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Silica sulfuric acid: an efficient reusable heterogeneous solid support for the synthesis of 3*H*,3′*H*-spiro[benzofuran-2,1′isobenzofuran]-3,3′-diones under solvent-free condition

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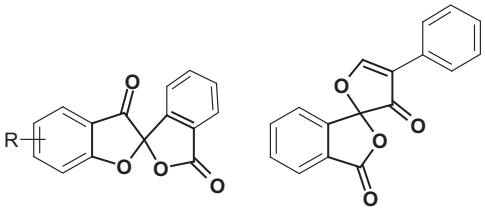
ABSTRACT

A highly efficient protocol for the library synthesis of biologically important 3*H*,3′*H*-spiro[benzofuran-2,1′isobenzofuran]-3,3′-diones has been developed by employing silica sulfuric acid (SSA) as solid acid support under solvent-free condition. The dual characteristics of SSA, as an activating agent as well as oxidizing agent, have been well exposed in these syntheses. The intrinsic advantages of the methodology are the use of solvent-free reaction condition without using any toxic reagents or metal catalyst, operational simplicity, recyclability of the solid support, good availability of the starting materials, and excellent yields which make the method attractive, economic, and 'benign by design'.

Spirocyclic systems containing one carbon atom common to two rings are structurally interesting.[1] Spiro substructure has immense importance not only in the field of medicinal chemistry, but also in material science for the preparation of organic LED.[2] Spiroheterocycles are particularly interesting because the conformational restriction associated to the structural rigidity affects considerably their biological activity.[3] Especially, 3*H*,3′*H*-spiro[benzofuran-2,1′isobenzofuran]-3,3′-diones (**A**, Fig. 1) are such intriguing examples of spiroheterocycles with substantial potentiality. The core structure of **A** is known to be present in synthetic compounds such as Fluorescamine (Fig. 1), a well known fluorescent probe for amino acid peptides, proteins, and primary amines.[4] However, a literature survey reveals that, very few earlier reports describe the preparation of 3*H*,3′*H*-spiro[benzofuran-2,1′isobenzofuran]-3,3′-diones (**A**). In addition, these reactions suffer from some serious limitations such as requiring the use of highly hazardous SeO_2,[5] or through multistep route with low yield.[6] Recently, Jung and co-workers have reported microwave-assisted and molecular-iodine mediated oxidative procedure to build the skeleton and showed its biological application as the inhibitors of influenza virus infection.[7] Although this method is superior to the previous reports in terms of derivatization of products and yields, still it has several drawbacks such as: solvent-mediated high energy consuming process (150 °C) with long reaction time (2–6 h), burdensome product isolation procedure, use of high loading of molecular-iodine for several derivatives, and non-reusability of catalyst etc. Therefore, the development of a versatile, simple, and environmentally friendly synthetic methodology is needed.[8]

In recent years, the use of solid acidic support/catalysts has offered important advantages in organic synthesis, for example operational simplicity, environmental compatibility, non-toxicity, reusability, low cost, and ease of isolation.[9] In this regard, silica sulfuric acid (SSA), a product that is easily synthesized from silica gel and chlorosulfonic acid,[10] has shown immense potentiality as an efficient and easily retrievable solid support/catalyst in various important organic syntheses under solvent-free conditions.[11] SSA



A **Flourescamine**

Figure 1. Representative compound with core spiro structure.

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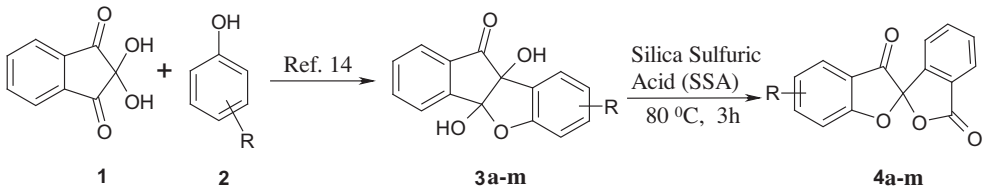
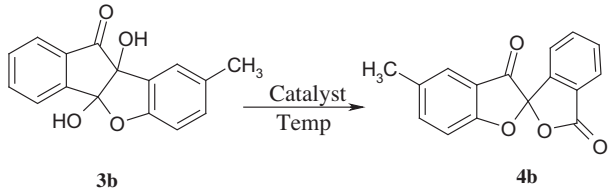


Scheme 1. Synthesis of 3*H*,3′*H*-spiro[benzofuran-2,1′isobenzofuran]-3,3′-diones **4** from ninhydrin.

is easier to handle than sulfuric acid and can readily be separated from the products by simple filtration. Therefore, in continuation of our research work on the synthesis of ninhydrin based bio-active heterocycles[12] and development of green synthetic methodologies,[13] we wish to report an environmentally benign protocol for the synthesis of 3*H*,3′*H*-spiro[benzofuran-2,1′isobenzofuran]-3,3′-diones using silica sulfuric acid as solid acid support under solvent-free condition.

Initially a series of monoarylated adducts of ninhydrin 4b,9b-dihydroxy-4b,9b-dihydro-5-oxa-indeno[2,1-*a*]inden-10-ones (**3**, Scheme 1) were synthesized by refluxing the appropriate phenols and ninhydrin in acetic acid for 7–8 h.[14] The products preferentially remain in the cyclic hemiketal form **3**. Previously, we have reported that the base catalyzed rearrangement of **3** can produce potentially bioactive benzofuroisocoumarins.[12d] Therefore we became interested in examining whether compounds **3** could undergo acid catalyzed rearrangement. Surprisingly, when compounds **3** were soaked on silica sulfuric acid surface and heated, 3*H*,3′*H*-spiro[benzofuran-2,1′isobenzofuran]-3,3′-diones (**4**) were obtained as rearranged products (Scheme 1).[15]



Scheme 2. Reaction optimization for the synthesis of 5-methyl-3*H*,3′*H*-spiro[benzofuran-2,1′isobenzofuran]-3,3′-dione (**4b**).

In our initial studies, we attempted to optimize the reaction condition taking 4b,9b-dihydroxy-8-methyl-4b,9b-dihydro-5-oxa-indeno[2,1-*a*]inden-10-one (**3b**) as model substrate in the presence of different solvents, solid supports, and catalysts at different temperatures (Scheme 2, Table 1). At first, we refluxed **3b** in the presence of various polar protic solvents for example water, ethanol without using any catalyst for a prolonged reaction time (24 h),

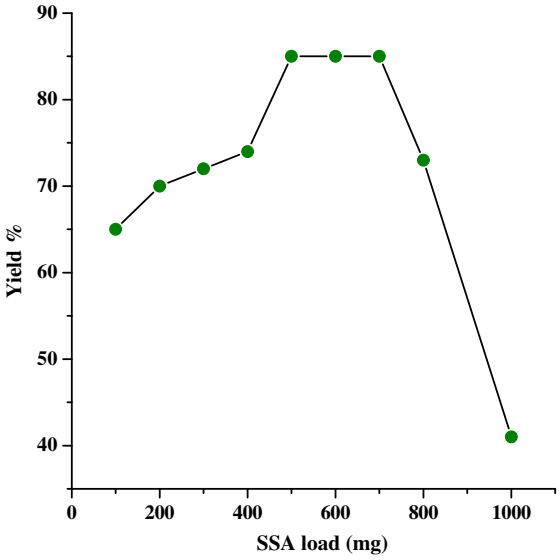


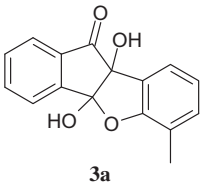
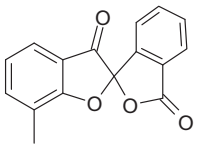
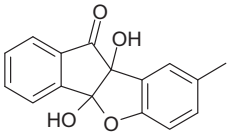
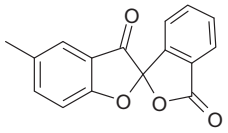
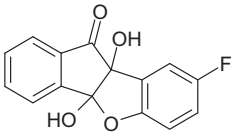
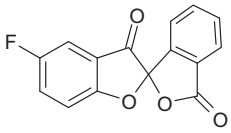
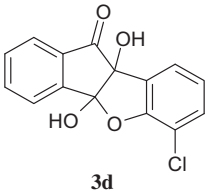
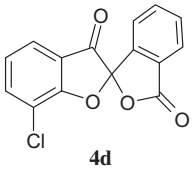
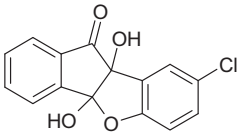
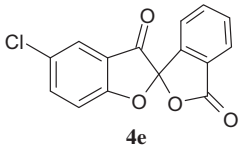
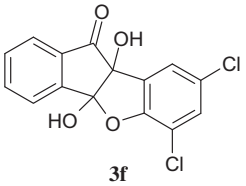
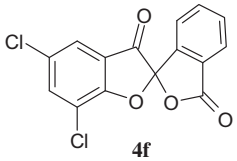
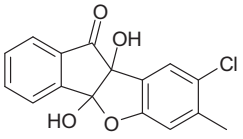
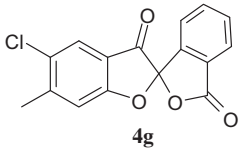
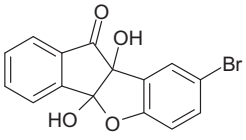
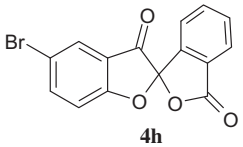
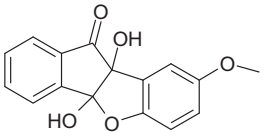
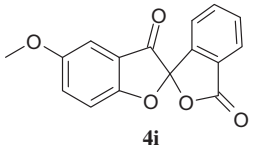
Figure 2. SSA load optimization study.

Table 1
Optimization of reaction conditions for the synthesis of **4b** from **3b**. The bold values indicates the maximum yield of the product at that particular reaction condition

Entry	Solvent	Catalyst/solid support	Catalyst load	Temperature (°C)	Time (h)	Yield[a] (%)
1	H_2O	—	—	100	24	—
2	EtOH	—	—	90	24	—
3	EtOH	Triethanolamine	20 mol %	90	24	—
4	AcOH	H_2SO_4	0.5 ml	120	4	45
5	AcOH	Triflic acid	0.5 ml	120	24	—
6	H_2O	PEG-OSO_3H	20 mol %	100	24	—
7	—	Basic alumina	500 mg	100	24	—
8	—	Melamine sulfonic acid (MSA)	500 mg	100	24	—
9	—	PEG-OSO_3H	500 mg	100	24	—
10	—	Silica sulfuric acid (SSA)	500 mg	100	0.5	24
11	—	SSA	500 mg	90	3	77
12	—	**SSA**	**500 mg**	**80**	**3**	**85**
13	—	SSA	500 mg	70	5	65
14	—	SSA	100 mg	80	3	65
15	—	SSA	200 mg	80	3	70
16	—	SSA	300 mg	80	3	72
17	—	SSA	400 mg	80	3	74
18	—	SSA	600 mg	80	3	85
19	—	SSA	700 mg	80	3	85
20	—	SSA	800 mg	80	3	73
21	—	SSA	1000 mg	80	3	41

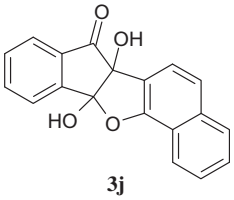
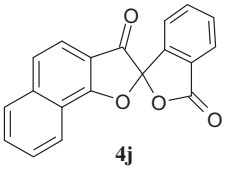
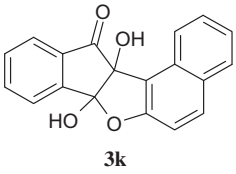
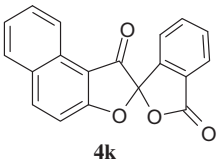
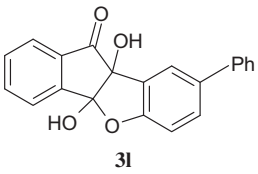
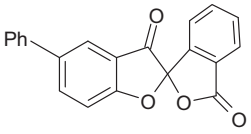
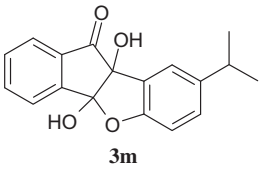
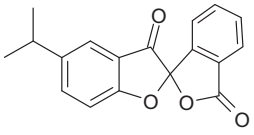
[a] Isolated yield.

Table 2
Formation of 3*H*,3′*H*-spiro[benzofuran-2,1′isobenzofuran]-3,3′-diones **4** from **3**

Entry	Adduct	Product	Yield[a] (%)	Literature mp[7]/observed mp (°C)
1	 **3a**	 **4a**	76	155–157/154–156
2	 **3b**	 **4b**	85	166–168/170–172
3	 **3c**	 **4c**	80	162–164
4	 **3d**	 **4d**	78	200–202/196–198
5	 **3e**	 **4e**	83	162–165/160–162
6	 **3f**	 **4f**	79	198–200
7	 **3g**	 **4g**	81	296–298
8	 **3h**	 **4h**	85	180–182
9	 **3i**	 **4i**	77	178–180

(*continued on next page*)

Table 2 (*continued*)

Entry	Adduct	Product	Yield[a] (%)	Literature mp[7]/observed mp (°C)
10	 **3j**	 **4j**	71	187–189/184–186
11	 **3k**	 **4k**	75	223–225/220–222
12	 **3l**	 **4l**	78	202–204/198–200
13	 **3m**	 **4m**	87	228–230

[a] Isolated yield.

but no change in the substrate was observed (Table 1, entries 1 and 2). Same result was observed on employing triethanolamine as catalyst in ethanol under the same reaction condition (Table 1, entry 3). Interestingly, when the acidity of the reaction medium was enhanced by using AcOH as solvent and H_2SO_4 as catalyst, TLC study revealed the formation of a new product after 4 h at reflux (Table 1, entry 4). The product was isolated, purified and the structure of the product **4b** was assigned and confirmed by IR, ^{1}H NMR, ^{13}C NMR spectroscopy, elemental analysis, and also by matching the melting point of the product with the reported value.[7] This observation incited us to carry out the conversion in the presence of other acid catalysts. However polymeric acid-surfactant combined catalyst, PEG-OSO_3H, and triflic acid failed to serve the purpose under similar reaction condition (Table 1, entries 5 and 6). Literature survey reveals that many reactions proceed adeptly under solvent-free condition. Indeed in many cases, solid state organic reactions occur efficiently and more selectively than those counterparts performed in solution.[16–18] In fact, one important facet of green chemistry is the eradication of solvents in chemical processes. So for the synthesis of our target compound **4b**, several solid supports under solvent-free condition were also selected (e.g. basic alumina, MSA, PEG-OSO_3H) (Table 1, entries 7–9). The reaction did not proceed at all by using these solid supports but formation of the product was observed on SSA. However, the reaction mixture began to char after 0.5 h at high temperature (100 °C) and considerable amounts of impurities were formed (Table 1, entry 10). Gratifyingly, upon lowering the temperature from 100 to 80 °C, the yield of the product **4b** (~85%) improved notably (Table 1, entries 11 and 12). Since SSA had emerged as the most efficient solid support, we studied the influence of its stoichiometry on the yield of the reaction. This work revealed that the yield of the product increased smoothly with an increase of SSA load up to 500 mg and then remained unaltered up to 700 mg. A further increase of SSA load resulted in a sharp drop in the product yield (Table 1, entries 12–21, Fig. 2). At high loading of SSA, due to the strong acidity, the reaction mixture charred considerably at 80 °C causing low yield of the product. Therefore, best yield of **4b** (85 %) was achieved when 1 mmol **3b** was heated with 500 mg of SSA at 80 °C for 3 h under solvent-free condition. With the optimized condition in hand, the scope and generality of this protocol were next assessed by employing

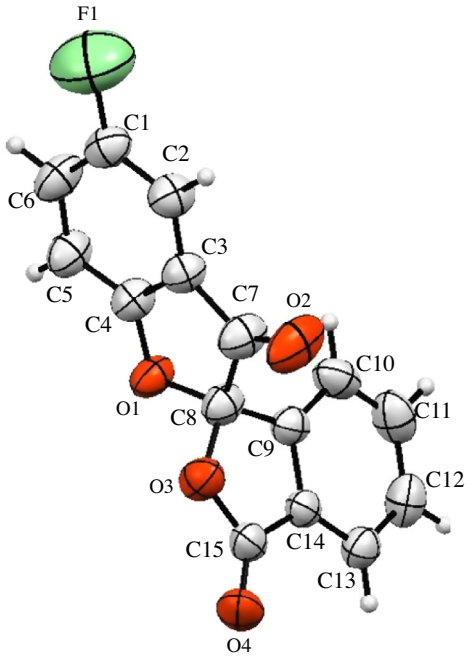


Figure 3. ORTEP diagram of compound **4c** with atom numbering scheme. Thermal ellipsoids are shown at the 50% probability. (CCDC No. 962441).

various dihydroxy indenofuranone derivatives **3a–m** (Table 2). Though the yields (for electron donating substituents) are comparable to those of the previously reported method,[7] the present methodology is more advantageous in many aspects: (a) eradication of solvent by employing SSA as solid acid support, (b) Reduction of reaction temperature (from 150 to 80 °C), (c) Generality of the process as it is compatible with both electron withdrawing and electron donating substituents, (d) Easier isolation/purification

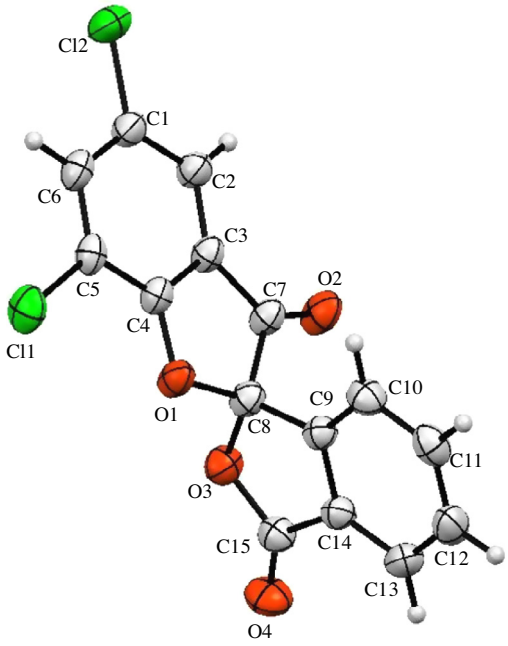


Figure 4. ORTEP diagram of compound **4f** with atom numbering scheme. Thermal ellipsoids are shown at the 50% probability. (CCDC No. 970679).

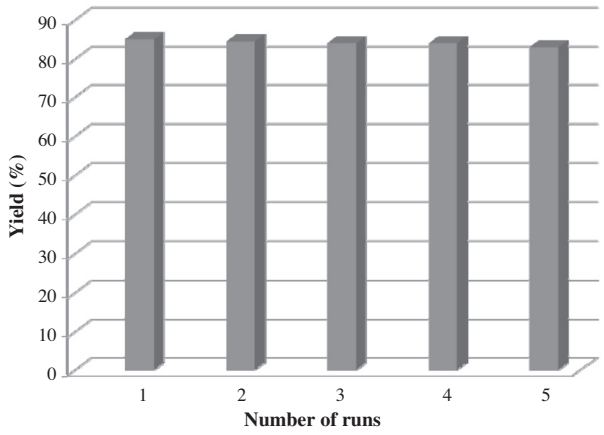
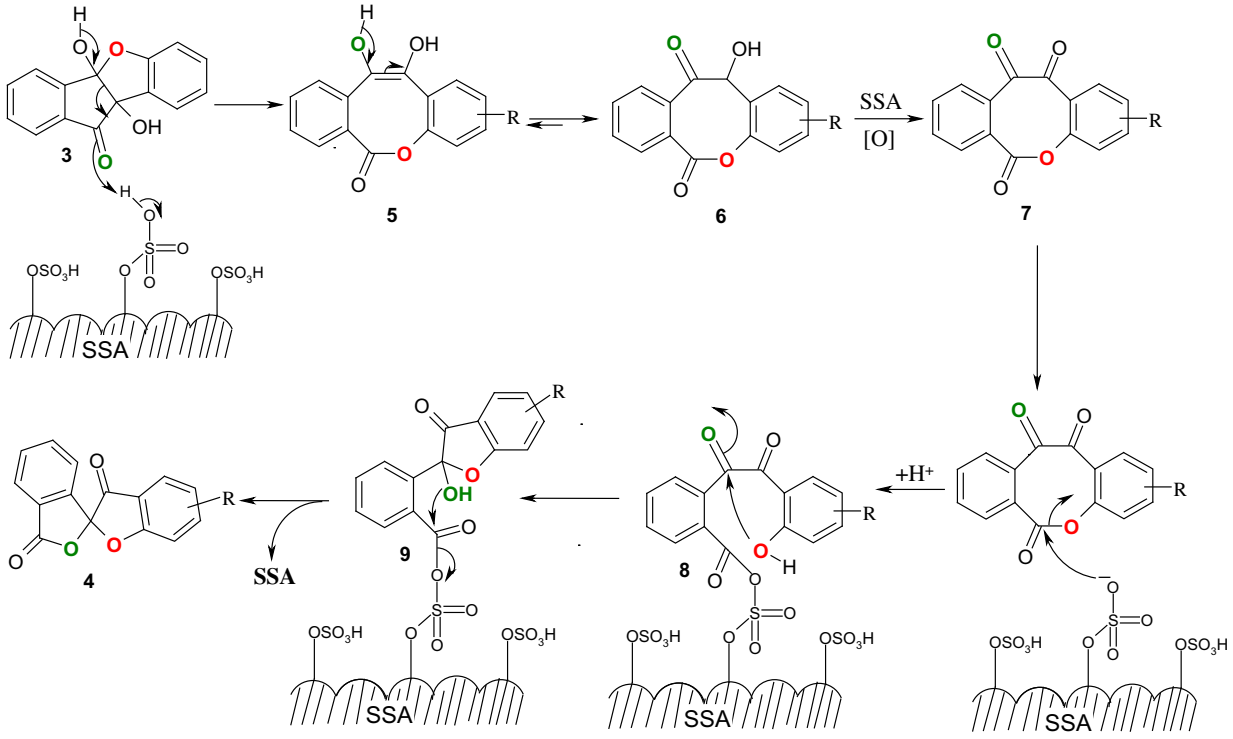


Figure 5. Reusability of SSA for the synthesis of 5-methyl-3*H*,3′*H*-spiro[benzofuran-2,1′-isobenzofuran]-3,3′-dione (**4b**).

of the products with shorter reaction time (3 h). In all cases, the final products were confirmed by IR, ^{1}H NMR, ^{13}C NMR spectroscopy, and also by comparing the melting points of **4** with the reported values.[7] Further the elucidation of X-ray crystal structure of compounds **4c** (Fig. 3) and **4f** (Fig. 4) confirms the product formation.[19]

A probable mechanistic pathway for the formation of **4** has been proposed emphasizing the dual role of SSA as a proton transferring agent, as well as oxidizing agent in Scheme 3.[7] At first, protonation of the carbonyl group from the sulfonic group of SSA surface of the bicyclo[3.3.0]octano system **3** initiates the breaking of the central C–C bond to afford an eight-membered lactone intermediate **5** which tautomerizes to keto form **6**. Subsequently, α-hydroxyketo intermediate **6** undergoes SSA catalyzed oxidation[20] to form 1,2-dicarbonyl species **7**. The nucleophilic attack of $-OSO_3^-$ of SSA at the lactonic carbonyl of **7** leads to the cleavage of lactone



Scheme 3. Plausible mechanism for the formation of **4** on the surface of SSA.

linkage producing the ring open substrate **8**. The intramolecular attack of the phenolic hydroxyl group of **8** to the carbonyl group enables the formation of 2-phenylhydroxyfuranone **9**. Finally, the hydroxyl group attacks the carbonyl carbon of the *ortho* ester leading to the formation of spiro lactones **4**.

Furthermore, we have performed the recovering and reusability test of SSA for the formation of **4b**. At first, **3b** was dissolved in minimum quantity of chloroform, soaked on the surface of SSA, and heated for 3 h at 80 °C. The desired product **4b** was isolated easily with ethylacetate by ultrasonication of the reaction mixture. The recovered solid support SSA was reused five times, and the yield of the product **4b** varied from 85% to 83%, indicating unaltered reactivity and efficiency of SSA even after repeated application (Fig. 5).

In conclusion, we have developed a facile and convenient methodology for the preparation of 3*H*,3′*H*-spiro[benzofuran-2,1′isobenzofuran]-3,3′-diones using silica sulfuric acid (SSA) as solid acid support under solvent-free condition. The intrinsic advantages of the present process are easy and clean preparation of the solid acid support SSA without tedious work-up procedure and the energy efficient expedient protocol. The present methodology addresses the current drive toward green chemistry and will be attractive to chemists due to good yields, high atom-economy, and reusability of the solid support.

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Supplementary data

Supplementary data (preparational method and characterizations of SSA, and detailed analytical data (IR, ^{1}H, ^{13}C data of compounds **4**)) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2014.01.109.

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15. *General procedure for the synthesis of 4b,9b-dihydroxy-4b,9b-dihydro-5-oxa-indeno[2,1-a]inden-10-ones* (***3a–m***): 4b,9b-Dihydroxy-4b,9b-dihydro-5-oxa-indeno[2,1-*a*]inden-10-ones (**3a–m**) were synthesized according to previously reported procedure.[14]
Typical procedure for the synthesis of 5-methyl-3H,3′H-spiro[benzofuran-2,1′-isobenzofuran]-3,3′-dione (**4b**): 4b,9b-Dihydroxy-8-methyl-4b,9b-dihydro-5-oxa-indeno[2,1-*a*]inden-10-one (**3b**) (0.268 g, 1 mmol) was dissolved in minimum quantity of chloroform in a round bottom flask and then soaked on silica sulfuric acid (500 mg) by stirring for 10 min. The thoroughly mixed reaction mixture was dried under vacuum and then heated around 80 °C on an oil bath for 3 h under continuous stirring, until the complete disappearance of dihydroxy-indenobenzofuran was observed (as monitored by TLC). The solid mass was then cooled to room temperature and ethylacetate (10 ml) was added to isolate the product by ultra-sonication. The separated organic phase was concentrated to get the crude product which was purified over silica gel column chromatography (ethyl acetate/hexanes) (~1:10) to afford the spiro-compounds (**4a–m**).
Representative spectral data of compounds: 5,7-Dichloro-3H,3′H-spiro[benzofuran-2,1′-isobenzofuran]-3,3′-dione (**4f**): ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.02–8.00 (m, 1H), 7.78–7.73 (m, 2H), 7.66 (d, J = 2.1 Hz, 1H), 7.41–7.39 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.7, 166.1, 165.2, 141.3, 138.7, 135.3, 132.3, 129.7, 126.9, 126.4, 123.4, 122.6, 120.9, 120.2, 104.9; IR (KBr): 1780, 1711 cm^{-1}; Anal. Calcd for $C_{15}H_6Cl_2O4$: C, 56.11; H, 1.88. Found C, 55.98; H, 1.78.
5-Bromo-3H,3′H-spiro[benzofuran-2,1′-isobenzofuran]-3,3′-dione (***4h***): ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.99–7.96 (m, 1H), 7.89–7.82 (m, 2H), 7.74–7.68 (m, 2H), 7.41–7.36 (m, 1H), 7.15 (d, J = 8.71 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.1, 169.9, 168.7, 142.2, 135.2, 132.1, 131.9, 128.2, 127.0, 126.2, 122.5, 120.3, 116.4, 115.4, 104.1; IR (KBr): 1792, 1734 cm^{-1}; Anal. Calcd for $C_{15}H_7Br_1O4$: C, 54.41; H, 2.13. Found C, 54.32; H, 2.04.
5-Isopropyl-3H,3′H-spiro[benzofuran-2,1′-isobenzofuran]-3,3′-dione (**4m**): ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.14–8.11 (m, 1H), 7.74–7.71 (m, 2H), 7.51–7.48 (m, 1H), 7.01 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 6.92 (d, J = 8.1 Hz, 1H), 6.08 (d, J = 1.5 Hz, 1H), 2.50–2.46 (m, 1H), 0.84 (d, J = 6.9 Hz, 3H), 0.75 (d, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.2, 167.2, 165.1, 148.8, 143.1, 135.1, 131.4, 128.5, 127.1, 126.0, 124.8, 124.1, 122.6, 117.1, 103.3, 33.2, 24.0, 23.1; IR (KBr): 1773 cm^{-1}; Anal. Calcd for $C_{18}H_{14}O_4$: C, 73.46; H, 4.79. Found C, 73.32; H, 4.71.
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19. Crystallographic data for the structure **4c** and **4f** in this Letter have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 962441 and CCDC 970679, respectively. Copies of the data can be obtained, free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (Fax: +44 01223 336033 or e-mail: deposit@ccdc.cam.ac.uk).
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