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Ali Alinasab Amiri, Shahrzad Javanshir, *Zahra Dolatkhah and Mohammad G. Dekamin

SO$_3$H-Functionalized Mesoporous Silica Materials (SO$_3$H-FMSM), as an efficient, mild, recoverable and environmentally friendly heterogeneous mesoporous nanocatalyst has been used to synthesize 2H-indazolo[2,1-b]phthalazine-1,6,11-trione derivatives in a one-pot three-component condensation reaction of 2,3-dihydropthalazine-1,4-dione, dimedone, and benzaldehyde derivatives under thermal solvent-free (SF) conditions in excellent yields and short reaction times.

**Introduction**

During recent years, multicomponent Reactions (MCRs) have become progressively popular tools to assure sufficient molecular diversity and complexity, and simultaneously ensure an atom-economy and straightforward reaction design for substantial minimization of waste, labor, time, and cost, thus leading to useful heterocyclic scaffold for the construction of various chemical libraries of ‘drug like’ molecules.  

The preparation and synthesis of new heterocyclic compound has always been a topic of great interest owing to their wide applicability. Aza heterocycles are an important class of compound that have many usage in pharmaceutical, agrochemical, and functional materials. Among a large diversity of aza heterocyclic compounds, heterocycles containing phthalazine portion are of interest because of their several pharmacological and biological activities such as cytotoxic, anti-inflammatory, anticancer, anticonvulsant, antifungal, antimicrobial, vasorelaxant, cardiotonic, and also unique electrical and optical properties. Despite many methods being available for the synthesis of phthalazine derivatives, their broad utility has accentuated the need to develop new synthetic routes for N-heterocycles containing the phthalazine moiety.

In recent years, several three-component reactions (3-CRs) have been reported for the preparation of 2H-indazolo[2,1-b]phthalazine-1,6,11-triones in the presence of an acid or base such as TMSCl, H$_2$SO$_4$, phosphomolybdic acid (PMA)-SiO$_2$, I$_2$, S-Camphorsulfonic acid (S-CSA), poly(N-bromo-N-ethylbenzene-1,3-disulfonamid) (PBBS), ceric ammonium nitrate (CAN), magnetic nanoparticle immobilized N-propylsulfamic acid (MNP-PSA), ZrOCl$_2$, H$_2$O$_2$, Fe$_3$O$_4$, sulfuric acid nanoparticles and SBA-15/2,2,2-trifluoroethanol adduct (SBA-15/TFE) via condensation of an aldehyde, 2,3-dihydropthalazine-1,4-dione, and dimedone. Nevertheless, many of these methods have disadvantages such as low yields of products, long reaction times, harsh reactions conditions, exhausting work-ups leading to the generation of large amount of toxic metal- or halogen-containing waste, the requirement for an inert atmosphere and the use of stoichiometric or relativity expensive reagents. As a result, offering novel synthetic methods or improving them for the preparation of 2H-indazolo[2,1-b]phthalazine-1,6,11-trione derivatives could be of considerable importance.

The point of this presented protocol is to highlight the synergistic effects of the combined use of MCRs and reactions under solvent-free conditions with an efficient heterogeneous nanocatalyst for the development of a new eco-compatible for the synthesis of heterocycles. Regarding the fact that solvent-free reactions and preventing the formation of by-products and also raising the rate of reactions could provide a large number of factors needed for green chemistry, we have decided to synthesize 2H-Indazolo[2,1-b]phthalazinetrione derivatives using phthalhydrazide, dimedone and benzaldehyde derivatives with the exploitation of SO$_3$H-FMSM, as a recyclable heterogeneous mesoporous nanocatalyst in a one-pot multicomponent reaction in order to obtain more eligible efficiency and short reaction time (Scheme 1).

![Scheme 1](image)

**Scheme 1** Synthesis of 2H-indazolo[2,1-b]phthalazine-1,6,11-triones by SO$_3$H-FMSM.
Results and Discussion

The synthesis and Characterisation of SO$_3$H-FMSM

MCM-41 is a family member of M41S mesoporous molecular silicates that has a regular hexagonal arrangement and is introduced as a solid substrate. Much attention to this substrate is due to its high surface area ($1000-1300$ m$^2$ g$^{-1}$), specific pore size (15-100 Å), and mechanical, thermal and hydrothermal (over 800 °C) stability. For as much as MCM-41 is a neutral catalyst, its surface can be modified by SO$_3$H functional group. The MCM-41 nanotube was modified by the SO$_3$H acidic group to create acidic sites on its surface. MCM-41 and SO$_3$H-FMSM were synthesized according to previously reported methods.$^{24,25}$ The SO$_3$H-FMSM was characterized by SEM (Scanning Electron Microscopy), EDX (Energy Dispersive X-ray) and FT-IR spectroscopy. In FT-IR spectroscopy (Fig. 1), the bands at 1250 cm$^{-1}$ and 1321 cm$^{-1}$ are due to the symmetric and asymmetric stretching vibrations of S=O of the sulfonic acid group. The broad band in the region of 3200-3400 cm$^{-1}$ is assigned to the O-H stretching vibration of hydroxyl groups. Moreover, a strong band at 1174 cm$^{-1}$ is assigned to the Si–O–Si asymmetric stretching vibrations and a band at 850 cm$^{-1}$ related to its symmetric stretching vibrations (Fig. 1).

Fig. 1 FT-IR spectrum of SO$_3$H-FMSM nanocatalyst.

In order to investigate the morphology of the catalyst structure, the SEM micrograph was used. As can be seen, nanoscale particles and pores of the catalyst is clearly evident (Fig. 2).

Fig. 2 The SEM micrographs of SO$_3$H-FMSM nanocatalyst.

EDX analysis is used to study the chemical composition and elemental analysis of solid samples. As shown in Fig. 3, nanocatalyst contains the sulfur, silicon and oxygen. It shows that our catalyst is formed and functionalized. The low angle XRD and BET analysis of SO$_3$H-FMSM were also provided in supplementary data. The specific surface area, pore volume and average pore diameter were obtained by the N$_2$ adsorption isotherms calculated by the BET and BJH method and found 1078 m$^2$ g$^{-1}$, 0.56 cm$^3$ g$^{-1}$ and 2.5 nm respectively before functionalization and 71.7 m$^2$ g$^{-1}$, 0.05 cm$^3$ g$^{-1}$ and 2.8 nm respectively after functionalization with SO$_3$H-groups. Pore volume are found lower than that of MCM-41 due to the functionalization. The results of N$_2$ adsorption isotherms also showed that SO$_3$H-FMSM exhibits typical type IV isotherm indicating that the mesoporous texture is largely maintained.

Optimization of reaction conditions

2,3-dihydrophthalazine-1,4-dione 1 as an initial material in this reaction, was synthesized according to the reported method.$^{26}$ It was characterized with FT-IR and $^1$H and $^{13}$CNMR spectroscopy.

For gaining the optimum conditions, a model reaction was selected that involved a mixture of 2,3-dihydrophthalazine-1,4-dione (1.0 mmol, 162.1 mg), dimedone (1.0 mmol, 140.1 mg) and 4-chlorobenzaldehyde (1.0 mmol, 140.6 mg) under various conditions such as ball milling without heating; sonication in ethanol as solvent in room temperature and thermal solvent-free conditions in the presence of SO$_3$H-FMSM (20.0 mg) (Scheme 2).

Scheme 2 Model reaction for the synthesis of 4b
The progress of the reaction monitored by thin-layer chromatography (TLC) indicated that the reaction was not completed and just the intermediate was formed after 30 minutes of ball milling and in the case of sonication the yield was low. However, under thermal condition, the reaction was completed after 30 min, and thus the thermal solvent-free conditions was selected as the best method (Table 1, Entry 3).

**Table 1** Study for selecting the best route for synthesis of 2H-indazolo[2,1-b]phthalazine-1,6,11-trione derivatives.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Path of the reaction</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ball milling</td>
<td>trace</td>
</tr>
<tr>
<td>2</td>
<td>30°, Ethanol, r.t.</td>
<td>30</td>
</tr>
<tr>
<td>3</td>
<td>Δ, Solvent-free</td>
<td>90</td>
</tr>
</tbody>
</table>

*Ultrasonic irradiation; bThermal condition

In order to obtain the optimum reaction temperature, the model reaction was studied at different temperatures using constant amount of catalyst. According to the results 110°C was selected as optimum temperature (Table 2).

To put in evidence the role and effect of the catalyst in the rate of reaction, the model reaction was carried out in the absence of any catalyst (Entry 1, Table 3). The results revealed that the yield of the reaction was very low and lapse of time hasn’t had significant impact on efficiency of reaction.

To evaluate the appropriate catalyst loading, the model reaction was carried out using different amount of catalyst. It was found that 20 mg was the most effective amount (Table 3, entry 5) and larger amounts of catalyst do not increase the reaction yield. The reaction was also done in the presence of 20 mg of MCM-41-Propyl-SO$_3$H as a comparative acidic catalyst. The result suggests that SO$_3$H-FMSM is more suitable for this reaction (Table 3, entry 8).

**Table 2** The temperature effect on efficiency and duration of synthesis of 2H-indazolo[2,1-b]phthalazine-1,6,11-trione derivatives.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Temperature (°C)</th>
<th>Time (min)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>70</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>70</td>
<td>55</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>85</td>
<td>30</td>
<td>88</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>25</td>
<td>93</td>
</tr>
<tr>
<td>5</td>
<td>110</td>
<td>18</td>
<td>95</td>
</tr>
<tr>
<td>6</td>
<td>120</td>
<td>18</td>
<td>94</td>
</tr>
</tbody>
</table>

*Isolated yields

To generalize the optimum conditions for the synthesis of 2H-indazolo[2,1-b]phthalazine-1,6,11-trione derivatives a one-pot reaction of 2,3-dihydrophtalazine-1,4-dione, dimedone and aromatic aldehydes (1:1:1) was carried out in the presence of 20 mg of SO$_3$H-FMSM at 110°C under solvent-free conditions for the appropriate time (Table 4). The results were excellent in terms of yields and product purity.

**Table 3** The catalyst effect study and amount of it on efficiency and duration of synthesis of 2H-indazolo[2,1-b]phthalazine-1,6,11-trione derivatives under thermal solvent-free conditions.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Amount catalyst (mg)</th>
<th>Time (min)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>-</td>
<td>180</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>SO$_3$H-FMSM</td>
<td>5</td>
<td>80</td>
<td>70</td>
</tr>
<tr>
<td>3</td>
<td>SO$_3$H-FMSM</td>
<td>10</td>
<td>60</td>
<td>80</td>
</tr>
<tr>
<td>4</td>
<td>SO$_3$H-FMSM</td>
<td>15</td>
<td>40</td>
<td>88</td>
</tr>
<tr>
<td>5</td>
<td>SO$_3$H-FMSM</td>
<td>20</td>
<td>18</td>
<td>95</td>
</tr>
<tr>
<td>6</td>
<td>SO$_3$H-FMSM</td>
<td>25</td>
<td>20</td>
<td>95</td>
</tr>
<tr>
<td>7</td>
<td>SO$_3$H-FMSM</td>
<td>30</td>
<td>20</td>
<td>93</td>
</tr>
<tr>
<td>8</td>
<td>MCM-41-Pr-SO$_3$H</td>
<td>20</td>
<td>60</td>
<td>88</td>
</tr>
</tbody>
</table>

*Isolated yields

**Proposed Mechanism**

A plausible mechanism for the reaction is shown in Scheme 2. The formation of 2H-indazolo[2,1-b]phthalazine-1,6,11-triones involves initial formation of intermediate (A) via a Knoevenagel condensation of dimedone and aromatic aldehyde catalyzed by SO$_3$H-FMSM. Subsequent Michael-type addition of the phthalhydrazide followed by cyclization affords the corresponding product (Scheme 2).

**Scheme 3** A plausible mechanism for the one-pot and three-component synthesis of 2H-indazolo[2,1-b]phthalazine-1,6,11-trione derivatives catalyzed by SO$_3$H-FMSM.

**Reusability of the catalyst**

The reusability of the catalyst was also investigate, for this purpose it was filtered by nano-paper filter and washed by hot ethyl acetate and ethanol, then dried at 50°C. The recycled catalyst was used for 4 runs without considerable loss of activity (Figure 4). The FT-IR spectrum of SO$_3$H-FMSM after recycling are given in supporting information. In order to show the merit of this work in comparison with other work recently reported, we compared the results of the synthesis of 2H-indazolo [2,1-b]phthalazine-1,6,11-trione derivatives in the presence of various catalysts, regarding the reaction time, temperature, reaction conditions and product yields (Table 5).
Recyclability of $\text{SO}_3\text{H}$-FMSM as a nanocatalyst in this reaction.

**Table 4** Three-components reaction for preparation of 2H-indazolo[2,1-b]phthalazine-1,6,11-trione derivatives at 110°C catalyzed by $\text{SO}_3\text{H}$-FMSM.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Aromatic aldehyde</th>
<th>Product</th>
<th>Time (min)</th>
<th>Yield* (%)</th>
<th>m.p. Found (°C)</th>
<th>m.p. Reported (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4a</td>
<td>20</td>
<td>93</td>
<td>202-204</td>
<td>204-206</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>4b</td>
<td>18</td>
<td>95</td>
<td>255-257</td>
<td>262-264</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>4c</td>
<td>22</td>
<td>95</td>
<td>265-267</td>
<td>264-266</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>4d</td>
<td>20</td>
<td>93</td>
<td>218-220</td>
<td>219-221</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>4e</td>
<td>15</td>
<td>95</td>
<td>224-227</td>
<td>223-225</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>4f</td>
<td>20</td>
<td>93</td>
<td>232-234</td>
<td>227-229</td>
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<tr>
<td>7</td>
<td>4g</td>
<td>20</td>
<td>93</td>
<td>264-266</td>
<td>270-272</td>
<td></td>
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<tr>
<td>8</td>
<td>4h</td>
<td>25</td>
<td>90</td>
<td>226-229</td>
<td>227-229</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>4i</td>
<td>22</td>
<td>92</td>
<td>214-216</td>
<td>218-220</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>4j</td>
<td>24</td>
<td>90</td>
<td>180-182</td>
<td>186-188</td>
<td></td>
</tr>
</tbody>
</table>


Table 5 Comparison of the performance of SO$_3$H-FMSM with other catalysts in synthesis of 2$H$-indazolo[2,1-b]phthalazine-1,6,11-trione derivatives.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Condition</th>
<th>Temp. (°C)</th>
<th>Time (min)</th>
<th>Yield (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TMSCl</td>
<td>(CH$_3$CN/DMF)</td>
<td>80</td>
<td>60</td>
<td>86.2</td>
<td>12</td>
</tr>
<tr>
<td>2</td>
<td>H$_2$SO$_4$</td>
<td>Ethanol/H$_2$O</td>
<td>80</td>
<td>30</td>
<td>88</td>
<td>13</td>
</tr>
<tr>
<td>3</td>
<td>H$_2$SO$_4$</td>
<td>[bmim]BF$_4$</td>
<td>80</td>
<td>35</td>
<td>90</td>
<td>13</td>
</tr>
<tr>
<td>4</td>
<td>PMA-SiO$_2$</td>
<td>Solvent free</td>
<td>80</td>
<td>40</td>
<td>91</td>
<td>14</td>
</tr>
<tr>
<td>5</td>
<td>I$_2$</td>
<td>Ethanol</td>
<td>80</td>
<td>25</td>
<td>90</td>
<td>15</td>
</tr>
<tr>
<td>6</td>
<td>(S)-CSA</td>
<td>Sonication</td>
<td>R.T.</td>
<td>40</td>
<td>82</td>
<td>16</td>
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<tr>
<td>7</td>
<td>PBBS</td>
<td>Solvent free</td>
<td>100</td>
<td>45</td>
<td>75</td>
<td>17</td>
</tr>
<tr>
<td>8</td>
<td>CAN</td>
<td>PEG-400$^a$</td>
<td>50</td>
<td>120</td>
<td>94</td>
<td>18</td>
</tr>
<tr>
<td>9</td>
<td>MNPs-PSA</td>
<td>Solvent free</td>
<td>100</td>
<td>25</td>
<td>93</td>
<td>19</td>
</tr>
<tr>
<td>10</td>
<td>ZrOCl$_2$.8H$_2$O</td>
<td>Solvent free</td>
<td>80</td>
<td>60</td>
<td>89</td>
<td>20</td>
</tr>
<tr>
<td>11</td>
<td>Fe$_3$O$_4$@Silica sulfuric acid</td>
<td>Solvent free</td>
<td>100</td>
<td>35</td>
<td>92</td>
<td>21</td>
</tr>
<tr>
<td>12</td>
<td>SBA-15/TFE</td>
<td>TFE$^b$</td>
<td>65</td>
<td>150</td>
<td>94</td>
<td>22</td>
</tr>
<tr>
<td>13</td>
<td>SO$_3$H-FMSM</td>
<td>Solvent free</td>
<td>110</td>
<td>18</td>
<td>95</td>
<td>This work</td>
</tr>
</tbody>
</table>

$^a$polyethylene glycol 400; $^b$ Trifluoroethanol

Conclusions

In summary, an efficient protocol for the one-step and one-pot synthesis of 2$H$-indazolo[2,1-b]phthalazine-1,6,11-trione derivatives has been described via a three-component condensation reaction of phthalhydrazide, dimeredone and aromatic aldehydes in the presence of SO$_3$H-FMSM as a recoverable heterogeneous nanocatalyst under thermal solvent-free conditions. The products of the reaction were obtained in excellent yields and in short reaction times. SO$_3$H-FMSM could be successfully recovered and recycled for four runs without any important diminution of activity.

Experimental

Instruments and characterization

All chemicals were purchased from Merck, Fluka, and Sigma-Aldrich companies and were used without further purification. Thin layer chromatography (TLC) was performed by using aluminum plates coated with silica gel 60 F-254 plates (Merck) using ethyl acetate and n-hexane (1:2) as eluents. The spots were detected either under UV light or by placing in an iodine chamber. Melting points were determined in open capillaries using an Electrothermal 9100 instrument. 1$H$ NMR (300 MHz) and 13$C$ NMR (75 MHz) spectra were recorded on a Bruker Avance DPX-300 instrument. The spectra were measured in DMSO-d$_6$ relative to TMS as internal standard. FT-IR spectra were obtained with a shimadzu 8400S with spectroscopic grade KBr. CHN were recorded on a CHN-OS analyzer (Perkin Elmer 2400, series II). Scanning electron microscopy (SEM) was recorded on a VEG//TESCAN WITH GOLD COATING, and energy dispersive X-ray spectroscopy (EDX) was recorded on a VEG//TESCAN-XMU.

General procedure for preparation of MCM-41

2.7 g diethylamine was added to 42 mL deionized water in a 500 mL beaker at room temperature while the mixture was stirred. After 10 min, 1.47 g cetyltributylammonium bromide (CTAB) was inchmeal added to the mixture about 30 min, until a clear solution was obtained. In the following, 2.1 g Tetraethyl orthosilicate as a silica precursor was added drop-wise to the solution and the pH was adjusted to 8.5 by adding 1.0 M HCl solution slowly. After being stirred for 2 h, the white solid precipitate was filtered and washed with deionized water. The
obtained MCM-41 was dried at 45 °C for 12 h and then was
calced at 550 °C for 5 h to remove all the surfactant.  

General procedure for preparation of SO\textsubscript{3}H-FMSM

MCM-41 (1.0 g) and CH\textsubscript{2}Cl\textsubscript{2} (5.0 mL) were transferred to 100
mL round bottom flask equipped with a gas outlet tube and a
dropping funnel containing a solution of CISO\textsubscript{3}H (1.5 mL) in
CH\textsubscript{2}Cl\textsubscript{2} (10 mL). The chlorosulfonic acid solution was added
drop-wise to the flask containing over a period of 30 min at
room temperature while the mixture was being stirred.
Expulsion of evolved HCl gas from the reaction mixture was
conducted via the gas outlet tube into a NaOH solution. After
the completion of the reaction, the solvent was evaporated
under reduced pressure and the SO\textsubscript{3}H-FMSM was collected as a
greyish white solid. The amount of SO\textsubscript{3}H groups is
then calculated by titration: 0.5 g of the catalyst sample was added to 50 mL of
NaCl solution (200 g/L) and stirred at room temperature. The
concentration of acid sites of catalyst was determined by
titration: 0.5 g of the catalyst sample was added to 50 mL of
NaCl solution (200 g/L) and stirred at room temperature. The

General procedure for preparation of MCM-41-Propyl-SO\textsubscript{3}H

The MCM-41 (5 g) was added to a solution of
3-mercaptopropyl(trimethoxy)silane (10 mmol) in dry toluene and
refluxed for 24 h. The product was filtered off and washed with hot
toluene and dried at 110 °C for 5 h.

A procedure for the synthesis of 2,3-dihydrophthalalnine-1,4-dione

Hydrazine hydrate (NH\textsubscript{2}·H\textsubscript{2}O, 2.0 mmol) was added drop-
wise to a stirred, cold (ice-bath) solution of Phthalimide (2.98
g, 2.0 mmol) in ethanol (30 mL) over a period of 30 min. The
reaction mixture was stirred for 3 hours at 70 °C and then
allowed to cool to 0°C in an ice-water bath, causing the
formation of a white precipitate. The precipitate was then
collected by filtration, washed with ethanol, and dried under
vacuum at room temperature to give the required

General procedure for the synthesis of 2H-indazolo[2,1-b]
phthalalnine-1,6,11(13H)-triones catalyzed by the SO\textsubscript{3}H-FMSM
nanocatalyst

A pressurized seal tube equipped with a tiny magnetic stir bar
was charged with a mixture of 2,3-dihydrophthalalnine-1,4-
dione 1 (1.0 mmol, 162.1 mg), dimedone 2 (1.0 mmol, 140.1
mg) and aldehyde 3a-p (1.0 mmol) under solvent-free

Spectral data for the selected compounds:

Table 4, entry 1, 4a:

Yellow powder, m.p. 202-204 °C; IR (KBr): \( \nu \) 2920, 2862, 1680,
1577 cm\(^{-1}\); \(^1\)H NMR (300.13 MHz, DMSO): \( \delta \) 1.08 (s, 3H), 1.11
(s, 3H), 1.24 (s, 2H, CH\textsubscript{2}C), 3.04-3.16 (AB system, 2H,
CH\textsubscript{2}H\textsubscript{2}CO), 3.57-3.69 (dd, 4H, ArCl), 7.03-7.15
(m, 9H, aromatics) ppm; \(^13\)C NMR (75 MHz, CDCl\textsubscript{3}):
\( \delta \) 28.5, 28.6, 34.8, 38.2, 50.8, 64.1, 117.9, 127.4, 127.9,
128.3, 128.6, 128.8, 129.0, 133.5, 134.2, 134.6, 134.9, 150.4, 151.2
ppm; Anal. Calcd for C\textsubscript{23}H\textsubscript{18}ClN\textsubscript{2}O\textsubscript{3}: C, 67.92;
H, 4.7; N, 6.85%. Found: C, 67.8; H, 4.62; N, 6.81%.

Table 4, entry 2, 4b:

Yellow powder, m.p. 255-257 °C; IR (KBr): \( \nu \) 2920, 2862, 1680,
1577 cm\(^{-1}\); \(^1\)H NMR (300.13 MHz, DMSO): \( \delta \) 1.08 (s, 3H), 1.11
(s, 3H), 2.24 (s, 2H, CH\textsubscript{2}C), 3.04-3.16 (AB system, 2H,
CH\textsubscript{2}H\textsubscript{2}CO), 3.57-3.69 (dd, 4H, ArCl), 7.03-7.15
(m, 9H, aromatics) ppm; \(^13\)C NMR (75 MHz, CDCl\textsubscript{3}):
\( \delta \) 28.5, 28.6, 34.8, 38.2, 50.8, 64.1, 117.9, 127.4, 127.9,
128.3, 128.6, 128.8, 129.0, 133.5, 134.2, 134.6, 134.9, 150.4, 151.2
ppm; Anal. Calcd for C\textsubscript{23}H\textsubscript{18}ClN\textsubscript{2}O\textsubscript{3}: C, 67.92;
H, 4.7; N, 6.85%. Found: C, 67.8; H, 4.62; N, 6.81%.

Table 4, entry 5, 4e:

Yellow powder, m.p. 224-227 °C; IR (KBr): \( \nu \) 2920, 2955, 1689,
1654, 1632 cm\(^{-1}\); \(^1\)H NMR (300.13 MHz, DMSO): \( \delta \) 1.06 (s, 3H),
1.15 (s, 3H), 2.25 (s, 2H, CH\textsubscript{2}C), 3.02-3.16 (AB system, 2H,
CH\textsubscript{2}H\textsubscript{2}CO), 3.65 (s, 1H), 7.19-8.00 (dd, 4H, ArCl),
7.84-8.00 (m, 6H, aromatics) ppm; \(^13\)C NMR (75 MHz, CDCl\textsubscript{3}):
\( \delta \) 28.4, 28.8, 34.7, 37.9, 50.7, 64.3, 117.5, 123.8, 128.3,
128.8, 133.9, 134.7, 143.3, 148.0, 152.0, 154.6, 192.1
ppm; Anal. Calcd for C\textsubscript{23}H\textsubscript{18}ClN\textsubscript{2}O\textsubscript{3}: C, 66.15;
H, 4.59; N, 10.02%. Found: C, 66.21; H, 4.62; N, 9.99%.

Table 4, entry 8, 4h:

Yellow powder, m.p. 226-229 °C; IR (KBr): \( \nu \) 2958, 1667, 1628
1, \(^1\)H NMR (300.13 MHz, DMSO): \( \delta \) 1.08 (s, 3H), 1.10
(s, 3H), 1.22 (s, 3H), 2.26 (s, 2H, CH\textsubscript{2}Ph), 2.26 (s, 2H, CH\textsubscript{2}C),
3.03-3.20 (AB system, 2H, CH\textsubscript{2}H\textsubscript{2}CO), 6.28 (s, 1H),
7.22-7.38 (dd, 4H, ArMe), 7.92-8.25 (m, 4H, Ph); \(^13\)C NMR (75 MHz,
CDCl\textsubscript{3}):
\( \delta \) 21.3, 28.6, 29.0, 34.6, 38.0, 60.0, 64.8, 118.5, 127.3, 127.7,
127.9, 128.8, 129.0, 133.5, 133.6, 134.5, 138.4, 150.9, 154.1, 155.9, 192.3
ppm; Anal. Calcd for C$_{12}$H$_8$N$_2$O$_2$: C, 74.59; H, 5.77; N, 7.21%. Found: C, 74.61; H, 5.69; N, 7.31.

3,4-Dihydro-3,3-dimethyl-13-(3-hydroxyphenyl)-2H-indazolo[2,1-b]phthalazine-1,6,11(13H)-trione (Table 4, entry 13, 4m):

Yellow powder, m.p. 252-255 °C; IR (KBr): v 3351, 2954, 2890, 1667 cm$^{-1}$; $^1$H NMR (300.13 MHz, DMSO): δ 1.09 (s, 3H), 1.11 (s, 3H), 2.22 (s, 2H, CH$_2$C), 3.04-3.20 (AB system, 2H, CH$_2$CO), 5.91 (b, 1H, OH), 6.27 (s, 1H), 6.66-7.19 (m, 4H, ArOH), 7.70-7.77 (m, 2H, Ph), 8.20-8.31 (m, 2H, Ph); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 28.5, 28.6, 34.5, 37.9, 51.0, 64.6, 114.4, 115.8, 118.4, 118.6, 127.7, 127.9 (2), 128.9, 130.0, 133.5, 134.4, 138.0, 150.9, 154.1, 155.9, 192.2 ppm; Anal. Calcd for C$_{23}$H$_{19}$N$_4$O$_3$: C, 71.12; H, 5.22; N, 7.25%. Found: C, 71.13; H, 5.19; N, 7.28%.

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Supplementary data

Supplementary data associated with this article can be found, in the online version at http://dx.doi

Notes and references

Graphical Abstract

**SO$_3$H-Functionalized Mesoporous Silica Materials as Solid Acid Catalyst for Facile and Solvent-free Synthesis of 2H-Indazolo[2,1-b]phthalazine-1,6,11-trione Derivatives**

Ali Alinasab Amiri, Shahrzad Javanshir, Zahra Dolatkhah and Mohammad G. Dekamin

SO$_3$H-Functionalized Mesoporous Silica Materials (SO$_3$H-FMSM), as an efficient, recoverable and environmentally friendly heterogeneous mesoporous nanocatalyst has been used to synthesize 2H-indazolo[2,1-b]phthalazine-1,6,11-trione derivatives in a one-pot three-component condensation reaction of 2,3-dihydrophtalazine-1,4-dione, dimedone, and benzaldehyde derivatives under thermal solvent-free (SF) conditions.