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# Microwave-promoted efficient conversion of acetophenones to 1,3,5-triarylbenzenes catalyzed by $H_3PW_{12}O_{40}$ and nano-silica supported $H_3PW_{12}O_{40}$ as reusable catalysts

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#### 1. Introduction

In recent years, the chemical synthesis under solvent-free conditions has developed into a powerful methodology as it reduces the toxic waste produced and therefore becomes less harmful to the environment [1]. On the other hand, one of the major challenges facing chemists is to develop new synthetic transformations that are not only efficient and high-yielding but that are also environmentally benign [2]. Consequently, green chemistry and sustainability have received great attention in organic synthesis during the last decade [2–4].

The application of heterogeneous solid acid catalysts such as heteropoly acids (HPAs) have attracted extensive interest in recent times due to their easy recovery and reusability, non-corrosiveness, environmental benignity, non-hazardous nature, low cost and operational simplicity [5,6]. Heteropoly acids, especially  $H_3PW_{12}O_{40}$ , have received great attention among the acid catalysts, because of their high acid strength and selectivity properties [5,6]. A major disadvantage of bulk HPAs lies in their low specific surface area, less than 10 m<sup>2</sup> g<sup>-1</sup> that can be improved by supporting on oxidic carriers especially SiO<sub>2</sub> which is an inexpensive and non-corrosive neutral solid [7–9]. The support provides an opportunity to spread HPAs over a large surface area, which generally increases

#### ABSTRACT

 $H_3PW_{12}O_{40}$  and nano-silica supported  $H_3PW_{12}O_{40}$  were found to be efficient heterogeneous catalysts for the preparation of 1,3,5-triarylbenzenes via triple self condensation of acetophenones under microwave irradiation and solvent-free conditions. High yields, short reaction times, easy work-up, easy availability and handling, eco-friendly and reusability of the catalysts are the main aspects of the present method. The catalytic mechanism of 1,3,5-triarylbenzenes synthesis is also proposed.

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catalytic activity. Due to the unique properties of HPAs, various chemical transformations using these compounds as catalysts have been reported in the literature during the recent years [10–16].

1,3,5-Triarylbenzenes represent an important class of organic compounds because of their applications in the fields of electrode and electroluminescent devices [17], resisting materials [18] and conducting polymers [19]. These compounds can also be used as important intermediates for the synthesis of buck minster fullerenes, pharmaceuticals and conjugated star polyaromatics [20,21]. On this basis, a number of synthetic methods to approach 1,3,5-triarylbenzenes have been previously developed [22–34]. Although these methods have proved to be useful for the synthesis of these compounds, there are some limitations, including low yields, tedious workup, nonrecyclability of the catalyst, long reaction times and the use of stoichiometric amounts of catalysts which are expensive, moisture sensitive and toxic.

As a part of our ongoing efforts to explore environmentally benign synthetic reactions using HPA catalysts [35–40], herein we report a rapid, practical and efficient synthesis of 1,3,5-triarylbenzenes via a microwave-assisted cyclotrimerization of acetophenones catalyzed by  $H_3PW_{12}O_{40}$  (HPW) and nano-silica supported  $H_3PW_{12}O_{40}$  under solvent-free conditions (Scheme 1).

#### 2. Experimental

All starting materials were purchased from Merck or Fluka chemical companies. All products were identified by comparison



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Scheme 1. Synthesis of 1,3,5-triarylbenzenes.

Table 1
Optimization of the reaction conditions for triple-self condensation of acetophenon

Entry	Catalyst (mmol)	T (°C)	Power (W)	Yield (%) <sup>a</sup>
1	H <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub> (0.15)	90	450	55
2	H <sub>4</sub> SiW <sub>12</sub> O <sub>40</sub> (0.15)	90	450	70
3	H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> (0.15)	90	450	93
4	H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> (0.17)	90	450	93
5	H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> (0.12)	90	450	73
6	H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> (0.15)	100	450	93
7	H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> (0.15)	80	450	81
8	H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> (0.15)	90	500	93
9	H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> (0.15)	85	400	85
10	$H_{3}PW_{12}O_{40}@nano-SiO_{2}(0.08)$	90	450	95
11	H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> @nano-SiO <sub>2</sub> (0.07)	90	450	95
12	$H_3PW_{12}O_{40}$ @nano-SiO <sub>2</sub> (0.05)	90	450	91

<sup>a</sup> Isolated yield.

of their physical and spectral data with those of authentic samples. Melting points were determined using Stuart Scientific SMP2 apparatus. IR spectra were recorded on a Shimadzu IR-435 spectrophotometer. <sup>1</sup>H NMR spectra were recorded in a CDCl<sub>3</sub> solution on a Bruker-Avance 400 MHz spectrometer. The microwave system used for these experiments includes the following items: Micro-SYNTH lab station, complete with glass door, dual magnetron system with pyramid-shaped diffuser, 1000 W delivered power, exhaust system, magnetic stirrer, "quality pressure" sensor for flammable organic solvents, ATCFO fiber optic system for automatic temperature control.

#### 2.1. Preparation of nano-silica supported H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>

The supported  $H_3PW_{12}O_{40}$  catalyst was prepared by the method of incipient wetness. To a solution of  $H_3PW_{12}O_{40}$  (0.4 g) in deionized water (50 mL), high surface area SiO<sub>2</sub> (Cabosil 20) support (1.6 g) was added and stirred for 24 h. The resulting pastes were dried at 100 °C and then calcined at 250 °C for 4 h [41–44].

## 2.2. General procedure for the synthesis of 1,3,5-triarylbenzenes in the presence of $H_3PW_{12}O_{40}$ and nano-silica supported $H_3PW_{12}O_{40}$ under MW irradiation

A mixture of acetophenone derivative (1 mmol) and  $H_3PW_{12}O_{40}$  (15 mol%) or nano-silica supported  $H_3PW_{12}O_{40}$  (7 mol%) was subjected to microwave irradiation (450 W) at 90 °C for the appropriate time according to Table 2. The progress of the reaction was monitored by TLC (eluent:ether/ethyl acetate, 6:1). After completion of the reaction, hot ethyl acetate (10 mL) was added and the catalyst was separated by filtration. The solvent was evaporated and the residue was recrystallized from ethanol or acetone to afford the pure 1,3,5-triarylbenzene.

#### 3. Results and discussion

3.1. Synthesis of 1,3,5-triarylbenzenes in the presence of  $H_3PW_{12}O_{40}$  and nano-silica supported  $H_3PW_{12}O_{40}$  under MW irradiation

The supported HPW@nano-SiO<sub>2</sub> catalyst was characterized by elemental analysis, FT-IR spectroscopy and SEM. The most

informative technique for the investigation of surface interaction between HPW and nano-SiO<sub>2</sub> is FT-IR spectroscopy (Fig. 1). The pure HPW displays bands at 1081 (P–O), 985 (W–O), 889 (W– Oc–W) and 801 cm<sup>-1</sup> (W–Ob–W). The FT-IR spectrum of HPW@nano-SiO<sub>2</sub> shows bands at 982 (W–O), 899 and 801 cm<sup>-1</sup> (W–O–W) and the band assigned to P–O vibrations is masked by nano-SiO<sub>2</sub> broad vibrations.

The UV–Vis spectra of HPW in CH<sub>3</sub>CN displayed an absorption peak at 255 nm, which is assigned to charge-transfer absorption in the heteropoly cage (Fig. 2A). This absorption peak was appeared in the solid-state UV–Vis spectra of catalyst and since pure nano-SiO<sub>2</sub> shows no UV absorption peak; therefore, these results indicated that primary Keggin structure has been introduced into the nanostructure framework (Fig. 2B).

The SEM image of the catalyst showed that the catalyst particles have sizes in the range of nanometers (Fig. 3).

The HPW loading on the supports, which were calculated from W content in supported HPW catalyst, was determined by neutron activation analysis. The amount of W loading on the supported catalyst was obtained about 0.068 mmol/g.

In order to optimize the reaction conditions, we carried out the cyclotrimerization of acetophenone and studied the effect of temperature, amount of catalyst and MW power (Table 1). First, the model reaction was examined in the presence of different heteropoly acids (15 mol%) as catalysts, among which H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> proved to be the most effective catalyst for this purpose. Investigation of different parameters in the model reaction indicated that the best yield of the desired product was obtained using 1:0.15 molar ratios of acetophenone and H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> with an applied power of 450 W at 90 °C after 18 min. Under the same reaction conditions, the catalytic activity of nano-silica supported H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> was also investigated and the best result was obtained using 0.07 mmol of the catalyst per mmol of acetophenone. Increasing the temperature, the amount of catalyst, reaction time and/or applying a higher power level failed to improve the yield, while decreasing these parameters led to reduced yield.

To explore the generality of the reaction, we extended our study with different acetophenones. The results of synthesis of a series of 1,3,5-triarylbenzenes in the presence of  $H_3PW_{12}O_{40}$  (15 mol%) are summarized in Table 2. This protocol tolerates a variety of acetophenones containing both electron-withdrawing and electron-donating substituents. The reactions are generally clean and the desired 1,3,5-triarylbenzenes were obtained in high yields (80–93%) and in very short reaction times (18–30 min). In order to show the influence of supporting on the reactivity of the catalyst, these reactions were performed in the presence of nano-silica supported  $H_3PW_{12}O_{40}$ . As shown in Table 2, the comparable results as with  $H_3PW_{12}O_{40}$  was obtained using only 7 mol% of supported catalyst. These results clearly revealed that the supporting HPA on nano-silica increases the specific surface area and therefore, the catalytic activity of the catalyst is increased.

In order to verify the effect of MW irradiation, some of these reactions were also carried out under thermal conditions at the same temperature (90 °C) used for the system under MW irradiation (Table 2, entries 1, 2 and 9). It was found that significantly lower yields (8–48%) were obtained under these conditions even after 8 h. These clearly showed that MW irradiation improved the results.

The acceleration of the reactions by microwave mainly results from two effects: thermal effect and specific microwave effect [45,46]. Thermal effect (dielectric heating) resulting from material-microwave interaction which allows fast and uniform distribution and conversion of microwave energy into heat. Specific microwave effect can be expected for the polar mechanism, when the polarity is increased during the reaction from the ground state (GS) towards the transition state (TS). For the reactions under

 Table 2

 Synthesis of 1,3,5-triarylbenzenes catalyzed by HPW and HPW@nano-SiO2.

$$3 \operatorname{Ar}^{O}_{CH_3} \xrightarrow{HPW (15 \text{ mol}\%) \text{ or } HPW @ \text{nano-SiO}_2 (7 \text{ mol}\%)}_{Solvent-free, MW (450 W), 90 °C} + 3 H_2O$$

Entry	Ar	Product	Time (min)	HPW Yield (%) <sup>a</sup>	HPW@nano-SiO <sub>2</sub> Yield (%) <sup>a</sup>
1			18 (480 <sup>b</sup> )	93 (45 <sup>b</sup> )	95 (48 <sup>b</sup> )
2	H <sub>3</sub> C-	CH <sub>3</sub>	22 (480 <sup>b</sup> )	83 (30 <sup>b</sup> )	85 (30 <sup>b</sup> )
3		H <sub>3</sub> C CH <sub>3</sub>	20 (480 <sup>b</sup> )	89 (35 <sup>b</sup> )	91 (38 <sup>b</sup> )
4	H <sub>3</sub> CO	OCH3	23 (480 <sup>b</sup> )	82 (20 <sup>b</sup> )	81 (18 <sup>b</sup> )
5		H <sub>3</sub> CO OCH <sub>3</sub>	20 (480 <sup>b</sup> )	87 (32 <sup>b</sup> )	89 (35 <sup>b</sup> )
6			28 (480 <sup>b</sup> )	82 (15 <sup>b</sup> )	85 (20 <sup>b</sup> )

(continued on next page)

Table 2 (continued)

Entry	Ar	Product	Time (min)	HPW Yield (%) <sup>a</sup>	HPW@nano-SiO <sub>2</sub> Yield (%) <sup>a</sup>
7			20 (480 <sup>b</sup> )	84 (30 <sup>b</sup> )	86 (30 <sup>b</sup> )
8	F	F F	28 (480 <sup>b</sup> )	80 (10 <sup>b</sup> )	84 (14 <sup>b</sup> )
9	CI		25 (480 <sup>b</sup> )	85 (12 <sup>b</sup> )	87 (15 <sup>b</sup> )
10	Br		28 (480 <sup>b</sup> )	84 (10 <sup>b</sup> )	84 (15 <sup>b</sup> )
11	I	Br Br	30 (480 <sup>b</sup> )	80 (8 <sup>b</sup> )	82 (10 <sup>b</sup> )
12			30 (480 <sup>b</sup> )	82 (8 <sup>b</sup> )	85 (10 <sup>b</sup> )
		CI			

<sup>a</sup> Isolated yield.

<sup>b</sup> Reaction was performed under thermal conditions.

investigation, it seems that stabilization of the transition state is more effective than that of the ground state, and therefore, the reactivity is enhanced as a result of decreased activation energy.

A plausible mechanism for the synthesis of 1,3,5-triarylbenzenes has been proposed in Scheme 2. The acetophenone was first converted to intermediates **A** and **B** in the presence of the catalyst. The reaction between these intermediates followed by dehydration produces  $\alpha,\beta$ -unsaturated carbonyl compound **C**. Activation of **C** by the catalyst and subsequent reaction with **A** provides **D** that on subsequent dehydration followed by prototropic shift in the presence of catalyst afforded **E**.  $6\pi$ -electrocyclization of **E** leads to **F** which upon dehydration produces the desired product **G** and releases the catalyst for the next catalytic cycle. On the other hand, the desired product was obtained by the reaction of  $\alpha,\beta$ -unsatu-



Fig. 1. The FT-IR spectrum of (A) pure nano-silica, (B) pure HPW and (C) HPW@nano-SiO<sub>2</sub>.



Fig. 2. UV-Vis spectrum of (A) pure HPW and (B) HPW@nano-SiO<sub>2</sub>.



Fig. 3. SEM image of HPW@nano-SiO<sub>2</sub>.

rated carbonyl compound  $\mathbf{C}$  with acetophenone under the same conditions. This is a good indication that the proposed mechanism is reasonable.

#### 3.2. Catalyst reusability

The catalyst recovery and reuse was evaluated taking the cyclotrimerization of acetophenone as a model reaction. After completion of the reaction, hot ethyl acetate was added and the catalyst was separated by simple filtration. The catalyst was dried at 100 °C and reused. The recovered catalyst can be used at least five consecutive times without significant loss in product yield (Table 3).

#### 3.3. Spectral data

3.3.1. 1,3,5-Triphenylbenzene (Table 2, entry 1)

Light yellow solid; m.p. 174–175 °C (Lit. [34] 175–176 °C). IR (KBr):  $v_{max}$  = 3061, 1595, 1476, 1452, 1026, 751, 699 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.34–7.53 (m, 9H, ArH), 7.71 (d, *J* = 8.2 Hz, 6H, ArH), 7.79 (s, 3H, ArH).

#### 3.3.2. 1,3,5-Tris(4-methylphenyl)benzene (Table 2, entry 2)

White solid; m.p. 176–177.5 °C (Lit. [24] 178 °C). IR (KBr):  $v_{max} = 3018, 2921, 1611, 1512, 1489, 1110, 813 cm^{-1}$ . <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 2.43$  (s, 9H, CH<sub>3</sub>), 7.29 (d, *J* = 8.0 Hz, 6H, ArH), 7.60 (d, *J* = 8.0 Hz, 6H, ArH), 7.74 (s, 3H, ArH).

#### 3.3.3. 1,3,5-Tris(4-isopropylphenyl)benzene (Table 2, entry 3)

White solid; m.p. 166–167 °C (Lit. [24] 166 °C). IR (KBr):  $v_{max}$  = 2957, 2867, 1637, 1509, 1457, 1362, 1054, 826 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.32 (d, *J* = 6.4 Hz, 18H, CH(CH<sub>3</sub>)<sub>2</sub>, 2.93–3.01 (m, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 7.36 (d, *J* = 7.6 Hz, 6H, ArH), 7.63 (d, *J* = 7.6 Hz, 6H, ArH), 7.76 (s, 3H, ArH).

#### 3.3.4. 1,3,5-Tris(4-methoxyphenyl)benzene (Table 2, entry 4)

White solid; m.p. 142–143 °C (Lit. [25] 143 °C). IR (KBr):  $v_{max}$  = 2954, 2917, 2849, 1603, 1463, 1377, 1261, 1099, 803 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.81 (s, 9H, OCH<sub>3</sub>), 6.92–7.60 (m, 12H, ArH), 7.75 (s, 3H, ArH).

#### 3.3.5. 1,3,5-Tris(4-cyclohexylphenyl)benzene (Table 2, entry 5)

Light yellow solid; m.p. 230–232 °C. IR (KBr):  $v_{max} = 3022, 2922, 2850, 1591, 1509, 1447, 1396, 998, 906, 823, 783 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): <math>\delta = 1.29-1.35$  (m, 6H, CH<sub>2</sub>), 1.42–1.50 (m, 12H, CH<sub>2</sub>), 1.91 (d, J = 11.9 Hz, 6H, CH<sub>2</sub>) 1.97 (d, J = 11.9 Hz, 6H, CH<sub>2</sub>), 2.59–2.60 (m, 3H, CH),7.35 (d, J = 8.1 Hz, 6H, ArH), 7.64 (d, J = 8.1 Hz, 6H, ArH), 7.77 (s, 3H, ArH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 26.60, 27.35, 34.91, 44.71, 125.07, 127.63, 127.70, 139.24, 142.53, 147.86.$  MS (EI): m/z = 552.38 (18.54, [M<sup>+</sup>], 207.16 (17.81), 83.27 (41.67), 69.20 (52.08), 57.21 (71.67), 55.14 (100)).

#### 3.3.6. 1,3,5-Tris(bipheny)benzene (Table 2, entry 6)

White solid; m.p. 239–240 °C (Lit. [33] 236.2–238 °C). IR (KBr):  $v_{max}$  = 3025, 1590, 1486, 1380, 1217, 1005, 829, 766, 695 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.36–7.52 (m, 10H, ArH), 7.57–7.85 (m, 17H, ArH), 7.90 (s, 3H, ArH).

#### 3.3.7. 1,3,5-Tris(2-naphthyl)benzene (Table 2, entry 7)

Light yellow solid; m.p. 240–241 °C (Lit. [34] 241–242 °C). IR (KBr):  $v_{max} = 3050$ , 1598, 1507, 854, 747 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.45-7.55$  (m, 6H, ArH), 7.91–8.02 (m, 12H, ArH), 8.08 (s, 3H, ArH), 8.23 (s, 3H, ArH).

#### 3.3.8. 1,3,5-Tris(4-fluorophenyl)benzene (Table 2, entry 8)

White solid; m.p. 237–238 °C (Lit. [31] 238–240 °C). IR (KBr):  $v_{max}$  = 3059, 1605, 1509, 1448, 1222, 1158, 823, 772 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.18 (t, *J* = 8.4 Hz, 6H, ArH), 7.63–766 (m, 6H, ArH), 7.67 (s, 3H, ArH).

#### 3.3.9. 1,3,5-Tris(4-chlorophenyl)benzene (Table 2, entry 9)

White solid; m.p. 245–246 °C (Lit. [25] 246 °C). IR (KBr):  $v_{max}$  = 3046, 1599, 1492, 1382, 1092, 1011, 814 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.46 (d, *J* = 8.4 Hz, 6H, ArH), 7.61 (d, *J* = 8.4 Hz, 6H, ArH), 7.70 (s, 3H, ArH).

#### 3.3.10. 1,3,5-Tris(4-bromophenyl)benzene (Table 2, entry 10)

White solid; m.p. 260–261 °C (Lit. [31] 260–261 °C). IR (KBr):  $v_{max}$  = 3043, 1595, 1489, 1379, 1075, 1007, 809 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.55 (d, *J* = 8.4 Hz, 6H, ArH), 7.62 (d, *J* = 8.4 Hz, 6H, ArH), 7.70 (s, 3H, ArH).

#### 3.3.11. 1,3,5-Tris(4-iodophenyl)benzene (Table 2, entry 11)

Dark brown solid; m.p. 264–265 °C (Lit. [24] 265 °C). IR (KBr):  $v_{max}$  = 3055, 1593, 1485, 1376, 1003, 809 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.41 (d, *J* = 8.0 Hz, 6H, ArH), 7.69 (s, 3H, ArH), 7.82 (d, *J* = 8.0 Hz, 6H, ArH).

#### 3.3.12. 1,3,5-Tris(3-chlorophenyl)benzene (Table 2, entry 12)

White solid; m.p. 171 °C (Lit. [29] 171–172 °C). IR (KBr):  $v_{max}$  = 3059, 1592, 1484, 1381, 1101, 1079, 861, 771, 684 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.39–7.42 (m, 3H, ArH), 7.45 (d, *J* = 7.2 Hz, 3H, ArH), 7.58 (d, *J* = 7.2 Hz, 3H, ArH), 7.69 (s, 3H, ArH), 7.75 (s, 3H, ArH).





#### Table 3

Investigation of catalyst reusability in cyclotrimerization of acetophenone.<sup>a</sup>



<sup>a</sup> Reaction conditions: acetophenone (1 mmol), HPW (0.15 mmol) or HPW@nano-SiO<sub>2</sub> (0.07 mmol), applied power (450 W), 90 °C and 18 min. <sup>b</sup> Isolated yield.

86

85

86

84

#### 4. Conclusion

In conclusion, we have demonstrated an efficient microwavepromoted synthesis of 1.3.5-triarylbenzenes via a one-pot cyclotrimerization of structurally diversified acetophenones catalyzed by H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> and nano-silica supported H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> under solventfree conditions. The prominent advantages of this new methodology are the reusability of the catalysts, the operational simplicity, high yields of the products, fast reaction and green synthesis avoiding toxic reagents and solvents. Thus, it provides a better and more practical alternative to the existing methodologies for the synthesis of 1,3,5-triarylbenzenes

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