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Pyridine-grafted graphene oxide: a reusable acid– base bifunctional catalyst for the one-pot synthesis of β-phosphonomalonates *via* a cascade Knoevenagel–phospha Michael addition reaction in water⁺

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Introduction

The "greening" of global chemical processes has become an important task of modern synthetic chemistry. One major drawback in modern chemical production processes is the use of highly toxic and flammable organic solvents.1 Learning from living systems, there has been a growing interest in the development of water medium organic synthesis since water is safe, renewable, nontoxic and nonflammable.² Moreover, the organic synthesis process is usually comprised of iterative reactions.³ The iterative reaction is generally conducted individually and step-by-step with the corresponding catalyst. After each step of reaction, the product and catalyst are isolated and purified, followed by adding a new catalyst and other reactants as well as solvent media for the subsequent step of the cascade reaction.⁴ Obviously, this is the most time- and cost-demanding and waste-producing manual operation.5 To reduce the number of purification steps and improve overall efficiency, the use of onepot chemical reactions has been recognized as a promising approach. However, the difficulties associated with the design of well-controlled isolated catalytic centres which are able to catalyze each reaction step efficiently, limit the wide range of general applications for one-pot chemical processes.6 Learning from enzymes, most studies have focused on homogeneous catalysts with multiple kinds of active sites for synergistically driving one-pot cascade reactions.7 Obviously, the use of both strong acidic and basic species in a homogeneous one-pot

A new acid–base bifunctional catalyst was synthesized by postgrafting of pyridine onto GO. This new catalyst was characterized by different methods such as FT-IR, XRD, TGA, TEM, SEM, EDS, UV-Vis and elemental analysis and employed as a reusable acid–base bifunctional catalyst for the one-pot synthesis of β -phosphonomalonates *via* a cascade Knoevenagel–phospha Michael addition reaction of aldehydes, malononitrile and dialkyl phosphites in water.

reaction is impossible due to the neutralization that forms inactive salts. In addition, recovery and reuse of both catalytic species are often problematic in homogeneous systems.8 To address this dilemma, heterogeneous catalysts recently attracted much attention for their remarkable advantages of easier recycling and fixing acidic and basic groups to avoid neutralization reaction.9 Solid matrixes such as silica, clay, and polymer are the common solid materials which have been used for hosting acidic and basic functions.10 There are several evident barriers in the synthesis of these bifunctional catalysts such as the tedious protection-deprotection procedures or the uncontrollable and inhomogeneous positioning of catalytically active species.11 Therefore, the development of a simple and efficient method for the fabrication of robust acid-base bifunctional heterogeneous catalysts to synthesis complex molecules in one step is urgently needed.

Graphene and related two-dimensional sp²-hybridized materials have invoked incredible research interest owing to their inherent optical, electrochemical and mechanical properties.12 Graphene oxide (GO), the oxygenated graphene sheets covered with hydroxyl, epoxy and carboxyl groups offers excellent aqueous dispersity, acidic properties and tremendous opportunities for further chemical modifications.13 Notably, GO exhibits as solid acid owing to the existence of carboxylic acids on the edges. Taking advantage of the presence of intrinsic carboxylic acids on GO, acid-base bifunctional GO catalysts have been synthesized by a simple postgrafting of basic functional groups onto GO.14 The acid-base bifunctional GO catalysts have exhibited excellent activity in one-pot cascade reactions owing to the unique two dimensional structure with low mass transfer limitation and suitable surface acidity of GO. Meanwhile, these heterogeneous catalysts could be easily recycled and reused repetitively.15 However, despite the excellent

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catalytic activity and reusability of bifunctional GO catalysts, rare studies reaches GO functionalization and catalytic performances in cooperative catalysis, even though this area has immense potential.

Within organophosphorus compounds, phosphonates are an important class of molecules. They have broad applications in catalysis,16 medicinal,17 and material chemistry.18 There are several methods for the synthesis of phosphonates. Among various methods to generate P-C bonds, the conjugate addition of phosphorus nucleophiles to activated alkenes (phospha-Michael reaction) holds a fundamental position in the phosphonate synthesis.¹⁹ These protocols proceed through two-pot procedure in which P-C and C-C bond formations occur in separate steps. Actually, these methods are not multicomponent reactions and use of a Knoevenagel adduct as starting material is required.²⁰ Over the last few years, coupling of P-C and C-C bond forming events during one-pot phosphonate synthesis has been attracted much attention in organophosphorus synthesis. To date, Brønsted/Lewis acids, bases, ionic liquids and micellar solution have been reported for the one-pot synthesis of β-phosphonomalonates via cascade Knoevenagel-phospha Michael addition reaction.21 Even though, phospha-Michael addition could be proceed by these methods, most of the existing protocols suffer from limitations such as low yields, long reaction times, using hazardous organic solvents or unrecyclable and/or expensive catalysts and tedious work-up procedures leading to copious amount of toxic wastes. Additionally, in most of these methods, poisonous and nasty smell trialkyl phosphites is used as the phosphorus nucleophile and few example employ dialkyl phosphites, which fulfils the criteria of atom economy.^{21g,h,22} More importantly, in spite of the prominence of bifunctional catalysts for efficient promotion of one-pot cascade reactions, the reports for one-pot synthesis of β-phosphonomalonates catalyzed by bifunctional catalysts are rare in the literature.^{20b,22} Therefore, a simple and green procedure for one-pot synthesis of β-phosphonomalonates catalyzed by an efficient, inexpensive and reusable bifunctional catalyst employing diethyl phosphite as the phosphorous component remains a major challenge in organophosphorus synthesis.

In this paper, in continues of our recent works on the development of new heterogeneous catalysts²³ and to benefit the efficiency of bifunctional catalysts in one-pot cascade reactions, we report the synthesis of pyridine-grafted GO as a new acid-base bifunctional catalyst (Py–GO, Scheme 1) by post-grafting of pyridine onto GO. This new catalyst was characterized by different methods such as Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), thermogravimetric analysis (TGA), transmission electron microscopy (SEM), scanning electron microscopy (SEM), energy dispersive



Scheme 1 Pyridine-grafted GO (Py-GO).

spectroscopy (EDS), ultraviolet-visible spectroscopy (UV-Vis) and elemental analysis and employed as a reusable acid-base bifunctional catalyst for the one-pot synthesis of β -phosphonomalonates *via* cascade Knoevenagel-phospha Michael addition reaction in water.

Results and discussion

Synthesis and characterization of Py-GO

Pyridine-grafted GO (Py–GO) was synthesized by the procedure outlined in Scheme 2. As indicated in Scheme 2, GO was reacted with an appropriate concentration of 3-mercaptopropyl trimethoxysilane to give mercapto-functionalized GO. The obtained mercapto-functionalized GO was subjected to react with 3-(chloromethyl)pyridine hydrochloride to obtain Py–GO. The synthesized Py–GO was characterized by FT-IR, XRD, TGA, TEM, SEM, EDS, UV-Vis and elemental analysis.

FT-IR spectra of GO and Py–GO are shown in Fig. 1a and b, respectively. Vibration peaks with a strong intensity at 3400, 1710, 1610, 1200, and 1050 cm⁻¹ in the FT-IR spectrum of GO were assigned to the stretching vibrations of O–H, C=O, C=C, C–OH and C–O–C bonds, respectively. These peaks reveal the presence of hydroxyl, carboxyl, and epoxy groups on the GO. In the spectrum of Py–GO, typical bands at about 2900 and 2830 attributed to C–H stretching vibrations from the silane chain. A peak at 1570 cm⁻¹ was observed, which was related to the stretching vibrations of C=C bonds. Si–O–Si and Si–O–C stretching modes of silane chain were indicated as a strong broad doublet at about 1110 and 1030 cm⁻¹. An absorption band at 1430 cm⁻¹ due to the ring stretching vibration of C=N was also seen (Fig. 1b). These results indicated that pyridine was successfully grafted onto GO.

The XRD pattern of GO (Fig. 2a) shows a sharp peak at $2\theta = 11.9^{\circ}$ with *d*-spacing of 0.73 nm, which can be ascribed to the (0 0 1) of GO, suggesting that graphite powder was oxidized to GO. As reported usually, the natural graphite reveals a basal reflection (0 0 2) peak at $2\theta = 26.6^{\circ}.^{24}$ In Py–GO, the diffraction peak (0 0 1) became very weak and broad appeared at $2\theta = 8.2^{\circ}$



Scheme 2 Synthesis of Py-GO.



Fig. 1 FT-IR spectra of (a) GO and (b) Py-GO.



Fig. 2 XRD patterns of (a) GO and (b) Py-GO

with *d*-spacing of 1.0 nm (Fig. 2b), which indicates that the organic groups were successfully tethered onto the GO. Another weak and broad diffraction peak centred at around 22.5° emerged for Py–GO, indicating that a part of the GO was changed into graphene.²⁵

The thermal decomposition of Py–GO and GO was examined by thermogravimetric analysis (Fig. 3a and b). As shown in Fig. 3a, Py–GO has a 2.6% mass loss below 145 °C, resulting from the evaporation of adsorbed water and a 6.8% mass loss from 145 to 280 °C, which is due to the removal of the oxygencontaining functional groups. The mass loss of GO is obviously higher than that of Py–GO (Fig. 3b), especially the second mass loss, which demonstrates an obvious decrease in the amount of oxygen-containing functional groups and a profound reduction of GO in Py–GO. The last mass loss of 13.4% is found around 400 °C in the TGA of Py–GO that is caused by the decomposition of organic parts located on its surface.

Elemental analysis showed that loading of pyridine on the GO was 0.9 mmol g^{-1} based on nitrogen content (N = 1.27%).



Fig. 3 TGA curve of (a) Py-GO and (b) GO.

The TEM image of Py–GO is shown in Fig. 4a. It is evident from Fig. 4a that the immobilized catalyst has a layered structure. The crumpled nanosheet can be seen in both TEM and SEM images (Fig. 4b and c) due to an agglomerated phase. EDS mapping demonstrates that S, O, and N elements (Fig. 4d–f) are homogeneously distributed on the surface of Py–GO, which indicates that sulfur and pyridine groups are homogeneously anchored on GO. The crumpling characteristic of the Py–GO, along with the homogeneous distribution of the active sites should be benefit for its catalytic performances, because reactants and products can easily access or leave the active sites on both sides of the two-dimensional with limited mass transfer resistance.

The UV-Vis spectrum of GO (Fig. 5a) shows a strong absorption peak at 230 nm, which is attributed to the $\pi \rightarrow \pi^*$ transition of graphite C–C bonds and a shoulder at ~300 nm is assigned to the $n \rightarrow \pi^*$ transition of C=O. The loading of pyridine leads to significant changes in the absorption spectrum of GO (Fig. 5b). An absorption peak at 230 nm in GO was shifted to 280 nm in Py–GO revealing the grafting of pyridine onto GO.

One-pot synthesis of β -phosphonomalonates catalyzed by Py–GO

In continuous of our recent research programs on the development of novel methods for the synthesis of phosphonate derivatives, $^{21a-d,i-k,26}$ in this paper, we have studied the applicability of pyridine grafted GO (Py–GO) as a new acid–base bifunctional catalyst for the one-pot synthesis of β -phosphonomalonates *via*



Fig. 4 (a) TEM image, (b and c) SEM images of Py-GO and the corresponding quantitative EDS element mapping of (d) S, (e) O and (f) N.

Fig. 5



cascade Knoevenagel-phospha Michael addition reaction of

aldehydes, malononitrile and diethyl phosphite. At first, one-pot reaction of benzaldehyde, malononitrile and diethyl phosphite was chosen to optimize the reaction conditions such as solvents and molar ratio of the catalyst at 100 °C (Table 1). We have found that in the presence of 3 mol% of Py-GO, the corresponding β -phosphonomalonate was obtained in the best yield at 100 °C under aqueous conditions (entry 2). By lowering the amount of the catalyst to 1 mol%, the desired product was obtained in lower yield (entry 7). A similar reaction at a lower temperature required longer reaction time and produced the desired product in lower yield (Table 1, entry 8). In order to show the role of Py-GO as an acid-base bifunctional catalyst, similar reactions in the absence of the catalyst and in the presence of G, GO, pyridine and a mixture of pyridine and GO were also examined (Table 1, entries 9-13). It was found that no reaction was occurred in the absence of any catalyst, and lower yields (20-65%) of the desired product were achieved by G, GO (with acidic sites), pyridine (as a base) and a mixture of pyridine and GO. The high catalytic activity of Py-GO for this

one-pot cascade reaction, clearly demonstrates a cooperative behaviour of intrinsic carboxylic acids and pyridine active sites on the same framework in Py–GO.

To confirm the generality of the present method, we next examined the reaction of a variety of aldehydes with malononitrile and diethyl phosphite under the optimized reaction conditions. The results of this study are depicted in Table 2.

As indicated in Table 2, benzaldehyde and different substituted benzaldehydes containing electron-donating and electron-withdrawing groups underwent one-pot reaction and gave the corresponding β -phosphonomalonates in good to high yields (entries 1–10). The reaction of aliphatic aldehydes proceeded well and produced the desired products in good yields in longer reaction time, probably due to their relatively weaker electrophilicity (entries 11 and 12).

Furthermore, we have evaluated the generality of the presented method for the one-pot synthesis of β-phosphonomalonates from 4-chlorobenzaldehyde with different phosphite esters and active methylene compounds (Table 3). As it is shown in Table 3, both the yields and the reaction time of 4-chlorobenzaldehyde and malononitrile with different phosphite esters are relatively dependent of the phosphorus compound (entries 1-5). The reaction proceeded with higher yield in shorter reaction time using dialkyl phosphites (entries 1 and 2) compared with trialkyl phosphites (entries 3-5). The higher activity of dialkyl phosphites is might be due to the role of the basic sites of Py-GO catalyst to accelerate phospha-Michael addition step by P-H bond deprotonation. In addition to malononitrile, some other active methylene compounds were also examined to carry out the reaction with 4-chlorobenzaldehyde and diethyl phosphite (entries 6-8). The results showed that the reaction involving ethyl cyano acetate worked well and the desired product was obtained in 70% yield.

 Table 1
 One-pot reaction of benzaldehyde, malononitrile and diethyl phosphite under different conditions

 $\overset{R}{\underset{H}{\longrightarrow}} O + \overset{CN}{\underset{CN}{\overset{H}{\longrightarrow}}} \overset{H}{\underset{H}{\overset{HP(OEt)_2}{\longrightarrow}}} \underbrace{\overset{Py-GO(3 \text{ mol}\%)}{\underset{H_2O, 100 \ ^{\circ}C}{\overset{(EtO)_2P}{\overset{V}{\longrightarrow}}}} \overset{O}{\underset{R}{\overset{CN}{\longleftarrow}} \overset{CN}{\underset{CN}{\overset{CN}{\longrightarrow}}}$

Table 2 Synthesis of a variety of β -phosphonomalonates catalyzed by

Py-GO

R = aryl, alkyl

Entry	Aldehyde	Product	Time (h)	Yield ^a (%)
1	Benzaldehvde	1	1	90
2	4-Methylbenzaldehyde	2	1	80
3	4-Methoxybenzaldehyde	3	1	73
4	3-Methoxybenzaldehyde	4	1	78
5	4-Chlorobenzaldehyde	5	1	87
6	3-Chlorobenzaldehyde	6	1	80
7	2-Chlorobenzaldehyde	7	2	73
8	4-Bromobenzaldehyde	8	1	82
9	3-Bromobenzaldehyde	9	1	68
10	4-Hydroxybenzaldehyde	10	2	85
11	Butyraldehyde	11	3	75
12	Heptanaldehyde	12	3	70

 a Isolated yield. Reaction conditions: aldehyde (1 mmol), malononitrile (1 mmol), diethyl phosphite (2 mmol), catalyst (3 mol%), H₂O (3 mL), 100 °C. All of the products are known.^{20b,e,21c,g,k}

hite under different conditions $\stackrel{Ph}{\longrightarrow} O + \underbrace{\stackrel{CN}{\leftarrow} N}_{H} + \frac{\stackrel{O}{H}}{HP(OEt)_2} \xrightarrow{Catalyst} \stackrel{(EtO)_2 P'}{\longrightarrow} \stackrel{O}{\longleftarrow} O$

Entry	Catalyst	Solvent	Time (h)	Yield ^a (%)
1	P_{V-GO} (3 mol%)	DMF	1	60
2	Pv-GO (3 mol%)	H ₂ O	1	90
3	Pv-GO (3 mol%)		2	78
4	Py-GO (3 mol%)	EtOH	2	73
5	Py-GO (3 mol%)	CH ₃ CN	2	52
6	Py-GO (3 mol%)	Toluene	2	30
7	Py–GO (1 mol%)	H_2O	1	80
^b 8	Py-GO (3 mol%)	H_2O	2	75
^c 9		H_2O	3	_
10	G (3 mol%)	H_2O	3	20
11	GO (0.03 g)	H_2O	3	53
12	Pyridine (27 µL)	H_2O	3	30
13	Pyridine $(27 \ \mu L) + GO (0.03 \ g)$	H ₂ O	3	65

^{*a*} Isolated yield. Reaction conditions: benzaldehyde (1 mmol), malononitrile (1 mmol), diethyl phosphite (2 mmol), catalyst, temperature = $100 \,^{\circ}$ C. ^{*b*} Temperature = $80 \,^{\circ}$ C. ^{*c*} No catalyst.

1-10

Table 3 One-pot synthesis of β -phosphonomalonates from 4-chlorobenzaldehyde with different phosphite esters and active methylene compounds catalyzed by Py–GO



Entry	Phosphite ester	Х	Y	Product	Time (h)	Yield ^a (%
1	$HP(O)(OEt)_2$	CN	CN	5	1	87
2	$HP(O)(O-iso-Pr)_2$	CN	CN	13	1	80
3	$P(OMe)_3$	CN	CN	14	1	68
4	P(O-iso-Pr) ₃	CN	CN	13	3	50
5	$P(OEt)_3$	CN	CN	5	1	65
6	$HP(O)(OEt)_2$	CN	CO_2Et	15	2	70
7	$HP(O)(OEt)_2$	CO_2Et	CO_2Et	_	24	b
8	$HP(O)(OEt)_2$	Н	NO_2	—	24	0

^{*a*} Isolated yield. Reaction conditions: 4-chlorobenzaldehyde (1 mmol), active methylene group (1 mmol), phosphite ester (2 mmol), catalyst (3 mol%), H_2O (3 mL), 100 °C. All of the products are known.^{19a,20b,21g b} Trace.

However, no product was produced when diethyl malonate or nitromethane were used in this one-pot reaction under the same conditions.

Because the recycling of the catalyst are important issues from both practical and economical viewpoints, we next investigated the reusability of the Py-GO catalyst in the reaction of benzaldehyde, malononitrile with diethyl phosphite under the optimized reaction conditions (Fig. 6). After 1 h in each run, the catalyst was easily recovered from the reaction mixture by centrifugation and reused after washing with EtOAc and drying. As seen in Fig. 6, Py-GO showed excellent catalytic performance upon at least six runs. FT-IR spectrum of the catalyst after six times reuse (Fig. 7) was compared with that of the fresh catalyst (Fig. 1b). Comparison of the FT-IR spectra of the fresh and reused catalyst persuasively validates that the structure of the Py-GO remains unchanged after the coupling reaction (Fig. 7). Furthermore, elemental analysis of Py-GO was carried out after six times reuse and the results showed that the loading amount of the catalyst remained intact.

To check whether any pyridine leached out from the solid catalyst to the solution, after proceeding of 60% of the coupling



Fig. 6 Reusability of the Py–GO in the coupling reaction of benzaldehyde, malononitrile and diethyl phosphite under the optimized reaction conditions.



Fig. 7 FT-IR spectrum of Py-GO after six times reuse.

reaction of benzaldehyde, malononitrile and diethyl phosphite in water at 100 °C, the mixture was centrifuged to remove the solid catalyst. Then the mother solution was allowed to react for another 3 h under the same reaction conditions. In the absence of the catalyst, any increase in the conversion value was not detected. It demonstrated that any pyridine leaching from Py– GO to the solution was not occurred and the present catalysis was heterogeneous in nature.

A plausible mechanism for the one-pot reaction of aldehydes, malononitrile and diethyl phosphite in the presence of Py–GO is depicted in Scheme 3. The process represents a typical cascade reaction by double-activation. In the initial step of the catalytic cycle, the acid sites present in the GO activate the carbonyl group in the aldehyde and the basic sites activate the malononitrile to form the Knoevenagel product. In the second step, the cyanogroup in the Knoevenagel product were activated by the acid sites in the catalyst. Diethyl phosphite was deprotonated by basic sites of Py–GO. The activated α , β -unsaturated malonate underwent Michael addition with deprotonated phosphorus nucleophile to give the corresponding β -phosphonomalonate.

In order to show the cooperative behaviour of intrinsic carboxylic acids and pyridine active sites on the same framework of Py–GO in these reactions, we have performed the one-pot reaction of benzaldehyde, malononitrile, and diethyl phosphite in the presence of a catalytic amount of solid catalysts (3 mol%)



Scheme 3 A plausible mechanism for the one-pot reaction of aldehydes, malononitrile and diethyl phosphite catalyzed by Py–GO.

Table 4 Comparison of the catalytic activity of Py–GO with various reported acidic and basic catalysts for the synthesis of β -phosphonomalonate 1

Entry	Catalyst	Time (h)	Yield ^a (%)	TON^b	TOF
1	NPS-γ-Fe ₂ O ₃	5	20	6	1
2	γ-Fe ₂ O ₃ -La(OTf) ₂	3	40	13	4
3	HClO ₄ -SiO ₂	10	20	6	0.6
4	AP-SiO ₂	5	10	3	0.6
5	Py-\gamma-Fe ₂ O ₃	3	55	18	6
6	Piperidine-MNPs	3	40	13	4
7	Piperazine-MNPs	3	58	19	6
8	$Py-GO^d$	1	90	30	30

^{*a*} Isolated yield, reaction conditions: benzaldehyde (1 mmol), malononitrile (1 mmol), diethyl phosphite (2 mmol), catalyst (3 mol%), temperature = 100 °C. ^{*b*} TON = turnover number = ratio of moles of product to moles of catalyst. ^{*c*} TOF = turnover frequency = TON per hour. ^{*d*} This work.

including acidic [*n*-propylsulfonated- γ -Fe₂O₃ (NPS- γ -Fe₂O₃),^{21a} γ -Fe₂O₃-La(OTf)₂ (ref. 21*b*) and HClO₄/SiO₂ (ref. 20*c*)] and basic catalysts [3-aminopropylated-SiO₂ (AP-SiO₂),^{21c} Py- γ -Fe₂O₃,^{23c} piperidine- γ -Fe₂O₃ and piperazine- γ -Fe₂O₃ (ref. 21*d*)] (Table 4). As is evident from Table 4, Py–GO as an acid–base bifunctional catalyst is the most effective catalyst in terms of TON and TOF leading to the formation of β -phosphonomalonates.

Experimental

Chemicals were purchased from Merck Chemical Company. NMR spectra were recorded on a Bruker Advance DPX-400 and 250 in CDCl₃ as solvent and TMS as internal standard. The purity of the products and the progress of the reactions were accomplished by TLC on silica-gel polygram SILG/UV254 plates. FT-IR spectra were recorded on a Shimadzu Fourier Transform Infrared Spectrophotometer (FT-IR-8300). TEM analysis was performed using TEM microscope (Philips CM30). Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were determined by using a SEM Phenom, model PROX. Thermogravimetric analysis (TGA) was performed using a Shimadzu thermogravimetric analyzer (TG-50). Elemental analysis was carried out on a Costech 4010 CHNS elemental analyzer. Power X-ray diffraction (XRD) was performed on a X'Pert Pro MPD diffractometer with Cu K α (λ = 0.154 nm) radiation. The UV-Vis spectra were carried out by using a Shimadzu UV-160 A spectrophotometer.

Synthesis of graphene oxide (GO)

A 9 : 1 mixture of concentrated H_2SO_4/H_3PO_4 (360 : 40 mL) was added to a mixture of graphite flakes (3.0 g) and KMnO₄ (18.0 g). The reaction was then heated to 50 °C and stirred for 12 h. The reaction was cooled to rt and poured onto ice (~400 mL) with 30% H_2O_2 (3 mL). Finally, the resulting oxidized product was collected by centrifuging, washing abundantly with 5% HCl solution and deionized water and dried under vacuum.

Synthesis of mercapto-functionalized GO

A mixture of GO (2 g) in toluene (40 mL) was sonicated for 30 min. 3-Mercaptopropyl trimethoxysilane (0.5 mL) was added to the dispersed GO in toluene, slowly heated to 105 °C and stirred at this temperature for 20 h. The resulting mercapto-functionalized GO was centrifuged, washed 3 times with methanol, ethanol and $\rm CH_2Cl_2$ and dried under vacuum.

Synthesis of pyridine-grafted GO (Py-GO)

3-(Chloromethyl)pyridine hydrochloride (0.15 g) and triethylamine (0.13 mL) were added to mercapto-functionalized GO (1.7 g) in toluene (15 mL), and the mixture was refluxed for 18 h. The solid material was then centrifuged, washed with water, methanol, CH_2Cl_2 and dried under vacuum.

General procedure for the synthesis of βphosphonomalonates

A mixture of aldehyde (1 mmol), malononitrile (1 mmol), diethyl phosphite (2 mmol) and Py–GO (3 mol%) was refluxed at 100 °C for an appropriate time (Table 2). The catalyst was separated by centrifugation. The supernatant was extracted with ethyl acetate (3 \times 10 mL). The organic layer was dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure, and the resulting product (1–15) was purified by chromatography on silica (*n*-hexane/EtOAc: 1/1).

Conclusion

We have successfully synthesized a new inexpensive and reusable acid–base bifunctional catalyst by postgrafting of pyridine onto GO. This pyridine-grafted GO was successfully used as an acid–base cooperative catalyst for the one-pot synthesis of β -phosphonomalonates *via* cascade Knoevenagel–phospha Michael addition reaction of aldehydes, malononitrile and dialkyl phosphites in water. Efficiency and reusability of the catalyst and using aqueous conditions make this protocol a green process for the synthesis of β -phosphonomalonates in good to high yields. Employment of odourless dialkyl phosphite, which fulfils the criteria of atom economy, instead of nasty smell trialkyl phosphite is the other advantage of this protocol.

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