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Multifunctional Catalysis of Nanosheet Defective Molybdenum Sulfide Basal Planes for Tandem Reactions involving Alcohols and Molecular Hydrogen

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ABSTRACT

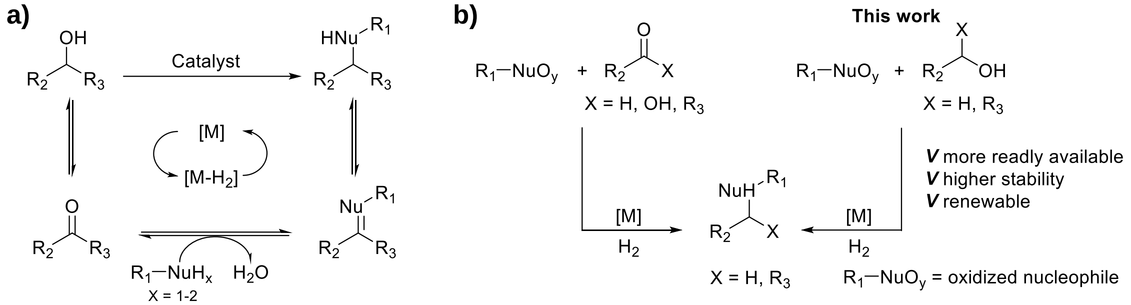
Establishing tandem catalytic synthetic strategies based on the use of readily available, stable and renewable feedstocks is of great significant for the sustainable advancement of chemical-related industries. The key to success largely relies on applying efficient multifunctional catalysts that allow carrying out one-pot single-step synthesis. In this work, we have demonstrated that defect engineered basal planes of a molybdenum sulfide nanomaterial ($\{Mo_3S_4\}_n$) offer a multifunctional catalytic platform for chemical process intensification. By applying this catalyst, besides borrowing hydrogen-type processes, herein exemplified for the thioetherification of alcohols, we have also disclosed novel and rare coupling reactions requiring hydrogen activation and alcohol dehydrogenation processes in a one-pot fashion. More specifically, oxidized nucleophiles, such as *o*-dinitroarenes and dinitrophenyl disulfides, are reacted with alcohols in the presence of H_2 to yield respectively benzimidazoles and benzothiazoles. The uncommon catalytic reactivity of $\{Mo_3S_4\}_n$ arises from the presence of coordinatively unsaturated molybdenum and sulfide species, which work as Lewis acid and Lewis basic sites, respectively. As suggested by in-situ Infrared (IR) spectroscopy investigations, the alcohol dehydrogenation involves the participation of both types of active sites, while the H_2 dissociation takes place on coordinatively unsaturated sulfide species.

INTRODUCTION

The development of synthetic processes that combine efficiency, reduced cost, and low environmental impact is essential for the sustainable advancement of bulk and fine chemical industries. Catalysis is a key discipline offering versatile and efficient strategies for sustainability. For instance, it enables the development of domino or tandem processes involving multiple catalytic events in a one-pot fashion, thus avoiding separation and purification intermediate steps associated with stop-and-go syntheses.[1-10]

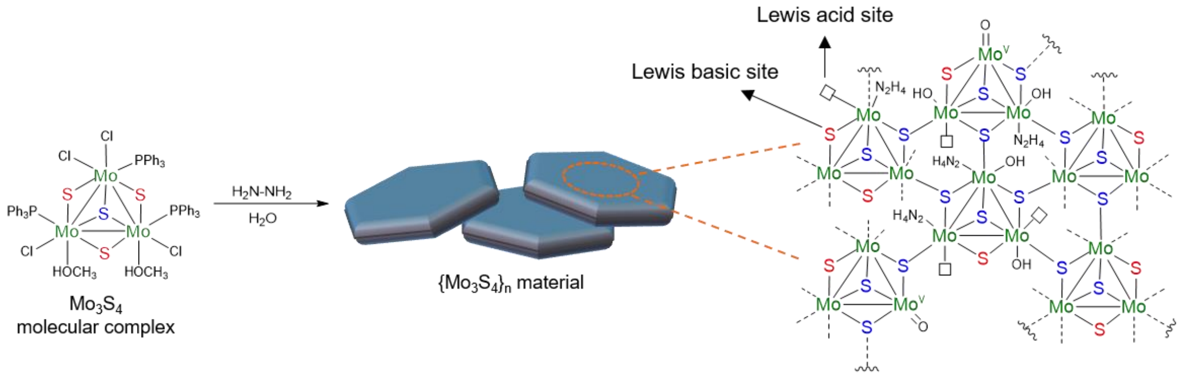
Among the well-established domino catalytic transformations available to obtain value-added molecules, transition metal-catalyzed hydrogen autotransfer (also known as borrowing hydrogen) processes involving alcohols as starting materials occupy a central place in the repertoire of sustainable synthetic methodologies.[11-22] In this reaction sequence, alcohols are used as both coupling partners and hydrogen source, thus avoiding the use of an additional reducing agent (Scheme 1a). Although it can be envisioned as an outstanding benefit, however, in terms of atomic efficiency, it limits the applicability of this synthetic strategy to processes requiring a low number of reduction events. Otherwise, large amounts of alcohols should be required to successfully accomplish the desired overall transformation. This means that the use of oxidized nucleophiles, which need to be in-situ reduced, is problematic. In such a cases, transition metal-catalyzed reductive coupling reactions involving carbonyl compounds (aldehydes,[23-34] ketones,[35-38] and even more challenging carboxylic acid derivatives[39-44]), instead of alcohols, and the use of the greenest reducing agent (i.e. molecular hydrogen) might allow for more benign and practical synthetic strategies.[45]

Alternatively, since alcohols are readily available, structurally diverse, stable, and many of them renewable, the development of catalytic reductive coupling processes whereby alcohols, instead of carbonyl compounds, can be in-situ dehydrogenated and converted into value-added compounds in the presence of a hydrogen atmosphere would be particularly interesting (Scheme 1b). Nevertheless, the reversibility nature of the alcohol dehydrogenation step under hydrogenative conditions could make the overall process challenging, which would become especially more complicated when the alcohol dehydrogenation and the hydrogen activation are competitive reactions that take place in the same active centers. In this scenario, the finding of a multifunctional solid catalyst that allows both reactions to be accomplished on different or, at least, on partially shared active sites would be advantageous.



Scheme 1. a) General mechanism for borrowing hydrogen synthetic processes using alcohols. b) Comparison of using carbonyl compounds (left) *versus* alcohols (right) for hydrogenative coupling reactions involving oxidized nucleophiles as substrates.

Recently, we reported an innovative synthetic strategy based on the use of molecular Mo_3S_4 cluster complexes as building entities, whereby a sulfur deficient molybdenum disulfide (MoS_2)-type nanomaterial, named $\{Mo_3S_4\}_n$, was prepared.[46] $\{Mo_3S_4\}_n$ comprises randomly agglomerated nanosheets displaying a high degree of structural defects on the edge positions and along the typically inactive basal planes. More specifically, these nanosheets are constituted by partially assembled Mo_3S_4 units, thus implying the existence of unsaturated bridging sulfide ligands and vacant coordination sites around the outer coordination sphere of molybdenum atoms, which are mainly occupied by hydroxyl and labile hydrazine ligands (see Scheme 2). Interestingly, application of this nanomaterial allowed for the establishment of a novel catalytic protocol for the direct synthesis of benzimidazoles by hydrogenative coupling of *o*-dinitroarenes with aldehydes. The partial removing of the bridging sulfide ligands, detected during the hydrogenative recycling investigations, as well as previous reported studies performed on Mo_3S_4 complexes,[47] suggest that these bridging sulfide moieties are the active centers where H_2 undergoes dissociative activation. Furthermore, these unsaturated sulfide ligands exhibit Lewis basic character, a fact that, in combination with the presence of readily formed vacant active sites around molybdenum atoms with Lewis acid properties, might make the nanomaterial $\{Mo_3S_4\}_n$ a potential candidate to be applied as a multifunctional catalyst for tandem processes requiring both hydrogenation and dehydrogenation reactions in a one-pot fashion.



Scheme 2. Schematic representation of defective basal planes of the nanomaterial $\{Mo_3S_4\}_n$ displaying vicinal Lewis acid and Lewis basic sites.

To go gradually deeper into this hypothesis, firstly, in this work we investigate the ability of the catalyst $\{Mo_3S_4\}_n$ to perform a conventional borrowing hydrogen strategy where the released hydrogen is used to successfully furnish the desired final product. The formation of carbon-sulfur bonds by dehydrogenative coupling of alcohols with thiols to synthesize thioethers was the selected reaction. These sulfur-containing compounds are important scaffolds widely found in natural products, drugs, and functional organic materials.[48-56] Among the known synthetic procedures for their preparation,[51, 57-122] the borrowing hydrogen thioetherification of alcohols offers compelling benefits avoiding issues associated with the formation of inorganic waste, low availability of starting materials, regioselectivity, and reactivity limitations ascribed to the poor leaving character of the hydroxyl functionality.

As far as we know, there are only two examples on this reaction mediated by heterogeneous catalysts, both reported by some of us. One of them is based on palladium nanoparticles supported on high-surface area magnesium oxide (MgO),[123] while the other one uses cobalt-molybdenum-sulfides as catalysts.[124] Herein, we apply the catalyst $\{Mo_3S_4\}_n$, whose non-noble metal nature along with its cobalt-promoter-free structure configuration displaying a high degree of active sites on the typically inactive basal planes, make the use of this sulfur-deficient MoS_2-type catalyst especially attractive. It is worth mentioning that MoS_2-derived catalysts have been applied for performing dehydrogenations[125-128] and transfer hydrogenations reactions,[129-133] but their use in a conventional borrowing hydrogen-type synthetic process remains scarce.[132]

As one of the most representative oxidized nucleophiles, nitroarenes are inexpensive, stable, and readily available compounds. Since their reduction represents the most convenient methodology to access primary aromatic amines, they are considered essential feedstocks for preparing aniline-derived fine chemicals by means of tandem transformations involving reduction reactions.[6, 8, 23-44, 134-135] Among many others, this is the case of benzimidazoles, a class of N-heterocyclic compounds with industrial interest within the fields of pharmaceuticals,[136-142] fertilizers,[143] polymers,[144-145] dyes,[146] and so on.[147-148] In fact, compared to the common use of *o*-phenylenediamines as starting reagents,[149-154] more shortcut approaches to prepare benzimidazoles have been developed starting from *o*-nitroanilines,[155-170] and even more interestingly, from *o*-dinitroarenes.[43, 46, 171-173] Nevertheless, the use of nitroarene-derived reagents in combination with alcohols as coupling reagents to access benzimidazoles is quite limited. To the best of our knowledge, the synthesis of benzimidazoles has been accomplished from o-nitroanilines through transition metal-catalyzed borrowing hydrogen methodologies,[161, 164-166, 168-170] and by means a synthetic strategy based on redox condensation reactions mediated by a Fe/S catalytic system.[158] On the contrary, no examples on the direct one-pot single-step synthesis of benzimidazoles (neither any other N-heterocyclic compounds) by reaction of *o*-dinitroarenes with alcohols have been reported to date. To this respect, it is worth mentioning that the use of a multifunctional catalyst based on Au/CeO_2, which is able to perform the one-pot reaction between *o*-dinitrobenzene and a vicinal diol derivative to give the corresponding quinoxaline. However, modification of reaction conditions was required in each of the reaction steps of the overall synthetic process.[134]

In this contribution, we apply the catalyst $\{Mo_3S_4\}_n$ to establish an unprecedented coupling synthetic strategy to access 2-substituted benzimidazoles, in which alcohols and *o*-dinitroarenes are reacted in the presence of molecular hydrogen. Advantageously, the fact of using an extra supply of hydrogen allows decreasing the amount of the alcohol-coupling reagent, as compared when the reaction is accomplished via a traditional borrowing hydrogen strategy. In-situ Infrared spectroscopy studies confirm the vital role of the multifunctional character of the catalyst $\{Mo_3S_4\}_n$, containing both Lewis acid and Lewis basic sites distributed along the basal planes, for the reaction to be successfully accomplished. In addition, in view of this uncommon catalytic behavior, we also generalize the applicability of the catalyst $\{Mo_3S_4\}_n$ to prepare other valuable benzene-fused heterocycles, such as 2-arylbenzothiazoles,[174-177] via this rare straightforward coupling reaction strategy combining alcohols, molecular hydrogen, and, in this particular case, 2,2'-dinitrodiphenyl disulfide.

RESULTS AND DISCUSSION

$\{Mo_3S_4\}_n$-Catalyzed Borrowing Hydrogen Thioetherification of Alcohols

Initially, to explore the ability of the catalyst $\{Mo_3S_4\}_n$ to conduct a conventional borrowing hydrogen-based synthetic strategy, we investigated the benzyl phenyl sulfide (**3aa**) formation by alkylation of benzenethiol (**1a**) with benzyl alcohol (**2a**). In accordance with the established borrowing-hydrogen process (Scheme 1a), $\{Mo_3S_4\}_n$ should be able to dehydrogenate the alcohol **2a** to benzaldehyde, to promote the nucleophilic attack of the thiol **1a** to the aldehyde, and to carry out the transfer hydrogenation to the formed transient hemithioacetal intermediate in order to finally afford the thioether **3aa** (Scheme S1).[123, 178-181]

The first catalytic experiment was performed under nitrogen atmosphere, in toluene, at 180 ºC, and using a slight excess of the alcohol **2a** (3 equiv.). In spite of benzaldehyde was present when the reaction was stopped (16 h), the initial thiol **1a** did not completely react (69% conv.) and the desired thioether **3aa** was afforded in a discrete yield (46%) together with phenyl disulfide (**4a**) as a byproduct (4% yield). Therefore, we decided to carry out a catalyst pre-activation treatment (180 ºC, 2 h, vacuum conditions) in the same autoclave with the aim to create Lewis acid sites at a higher extent by removing remaining water molecules, adsorbed on the catalyst surface, and labile hydrazine ligands from defective basal planes of $\{Mo_3S_4\}_n$. Characterization by combustion elemental analyses combined with inductively coupled plasma optical emission spectrometry (ICP-OES) measurements revealed a considerable decrease of the nitrogen content, *i.e.* hydrazine ligands, in the pre-activated catalyst (2.9%) when compared with the fresh one (10.0%), while the S/Mo molar ratio remains constant. To our delight, under otherwise the same reaction conditions but in the presence of the pre-activated catalyst, the thiol **1a** was fully converted into **3aa** in nearly quantitative yield (97%). Importantly, this result suggests that the Lewis acid sites offered by coordinatively unsaturated molybdenum centers located at the defective basal planes can play an important role not only in the alcohol dehydrogenation step, but also in the intermediate nucleophilic reaction by increasing the electrophilic nature of the carbonyl functionality, thus enhancing its reactivity.

Further evidences on the importance of presenting defective basal planes for the investigated reaction were gathered by using a sulfurized catalyst, named $\{Mo_3S_4\}_n$-S. Its structure configuration comprising stacked nanosheets is constituted by a hexagonal (2H)−trigonal (1T) mixed-phase of MoS_2 and non-sulfurized Mo_3S_4 domains to a lesser extent, which implies the presence of lesser defect-rich basal planes and a higher difficulty to be accessible as compared with $\{Mo_3S_4\}_n$.[46] Consequently, a considerable lower reaction rate for the formation of the desired thioether **3aa** was obtained when the sulfurized catalyst $\{Mo_3S_4\}_n$-S was used under otherwise the same reaction conditions (Figure S1). Reaction profiles for both catalysts reveal the formation of the disulfide **4a** as a primary product. Unlike $\{Mo_3S_4\}_n$-S, the concentration of **4a** reach a maximum in the presence of $\{Mo_3S_4\}_n$ and begins to decrease, thus indicating that the disulfide bond in **4a** is catalytically reduced to form the starting thiol **1a** again. It is also noteworthy that the catalyst $\{Mo_3S_4\}_n$ displays a higher catalytic activity (measured by the initial reaction rates normalized to the moles of metal) than that of the catalyst based on cobalt molybdenum sulfides previously reported for the same reaction (Figure S2).[124]

Other critical reaction parameters were investigated by decreasing the amount of the alcohol **2a**, the reaction temperature to 160 ^{0}C, and by testing different solvents (Table S1). In general, all these variations led to lower reactivity, being particularly remarkable the fact that considerable lower yields of **3aa** (18-31%) were achieved by using coordinating solvents, such as, butanol, 1,4-dioxane, acetonitrile, and tetrahydrofuran. Probably, it results from the partial blockage of the Lewis acid sites of the catalyst, thus limiting the alcohol dehydrogenation to benzaldehyde. Indeed, after reaction time, large amounts of the alcohol **2a** remained unreacted, and benzaldehyde was hardly detected. On the contrary, an enhanced yield of **3aa** (69%), but not higher than that for toluene, was afforded with the use of the structure-related and non-coordinating solvent o-xylene.

Then, the recyclability of $\{Mo_3S_4\}_n$ for the model reaction was explored under the previously optimized reaction conditions. Gratifyingly, no obvious decrease of the activity of $\{Mo_3S_4\}_n$ was observed (Figure 1), and full conversion of **1a** was achieved for five consecutive runs affording the thioether **3aa** in excellent yields (Figure S3). It is noticeable that no molybdenum leaching to the reaction medium occurred, as revealed by inductively coupled plasma optical emission spectrometry (ICP-OES) measurements of the filtrates after separating-off the catalyst by filtration. Although no obvious structural changes could be ascertained by transmission electron microscopy (TEM) and X-ray diffraction (XRD) spectroscopy (Figure S5-S6), ICP-OES measurements combined with elemental analysis revealed a slight decrease of the S/Mo molar ratio from 1.25 to 1.09 when comparing the fresh catalyst with the five-times-recycled one ($\{Mo_3S_4\}_n$-R'), respectively. The variation of the sulfur content was further investigated by X-ray photoelectron spectroscopy (XPS), which showed a small decrease in the area ratio of bridging to apical sulfur species (red and blue S in Scheme 2, respectively). This observation indicates that bridging sulfide ligands rather than the coordinatively saturated apical ones are involved in the borrowing hydrogen process, likely as basic active sites, being these only slightly vanished during catalysis (Figure S4 and Table S2).

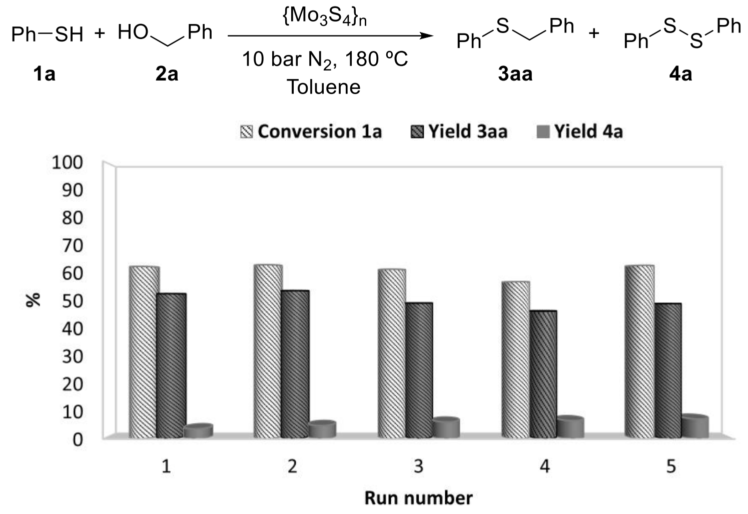
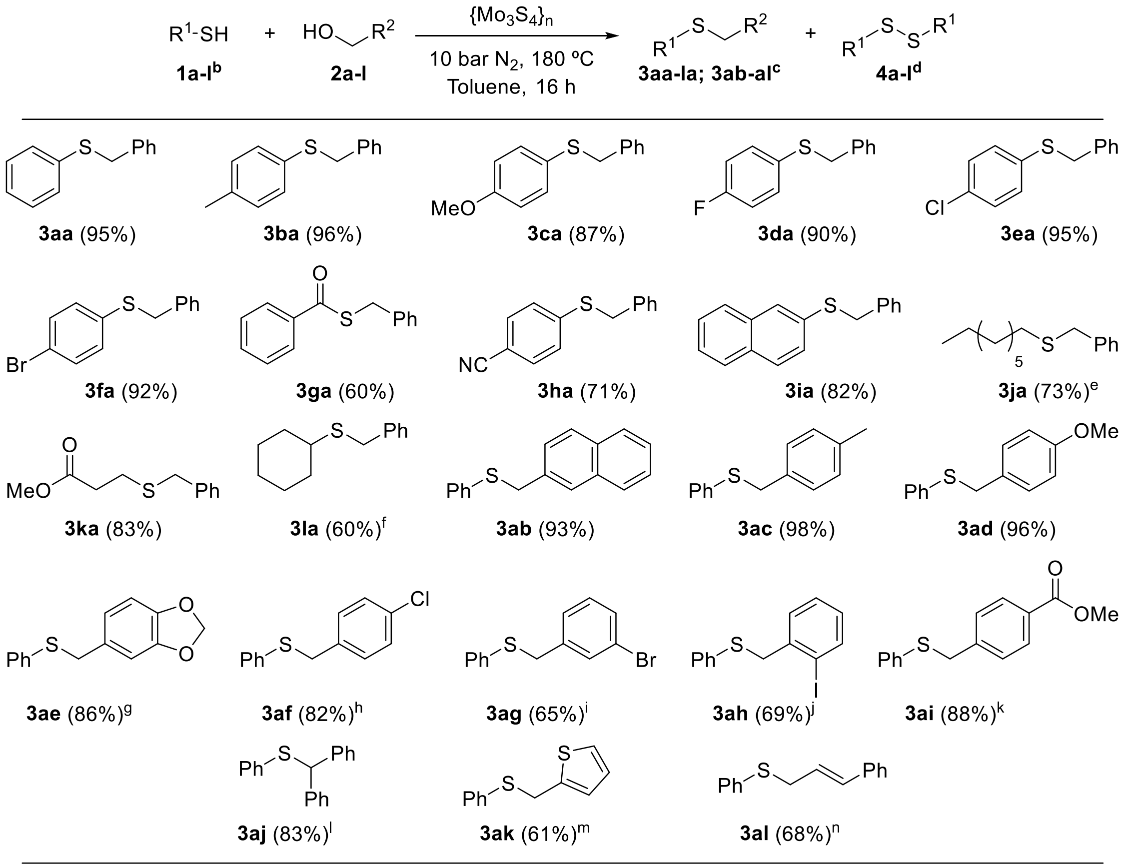


Figure 1. Recycling of catalyst $\{Mo_3S_4\}_n$ for the borrowing hydrogen synthesis of **3aa** by thioetherification reaction of **2a** with **1a**. Catalyst activation: 180 ºC, 2 h, vacuum; Reaction conditions: **1a** (0.25 mmol), **2a** (0.75 mmol), $\{Mo_3S_4\}_n$ (30 mg), toluene (3 mL), 10 bar N_2, 180 ºC, 6h. Conversions and yields determined by GC using hexadecane as an internal standard.

All the above results suggest that both coordinatively unsaturated molybdenum and bridging sulfide ligands with Lewis acid and Lewis basic character, respectively, participate as active centers for the borrowing hydrogen C–S bond formation reaction of thiols with alcohols.

Scheme 3. $\{Mo_3S_4\}_n$-catalyzed borrowing hydrogen synthesis of thioethers by reaction of various thiols with different alcohols[a]



[a]Catalyst activation: 180 ºC, 2h, vacuum; Reaction conditions: **1b-l** (0.25 mmol), **2a-l** (0.75 mmol), $\{Mo_3S_4\}_n$ (30 mg), toluene (3 mL), 10 bar N_2, 180 ºC, 16 h. [b]Conversion determined by GC using

n-hexadecane as an internal standard. [c]Yield of isolated products is given with full conversion of **1a**-**1l** unless otherwise stated. [d]Yield determined by GC using n-hexadecane as an internal standard. [e]88% conv. **1j**; **4j** (traces < 2%) [f]$\{Mo_3S_4\}_n$ (60 mg); 69% conv. **1l**; 2% yield **4l**. [g]5% yield **4a**. [h]90% conv. **1a**; 7% yield **4a**. [i]76% conv. **1a**; 3% yield **4a**. [j]**1a**; 19% yield **4a**. [k]$\{Mo_3S_4\}_n$ (60 mg); 94% conv. **1a**. [l]98% conv. **1a**; 16% yield **4a**. [m]92% conv. **1a**; 11% yield **4a**. [n]**2l** (1 mmol); 95% conv. **1a**; 23% yield **4a**.

Next, the catalytic performance of $\{Mo_3S_4\}_n$ to conduct this conventional borrowing hydrogen process was further explored by reaction of various thiols with benzyl alcohol (**2a**) under optimized conditions. As shown in Scheme 3, methyl- and metoxy-substituted aryl thiols reacted efficiently with **2a** affording the corresponding alkylated thiols **3ba** and **3ca** in 96 and 87% isolated yields, respectively. Likewise, the halogen-containing thioethers **3da**, **3ea** and **3fa** were accessed in excellent yields without dehalogenation-side reactions. Notably, aromatic-ring-attached reducible substituents, such as ketones and nitriles, were well tolerated and the desired functionalized products **3ga** and **3ha** could be isolated in satisfactory yields. Moreover, a thiol displaying benzene-fused aromatic rings, *i.e.* 2-naphtalene thiol, was successfully alkylated providing **3ia** in 82% isolated yield. Aliphatic thiols, either linear or cyclic, and even containing the sensitive ester group, also underwent efficiently the thioetherification reaction of **2a** (**3ja**-**3la**).

Furthermore, other structure-diverse thioethers were accessed by reacting the thiol **1a** with different alcohols. The thioether **3ab**, which originates from the use of naphthalene methanol as alkylating reagent, was isolated in 93% yield. The use of methyl-substituted and electron-rich benzyl alcohol derivatives resulted in the formation of the corresponding thioethers **3ac**, **3ad**, and **3ae** in excellent isolated yields. On the other hand, a slight decrease in the reaction efficiency was observed by using benzyl alcohols containing halogen substituents, which were well retained in the final thioethers (**3af-3ah**). Most likely, the electron-deficient nature of halogen groups reduces the alcohol reactivity limiting its ability to interact, and therefore to be activated, on the acid and basic sites present in $\{Mo_3S_4\}_n$. Moderate reactivity was also achieved by using an ester-functionalized benzyl alcohol, which could be overcome by increasing the catalyst loading. It is noteworthy that, in spite of the reducible character of the ester group, it was fully preserved, and the target thioether **3ai** was isolated in 88% yield. Exploring the scope further, reaction of **1a** with more challenging secondary alcohols as well as non-benzylic-type heterocyclic and allylic alcohol derivatives were investigated, resulting in good to moderate isolated yields of the thioethers **3aj**, **3ak**, and **3al** (83, 61, and 68%, respectively). On the contrary, low reactivity towards the desired thioether was achieved by using a non-activated aliphatic alcohol (Scheme S2).

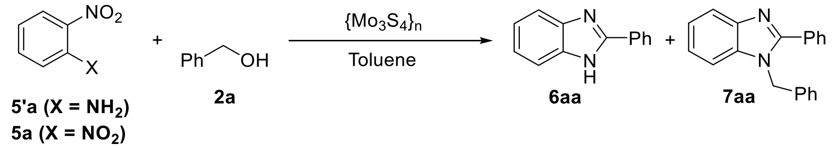
$\{Mo_3S_4\}_n$-Catalyzed Preparation of 2-substituted Benzimidazoles by Coupling Reaction of *o*-Dinitroarenes with Alcohols under Hydrogenative Conditions

After demonstrating good catalytic activity for the synthesis of thioethers by reaction of alcohols with thiols, we wondered if $\{Mo_3S_4\}_n$ would be able to catalyze borrowing hydrogen processes involving more hydrogen-demanding oxidized nucleophiles, such as for instance, nitro derivatives. More specifically, we were interested in the preparation of benzimidazoles, whose reaction mechanism in the presence of catalyst $\{Mo_3S_4\}_n$ preferentially involves the hydrogenation of the nitro to the amine functionalities, their condensation with the aldehyde (herein formed by alcohol dehydrogenation), and the cyclization of the imine intermediate followed by a dehydrogenation process, as previously reported (Schemes S3-S4).[46]

First, we investigated the coupling process of o-nitroaniline (**5'a**) with benzyl alcohol (**2a**) in the presence of $\{Mo_3S_4\}_n$, at 180 ºC, and under a N_2 atmosphere, reaction through which 2-phenyl-benzimidazole (**6aa**) was afforded in 95% yield together with traces (< 3%) of 1-benzyl-2-phenyl-

1H-benzo[d]imidazole (**7aa**) (Table 1, entry 1). Encouraged by this result and aimed to develop a more compacted synthetic route to benzimidazoles, we decided to explore the use of o-dinitrobenzene (**5a**), instead of o-nitroaniline (**5’a**), as a viable starting reagent. Under otherwise the same reaction conditions, but using a higher amount of **2a** (8 equiv.), **6aa** was obtained in 92% yield (Table 1, entry 2).

Table 1. Synthesis of 2-phenylbenzimidazole (**6aa**) by coupling reaction of nitro compounds (**5’a** or **5a**) with benzyl alcohol (**2a**) catalyzed by $\{Mo_3S_4\}_n$[a]



Entry	Substrate	Pressure N_2/H_2 (bar)	Temperature (°C)	Conversion (%)[b]	Yield 6aa (%)[b]
1[c]	**5’a**	10/0	180	>99	95
2[d]	**5a**	10/0	180	>99	92
3[e]	**5a**	10/0	180	>99	59
4[f]	**5a**	7/3	170	>99	97
5[f,g]	**5a**	7/3	170	>99	96
6[h]	**5a**	7/3	170	>99	94 (92)
7[i]	**5a**	7/3	170	>99	74
8[j]	**5a**	7/3	140	>99	86

[a]Catalyst activation: 180 ºC, 2h, vacuum; Reaction conditions: substrate (0.25 mmol), **2a** (1 mmol), $\{Mo_3S_4\}_n$ (30 mg), toluene (3 mL), 10 bar pressure (N_2+H_2), 16 h. [b]Determined by GC using hexadecane as an internal standard; Isolated yield in parenthesis. [c]Traces of **7aa** (< 3%) and 2,3-diphenylquinoxaline (< 2%) were detected. [d]**2a** (2 mmol); Traces of **7aa** (< 5%) and 2,3-

diphenylquinoxaline (< 2%) were detected. [e]**5'a** (22% yield) was detected. [f]Traces of **7aa** (< 2%) were detected. [g]**2a** (0.75 mmol). [h]**2a** (0.5 mmol). [i]**2a** (0.25 mmol); *o*-phenylenediamine (9%). [j]*o*-phenylenediamine and **5'a** (both in 3% yield) were detected.

Nevertheless, for atomic efficient reasons, we focused our efforts on developing a synthetic process without further increasing the amount of the alcohol **2a**. Hence, the preparation of 2-phenylbenzimidazole (**6aa**) by reaction of o-dinitrobenzene (**5a**) with **2a** (4 equiv.) was attempted in the presence of an extra supply of hydrogen pressure to guarantee the complete reduction of both nitro groups (Table 1, entries 3-4). Interestingly, the yield of the target benzimidazole **6aa** presented a volcano-type dependency with the hydrogen pressure, attaining the highest value of 97% yield at a 7/3 (N_2/H_2) bar pressure ratio (Figure S8). The increasing part of the volcano curve demonstrates that $\{Mo_3S_4\}_n$ works as a multifunctional catalyst able to conduct the hydrogen activation and dehydrogenation reactions in a one-pot fashion, both of them required to successfully achieve the desired benzimidazole product. On the other hand, the detrimental effect observed by further increasing the H_2 pressure likely originates from the reversibility nature of the alcohol dehydrogenation step under hydrogenative conditions (Scheme S5), and, most importantly, it might also suggest that both dehydrogenation and hydrogen activation processes take place on the same or, at least, on partially shared active sites.

Further optimization of reaction conditions allowed decreasing the amount of **2a** (up to 2 equiv.) without observing any significant negative impact on the yield of **6aa**, which was afforded in 94% yield (Table 1, entries 5-7). Remarkably, $\{Mo_3S_4\}_n$ was also active at lower temperature (140 ºC), but it showed lower reactivity toward the formation of the desired benzimidazole product (Table 1, entry 8). The use of other solvents different from toluene showed that o-xylene is a good solvent alternative for the investigated reaction, and again the utilization of coordinating solvents led to considerable detrimental results (Table S3).

With regard to the recycling experiments for this reaction, a decrease of the catalytic efficiency towards the formation of the desired benzimidazole **6aa** was observed along the reaction runs (Figure 2). In spite of this, excellent yields of **6aa** could be obtained for five consecutive runs at longer reaction times (Figure S9). Again, no molybdenum leached species were detected in the reaction filtrates. The characterization by ICP-OES measurements combined with elemental analysis of the recycled catalyst obtained after the complete sequence of runs (named $\{Mo_3S_4\}_n$-R''), unveiled that it has a smaller S/Mo molar ratio than the catalyst $\{Mo_3S_4\}_n$-R', previously obtained from the borrowing hydrogen C–S bond formation reaction run in the absence of an extra supply of hydrogen pressure (0.92 *vs* 1.09, respectively). Likewise, this decrease was also observed in the area ratio of bridging to apical sulfur species determined by XPS analysis (Figure S4 and Table S2; see also Figure S7 for electron microscopy characterization). These results clearly show that the use of hydrogen pressure promotes the vanishing of the unsaturated bridging sulfides rather than the apical ones, thus suggesting that the unsaturated bridging sulfides are the active centers where hydrogen is activated, as previously reported.[47]

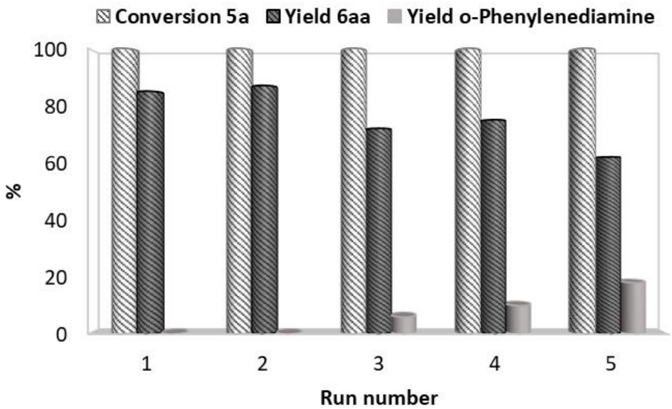


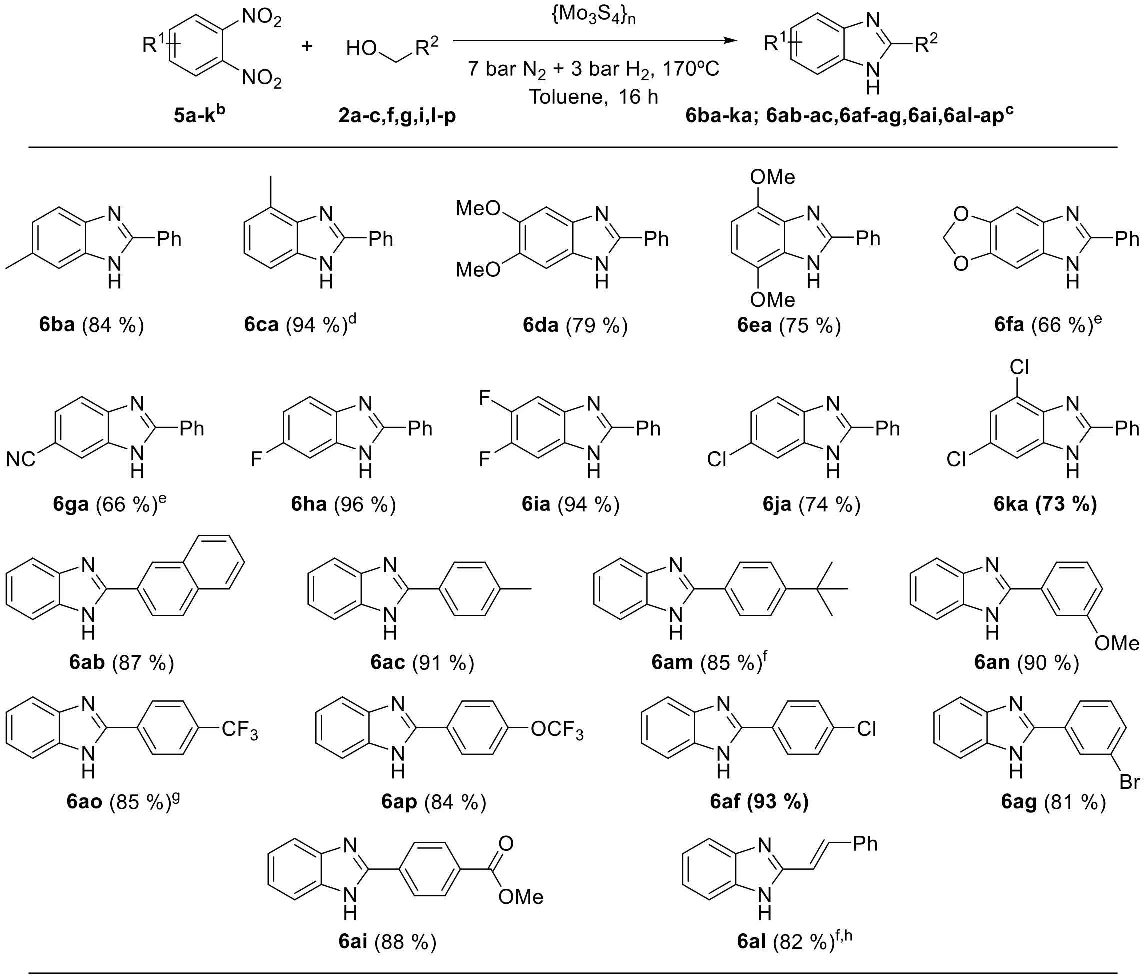
Figure 2. Recycling of catalyst $\{Mo_3S_4\}_n$ for the synthesis of **6aa** by coupling reaction of **5a** with **2a** in the presence of H_2. Catalyst activation: 180 ºC, 2 h, vacuum; Reaction conditions: **5a** (0.25

mmol), **2a** (0.5 mmol), $\{Mo_3S_4\}_n$ (30 mg), toluene (3 mL), 7 bar N_2 + 3 bar H_2, 170 ºC, 5 h. Conversions and yields determined by GC using hexadecane as an internal standard.

The substrate scope of this novel straightforward catalytic domino coupling process with regard to the functional group tolerance was first investigated by reacting different *o*-dinitroarenes with benzyl alcohol (**2a**) in the presence of hydrogen. As shown in Scheme 4, *o*-dinitroarenes functionalized with a methyl group afforded the corresponding benzimidazoles **6ba** and **6ca** in 84 and 94% yield, respectively. Good yields (75-79%) were also achieved for benzimidazoles **6da** and **6ea** furnished with metoxy groups attached to the dinitroarene-derived aromatic ring. When using a dinitroarene functionalized with a cyclic acetal, although a higher amount of the alcohol **2l** (4 equiv.) was needed, the desired benzimidazole **6fa** could be isolated in a moderate 66% yield. In the presence of a cyanide group, the coupling reaction proceeded in a similar manner, and to our delight, this sensitive moiety was well retained in the final benzimidazole product **6ga**. Fluoro-substituted benzimidazoles **6ha** and **6ia** were afforded in a comparably higher yield (≈ 95%) than those containing chloride groups (**6ja** and **6ka,** ≈ 74%), without observing dehalogenation products in any case.

Next, in order to demonstrate the general applicability of this methodology, we tested different benzyl alcohols as coupling partners. *O*-dinitrobenzene (**5a**) efficiently reacted with 2-naphthalenemethanol and various alkyl-substituted benzyl alcohols furnishing the desired benzimidazoles **6ab**, **6ac**, and **6am** in about 90% yield. In general, the introduction of both electron-donating and electron-withdrawing substituents on the aromatic ring of the benzyl alcohol had no significant influence on the efficiency of this methodology. Indeed, benzyl alcohols functionalized with the electron-donating metoxy group, as well as the electron-deficient trifluoromethyl, trifluorometoxy and halogen substituents displayed similar reactivity toward the formation of the corresponding benzimidazoles (**6an**, **6ao**, **6ap**, **6af**, **and 6ag**, respectively), which were isolated in remarkable high yields (81-93%). Again, dehalogenated products were not detected. Interestingly, the reducible ester group was fully retained in the desired product **6ai**, too. Furthermore, an allylic-type alcohol was also tested as coupling reagent and converted into the benzimidazole **6al** in 82% yield, in which the allylic C-C double bond was excellently retained.

Scheme 4. $\{Mo_3S_4\}_n$-catalyzed synthesis of benzimidazoles by reaction of various *o*-dinitroarenes with different alcohols[a]



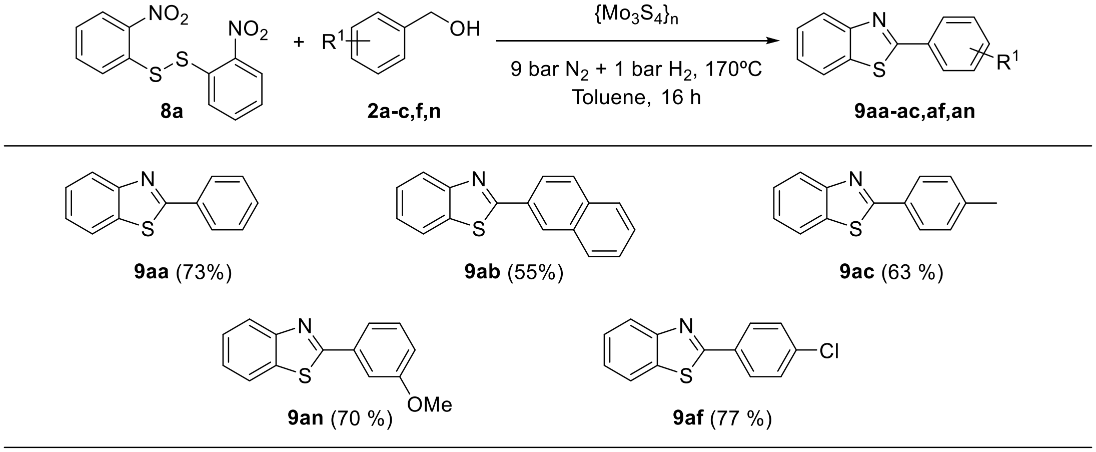
[a]Catalyst activation: 180 ºC, 2h, vacuum; Reaction conditions: **5a-k** (0.25 mmol), **2a-c,f,g,i,l-p** (0.5 mmol), $\{Mo_3S_4\}_n$ (30 mg), toluene (3 mL), 7 bar N_2 + 3 bar H_2, 170 ºC, 16 h. [b]Conversion

determined by GC using n-hexadecane as an internal standard. [c]Yield of isolated products is given with full conversion of **5a-k** unless otherwise stated. [d]3-methylbenzene-1,2-diamine (7%). [e]**2a** (1 mmol), 180 ºC. [f]*o*-phenylenediamine (4%). [g]*o*-phenylenediamine (9%) . [h]**2l** (1 mmol), 180 ºC.

$\{Mo_3S_4\}_n$-Catalyzed Coupling Reaction of Dinitrodiphenyl disulfides with Alcohols under Hydrogenative Conditions: Synthesis of Benzothiazoles

Based on the catalytic pattern of $\{Mo_3S_4\}_n$ observed for the formation of C-S and C-N bonds, we envisioned the possibility for a straightforward coupling reaction of 2,2'-dinitrodiphenyl disulfide (**8a**) with alcohols in the presence of molecular hydrogen to yield 2-arylbenzothiazoles (Scheme S6).[174-177] As shown in Scheme 5, benzyl alcohol (**2a**) and its derivatives functionalized with aryl, methyl, methoxy, and chloride substituents were successfully applied in this novel one-pot domino catalytic transformation affording the corresponding valuable benzene-fused heterocycles (**9aa**, **9ab**, **9ac**, **9an**, and **9af**, respectively) in moderate to good yields without further optimization.

Scheme 5. $\{Mo_3S_4\}_n$-catalyzed synthesis of 2-arylbenzothiazoles from 2,2'-dinitrodiphenyl disulfide, benzyl alcohols, and H_2[a]



[a]Catalyst activation: 180 ºC, 2h, vacuum; Reaction conditions: **8a** (0.125 mmol), **2b,c,f,n** (0.5 mmol), $\{Mo_3S_4\}_n$ (30 mg), toluene (3 mL), 9 bar N_2 + 1 bar H_2, 170 ºC, 16 h. [b]Conversion

determined by GC using n-hexadecane as an internal standard. ^{c}Yield of isolated products is given with full conversion of **8a** unless otherwise stated; Traces of the unclosed product, i.e. the thioaniline derivative, were detected in all reactions.

In-situ IR Spectroscopy Studies: Determining the role of Lewis and Basic Active Sites in $\{Mo_3S_4\}_n$

To shed light on the nature of the active sites responsible of the multifunctional character of the catalyst $\{Mo_3S_4\}_n$, different *in situ* IR spectroscopy studies were performed (Figure 3). Surprisingly, when the catalyst was treated with a N_2 flow at increasing temperature from 80 to 150 ºC (see the Experimental Section for further details and Figure S10), a broad band centered at 2188 cm^{-1} was perceived (Figure 3a). Notably, this IR band match well with the vibrational frequencies of S-H species,[182] whose formation likely arises from the decomposition of the hydrazine ligands attached to the outer coordination sphere of molybdenum atoms.[183] Further confirmation of the correct assignment of this band was obtained by isotopic S-D exchange by conducting an experiment flowing D_2. We have seen that the isotopic substitution not only took place on the S-H groups but also on the O-H functionalities present in $\{Mo_3S_4\}_n$ (see Scheme 1). As result, together with the absence of the S-H vibration band, the IR spectrum exhibits broad bands at 1553 cm^{-1}, associated with S-D bond species,[182] and at 2295, 2361, 2473, and 2595 cm^{-1}, corresponding to the vibration of O-D bonds. In the opposite, no changes were observed when the *in situ* IR experiment was performed with a H_2 flow, being the band associated with S-H species the only perceptible one.

In another sequential experiment, after treating the catalyst $\{Mo_3S_4\}_n$ at 150 ºC under a N_2 flow, benzyl alcohol (**2a**) was dosed under dynamic vacuum conditions and kept at this temperature for 2 h. In addition to the S-H vibration band at ~2188 cm^{-1}, a broad shoulder at 1652 cm^{-1} ascribed to

Mo-H species,[182] which are generated by alcohol to aldehyde dehydrogenation, was slightly discerned in the acquired IR spectrum (Figure 3b). On the contrary, it is remarkable that this band was not found in the experiment performed by flowing H_2 (Figure 3a). Subsequently, by cooling down to room temperature, a new band associated with the C=O vibration (1684 cm^{-1}) was also clearly observed in the IR spectrum, which signifies that adsorption of previously formed aldehyde species on the catalyst surface took placed. Interestingly, both, the C=O and Mo-H, IR bands rapidly disappeared when the temperature was increased up to 170 ºC, and only the C=O band was recovered by cooling down again to room temperature, thus inferring the re-adsorption of aldehyde species. The vanishing of the band associated to the Mo-H bond vibration with the increase of the temperature evidences the ability of these hydride species to be transferred, in this particular experiment, either by hydrogen spillover to form S-H species or by combination with these latter to generated molecular hydrogen.

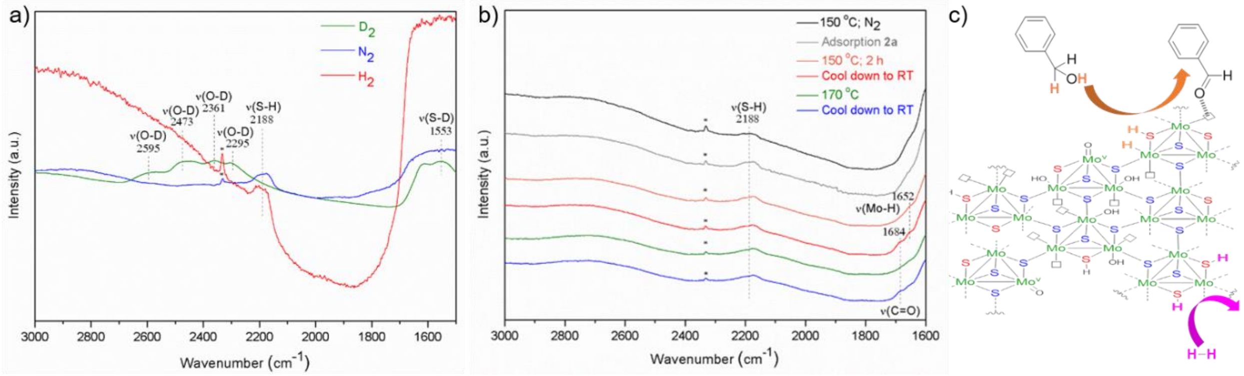


Figure 3. (a) IR spectra of $\{Mo_3S_4\}_n$ under a N_2 (blue), D_2 (green), and H_2 (red) flow at 150 ºC. (b) Evolution of the bands in the spectra of $\{Mo_3S_4\}_n$ for the sequential IR experiments at 150 ºC under a N_2 flow (black), after adsorption of **2a** (grey), by heating at 150 ºC for 2 h (orange), after cooling down to room temperature (red), by heating at 170 ºC (green), and after cooling down again to room temperature (blue). The band at 2330 cm^{-1}, marked with an asterisk, originates from residual CO_2 from the ambient. (c) Benzyl alcohol (**2a**) dehydrogenation to benzaldehyde over

Lewis acid and Lewis basic sites and H_2 activation over bridging sulfide ligands of activated $\{Mo_3S_4\}_n$.

From these results it can be concluded that, whereas H_2 activation takes places on non-coordinatively saturated sulfide species, i.e. on bridging sulfide ligands to form S-H,[47] the alcohol dehydrogenation involves the participation of these sulfide species as well as Mo centers with Lewis basic and Lewis acid character, respectively (Figure 3c). Moreover, it is also revealed that, once the alcohol is dehydrogenated, the resulting aldehyde is adsorbed/activated on Lewis acid Mo centers by interacting through the carbonyl group, thus being ready to condensate with the N- and S-derived nucleophiles. Interestingly, these spectroscopic results provide a clear explanation on the origin of the multifunctional behavior of $\{Mo_3S_4\}_n$. The fact that hydrogen and alcohols are activated on partially shared active sites is crucial to allow this catalyst to be active catalyzing single-step coupling reactions requiring both hydrogen activation and dehydrogenation reactions in a one-pot fashion.

CONCLUSIONS

In summary, we have demonstrated the multifunctional catalytic behavior of defective basal planes of a sulfur-deficient molybdenum disulfide-type catalyst ($\{Mo_3S_4\}_n$), which allows catalyzing not only conventional borrowing hydrogen processes, such as the thioetherification of alcohols, but also single-step coupling reactions requiring both hydrogen activation and dehydrogenation reactions in a one-pot fashion. More specifically, novel straightforward catalytic domino coupling processes have been established for the synthesis of benzimidazoles and benzothiazoles by reacting *o*-dinitroarenes and dinitrophenyl disulfide, respectively, with alcohols in the presence of molecular hydrogen.

The origin of this rare catalytic behavior has been investigated by in-situ IR spectroscopy studies, which revealed that hydrogen activation and alcohol dehydrogenation reactions take place on partially shared active sites. Whereas non-coordinatively saturated sulfide species, i.e. bridging sulfide ligands, are proposed to be the responsible active species for H_2 dissociation, the alcohol to aldehyde dehydrogenation involves the participation of these sulfide species as well as Mo centers with Lewis basic and Lewis acid character, respectively. In addition, Lewis acid molybdenum centers have resulted to play an important role by further enhancing the reactivity of the formed aldehyde intermediate species, thus promoting their condensation with the used N- and S-derived nucleophiles.

Importantly, by means this work we have broadened the toolbox of useful synthetic transformations mediated by defective basal planes-promoted molybdenum sulfide-derived catalysts. The aforementioned synthetic strategies, combining oxidized nucleophiles, alcohols, and molecular hydrogen, offer convenient alternatives to traditional reductive coupling reactions involving carbonyl compounds, and we are convinced that these will find increasing applications related with the use of renewable feedstocks.

EXPERIMENTAL SECTION

General procedure for the borrowing hydrogen thioetherification of alcohols

Reactions were performed in a 12 mL stainless steel autoclave equipped with a Teflon liner, a pressure controller, and a cannula provided with a valve system. Once the autoclave containing a stirring bar and the corresponding amount of the catalyst $\{Mo_3S_4\}_n$ (30 mg) was tightly sealed, it was connected to a pressure pump and kept under dynamic vacuum conditions at 180 ºC for 2 h in order to carry out the catalyst activation treatment. After activation, the autoclave was cooled down to room temperature, and, without opening the autoclave, it was sequentially charged through the cannula with the thiol (0.25 mmol), alcohol (0.75 mmol), *n*-hexadecane (30 μL) and toluene (3 mL). Then, the autoclave was three-times purged with N_2, pressurized to 10 bar N_2, and placed into a preheated aluminum block located on a heating plate, which was previously set to 180ºC and 700 rpm of stirring speed. After 16 h, the autoclave was cooled down to room temperature and carefully depressurized. The reaction mixture was diluted with ethyl acetate and an aliquot was taken for GC analysis. To determine the isolated yields, the diluted reaction mixture was filtered to separate off the catalyst, and then purified by preparative TLC plates silica gel (20 cm × 20 cm; 500 μm) with hexane/ethyl acetate mixtures affording the corresponding thioethers in the reported yields. The kinetic experiments were performed by taking samples (25 μL) through the cannula at different reaction times, and analyzed by GC. For the catalyst recycling experiments, the catalyst was recovered after each reaction by centrifugation and decantation, washed with ethyl acetate, diethyl ether, dried at ambient conditions, and used for the next run.

General procedure for the synthesis of 2-substituted benzimidazoles by coupling reaction of *o*-dinitroarenes with alcohols under hydrogenative conditions

The general procedure described above was applied with minor modifications. Once the catalyst is activated and the autoclave is at room temperature, it was charged through the cannula with a toluene (3 mL) solution containing the corresponding o-dinitroarene (0.25 mmol), the alcohol (0.5 mmol), and hexadecane (30 μL). Then, the autoclave was three-times purged with N_2, pressurized to 10 bar (7 bar N_2 + 3 bar H_2), and placed into a preheated aluminum block located on a heating plate, which was previously set to 170ºC and 700 rpm of stirring speed. After 16 h, the autoclave was cooled down to room temperature and carefully depressurized. The reaction mixture was diluted with ethanol and an aliquot was taken for GC analysis. To determine the isolated yields, the diluted reaction mixture was filtered to separate off the catalyst, and then purified by silica gel column chromatography (n-hexane/ethyl acetate) to give the isolated products in the reported yields. For the catalyst recycling experiments, the catalyst was recovered after each by centrifugation and decantation, washed with ethanol, diethyl ether, dried at ambient conditions, and used for the next run.

General procedure for the synthesis of benzothiazoles by coupling reaction of dinitrodiphenyl disulfides with alcohols under hydrogenative conditions

Again, the general procedure described above for the synthesis of benzimidazoles was applied with minor modifications. In this case, the injected toluene (3 mL) solution contained 2,2'-dinitrodiphenyl disulfide (0.125 mmol), the alcohol (1 mmol), and hexadecane (30 µL). Then, the autoclave was three-times purged with N_2, pressurized to 10 bar (9 bar N_2 + 1 bar H_2), and placed into a preheated aluminum block located on a heating plate, which was previously set to 170ºC and 700 rpm of stirring speed. After 16 h, the autoclave was cooled down to room temperature and carefully depressurized. The reaction mixture was diluted with ethyl acetate and an aliquot was taken for GC analysis. To determine the isolated yields, the diluted reaction mixture was filtered to separate off the catalyst, and then purified by preparative TLC plates silica gel (20 cm × 20 cm; 500 µm) with hexane/ethyl acetate mixtures affording the corresponding benzothiazoles in the reported yields.

FTIR in-situ analysis

IR spectra were recorded with a Thermo is50 FTIR spectrometer equipped with a DTGS detector and acquired at 4 cm^{-1} resolution (32 scans). A homemade quartz IR cell allowing in-situ treatments in controlled atmospheres and temperatures from 25 to 170 °C was connected to a vacuum system with gas dosing facility. Self-supported pellets (ca. 10 $mg \cdot cm^{-2}$) were prepared from the sample powders and treated at 80 ºC under dynamic vacuum conditions (10^{-4} mbar) for

1.5 h. After activation, the pellet was treated in N_2 flow (10 mL·min^{-1}) at 80 ºC, 120 ºC, and 150 ºC for 1 h at each of the temperatures. For the experiment with D_2 flow, the treatment of the pellet was the same. In the case of the experiment with H_2, after activation, the sample was only treated in H_2 flow (10 mL·min^{-1}) at 150 ºC for 1 h.

For the sequential IR experiment, the temperature was increased up to 150 ºC under a N_2 flow (10 mL·min^{-1}), immediately followed by evacuation (10^{-4} mbar) at this temperature. Then, benzyl alcohol (**2a**) was dosed at 1.8 mbar, kept at this temperature for 2 h, and cooled down to room temperature for 5 min. Next, the temperature was increased up to 170 ºC, and cooled down again to room temperature. IR spectra were recorded at each step.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge at https://pubs.acs.org.

General information on methods for characterization, extended catalytic data for the $\{Mo_3S_4\}_n$-catalyzed borrowing hydrogen thioetherification of alcohols, additional characterization of the five-times-recycled catalysts $\{Mo_3S_4\}_n$-R’ and $\{Mo_3S_4\}_n$-R’’, extended catalytic data for the $\{Mo_3S_4\}_n$-catalyzed synthesis of 2-substituted benzimidazoles, sustainability merits, characterization data of the isolated thioethers, benzimizadoles, and benzothiazoles.

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Authors Contribution

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

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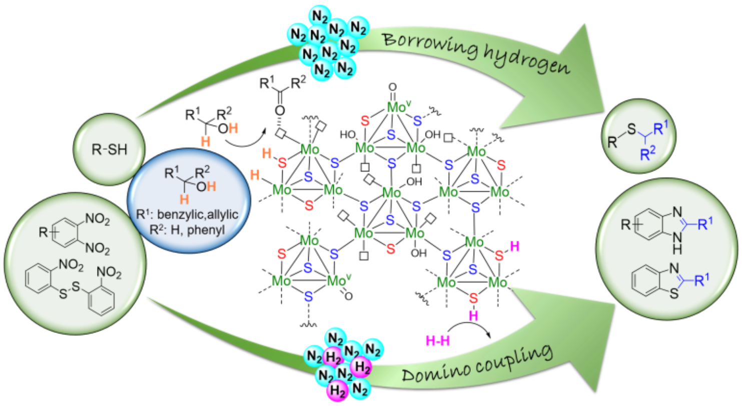
TOC/ABSTRACT GRAPHIC



SYNOPSIS**:** Complementary to known reductive reactions using carbonyl compounds, straightforward domino synthetic processes involving alcohols are established by applying a defect engineered molybdenum sulfide catalyst.