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# Nano-titania-supported sulfonic acid catalyzed synthesis of 2-arylbenzothiazole derivatives under solvent free conditions

Ali Amoozadeh<sup>a</sup>, Rahmat Allah Azadeh<sup>a</sup>, Salman Rahmani<sup>a</sup>, Mehdi Salehi<sup>a</sup>, Maciej Kubicki<sup>b</sup> & Grzegorz Dutkiewicz<sup>b</sup>

<sup>a</sup> Department of Chemistry, Semnan University, Semnan, Zip Code: 35131-19111, Iran

<sup>b</sup> Faculty of Chemistry, Adam Mickiewicz University, Umultowska 89b, 61-614 Poznan, Poland Accepted author version posted online: 16 Apr 2015.

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#### NANO-TITANIA-SUPPORTED SULFONIC ACID CATALYZED SYNTHESIS OF 2-ARYLBENZOTHIAZOLE DERIVATIVES UNDER SOLVENT FREE CONDITIONS

Ali Amoozadeh<sup>a</sup>\*, Rahmat Allah Azadeh<sup>a</sup>, Salman Rahmani<sup>a</sup>\*, Mehdi Salehi<sup>a</sup>, Maciej Kubicki<sup>b</sup>, Grzegorz Dutkiewicz<sup>b</sup>

<sup>a</sup> Department of Chemistry, Semnan University, Semnan, Semnan, Zip Code: 35131-19111, Iran,
 Fax: +98 (233) 3354110, Tel.: +98 (233) 3366177, e-mail: aamozadeh@semnan.ac.ir,
 s rahmani@semnan.ac.ir

<sup>b</sup> Faculty of Chemistry, Adam Mickiewicz University, Umultowska 89b, 61-614 Poznan, Poland

**Abstract:** Nano-titania-supported sulfonic acid (n-TSA) has been used as an efficient, inexpensive and reusable heterogeneous nano catalyst for synthesis of 2-arylbenzothiazole derivatives under solvent free condition. The reaction works very well, with good to excellent yields, for different aromatic aldehydes with both electron withdrawing and electron donating groups. Easy preparation and separation of catalyst, simply workup procedure, clean reaction and reusability of the catalyst up to 7 times without appreciable loss of its catalytic activity are undoubtful advantages of this work.

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#### INTRODUCTION

In recent years, heterogeneous solid acid catalysts have gained importance in organic synthesis due to several advantages such as operational simplicity, no toxicity, reusability and ease of isolation after completion of the reaction.<sup>1</sup> In this context the use of nanoparticles as heterogeneous catalysts have attracted considerable attention because of the interesting structural features and high levels of catalytic activity associated with these materials.<sup>2,3</sup>

2-Arylbenzothiazole and their derivatives compose a very important group of heterocyclic compounds.<sup>4</sup> They are well known for their biological and pharmaceutical activities such as antitumor,<sup>5</sup> anticancer,<sup>6</sup> antimicrobial,<sup>7</sup> antimalarial,<sup>8</sup> antiglutamate/antiparkinson.<sup>9</sup> In addition some of these compound exhibit nonlinear optical,<sup>10</sup> luminescent<sup>11</sup> and fluorescent<sup>12</sup> properties.

Numerous methods have already been reported for the synthesis of 2-arylbenzothiazoles. The classical one involves condensation of 2-aminothiophenol with substituted aldehydes, carboxylic acids, acyl chlorides,<sup>13</sup> estersor nitriles.<sup>14</sup> On the other hand, the most common method for such synthesis involves condensation of aldehydes with 2-aminothiophenol in the presence of various catalysts such as  $I_2/DMF$ ,<sup>15</sup>  $O_2$  or  $H_2O_2$  in the presence of scandium triphtalate (Sc(OTf)<sub>3</sub>),<sup>16</sup> MnO<sub>2</sub>/SiO<sub>2</sub>,<sup>17</sup> *p*-TsOH or graphite supported on solid mineral under microwave irradiation,<sup>18</sup> 1-phenyl-3-methylimidazoliumbromide [PmIm]Br under microwave irradiation,<sup>19</sup> solid hetero poly acid supported on silica gel,<sup>20</sup> cerium (IV) ammonium nitrate (CAN),<sup>21</sup> activated carbon (shirasagi KL or DARCO<sup>®</sup> KB) under oxygen atomosphere<sup>22</sup> and dowex 50W.<sup>23</sup>

We have recently reported nano-titania-supported sulfonic acid (n-TSA)<sup>24</sup> as a new and efficient solid acid catalyst in organic reactions.

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#### **RESULTS AND DISCUSSION**

In continuation of our studies on developing inexpensive and environmentally benign methodologies for synthesis of heterocyclic compounds and organic reactions<sup>25,26</sup> and to extend our knowledge about the applicability of our new catalyst, we have decided to investigate the possibility of synthesizing 2-arylbenzothiazole derivatives by one-pot condensation reaction strategy in presence of n-TSA under solvent free conditions. In order to examine the catalytic activity of n-TSA, we have begun with the condensation of 2-aminothiophenol (1) with benzaldehyde (2) (Scheme 1).

To optimize the reaction conditions, amount of the n-TSA, different temperatures and solvents were screened. Initially, the limitation of catalyst amount was examined.

The obtained results showed that by increasing the catalytic load of n-TSA from 0.00 to 0.099 mmol, the yield has improved from 25% to 92%, but further increasing of the catalyst amount did not improve the yield (Table 1). In order to evaluate the effect of the catalyst particle size and acidity on the catalytic activity, the obtained results were compared with those obtained using other titanium dioxide bases such as unmodified nano-TiO<sub>2</sub>, unmodified bulk TiO<sub>2</sub> and modified-bulk TiO<sub>2</sub> (prepared by procedure reported earlier<sup>27</sup>). The obtained yields were 8, 4 and 65%, respectively. These results showed clearly that n-TSA worked very well for this reaction, so we have selected it.

In the next step, the effect of temperature in presence of 0.099 mmol of n-TSA was investigated. The results showed that the best temperature is 70 °C. By increasing the temperature to 90 °C, the achieved yields decreased. So the further experiments were performed at 70 °C.

#### <sup>4</sup> ACCEPTED MANUSCRIPT

Eventually, to making sure that the solvent free condition is appropriate, we investigated the effect of different solvents such as  $H_2O$ , PEG, Toluene, Et-OH and  $CH_3CN$  at 70 °C (Table 2). The results showed that by using of these solvents caused significantly lower yields, and longer reaction times did not improve the yields. It seems that among these solvents, Et-OH provided the best yield but as solvent free conditions are more valuable (also from the point of view of so-called green chemistry), so we chose this possibility.

Now, with optimized conditions (n-TSA (0.099 mmol) as catalyst in solvent free at 70 °C), we have performed some experiments to develop the scope of this procedure. For this purpose, the condensation between 2-aminothiophenol and various aromatic aldehydes (including aromatic aldehydes with electron-releasing, electron-withdrawing and halogen substituents) were carried out to provide corresponding products in good to excellent yields. Entertainingly, by present procedure the synthesized 2-arylbenzothiazole derivatives were prepared purely without any byproducts. The results are summarized in Table 3.

As indicated in Table 3, the reaction works easily for a variety of aldehydes with both electron-donating and electron-withdrawing groups to give corresponding 2-arylbenzothiazole derivatives in good to excellent yields (85-96%). In almost all cases, the reactions proceeded smoothly within 15-50 min. It seems that the reaction for aldehydes with strong withdrawing groups like 4-fluoro, 4-bromo and nitro is very fast (Table 3, products **3f**, **3g** and **3j-3l**). This could be justified by regarding the proposed mechanism<sup>28</sup> (Figure. 1). It seems that the rate determining step must be the nucleophilic attack of sulfur ion pair on to carbonyl group of aldehydes.

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Various methods have been reported for the synthesis of 2-arylbenzothiazoles, including, condensation of aromatic aldehydes and 2-aminothiophenol in presence of different catalysts. A comparison between the result of the proposed catalyst and some of the recently used catalysts for synthesis of 2-arylbenzothiazole derivatives is summarized in Table 2.

Although, some of these methods have convenient protocols with good to high yields, the majority of these methods suffer at least from one of the following disadvantages such as the use of toxic organic solvents, excess reagents, long reaction time and harsh reaction conditions. Table 2 shows that the heterogeneous solid acid catalyst of nano-TiO<sub>2</sub>-SO<sub>3</sub>H is the best in comparison to the other mentioned catalysts. The proposed new catalyst has some advantages in comparison with the other catalyst including shorter reaction time, easy separation and low consumption of organic solvents, reusability and ability to perform reactions in solvent free conditions. It is a stable solid acid catalyst with high densities of sulfuric acid groups that can be easily synthesized in the laboratory and can be reused for several times.

To test the reusability of catalyst and green chemistry aspects, the reaction mixture was washed with hot ethanol, catalyst was separated with centrifuge and dried at 50 °C for 2h. The condensation of 1 (1 mmol) and 2 (1 mmol) was repeated with recovered catalyst without any loss of activity. The catalyst could be efficiently recovered and recycled up to seven times without suffering any significant drop in its catalytic activity or the yield for the reaction (90-92%) (Figure S 1, Supplemental Materials)

The characterization of the nano- $TiO_2$ - $SO_3H$  before and after reuse 7 times showed the same particle size by scanning electron microscopy (Fig. 2b)

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#### **Crystal Structure Description of Compound 3c**

The asymmetric part of the unit cell of **3c** contains four symmetry-independent molecules; their geometrical features differ only slightly. Figure 3 shows a perspective view of one of the molecules and an overlay comparison is provided in Figure S 2 (Supplemental Materials). The lengths of two C-S bonds differ, and the difference is statistically important: for the S1-C9 bond the mean value for the four molecules is 1.728(3) Å, while for S1-C2 it is 1.753(4) Å. The mean value of the C-S-C angle is  $89.32(13)^{\circ}$  (Table S 1, Supplemental Materials). These values compare well with those found for instance in arylbenzothiazole derivatives.<sup>29,30</sup> Benzothiazole and phenyl groups are planar within the experimental errors and the dihedral angles between appropriate planes are small, ranging from  $0.62(8)^{\circ}$  in molecule D to  $5.96(7)^{\circ}$  in molecule A. The title compound has no other intermolecular contacts of structural significance than weak  $\cdots$  (centroid-to-centroid distances longer than 3.57Å) and van der Waals contacts.

#### **EXPERIMENTAL SECTION**

**Materials and Instruments:** Chemicals were purchased from the Merck chemical companies. Thin-Layer Chromatography (TLC) on commercial plates of silica gel 60 F254 was used to monitor the progress of reactions. The products were characterized by FT-IR spectra, <sup>1</sup>H NMR, <sup>13</sup>C NMR. FT-IR spectra were recorded on Shimadzu FT-IR 8400 instrument. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker Advance Spectrometer 400 MHz using CDCl<sub>3</sub> as solvent. The chemical shifts are expressed in parts per million (ppm) and tetramethylsilane (TMS) was used as an internal reference. Elemental analyses were performed by Perkin Elmer CHN analyzer, 2400 series II. Melting points were recorded on a THERMO SCIENTIFIC 9100 apparatus. The Supplemental Materials contains sample <sup>1</sup>H and <sup>13</sup>C NMR spectra for 3m (Figures S 3 6 S 4)

#### <sup>7</sup> ACCEPTED MANUSCRIPT

**Preparation of nano-TiO<sub>2</sub>-SO<sub>3</sub>H (n-TSA):** A suction flask equipped with a constant-pressure dropping funnel and a gas inlet tube for conducting HCl gas over an adsorbing solution (i.e., water) was used, charged with the titania nanoparticles (4 g). Chlorosulfonic acid (1 mL, 15 mmol) was added drop wise over a period of 30 min at room temperature. HCl gas immediately evolved from the reaction vessel. Stirring was continued HCl evolution was seized. After the addition was completed, the mixture was shaken for 30 min. A gray solid of nano-titania-supported sulfonic acid was obtained.

The prepared n-TSA stored in vacuum desiccator over anhydrous silica gel, then, was dried in 120 °C for 6 hours. The mmol of  $H^+$  per gram of catalyst (4.5 mmol/g of n-TSA) was determined by the titration of 0.1 gram of sample with a standard solution of NaOH (0.1 N).<sup>26</sup>

General Procedure for preparation of benzothiazole derivatives: In a typical experiment, 2aminothiophenole (1 mmol), aromatic aldehyde (1 mmol) and catalyst (0.099 mmol) in solvent free condition were taken in a 25 ml round bottomed flask and was stirred at 70 °C for an appropriate time. The reaction mixture was cooled, eluted with hot ethanol (5 mL) and was centrifuged and filtrated to collect the formed precipitate. The crude product was recrystallized from ethanol to yield pure benzothiazole derivatives.

#### Spectral data of 2-(naphthalen-3-yl)benzo[d]thiazole (3m)

Colorless Crystal (yield 91%), M.P: 127-130 °C; IR (KBr) Cm<sup>-1</sup>: 3065,1496,1427, 1357, 1118, 979, 732;<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 8.59-8.60 (d, J= 0.8 Hz, 1H, Ar), 8.23-8.26 (dd, J= 8.6 and 1.6 Hz, 1H, Ar), 8.13-8.16 (dq, J= 8.2 and 0.4 Hz, 1H, Ar), 7.96-8.02 (m, J= 0.4-6 Hz, 3H, Ar), 7.90-7.93 (m, J= 1.2-5.2 Hz, 1H, Ar), 7.58-7.61 (m, J= 1.2-4.8 Hz, 2H, Ar), 7.52-7.58 (dd, J= 7.8 and 1.2 Hz, 1H, Ar) 7.42-7.46 (td, J= 7.6 and 1.2 Hz, 1H, Ar). <sup>13</sup>C NMR (100 MHz,

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CDCl<sub>3</sub>): 121.7 (C 13, C 14), 123.2 (C 17), 124.4 (C 12), 125.3 (C 16), 126.4 (C 11), 126.9 (C 8), 127.5 (C 7), 127.6 (C 9), 127.9 (C 6), 128.8 (C 10), 130.9 (C 5), 133.2 (C 4), 134.6 (C 15), 135.1 (C 3), 154.2 (C 2), 168.1 (C 1). Anal. Calc. for C<sub>17</sub>H<sub>11</sub>NS, C, 78.13; H, 4.24: N, 5.36; Found: C, 78.26, H, 4.36, N, 5.48.

#### **Crystallographic Data Collection and Structure Determination**

Diffraction data of the compounds1(**3c**) were collected at room temperature by the -scan technique on an Agilent Technologies Xcalibur four-circle diffractometer with Eos CCD-detector and graphite-monochromatized MoK radiation source (= 0.71073 Å). The data were corrected for Lorentz-polarization as well as for absorption effects.<sup>31</sup> Precise unit-cell parameters were determined by a least-squares fit of 5846 reflections of the highest intensity, chosen from the whole experiment. The structure was solved with SIR92<sup>32</sup> and refined with the full-matrix least-squares procedure on F<sup>2</sup> by SHELXL97.<sup>33</sup> Hydrogen atoms were placed geometrically and refined as riding model with U<sub>iso</sub> set at 1.2 times U<sub>eq</sub> for appropriate carrier atoms. Relevant crystal data are listed in Table 5, together with refinement details.

#### CONCLUSIONS

In summary, nano-titania-supported sulfonic acid has been used as a heterogeneous nano catalyst for the synthesis of 2-arylbenzothiazole derivatives in solvent-free conditions. This reaction leads to appropriate products in good to excellent yields. This new reported method has some advantages such as easy preparation and high efficiency of catalyst, operational simplicity, mild reaction conditions, easy puriŁcation, high yields of products, no environmental hazards and reusability of the catalyst for at least 7 times.

#### ACKNOWLEDGMENTS

#### <sup>9</sup> ACCEPTED MANUSCRIPT

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Entr	Catalyst (mmol)	Time	Yield <sup>b</sup>
У	Catalyst (IIIII01)	(min)	(%)
1	Catalyst Free	60	25
2	Nano-Ti $O_2SO_3H$ (0.012)	30	43
3	Nano-Ti $O_2SO_3H$ (0.025)	30	51
4	Nano-TiO <sub>2</sub> SO <sub>3</sub> H (0.050)	30	68
5	Nano-TiO <sub>2</sub> SO <sub>3</sub> H (0.074)	30	85
6	Nano-TiO <sub>2</sub> SO <sub>3</sub> H ( $0.099$ )	30	92
7	Nano-TiO <sub>2</sub> SO <sub>3</sub> H $(0.124)$	30	91
8	Nano TiO <sub>2</sub> (0.099)	60	8
9	Bulk TiO <sub>2</sub> (0.099)	60	4
10	Bulk-TiO <sub>2</sub> SO <sub>3</sub> H (0.099)	60	65

Table 1 The effect of different conditions on synthesis of 2-phenylbenzothiazoles<sup>a</sup>.

<sup>a</sup> Reaction Condition: **1** (1 mmol), **2** (2 mmol) at 90 °C under solvent free condition.

<sup>b</sup> Isolated yield.

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Entry	Temp. (°C)	Solvent	Time (min)	Yield <sup>b</sup> (%)
1	RT	-	30	32
2	50	-	30	63
3	60	-	30	76
4	70	-	30	92
5	80	-	30	91
6	90	-	30	90
7	70	Toluene	60	35
8	70	PEG- 400	60	45
9	70	$H_2O$	60	55
10	70	CH <sub>3</sub> CN	60	75
11	70	EtOH	60	85

Table 2 The effect of different conditions on synthesis of 2-phenylbenzothiazole<sup>a</sup>.

<sup>a</sup> reaction condition: **1** (1 mmol), **2** (1 mmol) and n-TSA (0.099 mmol).

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Entr	2	Draduat	Time	$\mathbf{V}_{i}$	Melting Point (°C)	
У	2	Product	(min)	rield (%)	Found	Reported
1	$-C_6H_5$	<b>3</b> a	30	92	111-114	112-115 <sup>34</sup>
2	$2-Cl-C_6H_4$	<b>3</b> b	40	87	73-77	$72-74^{1}$
3	$4-Cl-C_6H_4$	3c	40	91	114-116	$116-117^{1}$
4	$2-HO-C_6H_4$	3d	20	86	129-131	126-128 <sup>35</sup>
5	$4-HO-C_6H_4$	<b>3e</b>	15	87	225-227	226-227 <sup>35</sup>
6	$4-F-C_6H_4$	<b>3</b> f	15	90	101-103	$102 - 103^{1}$
7	$4-Br-C_6H_4$	3g	20	90	130-132	130-131 <sup>35</sup>
$8^{\rm c}$	$4-H_3C-C_6H_4$	3h	45	93	86-88	$85-87^{1}$
9	$4-H_3CO-C_6H_4$	<b>3i</b>	35	96	119-121	$120-122^{1}$
10	$2-O_2N-C_6H_4$	3ј	20	85	132-134	132-135 <sup>34</sup>
11	$3-O_2N-C_6H_4$	3k	15	89	184-186	180-183 <sup>35</sup>
12	$4-O_2N-C_6H_4$	31	10	93	223-226	$226-228^{1}$
13 <sup>d</sup>	2-Naphtaldehyde	3m	20	91	127-130	Not
15	2-Maphaldenyde	5111	20	71	127-130	Reported
14	Thiophen-2-	3n	20	80	102-104	102-103 <sup>34</sup>
14	Carbaldehyde	011				

Table 3 Synthesis of 2-arylbenzothiazoles by n-TSA as a reusable nano catalyst.<sup>a</sup>

<sup>a</sup> Reaction condition: **1** (1 mmol) **2** (1 mmol) and n-TSA (0.099 mmol) in solvent-free at 70 °C.

<sup>b</sup> Isolated yield.

<sup>c</sup> New single crystal: characterized by Xcalibur four-circle diffractometer.

<sup>d</sup> New compound: characterized by FT-IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and elemental analysis.

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Table 4 Comparison of the characteristic of new reported method with other methods for

Entry	Catalyst	Amount of Catalyst	Time (min)	Condition	Solvent	Yield (%)
1	Baker's Yeast <sup>36</sup>	2 g	1440	RT	$CH_2Cl_2$	75
2	HMTA-Bromine <sup>34</sup>	10 mol%	360	RT	CH <sub>3</sub> CN	85
3	$NH_4Cl^{28}$	70 mol%	30	RT	MeOH/H <sub>2</sub> O	84
4	$SSA^1$	100 mg	12	Microwave (45 W)	-	90
5	$H_2SO_4.SiO_2^{35}$	5 mg	25	RT	EtOH	80
6	CH <sub>3</sub> -SO <sub>3</sub> H <sup>37</sup>	15 mol%	30	Microwave (230 °C)	1,2- Cl <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	93
7	Nano BF <sub>3</sub> /SiO <sub>2</sub> <sup>38</sup>	25 mol%	30	RT	EtOH	85
8	Indion-190 Resin <sup>39</sup>	10%/weight	240	70 °C	EtOH	90
9	Present method	0.016 g	30	70 °C	-	92

synthesis of 2-arylbenzothiazoles.

### <sup>17</sup> ACCEPTED MANUSCRIPT

 Table 5 Crystal information of 3c

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Crystal structure and data refinement parameters for 3c			
Formula	C <sub>13</sub> H <sub>8</sub> ClNS		
Formula Weight	245.72		
Crystal System	Triclinic		
Space group	P-1		
a (Å)	11.1540(6)		
b (Å)	14.3104(8)		
c (Å)	15.0501(7)		
(°)	95.626(4)		
(°)	106.740(5)		
γ (°)	100.092(5)		
V (Å <sup>3</sup> )	2236.6(2)		
$D_x (g/cm^3)$	1.46		
F(000)	1008		
μ (/mm)	0.50		
$\theta$ range (°)	3.0-25.0		
hkl range	-12 Öh Ö13 -17 Ök Ö17 -17 ÖI Ö15		
Reflection			
Collected	18271		
Unique (R <sub>int</sub> )	7862 (0.029)		
With $I > 2\sigma(I)$	6091		
No. of parameters	577		
$R(F)[I > 2\sigma(I)]$	0.039		
$wR(F^2)[I > 2\sigma(I)]$	0.097		
R(F) [all data]	0.057		
w $R(F^2)$ [all data]	0.104		

<sup>18</sup> ACCEPTED MANUSCRIPT

Goodness of fit	1.08
Min/Max $\Delta \rho$ (e/Å <sup>3</sup> )	0.30/-0.34
CCDC No.	1021332

# <sup>19</sup> ACCEPTED MANUSCRIPT



Scheme 1

# <sup>20</sup> ACCEPTED MANUSCRIPT



Figure 1: Possible mechanism for synthesis of 2-arylbenzothiazoles derivatives.

# <sup>21</sup> ACCEPTED MANUSCRIPT



Figure 2: The SEM images of n-TSA before use (a) and after reuse 7 times (b).

### <sup>22</sup> ACCEPTED MANUSCRIPT



**Figure 3:** Perspective view of molecule A found in the structure of **3c**; the ellipsoids are drawn at 50% probability level, hydrogen atoms are shown as spheres of arbitrary radii.

# <sup>23</sup> ACCEPTED MANUSCRIPT