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# Solvent-Free Condensation Reactions To Synthesize Five-Membered Heterocycles Containing the Sulfamide Fragment

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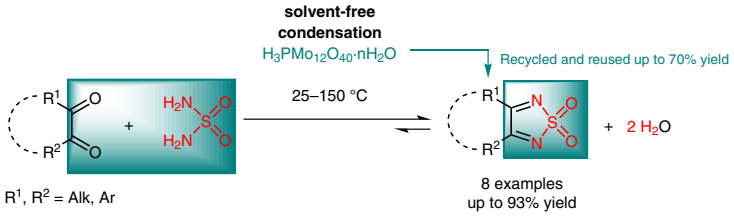


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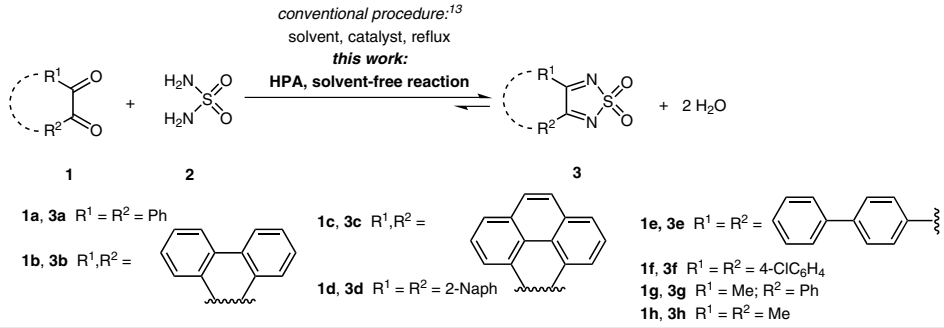
**Abstract** We report a study of the solvent-free condensation reaction of 1,2-dicarbonyl compounds with sulfamide catalyzed by a Keggin-type acid ($H_3PMo_{12}O_{40}·nH_2O$, MPA) to obtain 3,4-disubstituted 1,2,5-thiadiazole 1,1-dioxide derivatives. Some reactions were also performed in solution or using nano-sized silica-supported MPA catalyst in order to compare the results under different experimental conditions. Effects of the temperature used for the thermal pretreatment of the catalyst, the reaction temperature, the molar ratios sulfamide/1,2-dicarbonyl compound and MPA/1,2-dicarbonyl compound, and alternative experimental procedures on the yield of the reaction product were investigated. Under suitable experimental conditions eight compounds were obtained in good yields. The catalyst was recycled and reused, but with some loss of its catalytic activity. The presented synthetic method is a simple, clean, and environmentally friendly alternative for synthesizing different 1,2,5-thiadiazole 1,1-dioxide derivatives.

**Key words** heterocycles, solvent-free reaction, condensation, acid catalysis, heteropolyacids, 1,2-dicarbonyl compounds, sulfamide

Numerous and varied heterocyclic compounds that contain the sulfamide fragment (>$NSO_2N$<) exhibit a broad spectrum of physiological activities and they are also used as components of fungicide and insecticide mixtures, as detergents, and in photography.[1] In particular five-membered thiadiazole heterocyclic compounds have been used in organic synthesis,[2] in medicine,[3] in agrochemistry as potent pesticides,[4] and the high value of these building blocks for the generation of n-type conjugated organic materials has been emphasized.[5] Recently, our group reported for the first time on the capacity of two 3,4-disubstituted 1,2,5-thiadiazole 1,1-dioxide derivatives as corrosion inhibitor for copper and mild steel in acid medium,[6,7] and on the ability of some other derivatives as acceptor molecules that give stable radical anions.[8,9]

One of the most general procedures for the synthesis of heterocyclic compounds based on sulfamides involves their condensation with carbonyl compounds.[10–12] For the preparation of 3,4-disubstituted 1,2,5-thiadiazole 1,1-dioxide derivatives, the more general reaction is the condensation of the 1,2-dicarbonyl compounds **1** with sulfamide (**2**) (Scheme 1) in solution catalyzed by strong mineral acids.[13–15] To overcome the use of strong acids, an efficient and mild access to these 1,2,5-thiadiazole heterocycles using *N*,*N*′-bis(trimethylsilyl)sulfamide and **1** promoted by $BF_3·OEt_2$ was recently reported by Zezschwitz et al.[16] Also, Erturk and Bekdemir[17] performed a microwave-assisted synthesis for the condensation reaction of **1** with **2** in absolute EtOH.

It is well known that conventional strong mineral acids are corrosive and pose risks in handling, disposal, and regeneration due to their corrosive and toxic nature. A major source of waste in the fine chemicals industry is derived from the widespread use of liquid mineral acids and a variety of Lewis acids. They cannot easily be recycled and generally end up, via a hydrolytic workup, as waste streams containing large amounts of inorganic salts. Their replacement by recyclable solid acids would afford a significant reduction in waste. Waste prevention and environmental protection are imperative requirements in an overcrowded world of increasing demands. Synthetic chemistry continues to develop chemical procedures for obtaining products with less environmental impact. One of the more promising approaches is solvent-free organic synthesis.




**Scheme 1** Synthesis of **3** by condensation reaction of **1** with **2**, catalyzed by HPA under solvent-free conditions

Catalysis by heteropolyacids (HPAs) is a field of increasing importance worldwide.[18] Advances are being carried out both in basic investigation and in fine chemicals processes.[19,20] HPAs are good acid catalysts in homogeneous and heterogeneous media.[21] These solid catalysts have many advantages over liquid acid catalysts. The Brønsted acidity of HPAs compared to mineral acids leads to rates per proton that are usually significantly higher for HPAs. They are non-corrosive and are environmentally benign, presenting fewer disposal problems. Solid HPAs have attracted much attention in organic synthesis owing to easy workup procedures, easy filtration, and minimization of cost and waste generation due to reuse and the possibility of catalyst recycling.[22] Reactions catalyzed both in homogeneous or heterogeneous systems have been reviewed by many researchers.[23,24] There are various different structural types of HPAs, but for acid catalysts in common catalytic applications the commercial Keggin-type HPAs are often used, especially owing to their availability, and chemical and thermal stability.[25,26]

Supported HPA catalysts are important for applications because bulk HPAs have a low specific surface. The acidity and catalytic activity of supported HPAs depend on the type of the carrier, the HPA loading, pretreatment conditions, etc., the most frequently used carrier being silica. Silica is relatively inert towards HPAs, the thermal stability of HPA on silica seems to be comparable to or slightly lower than that of the parent HPA.[27]

To the best of our knowledge, in the literature there is no information on synthetic procedures for the preparation of **3** (Scheme 1) using HPAs as strong acid catalysts or the use of solvent-free reactions for the synthesis of such derivatives. The present work focuses on the study of the condensation reaction of **1a**–**h** (Scheme 1) with **2** catalyzed by a Keggin-type HPA, molybdophosphoric acid ($H_3PMo_{12}O_{40}{\cdot}nH_2O$, MPA), in the absence of solvent (solvent-free reaction, Table 1, entries 2–5, 7–10, 12, 13, and 15–23), to obtain derivatives **3a**–**h** (Scheme 1). Some reactions were also performed in absolute EtOH solution (entry 11) in order to compare the results under both different experimental conditions. Effects of the process variables, such as the temperature used for the thermal pretreatment of the catalyst, the reaction temperature, the molar ratios **2**/**1** and MPA/**1**, the time of contact between **1** and MPA previous to the addition of **2**, and the different experimental procedures, on the yield of the reaction product were investigated with the aim of obtaining **3** with the best yields. Suitable experimental conditions to prepare **3a**–**h** (Scheme 1) generally in good yields were found.

The scope, generality of the method, and molar yields for the products **3a**–**h** are illustrated with several examples in Table 1. The experimental conditions are also shown in Table 1 and in its footnotes. For comparison, data from the literature[13,28] (entries 1 and 14) are also included in this table. In this work, yields of **3** are similar to or improved compared to those reported in the literature. The reaction times shown in Table 1 should be considered with caution, because the initial mass of **1** employed in the assays and the reactors were not the same for all experiments. Three experimental procedures were assayed for solvent-free reactions (procedures A–C).

Results shown in Table 1 indicate that the appropriate MPA/**1** and **2**/**1** molar ratios and reaction temperature to obtain a better yield of **3** depend on the chemical structure of **1** and on the previous thermal treatment of the catalyst.

When the isolation of **3** from the solid reaction mixture (solvent-free reaction) was carried out by extraction with $CH_2Cl_2$, the practical molar yield was similar to that obtained when water was used. The use of water for the isolation is recommended because it is chemically sustainable. When water is used, MPA and **2** are soluble in the aqueous phase, while if $CH_2Cl_2$ is employed, they remain as an insoluble solid residue.

3,4-Diphenyl-1,2,5-thiadiazole 1,1-dioxide (**3a**) was synthesized following procedure A. The condensation reaction took place at an appreciable rate when MPA$^{70\,°C}$ was used as the catalyst (MPA$^{70\,°C}$/**1a**: 0.02; **2**/**1a**: 1.2) at 70 °C, but the reaction remained incomplete even after a prolonged reaction time (908 h). Increasing the excess of **2**, using ca. three times the stoichiometric amount, and the molar ratio MPA$^{70\,°C}$/**1a**: 0.43 (entry 2) the reaction went to completion and the yield of **3a** was slightly higher (53%)

**Table 1** Condensation of 1,2-Dicarbonyl Compounds **1** with Sulfamide **2** Catalyzed by MPA, under Various Conditions

| Entry | **1** (mmol) | Conditions[a] | Temp (°C) | Time (h) | Ratio[b] **2**/**1** | Ratio[c] MPA$^{T\,°C}$/**1** | **3** | Yield[d] (%) |
|---|---|---|---|---|---|---|---|---|
| 1 | **1a** (50) | EtOH | reflux | 2 | 1.0 | HCl(g) | **3a** | 51[13] |
| 2 | **1a** (0.25) | –[e] (A) | 70 | 29 | 3.1 | 0.43 (MPA$^{70\,°C}$) | **3a** | 53[f] |
| 3 | **1a** (0.50) | –[e](A/B) | 70 | 96 | 6.6 | 0.23 (MPA$^{150\,°C}$) | **3a** | 91[f] (75)[f] |
| 4 | **1a** (0.52) | –[e] (B/C) | 70 | 100 | 2.3 | 0.23 (MPA$^{150\,°C}$) | **3a** | 91[f] (83)[f] |
| 5 | **1a** (0.50) | –[e] (B/C) | 70 | 144 | 1.3 | 0.11 (MPA$^{300\,°C}$) | **3a** | 93[f] (82)[f] |
| 6 | **1b** (10) | EtOH | reflux | 1 | 1.0 | HCl(g) | **3b** | 82[28] |
| 7 | **1b** (0.27) | –[e] (A) | 120 | 31 | 9.0 | 0.064 (MPA$^{150\,°C}$) | **3b** | 64[f,g] |
| 8 | **1b** (0.48) | –[e] (A) | 150 | 7 | 9.0 | 0.062 (MPA$^{150\,°C}$) | **3b** | 85[f] |
| 9 | **1b** (0.48) | –[e] (A) | 150 | 7 | 9.0 | 0.062 (MPA$^{150\,°C}$) | **3b** | 85 |
| 10 | **1b** (0.52) | –[e] (A) | 150 | 3.5 | 9.0 | 0.04 (MPA$^{300\,°C}$) | **3b** | 86[f] |
| 11 | **1b** (0.33) | abs. EtOH[h] | reflux | 10 | 7.8 | 0.06 (MPA$^{150\,°C}$) | **3b** | 84 |
| 12 | **1c** (0.13) | –[e] (A) | 150 | 28 | 14.6 | 0.18 (MPA$^{150\,°C}$) | **3c** | 37[f,g] |
| 13 | **1c** (0.17) | –[e] (A) | 150 | 15 | 14.6 | 0.011 (MPA$_{supp}$$^{150\,°C}$)[i] | **3c** | 70[f] |
| 14 | **1d** (5.4) | EtOH | reflux | 15 | 5.4 | HCl$_{(g)}$ | **3d** | 70[29] |
| 15 | **1d** (0.066) | –[e] (A) | 150 | 94 | 10.4 | 0.080 (MPA$^{150\,°C}$) | **3d** | 71[f] |
| 16 | **1e** (0.28) | –[e] (A) | 150 | 97 | 9.0 | 0.074 (MPA$^{150\,°C}$) | **3e** | 58[f] |
| 17 | **1e** (0.14) | –[e] (C) | 150 | 8 | 9.0 | 0.069 (MPA$^{300\,°C}$) | **3e** | 60[f] |
| 18 | **1f** (0.39) | –[e] (A/B) | 150 | 95 | 9.0 | 0.025 (MPA$^{150\,°C}$) | **3f** | 49[f] (40)[f] |
| 19 | **1g** (1.68) | –[e] (A) | r.t. | 70 | 1.2 | 0.008 (MPA$^{150\,°C}$) | **3g** | 86[f] |
| 20 | **1h** (2.36) | –[e] (A) | r.t. | 52 | 1.2 | 0.008 (MPA$^{150\,°C}$) | **3h** | 83[f] |
| 21 | **1b** (0.48) | –[e] (A, a) | 150 | 68 | 13.0 | 0.062 (MPA$^{150\,°C}$) | **3b** | 15[f] |
| 22 | **1b** (0.49) | –[e] (A, b) | 150 | 7.5 | 9.2 | 0.060 (MPA$^{300\,°C}$)[j] | **3b** | 70[f] |
| 23 | **1a** (0.13) | –[e] (B/C, b) | 70 | 530 | 5.1 | 0.21 (MPA$^{150\,°C}$)[j] | **3a** | 42[f] |

[a] Procedure is in parentheses.
[b] Ratio **2**/**1** mmol/mmol.
[c] Ratio MPA$^{T\,°C}$/**1** mmol/mmol
[d] Yield of **3** calculated recovered **1** (yield based on initial amount of **1**).
[e] Solvent-free reaction.
[f] Reaction product extracted with $CH_2Cl_2$.
[g] Incomplete reaction.
[h] Homogeneous catalysis.
[i] Nano-sized silica-supported MPA$^{150\,°C}$.
[j] Recycled catalyst.

than that published in the literature (51%,[13] entry 1), but increasing the excess of **2** (**2**/**1a**: 6.6, result not shown) did not improve the yield. Similar yields resulted when **3a** was isolated by procedures (i, with water) or (ii, with $CH_2Cl_2$). The low yield of **3a** and the weight loss of the solid reaction mixture observed during the experiments were assumed as a result of evaporation of **1a** and **2**. Then we decided to use a sublimator as the reactor (procedure B). Using it both compounds were recovered from the cold finger.

Using MPA$^{150\,°C}$ as the catalyst and working as in procedure A/B, the yield of **3a** was 91% based on recovered **1a** or 75% based on **1a** initially added (entry 3). Following procedure B/C, to get the same yield for **3a** (entry 4) it was necessary to use a smaller amount of **2** than that used in procedure A/B.

An increase in the temperature of the thermal pre-treatment of MPA to 300 °C (MPA$^{300\,°C}$) slightly improved the yield for **3a**: 93%, still using low MPA$^{300\,°C}$/**1a** (0.11) and **2**/**1a** (1.3) molar ratios following procedure B/C (entry 5 vs. 4). An increase in the reaction temperature to reduce reaction time is not convenient (results not shown) because of the evaporation of **1a** and **2**.

It can be concluded that the best procedure to synthesize **3a** is procedure B/C, MPA$^{300\,°C}$, **2**/**1a** and MPA/**1a** molar ratios 1.3 and 0.11, respectively, at 70 °C (entry 5). This work resulted in an improved yield of **3a** compared to that reported in the literature (51%,[13] 87%,[16] or 66%[17]). The reaction times in solvent-free reactions catalyzed by MPA are longer than those measured following the guidelines in refs. 13 and 17, and we are currently investigating improvements to the technique that would shorten the reaction

times. We are using a nano-sized silica-supported MPA catalyst ($MPA_{supp}$) to obtaining a high specific surface. The results so far obtained are very encouraging, e.g. **3a** was prepared in 90% yield with $MPA_{supp}^{150\,°C}$/**1a**: 0.1, **2**/**1a**: 6.6, 48 h, at 70 °C (results not shown).

Phenanthro[9,10-*c*][1,2,5]thiadiazole 2,2-dioxide (**3b**); Table 1 (entry 6) shows the published results for the traditional synthesis of **3b**.[28] In solvent-free reactions using $MPA^{150\,°C}$ ($MPA^{150\,°C}$/**1b**: 0.06) and a high **2**/**1b** molar ratio: 9, at 120 °C, the reaction was not complete after 31 h (entry 7). However, the yield for **3b** was 85% at a reaction temperature of 150 °C and under other similar experimental conditions (entry 8). The same yields resulted from isolating **3b** by procedures (i) or (ii) (entries 8 and 9). Using pretreatment of the heteropolyacid at higher temperature ($MPA^{300\,°C}$) and with a lower $MPA^{300\,°C}$/**1b** molar ratio: 0.04 gave **3b** in 86% yield in a lower reaction time (3.5 h) (entry 10). Results from experiments performed to compare procedures A and C shown that for the synthesis of **3b** both procedures give similar yields. A similar yield for **3b** (84%, entry 11) was reached in a longer reaction time when the reaction was performed in EtOH solution (homogeneous catalysis) by heating to mild reflux, and using a high $MPA^{150\,°C}$/**1b**: 0.060 and a lower **2**/**1b**: 7.8 molar ratio. The results show that the catalyst in EtOH solution is not as effective as in solvent-free reactions.

It can be concluded that the best results are obtained for solvent-free reactions with the following experimental conditions: $MPA^{300\,°C}$, with molar ratios $MPA^{300\,°C}$/**1b**: 0.04 and **2**/**1b**: 9.0 and 150 °C as reaction temperature. The best yield for **3b** (86%, entry 10) and the reaction time obtained in this work are somewhat higher that published in the literature[28] (82%, entry 6). The reaction times for the synthesis of **3b** performed in solution of EtOH/MPA are higher than under solvent-free reactions, but product yields are similar. The higher concentration of reactants in the absence of solvents usually leads to more favorable kinetics than in solution. Protons in the surface layer of acidic MPA were much more active than protons from MPA in homogeneous solution. The very large excess of **2** necessary for the synthesis of **3b** be complete is rationalized by evaporation of **2** at 150 °C. As discussed, the large excess of **2** required for the reaction to go to completion can be recovered and reused if the reaction is performed in a sublimator (procedure B).

Pyreno[4,5-*c*][1,2,5]thiadiazole 10,10-dioxide (**3c**); qualitative assay shows that in a solvent-free reaction using $MPA^{70\,°C}$ with $MPA^{70\,°C}$/**1c**: 0.10 and **2**/**1c**: 10.3, for 23 h at 70 °C, the formation of **3c** and the disappearance of **1c** were not observed (TLC). $MPA^{150\,°C}$ was tested with $MPA^{150\,°C}$/**1c**: 0.18 at a higher reaction temperature (150 °C). Even using a high **2**/**1c** ratio (14.6) for 28 h, the reaction did not go to completion and **3c** was obtained in low yield (37%, entry 12). The formation of a byproduct was observed (TLC) when **1c** was still present in the reaction mixture, and for this reason the reaction was considered finished. With the aim of decreasing the reaction time, we worked with $MPA_{supp}^{150\,°C}$ with a low $MPA_{supp}^{150\,°C}$/**1c** molar ratio (0.011) at the same reaction temperature. By using $MPA_{supp}^{150\,°C}$, the yield obtained (70%, entry 13) was twice as high as that obtained using unsupported $MPA^{150\,°C}$, the reaction time decreased, and moreover, the formation of the byproduct was only observed at the end of the reaction time.

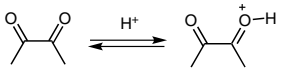
3,4-Di(2-naphthyl)-1,2,5-thiadiazole 1,1-dioxide (**3d**) and 3,4-di(biphenyl-4-yl)-1,2,5-thiadiazole 1,1-dioxide (**3e**); compound **3d** was previously synthesized in our laboratory[29] in 70% yield (entry 14) following the general procedure reported by Wright.[13] Now **3d** was prepared from **1d** in a solvent-free reaction catalyzed by $MPA^{150\,°C}$ (entry 15) following procedure A. The molar yield for **3d** (71%) was marginally higher and the reaction time was ca. six times longer than the published one.[29] Similar experimental conditions were employed for the synthesis of **3e**, but the compound was obtained in 58% yield (entry 16), lower than that for **3d**. The reaction was also performed using $MPA^{300\,°C}$ following procedure C and although the yield of **3e** (entry 17) was improved only slightly, the reaction time was shorter.

3,4-Bis(4-chlorophenyl)-1,2,5-thiadiazole 1,1-dioxide (**3f**); experiments were carried out without solvent, following procedure A/B using $MPA^{150\,°C}$. For the assays performed with **2**/**1f**: 9.9, and $MPA^{150\,°C}$/**1f**: 0.083–0.17 at 70–100 °C, the condensation reaction did not take place even over an extended period (193 h). With molar ratio **2**/**1f**: 9.0 and $MPA^{150\,°C}$/**1f**: 0.025, but increasing the reaction temperature to 150 °C, the reaction product **3f** was obtained in a 49% yield (based on recovered **1f**) (entry 18). Compounds **1f** and **2** were recovered from the cold finger of the sublimator.

For the synthesis of 3-methyl-4-phenyl-1,2,5-thiadiazole 1,1-dioxide (**3g**) and 3,4-dimethyl-1,2,5-thiadiazole 1,1-dioxide (**3h**), only procedure A was assayed using $MPA^{150\,°C}$. Reaction products **3g**,**h** were obtained in good yields [86% (**3g**) and 83% (**3h**)] (entries 19 and 20) using the ratios $MPA^{150\,°C}$/**1g**,**h**: 0.008 and **2**/**1g**,**h**: 1.2, at ca. 25 °C. Should be observed that as **1g**,**h** are liquids at room temperature and their boiling points are ca. 100 °C, it is not possible work at a higher reaction temperature. Yields for both compounds are higher than that reported in the literature (29%[13] and 74%[6] for **3g** and **3h**, respectively).

Compounds **3a**–**d**,**g**,**h** were synthesized in good yields, but yields were only moderate for **3e**,**f**. Reaction times were in general long, particularly for **3a**,**d**–**h**, while for **3b**,**c** the reaction times were shorter. Compounds **3a**,**d**–**f** are 3,4-disubstituted with the substituents containing separated π-electronic systems, and while **3b**,**c** are derivatives that are 3,4-disubstituted where the substituents have a connected π-electronic system.[30] Compounds **3g**,**h** are alkyl-aryl and alkyl-alkyl 3,4-disubstituted 1,2,5-thiadiazole 1,1-dioxide derivatives and are not included in the above classification.

The condensation reaction involves an addition of the nucleophile to the carbonyl groups and then elimination of two molecules of water to yield the five-membered heterocycle **3**. Acids catalyze the addition of weak nucleophiles, such as **2**, to carbonyl compounds by protonating the carbonyl oxygen atoms. This makes the carbonyl carbon more electrophilic and reactive thereby enhancing its susceptibility to attack by nucleophiles. The dicarbonyl compound precursors of **3b**,**c** can better stabilize the positive charge by resonance in the conjugated acid than in dicarbonyl compound precursors of **3a**,**d**–**h**, hence the protonation equilibrium (Scheme 2) for **1b**,**c** is more shifted to the right than for **1a**,**d**–**h**, and the concentration of the reactive conjugated acid is higher for **1b**,**c**. The elimination reactions may also be catalyzed by acids, but the effect of the aromatic substituent on the positive charge will be minor (only inductive effect).




**Scheme 2**

In a previous paper[29] we reported the efficient formation of a 9,10-dihydrophenanthrene polycyclic system fused to a 1,2,5-thiadiazole 1,1-dioxide via the formation of an aryl–aryl bond using strong Brønsted and Lewis acids, at different temperatures (–80 to 25 °C). The syntheses of **3b** and the novel asymmetric naphtho[2′,1′:3,4]anthra[1,2-*c*][1,2,5]thiadiazole 8,8-dioxide from **3a** and **3d**, respectively, employing concentrated sulfuric or chlorosulfonic acids, or $AlCl_3$ as catalysts, were compared.[29] We also looked[29] at the synthesis of **3b** in a domino-type reaction directly from **1a** and **2**, the same reagents employed in the traditional synthesis of **3a**.[13] In concentrated sulfuric acid we obtained **3b** in 55% yield. The reaction rate was low at room temperature, but increased at higher temperatures (<100 °C). As it is reported than HPAs present an acid force stronger than the strong mineral acids used conventionally,[31] we considered the possibility of preparing **3b** by cyclization of **3a** using $MPA_{supp}^{150\ °C}$ as catalyst (molar ratio $MPA_{supp}^{150\ °C}$/**3a**: 0.2 at 150 °C). After a reaction time of 171 h, the original mass of **3a** was recovered unchanged. The formation of **3b** as a by-product was also not observed (TLC) under the conditions shown in entries 2–5. Under the experimental conditions investigated in this work, the carbonyl compounds are protonated by the MPA, but the thiadiazole products are not, and thus the intramolecular cyclization is not possible (see proposed reaction mechanism[29]).

Reusability of MPA. The MPA was recovered after the synthesis and reused as a catalyst in the condensation reactions. Two procedures (a) and (b) were tested. The best results were obtained by procedure (b).

Following procedure (a). A fine powdered solid mixture of thermally pretreated residual solid (150 °C, 24 h) and **1a** in the same ratio as the original experiment (entry 3) was heated at the reaction temperature (70 °C) for 262 h, but the reaction to give **3a** did not occur. No reaction occurred after further addition of **2** (**2**/**1a**: 9.0) after 528 h, at the same reaction temperature. For compound **3b** the residual solid from assay entry 8 was thermally pretreated at 150 °C, for 24 h and **1b** was added in the same ratio as the original experiment. After 48 h at 150 °C the reaction did not occur, but after further addition of **2** (**2**/**1b**: 13.0) the reaction take place (entry 21), but **3b** was isolated in a low yield.

The catalyst recycled by the above procedure (a) showed substantial loss in its catalytic activity, but when recycled by procedure (b), it showed a better catalytic activity although the yields of **3** were lower and reaction times were longer than in the original reactions. As typical examples, **3a** in 42% yield for the reused catalyst (entry 23) vs. 91% (entry 4) for the original experiment; **3b** in 70% yield for the reused catalyst (entry 22) vs. 86% for the original experiment (entry 10).

The above results suggest that **2** deactivates the catalyst and it is necessary to remove **2** from the catalyst to be reused. Procedure C is recommended to reuse the catalyst with a minimal loss of MPA during the washing with water. As a typical example compare entries 3–5 in Table 1 (for **3a**). When the reaction is complete, the small excess of **2** is removed with a minimum volume of water and thus the minimum quantity of MPA is lost. When isolation of **3** was performed using water, the catalyst and **2** were soluble in the aqueous phase. After evaporation of the water solvent, the residual solid was treated as described above.

This work provides a new alternative of low ecological demand for the synthesis of 3,4-disubstituted 1,2,5-thiadiazole 1,1-dioxides that restricts the use of solvent and eliminates the employment of strong mineral acids that are corrosive and harmful to the environment. The reaction products are obtained in good yield, they are easy to isolate, and the crude product only contains traces of impurities. The catalyst is recovered and reused though with some loss of its catalytic activity. To recover the catalyst it is necessary to eliminate sulfamide (**2**) that remains together with the heteropolyacid after the isolation of the reaction product. The thermal pretreatment of the catalyst has a marked effect on the rate of the reaction, as well as on the ratio MPA/**1**. Results show that the best experimental conditions depend on the structure of the dicarbonyl compound. However, a general tendency is observed in the examples of the reaction scope. Procedure C in which the dicarbonyl compound and the solid catalyst in a fine powdered mixture (or a paste for liquid dicarbonyl compounds) is left in contact for a time before an excess of sulfamide is added is, in general, preferred, although in some examples similar results are obtained following the procedure A (both reagents and the catalyst are mixed together). The use of a conventional sub-

limator as reactor may be considered as suitable because the excess sulfamide and some dicarbonyl compounds (e.g., benzyl in this work) may be deposited on the cold finger and may be recovered and reused. The highest yields of the products were obtained using catalyst pretreated at 300 °C. A lower temperature (150 °C) may be used without significant loss of the yields, but a higher catalyst/dicarbonyl compound molar ratio is necessary. The optimal general reaction temperature is 150 °C, but for some products a lower temperature (70 °C or room temperature) is sufficient. Under the experimental conditions investigated, the dicarbonyl compounds are protonated by the MPA, but the thiadiazole products are not.

All the chemicals were of analytical grade. Abs. EtOH, $CH_2Cl_2$, anhyd $Na_2SO_4$, benzil (**1a**), phenanthrene-9,10-dione (**1b**), 1-phenylpropane-1,2-dione (**1g**), biacetyl (**1h**), and **2** were purified by standard methods.[32] Pyrene-4,5-dione (**1c**) was synthesized in our laboratory by a literature procedure[33] with modification (exclusion of light and under $N_2$ atmosphere) that gave a better yield (60%) than the published one (46%).[33] 1,2-Di(2-naphthyl)ethane-1,2-dione (**1d**), 1,2-di(biphenyl-4-yl)ethane-1,2-dione (**1e**), and 1,2-bis(4-chlorophenyl)ethane-1,2-dione (**1f**) were synthesized from the corresponding benzoin by $CuSO_4$ oxidation,[34] and the benzoin was obtained by the reaction known as benzoin condensation from the corresponding aromatic aldehyde.[35] MPA (99.9%, from Aldrich) was thermally pretreated immediately before use (*vide infra*), nano-sized silica (from Sigma-Aldrich), particle size 7 nm, surface area 390 ± 40 $m^2\ g^{-1}$, was employed to support MPA, and distilled water deionized by the system Milli Pore-MilliQ was used for all the procedures.

Compounds **3a**–**d**,**f**–**h** (see Scheme 1) are known compounds.[5,8,9,13,29] They were synthesized by our research group using the conventional technique[13] suitably modified for better yields and/or by procedures designed by our working group.[29] Physical properties, spectroscopic data, and X-ray crystal structure analysis measured for compounds **3** synthesized in this work were compared with those of the authentic samples and with data previously published by us or by other authors, except for **3e**, and found to be identical. Synthesis, physical properties, spectroscopic data (FT-IR, $^1H$ and $^{13}C$ NMR, and UV-vis) and X-ray crystal structure analysis for **3e** have not been previously published. For TLC, Silica gel 60 F254 plates from Merck were used and examined under UV light irradiation (254, 365, and 200–800 nm). Melting points were determined using the capillary tube method by a Melting Point Apparatus B-545 (Büchi, Flawil, Switzerland) and are uncorrected. FT-IR spectra were recorded in KBr pellets on a Perkin Elmer FTIR spectrophotometer or a FTIR Thermo Scientific Nicolet 8700, and the UV-vis spectral measurements were made with a Shimadzu-1800 spectrophotometer equipped with a thermostatic cell holder. Teflon-stoppered quartz cells with a 1-cm optical path were used. $^1H$ and $^{13}C$ NMR spectra were recorded on Bruker 200 or 400 MHz spectrometers. Elemental analysis were performed by the Unidad de Microanálisis y Métodos Físicos Aplicados a Química Orgánica (UMYMFOR), Facultad de Ciencias Exactas, UBA using an Elemental Analyzer CE440.

### Preparation of MPA Catalyst

Commercial MPA was treated at different temperatures in order to enhance the acid strength: 70, 150, or 300 °C ($MPA^{70\ °C}$, $MPA^{150\ °C}$, and $MPA^{300\ °C}$, respectively), for 24 h and was maintained in a vacuum desiccator at r.t., immediately before use.

The nano-sized, silica-supported MPA catalyst ($MPA_{supp}$) was prepared by wet impregnation. Nanosilica was added to a solution of MPA in acetone solvent in order to obtain a catalyst containing 40 g MPA/140 g catalyst. The suspension was allowed to stand with magnetic stirring for 15 min, and then the solvent was evaporated. The yellow solid obtained was dried under reduced pressure at r.t. for 8 h. Before use, $MPA_{supp}$ was pre-treated at 150 °C ($MPA_{supp}^{150\ °C}$), for 24 h and maintained in a vacuum desiccator at r.t., immediately before performing the experiments.

### General Synthetic Procedure

Condensation reactions were carried out in the temperature range 25–150 °C. The used molar ratios of reactants and catalyst were: **2**/**1** 1.0–14.6; MPA/**1** 0.008–0.43. The course of the reactions was routinely monitored by TLC. A small sample of the reaction mixture (solvent-free reactions: ca. 0.2 mg; reactions in solution: ca. 0.1 mL) was treated with $CH_2Cl_2$ (ca. 1 mL), sonicated and the supernatant was analyzed by TLC. Completion of the reaction was judged by the disappearance of the TLC spot of the reagent **1a**–**h**. A few experiments were stopped before the complete disappearance of **1** (Table 1, entries 7 and 12). Longer heating did not lead to decomposition of the reaction products **3**.

### Solvent-Free Reaction; Procedure A

A fine powdered mixture (or a paste for liquids **2**) of **1**, MPA, and **2** placed in a Pyrex glass centrifuge tube (size: 107–109 mm, diameter: 16–17 mm, style type: rimless) was kept at 25–150 °C until the reaction was complete. Occasionally the mixture was allowed to cool to r.t. in a desiccator and then was again finely pulverized.

### Solvent-Free Reaction; Procedure B

In some experiments for the preparation of **3a** and **3f** the centrifuge tube was replaced by a conventional sublimator at atmospheric pressure. When the reaction was performed according to this procedure some of the initial **1a**,**f** and **2** mass were deposited on the cold finger of the sublimator and were recovered, recrystallized and reused in other experiments. The solid removed from the cold finger of the sublimator was washed with water or $CH_2Cl_2$ (with water: **2** was soluble and **1** was insoluble; with $CH_2Cl_2$: **2** was insoluble and **1** was soluble).

### Solvent-Free Reaction; Procedure C

A procedure slightly different than procedure A was also tested (as examples, Table 1 entries 5, 17, and 23). A homogeneous fine powdered mixture of **1** and MPA was left at the reaction temperature for ca. 18 h, then the mixture was allowed to cool to r.t. in the desiccator, **2** was added and the solid mixture was again pulverized and heated at the reaction temperature.

At the end of the reaction for the three above procedures, the solid mixture was allowed to cool to r.t. in the desiccator. Two procedures for the isolation of the reaction product were tested: (i) ice water (200–500 mL) was added or (ii) the solid reaction mixture was extracted with $CH_2Cl_2$ (total volume 150–250 mL: 10 × 15–25 mL). The residual solid after the extractions was reserved and reutilized. (i) Addition of ice water: the insoluble solid was filtered, washed with copious amounts of cold $H_2O$, and dried under reduced pressure at 40 °C to constant weight. (ii) Extraction with $CH_2Cl_2$: the combined organic extracts were washed with $H_2O$, dried (anhyd $Na_2SO_4$) and then the solvent was evaporated under reduced pressure at r.t. yielding a solid

that was dried under reduced pressure at 40 °C to constant weight. Using both procedures (i) and (ii) crude **3a** was obtained as a chromatographically (TLC) pure product, but in crude **3b**–**h** products traces (TLC) of unknown by products were present. Pure **3b**–**f** were obtained by the following procedures: **3b**, recrystallization (boiling acetone); **3c**, repeated washing with warm EtOH; **3d**, recrystallization (boiling $CH_2Cl_2$); **3e**, repeated washing with EtOH; **3f**, repeated washing with *n*-hexane, and **3g**,**h**, recrystallization (boiling benzene with drops of TFA). When $MPA_{supp}$ was used for **3c** preparation, the isolation of the reaction product was performed by extraction with $CH_2Cl_2$ to not destroy the supported catalyst.

### Reactions in EtOH Solution

A fine powdered solid mixture of **1b** (60 mg, 0.33 mmol) and $MPA^{150\,°C}$ (36 mg, 0.02 mmol) was added to abs EtOH (45–50 mL) contained in a Pyrex glass round-bottom flask (100-mL volume). The initial yellow homogeneous solution turned green after 45 min of heating to mild reflux. Then, excess of **2** (250 mg, 2.6 mmol) was added, and the solution was allowed to stand with magnetic stirring under heating to mild reflux. When the reaction was complete (TLC), the heterogeneous solution (MPA was soluble in EtOH) was allowed to cool to r.t., and then was left in a refrigerator overnight. The solid (**3b**) was filtered, washed with cold water, then with cold EtOH, dried to constant weight and was recrystallized from boiling acetone.

### Reusability of MPA

The catalyst was assayed to be recovered and to be reused in the reactions for **3**. After the extraction of **3** from the solid reaction mixture with $CH_2Cl_2$, the residual solid contains MPA and the excess of **2**. The residual solid was treated by the following two different procedures: (a) The residual solid was dried and thermally pre-treated under the same conditions as for the original reaction. (b) The residual solid was washed with a small volume of water [MPA solubility in water: 0.0169 g/mL at r.t. (ratio: 5 mL water/g residual solid) and **2** is freely water soluble]. **2** passed to the aqueous phase, and a small amount (8%) of MPA was lost in water during the washing. A suitable volume of water was added to the residual solid and then it was centrifuged for 20 min at 4300 rpm (ROLCO I-2036 centrifuge), the aqueous phase was separated and the washed residual solid was dried for 48 h at 70 °C in an oven at reduced pressure at r.t. up to constant weight. Finally, the catalyst thus recovered was thermally pretreated under the same experimental conditions as the original test and was reused.

The synthetic procedures that gave the best results are detailed below; physical and spectroscopic data for all known compounds are given in the Supporting Information.

### 3,4-Diphenyl-1,2,5-thiadiazole 1,1-Dioxide (3a) (Table 1, Entry 5)

Following procedure B/C, a fine powered mixture of **1a** (105.2 mg, 0.50 mmol), $MPA^{300\,°C}$ (91.3 mg, 0.05 mmol), and **2** (60.6 mg, 0.60 mmol) was kept in a conventional sublimator at atmospheric pressure and 70 °C until the reaction was complete (144 h). At the end of the reaction the solid mixture was allow to cool to r.t. The solid mixture was extracted with water or $CH_2Cl_2$ following procedures (i) or (ii). The solid removed from the cold finger of the sublimator with $CH_2Cl_2$ was **1a** (7.9 mg, 0.04 mmol). The crude **3a** [116.3 mg, 0.43 mmol, 93% (based on recovered **1a**)] was a pure product (TLC).

### Phenanthro[9,10-*c*][1,2,5]thiadiazole 2,2-Dioxide (3b) (Table 1, Entry 10)

Following procedure A, a fine powered mixture of **1b** (108.2 mg, 0.52 mmol), $MPA^{300\,°C}$ (37.0 mg, 0.020 mmol), and **2** (445.2 mg, 4.64 mmol) was kept at 150 °C until the reaction was complete (3.5 h). At the end of the reaction the solid mixture was allow to cool to r.t. in a desiccator. The solid mixture was treated with water or extracted with $CH_2Cl_2$ following procedures (i) or (ii) yielding **3b** (120.2 mg, 0.48 mmol, 86%).

### Pyreno[4,5-*c*][1,2,5]thiadiazole 10,10-Dioxide (3c) Using $MPA_{supp}^{150\,°C}$ (Table 1, Entry 13)

Following procedure A, a fine powered mixture of **1c** (50.0 mg, 0.17 mmol), $MPA_{supp}^{150\,°C}$ (15.4 mg, 0.0024 mmol of MPA), and **2** (403.1 mg, 4.19 mmol) was kept at 150 °C until the reaction was complete (15 h). At the end of the reaction, the solid mixture was allow to cool to r.t. in a desiccator. The solid mixture was extracted with $CH_2Cl_2$ following procedure (ii) yielding **3c** (44.1 mg, 0.15 mmol, 70%).

### 3,4-Di(2-naphthyl)-1,2,5-thiadiazole 1,1-Dioxide (3d) (Table 1, Entry 15)

Following procedure A, a fine powered mixture of **1d** (20.4 mg, 0.066 mmol), $MPA^{150\,°C}$ (9.7 mg, 0.0053 mmol), and **2** (65.5 mg, 0.688 mmol) was kept at 150 °C until the reaction was complete (94 h). At the end of the reaction, the solid mixture was allow to cool to r.t. The solid mixture was extracted with $CH_2Cl_2$ following procedure (ii) yielding a solid (17.3 mg, 0.047 mmol, 71%).

### 3,4-Di(biphenyl-4-yl)-1,2,5-thiadiazole 1,1-Dioxide (3e) (Table 1, Entry 17)

Following procedure C, a fine powered mixture of **1e** (50.1 mg, 0.14 mmol), $MPA^{300\,°C}$ (17.8 mg, 0.0097 mmol) and **2** (129.1 mg, 1.34 mmol) was kept at 150 °C until the reaction was complete (8 h). At the end of the reaction, the solid mixture was allow to cool to r.t. in a desiccator. The solid mixture was extracted with $CH_2Cl_2$ following procedure (ii) yielding **3e** (35.3 mg, 0.084 mmol, 60%) as a bright yellow crystalline solid; mp 270.5–271.0 °C.

FT-IR (KBr): 3070–3010, 1600, 1580, 1570, 1540, 1380, 1270, 1190, 1180, 1000, 980, 850, 790, 765, 740, 690, 640, 560, 530, 515 $cm^{-1}$.

$^1H$ NMR (200 MHz, DMSO-$d_6$): δ = 8.54–7.44 (complex multiplet, $C_{Ar-H}$).

$^{13}C$ NMR (50 MHz, DMSO-$d_6$): δ = 167.2 (heterocyclic $sp^2$ C-atoms), 144.5–125.9 (several signals $C_{Ar}$).

UV-vis (MeCN): λ (ε, L $mol^{-1}$ $cm^{-1}$) = 261 ($3.2 \times 10^4$), 369 nm ($2.02 \times 10^4$).

UV-vis (EtOH): λ (ε, L $mol^{-1}$ $cm^{-1}$) = 258 ($2.5 \times 10^4$), 316 nm ($2.6 \times 10^4$).

Anal. Calcd for $C_{26}H_{18}N_2O_2S$: C, 73.93; H, 4.27; N, 6.64; S, 7.58. Found: C, 74.75; H, 4.33; N, 6.75; S, 7.65.

### Crystal Structure for 3e

Single crystals of **3e** were obtained from MeCN solutions by slow evaporation of the solvent. Single crystal X-ray data were obtained with a KappaCCD diffractometer, using ϕ and ω scans and graphite monochromated MoKα radiation (λ = 0.71073 Å) in the θ range from 3.33 to 25.00°. The structure was solved by direct and Fourier methods and the final molecular model obtained by full-matrix least-squares refinement on $F^2$ of the non-hydrogen atoms employing the SHELXS-97[36] and SHELXL-97[37] programs. An ORTEP diagram of **3e** is presented in Figure 1. Detailed X-ray crystal structure data are available in the Supporting Information.

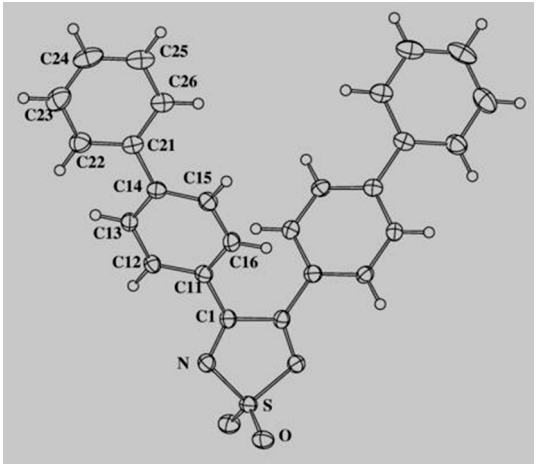



**Figure 1** ORTEP molecular drawing for **3e**. The molecule is sited on a two-fold crystallographic axis. The figure shows the atomic labeling of one independent half of the molecule.

### 3,4-Bis(4-chlorophenyl)-1,2,5-thiadiazole 1,1-Dioxide (3f) (Table 1, Entry 18)

Following procedure A/B, a fine powered mixture of **1f** (109.5 mg, 0.39 mmol), MPA$^{150\,°C}$ (18.05 mg, 0.0099 mmol), and **2** (337.5 mg, 3.516 mmol) was kept in a conventional sublimator at atmospheric pressure and 150 °C until the reaction was complete (95 h). The solid mixture at r.t. was extracted with $CH_2Cl_2$ following procedure (ii), yielding a solid that was dried under reduced pressure at 40 °C. The crude **3f** was obtained with traces of unknown byproducts [52.8 mg, 0.155 mmol, 40%, 49% (based on recovered **1f**). The solid removed from the cold finger of the sublimator with $CH_2Cl_2$ was **1f** (21.0 mg, 0.075 mmol).

### 3-Methyl-4-phenyl-1,2,5-thiadiazole 1,1-Dioxide (3g) (Table 1, Entry 19)

Following procedure A, a fine powered mixture of **2** (195.7 mg, 2.040 mmol), MPA$^{150\,°C}$ (22.4 mg, 0.0122 mmol), and **1g** (248.1 mg, 0.2 mL, 1.676 mmol) was kept at r.t. until the reaction was complete (70 h). At the end of the reaction the solid mixture was extracted with $CH_2Cl_2$ and procedure (ii) was followed. Solid **3g** (301.4 mg, 1.449 mmol, 86%; Lit.[13] 29%).

### 3,4-Dimethyl-1,2,5-thiadiazole 1,1-Dioxide (3h) (Table 1, Entry 20)

Following procedure A, a fine powered mixture of MPA$^{150\,°C}$ (38.9 mg, 0.021 mmol), **2** (301.3 mg, 3.13 mmol), and **1h** (203.6 mg, 0.2 mL, 2.358 mmol), was kept at r.t. until the reaction was complete (52 h). At the end of the reaction the solid mixture was treated as in procedure (ii) yielding a solid (285.1 mg, 1.953 mmol, 83%; Lit.[28] 74%).

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## Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0035-1561371.

## References

(1) Gazieva, G. A.; Kravchenko, A. N.; Lebedev, O. V. *Russ. Chem. Rev.* **2000**, *69*, 221.
(2) Clerici, F. *Adv. Heterocycl. Chem.* **2002**, *83*, 71.
(3) Robichaud, A. J. *Curr. Top. Med. Chem.* **2006**, *6*, 553.
(4) Dungan, L. B.; Rowley, E. G.; Dixson, J. A.; Ali, S. F.; Crawford, S. D.; Sehgel, S.; Whiteside, M. P.; Zydowsky, T. M.; Yeager, W. H. PCT Int. Appl. WO 6858, **2005**; *Chem. Abstr.* **2005**, *142*, 150261.
(5) Linder, T.; Badiola, V.; Baumgartner, T.; Sutherland, T. C. *Org. Lett.* **2010**, *12*, 4520.
(6) Grillo, C. A.; Mirífico, M. V.; Morales, M. L.; Reigosa, M. A.; Fernández Lorenzo de Mele, M. *J. Hazard. Mater.* **2009**, *170*, 1173.
(7) Banera, M. J.; Caram, J. A.; Gervasi, C. A.; Mirífico, M. V. *J. Appl. Electrochem.* **2014**, *44*, 1337.
(8) Mirífico, M. V.; Caram, J. A.; Gennaro, A. M.; Cobos, C. J.; Vasini, E. J. *J. Phys. Org. Chem.* **2009**, *22*, 964.
(9) Mirífico, M. V.; Caram, J. A.; Gennaro, A. M.; Cobos, C. J.; Vasini, E. J. *J. Phys. Org. Chem.* **2011**, *24*, 1039.
(10) Lee, C-H.; Korp, J. D.; Kohn, H. *J. Org. Chem.* **1989**, *54*, 3077.
(11) Esser, T.; Karu, A. E.; Toia, R. F.; Casida, J. E. *Chem. Res. Toxicol.* **1991**, *4*, 162.
(12) Alberola, A.; Andres, J. M.; Gonzalez, A.; Pedrosa, R.; Vicente, M. *Synthesis* **1991**, 355.
(13) Wright, J. B. *J. Org. Chem.* **1964**, *29*, 1905.
(14) Koutentis, P. A. In *Comprehensive Heterocyclic Chemistry III*; Vol. 5; Katritzky, A. R.; Ramsden, C. A.; Scriven, E. F. V.; Taylor, R. J. K., Eds.; Elsevier: Oxford, **2008**, 516.
(15) Xie, Y.; Shuku, Y.; Matsushita, M. M.; Awaga, K. *Chem. Commun.* **2014**, *50*, 4178.
(16) Schüttler, C.; Li-Böhmer, Z.; Harms, K.; von Zezschwitz, P. *Org. Lett.* **2013**, *15*, 800.
(17) Erturk, A. G.; Bekdemir, Y. *Phosphorus, Sulfur Silicon Relat. Elem.* **2014**, *189*, 285.
(18) Bennardi, D. O.; Romanelli, G. P.; Sathicq, A. G.; Autino, J. C.; Baronetti, G. T.; Thomas, H. J. *Appl. Catal., A* **2011**, *404*, 68.
(19) Heravi, M.; Sadjadi, S. *J. Iran. Chem. Soc.* **2009**, *6*, 1.
(20) Romanelli, G. P.; Autino, J. C. *Mini-Rev. Org. Chem.* **2009**, *6*, 359.
(21) Firouzabadi, H.; Jafari, A. A. *J. Iran. Chem. Soc.* **2005**, *2*, 85.
(22) Heravi, M. M.; Derikvand, F.; Haeri, A.; Oskoie, H. A.; Bamoharram, F. F. *Synth. Commun.* **2008**, *38*, 135.
(23) Okuhara, T. *Catal. Today* **2002**, *73*, 167.
(24) Mizuno, N.; Misono, V. *Curr. Opin. Solid State Mater. Sci.* **1997**, *2*, 84.
(25) Takana, K.; Koda, F. *Chem. Rev.* **2000**, *100*, 1025.
(26) Rostami, M.; Khosropour, A.; Mirkhani, V.; Moghadam, M.; Tangestaninejad, S.; Mohammadpoor-Baltork, I. *Appl. Catal., A* **2011**, *397*, 27.
(27) Kozhevnikov, I. *J. Mol. Catal. A: Chem.* **2007**, *262*, 86.
(28) Vorreither, K.; Ziegler, E. *Monatsh. Chem.* **1965**, *96*, 216.
(29) Svartman, E. L.; Rozas, M. F.; Piro, O. E.; Castellano, E. E.; Mirífico, M. V. *Synthesis* **2006**, 2313.
(30) Svartman, E. L.; Caram, J. A.; Mirífico, M. V.; Vasini, E. J. *Can. J. Chem.* **1999**, *77*, 511.
(31) Marcì, G.; García-López, E. I.; Palmisano, L. *Eur. J. Inorg. Chem.* **2014**, 21.

(32) Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*, 4th ed.; Butterworth Heinemann: Oxford, **1997**.
(33) Harris, F. W.; Zhang, D.; Hu, J. *J. Org. Chem.* **2005**, *70*, 707.
(34) Vogel, A. I. *A Textbook of Practical Organic Chemistry*; Longmans Green: London, **1948**, 679.
(35) Gomberg, M.; Van Natta, F. J. *J. Am. Chem. Soc.* **1929**, *51*, 2238.
(36) Sheldrick, G. M. *SHELXS-97 Program for Crystal Structure Resolution*; University of Göttingen: Germany, **1997**.
(37) Sheldrick, G. M. *SHELXS-97 Program for Crystal Structure Analysis*; University of Göttingen: Germany, **1997**.