MICROWAVE-PROMOTED SOLVENT FREE ONE-POT SYNTHESIS OF TRIAZOLO[1,2-A]INDAZOLE-TRIONES CATALYZED BY SILICA-SUPPORTED LA₀.₅CA₀.₅CrO₃ NANOPARTICLES AS A NEW AND REUSABLE PEROVSKITE-TYPE OXIDE

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ABSTRACT. Microwave assisted solvent free synthesis of triazolo[1,2-a]indazole-1,3,8-triones through one-pot three-component reaction of didecene, phenyl urazole and aromatic aldehydes is presented. The reaction process was catalyzed by La₀.₅Ca₀.₅CrO₃ and silica-supported La₀.₅Ca₀.₅CrO₃ nanoparticles as new perovskite-type catalysts. The nano catalyst was studied by XRD, SEM and IR characterization tools. Some advantages of the proposed approach include high yield, being eco-friendly, procedure convenience and reusability of the catalyst.

KEY WORDS: One-pot reaction, Triazolo[1,2-a]indazole trione, Perovskite oxide, Nano catalyst, Microwave, Solvent-free

INTRODUCTION

Nitrogen-containing heterocyclic compounds (NCHCs) have some roles in organizing many chemical reactions and providing some specific properties. These compounds can be found as the moiety of many natural products and pharmaceuticals that are essential for biological processes and enhancing life quality [1]. Among different types of NCHCs, the molecules that contain a urazole (1,2,4-triazolidine-3,5-dione) ring in their structures have attached more interest since they are members of an important category of non-natural and natural products [2]. Moreover, many urazole containing compounds have been confirmed to exhibit noticeable biological properties, in addition to being successful for clinical applications [3, 4]. Furthermore, urazole derivatives can act as anticonvulsant agents [5], demonstrate fungicidal activity [6], and catalyze radical polymerization reactions [7].

In the areas of modern organic chemistry and synthesis of heterocyclic compounds, a powerful and efficient method has been recently developed, which involves multi-component reactions (MCRs). Through MCRs, complex organic molecules can be synthesized from some simple and accessible starting materials. The outstanding advantages of MCRs are its high efficiency, short procedure time and excluding the requirement of intermediate isolation [8]. MCRs are considered as eco-friendly processes as they decrease energy consumption, number of the required synthesis steps, procedures duration and lateral products [9, 10]. Therefore, discovering novel MCRs and improving the currently known MCRs by employing reusable catalysts are of significant interest [11, 12].

In the last decade, indazole trione derivatives are synthesized by one-pot multicomponent reactions [13, 14]. With the same purpose, triazolo[1,2-a]indazole-1,3,8-triones are synthesized by one-pot three-component condensation of didecene, phenyl urazole and aromatic aldehydes by using various catalyst [15-19]. However, most of these reactions are suspended with one or more damage, such as low yields, high temperature requirement, longer reaction time, use of expensive reagents and catalysts, use of harmful solvents, and tedious work-up.

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Perovskite-type oxides (PTOs) are one of the best studied groups of oxides. Usually, PTOs are recognized with ABO$_3$ formulas ordered in cubic structures, where A and B are denoted to metal cations. The extent of structural defects and oxygen amounts of PTOs depend on their compositions since PTOs present a wide variety of structural stability, and their A and B metal cations can be replaced by other metal cations, partially. The A-site is usually occupied by the bigger cation and coordinates with 12 oxygen anions. The A-site cation is often one of the La, Sm or Pr rare, Sr, Ba or Ca alkaline, or Na or K alkali earth metal cations. One the other hand, the B-site is occupied by a transition metal cation with a smaller cationic radius, typically. B-site cations fill up the octahedral gaps that are accessible within oxygen framework of PTOs [20]. In fact, interest in crystal structures of PTOs has roots in their various and ever surprising properties and their flexibilities to match almost all outlined elements [21, 22]. Due to the thermal stability of PTOs and variation in their physical and chemical properties, which can be controlled by choosing different A or B-site elements, PTOs are widely used as homogeneous or heterogeneous catalysts [23, 24]. PTOs have different kinds of attributes, such as adsorption, acid-base, and redox properties. Consequently, they can be considered as interesting catalysts with different properties [25].

In this work, we synthesized and characterized the PTO nanoparticles (NPs) of La$_{0.5}$Ca$_{0.5}$CrO$_3$ (LCCO) and silica-supported La$_{0.5}$Ca$_{0.5}$CrO$_3$ (S-LCCO), and used them as new heterogeneous catalysts to synthesize substituted indazols through one-pot condensation of dimeredone, urazole and aromatic aldehyde components under microwave irradiation and solvent-free conditions. The conducted MCR processes lasted in short times and gave high conversions and product selectivity values (Scheme 1). Furthermore, they enabled recovery of the catalyst and the products and provided an efficient route to prepare a range of products.

![Scheme 1. Triazolo[1,2-a]indazole-triones synthesis catalyzed by LCCO or S-LCCO NPs under microwave irradiation solvent-free conditions.](image)

**EXPERIMENTAL**

**Materials and equipment**

All reagents and materials were purchased from Aldrich and Merck companies and were utilized without any further purification. The microwave treated reactions were carried out in a milestone reactor (Italy). An Electro thermal type 9100 melting point apparatus was used to determine the melting point of the chemicals with no corrections. Also, Thermo Nicolet AVATAR-370 and Bruker DRX400 spectrometers were employed to record FT-IR and $^1$H NMR spectra.

**Synthesis of La$_{0.5}$Ca$_{0.5}$CrO$_3$ (LCCO) nanoparticles**

In order to synthesize La$_{0.5}$Ca$_{0.5}$CrO$_3$ NPs, proportional amounts of Ca(NO$_3$)$_2$.4H$_2$O, La(NO$_3$)$_3$.6H$_2$O and Cr(NO$_3$)$_3$.9H$_2$O were dissolved in 20 mL deionized water. The obtained
metal solution was mixed with citric acid at room temperature and its temperature was elevated to approximately 75 °C to evaporate its excess water. In this way, a gel was formed. The gel was dried by annealing to 110 °C in an oven and keeping it at this temperature for 10 h. In the last step, the dried gel was powdered by an agate mortar and calcinated in air for 9 h, at 750 °C (heating rate: 3 °C/min). This process helped to remove most residual carbons and obtain cubic perovskite phase.

Preparation of silica-supported La0.5Ca0.5CrO3 (S-LCCO) nanoparticles

Initially, silica was put into oven for 2 h, at 90 °C. Then, 0.2 g La0.5Ca0.5CrO3 NP and 0.8 g silica were rubbed into a glass mortar for about 1 h to obtain a bright and heterogeneous mixture of S-LCCO (20% w/w).

Typical solvent-free procedure of triazolo[1,2-a]indazole-triones synthesis under microwave irradiation

A mixture of dimedone (1, 1 mmol), 4-phenylazoazole (2, 1 mmol), aromatic aldehyde (3a-h, 1 mmol) and S-LCCO nano perovskite (0.01 g) was mixed in a high-pressure Teflon reactor, which was equipped with a magnetic stirrer and an optical fiber, which was implemented to control the reaction's temperature. The reaction mixture was irradiated by 400 W microwave at 80 °C, for the specified reaction times. TLC with n-hexan:ethylacetate eluent was used to monitor the progress of the reactions. After reaction completion and cooling, the reaction mixtures were filtered and washed with ethanol to separate the catalyst. First, 10 mL water was added to the solution. Then, EtOH/H2O (4:1) was added to crystallize the water insoluble crude products. Then the crystals were filtered to achieve pure products (4a-h). The physical and spectroscopic data of the products were collected to compare their properties with those of authentic samples and confirm their structures.

Analytical data for selected compounds

6,6-Dimethyl-2,9-diphenyl-6,7-dihydro-[1,2,4]triazolo[1,2-a]indazole-1,3,8(2H,5H,9H)-trione (4a). White powder; m.p. 187–189 °C; IR (KBr) (v max cm⁻¹): 2956, 2926, 1720, 1679, 1595, 1372; ¹H NMR (300 MHz, CDCl3): δ 1.22 (s, 6H, 2CH3), 2.33 (s, 2H, CH2), 2.93 (2H, AB system, ²JH-H = 18.0 Hz, CH3) 5.54 (s, 1H, CH–Ar), 7.07–8.01 (m, 10H, Ar) ppm; ¹³C NMR (75 MHz, CDCl3): δ 28.3, 28.7, 34.8, 35.5, 51.3, 64.1, 120.1, 125.6, 127.1, 128.8, 128.9, 129.3, 130.7, 136.8, 149.0, 150.7, 151.0, 192.0 ppm.

(4-Chlorophenyl)-6,6-dimethyl-2-phenyl-6,7-dihydro-[1,2,4]triazolo[1,2-a]indazole-1,3,8(2H,5H,9H)-trione (4d). White powder; m.p. 167–169 °C; IR (KBr) (v max cm⁻¹): 3050, 2950, 2960, 1610, 1200; ¹H NMR (300 MHz, CDCl3): δ 1.20 (s, 6H, 2CH3), 2.44 (s, 2H, CH2), 2.90 (2H, AB system, ²JH-H = 18.7 Hz, CH3) 5.61 (s, 1H, CH–Ar), 7.08–7.87 (m, 9H, Ar) ppm; ¹³C NMR (75 MHz, CDCl3): δ 28.2, 28.7, 34.7, 35.5, 51.2, 63.5, 119.7, 125.6, 128.6, 128.8, 129.0, 129.4, 130.7, 134.6, 135.6, 149.1, 151.0, 151.3, 192.0 ppm.

(2-Chlorophenyl)-6,6-dimethyl-2-phenyl-6,7-dihydro-[1,2,4]triazolo[1,2-a]indazole-1,3,8(2H,5H,9H)-trione (4e). White powder; m.p. 174–178 °C; IR (KBr) (v max cm⁻¹): 2956, 2928, 2720, 1676, 1650, 1380; ¹H NMR (300 MHz, CDCl3): δ 1.21 (s, 6H, 2CH3), 2.45 (s, 2H, CH2), 2.92 (2H, AB system, ²JH-H = 18.3 Hz, CH3) 5.47 (s, 1H, CH–Ar), 6.99–7.48 (m, 9H, Ar) ppm; ¹³C NMR (75 MHz, CDCl3): δ 28.3, 28.9, 34.6, 35.4, 51.2, 63.6, 118.5, 125.8, 127.6, 128.7, 129.3, 130.5, 130.7, 130.8, 131.3, 131.9, 132.8, 148.4, 150.0, 150.7, 191.8 ppm.

RESULTS AND DISCUSSION

Catalyst characterization

The XRD pattern of the calcined LCCO powder is displayed in Figure 1. The obtained XRD peaks are attributed to perovskite La$_6$Ca$_4$CrO$_{12}$, according to the standard XRD spectra [24]. Positions of these peaks approve successful synthesis of perovskite-type phase through the adopted sol-gel method while their sharpness indicates achievement of high crystallinity after calcinating the LCCO NPs for 9 h at 750 °C. Based on the XRD peaks, it can be declared that the perovskite crystals are cubic with $a = 3.8800$ Å, $b = 3.8800$ Å and $c = 3.8800$ Å crystal parameters. Crystallite sizes of the LCCO NPs were calculated to be about 35 nm by applying the Scherer’s equation to the (110) XRD peak. In the Scherers equation, $K$ is a constant, $\lambda$ is the wavelength of the radiation, $\beta$ is the full-width at half maximum and $\theta$ is the diffraction angle.

$$D = \frac{K\lambda}{\beta \cos \theta}$$

Figure 1. XRD spectra of LCCO.

Morphology of the NPs was studied by SEM analysis. Figure 2 exhibits the SEM micrograph of the LCCO particles synthesized using the modified sol-gel method of Pechini. As Figure 2 shows, the surface of the sample is porous and uniform while its pore sizes vary from 30 to 70 nm. Also, the surface seems to be fully covered by the grown particles [26]. It is noteworthy that larger particle geometrics with appropriate pore size are more useful for liquid-phase catalysis of oxidation reactions due to the convenience of solid-liquid separation and, therefore, enhanced reusability of the catalyst.

FT-IR spectra of the LCCO and S-LCCO samples were recorded over the range of 400 to 4000 cm$^{-1}$. Figure 3a illustrates the FT-IR spectrum of the LCCO NPs. The broad band observed at 3438 cm$^{-1}$ refers to the O–H stretching mode [27] of the water molecules that have occluded into the precursor gel. Also, the 1621 cm$^{-1}$ IR band corresponds to the bending mode of the H$_2$O molecules. Several bands at 423, 603 and 894 cm$^{-1}$ and one shoulder at 719 cm$^{-1}$ are observed in Figure 3a, which are attributed to the $\nu_{\text{M-O}}$ stretching and $\delta_{\text{O-M-O}}$ bending vibrational modes of the perovskite oxides, respectively [28-30]. Figure 3b depicts the FT-IR spectrum of S-LCCO with 3440 cm$^{-1}$ and 1635 cm$^{-1}$ IR bands that are related to the stretching and bending modes of H$_2$O molecules, respectively. The broad but very strong peak that has risen at 1091 cm$^{-1}$ and the shoulder at 1180 cm$^{-1}$ are ascribed to the TO and LO Si-O-Si asymmetric stretching vibrational modes. The Si-O- stretching mode of the silanol groups can be distinguished by the IR band of 950 cm$^{-1}$. The 800 cm$^{-1}$ and 467 cm$^{-1}$ bands are associated with the Si-O-Si symmetric

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stretching and O-Si-O bending vibrations, respectively. Moreover, the 603 cm\(^{-1}\) (strong), and 696 and 890 cm\(^{-1}\) (shoulder) peaks corresponding to LCCO perovskite coated on SiO\(_2\) are clearly observed in this spectrum.

Figure 2. SEM images of LCCO.

Figure 3. FT-IR spectra of LCCO (a) and S-LCCO (b).

Application of $La_{0.5}Ca_{0.5}CrO_3$ nanoparticles to catalytic synthesis of triazolo[1,2-a]indazole-trione derivatives

This study is an effort to continue our previous works on heterogeneous catalysis of organic reactions by acidic solid catalysts [31-35]. In this respect, triazolo[1,2-a]indazole-triones (4a-h) are synthesized through one-pot condensation of dimedone (1), phenyl urazole (2) and aromatic aldehydes (3a-h) in the presence of LCCO and S-LCCO NPs, as new catalysts. To optimize reaction time, temperature and catalyst amount, the three-component reaction of dimedone, phenyl urazole and benzaldehyde was selected, as a model MCR, and studied under different conditions (Table 1).

Table 1. Optimization of the reactions based on the synthesis of triazolo[1,2-a]indazole-trione under different conditions*.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst/amount (g)</th>
<th>Condition/temperature (°C)</th>
<th>Time (min)</th>
<th>Yield (%)b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>LCCO/0.01</td>
<td>H_2O/reflux</td>
<td>120</td>
<td>Trace</td>
</tr>
<tr>
<td>2</td>
<td>LCCO/0.01</td>
<td>EtOH/reflux</td>
<td>120</td>
<td>54</td>
</tr>
<tr>
<td>3</td>
<td>LCCO/0.01</td>
<td>EtOAc/reflux</td>
<td>120</td>
<td>39</td>
</tr>
<tr>
<td>4</td>
<td>LCCO/0.01</td>
<td>CHCl_3/reflux</td>
<td>120</td>
<td>47</td>
</tr>
<tr>
<td>5</td>
<td>LCCO/0.01</td>
<td>CHCN/reflux</td>
<td>120</td>
<td>52</td>
</tr>
<tr>
<td>6</td>
<td>0.0</td>
<td>Solvent-free/80</td>
<td>120</td>
<td>Trace</td>
</tr>
<tr>
<td>7</td>
<td>LCCO/0.005</td>
<td>Solvent-free/t.r.</td>
<td>120</td>
<td>Trace</td>
</tr>
<tr>
<td>8</td>
<td>LCCO/0.005</td>
<td>Solvent-free/80</td>
<td>120</td>
<td>41</td>
</tr>
<tr>
<td>9</td>
<td>LCCO/0.01</td>
<td>Solvent-free/80</td>
<td>30</td>
<td>58</td>
</tr>
<tr>
<td>10</td>
<td>LCCO/0.02</td>
<td>Solvent-free/80</td>
<td>30</td>
<td>60</td>
</tr>
<tr>
<td>11</td>
<td>S-LCCO 10% w/w/0.01</td>
<td>Solvent-free/80</td>
<td>20</td>
<td>57</td>
</tr>
<tr>
<td>12</td>
<td>S-LCCO 20% w/w/0.01</td>
<td>Solvent-free/80</td>
<td>20</td>
<td>75</td>
</tr>
<tr>
<td>13</td>
<td>S-LCCO 30% w/w/0.01</td>
<td>Solvent-free/80</td>
<td>20</td>
<td>76</td>
</tr>
<tr>
<td>14</td>
<td>S-LCCO 20% w/w/0.01</td>
<td>Solvent-free/MW (400 W)</td>
<td>2</td>
<td>46</td>
</tr>
<tr>
<td>15</td>
<td>S-LCCO 20% w/w/0.01</td>
<td>Solvent-free/MW (400 W)</td>
<td>4</td>
<td>91</td>
</tr>
<tr>
<td>16</td>
<td>S-LCCO 20% w/w/0.01</td>
<td>Solvent-free/MW (400 W)</td>
<td>5</td>
<td>90</td>
</tr>
<tr>
<td>17</td>
<td>S-LCCO 20% w/w/0.02</td>
<td>Solvent-free/MW (400 W)</td>
<td>4</td>
<td>92</td>
</tr>
</tbody>
</table>

*Reaction conditions: dimedone 1 (1 mmol), phenyl urazole 2 (1 mmol) and benzaldehyde 3a (1 mmol). *Isolated yield.

Since solvent may play an important role in this process, different solvents were evaluated. According to the results, solvent has a negative impact on efficiencies of the catalysts. So that, product yields were lower in acetonitrile, ethanol, chloroform, ethyl acetate and water (Table 1, entries 1-5) while the highest yield and the shortest reaction time was observed for the solvent-free process at 80 °C.

The optimum reaction condition was determined as microwave-assisted solvent-free catalysis using 0.01 g of S-LCCO 20% w/w, after exhaustive screening of various reaction conditions. At the optimum condition, 91% yield was acquired for synthesis of triazolo[1,2-a]indazole-trione (4a) from condensation of dimedone (1), phenyl urazole (2) and benzaldehyde (3a) (Table 1, entry 15).

To compare the performance of the S-LCCO perovskite oxide in the synthesis of 6,6-dimethyl-2,9-diphenyl-6,7-dihydro-[1,2,4]triazolo[1,2-a]indazole-1,3,8(2H,5H,9H)-trione with activities of other catalysts reported in literature, some of the results are summarized in Table 2. The results show that the S-LCCO NPs are more efficient than the reported catalysts, based on the obtained reaction times and product yields (entry 9).

Microwave-promoted solvent free one-pot synthesis of triazolo[1,2-a] indazole-triones

Table 2. Comparison of S-LCCO with reported catalysts in the reaction of dimedone, phenyl urazole, and benzaldehyde.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst/amount (g)</th>
<th>Condition/temperature (°C)</th>
<th>Time (min)</th>
<th>Yield (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>P₂O₅/SiO₂</td>
<td>Solvent-free/80</td>
<td>240</td>
<td>57</td>
<td>15</td>
</tr>
<tr>
<td>2</td>
<td>NaHSO₄·SiO₂</td>
<td>Solvent-free/80</td>
<td>360</td>
<td>46</td>
<td>15</td>
</tr>
<tr>
<td>3</td>
<td>InCl₃</td>
<td>Solvent-free/80</td>
<td>180</td>
<td>50</td>
<td>15</td>
</tr>
<tr>
<td>4</td>
<td>(NH₄)₂MoO₄·H₂O</td>
<td>Solvent-free/80</td>
<td>180</td>
<td>26</td>
<td>15</td>
</tr>
<tr>
<td>5</td>
<td>SiO₂·OSO₄·H</td>
<td>Solvent-free/80</td>
<td>240</td>
<td>81</td>
<td>15</td>
</tr>
<tr>
<td>6</td>
<td>H₃SiW₁₂O₄₀</td>
<td>Solvent-free/80</td>
<td>70</td>
<td>88</td>
<td>16</td>
</tr>
<tr>
<td>7</td>
<td>Nanosilica sulfuric acid</td>
<td>Solvent-free/80</td>
<td>30</td>
<td>80</td>
<td>17</td>
</tr>
<tr>
<td>8</td>
<td>p-TSA</td>
<td>Solvent-free/80</td>
<td>30</td>
<td>78</td>
<td>18</td>
</tr>
<tr>
<td>9</td>
<td>S-LCCO 20% w/w/0.01</td>
<td>Solvent-free/MW (400 W)</td>
<td>4</td>
<td>91</td>
<td></td>
</tr>
</tbody>
</table>

This work

*Reaction conditions: dimedone 1 (1 mmol), phenyl urazole 2 (1 mmol) and benzaldehyde 3a (1 mmol). *Isolated yield.

Table 3. Synthesis of triazolo[1,2-a]indazole-1,3,8-triones using silica-supported La₀.₃Ca₀.₇CrO₄ NPs.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ar</th>
<th>Product</th>
<th>Yield (%)</th>
<th>M.P. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C₆H₅</td>
<td>4a</td>
<td>91</td>
<td>187-189/188-190 [18]</td>
</tr>
<tr>
<td>2</td>
<td>4-NO₂C₆H₄</td>
<td>4b</td>
<td>92</td>
<td>176-178/175-177 [18]</td>
</tr>
<tr>
<td>3</td>
<td>3-NO₂C₆H₄</td>
<td>4c</td>
<td>90</td>
<td>124-126/126-128 [18]</td>
</tr>
<tr>
<td>4</td>
<td>4-ClC₆H₄</td>
<td>4d</td>
<td>91</td>
<td>167-169/166-168 [18]</td>
</tr>
<tr>
<td>5</td>
<td>2-ClC₆H₄</td>
<td>4e</td>
<td>84</td>
<td>174-176/173-175 [18]</td>
</tr>
<tr>
<td>6</td>
<td>4-MeC₆H₄</td>
<td>4f</td>
<td>93</td>
<td>161-163/160-162 [18]</td>
</tr>
<tr>
<td>7</td>
<td>4-MeOCC₆H₄</td>
<td>4g</td>
<td>94</td>
<td>177-180/176-180 [19]</td>
</tr>
<tr>
<td>8</td>
<td>4-BrC₆H₄</td>
<td>4h</td>
<td>92</td>
<td>184-186/185-186 [17]</td>
</tr>
</tbody>
</table>

*Reaction conditions: dimedone 1 (1 mmol), phenyl urazole 2 (1 mmol), benzaldehyde 3a (1 mmol) and S-LCCO 20% w/w (0.01 g), under solvent-free conditions using MW irradiation after 4 min. *Isolated yield.

Figure 4. Reusability of the catalyst.

Also, a series of triazolo[1,2-a]indazoletriones derivatives, i.e. 4a-h, were optimally synthesized (Table 3). It can be observed that all MCRs that were carried out for the reactions of aldehydes substituted with electron-donating or electron-withdrawing groups have ended up with successful product synthesis and good to excellent yields. The 4a-h compounds were found to be stable and their structures were validated by ¹H-NMR and FT-IR spectroscopies.

Ease of catalyst recovery is one of the most significant features of the outlined approach. To reuse the catalyst, it was removed from the mixture of the completed reaction by filtration, washed with chloroform and ethanol and dried at 80 °C. No considerable loss of catalytic activity was detected by reusing the catalyst for several subsequent catalytic reactions, even after four runs (Figure 4).

At the end, a reaction mechanism was proposed for formation of triazolo[1,2-a]indazole-1,3,8-trione heterocyclic compounds in Scheme 2. At first, in the presence of the perovskite oxide particles, one dimedone molecule attaches to the case aldehyde by Knoevenagel condensation. Then, Michael addition reaction takes place and an urazole molecule adds to this intermediate. Finally, intra-molecular cyclization and water elimination advance the second intermediate towards the product of interest.

CONCLUSION

In this paper, novel perovskite oxide nanoparticles are prepared to synthesize substituted triazolo[1,2-a]indazole-trione compounds through three-component cyclo-condensation reaction of urazole, dimedone and aldehyde under microwave irradiation solvent-free conditions. Findings demonstrated that La<sub>0.5</sub>Ca<sub>0.5</sub>CrO<sub>3</sub> and silica-supported La<sub>0.5</sub>Ca<sub>0.5</sub>CrO<sub>3</sub> are efficient, re-
usable and green acidic solid catalysts that can provide excellent yields, convenience of operation, short reaction times and easy catalyst recovery.

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