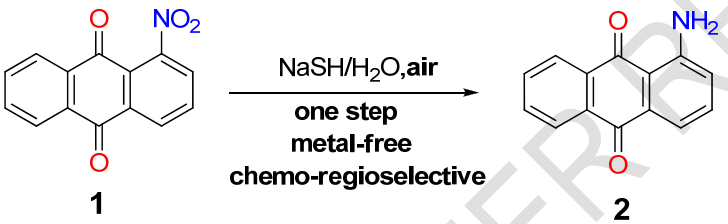
Original Research Article

A green and scalable synthesis of 1-amino anthraquinone

Abstract 1-amino anthraquinone **(2)** is the most important intermediate in the synthesis of acid dyes. This paper presents a new method for the preparation of title compound **(2)** in a highly chemo- and regioselective reduction of 1-nitro anthraquinone **(1)** by NaHS in water under mild conditons. This protocol is clean, operationally simple, easy work-up and could be applied in the industrial production .

Graphical_Abstract



Keywords nitroanthraquinone, aminoanthraquinone, reduction

1. Introduction

1-Amino anthraquinone (**2**) is one of the most important intermediates in the synthesis of functional dyes.[1] To date, a variety of methods for the the synthesis of 1-amino anthraquinone (**2**) have been disclosed, most of these protocols employing 1-nitro anthraquinone (**1**) as a starting material.[2] 1-amino anthraquinone (**2**) can be obtained by single–step reduction from compound (**1**). These reductants include ammonium formate,[3] sodium sulfate(Na_2S),[1] sodium borohydride ($NaBH_4$),[4], Gold-Catalyzed CO-H_2O system[5] and bis(cyclopentadienyl)titanium(IV) dichloride-indium system[6]. However, none of these reagent is siutable for industrial production due to drawbacks like high cost, toxic substance, complex work-up, etc. In

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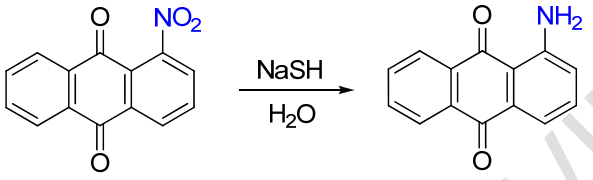
recent years, the demand for 1-amino anthraquinone (**2)** in the dye industry has been increased rapidly. Hence, it is important to developed an efficient and scalable method for synthesis of 1-amino anthraquinone (**2)**.

As shown in **Scheme 1,** we reported here a facial, green and scalable method for the preparation of 1-amino anthraquinone (**2)** by using NaHS as a reductant, the solvant water meets the requirements of green chemistry and it should be suitable for industrial production.



1 **2**

Scheme 1. Synthesis of compound 2

2. Experimental section

All reactions were monitored by TLC, Melting points were measured on Melting Point M-565 (BUCHI). NMR and mass spectra were recorded on a Bruker Avanc III-HD 400 NMR and a TripleTOF Mass spectrometers, respectively. All reagents: e.g. $Na_2S\cdot 9H_2O$, NaSH, $NaBH_4$, $Na_2S_2O_4$ were purchased from Adamas, P. R. China, and used without further purification.

Synthesis of 1-amino anthraquinone (**2)**

A 250 mL three-necked flask is equipped with a stirrer and thermometer and a dropping funnel. The flask is charged with a solution of NaSH (3.00 g, 0.05 mol) in water (15 mL) and stirred at 60 ^{o}C for 1h. Then 1-nitro anthraquinone (**1**) powder (3.04 g, 0.01 mol) was added over 10 minutes and the reaction mixture quickly turned to red. The mixture was stirred at 60 ^{o}C for another 1h and the progress of the reaction was monitored by TLC. The reaction mixture was filtered and the red precipitates were washed with water, and recrystallization from ethanol to give compound **2** as a red powder (2.79 g, yied 92%), m.p. 253 ^{o}C (lit[6]253-255°C)

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^{1}H NMR (400 MHz, $CDCl_3$): δ8.30 (d, *J* = 8.0 Hz, 1H), 8.26 (d, *J* = 8.0 Hz, 1H), 7.78 (t, *J* = 8.0 Hz, 1H), 7.73 (t, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.87 (s, 2H).

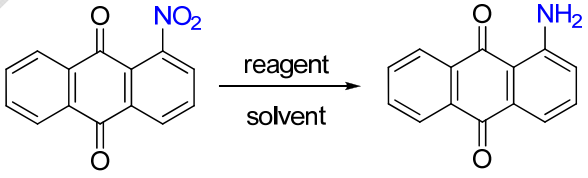
^{13}C NMR (100 MHz, $CDCl_3$): δ185.3, 183.6, 151.0, 134.8 (2**C**), 134.4, 134.0, 133.2 (2**C**), 126.8 (2**C**), 123.1, 117.3, 113.7.

MS(ESI): m/z = 224 (M+H)

3. Results and discussion

The key factor to obtain compound **2** is how to efficent selectivly redution the nitro-group of compound **1** without affecting the carbonyl group. We investaged the effects of different reagents and solvents, the results were shown in **Table 1**. The reaction solvent plays an important role in this reaction, water is better than alcohols or the alcohol solutions. Both Na_2S and NaHS can be severed as a good reducing agents, but when the reaction scale is kilogram level, we found that Na_2S is difficult to agitate in the 5L three round-bottomed flasks, while NaHS do not have this problem. Based on this point, NaHS is much more suitable in industrial large-scale production. The poor solubility of sulfide in ethanol lead to a decrease of yield. We also examed reagents $NaBH_4$ and $Na_2S_2O_4$, which gave compound **2** in 45% and 35% yield respectively. The optimal condition was using $AgNO_3$ (40%), and $K_2S_2O_8$ (2 equiv) in water at 60 °C for 2 h (entry 4, **Table 1**).

Table 1. Reduction of 1-nitroanthraquinone (**1**) udner different conditions



1 **2**

Entry	Reagent	Solvent(v/v)	Temperature(°C)	Yied(%)
1	$Na_2S\cdot 9H_2O$	H_2O	60	80%
2	$Na_2S\cdot 9H_2O$	EtOH	60	35%
3	$Na_2S\cdot 9H_2O$	EtOH/ H_2O(1/1)	60	63%
4	**NaSH**	**H_2O**	**60**	**92%**
5	NaSH	EtOH	60	24%
6	NaSH	EtOH/ H_2O(1/1)	60	59%

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7	$NaBH_4$	isopropanol	60	45%
8	$Na_2S_2O_4$	EtOH	60	35%

Reaction Conditions: compound **1** (0.05mol), reagent (2 equiv), 2 hour under open air

4. Conclusions

In summary, a NaHS-mediated new method for the synthesis of 1-amino anthraquinone **(2)** has been developed. This protocol is easily operational, efficient, and is amenable to the kilogram-scale synthesis of compound **(2)**. This chemistry also provided a new selectivly redution of aromatic nitro-group without using metal catalyst.

References

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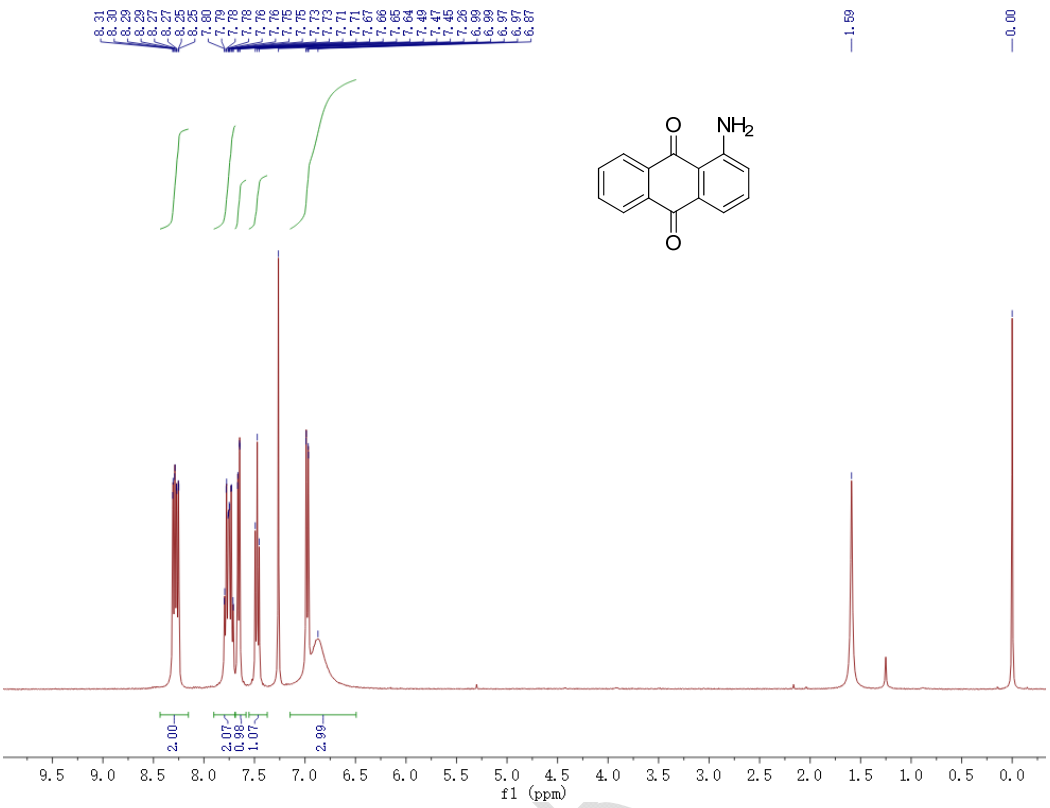
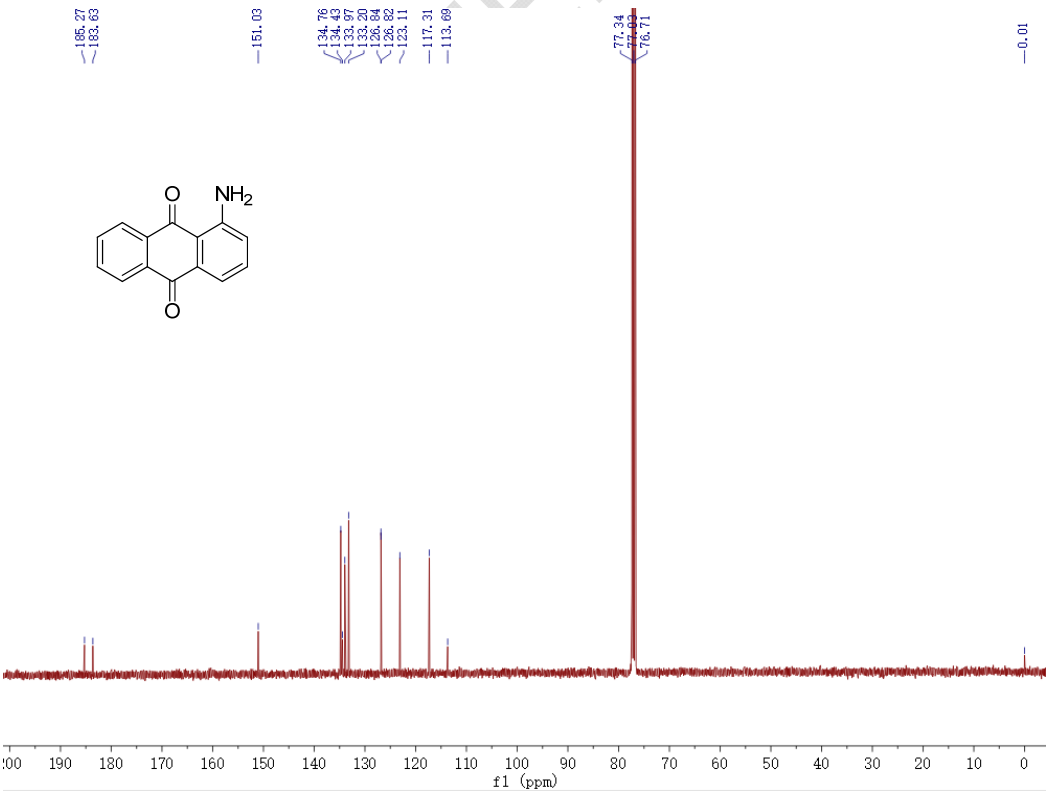


98

99 ^{1}H NMR of compound 2



100

101 ^{13}C NMR of compound 2

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