



## Short Communication

## Use of iodine doped polyaniline salt in the stereoselective synthesis of 2-methyl-4-substituted-1,2,3,4-tetrahydroquinoline derivatives

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## ABSTRACT

Polyaniline–iodine salt is proved as a simple, efficient, versatile, recyclable and eco-friendly polymer based solid acid catalyst in the reaction between aromatic amines and *N*-vinyl pyrrolidone/*N*-vinyl caprolactam under solvent free condition. Polyaniline salts such as polyaniline-sulfate, polyaniline-hydrochloride and polyaniline-perchlorate are also catalyzing this reaction smoothly.

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## 1. Introduction

The tetrahydroquinoline scaffold is existing in many natural products or synthetic materials and its derivatives exhibit a broad range of biological activities in various fields [1–3]. In particular, 4-aminoquinoline ring systems represent an important class of compounds [4] that has been shown to have interesting pharmacological properties such as antimalarial [5], analgesic [6,7], anti-inflammatory [8], antitumor [9] and antihypertensive agents [10] as non-nucleoside HIV-1 inhibitors [11,12] and as reversible inhibitors of (H<sup>+</sup>/K<sup>+</sup>)-ATPase [13]. The biological activity of these substituted tetrahydroquinolines has attracted continuous interest in developing new methods for their synthesis [14]. Among those efficient protocols towards the imino-Diels–Alder reaction between *N*-aryl imines and electron-rich dienophiles is probably a most powerful synthetic tool for the construction of nitrogen-containing heterocyclic compounds including substituted tetrahydroquinolines [15], due to its efficiency and the ready availability of starting materials.

2-Methyl,4-substituted tetrahydroquinoline derivatives have usually been synthesized from the reaction of substituted aniline and *N*-vinyl pyrrolidone (NVP) by the traditional method using acid catalysts [16–20]. According to the reference of Mahadeven et al. [16] using 4-nitro phthalic acid, the reactions were completed within 2–4 h with 88–94% yields in acetonitrile at 50 °C. However, reusability nature of this catalyst has not been reported. Subsequently, Hosamani et al. used copper pyridine dichloride as catalyst [17] under the same condition and obtained the product (90% yield) in 3 h with recyclability. The phosphotungstic acid catalyst reaction reported by Kavitha et al. [18]

mentioned the completion of reaction within 1 h with 75–79% of 2-methyl tetrahydroquinoline derivatives in acetonitrile at room temperature. Similarly, the report of indium trichloride catalyst [19] reaction was completed within 10–60 min. in water under reflux condition with higher yields. Very recently, Chen and Lee reported this reaction using FeCl<sub>3</sub> catalyst [20] in acetonitrile solvent at reflux condition and obtained the product in 74% yield in 8 h.

Thus, these reactions have some drawbacks like prolonged reaction time, non recoverable catalyst, toxic and expensive catalysts. Therefore, the search continues for a better catalyst for the synthesis of tetrahydroquinolines in terms of operational simplicity, reusability, low cost and green catalyst. In order to improve the synthetic methodology, polyaniline based solid acid catalysts have been used as better catalysts in the synthesis of *cis* 2-methyl-4-substituted tetrahydroquinoline derivatives.

## 2. Experimental

## 2.1. Instruments and characterization

Powder of PANI salt was pressed into disk of 13 mm diameter and about 1.5 mm thickness under pressure of 400 MPa. Resistance of the pellet was measured by two probe methods using 2010 digital multimeter (Keithley, Cleveland, Ohio, USA). FT-IR spectra of PANI salts were registered on a FT-IR spectrometer (Thermo Nicolet Nexus 670, USA) using the KBr pressed pellet technique. X-ray diffraction profiles for PANI salt powders were obtained on a Siemens/D-500 X-ray diffractometer, USA using Cu K $\alpha$  radiation, scan speed of 0.045°/min. Morphological studies of PANI salt powders were performed using Hitachi 3000N, Tokyo, Japan scanning electron microscope operating

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at 10 kV. The sample was mounted on a double-sided adhesive carbon disk and sputter-coated with a thin layer of gold to prevent sample from possible charging. The energy-dispersive X-ray (EDAX) spectroscopy was analyzed with an EDAX detector (Oxford LINK-ISIS 300) with Jest 520 microscope.  $^1\text{H}$  NMR spectra of all the products in DMSO- $d_6$  with TMS as internal standard were taken using Avance-500/Inova-400 instruments.

## 2.2. General procedure for preparation of polyaniline salt catalyst

Polyaniline base and polyaniline salts containing sulfate, perchlorate and hydrochloride were prepared by aqueous polymerization pathway via our earlier reported procedure [21]. Polyaniline-iodine salt was prepared by the following procedure. Polyaniline base (0.5 g) was added to 50 ml of acetonitrile solution containing 0.04 M iodine ( $\text{I}_2$ ) and the mixture was stirred at ambient temperature for 4 h. The resultant mixture was filtered, washed with acetonitrile followed by acetone until colorless filtrate and dried at 50 °C till a constant weight.

## 2.3. General procedure for polyaniline salt catalyzed domino tetrahydroquinoline synthesis

In a typical experiment, a mixture of aromatic amine (1 mmol), N-vinyl lactam (2 mmol) and PANI- $\text{I}_2$  catalyst (14 wt.% with respect to N-vinyl lactam) under solvent free conditions was stirred at 80 °C for 10 min. (Scheme 1) Then EtOAc was added to the reaction mixture, filtered and separated the catalyst. Organic layer was washed with water followed by brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated. The crude material was purified by column chromatography using silica gel (60–120 mesh) and eluted with petroleum ether: ethyl acetate (8:2). Isolated yield was calculated and the margins of error in these experiments are  $\pm 1\%$ . All the products were characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and mass spectroscopic data and compared with the literature values [16–20]. Recyclability experiment was carried out using the separated catalyst, wherein,

the separated catalyst was washed with acetone and dried in an oven for 50 °C for 2 h.

## 2.4. Spectral data

As representative systems, spectral data for the two compounds are given here.

### 2.4.1. *cis*-1-(6-Chloro-2-methyl-1,2,3,4-tetrahydroquinolin-4-yl) pyrrolidin-2-one

m.p. 150 °C.

IR (KBr)  $\text{cm}^{-1}$ : 3389 (N–H), 1670 (C=O).

$^1\text{H}$ NMR (DMSO- $d_6$ ):  $\delta$  1.26 (d, 3H,  $J=6.0$  Hz), 1.78 (ddd, 1H,  $J=12.6, 5.3, 2.5$  Hz), 1.93 (ddd, 1H,  $J=11.7, 5.8, 26.4$  Hz), 1.95–2.18 (m, 2H), 2.40–2.55 (m, 2H), 3.10–3.35 (m, 2H), 3.45–3.66 (m, 1H), 4.8 (brs, 1H, NH), 5.7 (dd, 1H,  $J=12.0, 6.0$  Hz), 6.43 (d, 1H,  $J=8.6$  Hz), 6.73 (s, 1H), 6.92 (dd, 1H,  $J=8.8$  Hz, 2.4 Hz) ppm.

$^{13}\text{C}$ NMR (DMSO- $d_6$ ):  $\delta$  18.0, 22.2, 31.8, 33.4, 42.8, 47.6, 47.3, 116.3, 120.3, 122.2, 126.0, 129.6, 144.1, 175.4 ppm.

MS  $m/z$ : 265.

### 2.4.2. *cis*-1-(6-Chloro-2-methyl-1,2,3,4-tetrahydroquinolin-4-yl)azepan-2-one

m.p. 124 °C.

IR (KBr)  $\text{cm}^{-1}$ : 3362 (N–H), 1654 (C=O).

$^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta$  1.13 (d,  $J$  6.0 Hz, 3H), 1.24–1.31 (m, 1H), 1.40–1.54 (m, 3H), 1.72–1.81 (m, 4 H), 2.37–2.42 (m, 1H), 2.73 (t,  $J$  12.4 Hz, 1H), 2.85–2.87 (m, 1H), 3.14–3.21 (m, 1H), 3.41–3.45 (m, 1H), 5.71–5.72 (m, 1H), 5.90 (s, 1H), 6.49 (d,  $J$  8.6 Hz, 1H), 6.63 (s, 1H), 6.91 (d,  $J$  8.5 Hz, 1H) ppm

$^{13}\text{C}$  NMR (DMSO- $d_6$ ):  $\delta$  21.9, 26.7, 32.8, 32.8, 33.2, 44.9, 44.6, 47.4, 50.9, 116.8, 119.2, 125.7, 126.3, 127.8, 144.1, 173.8 ppm

MS  $m/z$ : 293.

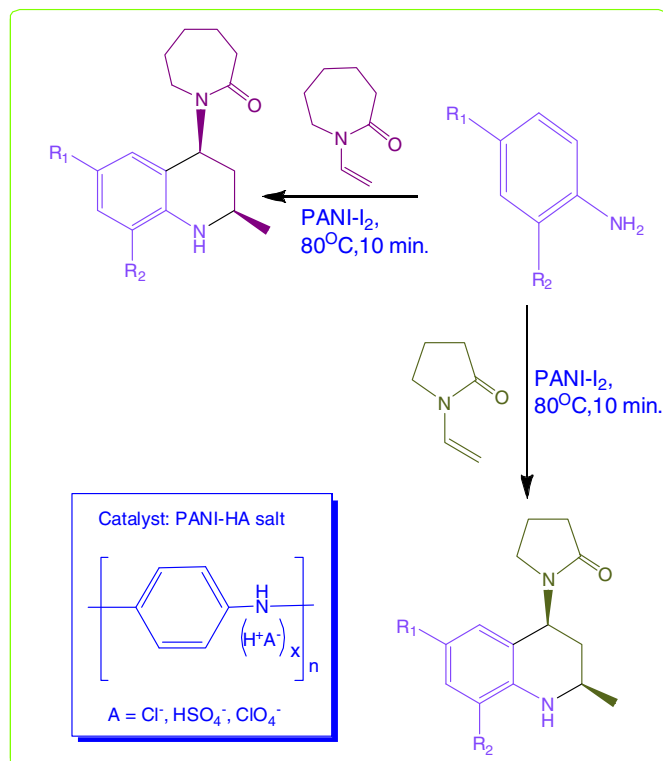
## 3. Results and discussion

Polyaniline (PANI) is one of the most widely studied conducting polymers for its technological applications in biosensors, gas sensors, super capacitors, batteries, electrochromic, electromagnetic shielding, light emitting devices, photovoltaic, ESD, etc. [22]. We have been using conducting polymer systems as polymer based solid acid catalysts in various organic transformations [23]. In continuation of our interest in the use of conducting polymer based solid acid catalysts, in this work, polyaniline-iodine salt was prepared by doping of polyaniline base with acetonitrile solution of iodine. This polyaniline-iodine salt was characterized by infrared, X-ray diffraction, scanning electron microscope, EDAX, conductivity and density measurements. Polyaniline-iodine salt is used as catalyst in the synthesis of 2-methyl-4-substituted-1,2,3,4-tetrahydroquinoline derivatives.

### 3.1. Characterization of polyaniline-iodine catalyst

#### 3.1.1. Infrared spectra of PANI- $\text{I}_2$

The infrared spectrum of PANI base, PANI- $\text{I}_2$  and recycled PANI- $\text{I}_2$  are shown in (Fig. 1). The major characteristic peaks obtained 2000 to 750  $\text{cm}^{-1}$  for the three polyaniline samples are reported in Table 1. Polyaniline base showed the ring stretching of quinoid (Q) and benzenoid ring (B) form at 1581 and 1495  $\text{cm}^{-1}$ , respectively. The C–N stretching band of an aromatic amine appears at 1375 and 1295  $\text{cm}^{-1}$  are attributed to stretching vibration of QBQ and QBB and BBQ respectively. Polyaniline shows a strong band at 1134  $\text{cm}^{-1}$ , which has been explained as electronic like absorption of  $\text{N}=\text{Q}=\text{N}$ . The C–H out-of-plane bending mode has been used as a key to identifying the type of substituted benzene. Polyaniline base showed a peak at 810  $\text{cm}^{-1}$  indicative of 1,4-disubstituted benzene. A similar observation has been reported in the literature for PANI base [24,25] On doping of polyaniline



**Scheme 1.** Synthesis of *cis* 2-methyl-4-substituted-1,2,3,4-tetrahydroquinolines using PANI- $\text{I}_2$  catalyst.

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