIGURE 4 2D (a) and 3D (b) AFM topography images of GO-SB-H<sub>2</sub>PMo



FIGURE 6 EDX analysis of GO-SB-H<sub>2</sub>PMo

dimedone, giving tetrahydrobenzo[*a*]xanthene-11-ones. For optimization of the reaction conditions, the reaction of  $\beta$ -naphthol **1**, 4-chlorobenzaldehyde **2b**, and dimedone **3** was investigated as a model. Different reaction parameters like catalyst amount, effect of media and influence of temperature were studied for the formation corresponding product **4b**. These results are summarized in Table 1. When the reaction was carried out without catalyst (Table 1, entry 1) under solvent-free conditions at high temperature, a low yield of the product was formed even after 120 min. However, when the reaction was performed in the presence of GO-SB-H<sub>2</sub>PMo, the desired product was obtained in moderate to high yields. Among the various

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solvents used such as  $H_2O$ , EtOH, EtOH/ $H_2O$ , MeOH,  $CH_3CN$ ,  $CH_2Cl_2$ ,  $CHCl_3$ , THF, and neat, the reaction proceeded most readily to give the highest yield of the product **4b** in shorter reaction times under solvent-free conditions. Increases in the amount of the catalyst and reaction temperature up to 5.1 mol% and 120 °C, respectively, led to an increase in the yield of the product **4b**. A further increase in temperature and catalyst amount did not improve the product yield. To show the merit of the GO-SB-H<sub>2</sub>PMo catalyst, the effect of Graphite, GO, and GO-SB was also investigated in the above model reaction in optimized conditions. The results are shown in Table 1 (entries 24–26). As depicted, GO-SB-H<sub>2</sub>PMo proved to be the better catalyst than others in terms of reaction time and yield.

Thereafter, to evaluate the applicability of the method, a variety of other aromatic aldehydes were used for the synthesis of a range of tetrahydrobenzo[a]xanthene-11-ones under optimized conditions. As shown in Table 2, all electron-rich as well as electron-poor aromatic aldehydes reacted successfully and gave the products in high yields within short reaction time. However, using aliphatic aldehydes, good yields of the products were obtained in longer reaction times.

The obtained results using GO-SB-H<sub>2</sub>PMo as a heterogeneous catalyst were compared with those of the other methods reported for the synthesis of tetrahy-drobenzo[a]xanthene-11-ones in the presence of various homogeneous, heterogeneous, and supported catalysts. This comparison is shown in Table 3. As can be seen, our reaction conditions showed a shorter reaction time with high yields of the desired products.



FIGURE 7 EDX elemental mapping of GO-SB-H<sub>2</sub>PMo

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**TABLE 1** Synthesis of 4b under different reaction conditions<sup>a</sup>

Entry	Catalyst (mol%)	Solvent	Temp. (°C)	Time (min)	Yield (%)	TON <sup>b</sup>	TOF $(min^{-1})^{c}$
1			120	120	15		
2	GO-SB-H <sub>2</sub> PMo (2.2)		80	9	55	25.00	2.78
3	GO-SB-H <sub>2</sub> PMo (2.2)		100	9	60	27.27	3.03
4	GO-SB-H <sub>2</sub> PMo (2.2)		120	8	68	30.91	3.86
5	GO-SB-H <sub>2</sub> PMo (3.7)		80	8	60	16.22	2.03
6	GO-SB-H <sub>2</sub> PMo (3.7)		100	7	69	18.65	2.66
7	GO-SB-H <sub>2</sub> PMo (3.7)		120	6	78	21.08	3.51
8	GO-SB-H <sub>2</sub> PMo (4.4)		80	7	75	17.05	2.44
9	GO-SB-H <sub>2</sub> PMo (4.4)		100	6	79	17.95	2.99
10	GO-SB-H <sub>2</sub> PMo (4.4)		120	5	85	19.32	3.86
11	GO-SB-H <sub>2</sub> PMo (5.1)		80	4	85	16.67	4.17
12	GO-SB-H <sub>2</sub> PMo (5.1)		100	3	91	17.84	5.95
13	GO-SB-H <sub>2</sub> PMo (5.1)		120	1	95	18.63	18.63
14	GO-SB-H <sub>2</sub> PMo (5.1)		140	1	94	18.43	18.43
15	GO-SB-H <sub>2</sub> PMo (5.5)		120	1	95	17.27	17.27
16	GO-SB-H <sub>2</sub> PMo (5.1)	H <sub>2</sub> O	Reflux	240	25	4.90	0.02
17	GO-SB-H <sub>2</sub> PMo (5.1)	EtOH	Reflux	90	80	15.69	0.17
18	GO-SB-H <sub>2</sub> PMo (5.1)	EtOH/H <sub>2</sub> O	Reflux	120	61	11.96	0.10
19	GO-SB-H <sub>2</sub> PMo (5.1)	MeOH	Reflux	100	48	9.41	0.09
20	GO-SB-H <sub>2</sub> PMo (5.1)	CH <sub>3</sub> CN	Reflux	110	77	15.10	0.14
21	GO-SB-H <sub>2</sub> PMo (5.1)	$CH_2Cl_2$	Reflux	110	79	15.49	0.14
22	GO-SB-H <sub>2</sub> PMo (5.1)	CHCl <sub>3</sub>	Reflux	110	75	14.71	0.13
23	GO-SB-H <sub>2</sub> PMo (5.1)	THF	Reflux	240	30	5.88	0.02
24	Graphite (5.1)		120	120	22	4.31	0.04
25	GO (5.1)		120	25	81	15.88	0.64
26	GO-SB (5.1)		120	20	84	16.47	0.82

<sup>a</sup>Reaction conditions:  $\beta$ -naphthol (1; 1 mmol), 4-chlorobenzaldehyde (2b; 1 mmol), and dimedone (3; 1 mmol).

<sup>b</sup>Turn Over Number.

<sup>c</sup>Turn Over Frequency.

The principle advantage of employing heterogeneous solid catalysts in organic transformations is their reusability which makes the method economically valuable, industrially profitable and environmentally sustainable. So, the recycling performance of GO-SB-H<sub>2</sub>PMo was investigated in the model reaction. After completion of the reaction, the mixture was cooled to room temperature and hot ethanol was added. The catalyst was easily separated by a simple filtration, washed with ethanol, dried at 70 °C under vacuum for 1 hr, and used for the next cycle. The recovered catalyst could be used at least nine times without any noticeable reduction in catalytic activity (Figure 8).

To show the catalyst's role, a plausible mechanism for this reaction may proceed as depicted in Scheme 3. It is proposed that the reaction occurs *via* initial formation of the *ortho*-quinone methide (*o*-QM) intermediate [**II**], prepared by condensation of  $\beta$ -naphthol **1** with aldehydes **2a-n** *via* the intermediate [**I**]. Subsequent Michael addition of the *o*-QM intermediate [**II**] with enolic form of dimedone **3** followed by addition of the phenolic hydroxyl moiety in intermediate [**III**] to the carbonyl group provides cyclic hemiketal intermediate [**IV**], which on dehydration afforded final products **4a-n**. As shown in Scheme 3, we propose that the catalyst GO-SB-H<sub>2</sub>PMo  $\equiv$  Cat. with several accessible Mo sites and P-O-H moieties can act as Lewis acid and Brønsted acid centres, respectively, and therefore activates the reactants and the intermediates in this reaction. Under these conditions, attempts to isolate the intermediates failed even after careful monitoring of the reactions. **TABLE 2** GO-SB-H<sub>2</sub>PMo catalyzed synthesis of tetrahydrobenzo[*a*]xanthene-11-ones **4a-n**<sup>a</sup>



<sup>a</sup>Reaction conditions: β-naphthol (1; 1 mmol), an aldehyde (2a-n; 1 mmol), dimedone (3; 1 mmol), GO-SB-H<sub>2</sub>PMo (5.1 mol%), 120 °C, solvent-free. <sup>b</sup>Turn Over Number.

<sup>c</sup>Turn Over Frequency.

**TABLE 3** Comparison of the efficiencies of different catalysts for the synthesis of tetrahydrobenzo[a]xanthene-11-ones

	Catalyst amount (mol%)	Conditions					
Catalyst		Solvent	T (°C)	Other	Time (min)	Yield (%)	Ref.
Trichloroisocyanuric acid	5		110		25-40	74–90	[39]
SO <sub>3</sub> H-functionalized ionic liquids	10		120		55-95	75–95	[40]
p-Dodecylbenzenesulfonic acid	10	$H_2O$	40-42	ultrasound	60-240	63–93	[41]
Ceric ammonium nitrate	5	CH <sub>2</sub> Cl <sub>2</sub> /EtOH	26	ultrasound	120-144	82-87	[42]
Ce (SO <sub>4</sub> ) <sub>2</sub> .4H <sub>2</sub> O	25		120		8-30	85–97	[43]
Zr-MCM-41	10		80		10-20	87–92	[44]
Metal oxide nanoparticles (TiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> , or Fe <sub>3</sub> O <sub>4</sub> )	20		110		8-30	80–97	[45]
Poly(N,N'-dibromo-N-ethylnaphtyl-2,7-sulfonamide)	5		110		30-120	70–96	[46]
Sulfonation of carbonized xylan-type hemicellulose	4.3		90		120	80–96	[47]
<i>N,N'-</i> dibromo- <i>N,N'-</i> 1,2-ethanediyl <i>bis(p-</i> toluenesulfonamide)	10		90		20-95	87–97	[48]
HBF <sub>4</sub> /SiO <sub>2</sub>	10		80		55-90	83–95	[49]
GO-SB-H <sub>2</sub> PMo	5.1		120		1-30	75–95	This work

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FIGURE 8 Reusability of GO-SB-H<sub>2</sub>PMo for the synthesis of compound 4b

### 3 | EXPERIMENTAL

All chemicals were purchased from Merck and Aldrich and used without further purification. Melting points were recorded with a Stuart SMP3 melting point apparatus. The <sup>1</sup>H NMR (300 MHz) spectra were recorded on a Bruker 300 FT spectrometer, in DMSO-d<sub>6</sub> as the solvent using tetramethyl silane (TMS) as internal standard. FT-IR spectra were obtained using a Tensor 27 Bruker spectrophotometer as KBr disks. Ultrasonication was performed using a Soltec sonicator at a frequency of 40 kHz and a nominal power of 260 W. FESEM analyses was done using a TESCAN BRNO-MIRA3 LMU. TEM analysis was performed using a Leo 912 AB microscope with an accelerating voltage of 120 kV. EDX analysis and elemental mapping were performed using a SAMX model instrument. The amount of molybdenum and phosphorus in the catalyst was determined using ICP-OES conducted with a Spectro Arcos model spectrometer.

### 3.1 | Preparation of GO nanosheets

GO nanosheets were prepared from natural graphite using Hummers method<sup>[10]</sup> with some modification. A mixture of graphite powder (5.0 g), sodium nitrate (NaNO<sub>3</sub>, 2.5 g), and concentrated sulfuric acid (115 ml, 98% H<sub>2</sub>SO<sub>4</sub>) was stirred in an ice bath at 0-5 °C for then potassium 15 min and permanganate (KMnO<sub>4</sub>,15.0 g) was slowly added. The stirring was continued for 2 hr while the temperature was kept in the range of 0-10 °C. The mixture was then transferred to a water bath and stirred at 35 °C for 30 min, forming a brownish grey thick paste. Afterwards, deionized water (230 ml) was slowly added to the paste and the suspension, now brown in color, was stirred at 95-98 °C for 15 min. The suspension was further diluted with warm deionized water (700 ml, 40 °C), followed with a drop by drop addition of 30% hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 50 ml). The mixture was centrifuged and the isolated vellow-brown cake was washed with diluted HCl (5 wt%) and deionized water several times until the pH became neutral. The solid graphite oxide was separated by centrifugation and dried at 60 °C under vacuum for 12 hr. The obtained graphite oxide (0.4 g) was dispersed in distilled water (400 ml) and sonicated in an ultrasonic bath cleaner (100 W) for 1 hr to exfoliate graphitic oxide. The complete exfoliation of graphite oxide is confirmed with the formation of light brown colored homogeneous dispersion GO. Afterwards, the GO solution was centrifuged for 20 min and then the supernatant was removed (to remove any unexfoliated graphitic oxide). The GO nanosheets were obtained after drying the sediment in a vacuum oven at 80 °C for 24 hr.



**SCHEME 3** Plausible mechanism for the formation of tetrahydrobenzo[a]xanthene-11-ones **4a-n** in the presence of GO-SB-H<sub>2</sub>PMo as catalyst

# 3.2 | Preparation of GO-NH<sub>2</sub>

The GO-NH<sub>2</sub> was prepared by grafting of APTS on GO nanosheets according to methods cited in the literature.<sup>[14,15]</sup> Briefly, the synthesized GO (1.0 g) was ultrasonically dispersed in anhydrous toluene (30 ml) at room temperature for 30 min and then APTS (3.0 mmol) was added. The mixture was heated under a N<sub>2</sub> atmosphere at 110 °C for 24 hr. The resultant solid was filtered and washed with toluene (3 × 10 ml), and dried at 50 °C under vacuum for 24 hr to give black powder of GO-NH<sub>2</sub>.

# 3.3 | Preparation of GO-SB

The resulting GO-NH<sub>2</sub> (1.0 g) was dispersed in absolute ethanol (60 ml) using an ultrasonic bath at room temperature for 30 min. This is followed by addition of benzil (3 mmol) and a few drops of glacial acetic acid. The mixture was heated under reflux for 5 hr. The solid was filtered and washed with absolute ethanol (3 × 10 ml) to remove the non-reacted benzil, and then dried at 40 °C under vacuum for 24 hr to give GO-SB.

# 3.4 | Preparation of GO-SB-H<sub>2</sub>PMo

GO-SB (0.5 g) was ultrasonically dispersed in absolute ethanol (20 ml) at 60 °C for 20 min.  $H_3PMo$  (2 mmol) was added to the suspension and sonication continued for another 1 hr at same temperature. The mixture was then refluxed for 10 hr. After cooling to room temperature, the solid was collected by filtration and repeatedly washed with absolute ethanol and dried under vacuum at 60 °C for 12 hr to form GO-SB-H<sub>2</sub>PMo.

# 3.5 | General procedure for synthesis of tetrahydrobenzo[*a*]xanthene-11-ones 4a-n catalyzed by GO-SB-H<sub>2</sub>PMo

A mixture of  $\beta$ -naphthol **1** (1 mmol), aldehyde (**2a-n**; 1 mmol), dimedone (**3**; 1 mmol), and GO-SB-H<sub>2</sub>PMo (70 mg) was heated in an oil bath at 120 °C. The reaction was monitored by TLC. Upon completion of the transformation, the reaction mixture was cooled to room temperature and hot ethanol was added. The catalyst was insoluble in hot ethanol and it could therefore be recycled by a simple filtration. The product was then collected from the filtrate after cooling to room temperature and recrystallized from ethanol to give compounds **4a-n** in high yields. All the products were characterized according to comparison of their melting points with those of authentic samples. IR and <sup>1</sup>H NMR spectral data for some

of the products are given in the supporting information (Figures S2-S9).

# 3.6 | Selected FT-IR and <sup>1</sup>H NMR data

# 3.6.1 | 9,9-Dimethyl-12-phenyl-8,9,10,12tetrahydrobenzo[*a*]xanthen-11-one (4a)

<sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>, ppm):  $\delta = 0.90$  (s, 3H, CH<sub>3</sub>), 1.08 (s, 3H, CH<sub>3</sub>), 2.14 (d, J = 16.1 Hz, 1H, one proton of diastereotopic protons in CH<sub>2</sub>), 2.36 (d, J = 16.1 Hz, 1H, one proton of diastereotopic protons in CH<sub>2</sub>), 2.66 (AB<sub>q</sub>,  $\Delta \nu = 28.5$  Hz,  $J_{AB} = 17.4$  Hz, 2H, CH<sub>2</sub>), 5.59 (s, 1H, pyran CH), 7.07 (t, J = 7.2 Hz, 1H, arom-H), 7.20 (t, J = 7.6 Hz, 2H, arom-H), 7.31 (d, J = 7.4 Hz, 2H, arom-H), 7.41–7.55 (m, 3H, arom-H), 7.93 (d, J = 8.7 Hz, 2H, arom-H), 8.06 (d, J = 8.3 Hz, 1H, arom-H); IR (KBr, cm<sup>-1</sup>)  $\nu = 2953$ , 1650, 1458, 1376, 1229, 1024, 811, 698.

# 3.6.2 | 12-(4-Chlorophenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one (4b)

<sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>, ppm):  $\delta = 0.90$  (s, 3H, CH<sub>3</sub>), 1.08 (s, 3H, CH<sub>3</sub>), 2.15 (d, J = 16.5 Hz, 1H, one proton of diastereotopic protons in CH<sub>2</sub>), 2.37 (d, J = 16.5 Hz, 1H, one proton of diastereotopic protons in CH<sub>2</sub>), 2.66 (AB<sub>q</sub>,  $\Delta \nu = 31.8$  Hz,  $J_{AB} = 17.4$  Hz, 2H, CH<sub>2</sub>), 5.61 (s, 1H, pyran CH), 7.26 (d, J = 8.6 Hz, 2H, arom-H), 7.33 (d, J = 8.6 Hz, 2H, arom-H), 7.41–7.55 (m, 3H, arom-H), 7.91–7.97 (m, 2H, arom-H), 8.02 (d, J = 8.2 Hz, 1H, arom-H); <sup>13</sup>C NMR (75 MHz, DMSO-d<sub>6</sub>, ppm):  $\delta = 26.72$ , 29.27, 32.39, 34.08, 40.70, 50.56, 113.27, 117.18, 117.65, 123.70, 125.56, 127.75, 128.61, 129.08, 129.83, 130.47, 130.99, 131.25, 131.58, 144.29, 147.63, 164.45, 196.41; IR (KBr, cm<sup>-1</sup>)  $\nu = 3072$ , 2951, 2872, 1648, 1482, 1370, 1227, 1089, 1018, 817, 750.

# 3.6.3 | 9,9-Dimethyl-12-(3-nitrophenyl)-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one (4 g)

<sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>, ppm):  $\delta = 0.89$  (s, 3H, CH<sub>3</sub>), 1.09 (s, 3H, CH<sub>3</sub>), 2.17 (d, J = 16.3 Hz, 1H, one proton of diastereotopic protons in CH<sub>2</sub>), 2.39 (d, J = 16.3 Hz, 1H, one proton of diastereotopic protons in CH<sub>2</sub>), 2.70 (AB<sub>q</sub>,  $\Delta \nu = 24.2$  Hz,  $J_{AB} = 17.4$  Hz, 2H, CH<sub>2</sub>), 5.81 (s, 1H, pyran CH), 7.43–7.56 (m, 4H, arom-H), 7.77 (dt, J = 7.9, 1.2 Hz, 1H, arom-H), 7.93–8.02 (m, 3H, arom-H), 8.07 (d, J = 8.2 Hz, 1H, arom-H), 8.19

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(t, J = 1.9 Hz, 1H, arom-H); <sup>13</sup>C NMR (75 MHz, DMSOd<sub>6</sub>, ppm):  $\delta = 26.66$ , 29.18, 32.44, 34.46, 40.67, 50.47, 112.82, 116.42, 117.68, 121.99, 123.03, 123.71, 125.70, 127.97, 129.13, 130.26, 130.87, 131.61, 135.32, 147.37, 147.75, 148.08, 164.92, 196.49; IR (KBr, cm<sup>-1</sup>) v = 2955, 1649, 1529, 1467, 1353, 1224, 1086, 1026, 812, 752.

# 3.6.4 | 12-(4-Methoxyphenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one (4 k)

<sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>, ppm):  $\delta = 0.91$  (s, 3H, CH<sub>3</sub>), 1.08 (s, 3H, CH<sub>3</sub>), 2.14 (d, J = 16.5 Hz, 1H, one proton of diastereotopic protons in CH<sub>2</sub>), 2.35 (d, J = 16.5 Hz, 1H, one proton of diastereotopic protons in CH<sub>2</sub>), 2.65 (AB<sub>q</sub>,  $\Delta \nu = 30.0$  Hz,  $J_{AB} = 17.3$  Hz, 2H, CH<sub>2</sub>), 3.64 (s, 3H, OCH<sub>3</sub>), 5.54 (s, 1H, pyran CH), 6.76 (d, J = 8.7 Hz, 2H, arom-H), 7.20 (d, J = 8.7 Hz, 2H, arom-H), 7.90–7.95 (m, 2H, arom-H), 8.05 (d, J = 8.3 Hz, 1H, arom-H); IR (KBr, cm<sup>-1</sup>)  $\upsilon = 2951$ , 1648, 1511, 1460, 1378, 1229, 1174, 1028, 832, 750.

## 3.6.5 | 12-(4-Hydroxyphenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one (4 1)

<sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>, ppm):  $\delta = 0.91$  (s, 3H, CH<sub>3</sub>), 1.07 (s, 3H, CH<sub>3</sub>), 2.14 (d, J = 16.1 Hz, 1H, one proton of diastereotopic protons in CH<sub>2</sub>), 2.34 (d, J = 16.1 Hz, 1H, one proton of diastereotopic protons in CH<sub>2</sub>), 2.63 (AB<sub>q</sub>,  $\Delta \nu = 29.2$  Hz,  $J_{AB} = 17.4$  Hz, 2H, CH<sub>2</sub>), 5.48 (s, 1H, pyran CH), 6.58 (d, J = 8.5 Hz, 2H, arom-H), 7.09 (d, J = 8.5 Hz, 2H, arom-H), 7.41–7.54 (m, 3H, arom-H), 7.88–7.94 (m, 2H, arom-H), 8.05 (d, J = 8.3 Hz, 1H, arom-H), 9.20 (s, 1H, OH); <sup>13</sup>C NMR (75 MHz, DMSO-d<sub>6</sub>, ppm):  $\delta = 26.71$ , 29.34, 32.36, 33.64, 40.71, 50.65, 114.06, 115.34, 117.63, 118.27, 123.83, 125.36, 127.49, 128.98, 129.28, 129.52, 131.17, 131.55, 135.93, 147.57, 156.03, 163.88, 196.42; IR (KBr, cm<sup>-1</sup>)  $\nu = 3224$ , 2953, 1649, 1600, 1512, 1463, 1376, 1231, 1023, 822, 752.

### 4 | CONCLUSIONS

In summary, GO-SB- $H_2$ PMo, as a new SB functionalized GO containing a phosphomolybdic counter-anion, was successfully prepared by grafting of APTS on GO nanosheets followed by condensation with benzil and finally reaction with  $H_3$ PMo. The structure of this new nanomaterial was confirmed using FT-IR spectroscopy,

FESEM, TEM, AFM, particle size distribution, EDX analysis, EDX elemental mapping, and ICP-OES. The new functionalized GO performed well as a catalyst in onepot synthesis of tetrahydrobenzo[*a*]xanthene-11-ones by reaction of  $\beta$ -naphthol with several aromatic or aliphatic aldehydes and dimedone under solvent-free conditions, giving high yields of the products within short reaction times. In addition, the catalyst is readily recovered by simple filtration and can be reused for subsequent reactions with no significant loss of its activity. Further applications of this new catalyst for other reaction systems are currently under investigation.

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