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## CuO/SnO<sub>2</sub> Mixed Metal Oxide: A Mild and Efficient Heterogeneous Catalyst for Synthesis of Phenylhydrazones

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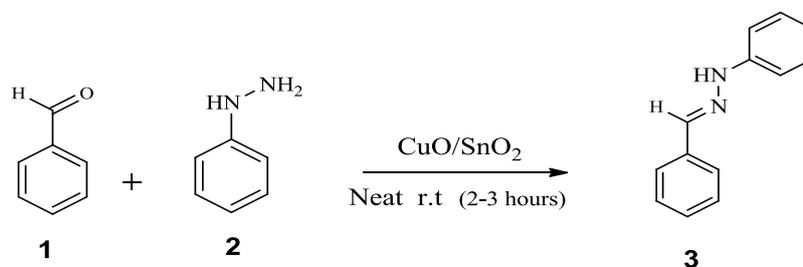
### ABSTRACT

Mixed metal oxide CuO/SnO<sub>2</sub> was considered as an apt heterogeneous catalyst for carbonyl group protection with phenyl hydrazine under solvent free condition at room temperature. The catalyst was recovered by easy filtration and reused for further reactions. The catalyst was prepared by wet impregnation method and characterized by XRD, SEM, EDX, FTIR and UV-DRS methods.

**Keywords:** Mixed metal oxide, CuO/SnO<sub>2</sub>, Benzaldehydes, Phenylhydrazones, Heterogeneous catalyst, Solvent free condition

### INTRODUCTION

Phenylhydrazones were synthesized from carbonyl compounds using phenylhydrazine. The phenylhydrazone compounds are the building blocks for the synthesis of some biologically important heterocyclic compounds. These compounds are widely employed as ligands for metal complexes. Previous methods used for protecting carbonyl compounds with phenyl hydrazine were: i) ZrOCl<sub>2</sub>·8H<sub>2</sub>O in acetonitrile [1]; ii) Acidic zeolite in hexane/methanol [2]; iii) Dowex polymer [3]; iv) Alumina as heterogeneous catalyst [4]; v) Different Lewis acids, like ZnCl<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> [5,6]; vi) Silica gel/sodium hydroxide [7]; vii) Solvent-free synthesis under microwave irradiation [8,9]; viii) Acid catalyst such as PSSA (polystyrene sulphonic acid) [10]; Mg(ClO<sub>4</sub>)<sub>2</sub> [11]; glacial CH<sub>3</sub>COOH [12]; ix) Bronsted Lewis acid catalyst [13]; x) Zeolite [14]; xi) Ultrasound [15]; and Ionic liquid [16]. These methodologies often require complex procedures, long reaction times, large quantities of organic solvents, high reaction temperatures and expensive organic solvents and highly corrosive. Therefore the development of novel easy and eco-friendly catalytic method was highly desirable. In recent years, heterogeneous catalysis has attracted much attention for various organic transformations. So we developed a novel facile method for protection of carbonyl compounds with phenyl hydrazine using CuO/SnO<sub>2</sub> under a solvent free condition (Scheme 1).



Scheme 1: Protection of carbonyl compounds with phenyl hydrazine

### EXPERIMENTAL

#### Materials

All aldehydes and phenylhydrazines were purchased from Aldrich and used without further purification.

### Physical measurements

The powder X-ray diffraction patterns were recorded on PANalytical B.V. Lelyweg 17602 EA Almelo the Netherlands instrument by using nickel-filtered CuK $\alpha$  radiation and scintillation counter detector. The scattered intensity data were recorded from 2 $\theta$  values scanning range from 10 to 80 by scanning at a scan speed of 2.000 (deg/min), sampling pitch 0.0200 deg and present time 60 s. Debye-Scherrer equation is used to determine average crystallite size of the particle. Scanning Electron Microscope (SEM) investigations performed on ZEISS Evo 18 oxford inca x-act penta FET Precision. FT-IR spectrum of the catalyst was recorded on a SHIMADZU model: A21005002961 spectrometer at ambient conditions. Self-supporting KBr pellets containing the catalyst samples were used to scan the spectra. UV-DRS spectra were recorded SHIMADZU UV-3600 for sample preparation using BaSO<sub>4</sub>. The <sup>1</sup>H NMR spectra were recorded at 400 MHz of Bruker Ultrashield (Avance-III) Nano Bay spectrometers using TMS as an internal standard.

### Catalyst preparation

The precipitate of Sn(OH)<sub>2</sub> was obtained by adding 0.1 M of NH<sub>4</sub>OH slowly into an aqueous solution of SnCl<sub>2</sub> at room temperature with stirring until the pH of the mother liquor reached about 8. The precipitate thus obtained then washed thoroughly with distilled water until no chloride ions were detected, filtered and dried for 12 hrs at 150°C. It was dried and solidified. Dissolved 5 g of Sn(OH)<sub>2</sub> in small amounts of water and taken the 5 wt% of Cu(NO<sub>3</sub>)<sub>2</sub> dissolved in water until a clear solution was obtained, mixed both the solutions and kept it on a water bath until water got evaporates completely and the precipitate was dried to 120°C and it was calcined in a kiln at 650°C for 4 hrs.

## RESULTS AND DISCUSSION

The FT-IR spectrum of Support SnO<sub>2</sub> and CuO/SnO<sub>2</sub> showed in Figure 1 exhibits three shoulders at 1738, 1366, and 1218 cm<sup>-1</sup>. The 2971 cm<sup>-1</sup> band intensity corresponding to the stretching vibration of hydroxyl groups decreased strongly and better-resolved bands are observed clearly at 686 cm<sup>-1</sup> which were characteristic of crystalline SnO<sub>2</sub>. From this, it was concluded that because of calcination condensation of hydroxyl groups of Sn(OH)<sub>4</sub> occurred leading to a crystallized sample of the species.

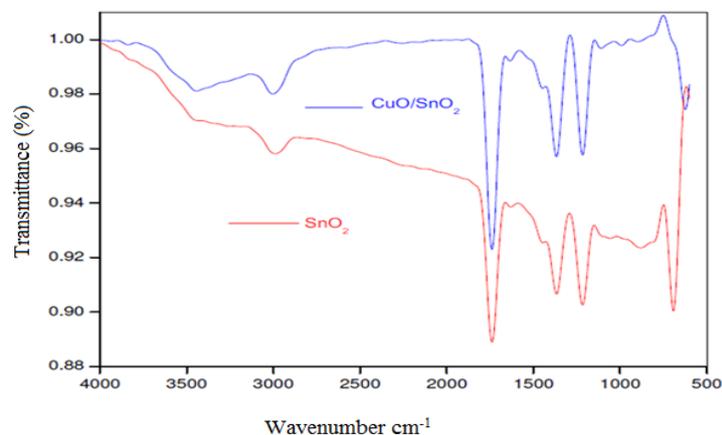


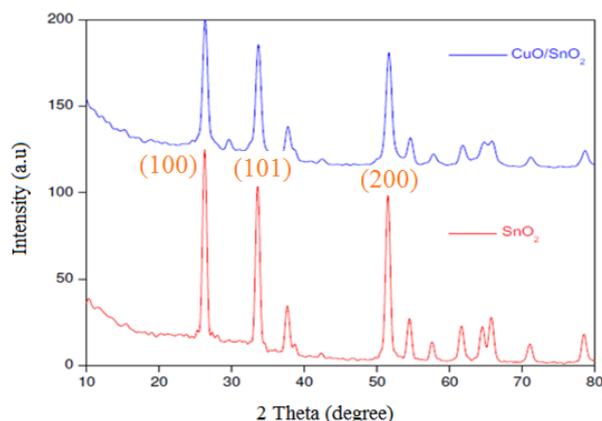
Figure 1: FTIR spectra of SnO<sub>2</sub> and CuO/SnO<sub>2</sub>

The powder X-ray diffraction patterns of SnO<sub>2</sub> and copper promoted SnO<sub>2</sub> samples calcined at 650°K are presented in Figure 2. In the figure, three intense peaks appeared at 2 $\theta$  values (26,<sup>o</sup> 33,<sup>o</sup> 51,<sup>o</sup>) can be associated with (100) (101) (200) h, k, l planes respectively indicates copper promoted SnO<sub>2</sub> is in tetragonal phase. The average particle size was calculated using the Scherer equation  $D=0.9 \lambda/\beta \cos\theta$  where D is the average crystalline size,  $\lambda$  is x-ray wavelength,  $\beta$  is (FWHM) diffraction line and  $\theta$  is the diffraction angle. The average crystalline size is 0.30  $\mu$ m for pure SnO<sub>2</sub> and copper promoted SnO<sub>2</sub> but does not have the same activity in the synthesis of phenyl hydrazones derivatives which were obtained in 2-3 hrs when copper promoted SnO<sub>2</sub> is used whereas pure SnO<sub>2</sub> was totally inactive.

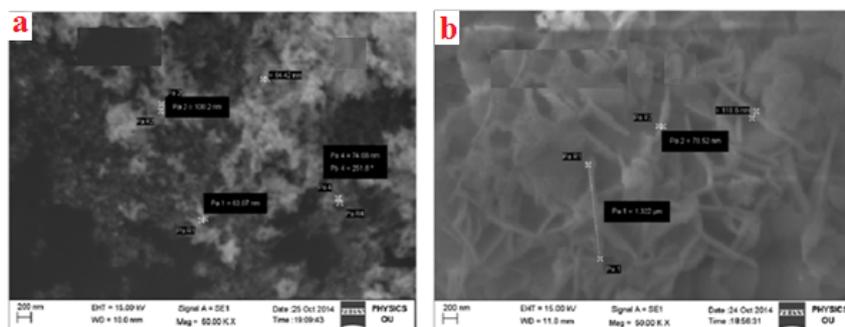
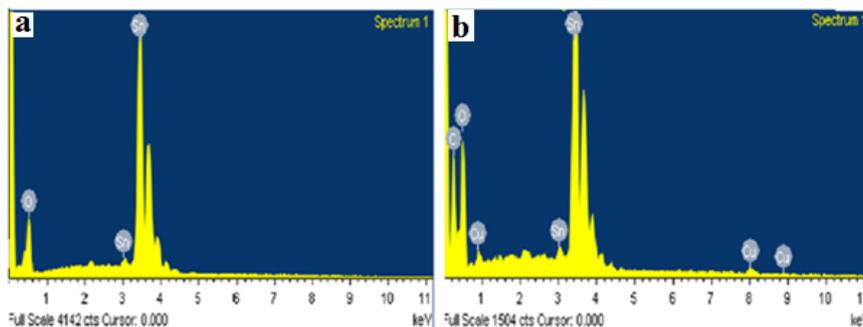
In Figure 3 SEM images of SnO<sub>2</sub> and CuO/SnO<sub>2</sub> were shown. There was no much difference in SEM photographs of SnO<sub>2</sub> and copper promoted SnO<sub>2</sub> catalyst indicating a small change in the structure of SnO<sub>2</sub> by incorporating copper. It was observed that particles were uniformly distributed all over the surface and spherical in shape. This result was agreement with XRD results of both the catalysts having a tetragonal phase with same crystallite size. Higher activity for copper promoted SnO<sub>2</sub> catalyst was due to uniform distribution of spherical particles all over the SnO<sub>2</sub>. The average crystalline size of the particles was observed to be same in both the samples from SEM photographs also.

In Figure 4 (a) EDX spectrum of pure SnO<sub>2</sub> and CuO/SnO<sub>2</sub> is shown. Pure SnO<sub>2</sub> exhibits peaks corresponding to Sn and O without any impurity whereas CuO/SnO<sub>2</sub> exhibits peaks corresponding to Cu, Sn, and O indicating incorporation of Copper into SnO<sub>2</sub>.

The UV-visible absorption edge of SnO<sub>2</sub> is obtained from the plots of absorbance against wavelength. The interception of the tangent on the descending part of the absorption peak of the wavelength axis gives the value of diffuse absorption edge (nm). The UV-visible DRS of SnO<sub>2</sub> and CuO/SnO<sub>2</sub> were presented in Figure 5 The absorption peak of SnO<sub>2</sub> can be easily found in the visible

Figure 2: XRD spectra of SnO<sub>2</sub> and CuO/SnO<sub>2</sub>

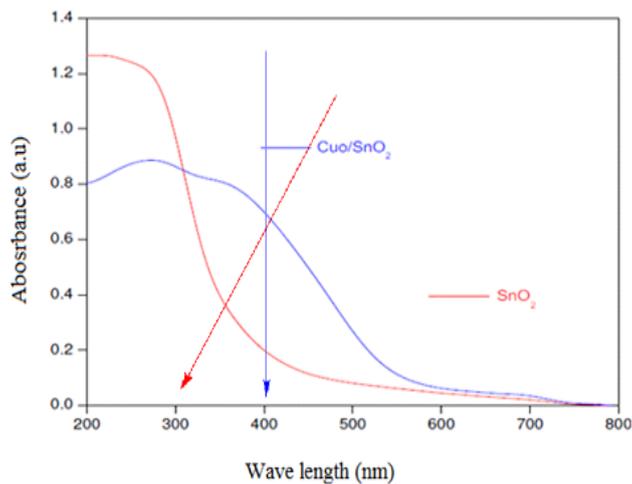
Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
26.3328	96.68	0.4723	3.38457	100.00
33.6468	75.63	0.5510	2.66371	78.23
51.6557	76.77	0.5510	1.76955	79.41

Figure 3 SEM images of a) SnO<sub>2</sub>, and b) CuO/SnO<sub>2</sub>Figure 4: EDX images of a) SnO<sub>2</sub>, and b) CuO/SnO<sub>2</sub>

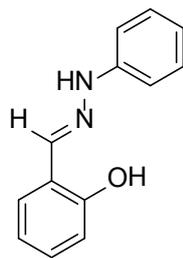
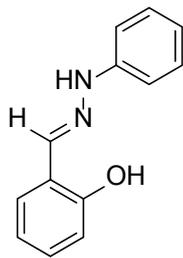
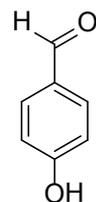
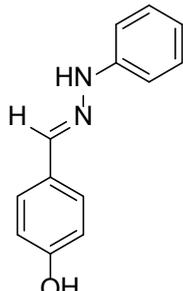
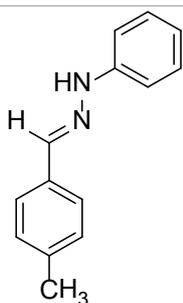
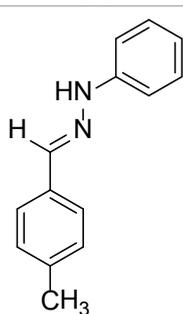
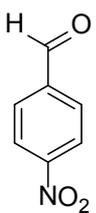
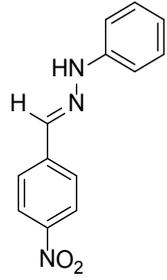
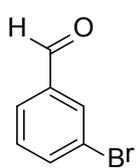
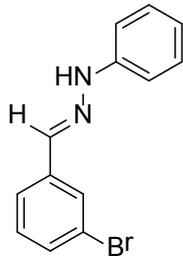
region. The wavelength for pure SnO<sub>2</sub> was about 300 nm, corresponding to a band gap of 4.13 eV, the band gap of the material can be estimated by using the formula:  $E_g = 1240/\lambda$ , where  $E_g$  is the band gap energy and  $\lambda$  is the wavelength of the absorption edge. A red shift was observed for the CuO/SnO<sub>2</sub> in which the absorption edge was shifted to 400 nm corresponding to a band gap of 3.1 eV. It is due to the incorporation of CuO.

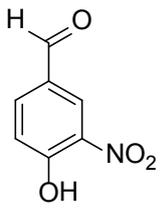
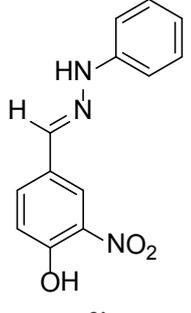
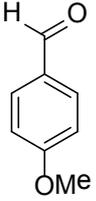
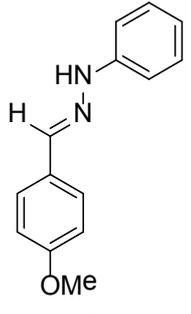
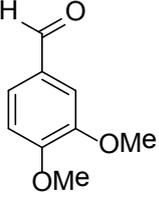
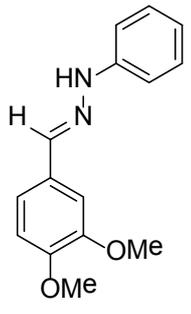
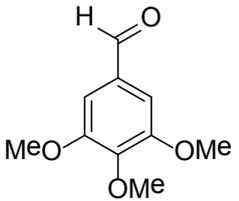
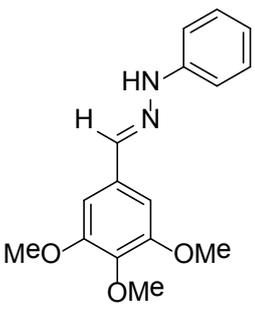
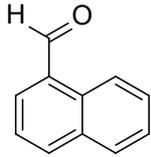
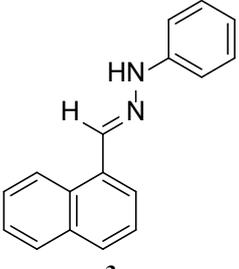
#### General procedure for the preparation of phenyl hydrazones by using CuO/SnO<sub>2</sub> catalyst

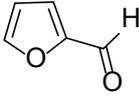
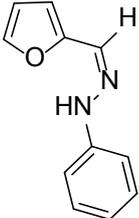
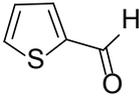
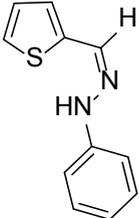
To a mixture of Phenylhydrazine (1 mmol), benzaldehyde (1.2 mmol) was added CuO/SnO<sub>2</sub> (5%, w/w) and the mixture was stirred at room temperature for the time indicated in Scheme 2. After completion of the reaction (indicated by TLC), EtOAc (10 mL) was added and the catalyst was separated by filtration. The filtrate was collected and concentrated. The residue was purified by column chromatography using the EtOAc and n-hexane (30:70) to obtain the pure product. The recovered catalyst was recycled for consecutive 3-4 times for the above reaction to furnish the product with a little variation in yields. All the products were characterized by IR and NMR mass spectroscopy and compared with those reported in the literature [17].

Figure 5: UV-DRS images of a) SnO<sub>2</sub> and b) CuO/SnO<sub>2</sub>

S. No	Reactant (1)	Products (2)	Time (Hours)	Yield (%)
1	 <b>1a</b>	 <b>3a</b>	2	95
2	 <b>1b</b>	 <b>3b</b>	2.30	90
3	 <b>1c</b>	 <b>3c</b>	3	85

4	 <b>1d</b>	 <b>3d</b>	2	90
5	 <b>1e</b>	 <b>3e</b>	3	92
6	 <b>1f</b>	 <b>3f</b>	3.5	85
7	 <b>1g</b>	 <b>3g</b>	2.5	78
8	 <b>1h</b>	 <b>3h</b>	3	80

9	 1i	 3i	3.5	85
10	 1j	 3j	2.5	80
11	 1k	 3k	3	75
12	 1l	 3l	2.5	70
13	 1m	 3m	3	80

14			2.5	90
15			3	90

<sup>a</sup>Conditions: **1a** (1.2 mmol), **2a** (1.0 mmol), 5wt% (10 mg) of catalyst, solvent free, room temperature, 2-3 h

**Scheme 2: Protection of carbonyl compounds with phenyl hydrazine under solvents free condition<sup>a</sup>**

#### Recovery of CuO/SnO<sub>2</sub>

After completion of the reaction the catalyst was separated by filtration and washed with ethanol 2-3 times to removal of organic residues, dried in an oven at 100-120°C for 10-11 h and the catalyst was reused for same reaction. After five cycles of reaction the catalyst mass checked it was found that the mass of CuO/SnO<sub>2</sub> didn't change significantly.

#### Spectral data: <sup>1</sup>H NMR and FTIR

**1) (Z)-1-Benzylidene-2-phenylhydrazine:** <sup>1</sup>H NMR (400 MHz CDCl<sub>3</sub>): δ, ppm=6.82 (t, 1H), 7.13 (d, 2H), 7.27 (d, 2H), 8.17 (s, 1H), 7.4 (s, 1H NH), 7.40-7.67 (m, 5H), IR (Kbr, cm<sup>-1</sup>): 3051, 1691, 1591, 1484, 1259, 1134, 912, 750.

**2) (Z)-1-(2-chlorobenzylidene)-2-phenylhydrazine:** <sup>1</sup>H NMR (400 MHz CDCl<sub>3</sub>): δ, ppm=7.40 (d, 2H), 7.46 (t, 3H), 7.30 (d, 1H), 6.82 (d, 1H), 7.13 (t, 2H), 7.27 (d, 1H), 8.17 (s, 1H), 7.4 (s, 1H, NH), 7.40-7.67 (m, 5H), IR (Kbr, cm<sup>-1</sup>): 3906, 3290, 3043, 1923, 1589, 1489, 1267, 1151, 848, 729.

**3) (Z)-1-(4-chlorobenzylidene)-2-phenylhydrazine:** <sup>1</sup>H NMR (400 MHz CDCl<sub>3</sub>): δ, ppm=7.30 (d, 2H), 7.20 (d, 2H), 8.17 (s, 1H), 7.4 (s, 1H NH), 7.40-7.67(m, 5H), IR (Kbr, cm<sup>-1</sup>): 3308, 3049, 2559, 1921, 1857, 1489, 1249, 1097, 827, 733.

**4) (Z)-2-((2-phenylhydrazono)methyl)phenol:** <sup>1</sup>H NMR (400 MHz CDCl<sub>3</sub>): δ, ppm=7.15 (d, 2H), 7.30 (t, 1H), 7.10 (d, 1H), 5.1 (s, 1H OH), 8.17 (s, 1H), 7.4 (s, 1H NH), 7.40-7.67 (m, 5H), IR (Kbr, cm<sup>-1</sup>): 3312, 3041, 1589, 1483, 1267, 1141, 931.

**5) (Z)-4-((2-phenylhydrazono)methyl)phenol:** <sup>1</sup>H NMR (400 MHz CDCl<sub>3</sub>): δ, ppm=7.40 (d, 2H) 7.0 (d, 2H) 5.1 (s, 1H OH), 8.17 (s, 1H), 7.4 (s, 1H NH), 7.40-7.67 (m, 5H), IR (Kbr, cm<sup>-1</sup>): 3296, 2926, 1687, 1487, 1250, 835, 742.

**6) (Z)-1-(4-methylbenzylidene)-2-phenylhydrazine:** <sup>1</sup>H NMR (400 MHz CDCl<sub>3</sub>): δ, ppm=7.40 (d, 2H), 7.15 (d, 2H), 2.20 (s, 3H CH<sub>3</sub>), 8.17 (s, 1H), 7.4 (s, 1H NH), 7.40-7.67 (m, 5H), IR (Kbr, cm<sup>-1</sup>): 3317, 3051, 2928, 2735, 1944, 1689, 1589, 1494, 1253, 1143, 1043.

**7) (Z)-1-(4-nitrobenzylidene)-2-phenylhydrazine:** <sup>1</sup>H NMR (400 MHz CDCl<sub>3</sub>): δ, ppm=7.70(d, 2H), 8.00 (d, 2H), 8.17 (s, 1H), 7.4 (s, 1H NH), 7.40-7.67 (m, 5H), IR (Kbr, cm<sup>-1</sup>):3292, 3051, 2426, 1795, 1510, 1145, 848, 734.

**8) (Z)-1-(3-bromobenzylidene)-2-phenylhydrazine:** <sup>1</sup>H NMR (400 MHz CDCl<sub>3</sub>): δ, ppm=7.50 (s, 1H), 7.30 (d, 1H), 7.40 (d, 2H), 8.17 (s, 1H), 7.4 (s, 1H NH), 7.40-7.67 (m, 5H), IR (Kbr, cm<sup>-1</sup>): 3315, 3051, 2928, 1813, 1685, 1529, 1493, 1249, 1141, 900, 784.

**9) (Z)-2-nitro-4-((2-phenylhydrazono)methyl)phenol:** <sup>1</sup>H NMR (400 MHz CDCl<sub>3</sub>): δ, ppm=8.1(s, 1H), 7.80 (d, 1H), 7.12 (d, 1H), 5.10 (s, 1H OH), 8.17 (s, 1H), 7.4 (s, 1H NH), 7.40-7.67 (m, 5H), IR (Kbr, cm<sup>-1</sup>): 3319, 3211, 3049, 2920, 1819, 1595, 1500, 1136, 839, 744.

**10) (Z)-1-(4-methoxybenzylidene)-2-phenylhydrazine:** <sup>1</sup>H NMR (400 MHz CDCl<sub>3</sub>): δ, ppm=7.52 (d, 2H), 7.10 (d, 2H), 3.5 (s, 3H CH<sub>3</sub>), 8.17 (s, 1H), 7.4 (s, 1H NH), 7.40-7.67 (m, 5H), IR (Kbr, cm<sup>-1</sup>): 3028, 1730, 1587, 1493, 1244, 1141, 1014, 864, 738.

**11) (Z)-1-(3,4-dimethoxybenzylidene)-2-phenylhydrazine:** <sup>1</sup>H NMR (400 MHz CDCl<sub>3</sub>): δ, ppm=7.40 (s, 1H), 7.10(d, 2H), 3.4 (s, 6H CH<sub>3</sub>), 8.17 (s, 1H), 7.4 (s, 1H NH), 7.40-7.67 (m, 5H), IR (Kbr, cm<sup>-1</sup>): 3302, 2941, 1682, 1593, 1494, 1250, 1140, 1020, 731.

**12) (Z)-1-phenyl-2-(3,4,5-trimethoxybenzylidene)hydrazine:** <sup>1</sup>H NMR (400 MHz CDCl<sub>3</sub>): δ, ppm=7.10 (d, 2H), 3.40 (9H CH<sub>3</sub>), 8.17 (s, 1H), 7.4 (s, 1H NH), 7.40-7.67 (m, 5H), IR (Kbr, cm<sup>-1</sup>):3068, 1587, 1054, 1249, 1136, 730.

**13) (Z)-1-(naphthalen-1-ylmethylene)-2-phenylhydrazine:** <sup>1</sup>H NMR (400 MHz CDCl<sub>3</sub>): δ, ppm=7.40-8.10 (m, 7H), 8.17 (s, 1H), 7.4 (s, 1H NH), 7.40-7.67(m, 5H), IR (Kbr, cm<sup>-1</sup>): 3304, 2833, 2040, 1695, 1593, 1491, 1024, 833, 742.

**14) (Z)-1-(furan-2-ylmethylene)-2-phenylhydrazine:** <sup>1</sup>H NMR (400 MHz CDCl<sub>3</sub>): δ, ppm=6.32(t, 1H), 6.50 (d, 1H), 7.20 (d, 1H), 8.17 (s, 1H), 7.4 (s, 1H NH), 7.40-7.67(m, 5H), IR (Kbr, cm<sup>-1</sup>): 3057, 1695, 1589, 1487, 1255, 1043, 727.

**15) (Z)-1-phenyl-2-(thiophen-2-ylmethylene)hydrazine:** <sup>1</sup>H NMR (400 MHz CDCl<sub>3</sub>): δ, ppm=7.05 (t, 1H), 7.40 (d, 1H), 7.40 (d, 1H), 8.17 (s, 1H), 7.4 (s, 1H NH), 7.40-7.67(m, 5H), IR (Kbr, cm<sup>-1</sup>): 2151, 1689, 1589, 1481, 1332, 1238, 1124, 1003, 842.

### CONCLUSION

We have developed a practical and convenient method for the facile synthesis of Phenylhydrazone derivatives with excellent yields. By using eco-friendly and economically viable mixed metal oxide heterogeneous catalyst CuO/SnO<sub>2</sub>. The significant features of this method involve avoiding organic solvents, reagents, acids, and bases. It was unfavorable for green chemistry the advantage of using this catalyst is an easy separation of catalyst and the product was obtained without any difficult like isolation and purification so this method is more appropriate for this reaction.

### ACKNOWLEDGMENTS

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