

# 2,4-Dioxo-1,3-diazaspiro[4,5]decane-3-sulfonic Acid as a Novel Solid Phase Halogen-free Acid Catalyst: Preparation, Characterization and Evaluation

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## ABSTRACT

N-sulfonated cyclohexylhydantoin (NSCH), a new N-sulfonic acid compound, was prepared and characterized using FT-IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, UV-Vis and TGA analysis. The potential catalyst efficiency was examined, using synthesis of chromene, xanthene and hydroquinoline derivatives under solvent-free conditions. All of the examined model reactions gave excellent yields, and required short reaction times. Simple catalyst preparation and work-up under mild reaction condition, with low cost and the ability to recover the catalyst for reuse without significant loss of activity are some of the notable advantages of the introduced catalyst.

## KEYWORDS

Hydantoin, N-sulfonated acidic catalyst, chromene, xanthene, hydroquinoline.

## 1. Introduction

Common Brønsted acid hydrogen containing catalysts such as sulfuric acid, p-toluene sulfonic acid, hydrochloric acid, hydrofluoric acid and phosphoric acid are used as catalysts to promote many organic synthetic reactions and industrial processes. However, the above-mentioned Brønsted acid catalysts generally result in homogeneous reaction mixtures, causing problems with separation from reaction media, resulting in some disadvantages such as negative environmental impact, wasting energy and increased chemical wastes production. For these reasons, solid acid catalysts have received considerable attention to replace such conventional homogeneous Brønsted acid catalysts, and have shown higher efficiency, operational simplicity, easy reusability, recoverability, non-corrosiveness and higher environmental acceptance.<sup>1–5</sup> Therefore, the development of solid acid catalysts could be very helpful for altering technologies using homogeneous acid catalysts. One of the simplest ways to access solid acidic materials is making use of nitrogen-containing organic compounds and introducing SO<sub>3</sub>H and HSO<sub>4</sub> groups as Brønsted acid functions into their chemical structure, which make them water soluble and enhance their polarity, which aids their use under solvent-free conditions. Many of such solid acid catalysts have been reported.<sup>6–10</sup>

Imidazolidine-2,4-diones (or hydantoins) are well known substructures found in a wide range of biologically active drugs and natural products.<sup>11</sup> From the synthetic point of view, hydantoins could be useful precursors for preparation of acidic catalysts because their acidic N-H could be replaced by the sulfonic acid functional group. Accordingly, sulfonic acid-functionalized hydantoin is now examined as a potential solid acid catalyst in the multicomponent synthesis of xanthenes, chromenes and hydroquinolines.<sup>12–14</sup>

Xanthene, chromene and hydroquinoline derivatives are important organic compounds with a wide range of applicability and biological activity.<sup>15–20</sup> Although some synthetic methodologies have been reported for each class of these compounds in the literature,<sup>21–32</sup> each with their own advantages, many of them

suffer from some disadvantages. The use of homogeneous acid catalysts may result in some difficulties with product separation and purification, low yield, long reaction time, use of toxic organic solvents and harsh reaction procedures. Therefore, we have developed a new and efficient catalyst to overcome these problems.

## 2. Experimental

### 2.1. General Procedure for the Synthesis of Cyclohexylhydantoin (CHH)

Cyclohexanone (5 mmol, 0.52 mL) and ammonium carbonate (10 mmol, 1 g) were added to 30 mL 1:1 ethanol/water. The mixture was heated at 60–70 °C until all of the ammonium carbonate dissolved. Then, a solution of potassium cyanide (10 mmol, 0.7 g) in 10 mL of distilled water was added dropwise over 10 min. After 48 h at 60–70 °C, the mixture was kept at room temperature for 45 min, and then below 0 °C for 2 h. The precipitate was filtered and recrystallized from ethanol. Finally, the desired hydantoin was obtained as needles (70%), mp 220–222 °C.<sup>33</sup>

### 2.2. General Procedure for the Synthesis of Cyclohexylhydantoin- N-sulfonic Acid (NSCH)

A mixture of cyclohexylhydantoin (2 mmol, 0.2 g) and dichloromethane (10 mL) was stirred at 0 °C for 2 h, generating a uniform white paste. Then chlorosulfonic acid (2 mmol, 0.25 mL) in dichloromethane (2 mL) was added over a period of 10 min at 0 °C. The resulting clear solution was kept at 0 °C for 2 h and then allowed to reach room temperature and stirred for a further 2 h. After evaporation of the dichloromethane, the residue was washed with diethyl ether (3 × 5 mL). The final precipitate was obtained (95%), mp 198 °C.

### 2.3. General Procedure for the Synthesis of Chromenes

To a mixture of dimedone (1 mmol), the benzaldehyde (1 mmol) and malonitrile (1.2 mmol) was added the NSCH catalyst (15 mg) and the mixture was stirred at 80 °C for the appropriate

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ate time. The reaction progress was monitored by TLC. After completion of the reaction, chloroform (10 mL) was used to extract the catalyst, and the residual product was recrystallized from ethanol.

#### 2.4. General Procedure for the Synthesis of Xanthenes

A mixture of, dimedone (2 mmol), the benzaldehyde (1 mmol). And the NSCH catalyst (15 mg) was stirred at 80 °C for a given time. At the end of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature. The catalyst was separated from the reaction mixture by addition of chloroform (10 mL), then the crude residue was recrystallized from ethanol.

#### 2.5. General Procedure for the Synthesis of Hydroquinolines

A stirred mixture of dimedone (1 mmol), benzaldehyde (1 mmol), ethyl acetoacetate (1 mmol), ammonium acetate (2 mmol) and the NSHH catalyst (15 mg) was heated at 80 °C and kept for a given time, and the reaction was monitored by TLC. The reaction mixture was cooled to room temperature and the catalyst separated from the reaction mixtures by addition of chloroform (10 mL). The crude product was recrystallized from ethanol.

#### 2.6. Optimizing Reaction Conditions for Tetrahydrochromene Synthesis

A mixture of dimedone (1 mmol), benzaldehyde (1 mmol) and malononitrile (1 mmol) was reacted in the presence of different amounts of NSCH in the temperature range 25–120 °C in the absence and presence of different solvents. The results are shown in Fig. 4a.

#### 2.7. Determination of the Acid Content of the Catalyst

The 0.04 M catalyst solution (20 mL) was titrated with the 0.05 M sodium hydroxide solution. The titration curve is given in

Fig. 3. As seen in Fig. 3, the titration reached the end point when 18 mL of the titrant was added to the catalyst solution. This amount of the titrant is nearly same as that (16 mL) which is needed to complete neutralization of the 20 mL of the 0.04 M solution of the catalyst according to the calculations below (Equation 1). These results showed that the catalyst contains one acidic proton, verifying its sulfonated NH group.

$$M_1 V_{1(\text{acid})} = M_2 V_{2(\text{base})}$$

$$0.04 \text{ (M)} \times 20 \text{ (mL)} = 0.05 \text{ (M)} \times V_2$$

$$V_2 = 16 \text{ mL}$$
(1)

### 3. Results and Discussion

#### 3.1. Catalyst Characterization

The structure of the cyclohexylhydantoin-N-sulfonic acid catalyst, which was synthesized as shown in Fig. 1, was characterized by FT-IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, TGA, DTG, and UV-Vis analysis.

The corresponding FT-IR spectra of cyclohexylhydantoin and cyclohexylhydantoin-N-sulfonic acid are shown in Fig. S11 (Fig. 1 in supporting information). In the case of cyclohexylhydantoin-N-sulfonic acid, the OH stretching band of the SO<sub>3</sub>H functional group appeared as broad bands between 3200 and 3700 cm<sup>-1</sup>, centred at 3414 cm<sup>-1</sup>. Characteristic absorption bands related to the SO<sub>2</sub> asymmetric and symmetric, S–N symmetric and S–OH bending vibrations appeared at 1262, 1176, 1069 and 879 cm<sup>-1</sup>.<sup>10</sup>

Thermogravimetric analysis of CHH and NSCH was carried out to investigate their structural stability during thermal changes. Fig. 2 displays a typical DTGA spectrum for CHH and NSCH. CHH shows a two-step thermal decomposition at 100 °C and 290 °C which corresponds to the loss of the moisture and complete decomposition of the CHH structure, respectively. In the case of NSCH, a three-step thermal decomposition appeared

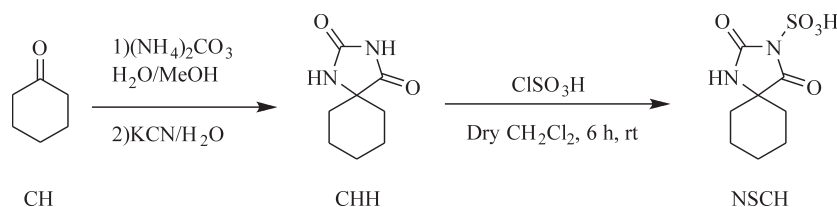


Figure 1 Synthesis of NSCH.

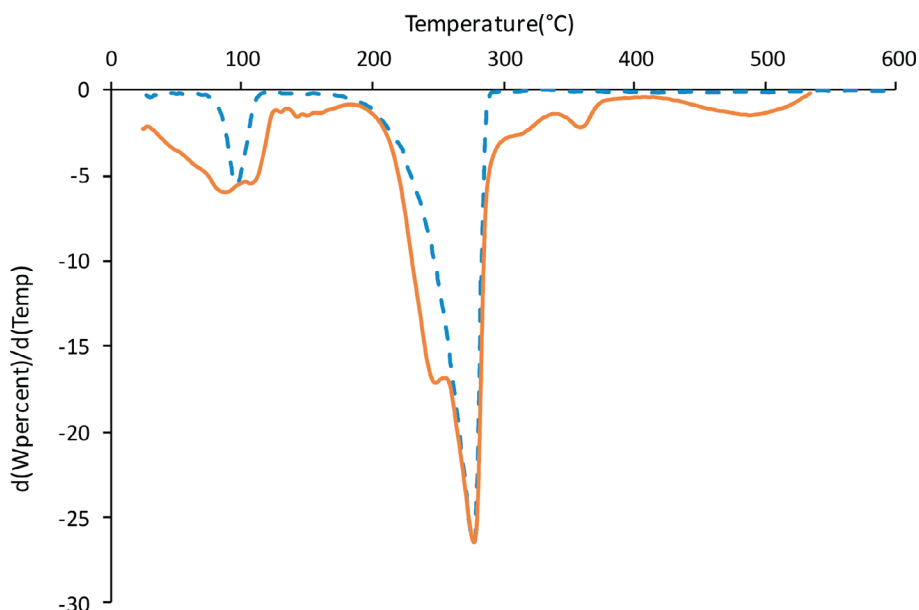


Figure 2 DTGA curves for CHH (– –) and NSCH (—).

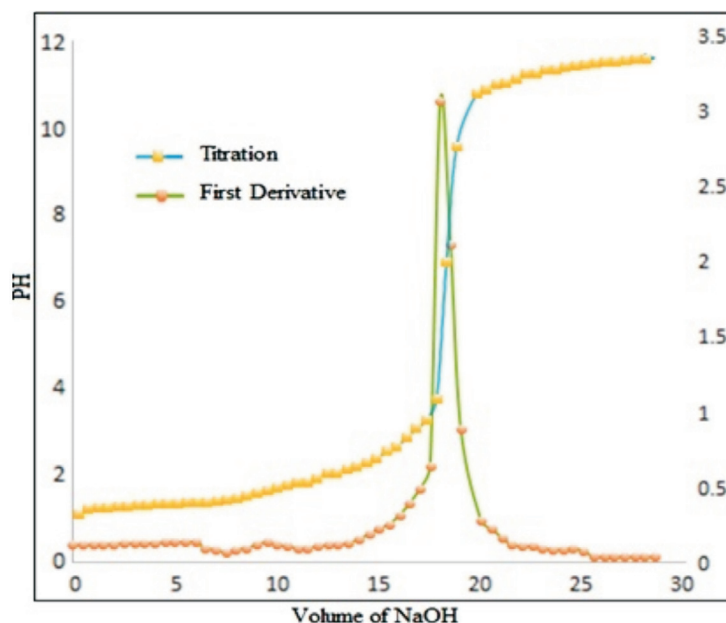


Figure 3 Titration and its first derivative curves of NSCH.

which includes firstly, weight loss in the range 30–120 °C, due to the removal of the local moisture. Secondly, the thermal decomposition of the sulfonic group appeared at 240 °C as a weight loss. The third decomposition, at 290 °C, corresponds to the complete decomposition of the NSCH. According to the DTGA results, the NSCH catalyst is thermally stable up to 240 °C.

<sup>1</sup>H NMR spectra of CHH and NSCH from 7 ppm to 12 ppm are shown in (Fig. SI2). The <sup>1</sup>H NMR spectrum of CHH displayed two singlet peaks at 10.54 and 8.38 ppm due to the hydrogens attached to the nitrogen atoms. After functionalization of CHH with chlorosulfonic acid, the NH peak at 10.54 was replaced by a new peak at 11.45 ppm, which corresponds to the newly attached SO<sub>3</sub>H proton. In addition, the <sup>13</sup>C NMR spectra of NSCH showed six peaks verifying its chemical structure.

### 3.2. Catalyst Acidity Power

One way to evaluate the acidic power of an acid in organic media is the use of the Hammett method (see equation below), using the UV-Vis technique.<sup>7</sup>

$$H_0 = \text{pK}(I)_{\text{aq}} + \log \left( \frac{[I]_s}{[IH^+]_s} \right)$$

In this equation  $\text{pK}(I)_{\text{aq}}$  represents the pKa value of an indicator in aqueous solution. The concentration of the indicator in protonated and deprotonated forms are represented as  $[IH^+]_s$  and  $[I]_s$ , respectively. The values of  $[I]_s/[IH^+]_s$  were easily obtained using the UV-Visible spectrum according to the Lambert–Beer's Law. In this study, the indicator and organic solvent are 4-nitroaniline ( $\text{pK}(I)_{\text{aq}} = 0.99$ ) and CCl<sub>4</sub>.

In the absence of the catalyst the mixture of the 4-nitroaniline and organic solvent shows the maximum absorbance at 330 nm with an intensity of ( $A_{\text{max}} = 2.2228$ ), while as the catalyst was added to this mixture the intensity of the maximum absorbance at 330 nm decreased to ( $A_{\text{max}} = 2.2616$ ). The decrease in the absorbance intensity of the indicator is due to the fact that some of the indicator molecules are protonated by the acidic protons which are supplied by the catalyst molecules, and the concentration of the non-protonated forms of the indicator molecules which are responsible for the absorption at 330 nm decreased. Table 1 lists the data obtained for the evaluation of the acidity power of the catalyst using Hammett acidity function.

Table 1 Calculation of the Hammett acidity function ( $H_0$ ) for NSSH.

Entry	Catalyst	$A_{\text{max}}$	$[I]_s/\%$	$[IH^+]_s/\%$	$H_0$
1	–	2.2228	100	0	–
2	NSSH	1.2616	56.76	43.24	1.108

Experiment conditions: 4-nitroaniline [ $\text{pK}(I)_{\text{aq}} = 0.99$ ],  $1.44 \times 10^{-4} \text{ mol L}^{-1}$  (10 mL), NSSH (10 mg), 25 °C.

### 3.3. Evaluation of the Catalytic Activity

After the characterization of NSCH, its catalytic activity was examined using it as solid acid catalyst to promote a number of synthetic organic reactions such as synthesis of the tetrahydrochromenes (Fig. 4a), xanthenes (Fig. 4b) and hydroquinolines (Fig. 4c).

The results showed that the optimum amount of the NMCH was 6 mol%, and by using this amount of the catalyst the reaction proceeded best under solvent-free conditions at 80 °C. In the absence of the catalyst, the reaction was incomplete, even after 24 h.

The yield of products from different benzaldehydes, under different reaction conditions, is shown in Table 2. The presence of electron-donating substituents in the benzaldehyde, e.g. entry 5 in Table 2 required longer reaction times.

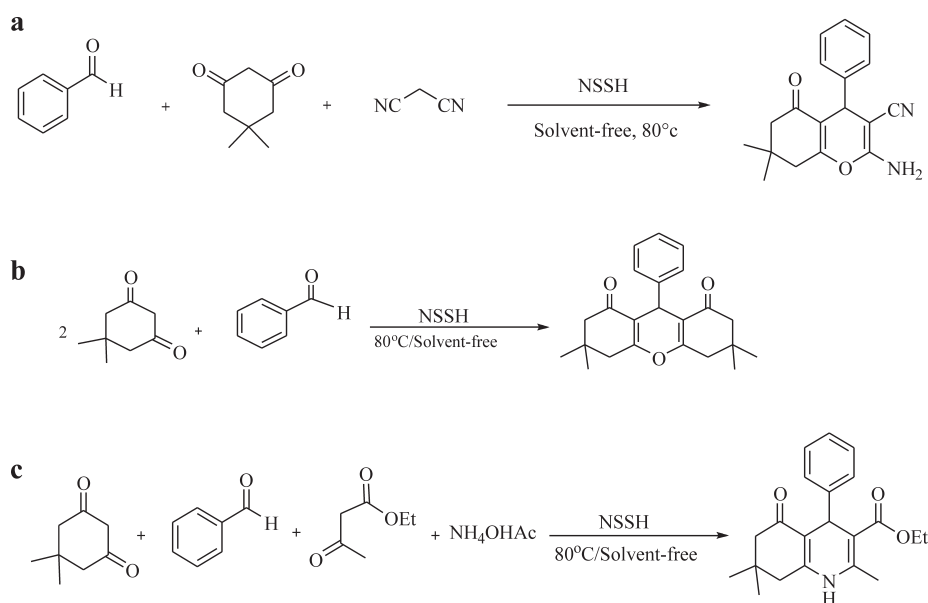
The proposed mechanism for tetrahydrochromene synthesis in the presence of NSCH is shown in Fig. SI3a.

Similarly, entries 13–17 report the optimized yields for the synthesis of 3,3,6,6-tetramethyl-1, 8-dioxooctahydroxanthenes from benzaldehyde derivatives (1 mmol) and dimedone (2 mmol) in presence of NSCH at 80 °C under solvent-free condition (Fig. 4b).

The synthesis of the hydroquinoline derivatives (Fig. 4c) was achieved efficiently from the benzaldehyde derivatives (1 mmol), dimedone (1 mmol) and ethyl acetoacetate (1 mmol) in the presence of NSCH at 80 °C under solvent-free condition. The results are listed in Table 2 (entries 18–22). Two alternative reaction pathways to achieve this outcome are shown in Fig. SI3c.

### 3.4. Reusability of the Catalyst

Recovery of the catalyst and its reuse were investigated under the optimized reaction procedure for the above three procedures. In each case, the catalyst was filtered off at the end of the



**Figure 4** Synthesis of tetrahydrochromenes (a), 1, 8-dioxooctahydroxanthenes (b) and hydroquinolines (c) catalyzed by NSCH at 80 °C.

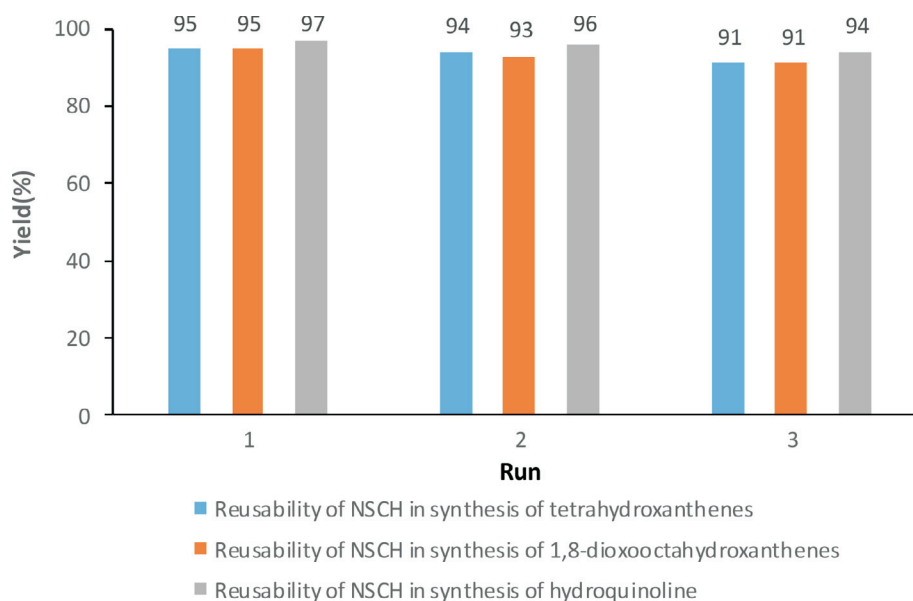
**Table 2** Synthesis of tetrahydrochromene (entries 1–12), 1, 8-dioxooctahydroxanthenes (entries 13–17) and hydroquinoline (entries 18–22) derivatives catalyzed by NSCH at 80 °C under solvent-free condition.

Entry	Aldehyde	Time/min	Yield/%	Found	Reported [ref]	Entry	Aldehyde	Time/min	Yield/%	Found	Reported [ref]
1	4H-C <sub>6</sub> H <sub>5</sub>	15	95	228–230	227–230 [12]	12	2Cl-C <sub>6</sub> H <sub>5</sub>	20	93	215–217	216–218 [12]
2	4F-C <sub>6</sub> H <sub>5</sub>	17	95	210–211	211–214 [12]	13	4H-C <sub>6</sub> H <sub>5</sub>	10	95	197–198	198–200 [9]
3	4Cl-C <sub>6</sub> H <sub>5</sub>	17	95	210–212	209–212 [12]	14	4Cl-C <sub>6</sub> H <sub>5</sub>	10	95	230–232	229–231 [9]
4	4Br-C <sub>6</sub> H <sub>5</sub>	17	95	195–197	197–200 [12]	15	4Br-C <sub>6</sub> H <sub>5</sub>	12	94	281–283	282–284 [9]
5	4OH-C <sub>6</sub> H <sub>5</sub>	28	94	204–206	204–207 [12]	16	4NO <sub>2</sub> -C <sub>6</sub> H <sub>5</sub>	10	96	220–224	220–222 [9]
6	4OMe-C <sub>6</sub> H <sub>5</sub>	20	95	210–211	211–214 [12]	17	3Me-C <sub>6</sub> H <sub>5</sub>	15	92	199–202	198–200 [9]
7	4NO <sub>2</sub> -C <sub>6</sub> H <sub>5</sub>	17	95	177–179	175–178 [12]	18	4H-C <sub>6</sub> H <sub>5</sub>	12	97	222–224	220–222 [7]
8	4CN-C <sub>6</sub> H <sub>5</sub>	17	95	223–225	211–214 [12]	19	4Cl-C <sub>6</sub> H <sub>5</sub>	15	92	242–244	241–243 [7]
9	4Me-C <sub>6</sub> H <sub>5</sub>	20	95	215–217	218–220 [12]	20	4Br-C <sub>6</sub> H <sub>5</sub>	15	94	246–248	248–252 [7]
10	4OEt-C <sub>6</sub> H <sub>5</sub>	23	96	223–225	225–227 [12]	21	4NO <sub>2</sub> -C <sub>6</sub> H <sub>5</sub>	15	93	241–243	238–240 [7]
11	3NO <sub>2</sub> -C <sub>6</sub> H <sub>5</sub>	17	95	210–212	210–213 [12]	22	4Me-C <sub>6</sub> H <sub>5</sub>	17	92	257–260	259–261 [7]

reaction, washed with ethanol, dried in an oven and reused for the same reaction. This process was repeated three times and no significant changes in the reaction time or yield were observed, verifying the practical recyclability of this catalyst (Fig. 5).

### 3.5. Comparison of the Reported Efficiency with Previous Work

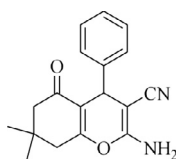
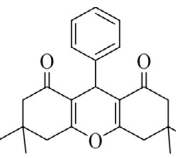
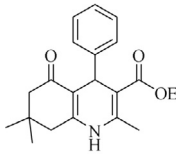
To evaluate the efficiency of our newly introduced procedures, comparison of the our results for the synthesis of chromenes,



**Figure 5** Reusability of the NSCH in the synthesis of tetrahydrochromenes, 1, 8-dioxooctahydroxanthenes and hydroquinoline.



**Table 3** Comparison of the results obtained from the synthesis of tetrahydrochromenes, 1, 8-dioxooctahydroxanthenes and hydroquinolines in the presence of NSCH with those obtained using other catalysts.

Product	Catalyst/loading	Reaction condition	Time/min	Yield/%	[ref]
	[PVPH]HSO <sub>4</sub> (14 mg)	EtOH:H <sub>2</sub> O/80 °C	10	96	[12]
	PPA-SiO <sub>2</sub> (10 mg)	H <sub>2</sub> O	13	80	[15]
	SiO <sub>2</sub> -Pr-SO <sub>3</sub> H (20 mg)	EtOH:H <sub>2</sub> O/reflux	15	97	[16]
	EDDA (90 mg)	Solvent-free/rt.	5	93	[21]
	SB-DABCO (6 mol%)	EtOH/rt	35	96	[22]
	NaBr (6 mol%)	Solvent-free/70 °C	10	95	[23]
	NSCH (6 mol%)	Solvent-free/80 °C	15	95	This work
	Silica sulfuric acid (30 mg)	Solvent-free/80 °C	60	97	[13]
	NSPVPS (20 mg)	Solvent-free/100 °C	10	98	[17]
	DSIMHS (0.25 mmol)	Solvent-free/55 °C	45	94	[18]
	PO(OSO <sub>3</sub> H) <sub>3</sub> (90 mg)	Solvent-free/80 °C	15	84	[24]
	SuSA (10 mg)	Solvent-free/80 °C	35	92	[25]
	P <sub>2</sub> O <sub>5</sub> /SiO <sub>2</sub> (12 mg)	Solvent-free/80 °C	90	97	[26]
	MSA (5 mol%)	Solvent-free/100 °C	60	96	[27]
	CAN/HY-zeolite (100 mg)	Solvent-free/80 °C	90	88	[28]
	Montmorillonite K10 (300 mg)	Solvent-free/100 °C	120	82	[29]
	NSCH (6 mol%)	Solvent-free/80 °C	15	95	This work
	Solecite (200 mg)	EtOH/reflux	45	93	[30]
	[PVPH]ClO <sub>4</sub> (40 mg)	Solvent-free/100 °C	8	97	[19]
	PZM-300 (0.25 mmol)	EtOH/reflux	40	94	[31]
	Cs <sub>2.5</sub> H <sub>0.5</sub> PW <sub>12</sub> O <sub>40</sub> (0.01 mmol)	TBAB/110 °C	6	92	[32]
	La <sub>2</sub> O <sub>3</sub> (10 mol %)	TFE/rt	60	90	[34]
	PS/PTSA (30 mg)	Solvent-free/60 °C	15	92	[20]
	SBA-Pr-SO <sub>3</sub> H (50 mg)	Solvent-free/100 °C	10	85	[35]
	Catalyst-free	H <sub>2</sub> O/reflux	8 h	96	[14]
	[DABCO](SO <sub>3</sub> H) <sub>2</sub> (Cl) <sub>2</sub>	Solvent-free/100 °C	45	87	[36]
	NSCH (6 mol%)	Solvent-free/80 °C	12	97	This work

xanthenes and hydroquinolines using NSCH as catalyst with the results reported previously in the literature were carried out (Table 3). The newly developed method herein reduced reaction times, excess use of the reagents, especially catalyst amount, and considerably improved on lengthy conditions for catalyst preparation.

#### 4. Conclusions

In summary, we have introduced a novel halogen-free solid acid catalyst, N-sulfonated cyclohexylhydantoin (NSCH), which has high acidic power and catalytic activity. The efficiency of the NSCH catalyst was evaluated in the synthesis of tetrahydrochromene, 1, 8-dioxooctahydroxanthene and hydroquinoline derivatives. The results clearly showed that the NSCH catalyst has high catalytic activity to enhance many of the organic synthetic reactions that require acidic conditions. The simple preparation of the catalyst, high availability of the starting materials, recyclability and reusability of the catalyst are advantages of this procedure. The solvent-free conditions, easy work-up and short reaction times are further advantages of the presented procedure.

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#### Conflict of interest

The authors declare no conflict of interest.

#### Supplementary Material

Supplementary information is provided in the online supplement.

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### **Supplementary material to:**

B. Khalili, A. Atashrazm and M. Rasoulia,

2,4-Dioxo-1,3-diazaspiro[4,5]decane-3-sulfonic Acid as a Novel Solid Phase Halogen-free Acid Catalyst: Preparation, Characterization and Evaluation,

*S. Afr. J. Chem.*, 2019, **72**, 195–200.

# Supporting Information

for

## **2,4-dioxo-1,3-diazaspiro[4,5]decane-3-sulfonic acid as a novel solid phase halogen free acid catalyst: preparation, characterization and evaluation**

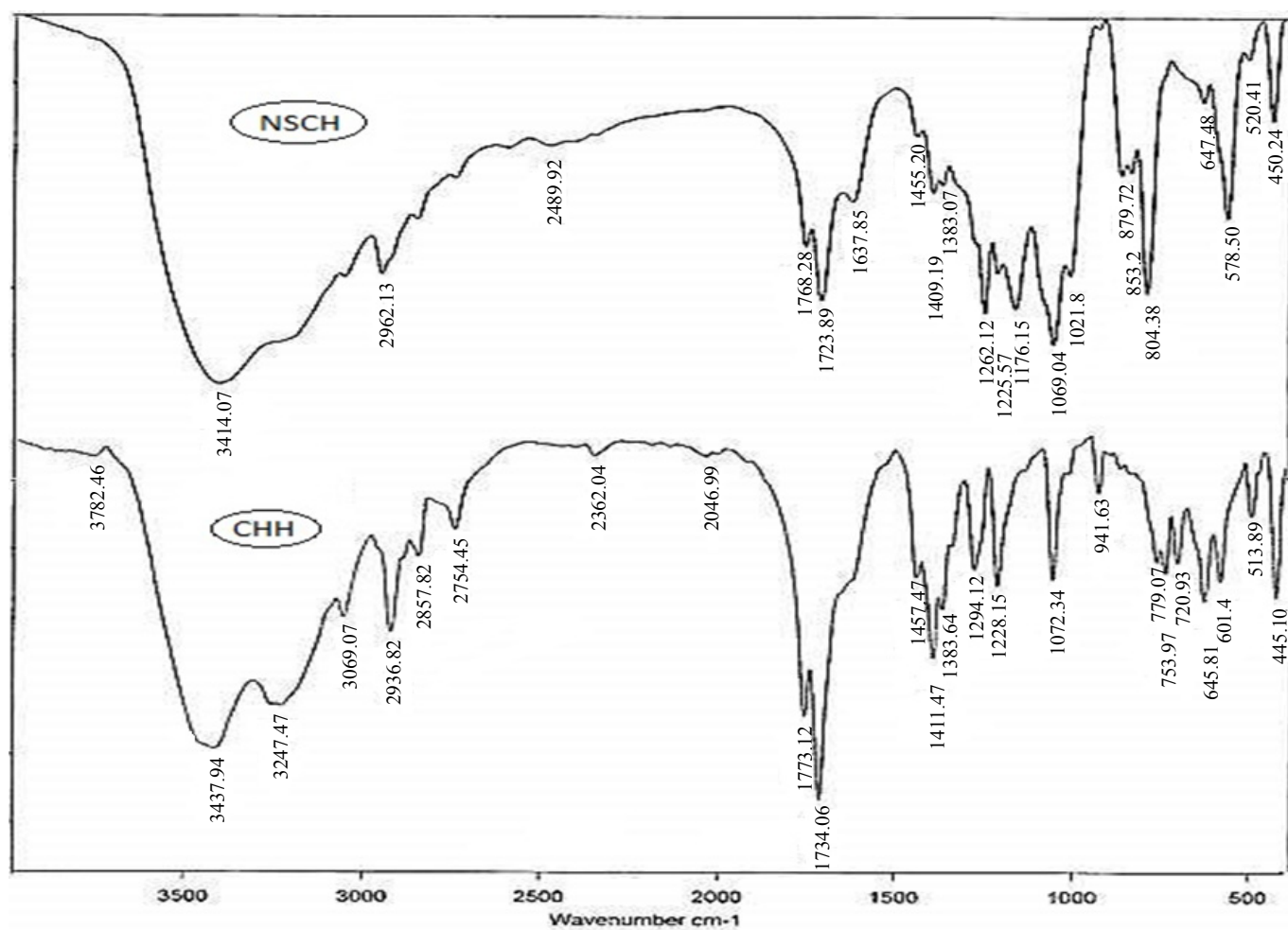
Behzad khalili\*, Aref Atashrazm and Mona Rasoulia

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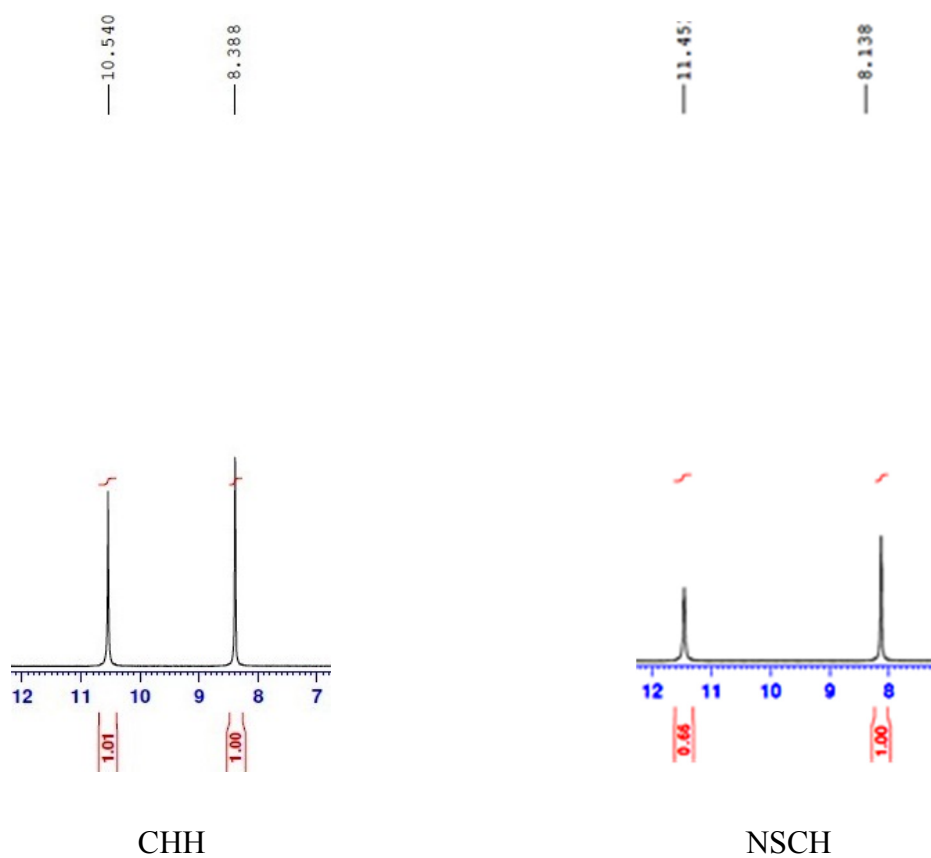
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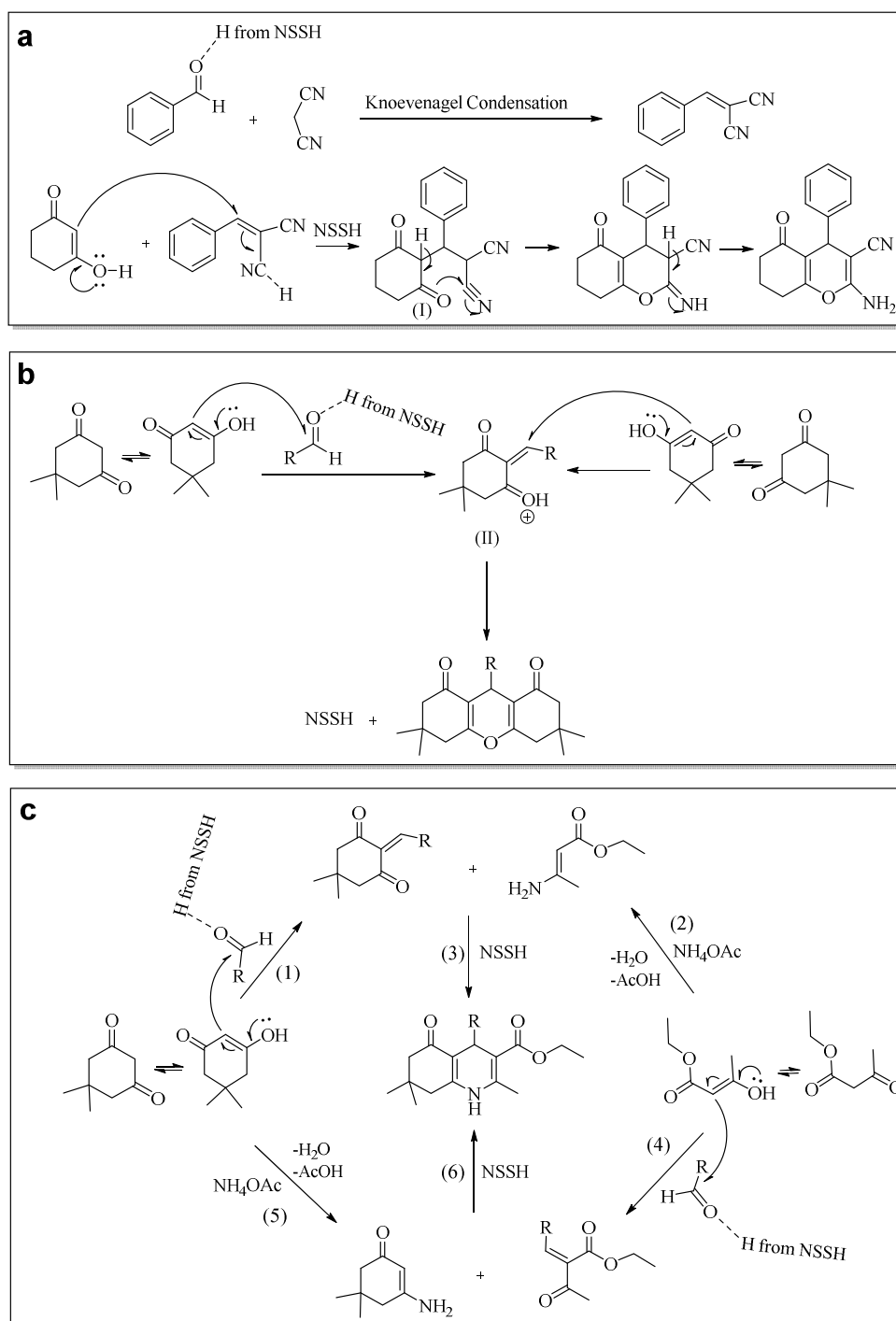




**Figure S11** FT-IR spectra of CHH and NSCH.



**Figure SI2**  $^1\text{H}$  NMR spectra of CHH and NSCH (from 7-12 ppm only).



**Figure SI3** Proposed mechanisms for the synthesis of tetrahydrochromene (**a**), 1,8-dioxooctahydroxanthene (**b**) and hydroquinoline (**c**) derivatives in the presence of NSCH.