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Graphene oxide as an active carbocatalyst for cyanation of quinoline and isoquinoline *N*-Oxides

Panpan Huang [a, 1], Xiangjun Peng [b, **, 1], Genhong Qiu [b], Keyang Yu [b], Hong Li [a], Lingting Kong [a], Jiaming Hu [a], Zhengwang Chen [a], Qing Huang [a, ***], Liangxian Liu [a, *]

[a] Department of Chemistry and Chemical Engineering, Gannan Normal University, Ganzhou, Jiangxi, 341000, PR China
[b] School of Pharmaceutical Science, Gannan Medical University, Ganzhou, Jiangxi, 341000, PR China

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ABSTRACT

Graphene oxide was found to be a highly efficient and cost-effective heterogeneous catalyst for the direct metal-free transformation of quinoline and isoquinoline *N*-oxides into the corresponding nitriles under mild conditions. This method is simple, economic and environmentally benign, representing a useful strategy for the convenient synthesis of α-cyano *N*-oxides that are difficult to prepare by transition-metal-free catalyzed methods. *In vitro*, compound **2s** exhibited good activities against T-24 cell lines with IC_{50} values in 10.23 ± 1.05 μM. Further studies investigated the mechanism of the effective inhibition of cell growth, including apoptosis ratio dection, cell cycle analysis, measurement of Ca^{2+} generation, ROS, and mitochondrial dysfunction.

1. Introduction

Heterocyclic *N*-oxides, especially heterocyclic aromatic *N*-oxides, often exhibit potent biological activities and are used as drugs [1,2] (Fig. 1). For example, isoquinoline alkaloid (**A**) was isolated from the leaves of *Neolitsea sericea* var. *aurata* Hayata, a plant native to Orchid Island, Taiwan [3a]. compound (**B**) was isolated from *Stigmatella aurantiaca* and utilized as a potent antibiotic [3b], Oxadiazole 2-oxide (**C**), identified from a quantitative high-throughput screen, was shown to inhibit a parasite enzyme, thioredoxin glutathione reductase (TGR), with activities in the low micromolar to low nanomolar range [3c], while compound (D) was designed, synthesized, and tested for their ability to inhibit p38α MAP kinase [2a]. On the other hand, the presence of a N—O bond also serves as an important handle to activate the heterocycle, thus allowing diverse functionalization of heterocycles, such as alkenylation [4], alkynylation [5], arylation [6], amidation [7], acetoxylation [8], and sulfonylation [9]. However, despite these advances, only a few examples have been reported for the cyanation of heterocyclic *N*-oxides, especially the transition-metal-free catalyzed cyanation reactions [10] (Scheme 1).

Recognizing the importance of heterocyclic *N*-oxides and C—H cyanation, we questioned whether carbon-based materials can be employed as benign catalysts to promote C—H cyanation of (iso) quinoline *N*-oxides as initial raw materials. We recognized that if such a process could be developed, it would represent a powerful method for the synthesis of (iso)quinoline *via* a direct and atomic economical strategy as well as it would open the door for numerous related transformations using the carbocatalysis platform. And the method avoided using the transition-metal, phosphorus reagent and base additives.

In recent years, graphene oxide (GO), which is usually prepared by oxidizing graphite and consists of hydrophilic oxygenated graphene sheets bearing oxygen functional groups on their basal planes and edges, have attracted much attention due to potential applications in plastic electronics, solar cells, optical materials and biosensors [11]. We recently reported a GO-promoted alkylation strategy to access 3,3′-bisindolylmethane derivatives and a GO/air oxidative strategy for the synthesis of *N*-acylisoindolin-1-one derivatives [12]. However, a high weight loading of GO relative to the substrate is usually required when GO was used as a substitute for metal catalysts [11c,13]. Thus, its potential as a catalyst in organic transformation remains relatively unexplored [14].

* Corresponding author.
** Corresponding author.
*** Corresponding author.
E-mail address: liuliangxian1962@163.com (L. Liu).
[1] These authors contributed equally to this work.

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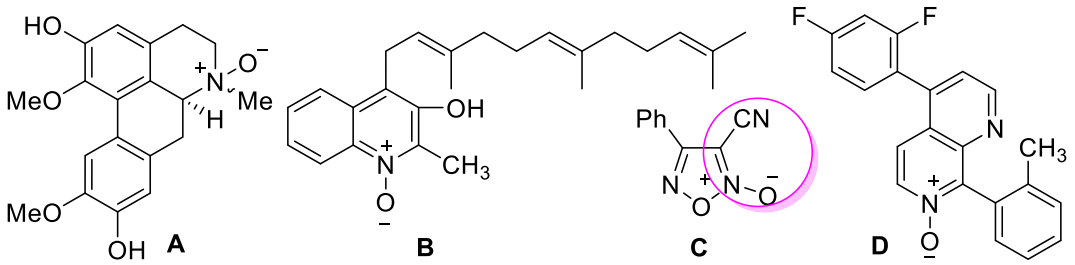
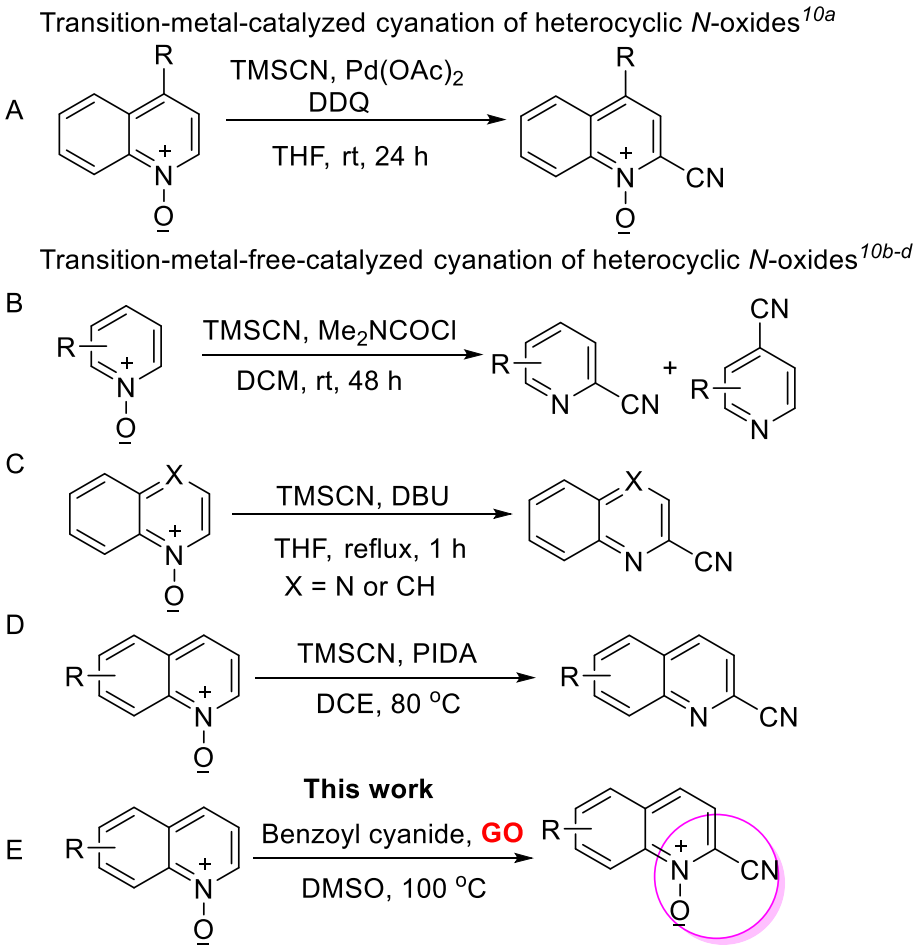


Fig. 1. Selected examples of bioactive natural products and compounds containing the N—O scaffold.



Scheme 1. Strategies for C2-cyanation of quinoline and other N-oxides.

Recently, Sun's group reported a regioselective synthesis of 2-cyanoquinoline derivatives by the $PhI(OAc)_2$ mediated N—O bond disruption and direct cyanation of quinoline *N*-oxide substrates [10d]. The reaction system featured an accelerator of N—O bond cleavage. In view of the potent biological activities from *N*-oxides, we want to preserve the N—O bond after *N*-oxides were functionalized. Based on the great versatility of aryl and heteroaryl nitriles in chemical transformations and their frequent appearance in natural products, biologically active products, pharmaceuticals, and specialty materials [15], as well as an inspirement from oxadiazole 2-oxide **c** as a TGR inhibitor, we herein report a green GO-catalyzed procedure for the cyanation of quinoline and isoquinoline *N*-oxides with benzoyl cyanide under metal-free and base-free reaction conditions, where the functionalization occurred at the 2-position of quinoline *N*-oxides and 1-position of isoquinoline *N*-oxides. Generally, the transition-metal-free catalyzed cyanation of *N*-oxides is accompanied by the N—O bond cleavage. To the best of our knowledge, this is the first example that GO as a carbocatalyst has been applied in the chemical transformations of heterocyclic *N*-oxides.

2. Results and discussion

The GO material used in this investigation was prepared by Hummers oxidation of graphite and subsequent exfoliation, as reported [16]. The obtained GO material was characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), visible Raman spectroscopy, atomic force microscopy (AFM), and infrared spectrum (IR) (see the Supporting Information).

Initially, we commenced our investigation by the reaction of

quinoline *N*-oxide (**1a**) with TMSCN as a model reaction. After extensive experimentation, the desired product **2a** was obtained in 25% yield when 50 wt % of GO was selected as a catalyst in dioxane at 100 °C for 8 h (Table 1, entry 1). It is important that the N—O bond cleavage is not occurring. To avoid producing hazardous HCN gas, replacing TMSCN with NH_4SCN, CH_3CN, 2-phenylacetonitrile, 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), azobisisobutyronitrile (AIBN) or *N*-cyano-N-phenyl-p-methylbenzenesulfonamide (NCTS) resulted in no reaction (Table 1, entries 2—6). However, the cyanation product **2a** was isolated in 56% yield by using benzoyl cyanide as a "CN" source (Table 1, entry 7). With the encouraging preliminary result, different solvents such as toluene, H_2O, EtOH, DMF, and DMSO, were investigated (Table 1, entries 8—12), and DMSO gave the best result with 89% yield (Table 1, entry 12). We also tried this reaction using graphite or graphene instead of GO. The results showed that graphite and graphene were inefficient (Table 1, entries 13 and 14).

As expected, the control experiments clearly showed that GO is essential for this reaction, as no cyanation product was observed in the absence of the GO catalyst (Table 1, entry 15). Subsequent efforts were directed toward optimizing the GO loadings (Table 1, entries 16 and 17). By lowering the catalyst loading to 40 wt %, it was observed that product could be isolated in 71% yield. However, further lowering catalyst loading to 30 wt % made the reaction become sluggish, which resulted in product **2a** in 33% yield along with 60% recovered starting material. The investigation on the effect of the reaction temperature proved that 100 °C was appropriate for this reaction (Table 1, entries 18 and 19). Finally, the best result was obtained by using GO (50 wt %) in DMSO at 100 °C for 8 h under air atmosphere.

After establishment of the optimal reaction conditions, we evaluated the generality of the GO- catalyzed cyanation, and the results are summarized in Table 2. We first examined the scope of differentially substituted quinoline *N*-oxides in the cyanation with benzoyl cyanide. As shown in Table 2, a wide range of quinoline *N*-oxides, including chloro, bromo, methyl, methoxy and nitro, can be employed as effective coupling partners. Generally, the introduction of electron-donating or electron-withdrawing groups at the C-5, -6, -7, or -8 position of the quinoline *N*-oxides all proceeded with the smooth coupling with benzoyl cyanide, affording the corresponding products in moderate to excellent yields and with good regioselectivity. Particularly compelling is the cyanation of 5-(phenylethynyl)quinolone *N*-oxide (**2o**), which proceeded in good yield despite the presence of an alkyne group. The structure of **2b** was confirmed by X-ray analysis (see the Supporting Information for more details).

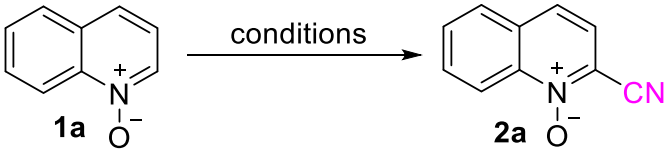
This methodology also proved applicable to isoquinoline *N*-oxides (**2p-2s**), which could proceed efficiently and afford the corresponding products in moderate to excellent yields and with good regioselectivity. Unfortunately, **1t** and **1u** were not converted into their target products.

In addition, the cyanations of other heteroarene *N*-oxides, such as 2,2-dimethyl-3,4-dihydro-2*H*-pyrrole 1-oxide **4,** with benzoyl cyanide was presented in Scheme 2.

GO as a carbocatalytic material could be easily scaled up because of its low-cost and abundantly available. In order to demonstrate the effectiveness of this new strategy, a gram scale reaction was performed under the standard conditions. 10 mmol **1a** and 15 mmol benzoyl cyanide were subjected to the reaction in the presence of GO (726 mg, 50 wt %) in 20 mL DMSO 100 °C under air atmosphere. After 8 h, the desired product **2a** was obtained in 85% yield, which demonstrated the practical application of this protocol to prepare 2-cyanoquinoline 1-oxides on a gram-scale (Scheme 3).

As we all know, one-pot synthesis can simplify a lot of processing procedure and reduce the loss of material compared to multi-step reactions. We envisaged that the cyanation of quinoline *N*-oxide could be realized in "one-pot" by starting with quinoline as substrate. We initiated our studies with quinoline as substrate and

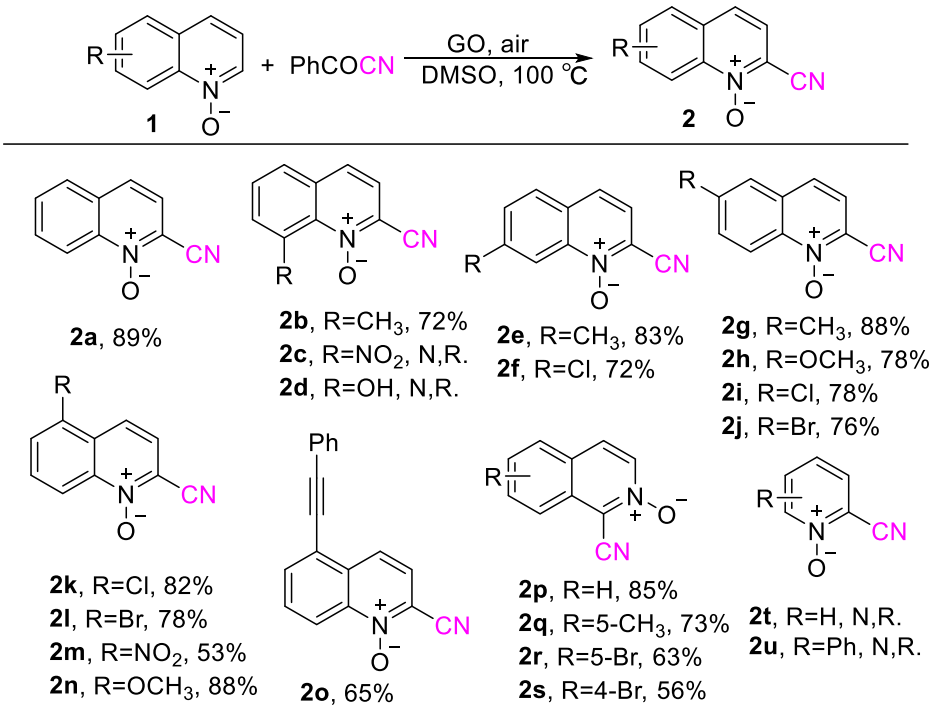
Table 1
Screening of the reaction conditions[a].



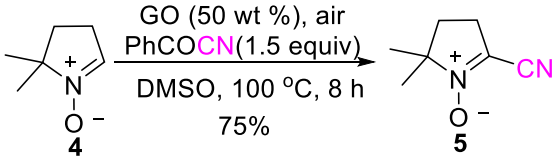
Entry	Catalyst (wt%)[b]	yano source	Solvent	T (°C)	Time (h)	Yield[c]
1	GO (50)	TMSCN (3 equiv)	1,4-dioxane	100	8	25
2	GO (50)	CH_3CN(3 equiv)	1,4-dioxane	100	24	0
3	GO (50)	$PhCH_2CN$(3 equiv)	1,4-dioxane	100	24	0
4	GO (50)	DDQ (3 equiv)	1,4-dioxane	100	24	0
5	GO (50)	AIBN (3 equiv)	1,4-dioxane	100	24	0
6	GO (50)	NCTS (3 equiv)	1,4-dioxane	100	24	0
7	GO (50)	benzoyl cyanide	1,4-dioxane	100	8	56
8	GO (50)	benzoyl cyanide	toluene	100	8	28
9	GO (50)	benzoyl cyanide	H_2O	100	8	N.R.
10	GO (50)	benzoyl cyanide	EtOH	100	8	N.R.
11	GO (50)	benzoyl cyanide	DMF	100	8	N.R.
12	GO (50)	benzoyl cyanide	DMSO	100	8	89
13	Graphite (50)	benzoyl cyanide	DMSO	100	24	N.R.
14	Graphene (50)	benzoyl cyanide	DMSO	100	24	N.R.
15	—	benzoyl cyanide	DMSO	100	24	N.R.
16	GO (40)	benzoyl cyanide	DMSO	100	8	71
17	GO (30)	benzoyl cyanide	DMSO	100	24	33
18	GO (50)	benzoyl cyanide	DMSO	90	8	80
19	GO (50)	benzoyl cyanide	DMSO	110	8	83

[a] Reaction conditions: A mixture of **1a** (0.3 mmol) and benzoyl cyanide (1.5 equiv) in solvent (1 mL) was placed in an oil bath under air atmosphere.
[b] With respect to the substrate **1a**.
[c] Isolated yield after purification by column chromatography.

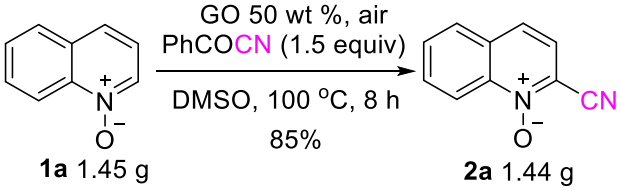
Table 2
Substrate scope of quinoline N-oxides with benzoyl cyanide[a,b].



[a] Reaction conditions: A mixture of N-oxides (0.3 mmol), GO (50 wt %) and benzoyl cyanide (1.5 equiv) in DMSO (1 mL) was placed in an oil bath at 100 °C under air atmosphere for 8 h [b] Isolated yield after purification by column chromatography.



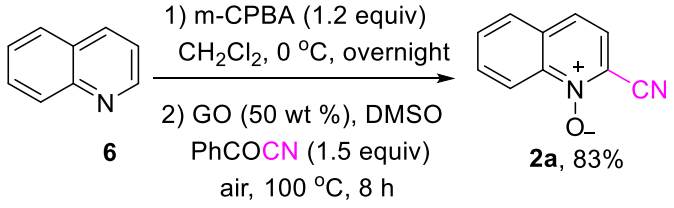
Scheme 2. The cyanation of pyrrole oxide with benzoyl cyanide.



Scheme 3. Scale-up reaction between 1a and benzoyl cyanide.

MCPBA as oxidant in CH_2Cl_2 at 0 °C for overnight. After completion of oxidation for the synthesis of the intermediate quinoline *N*-oxid **1a** and concentration, GO, benzoyl cyanide and DMSO were added, and the resultant mixture was stirred at 100 °C for 8 h. To our delight, **2a** was isolated in 83% yield after a lot of research (Scheme 4).

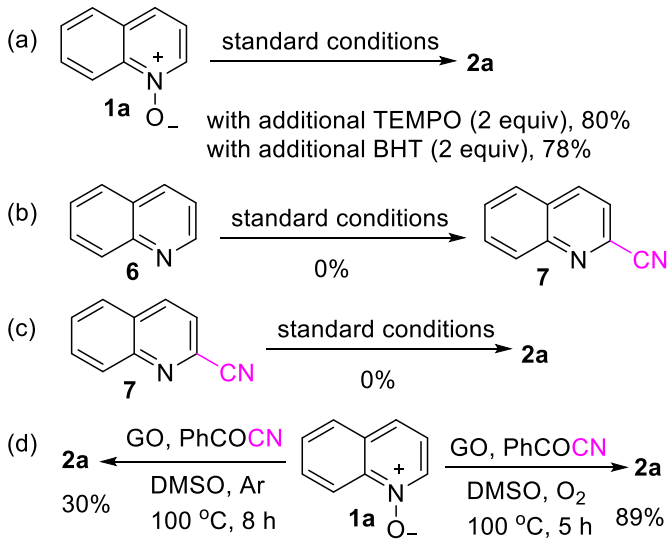
In order to gain some insight into the mechanism of this reaction, a series of control experiments were conducted as shown in Scheme 5. Initially, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) or butylated hydroxytoluene (BHT) as a radical inhibitor was added under the standard conditions. As expected, **2a** was isolated in good yields (80% and 78%, respectively) (Scheme 5a), suggesting that the reaction did not follow a free-radical pathway.



Scheme 4. One-pot synthesis of 2a using quinolone as substrate.

When the reaction of quinolone **6** instead of **1a** with benzoyl cyanide was performed under standard conditions, the product **2a** was not detected (Scheme 5b), which indicates that the oxidation of quinoline is the prerequisite condition. Furthermore, we used the substrate **7** to perform the reactions. Under the standard conditions, **2a** was not detected and **7** was basically recovered (Scheme 5c). These results indicated that **7** was not likely the key intermediate in this protocol and the N—O bond has been cut off during the reaction. These experimental results suggested that the reaction follows a different route [10d]. When the graphene instead of GO as the catalyst was also added under the standard conditions, no desired product was detected (Table 1, entry 14), confirming that the presence of abundant epoxide groups and carboxylic acid groups on GO was indispensable.

Because the GO-catalyzed cyanation of *N*-oxides was performed under open air, the role of molecular dioxygen in this reaction was explored. Notably, the reaction yield was not increased under an oxygen atmosphere, but a more rapid conversion of the starting material to the reaction product was observed. However, the product 2a was obtained only in 30% yield under an argon atmosphere (Scheme 5d). These results indicated that O_2 and GO are essential for the cyanation.



Scheme 5. Control experiments.

GO with high-oxygen content is usually labile at higher temperature. X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FT-IR) analysis showed that a large of epoxide groups and carbonyl functional groups are lost when GO participates the reaction (Fig. 2). For example, the results show a significant decrease in the intensity of C—O and C═O peaks in the high-resolution XPS spectra of the recycled (one time) catalyst samples (GO-r1) (Fig. 2a).

Furthermore, energy dispersive X-ray spectroscopy (EDXS) and X-ray photoelectron spectroscopy (XPS) were utilized to determine the carbon/oxygen content of the GO and recovered-GO. Table S1. (ESI†) shows the percentage of C was increased to 88.1% from 59.7%, while the O content was decreased to 10.5% from 39.7% (see the Supporting Information). The removal of oxygen functionalities is attributed to the effective removal of oxidative fragments and to a dehydration reaction driven by the high reaction temperature [17].

The catalyst reusability was examined using a GO catalyst, and the model substrates of **1a** and benzoyl cyanide. The sample was separated by filtration after the first reaction run and used for the second one under the same conditions. The desired product 2a was obtained only in 48% yield when the recovered-GO was used again as catalyst in the C—H cyanation of quinoline *N*-oxide, but the recovered-GO displays certain activity after 6 cycles (see the Supporting Information). The result indicates that the loss of epoxide groups and carbonyl functional groups results in a great decrease of recovered-GO catalytic activity, which suggests that GO with high-oxygen content is critical to this reaction.

On the basis of these experimental results and the relevant reports [10d,18], a plausible reaction pathway for this metal-free catalytic cyanation of quinoline *N*-oxide is shown in Scheme 6. Initially, the quinoline *N*-oxide is first activated by the hydroxyl groups and carbonyl functional groups on GO to generate a highly active electrophilic species [19]. Next, the highly active electrophilic species can be transformed into dearomatized intermediate **8** through regioselective nucleophilic attacks of cyanide ion (come from the hydrolysis of benzoyl cyanide) at α-carbon of quinoline. Finally, intermediate **8** underwent oxidation in the presence of GO and air to give intermediate **9**, followed by the dehydration of **9** to provide the 2-cyano product **2a**.

The *in vitro* antiproliferative activities of all prepared products was evaluated against T-24 (human bladder cancer), NCI—H460 (human lung cancer cell), HepG2 (human hepatocellular cancer), MGC-803 (human gastric cancer), Hela (human cervical cancer cells) and HL-7702 (human normal liver) cells, by MTT colorimetric assay to explore the potential pharmacological activity of synthesized compounds. Camptothecin (CPT) was used as a positive control (Table 3). The table showed that two products demonstrated moderate to favorable inhibition activity against these tumor cell lines. Among these compounds, **2s** showed the strongest activity with IC_{50} values of 10.23 ± 1.05, 13.67 ± 1.16, 15.69 ± 1.74, 14.53 ± 0.94 and 14.86 ± 1.63 μM against T-24, NCI—H460, HepG2, MGC-803, Hela cells, respectively (Table 3). The inhibiting effect of compound **2s** was more evident on tumor cells than that on normal human cells HL-7702.

The apoptosis effects of compound **2s** on T-24 cells were further studied on MTT assay results. T-24 cells were tested with compound **2s** at different concentrations (control, 5, 10 and 15 μM) for 24 h in Fig. 3. Treatment of 15 μM compound **2s** evidently increased the percentage of apoptotic T-24 cells to 15%. Cell viability significantly decreased at > 20 μM, and almost all of the T-24 cells died in 48 h.

The cell cycle distribution of compound **2s**-treated T-24 cells was examined by flow cytometry to investigate the inhibition effect of compound **2s** on cell proliferation through cell cycle arrest (Fig. 4). The percentage of T-24 cells at G1 phase was markedly decreased from 48.83% (control group) to 2.43% (15 μM) after incubation with compound **2s**. Meanwhile, cells in S phase decreased

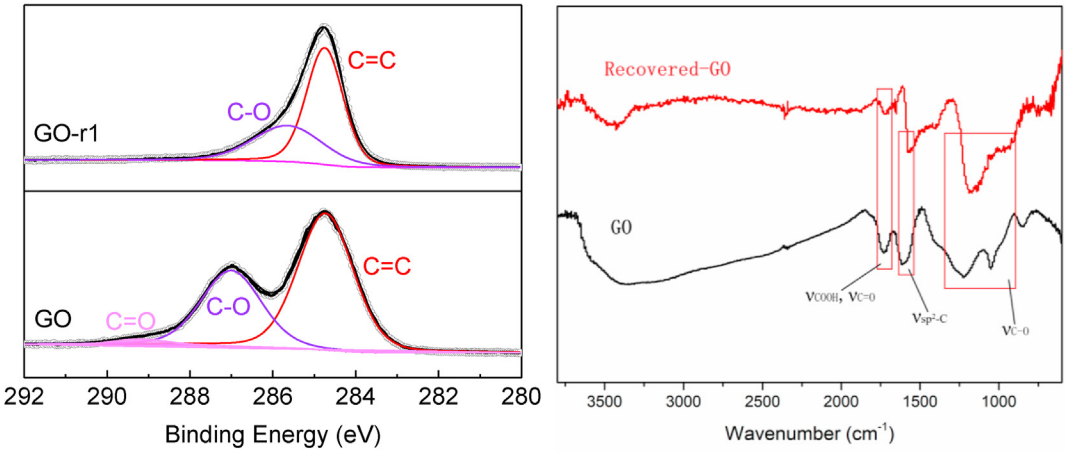
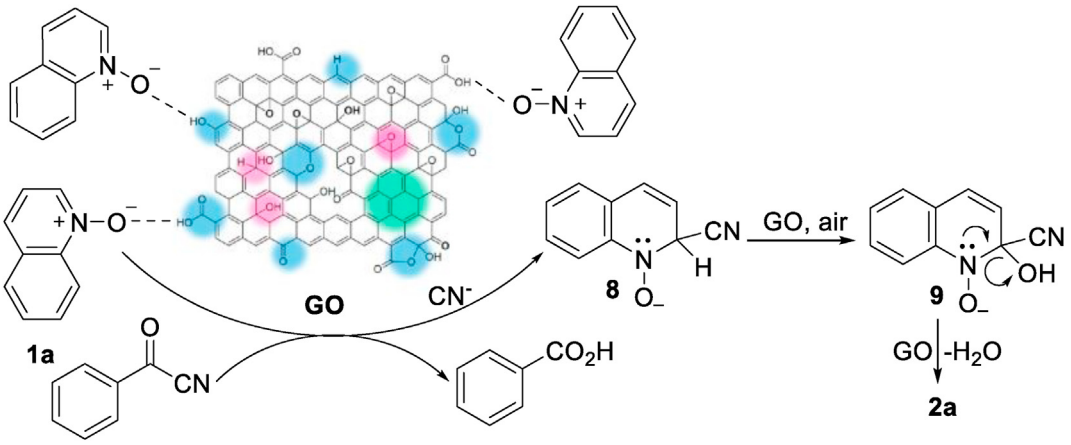


Fig. 2. a. XPS C1*s* spectra of GO and GO-r1(Recovered-GO); b. FT-IR spectrum of GO and Recovered-GO.



Scheme 6. Proposed reaction mechanism.

Table 3
The IC_{50} (μM)[a,b] values of antiproliferative activities.

Comp.	T-24	NCI−H460	HepG2	MGC-803	Hela	HL-7702
2◦	20.85 ± 1.06	22.17 ± 1.10	22.96 ± 1.54	20.98 ± 1.25	24.37 ± 1.47	60.87 ± 2.33
2s	**10.23 ± 1.05**	**13.67 ± 1.16**	**15.69 ± 1.74**	**14.53 ± 0.94**	**14.86 ± 1.63**	**41.53 ± 1.64**
CPT	3.15 ± 0.84	5.63 ± 0.94	4.12 ± 0.26	5.67 ± 1.21	3.46 ± 0.73	6.46 ± 0.83

[a] Data are expressed as means ± SD of three independent experiments.
[b] Compounds with IC_{50} (μM) values > 50 μM are considered inactive.

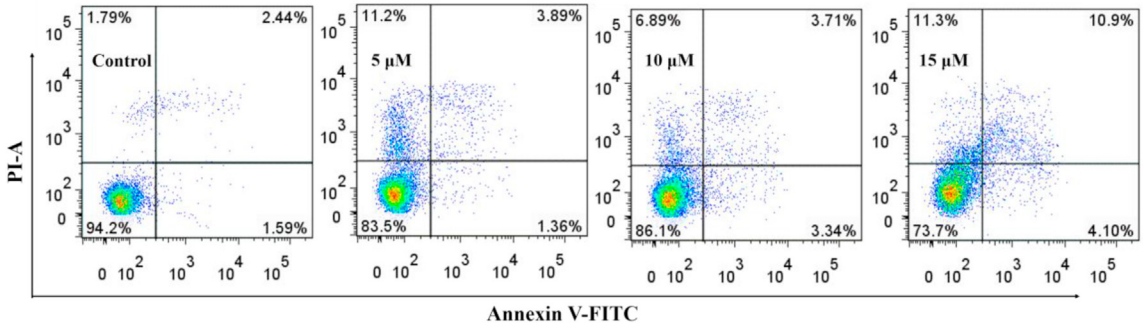


Fig. 3. Induction of apoptosis by compound 2s in T-24 cells.

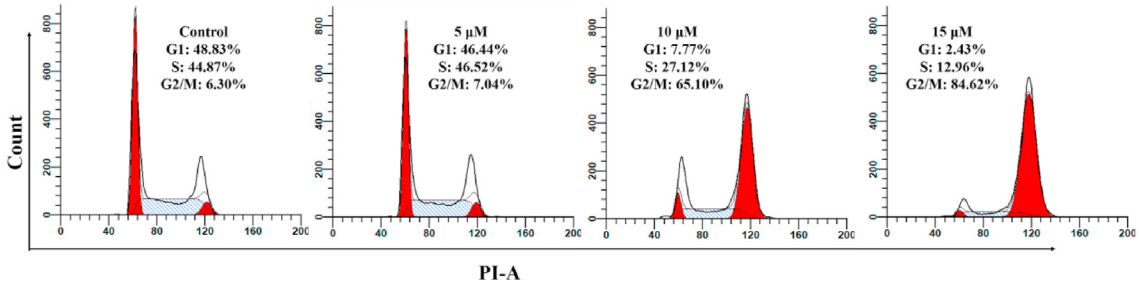


Fig. 4. Effects of 2s on cell cycle distribution in T-24 cells for 24 h.

from 44.87% to 12.96% (15 μM) in the control group. This finding indicates that compound **2s** caused a remarkable G1 phase arrest.

3. Conclusions

A new GO-catalyzed cyanation of quinoline and isoquinoline *N*-oxides with benzoyl cyanide was first developed, which provides an approach to prepare a variety of α-cyano quinoline and isoquinoline *N*-oxides under mild and neutral conditions without using any acid or base. This protocol is highly green and practical due to the use of inexpensive GO as the catalyst. Metal-free conditions, broad substrate scope with diverse substitution patterns,

and operational simplicity are noteworthy features of this protocol. Generally, the transition-metal-free catalyzed cyanation of *N*-oxides is accompanied by the N–O bond cleavage. Furthermore, compound **2s** induced T-24 apoptosis, decreased mitochondrial membrane potential, arrested cell cycle at the G1 phase, elevated intracellular reactive oxygen species level and intracellular free Ca^{2+} level in human bladder cancer cells.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2021.131964.

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