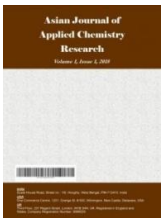

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A Green and Scalable Synthesis of 1-Amino Anthraquinone

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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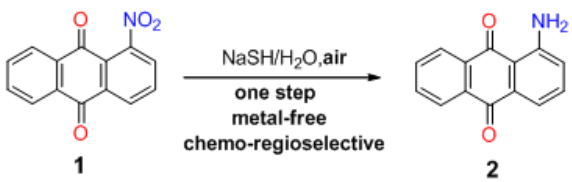
ABSTRACT

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 conditions. This protocol is clean, operationally simple, easy work-up and could be applied in the industrial production.

Graphical_Abstract



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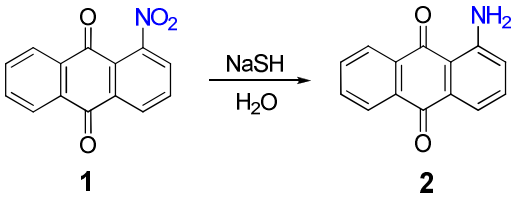
Keywords: Nitroanthraquinone; aminoanthraquinone; reduction.

1. INTRODUCTION

1-Amino anthraquinone [1] is one of the most important intermediates [2] in the synthesis of functional dyes [1]. To date, a variety of methods for the the synthesis of 1-amino anthraquinone [1] have been disclosed [3], most of these protocols employing 1-nitro anthraquinone [2] as a starting material [4]. 1-amino anthraquinone [1] can be obtained by single–step reduction from compound [2]. These reductants include ammonium formate,[5] sodium sulfate(Na_2S),[1] sodium borohydride ($NaBH_4$),[6], Gold-Catalyzed CO-H_2O system [7] and bis(cyclopentadienyl)titanium(IV) dichloride-indium system [8]. However, none of these reagent is suitable for industrial production due to drawbacks like high cost, toxic substance, complex work-up, etc.[9] In recent years, the demand for 1-amino anthraquinone (2) in the dye industry has increased rapidly. Hence, it is important to developed an efficient and scalable method for synthesis of 1-amino anthraquinone [1].

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, [10] the solvant water meets the requirements of green chemistry and it should be suitable for industrial production.



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 [11] .

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°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°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°C (lit[8]253-255°C)

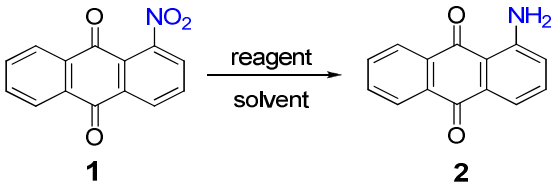
^{1}H NMR (400 MHz, $CDCl_3$): δ8.30 (d, *J* = 8.0 Hz, 1H), 8.26 (d, *J* = 8.0 Hz, 1H), 7.78 (t, *J* = 8.0 Hz, 1H), 7.73 (t, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.87 (s, 2H).

^{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 efficiently and selectively reduce the nitro-group of compound 1 without affecting the carbonyl group [12]. 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 severe 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 examined 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



Entry	Reagent	Solvent(v/v)	Temperature(°C)	Yied(%)
1	Na_2S	H_2O	60	80%
2	Na_2S	EtOH	60	35%
3	Na_2S	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%
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. CONCLUSION

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 provides a new selective reduction of aromatic nitro-group without using metal catalyst.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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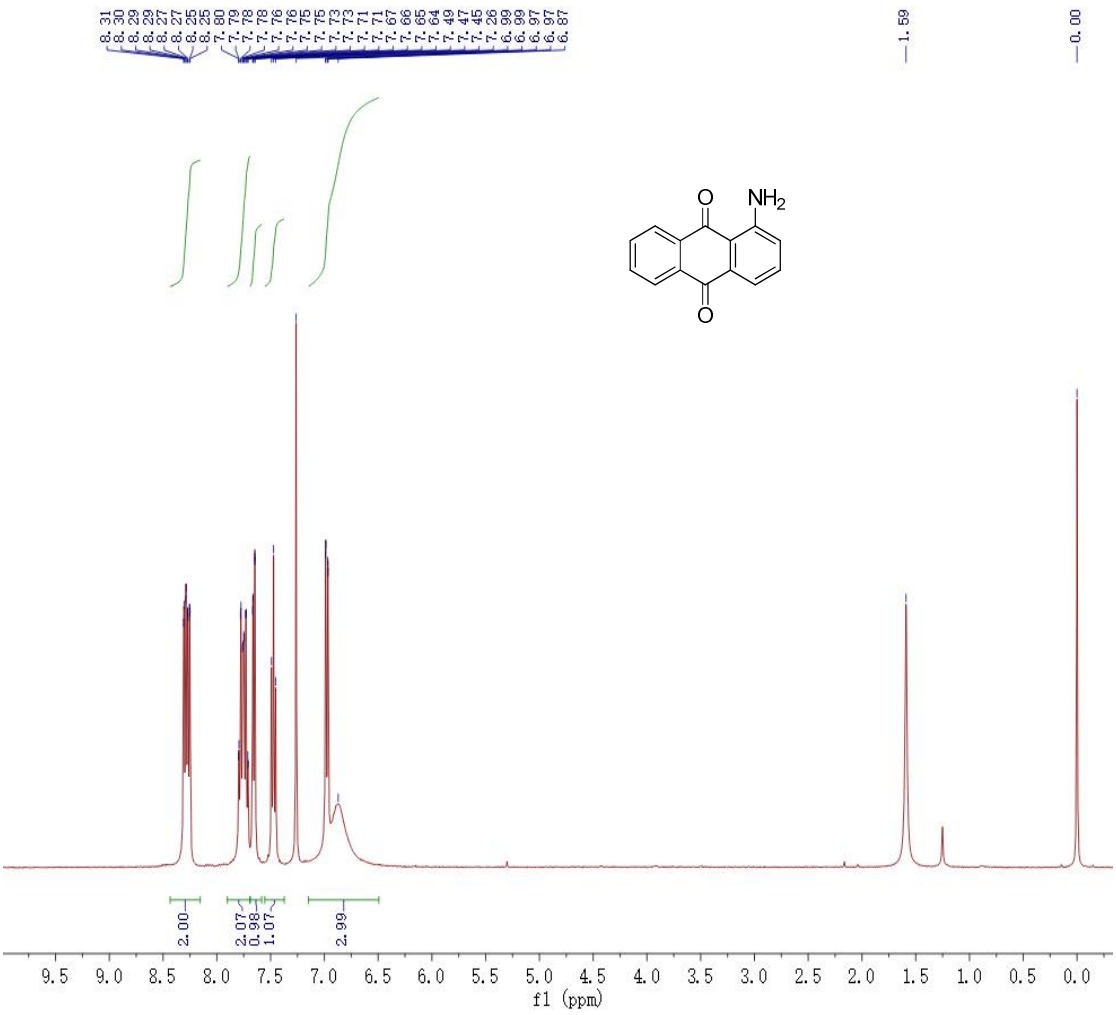
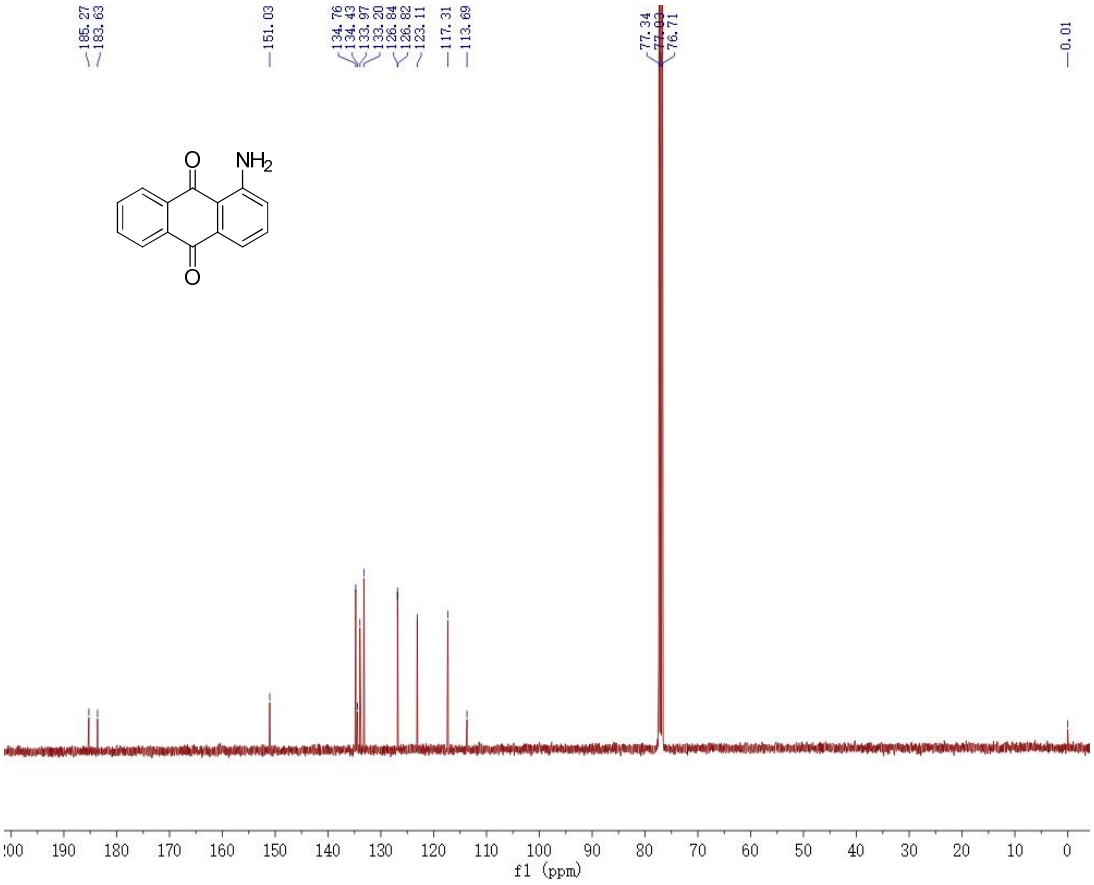
APPENDIX



^{1}H NMR OF COMPOUND 2



^{13}C NMR of compound 2

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