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DOI: 10.1039/C6RA19579B

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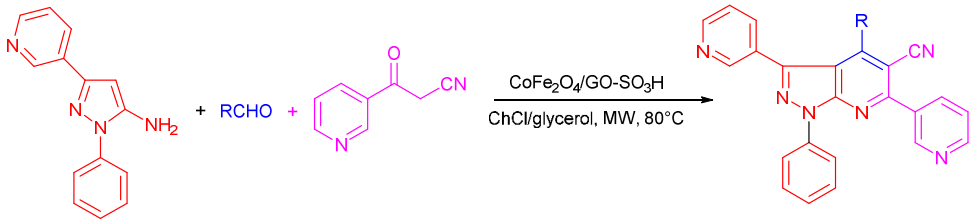
Graphical Abstract:

Magnetically separable graphene oxide anchored sulfonic acid: a novel, high efficient and recyclable catalyst for one-pot synthesis of 3,6-di(pyridin-3-yl)-1*H*-pyrazolo[3,4-*b*]pyridine-5-carbonitriles in deep eutectic solvent under microwave irradiation

Mo Zhang, Peng Liu, Yu-Heng Liu,* Ze-Ren Shang, Hai-Chuan Hu, Zhan-Hui Zhang*

A magnetic separable graphene oxide anchored sulfonic acid catalyst was prepared and applied for the synthesis of 3,6-di(pyridin-3-yl)-1*H*-pyrazolo[3,4-b]pyridine-5-carbonitriles via one-pot, three-component reaction of 1-phenyl-3-(pyridin-3-yl)-1H-pyrazol-5-amine with 3-oxo-3-(pyridin-3-yl)propanenitrile and aldehydes in choline chloride/glycerol under microwave irradiation.



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Magnetically separable graphene oxide anchored sulfonic acid: a novel, high efficient and recyclable catalyst for one-pot synthesis of 3,6-di(pyridin-3-yl)-1*H*-pyrazolo[3,4-*b*]pyridine-5-carbonitriles in deep eutectic solvent under microwave irradiation

Mo Zhang,[a] Peng Liu,[a] Yu-Heng Liu,[*a,b] Ze-Ren Shang,[a] Hai-Chuan Hu,[a] Zhan-Hui Zhang[*a]

Magnetically separable graphene oxide anchored sulfonic acid (Fe_3O_4-GO-SO_3H) nanoparticles were prepared and characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscope (TEM), and vibrating sample magnetometry (VSM) techniques. The synthesized heterogeneous material was found to exhibit high catalytic activity for synthesis of 3,6-di(pyridin-3-yl)-1*H*-pyrazolo[3,4-*b*]pyridine-5-carbonitriles via one-pot, three-component reaction of 1-phenyl-3-(pyridin-3-yl)-1*H*-pyrazol-5-amine with 3-oxo-3-(pyridin-3-yl)propanenitrile and aldehydes using choline chloride (ChCl)/glycerol as a green solvent under microwave irradiation. The catalytic system can be successfully reused eight times with no significant loss of its catalytic performance.

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DOI: 10.1039/C6RA19579B

Introduction

Pyrazolo[3,4-*b*]pyridines are a promising class of heterocyclic compounds and have received much attention due to their promising applications in diverse areas, such as pharmaceuticals,[1] dyes[2] and luminescence materials.[3] In addition, the compounds with pyrazolo[3,4-*b*]pyridine scaffold have also been reported to possess diverse biological activities, such as antimicrobial,[4] anti-biofilm,[5] antimicrobial,[6] and antioxidant[7], and they are also used as FGFR kinase inhibitors,[8] c-Met inhibitors,[9] potent dual orexin receptor antagonists,[10] anticancer agents[11] as well as corrosion inhibitors for metals and alloys in acid medium.[12] Several synthetic methods for the construction of these compounds and their structural analogues have been developed,[13] for example (1) condensation of pyrazole-5-amine derivatives and activated carbonyl groups in refluxing acetic acid,[1] (2) three-component reaction of aminopyrazoles, aldehydes, and (a) cycloketones,[14] (b) 1,3-dicarbonyl compounds,[15] (c) *N*-methyl-1-(methylthio)-2-nitroprop-1-en-1-amine,[16] (d) 3-(cyanoacetyl)indole,[17] (e) ethyl cyanoacetate,[18] (3) three-component reaction of aminopyrazole, isatin, and alkyl cyanoacetate using Et_3N as catalyst,[19] (4) four-component reaction of pyrazol-5-amines, aromatic amines, 4-hydroxy-6-methyl-2*H*-pyran-2-one, and cyclohexane-1,3-diones in the presence of acetic acid,[20] (5) A pseudo six-component reaction of ethyl acetoacetate, aldehyde, hydrazine and ammonium acetate.[21] Based on the importance of these structural frameworks, the further development of a versatile, more environmentally benign and practical protocol for synthesis of functionalized pyrazolo[3,4-*b*]pyridines using simple and readily available starting materials is highly desirable and valuable.

Due to its intriguing properties such as large surface area, high mechanical strength, unique layered structure, excellent physicochemical stability, strong covalent character and high flexibility, graphene oxide (GO) has been demonstrated to be good catalyst support for many catalytic applications.[22] The availability of oxygen-containing functional groups, such as hydroxyl, carboxyl, epoxide and carboxylic acid, on the GO sheets allows them to be functionalized with various organic and inorganic materials in covalent or non-covalent approaches. These oxygen functional groups in GO afford mild acidic and oxidative properties, and further functionalization of GO can make stronger acid sites on these carbons.[23] In this regard, sulfonic acid-functionalized GO materials have been developed and successfully used in organic transformations.[24-27] Despite their excellent catalytic performance in some organic reactions, traditional separation methods such as filtration or centrifugation were usually required for the recycling of catalysts. In address this issue, magnetic separation occurred as a feasible solution because it reduces loss of catalyst and makes the recovery and reusability of catalyst easier by magnetic force upon completion of the reaction.[28-31] Therefore, the incorporation of magnetic components on GO is most favoured and will provide high catalytic activity and improve separation efficiency.[32-33] Also, since conventional harmful organic solvents make several troubles relating to environmental pollution, replacement of these toxic solvents by green and environmentally benign media is also of key relevance.[34] Recently, deep eutectic solvents (DESs) have emerged as viable alternatives to traditional volatile organic solvents due to their advantages of low melting points, negligible vapour pressure, low flammability, biodegradable, simple and inexpensive preparation as well as ease of recyclability.[35-36] In addition, microwave-assisted organic reaction has become particularly

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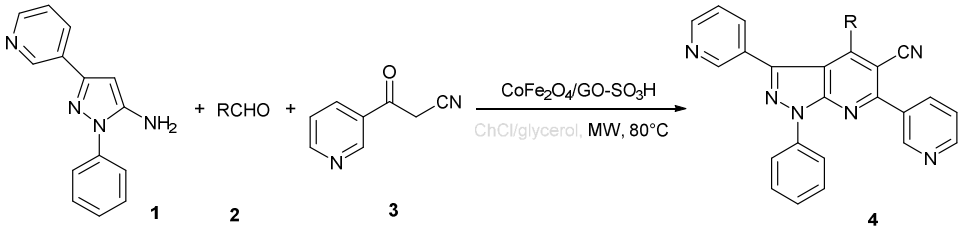
popular in recent years due to them offering the shorter reaction time and efficient routes for a large number of organic reactions.[37]

In consideration of these superiorities and based on our research interest in developing environmentally benign synthetic methodologies,[38-39] herein, we report for the first time, magnetically separable graphene oxide anchored sulfonic acid as catalyst for the synthesis of 3,6-di(pyridin-3-yl)-1*H*-pyrazolo[3,4-*b*]pyridine-5-carbonitriles via one-pot, three-component reaction of 1-phenyl-3-(pyridin-3-yl)-1*H*-pyrazol-5-amine with 3-oxo-3-(pyridin-3-yl)propanenitrile and aldehydes in choline chloride (ChCl)/glycerol under microwave irradiation (Scheme 1).



Scheme 1 Synthesis of 3,6-di(pyridin-3-yl)-1*H*-pyrazolo[3,4-*b*]pyridine-5-carbonitrile derivatives.

Results and discussion

As shown in Scheme 2, the catalyst $CoFe_2O_4$-GO-SO_3H was prepared in a three-step process. At first, graphene oxide (GO) was synthesized by oxidation of graphite powder according to a slightly modified Hummer's method. Then, the synthesized graphene oxide was suspended into water and treated with $FeCl_3$, $CoCl_2$ to obtain $CoFe_2O_4$/GO nanocomposites. High specific surface area of GO along with easily accessible oxygen-conating groups on GO sheets provided a better support for anchoring of $CoFe_2O_4$ NPs. Further the addition of chlorosulfonic acid into the $CoFe_2O_4$/GO suspension in dichloromethane yielded magnetically separable $CoFe_2O_4$-GO-SO_3H nanocomposites.

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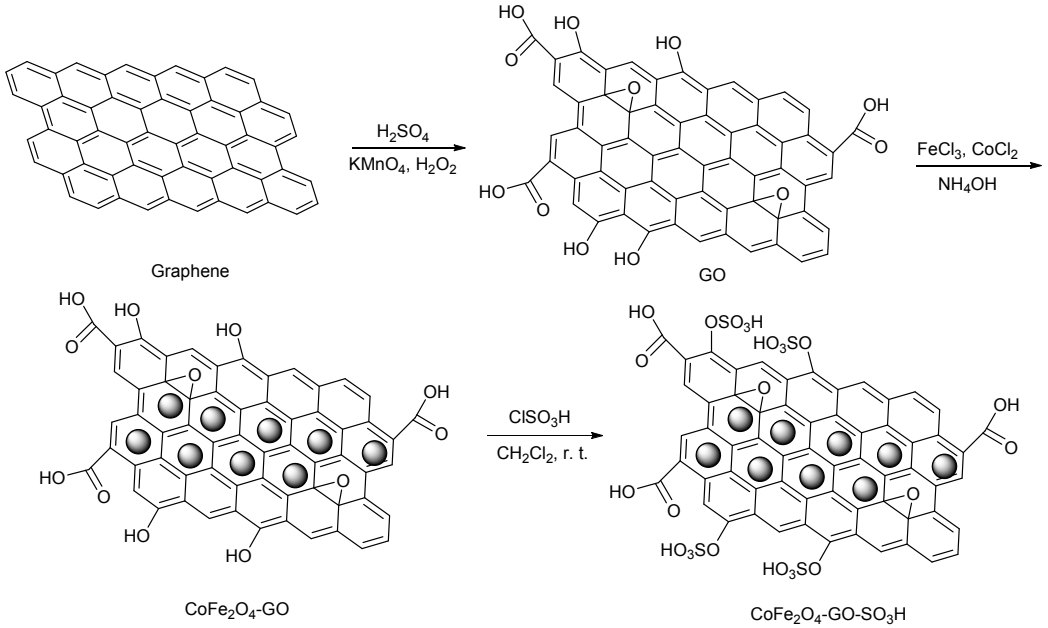

Scheme 2 Preparation of $CoFe_2O_4$-GO-SO_3H

The X-ray diffraction pattern of the $CoFe_2O_4$-GO-SO_3H nanoparticles is shown in Fig. 1. The main peaks in $CoFe_2O_4$-GO-SO_3H located at $2\theta = 18.20^o$, 30.10^o, 35.50^o, 43.10^o, 57.00^o and 62.60^o can be indexed to (111), (220), (311), (400), (511) and (440) planes of the cubic $CoFe_2O_4$ spinel structure (JCPDS 22-1086).[40] It is apparent that the crystal structure of the $CoFe_2O_4$ core was still well-maintained after functionalization.[41] However, no GO peaks were observed in XRD spectrum of $CoFe_2O_4$-GO-SO_3H indicating that GO was exfoliated due to crystal growth of $CoFe_2O_4$ between interlayer of GO sheets.[26] The prepared particle diameter are found to be 28.6 nm using the Debye–Scherrer's equation: $d = 0.89\lambda/\beta\cos\theta$, which was derived from full-width at half-maximum of the most intense peak corresponding to the (311) plane located at 43.10^o. The elemental composition of the $CoFe_2O_4$-GO-SO_3H sample was determined by energy dispersive spectrum (EDS) analysis. As it can be seen in Fig. 2, Fe, Co, O, C and S species have been observed in the catalyst. The content of the $CoFe_2O_4$ in $CoFe_2O_4$-GO and $CoFe_2O_4$-GO-SO_3H was found to be 85.75% and 78.48 wt%, respectively, as determined by atomic absorption spectroscopy (AAS).

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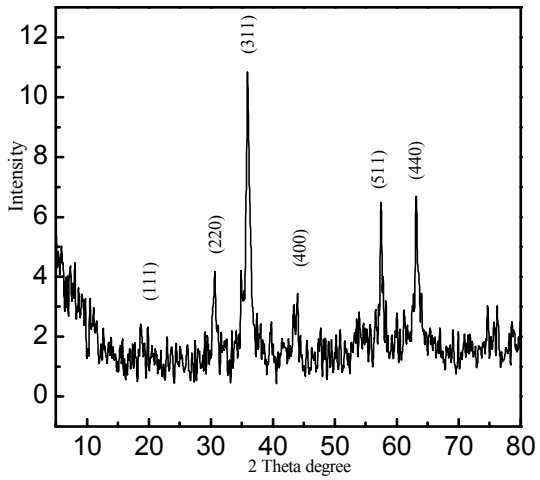

Fig. 1 XRD pattern of graphite (a), GO (b), and Fe_3O_4/GO-Mo (c).

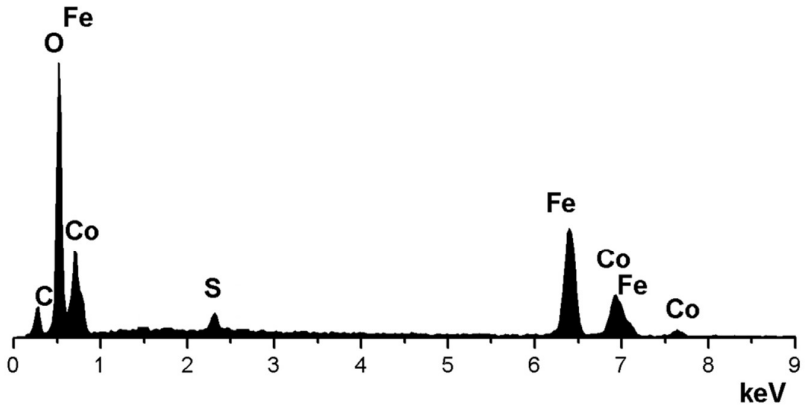

Fig. 2 EDS spectrum of Fe_3O_4/GO-Mo

The SEM and TEM images of $CoFe_2O_4$, $CoFe_2O_4$-GO and $CoFe_2O_4$-GO-SO_3H are represented in Fig. 3 and Fig. 4, respectively. These images confirm the formation of nanoparticles and that these nanoparticles are uneven-sized particles and most of the particles have a quasi-spherical shape. The TEM image of $CoFe_2O_4$-GO shows that $CoFe_2O_4$ nanoparticles distributed homogeneously throughout the graphene oxide surface. The TEM image of the $CoFe_2O_4$-GO shows that the graphene oxide sheets are decorated with large quantity of $CoFe_2O_4$. The average diameter of magnetic cores was estimated to be about 28.0 nm, which was in good agreement with the particle sizes calculated using the Debye–Scherrer's equation by XRD data.

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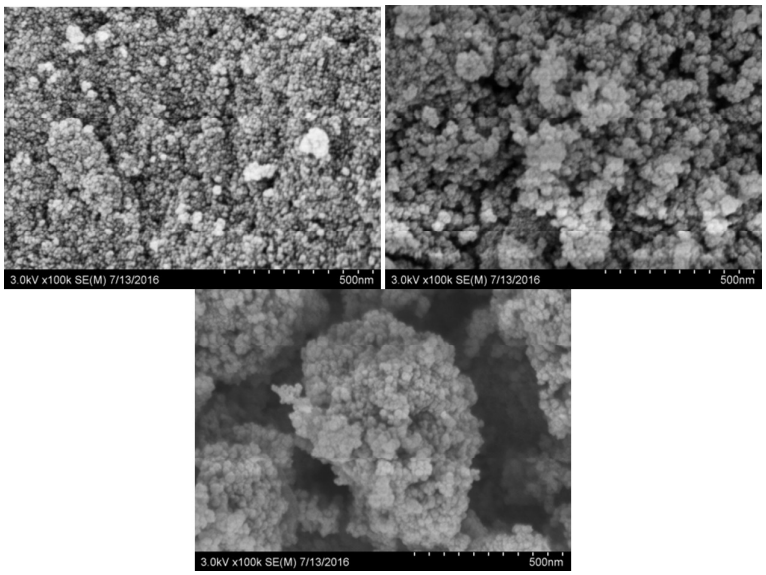
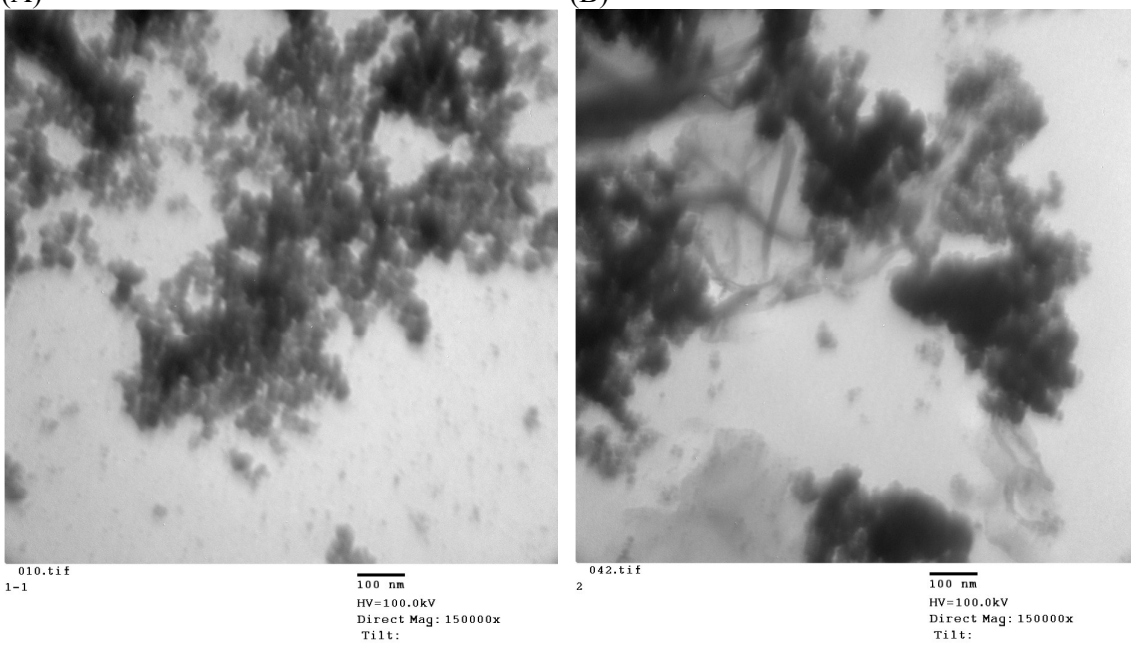


Fig. 3 SEM images of $CoFe_2O_4$ (left), $CoFe_2O_4$-GO (middle) and $CoFe_2O_4$-GO-SO_3H (right).

(A) (B)



(C)

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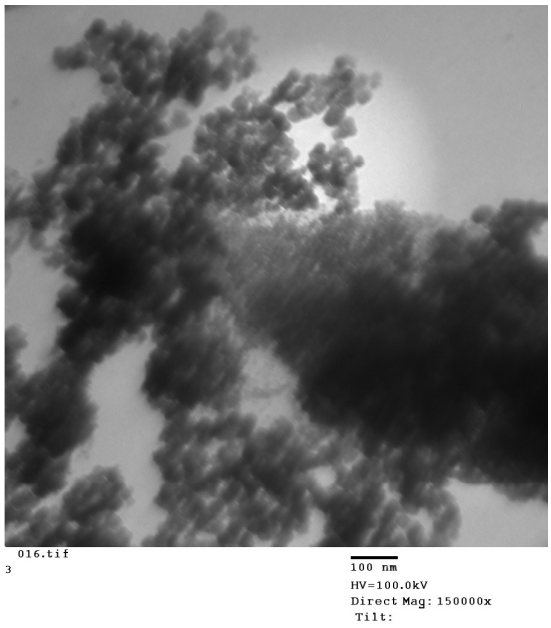

Fig. 4 TEM image of $CoFe_2O_4$ (A), $CoFe_2O_4$-GO (B) and $CoFe_2O_4$-GO-SO_3H (C).

The magnetic property of as synthesized $CoFe_2O_4$-GO-SO_3H was measured by using vibrating sample magnetometery (VSM) at room temperature. Magnetic measurement indicates the supermagnetic nature of the prepared $CoFe_2O_4$-GO-SO_3H and the saturation magnetization value is found to be 28.2 emu g^{-1} (Fig. 5). A suitable magnetic property of the prepared $CoFe_2O_4$-GO-SO_3H meets our objectives to design a more efficient and easily separable catalyst for organic reactions.

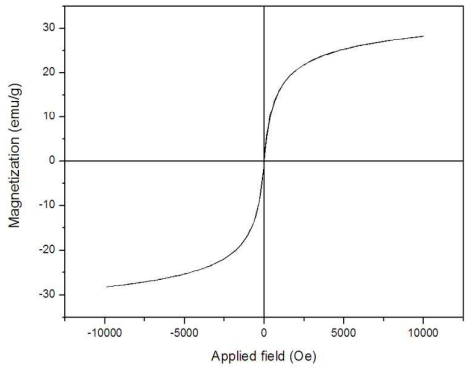

Fig. 5 Magnetization curve of $CoFe_2O_4$-GO-SO_3H.

The catalytic activity of the prepared catalyst was then evaluated in the model reaction of 1-phenyl-3-(pyridin-3-yl)-1*H*-pyrazol-5-amine, benzaldehyde and 3-oxo-3-(pyridin-3-yl)propanenitrile. As shown in Table 1, the desired product **4a** was obtained in 78% yield in the presence of $CoFe_2O_4$-GO-SO_3H in EtOH for 10 min under microwave irradiation (Table 1, entry 2). To further improve the yield, various reaction parameters such as solvents, microwave power, the amount of catalyst and temperature were evaluated systematically. Various solvents, including water, glucose, ChCl/L-(+)-tartaric acid, ChCl/glucose, ChCl/urea, ChCl/citric acid, ChCl/itaconic acid, ChCl/glycerol were investigated in the model reaction.

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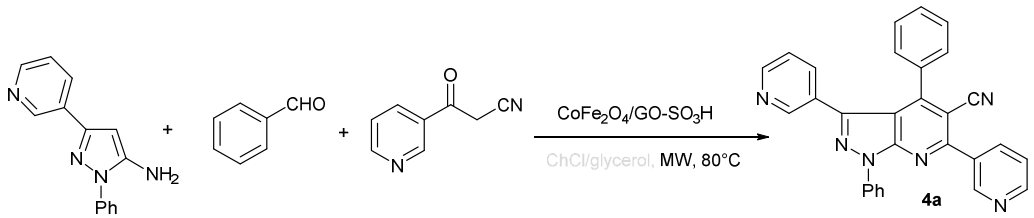
When glycerol was used, **4a** was obtained in 46% yield (entry 5). The yield of desired product was improved when deep eutectic solvent ChCl/glycerol was used. And, the product yield increased with the increasing proportion of glycerol in the deep eutectic solvent. We were pleased to find that ChCl/glycerol (1:3) was optimal and the reaction was completed with 10 min to give 95% yield of desired product (entry 13). Control experiments confirmed that, in the absence of any catalyst or the presence of $CoFe_2O_4$ or GO, the targeted product was obtained in very low yields, indicating that the acid catalyst was still playing the key role in the reaction. In addition, we found that the reaction is significantly accelerated when using microwave irradiation. The reaction under conventional heating condition needed longer time and the yield of the expected product was lower than under microwave irradiation (entry 17). The effect of microwave power on the reaction was also examined. The results showed that 700 W was the appropriate power for this reaction. Further examination of the amount of the catalyst revealed that 50 mg was the best loading for the reaction. Reducing the amount of catalyst to 30 mg led to slightly lower yield. A further increase the amount of catalyst to 80 mg did not affect the yield. A survey of the temperature was also conducted. The desired product **4a** was formed in 83% yield at 70 ^oC. And decreasing the temperature to room temperature did affect the reaction efficiency and the expected product was obtained in 35% yield (entry 22), while a higher temperature (90 ^oC, entry 26) was not advantageous for the yield either. Thus, the best result was obtained in ChCl/glycerol (1:3) at 80 ^oC in the presence of 50 mg $CoFe_2O_4$-GO-SO_3H under microwave irradiation (700 W).

As a further proof of the practical applicability of this methodology, the model reaction was scaled up to 50 mmol. The result indicated that the reaction proceeded successfully and the desired product **4a** could be obtained without decreasing the reaction efficiency (Table 1, entry 29).

Table 1 The effect of reaction condition on the reaction of 1-phenyl-3-(pyridin-3-yl)-1*H*-pyrazol-5-amine, benzaldehyde and 3-oxo-3-(pyridin-3-yl)propanenitrile[a]



Entry	Catalyst	Solvent	MW (W)	Temp (^oC)	Time (min)	Yield (%)[b]
1	no	ChCl/glycerol (1:3)	700	80	30	13
2	$CoFe_2O_4$/GO-SO_3H	no	700	80	30	12
3	$CoFe_2O_4$/GO-SO_3H	EtOH	700	reflux	10	78
4	$CoFe_2O_4$/GO-SO_3H	H_2O	700	80	10	25
5	$CoFe_2O_4$/GO-SO_3H	Glucose	700	80	10	46
6	$CoFe_2O_4$/GO-SO_3H	ChCl/L-(+)-tartaric acid (2:1)	700	80	10	37

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7	$CoFe_2O_4$/GO-SO_3H	ChCl/glucose	700	80	10	10
8	$CoFe_2O_4$/GO-SO_3H	ChCl/urea (1:2)	700	80	10	62
9	$CoFe_2O_4$/GO-SO_3H	ChCl/citric acid (1:2)	700	80	10	27
10	$CoFe_2O_4$/GO-SO_3H	ChCl/itaconic acid (1:1)	700	80	10	15
11	$CoFe_2O_4$/GO-SO_3H	ChCl/glycerol (1:1)	700	80	10	71
12	$CoFe_2O_4$/GO-SO_3H	ChCl/glycerol (1:2)	700	80	10	80
13	$CoFe_2O_4$/GO-SO_3H	ChCl/glycerol (1:3)	700	80	10	95
14	$CoFe_2O_4$	ChCl/glycerol (1:3)	700	80	20	26
15	GO	ChCl/glycerol (1:3)	700	80	20	40
16	$CoFe_2O_4$/GO	ChCl/glycerol (1:3)	700	80	10	52
17	$CoFe_2O_4$/GO-SO_3H	ChCl/glycerol (1:3)	0	80	120	86
18	$CoFe_2O_4$/GO-SO_3H	ChCl/glycerol (1:3)	400	80	40	91
19	$CoFe_2O_4$/GO-SO_3H	ChCl/glycerol (1:3)	500	80	15	91
20	$CoFe_2O_4$/GO-SO_3H	ChCl/glycerol (1:3)	600	80	15	93
21	$CoFe_2O_4$/GO-SO_3H	ChCl/glycerol (1:3)	800	80	10	95
22	$CoFe_2O_4$/GO-SO_3H	ChCl/glycerol (1:3)	700	20	60	35
23	$CoFe_2O_4$/GO-SO_3H	ChCl/glycerol (1:3)	700	30	60	42
24	$CoFe_2O_4$/GO-SO_3H	ChCl/glycerol (1:3)	700	50	20	68
25	$CoFe_2O_4$/GO-SO_3H	ChCl/glycerol (1:3)	700	70	10	83
26	$CoFe_2O_4$/GO-SO_3H	ChCl/glycerol (1:3)	700	90	10	95
27[c]	$CoFe_2O_4$/GO-SO_3H	ChCl/glycerol (1:3)	700	80	10	75
28[d]	$CoFe_2O_4$/GO-SO_3H	ChCl/glycerol (1:3)	700	80	10	95
29[e]	$CoFe_2O_4$/GO-SO_3H	ChCl/glycerol (1:3)	700	80	10	94

[a] Reaction was performed with 1-phenyl-3-(pyridin-3-yl)-1*H*-pyrazol-5-amine (1 mmol), benzaldehyde (1 mmol) and 3-oxo-3-(pyridin-3-yl)propanenitrile (1 mmol), catalyst (50 mg) in 1 ml solvent otherwise specified in the Table; [b] Isolated yields; [c] Catalyst (30 mg); [d] Catalyst (80 mg); [e] The reaction was carried out in 50 mmol scale.

With the optimized reaction conditions established, the scope and limitation of this protocol were further explored and representative results are summarized in Table 2. The $CoFe_2O_4$-GO-SO_3H-catalyzed three-component reaction showed good functional group tolerance and has proved to be a general method for the synthesis of 3,6-di(pyridin-3-yl)-1*H*-pyrazolo[3,4-*b*]pyridine-5-carbonitriles. A number of benzaldehydes, whether substituted by electron-rich or electron-poor groups on aromatic ring, reacted with 1-phenyl-3-(pyridin-3-yl)-1*H*-pyrazol-5-amine and 3-oxo-3-(pyridin-3-yl)propanenitrile to furnish the desired products **4a**-**4l** in high yields. Compared with the result of 4-methoxybenzaldehyde (**4d**, 95% yield), the yield of the reaction with 2-methoxybenzaldehyde (**4b**, 85% yield) was lower, which may be attributed to the steric hindrance. Delightfully, heteroaryl aldehydes, such as thiophene-2-carbaldehyde, isonicotinaldehyde and 1*H*-indole-3-carbaldehyde, were also suitable for this reaction, providing the

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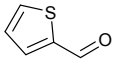
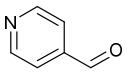
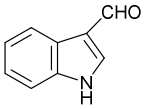
corresponding products **4m**-**4o** in high yields. Unfortunately, aliphatic aldehydes, such as cyclohexanecarbaldehyde and butyraldehyde, was also tested for this three-component reaction, the target product was not formed under same reaction conditions.

Table 2 Synthesis of 3,6-di(pyridin-3-yl)-1*H*-pyrazolo[3,4-*b*]pyridine-5-carbonitriles

Entry	R	Product	Time (min)	Yield (%)[a]	mp (^{o}C)
1	PhCHO	**4a**	10	94	134-135
2	2-$MeOC_6H_4CHO$	**4b**	15	85	256-257
3	3-$MeOC_6H_4CHO$	**4c**	10	93	246-247
4	4-$MeOC_6H_4CHO$	**4d**	10	95	230-232 (231-233)[6]
5	4-MeC_6H_4CHO	**4e**	10	94	188-190
6	3-ClC_6H_4CHO	**4f**	10	93	220-221
7	4-ClC_6H_4CHO	**4g**	10	95	223-225
8	3-BrC_6H_4CHO	**4h**	10	95	229-230
9	4-BrC_6H_4CHO	**4i**	10	95	138-139
10	2-$NO_2C_6H_4CHO$	**4j**	15	84	258-259
11	3-$NO_2C_6H_4CHO$	**4k**	10	94	230-231
12	4-$NO_2C_6H_4CHO$	**4l**	10	93	118-120
13		**4m**	10	89	127-128
14		**4n**	10	90	198-199
15		**4o**	10	88	230-231

[a] Isolated yield.

A plausible mechanism for the formation of 3,6-di(pyridin-3-yl)-1*H*-pyrazolo[3,4-*b*]pyridine-5-carbonitriles (**4**) in the presence of $CoFe_2O_4$-GO-SO_3H is depicted in Scheme 3. The formation of these products can be visualised by initial Knoevenagel condensation of aldehyde (**2**) and 3-oxo-3-(pyridin-3-yl)propanenitrile (**3**) to afford the intermediate (**I**). The $CoFe_2O_4$-GO-SO_3H activated intermediate **I**, which subsequently undergoes Michael addition of 1-phenyl-3-(pyridin-3-yl)-1*H*-pyrazol-5-amine (**1**) via attack of the nucleophilic C-4 of the pyrazolamine, followed by cyclization and loss of H_2O to afford the desired products **4**. It is pertinent to note that $CoFe_2O_4$-GO-SO_3H catalyses the above transformation efficiently, whilst either $CoFe_2O_4$ or GO give the product in low yield (Table 1). This suggests that the presence of sulfonic acid functional group in the catalyst molecule is crucial for the success of this transformation.

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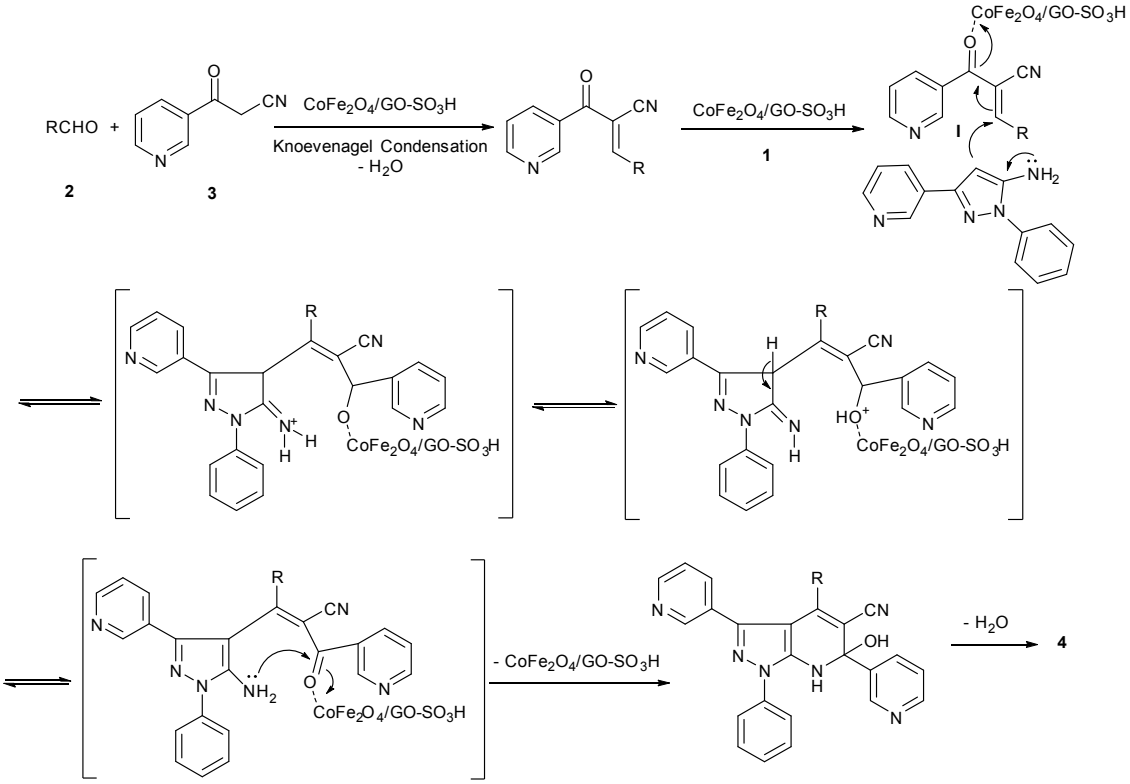

Scheme 3 Plausible mechanism for synthesis of **4**

Finally, the recovery and reusability of catalytic system were investigated in model reaction under the optimized reaction conditions. After completion of the reaction, the reaction mixture was cooled to room temperature, then, the catalyst was separated magnetically, and washed with ethyl acetate and water, dried under vacuum. Then, water was added to reaction mixture to dissolve DES. The formed solid product was collected by filtration. The water of the aqueous phase containing the DES, was evaporated under reduced pressure in order to recover the DES. The recover DES and catalyst were reused in model reaction to the next round. The catalytic system was found to be effective for up to eight consecutive runs without any significant loss in its catalytic activity and stability (Fig. 6).

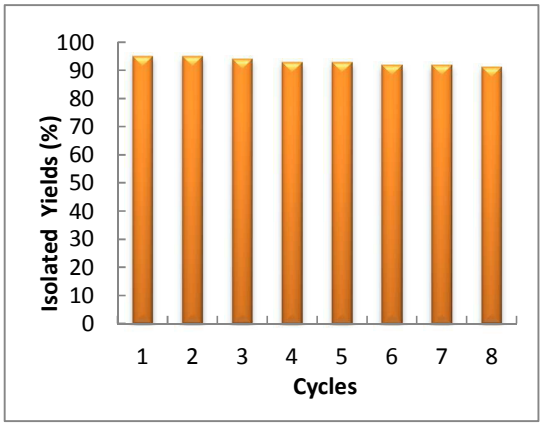

Fig. 6 Reusability of the $CoFe_2O_4$-GO-SO_3H in ChCl/glycerol catalytic system in the model reaction.

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Conclusion

In summary, a novel magnetically separable graphene oxide anchored sulfonic acid catalyst has been successfully prepared and used as an efficient heterogeneous catalyst for synthesis of 3,6-di(pyridin-3-yl)-1*H*-pyrazolo[3,4-*b*]pyridine-5-carbonitriles via one-pot, three-component reaction of 1-phenyl-3-(pyridin-3-yl)-1*H*-pyrazol-5-amine, 3-oxo-3-(pyridin-3-yl)propanenitrile and aldehydes in ChCl/ glycerol under microwave irradiation. The main highlights of this methodology are simplicity in the catalyst preparation, high yields, short reaction times, eco-friendliness, an easy work-up procedure, avoidance of toxic solvent, and applicability for large-scale synthesis. Particularly, catalytic system could be easily recovered and reused eight successive times without considerable loss of its activity, conferring great potential for industrial application.

Experimental section

General information

All reagents and materials used in this work were obtained from commercial sources and utilized as received without further purification. Microwave irradiation was carried out with a XH-300A Microwave Synthesizers from Beijing Science and Technology Development Co., Ltd, China. Melting points were measured with an X-5 apparatus and were uncorrected. ^{1}H NMR and ^{13}C NMR (500 and 125 MHz, respectively) spectra were acquired on a Bruker Avance III 500 spectrometer using TMS as internal standard. The nanostructures were characterized by a PANalytical X'Pert Pro X-ray power diffraction (XRD) diffractormeter employing a scanning rate of 0.05 ^{o}/s from 20 to 80º using Cu-Kα radiation as the X-ray source. Transmission electron microscope (TEM) and energy dispersive X-ray spectroscopy (EDX) analyses were carried out on a Hitachi H-7650 instrument operating at 80 KV. Scanning electron microscope (SEM) images of samples were obtained from a Hitachi S-4800 instrument. Magnetic properties of the samples were measured using a Physical Property Measurement System (PPMS-6700).

Preparation of graphene oxide (GO)[42]

Graphene oxide was prepared by the modified procedure reported by Hummers and Offeman.[43] In a typical procedure, 36.0 mL of concentrated H_2SO_4 (95%) was added into a round-bottomed flask and cooled in an ice bath. Then, 1 g of graphite powder and 300 mg of $NaNO_3$ were added with vigorous stirring to avoid agglomeration. After the graphite powder was well dispersed, 5.0 g of $KMnO_4$ was slowly added over 2 h under stirring at 8–10°C. The ice bath was then removed and the mixture was stirred at room temperature for 8 h. After that, 45 mL of distilled water was added, and the temperature was maintained at 95 °C for 1 h. After the temperature was reduced to 50 °C, 10.0 mL of 30 % H_2O_2 was added to the mixture so as to eliminate the excess MnO_4^-. The resulting GO was separated by filtration, washed successively with distilled water and 5% HCl solution repeatedly until sulfate could not be detected with $BaCl_2$, and then finally dried under vacuum at 50 °C for 24 h.

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Synthesis of $CoFe_2O_4$-GO nanocomposite

0.1 g GO was dispersed into 100 mL of deionized water with sonication for 30 min. Then, the aqueous solution of 2.70 g of $FeCl_3 \cdot 6H_2O$ and 1.19 g of $CoCl_2 \cdot 6H_2O$ (50 ml) was slowly added into the mixture. The mixture was stirred strongly at 80 °C for 2 h, and then 25 % ammonia solution was added until the pH increased to 12. The reaction mixture was then continually stirred under refluxing condition for 1 h. After cooling the solution to room temperature, the $CoFe_2O_4$-GO NPs were collected using a permanent magnet and washed with water and ethanol, then dried under vacuum at 60 ^oC for 24 h.

Preparation of $CoFe_2O_4$-GO-SO_3H

$CoFe_2O_4$-GO-SO_3H was prepared by the reaction of $CoFe_2O_4$-GO and chlorosulfonic acid. In an ice bath, $CoFe_2O_4$-GO (1.0 g) was suspended in dichloromethane (5 mL) in a 100 mL round bottom flask equipped with a gas outlet tube and a dropping funnel containing a solution of chlorosulfonic acid (0.5 g, 4.3 mmol) in dichloromethane (15 mL). With continuous stirring, chlorosulfonic acid solution was added dropwise to the mixture during 30 min. After the complete of the addition, the mixture was stirred for 1 h at room temperature until all HCl was removed from reaction vessel. Then, the catalyst was separated by magnetic decantation and washed several times with CH_2Cl_2 and ethanol, and dried under vacuum at 60 °C for 2 h.

General procedure for synthesis of 3,6-di(pyridin-3-yl)-1*H*-pyrazolo[3,4-*b*]pyridine-5-carbonitriles

A mixture of 1-phenyl-3-(pyridin-3-yl)-1*H*-pyrazol-5-amine (1 mmol), 3-oxo-3-(pyridin-3-yl)propanenitrile (1 mmol), and aldehydes (1 mmol) and Fe_3O_4-GO-SO_3H (50 mg) in ChCl/glycerol (1:2, 1 ml) was stirred under microwave irradiation at 80 °C for an appropriate time. After completion of the reaction (monitored by TLC), the mixture was cooled to room temperature. The catalyst was separated using an external magnet and washed with ethyl acetate followed by water, and dried under vacuum and reused directly for the next round of reaction. After that, water (5 mL) was added to reaction mixture to dissolve DES. The formed solid product was collected by filtration and recrystallized from ethanol to afford the pure product.

Characterization data

1,4-Diphenyl-3,6-di(pyridin-3-yl)-1*H*-pyrazolo[3,4-*b*]pyridine-5-carbonitrile (**4a**). Light yellow crystals; ^{1}H NMR (DMSO-d_6, 500 MHz) δ = 7.15 (dd, *J* = 7.5, 4.5 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.44-7.47 (m, 5H), 7.65-7.70 (m, 3H), 8.30 (d, *J* = 7.5 Hz, 2H), 8.35 (s, 1H), 8.44-8.47 (m, 2H), 8.83 (d, *J* = 4.5 Hz, 1H), 9.21 (d, *J* = 2.0 Hz, 1H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz) δ = 103.1, 113.0, 117.6, 122.4, 123.1, 124.0, 127.8, 128.7, 129.9, 130.5, 133.4, 133.9, 136.5, 137.4, 138.4, 144.6, 149.6, 150.2, 150.3, 151.5, 152.8, 158.4 ppm; HRMS (ESI, m/z): calcd. for $C_{29}H_{19}N_6$ $[M+H]^+$: 451.1671; found: 451.1665.

4-(2-Methoxyphenyl)-1-phenyl-3,6-di(pyridin-3-yl)-1*H*-pyrazolo[3,4-*b*]pyridine-5-carbonitrile (**4b**). Light yellow crystals; ^{1}H NMR (DMSO-d_6, 500 MHz) δ = 3.36 (s, 3H), 6.82 (d, *J* = 8.5 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 7.16 (dd, *J* = 7.5, 4.5 Hz, 1H), 7.43-7.51 (m, 4H), 7.64-7.69 (m, 3H), 8.29 (d, *J* = 8.0 Hz, 2H), 8.39 (s, 1H), 8.44 (d, *J* = 8.0 Hz, 1H), 8.48 (d, *J* = 4.5 Hz, 1H), 8.81 (d, *J* = 4.5 Hz, 1H), 9.20 (s, 1H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz) δ = 55.6, 103.7, 111.7, 113.3, 121.1, 122.5, 123.0, 124.0, 127.9, 130.0,

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DOI: 10.1039/C6RA19579B

131.2, 132.7, 134.0, 136.1, 137.5, 138.4, 145.0, 149.2, 149.8, 150.2, 151.4, 156.2, 158.5 ppm; HRMS (ESI, m/z): calcd. for $C_{30}H_{21}N_6O$ $[M+H]^+$: 481.1777; found: 481.1817.

4-(3-Methoxyphenyl)-1-phenyl-3,6-di(pyridin-3-yl)-1*H*-pyrazolo[3,4-*b*]pyridine-5-carbonitrile (**4c**). Yellow crystals; ^{1}H NMR (DMSO-d_6, 500 MHz) δ = 3.54 (s, 3H), 6.94 (s, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 7.5 Hz, 1H), 7.19 (dd, *J* = 7.5, 4.5 Hz, 1H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.46-7.49 (m, 2H), 7.64-7.70 (m, 3H), 8.28 (d, *J* = 8.0 Hz, 2H), 8.38 (s, 1H), 8.45 (d, *J* = 8.0 Hz, 1H), 8.49 (d, *J* = 8.0 Hz, 1H), 8.82 (d, *J* = 4.5 Hz, 1H), 9.21 (s, 1H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz) δ = 55.6, 103.0, 115.4, 116.7, 122.1, 122.5, 123.1, 124.0, 127.9, 130.0, 134.0, 134.5, 136.5, 137.5, 138.4, 144.6, 149.5, 149.7, 150.3, 151.5, 152.5, 158.5, 159.3 ppm; HRMS (ESI, m/z): calcd. for $C_{30}H_{21}N_6O$ $[M+H]^+$: 481.1777; found: 481.1801.

4-(4-Methoxyphenyl)-1-phenyl-3,6-di(pyridin-3-yl)-1*H*-pyrazolo[3,4-*b*]pyridine-5-carbonitrile (**4d**). Light brown crystals; ^{1}H NMR (DMSO-d_6, 500 MHz) δ = 3.79 (s, 3H), 6.87 (d, *J* = 8.0 Hz, 2H), 7.20-7.24 (m, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.45-7.51 (m, 2H), 7.63-7.70 (m, 3H), 8.29 (d, *J* = 8.0 Hz, 2H), 8.36 (s, 1H), 8.44 (d, *J* = 7.5 Hz, 1H), 8.50 (d, *J* = 4.5 Hz, 1H), 8.62 (d, *J* = 4.5 Hz, 1H), 9.21 (s, 1H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz) δ = 55.9, 114.2, 117.9, 122.3, 123.1, 124.0, 125.3, 127.7, 127.9, 129.9, 131.7, 134.0, 136.6, 137.5, 138.4, 144.6, 149.6, 150.2, 151.4, 152.7, 158.5, 161.2 ppm; HRMS (ESI, m/z): calcd. for $C_{30}H_{21}N_6O$ $[M+H]^+$: 481.1777; found: 481.1797.

1-Phenyl-3,6-di(pyridin-3-yl)-4-(*p*-tolyl)-1*H*-pyrazolo[3,4-*b*]pyridine-5-carbonitrile (**4e**). Dark yellow crystals; ^{1}H NMR (DMSO-d_6, 500 MHz) δ = 2.33 (s, 3H), 7.12-7.13 (m, 3H), 7.42-7.46 (m, 2H), 7.63-7.65 (m, 3H), 7.83 (d, *J* = 7.0 Hz, 2H), 8.29-8.35 (m, 3H), 8.45-8.48 (m, 2H), 8.82 (s, 1H), 9.20 (s, 1H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz) δ = 21.6, 103.0, 113.1, 117.7, 122.4, 123.0, 127.8, 128.6, 129.2, 129.5, 129.9, 130.5, 134.0, 136.5, 137.4, 138.5, 140.4, 143.4, 144.6, 149.6, 150.2, 151.4, 153.0, 158.4, 167.7 ppm; HRMS (ESI, m/z): calcd. for $C_{30}H_{21}N_6$ $[M+H]^+$: 465.1777; found: 465.1750.

4-(3-Chlorophenyl)-1-phenyl-3,6-di(pyridin-3-yl)-1*H*-pyrazolo[3,4-*b*]pyridine-5-carbonitrile (**4f**). Light yellow crystals; ^{1}H NMR (DMSO-d_6, 500 MHz) δ = 7.21 (dd, *J* = 7.5, 4.5 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.45-7.53 (m, 5H), 7.62-7.68 (m, 3H), 8.27 (d, *J* = 8.0 Hz, 2H), 8.33 (s, 1H), 8.44 (d, *J* = 8.0 Hz, 1H), 8.49 (d, *J* = 8.0 Hz, 1H), 8.80 (d, *J* = 4.5 Hz, 1H), 9.29 (s, 1H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz) δ = 103.0, 112.9, 117.5, 122.4, 123.2, 124.0, 127.6, 127.9, 128.7, 130.0, 133.6, 133.8, 135.1, 136.6, 137.5, 138.3, 144.5, 149.9, 150.2, 151.0, 151.6, 158.4 ppm; HRMS (ESI, m/z): calcd. for $C_{29}H_{18}ClN_6$ $[M+H]^+$: 485.1281; found: 485.1292.

4-(4-Chlorophenyl)-1-phenyl-3,6-di(pyridin-3-yl)-1*H*-pyrazolo[3,4-*b*]pyridine-5-carbonitrile (4g). Light yellow crystals; ^{1}H NMR (DMSO-d_6, 500 MHz) δ = 7.24 (dd, *J* = 8.0, 5.0 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.47-7.50 (m, 3H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.65-7.71 (m, 3H), 8.30 (d, *J* = 8.0 Hz, 2H), 8.36 (s, 1H), 8.46 (d, *J* = 8.0 Hz, 1H), 8.53 (dd, *J* = 4.5, 1.5 Hz, 1H), 8.83 (dd, *J* = 4.5, 1.5 Hz, 1H), 9.21 (d, *J* = 1.5 Hz, 1H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz) δ = 103.1, 113.1, 117.5, 122.5, 123.1, 124.0, 127.7, 127.9, 128.8, 130.0, 131.8, 132.2, 133.9, 135.6, 136.7, 137.4, 138.4, 144.5, 149.8, 150.2, 151.5, 158.4 ppm; HRMS (ESI, m/z): calcd. for $C_{29}H_{17}ClN_6Na$ $[M+Na]^+$: 507.1101; found: 507.1065.

4-(3-Bromophenyl)-1-phenyl-3,6-di(pyridin-3-yl)-1*H*-pyrazolo[3,4-*b*]pyridine-5-carbonitrile (4h). Yellow crystals; ^{1}H NMR (DMSO-d_6, 500 MHz) δ = 7.24 (dd, *J* = 8.0, 4.5 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 1H),

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7.46-7.51 (m, 3H), 7.61-7.10 (m, 5H), 8.28 (d, *J* = 8.0 Hz, 2H), 8.36 (s, 1H), 8.45 (d, *J* = 8.0 Hz, 1H), 8.52 (d, *J* = 4.5 Hz, 1H), 8.83 (d, *J* = 4.5 Hz, 1H), 9.21 (s, 1H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz) δ = 103.0, 112.9, 117.6, 122.5, 123.2, 124.1, 128.0, 130.0, 130.8, 131.4, 132.2, 132.9, 133.3, 135.3, 136.1, 136.7, 138.2, 144.5, 149.6, 150.0, 150.2, 150.9, 151.6, 158.4 ppm; HRMS (ESI, m/z): calcd. for $C_{29}H_{18}BrN_6$ $[M+H]^+$: 529.0776; found: 529.0742.

4-(4-Bromophenyl)-1-phenyl-3,6-di(pyridin-3-yl)-1*H*-pyrazolo[3,4-*b*]pyridine-5-carbonitrile (4i). Light yellow crystals; ^{1}H NMR (DMSO-d_6, 500 MHz) δ = 7.23 (dd, *J* = 8.0, 4.5 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.51-7.55 (m, 3H), 7.64-7.70 (m, 3H), 8.30 (d, *J* = 8.0 Hz, 2H), 8.35 (s, 1H), 8.45 (d, *J* = 8.0 Hz, 1H), 8.53 (d, *J* = 4.5 Hz, 1H), 8.83 (d, *J* = 4.5 Hz, 1H), 9.21 (s, 1H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz) δ = 103.0, 113.0, 117.5, 122.4, 123.2, 124.0, 127.7, 127.9, 129.9, 131.0, 132.0, 132.5, 133.8, 136.7, 137.4, 138.3, 144.5, 149.8, 150.2, 151.6, 158.4 ppm; HRMS (EI, m/z): calcd. for $C_{29}H_{17}BrN_6$ $[M]^+$: 528.0698; found: 528.0715.

4-(2-Nitrophenyl)-1-phenyl-3,6-di(pyridin-3-yl)-1*H*-pyrazolo[3,4-*b*]pyridine-5-carbonitrile (4j). Light yellow crystal; ^{1}H NMR (DMSO-d_6, 500 MHz) δ = 7.19 (dd, *J* = 8.0, 4.5 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.49-7.51 (m, 1H), 7.61-7.68 (m, 4H), 7.97 (d, *J* = 7.5 Hz, 1H), 8.12-8.29 (m, 5H), 8.40 (dd, *J* = 5.0, 1.5 Hz, 1H), 8.42-8.45 (m, 1H), 8.79 (dd, *J* = 5.0, 1.5 Hz, 1H), 9.19 (d, *J* = 2.0 Hz, 1H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz) δ = 103.0, 113.1, 117.5, 122.5, 123.3, 124.1, 125.2, 125.3, 127.5, 128.0, 130.0, 130.7, 133.8, 134.5, 136.5, 136.9, 137.5, 138.3, 144.3, 147.5, 149.8, 149.9, 150.0, 150.2, 151.7, 158.4 ppm; HRMS (ESI, m/z): calcd. for $C_{29}H_{18}N_7O_2$ $[M+H]^+$: 496.1522; found: 496.1442.

4-(3-Nitrophenyl)-1-phenyl-3,6-di(pyridin-3-yl)-1*H*-pyrazolo[3,4-*b*]pyridine-5-carbonitrile (4k). Light brown crystals; ^{1}H NMR (DMSO-d_6, 500 MHz) δ = 7.17 (dd, *J* = 7.5, 4.5 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.52 (d, *J* = 7.5 Hz, 1H), 7.63-7.70 (m, 4H), 8.00 (d, *J* = 7.5 Hz, 1H), 8.24-8.31 (m, 5H), 8.42 (d, *J* = 4.0 Hz, 1H), 8.46 (d, *J* = 7.5 Hz, 1H), 8.81 (d, *J* = 4.5 Hz, 1H), 9.21 (s, 1H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz) δ = 103.0, 113.1, 117.5, 122.5, 123.3, 124.1, 125.2, 125.4, 127.5, 128.0, 130.0, 130.7, 133.8, 134.5, 136.5, 136.9, 137.5, 138.3, 144.3, 147.5, 149.8, 149.9, 150.0, 150.2, 151.7, 158.4 ppm; HRMS (ESI, m/z): calcd. for $C_{29}H_{18}N_7O_2$ $[M+H]^+$: 496.1522; found: 496.1512.

4-(4-Nitrophenyl)-1-phenyl-3,6-di(pyridin-3-yl)-1*H*-pyrazolo[3,4-*b*]pyridine-5-carbonitrile (4l). Dark yellow crystals; ^{1}H NMR (DMSO-d_6, 500 MHz) δ = 7.21 (dd, *J* = 8.0, 5.0 Hz, 1H), 7.48-7.53 (m, 2H), 7.68 (t, *J* = 7.5 Hz, 2H), 7.72 (t, *J* = 5.0 Hz, 1H), 7.76 (d, *J* = 8.5 Hz, 2H), 8.18 (d, *J* = 8.5 Hz, 2H), 8.30 (d, *J* = 7.5 Hz, 2H), 8.34 (d, *J* = 2.0 Hz, 1H), 8.46 (dd, *J* = 4.5, 2.0 Hz, 2H), 8.53 (dd, *J* = 4.5, 2.0 Hz, 1H), 9.22 (d, *J* = 2.0 Hz, 1H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz) δ = 102.8, 113.0, 117.2, 121.2, 122.4, 123.2, 123.6, 124.0, 127.5, 127.9, 130.0, 131.7, 133.7, 136.7, 137.4, 138.3, 139.8, 144.3, 148.7, 149.7, 149.9, 150.2, 150.4, 151.6, 158.3 ppm; HRMS (ESI, m/z): calcd. for $C_{29}H_{18}N_7O_2$ $[M+H]^+$: 496.1522; found: 496.1535.

1-Phenyl-3,6-di(pyridin-3-yl)-4-(thiophen-2-yl)-1*H*-pyrazolo[3,4-*b*]pyridine-5-carbonitrile (4m). Dark green crystal; ^{1}H NMR (DMSO-d_6, 500 MHz) δ = 7.17 (dd, *J* = 5.0, 4.5 Hz, 1H), 7.26 (dd, *J* = 7.5, 4.5 Hz, 1H), 7.32 (d, *J* = 2.5 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.59-7.67 (m, 4H), 7.78 (d, *J* = 4.5 Hz, 1H), 8.24 (d, *J* = 7.5 Hz, 2H), 8.41 (d, *J* = 7.5 Hz, 1H), 8.44 (d, *J* = 1.5 Hz, 1H), 8.52 (dd, *J* = 4.5, 1.5 Hz, 1H), 8.79 (dd, *J* = 4.5, 1.5 Hz, 1H), 9.16 (d, *J* = 1.5 Hz, 1H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz) δ = 102.9, 113.0, 117.2, 121.2, 122.4, 123.0, 123.6, 124.1, 127.4, 130.7, 131.6, 133.7, 136.8, 137.6, 139.8, 144.3, 149.0, 150.1,

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DOI: 10.1039/C6RA19579B

150.3, 151.5, 158.4 ppm; HRMS (EI, m/z): calcd. for $C_{27}H_{16}N_6S$ $[M]^+$: 456.1157; found: 456.1169.

1-Phenyl-3,4,6-tri(pyridin-3-yl)-1*H*-pyrazolo[3,4-*b*]pyridine-5-carbonitrile (4n). Light yellow crystal; ^{1}H NMR (DMSO-d_6, 500 MHz) δ = 7.16 (dd, *J* = 7.5, 4.5 Hz, 1H), 7.43-7.46 (m, 3H), 7.51 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.61-7.67 (m, 3H), 8.24 (d, *J* = 8.0 Hz, 2H), 8.35 (d, *J* = 2.0 Hz, 1H), 8.41 (dt, *J* = 8.0, 2.0 Hz, 1H), 8.46 (dd, *J* = 4.5, 2.0 Hz, 1H), 8.50-8.51 (m, 2H), 8.79 (dd, *J* = 5.0, 2.0 Hz, 1H), 9.17 (d, *J* = 2.0 Hz, 1H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz) δ = 102.7, 103.0, 117.2, 122.5, 123.2, 124.0, 124.3, 127.4, 128.0, 130.0, 133.7, 136.7, 137.4, 138.2, 141.1, 144.4, 149.7, 149.9, 150.2, 151.6, 158.3 ppm; HRMS (EI, m/z): calcd. for $C_{28}H_{17}N_7$ $[M]^+$: 451.1545; found: 451.1549.

1-Phenyl-3,6-di(pyridin-3-yl)-4-(pyridin-4-yl)-1*H*-pyrazolo[3,4-*b*]pyridine-5-carbonitrile (4o). Dark green crystal; ^{1}H NMR (DMSO-d_6, 500 MHz) δ = 7.31-7.44 (m, 3H), 7.58-7.66 (m, 5H), 8.26-8.29 (m, 3H), 8.37 (d, *J* = 8.0 Hz, 1H), 8.59 (d, *J* = 8.0 Hz, 1H), 8.73 (d, *J* = 4.5 Hz, 1H), 8.78 (d, *J* = 4.0 Hz, 1H), 9.12 (s, 1H), 9.38 (s, 1H), 9.61 (s, 1H), 11.70 (brs, 1H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz) δ = 115.0, 121.4, 122.1, 124.7, 126.5, 126.9, 127.2, 128.4, 129.8, 131.1, 131.5, 134.9, 136.1, 139.2, 141.7, 148.2, 150.2, 150.3, 150.7, 169.1 ppm; HRMS (EI, m/z): calcd. for $C_{31}H_{19}N_7$ $[M]^+$: 489.1702; found: 489.1700.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (21272053), the Natural Science Foundation of Hebei Province (B2015205182 and H2015206393) and the Natural Science Foundation of Hebei Education Department (QN 2014126).

References

1 A. Ghaedi, G. R. Bardajee, A. Mirshokrayi, M. Mahdavi, A. Shafiee and T. Akbarzadeh, *RSC Adv.*, 2015, **5**, 89652-89658.

2 J. H. Chen, W. M. Liu, J. J. Ma, H. T. Xu, J. S. Wu, X. L. Tang, Z. Y. Fan and P. F. Wang, *J. Org. Chem.*, 2012, **77**, 3475-3482.

3 S. P. Patil, D. P. Shelar and R. B. Toche, *J. Fluoresc.*, 2012, **22**, 31-41.

4 M. S. Salem and M. A. M. Ali, *Biol. Pharm. Bull.*, 2016, **39**, 473-483.

5 P. Nagender, G. M. Reddy, R. N. Kumar, Y. Poornachandra, C. G. Kumar and B. Narsaiah, *Bioorg. Med. Chem. Lett.*, 2014, **24**, 2905-2908.

6 M. A. El-borai, H. F. Rizk, M. F. Abd-Aal and I. Y. El-Deeb, *Eur. J. Med. Chem.*, 2012, **48**, 92-96.

7 M. A. El-Borai, H. F. Rizk, D. M. Beltagy and I. Y. El-Deeb, *Eur. J. Med. Chem.*, 2013, **66**, 415-422.

8 B. Zhao, Y. X. Li, P. Xu, Y. Dai, C. Luo, Y. M. Sun, J. Ai, M. Y. Geng and W. H. Duan, *ACS Med. Chem. Lett.*, 2016, **7**, 629-634.

9 N. Liu, Y. F. Wang, G. C. Huang, C. H. Ji, W. Fan, H. T. Li, Y. Cheng and H. Q. Tian, *Bioorg. Chem.*, 2016, **65**, 146-158.

10 D. Behnke, S. Cotesta, S. Hintermann, M. Fendt, C. E. Gee, L. H. Jacobson, G. Laue, A. Meyer, T. Wagner, S. Badiger, V. Chaudhari, M. Chebrolu, C. Pandit, D. Hoyer and C. Betschart, *Bioorg. Med. Chem. Lett.*, 2015, **25**, 5555-5560.

View Article Online
DOI: 10.1039/C6RA19579B

11 K. Chavva, S. Pillalamarri, V. Banda, S. Gautham, J. Gaddamedi, P. Yedla, C. G. Kumar and N. Banda, *Bioorg. Med. Chem. Lett.*, 2013, **23**, 5893-5895.

12 A. Dandia, S. L. Gupta, P. Singh and M. A. Quraishi, *ACS Sustainable Chem. Eng.*, 2013, **1**, 1303-1310.

13 D. K. Dodiya, A. R. Trivedi, V. B. Kataria and V. H. Shah, *Curr. Org. Chem.*, 2012, **16**, 400-417.

14 Z. Chen, Y. X. Shi, Q. Q. Shen, H. X. Xu and F. R. Zhang, *Tetrahedron Lett.*, 2015, **56**, 4749-4752.

15 P. Gunasekaran, S. Indumathi and S. Perumal, *RSC Adv.*, 2013, **3**, 8318-8325.

16 P. Gunasekaran, P. Prasanna and S. Perumal, *Tetrahedron Lett.*, 2014, **55**, 329-332.

17 M. Mamaghani, K. Tabatabaeian, M. Bayat, R. H. Nia and M. Rassa, *J. Chem. Res.*, 2013, 494-498.

18 A. Dandia, S. L. Gupta and V. Parewa, *RSC Adv.*, 2014, **4**, 6908-6915.

19 A. Rahmati, T. Kenarkoohi and H. R. Khavasi, *ACS Comb. Sci.*, 2012, **14**, 657-664.

20 X. J. Tu, W. J. Hao, Q. Ye, S. S. Wang, B. Jiang, G. G. Li and S. J. Tu, *J. Org. Chem.*, 2014, **79**, 11110-11118.

21 J. Safaei-Ghomi, R. Sadeghzadeh and H. Shahbazi-Alavi, *RSC Adv.*, 2016, **6**, 33676-33685.

22 L. Zhang, S. T. Gao, W. H. Liu, R. X. Tang, N. Z. Shang, C. Wang and Z. Wang, *Chin. J. Org. Chem.*, 2014, **34**, 1542-1548.

23 J. Safari, S. Gandomi-Ravandi and S. Ashiri, *New J. Chem.*, 2016, **40**, 512-520.

24 M. M. Antunes, P. A. Russo, P. V. Wiper, J. M. Veiga, M. Pillinger, L. Mafra, D. V. Evtuguin, N. Pinna and A. A. Valente, *ChemSusChem*, 2014, **7**, 804-812.

25 B. Garg, T. Bisht and Y. C. Ling, *RSC Adv.*, 2014, **4**, 57297-57307.

26 P. P. Upare, J. W. Yoon, M. Y. Kim, H. Y. Kang, D. W. Hwang, Y. K. Hwang, H. H. Kung and J. S. Chang, *Green Chem.*, 2013, **15**, 2935-2943.

27 J. X. Zhou, Y. Wang, X. W. Guo, J. B. Mao and S. G. Zhang, *Green Chem.*, 2014, **16**, 4669-4679.

28 R. K. Sharma, S. Dutta, S. Sharma, R. Zboril, R. S. Varma and M. B. Gawande, *Green Chem.*, 2016, **18**, 3184-3209.

29 R. K. Sharma, M. Yadav, Y. Monga, R. Gaur, A. Adholeya, R. Zboril, R. S. Varma and M. B. Gawande, *ACS Sustainable Chem. Eng.*, 2016, **4**, 1123-1130.

30 B. Karimi, F. Mansouri and H. M. Mirzaei, *ChemCatChem*, 2015, **7**, 1736-1789.

31 D. Wang and D. Astruc, *Chem. Rev.*, 2014, **114**, 6949-698.

32 H. Woo, J. W. Kim, M. Kim, S. Park and K. H. Park, *RSC Adv.*, 2015, **5**, 7554-7558.

33 X. Q. Xiong, H. X. Chen, Z. K. Tang and Y. B. Jiang, *RSC Adv.*, 2014, **4**, 9830-9837.

34 *(a)* Y. L. Gu and F. Jerome, *Chem. Soc. Rev.*, 2013, **42**, 9550-9570; *(b)* R. Y. Guo, P. Wang, G. D. Wang, L. P. Mo and Z. H. Zhang, *Tetrahedron*, 2013, **69**, 2056-2061; *(c)* B. L. Li, P. H. Li, X. N. Fang, C. X. Li, J. L. Sun, L. P. Mo and Z. H. Zhang, *Tetrahedron*, 2013, **69**, 7011-7018.

35 *(a)* P. Liu, J. W. Hao, L. P. Mo and Z. H. Zhang, *RSC Adv.*, 2015, **5**, 48675-48704; *(b)* J. Garcia-Álvarez, *Eur. J. Inorg. Chem.*, 2015, 5147-5157; *(c)* D. A. Alonso, A. Baeza, R. Chinchilla, G. Guillena, I. M. Pastor and D. J. Ramón, *Eur. J. Org. Chem.*, 2016, 612-632; *(d)* X. Q. Xiong, Q. Han, L. Shi, S. Y. Xiao and C. Bi, *Chin. J. Org. Chem.*, 2016, **36**, 480-489; *(e)* E. L. Smith, A. P. Abbott and K. S. Ryder, *Chem. Rev.*, 2014, **114**, 11060-11082; *(f)* P. H. Li, F. P. Ma, P. Wang and Z. H. Zhang, *Chin. J. Chem* . 2013, **31**, 757-763.

View Article Online
DOI: 10.1039/C6RA19579B

36 *(a)* H. C. Hu, Y. H. Liu, B. L. Li, Z. S. Cui and Z. H. Zhang, *RSC Adv.*, 2015, **5**, 7720-7728; *(b)* J. Lu, X. T. Li, E. Q. Ma, L. P. Mo and Z. H. Zhang, *ChemCatChem*, 2014, **6**, 2854-2859; *(c)* P. Liu, J. W. Hao and Z. H. Zhang, *Chin. J. Chem.* 2016, **34**, 637-645; *(d)* P. Liu, J. W. Hao, S. J. Liang, G. L. Liang, J. Y. Wang and Z. H. Zhang, *Monatsh. Chem.*, 2016, **147**, 801-808.

37 A. K. Rathi, M. B. Gawande, R. Zboril and R. S. Varma, *Coord. Chem. Rev.*, 2015, **291**, 68-94.

38 *(a)* P. H. Li, B. L. Li, Z. M. An, L. P. Mo, Z. S. Cui and Z. H. Zhang, *Adv. Synth. Catal.*, 2013, **355**, 2952-2959; *(b)* X. N. Zhao, G. F. Hu, M. Tang, T. T. Shi, X. L. Guo, T. T. Li and Z. H. Zhang, *RSC Adv.*, 2014, **4**, 51089-51097; *(c)* J. Lu, E. Q. Ma, Y. H. Liu, Y. M. Li, L. P. Mo and Z. H. Zhang, *RSC Adv.*, 2015, **5**, 59167-59185; *(d)* M. Zhang, J. Lu, J. N. Zhang and Z. H. Zhang, *Catal. Commun.*, 2016, **78**, 26-32; *(e)* X. N. Zhao, H. C. Hu, F. J. Zhang and Z. H. Zhang, *Appl. Catal. A: Gen.*, 2014, **482**, 258-265; *(f)* P. H. Li, B. L. Li, H. C. Hu, X. N. Zhao and Z. H. Zhang, *Catal. Commun.*, 2014, **46**, 118-122.

39 *(a)* B. L. Li, H. C. Hu, L. P. Mo and Z. H. Zhang, *RSC Adv.*, 2014, **4**, 12929-12943; *(b)* X. T. Li, Y. H. Liu, X. Liu and Z. H. Zhang, *RSC Adv.*, 2015, **5**, 25625-25633; *(c)* R. Y. Guo, Z. M. An, L. P. Mo, S. T. Yang, H. X. Liu, S. X. Wang and Z. H. Zhang, *Tetrahedron*, 2013, **69**, 9931-9938; *(d)* X. T. Li, A. D. Zhao, L. P. Mo and Z. H. Zhang, *RSC Adv.*, 2014, **4**, 51580-51588; *(e)* R. Y. Guo, Z. M. An, L. P. Mo, R. Z. Wang, H. X. Liu, S. X. Wang and Z. H. Zhang, *ACS Comb. Sci.*, 2013, **15**, 557-563; *(f)* H. J. Wang, X. N. Zhang and Z. H. Zhang, *Monatsh. Chem.*, 2010, **141**, 425-430; *(g)* H. J. Wang, J. Lu and Z. H. Zhang, *Monatsh. Chem.*, 2010, **141**, 1107-1112.

40 B. L. Li, M. Zhang, H. C. Hu, X. Du and Z. H. Zhang, *New J. Chem.*, 2014, **38**, 2435-2442.

41 R. Dhanda and M. Kidwai, *RSC Adv.*, 2016, **6**, 53430-53437.

42 M. Zhang, ,Y. H. Liu, Z R. Shang, H. C. Hu and Z. H. Zhang, *Catal. Commun.*, 2017, **88**, 39-44.

43 W. S. Hummers Jr. and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.