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ARTICLE

Graphene oxide nanosheets as metal-free catalyst in the three-component reactions based on aryl glyoxals to generate novel pyranocoumarins

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Graphene oxide (GO) was prepared and employed as a novel, recyclable and safe catalyst for the one-pot, three-component condensations of 4-hydroxycoumarin with aryl glyoxals and malononitrile to produce new pyranocoumarins. Catalyst loadings can be as low as 0.005 g to give high yields of the corresponding products. This novel method has many advantages, such as the high product yield and simple work-up procedure.

Introduction

Metal-free carbon-based catalysts have some advantages over metal catalysts, such as high efficiency, environmental compatibility, low energy consumption, and corrosion resistance.[1] For example, graphene oxide (GO) is an inexpensive metal-free material which has recently been used as an oxidative catalyst in chemical transformations.[2] Despite the merits, the application of GO as catalyst in synthetic chemistry remains unexplored. Using GO nanosheets as a non-oxidative catalyst to promote and facilitate organic reactions in particular the three-component condensations of the active methylenes is a new area with outstanding potential.[3]

Recently, many organic chemists have focused on the multicomponent processes since they can enable direct access to a wide spectrum of structurally related, drug-like compounds. In addition, oxygen-containing heterocyclic compounds play a fundamental role in the context of both chemistry and biology. For example, pyrans and coumarins are prevalent heterocycles in numerous natural and synthetic products and possess significant biological activities.[4,5]

Pyrano-fused coumarins (pyranocoumarins) are natural products that exhibit important biological properties, such as antifungal, insecticidal, anticancer, anti-HIV, anti-inflammatory, and antibacterial activities.[6-9] Despite having several possible arrangements between the pyran and the coumarin rings, the synthesis of pyrano[3,2-*c*]coumarins has received more attention due to high activity of the pyrone part of coumarin.[10] Great efforts have therefore been made to find convenient strategies to synthesize pyranocoumarins. The three-component reaction of aromatic aldehydes, malononitrile, and hydroxycoumarins is the most common method, which has been widely developed and modified in recent years.[11-14]

To the best of our knowledge, there is no report on the synthesis of pyranocoumarins containing aroyl groups from aryl glyoxals.

In this report, we describe the synthesis of new pyranocoumarins using a three component reaction in the presence of catalytic amount of GO.

Experimental

Methods and Materials

Chemicals were purchased from Merck and Aldrich chemical companies. Aryl glyoxals were prepared as described previously .[15] GO was prepared using a modification of Hummers method from flake graphite (Merck Company).[16-18] IR spectra were recorded on a FT-IR JASCO-680 and the ^{1}H NMR spectra were obtained on a Bruker DPX-400 or 300 MHz Avance 2 instrument. The varioEl CHNS was also used for elemental analysis. Scanning electron micrographs (SEM) were obtained using a Cambridge S-360 instrument with an accelerating voltage of 20 kV. The powder X-ray diffraction (XRD) pattern was obtained by a Bruker AXS (D8, Avance) instrument employing the reflection Bragg-Brentano geometry with CuKα radiation. The structure of the products was confirmed on the basis of IR, NMR spectroscopic data, and elemental analysis.

General procedure for the preparation of GO

A flask containing graphite (1 g) and $NaNO_3$ (0.75 g) was placed in an ice-water bath. H_2SO_4 (75 mL) was added with stirring and then $KMnO_4$ (4.5 g) was slowly added over about 1 h. After vigorously stirring for 5 days at room temperature, 5 % H_2SO_4 (140 mL)

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aqueous solution was added over about 1 h with stirring, and the temperature was kept at 98 °C. The temperature was reduced to 60 °C, 3 mL of H_2O_2 (30 wt% aqueous solution) was added, and the mixture was stirred for 2 h at room temperature. As prepared, GO was suspended in ultra-pure water to give a brown dispersion, which was subjected to dialysis to completely remove residual salts and acids. The resulting purified GO powders were collected by centrifugation and air-dried. GO powders were dispersed in water to create a 0.05 wt% dispersion. The dispersion was then exfoliated through ultrasonication for 1 h, which the bulk GO powders were transformed into GO nanoplatelets.

General procedure for the synthesis of 4

To a 25 mL round-bottomed flask, was added 4-hydroxycoumarin (1.0 mmol), aryl glyoxal (1 mmol), malononitrile (1.2 mmol), EtOH/H_2O (1:1, 10 mL), and GO (0.005 g). The reaction was stirred at room temperature for 30 min, then, vigorously stirred under reflux for the specified time (Table 1). The progress of the reaction was monitored by TLC. After completion, the reaction mixture was cooled to room temperature and the precipitates were filtered, dried, and dissolved in hot EtOH/THF (3:1) to separate the catalyst. The solvent was removed under reduced pressure and the pure product was obtained after recrystallization from EtOH/THF (3:1).

Spectral data

Compound ***4a:*** IR (KBr) $\tilde{\nu}$ = 3402, 3292, 2201, 1708, 1678, 1606, 1373, 1064 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz): δ = 8.16 (s, 2H, J = 7.2 Hz), 7.90 (dd, 1H, J_1 = 8.2, J_2 = 1.6 Hz), 7.81-7.73 (m, 2H), 7.69 (s, 2H), 7.62 (t, 2H, J = 8.2 Hz), 7.57-7.53 (m, 2H), 5.42 (s, 1H); ^{13}C NMR (DMSO-d_6, 75 MHz): δ = 198.12, 160.08, 159.55, 154.72, 152.11, 135.34, 134.13, 133.35, 129.13, 128.89, 125.03, 122.15, 118.54, 116.83, 112.58, 101.91, 51.91, 37.14; Anal. Calcd. for $C_{20}H_{12}N_2O_4$: C, 69.76; H, 3.51; N, 8.14. Found: C, 69.55; H, 3.41; N, 8.09.

Compound ***4b:*** IR (KBr) $\tilde{\nu}$ = 3474, 3404, 2205, 1712, 1677, 1595, 1371, 1218, 1061 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz): δ = 8.27 (m, 2H), 7.90 (dd, 1H, J = 8.2, 1.8 Hz), 7.82-7.76 (m, 1H), 7.70 (s, 2H), 7.58-7.53 (m, 2H), 7.46 (t, 2H, J = 8.8 Hz), 5.44 (s, 1H); ^{13}C NMR (DMSO-d_6, 75 MHz): δ = 196.77, 160.08, 159.54, 154.74, 152.13, 133.37, 132.32, 132.19, 125.04, 122.17, 118.50, 116.84, 116.15, 115.86, 112.58, 101.76, 51.85, 37.19; Anal. Calcd. for $C_{20}H_{11}FN_2O_4$: C, 66.30; H, 3.06; N, 7.73. Found: C, 66.37; H, 3.00; N, 7.61.

Compound ***4c:*** IR (KBr) $\tilde{\nu}$ = 3319, 3186, 3027, 2871, 2205, 1713, 1673, 1587, 1375, 1058, 759 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz): δ = 8.20 (d, 2H, J = 8.4 Hz), 7.89 (dd, 1H, J_1 = 8.2, J_2 = 1.4 Hz), 7.81-7.69 (m, 5H), 7.57-7.52 (m, 2H), 5.43 (s, 1H); ^{13}C NMR (DMSO-d_6, 75 MHz): δ = 197.28, 160.08, 159.54, 154.75, 152.13, 139.22, 134.13, 133.39, 130.99, 129.07, 125.04, 122.18, 118.49, 116.83, 112.55, 101.64, 51.70, 37.26; Anal. Calcd. for $C_{20}H_{11}ClN_2O_4$: C, 63.42; H, 2.93; N, 7.40. Found: C, 63.61; H, 2.99; N, 7.35.

Compound ***4d:*** IR (KBr) $\tilde{\nu}$ = 3316, 3186, 3027, 2871, 2203, 1715, 1673, 1582, 1374, 1057, 620 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz): δ = 8.10 (d, 2H, J = 8.6 Hz), 7.91-7.76 (m, 4H), 7.71 (s, 2H), 7.58-7.53 (m, 2H), 5.42 (s, 1H); ^{13}C NMR (DMSO-d_6, 75 MHz): δ = 197.51, 159.54, 154.75, 152.14, 134.45, 133.40, 132.04, 131.05, 125.05, 122.19, 116.84, 112.55, 101.64, 51.70, 37.25; Anal. Calcd. for $C_{20}H_{11}BrN_2O_4$: C, 56.76; H, 2.62; N, 6.62. Found: C, 56.89; H, 2.51; N, 6.58.

Compound ***4e:*** IR (KBr) $\tilde{\nu}$ = 3415, 3086, 2928, 2197, 1712, 1673, 1609, 1525, 1385, 1352, 1063 cm^{-1};^1H NMR (DMSO-d_6, 300 MHz): δ = 8.83 (t, 1H, J = 1.8 Hz), 8.65 (d, 1 H, J = 7.8 Hz), 8.61-8.57 (m, 1H), 7.98-7.89 (m, 2H), 7.82-7.77 (m, 3H), 7.59-7.53 (m, 2H), 5.57 (s, 1H); ^{13}C NMR (DMSO-d_6, 75 MHz): δ = 197.01, 160.15, 159.57, 154.81, 152.16, 148.17, 136.61, 135.29, 133.51, 130.91, 128.39, 125.11, 123.17, 122.22, 118.51, 116.89, 112.50, 101.33, 51.24, 37.65; Anal. Calcd. for $C_{20}H_{11}N_3O_6$: C, 61.70; H, 2.85; N, 10.79. Found: C, 61.88; H, 2.77; N, 10.83.

Compound ***4f:*** IR (KBr) $\tilde{\nu}$ = 3461, 3336, 2192, 1720, 1681, 1613, 1517, 1383, 1326, 1070, 1064 cm^{-1}. ^1H NMR (DMSO-d_6, 300 MHz): δ = 8.46-8.38 (m, 4H), 7.90 (dd, 1H, J = 8.2, 1.4 Hz), 7.82-7.77 (m, 3H), 7.59-7.54 (m, 2H), 5.51 (s, 1H). ^{13}C NMR (DMSO-d_6, 75 MHz): δ = 197.79, 160.15, 159.56, 154.81, 152.17, 150.49, 140.22, 133.50, 130.43, 125.10, 124.01, 122.24, 116.88, 112.51, 101.33, 51.24, 37.98; Anal. Calcd. for $C_{20}H_{11}N_3O_6$: C, 61.70; H, 2.85; N, 10.79. Found: C, 61.79; H, 2.72; N, 10.71.

Compound ***4g:*** IR (KBr) $\tilde{\nu}$ = 3477, 3344, 3072, 2934, 2196, 1721, 1674, 1577, 1386, 1065 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz): δ = 7.90 (dd, 1H, J_1 = 8.2, J_2 =1.8 Hz), 7.815-7.75 (m, 2H), 7.70 (s, 2H), 7.62 (t, 1H, J = 2.4 Hz), 7.57-7.52 (m, 3H), 7.32 (dd, 1H, J_1 = 7.8, J_2 = 2.1 Hz), 5.40 (s, 1H), 3.87 (s, 3H); ^{13}C NMR (DMSO-d_6, 75 MHz): δ = 197.77, 160.04, 159.61, 159.44, 154.73, 152.13, 136.69, 133.34, 130.02, 125.02, 122.16, 121.68, 120.22, 118.57, 116.82, 113.52, 112.60, 101.96, 55.39, 52.02, 37.41; Anal. Calcd. for $C_{21}H_{14}N_2O_5$: C, 67.38; H, 3.77; N, 7.48. Found: C, 67.48; H, 3.70; N, 7.56.

Compound ***4h:*** IR (KBr) $\tilde{\nu}$ = 3426, 3320, 2926, 2200, 1714, 1673, 1597, 1383, 1062 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz): δ = 8.15 (d, 2H, J = 9.0 Hz), 7.89 (dd, 1H, J_1 = 8.2, J_2 = 1.4 Hz), 7.80-7.74 (m, 1H), 7.65 (s, 2H), 7.57-7.52 (m, 2H), 7.14 (d, 2H, J = 9.0 Hz), 5.36 (s, 1H), 3.90 (s, 3H); ^{13}C NMR (DMSO-d_6, 75 MHz): δ = 196.24, 163.92, 160.04, 159.50, 154.67, 152.08, 133.26, 131.65, 128.10, 124.99, 122.12, 118.62, 116.79, 114.12, 112.62, 102.10, 55.65, 52.28, 36.72; Anal. Calcd. for $C_{21}H_{14}N_2O_5$: C, 67.38; H, 3.77; N, 7.48. Found: C, 67.40; H, 3.73; N, 7.40.

Compound ***4i:*** M.p. 271-273 °C; IR (KBr) $\tilde{\nu}$ = 3477, 3327, 3050, 2923, 2191, 1727, 1674, 1573, 1381, 1177 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz): δ = 8.37 (m, 2H), 8.24 (d, 1H, J = 8.4 Hz), 8.09-8.05 (m, 1H), 7.92 (dd, 1H, J = 8.2, J_2 = 1.8 Hz), 7.83-7.70 (m, 4H), 7.66-7.54 (m, 4H), 5.43 (s, 1H); ^{13}C NMR (DMSO-d_6, 75 MHz): δ = 200.33, 160.26, 159.65, 154.68, 152.21, 134.20, 133.46, 133.39, 133.29, 129.87, 129.08, 128.56, 128.03, 126.59, 125.10, 125.05, 124.76, 122.20, 118.33, 116.86, 112.63, 101.71, 51.45, 38.65; Anal. Calcd. for $C_{24}H_{14}N_2O_4$: C, 73.09; H, 3.58; N, 7.10. Found: C, 73.13; H, 3.55; N, 7.01.

Compound ***4j:*** IR (KBr) $\tilde{\nu}$ = 3428, 3321, 2938, 2199, 1714, 1674, 1631, 1597, 1569, 1382, 1172 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz): δ = 8.44 (S, 1H), 7.98-7.95 (m, 2H), 7.84-7.82 (d, 1H, J = 8.4 Hz), 7.76-7.72 (m, 1H), 7.62-7.52 (m, 3H), 7.49-7.42 (m, 2H), 7.39 (S, 2H), 7.33 (d, 1H, J = 7.2 Hz), 5.47 (s, 1H); ^{13}C NMR (DMSO-d_6, 75

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MHz): δ = 199.66, 159.56, 157.85, 153.82, 152.05, 133.27, 132.93, 130.93, 128.47, 127.43, 126.18, 126.13, 126.02, 125.85, 125.75, 124.74, 123.43, 122.45, 119.15, 116.61, 112.96, 104.65, 53.62, 37.27; Anal. Calcd. for $C_{24}H_{14}N_2O_4$: C, 73.09; H, 3.58; N, 7.10. Found: C, 73.17; H, 3.60; N, 7.04.

Results and discussion

Graphene oxide sheets were synthesized by a modified Hummers method as described in the Experimental section. Scanning electron microscopy was used to observe the morphology of the GO nanoplatelets. Fig. 1 is the SEM images of GO nanoplatelets showing crumpled thin layers with wrinkles and folds on the surface of GO.

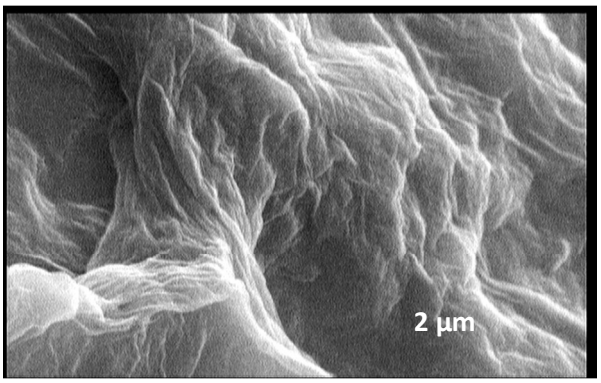


Fig. 1. SEM image of GO.

Fig. 2 shows the XRD pattern of the bulk GO in its dry state. In the XRD pattern, the clear diffraction bands centered at 2θ ~ 10° corresponding to the (002) plane of the GO. Pure graphite shows a diffraction peak at 2θ = 26.3º, corresponding to an interlayer spacing of about 0.335 nm. Elimination of this peak at 26.3º and appearance of the peak at 10º indicates complete oxidation of graphite to GO.

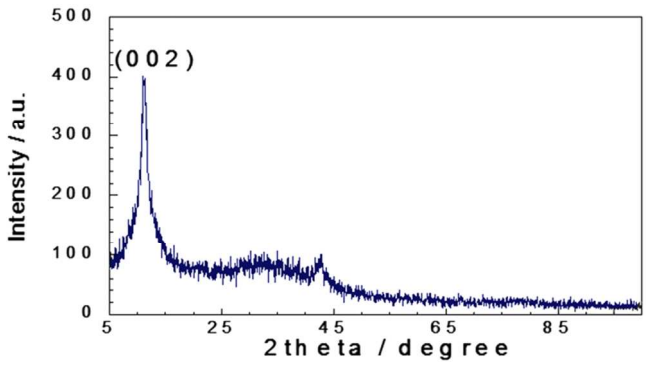
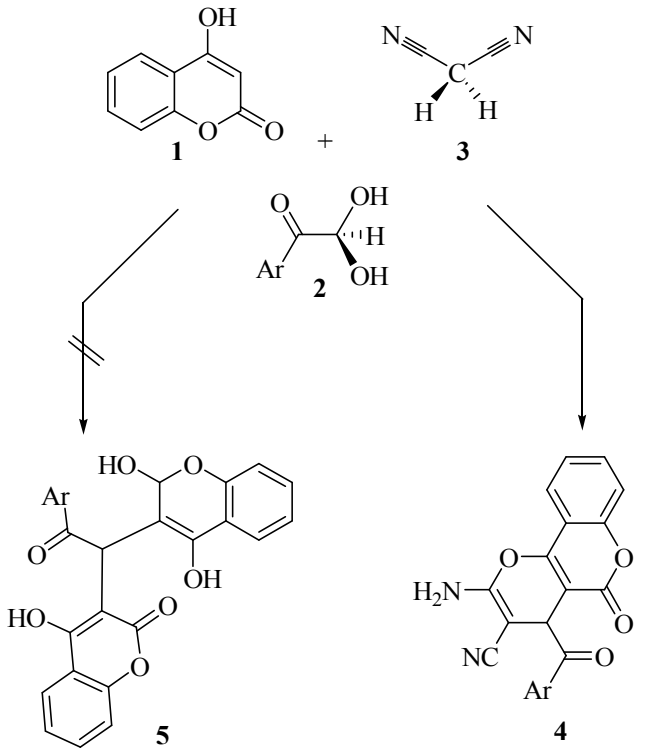


Fig. 2. XRD pattern of GO.

As part of an ongoing research program aiming to find novel methods within organic chemistry, we have synthesized a small library consisting of some heterocyclic compounds containing coumarin nucleus.[19-22] We have also developed new routes to novel benzofuran and pyrimidopyridazines starting from aryl glyoxals.[23,24]

Here, we describe a graphene oxide catalyzed three-component condensation of 4-hydroxycoumarin (**1**) and a series of aryl glyoxals **4** with malononitrile (**3**) (Scheme 1).



Conditions: EtOH/H_2O (1:1), GO (0.005 g), r.t. to reflux

Scheme 1. Synthesis of pyranocoumarins using GO.

The reaction showed selectivity towards the desired product **4** rather than biscoumarins **5**.

A brief investigation on the reaction conditions was carried out through the synthesis of compound **4a** as a model. Since phenyl glyoxal does not bear any substitution on the benzene ring, this substrate will not demonstrate substitution effects, suggesting that it can be considered as a suitable substrate in the model reaction with **1** and **2**. Based on similar reactions,[25] a mixture of EtOH/H_2O (1:1) was employed as solvent.

A catalyst-free reaction was performed at room temperature and the reaction led to undesired and non-isolable products after 180 min. Increasing the reaction temperature did not affect the progress of the reaction markedly. Using common basic catalysts such as NaOH and Na_2CO_3 was also shown to be ineffective. The use of a mild acid like GO, however, was also found to be a suitable catalyst at RT to 80 ºC. Fig. 3 shows optimization of catalyst loading on the model reaction.

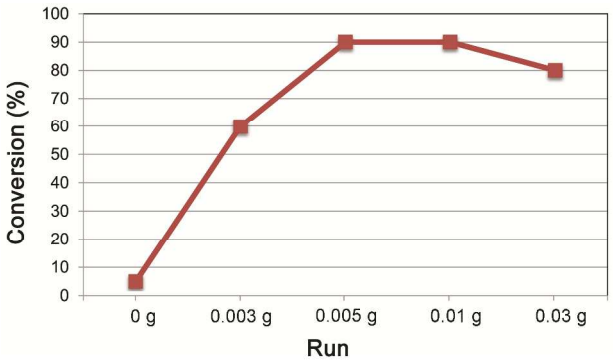


Fig. 3. Optimization of catalyst amount.

By choosing GO (0.005 g) as catalyst, several common solvents were further surveyed. Aprotic solvents such as CH_2Cl_2, THF, and CH_3CN did not show desirable results and they were relatively detrimental to the reaction. Although the H_2O is a green solvent, it is not suitable for use in this type of reactions. EtOH and MeOH gave good yields but had issues with safety and expense; a mixture of EtOH/H2O (1/1) proved to be the optimum solvent. After evaluation and screening, the generality of the reaction was examined under the optimized conditions (Table 1).

Table 1. Synthesis of **4** using GO as catalyst.

Entry	Ar	Yield[a] (%)	Time (min)	Mp (ºC)
4a	C_6H_5	90	60	272-274
4b	4-F-C_6H_4	92	65	253-255
4c	4-Cl-C_6H_4	88	80	263-265
4d	4-Br-C_6H_4	90	75	263-265
4e	3-NO_2-C_6H_4	85	85	248-250
4f	4-NO_2-C_6H_4	87	70	273-275
4g	3-MeO-C_6H_4	85	85	268-270
4h	4-MeO-C_6H_4	87	80	266-268
4i	1-Naphthyl	93	65	271-273
4j	2-Naphthyl	95	70	278-280

[a] Yield of isolated products.

It was observed that the process can tolerate both electron-withdrawing and electron-donating group on the benzene ring. In all cases, the reactions proceeded efficiently at RT to 80 ºC in EtOH/H_2O to afford the corresponding products in good to excellent yields. We also tested alkyl cyanoacetates in order to extend the application of active methylene compounds. However, using ethyl/methyl cyanoacetate did not lead to the desired heterocycles, but instead gave a dark mixture containing a complex product mixture.

All compounds **4a-j** were unknown and completely characterized by IR and NMR spectroscopy as well as elemental analysis. The data were in good agreement with the expected structures. For example, the ^{1}H NMR spectrum of compound **4g** shows the signals for aromatic protons at the range of δ = 7.91-7.31 ppm. Also, a singlet signal at δ = 7.69 ppm corresponds to amine protons. The two sharp singlet signals at δ = 5.40 ppm and δ = 3.87 ppm correspond to the methine and methyl protons respectively. Moreover, the ^{13}C NMR spectrum of compound **4g** confirms the validity of the suggested structure. Briefly, this spectrum shows 21 signals as expected. The IR spectrum of compound **4g** contains a characteristic absorption band of the conjugated cyano-group in the 2196 cm^{-1} region.

Due to incomplete insight into the mechanistic aspects of the GO, the exact mechanism of the reaction remains unclear. Based on recently published review articles[26,27] suggesting the possible mechanistic pathways for GO in organic reactions, it is probable that active sites of the catalyst are acidic and carbonyl groups. However, protons and hydrogen bonding can activate the hydroxyl groups of aryl glyoxal and promote the reactions.

If the catalyst was recyclable,[28,29] it would improve both the environmental impact and the economic profile of the current method. As shown in Fig. 4, the catalyst could successfully be used for four runs during which loss of the catalytic activity was minimal. Moreover, the catalyst could directly be reused after filtering.

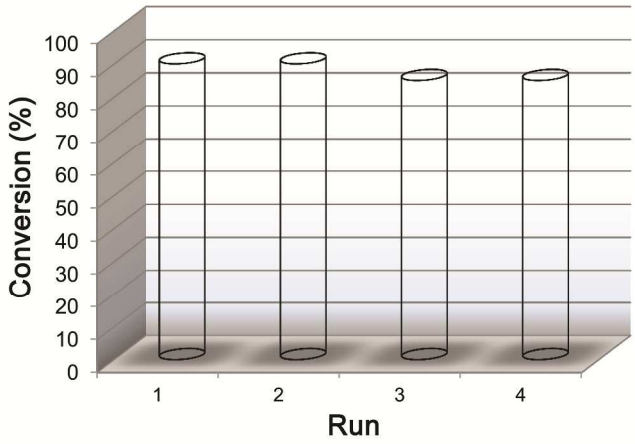


Fig. 4. Recyclability of the GO in the synthesis of **4a**. (Reaction time = 60 min).

Conclusions

In summary, the reaction of 4-hydroxycoumarin with aryl glyoxals and malononitrile in the presence of graphene oxide provides a simple one-pot entry to the synthesis of new pyranocoumarins of potential pharmaceutical and synthetic interest. This method may have some advantages such as, the use of a safe and recyclable catalyst, avoidance of toxic solvents, high product yields, short reaction times, and an easy work-up procedure. Finally, the presence of transformable functionalities in the products may also make them potentially useful for further synthetic manipulations.

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Notes and references

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