RESEARCH ARTICLE doi.org/10.1002/adsc.202401387 ADVANCED SYNTHESIS & CATALYSIS

γ-Terpinene: Biorenewable Reductant for the Molybdenum-Catalyzed Reduction of Sulfoxides, *N*-Oxides and Nitroarenes

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Manuscript received: November 8, 2024; Revised manuscript received: January 16, 2025;
Version of record online: Februar 5, 2025

Supporting information for this article is available on the WWW under https://doi.org/10.1002/adsc.202401387

Abstract: A molybdenum-catalyzed deoxygenation of sulfoxides, pyridine and quinoline *N*-oxides, *N*-hydroxybenzotriazoles, as well as the reduction of nitroarenes to anilines, has been developed using monocyclic terpenes such as γ-terpinene as an environmentally benign hydrogen surrogate. The only byproducts generated are water and *p*-cymene, under neat reaction conditions in which the terpene acts as both solvent and reducing agent. These features make this approach a highly attractive and sustainable alternative for the reduction of S-O and N-O containing compounds. Additionally, the reaction exhibited excellent chemoselectivity, tolerating a wide variety of functional groups.

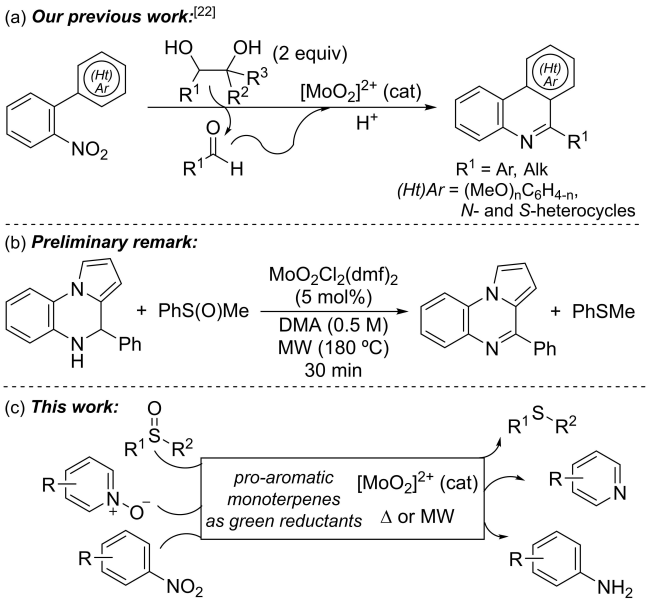
Keywords: γ-terpinene; molybdenum; reduction; sulfoxides; nitroarenes

Introduction

The efficient and economical utilization of renewable resources to produce value-added chemicals is crucial to developing synthetic methods.[1] In this sense, designing more efficient and sustainable reduction procedures, such as those performed in bio-derived solvents or under solvent-free conditions, combined with greener reducing agents, has garnered increasing attention.[2] For example, despite notable advances in the reduction of sulfoxides to sulfides,[3] the development of more sustainable approaches still remains an intriguing area of research.[4] Similarly, the more challenging reduction of inexpensive and readily available nitroarenes is a key reaction under constant evolution that enables the synthesis of valuable aromatic amines, which are pivotal intermediates in the production of nitrogen-containing biologically active compounds, dyes, polymers, agrochemicals,[5]… Molecular hydrogen is typically regarded as the reducing agent of choice in different reduction reactions, such as the hydrogenation of unsaturated compounds, given its inherent atom economy.[6] Nevertheless, hydrogen atom transfer (HAT) reactions have also emerged as appealing reduction strategies, offering notable control over regio-, chemo- and stereoselectivity[7] without requiring the use of highly flammable hydrogen gas. In this field, pro-aromatic reagents have proved to be suitable reducing agents, with Hantzsch esters demonstrating excellent reactivity and being among the most widely used systems.[8] However, simpler 1,4-cyclohexadienes have gained broader application in recent years.[9] Among these, γ-terpinene, a monocyclic terpene derived from biomass feedstocks,[10] has emerged as an efficient hydrogen atom source in a few recent examples.[11,12] In this sense, Lewis acid electron-deficient triarylboranes or frustrated Lewis pairs catalyze the ionic transfer hydrogenation of imines[11a] or silyloxyalkenes,[11b] respectively. Additionally, carbon-centered radicals have been efficiently reduced using γ-terpinene as a green and sustainable reductant.[12] Despite these elegant examples, the use of γ-terpinene and related terpenes as green reducing agents remains underexplored, particularly in deoxygenation processes.

On the other hand, deoxygenation reactions catalyzed by inexpensive and accessible dioxomolybdenum complexes have shown broad applicability in various transformations.[13] Our group has studied the deoxygenation of substrates containing the $^{+}$S–O^{-} and $^{+}$N–O^{-} units,

employing different reducing agents such as phosphites,[14] phosphines,[15] or thiols.[16] Similarly, silanes,[17] boranes,[18] and molecular hydrogen (50 bar)[19] have proved to be effective in the deoxygenation of sulfoxides and *N*-oxides, and even nitroarenes when molecular hydrogen was used.[19b] More recently, we discovered that glycols could serve as more environmentally benign reductants.[20] Besides, this approach enables the design of efficient cascade reactions.[21] Following a waste recycling strategy, we have reported a catalytic domino process for the direct synthesis of several types of *N*-polyheterocycles from nitroarenes and environmentally friendly glycols (Scheme 1a).[22] In this report, while conducting mechanistic studies to explain the use of only two equivalents of glycols as reductants, we observed that 4-phenyl-4,5-dihydropyrrolo[1,2-*a*]quinoxaline could efficiently function as a reducing agent in the presence of a Mo(VI) catalyst, as shown by the deoxygenation of methyl phenyl sulfoxide to the corresponding sulfide (Scheme 1b). Based on this result, and in search of greener oxygen-acceptors, we envisaged that pro-aromatic monoterpenes could serve as effective reducing agents for molybdenum-catalyzed deoxygenation reactions, considering their availability, low cost, and bio-renewable nature (Scheme 1c).



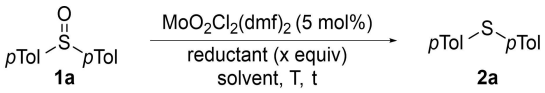
Scheme 1. Previous and present work.

Results and Discussion

Reduction of Sulfoxides

Initially, *p*-tolyl sulfoxide (**1 a**) was selected as the model starting material (Table 1), using DMA as solvent, and a screening of several potential reducing agents was conducted (see SI for more details). Different commercially available monoterpenes, such as γ-terpinene, α-phellandrene, α-terpinene, and terpinolene demonstrated high efficiency, achieving complete conversion of **1 a** to sulfide **2 a** under conventional heating at 180 °C (entries 1-4). Interestingly, limonene and bicyclic β-pinene were also reactive, though less effective than the previously mentioned monoterpenes, even with extended reaction times (entries 5 and 6). For comparison, Hantzsch ester was

Table 1. Optimization of the Mo-catalyzed reduction of sulfoxide **1 a** with monoterpenes.[a]



Entry	Reductant	x	Solvent	T [°C]	t (h)	Conversion [%][b]	**2 a** [%][b]
1	γ-terpinene	2	DMA	180	8	100	>95
2	α-phellandrene	2	DMA	180	8	100	>95
3	terpinolene	2	DMA	180	8	100	>95
4	α-terpinene	4	DMA	180	8	100	>95[c]
5	(+)-limonene	2	DMA	180	19	43	41
6	β-pinene	2	DMA	180	19	50	47[d]
7	Hantzsch ester	2	DMA	180	8	52	48
8	γ-terpinene	2	DMA	160	8	85	80[d]
9	γ-terpinene	12	–	160	2	100	>95
10	γ-terpinene	6	–	160	2	100	>95
11[e]	γ-terpinene	12	–	160	0.3	100	>95

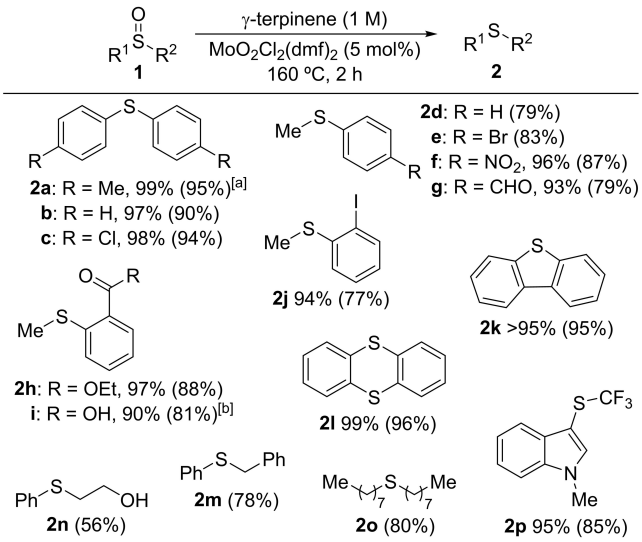
[a] Reaction conditions: **1 a** (0.3 mmol), under air.
[b] Determined by ^{1}H-NMR analysis using 1,3,5-trimethoxybenzene as internal standard.
[c] When 2 equiv. of α-terpinene were used a 75% conversion was observed.
[d] Trace amounts of di-*p*-tolyl sulfone (**S1a**) were detected as byproduct.
[e] Performed under microwave irradiation.

tested as well, but under these conditions, only about 50% conversion was observed (entry 7). This initial screening of pro-aromatic oxygen-acceptors prompted us to select γ-terpinene as the optimal reductant due to its low cost, wide availability, and the generation of *p*-cymene as the sole byproduct. Reducing the reaction temperature resulted in slightly lower conversion and the appearance of di-*p*-tolyl sulfone (**S1a**) as by-product, likely due to a competitive disproportionation reaction of the sulfoxide (entry 8). At this point, we wondered if γ-terpinene might function not only as reducing agent but also as the solvent in the reaction. Gratifyingly, when 12 equiv. of the monoterpene (0.5 M) were added, complete conversion of the sulfoxide was achieved in just 2 h (entry 9). Additionally, reducing the amount of γ-terpinene to 6 equiv. (1 M) still gave satisfactory results, with a quantitative yield of **2 a** (entry 10). Under these conditions, no sulfone byproduct was detected. Finally, the use of microwave irradiation enabled the shortening of the reaction time to 20 min with equal performance (entry 11).

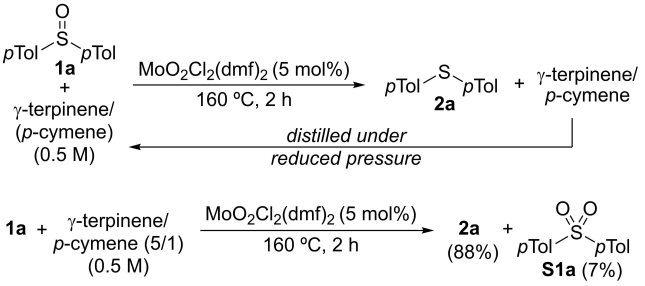
With the optimized reaction conditions established (Table 1, entry 10), the substrate scope was explored (Scheme 2). First, sulfoxides bearing two aromatic groups were subjected to the reaction conditions, yielding the corresponding sulfides **2 a-c** in excellent yields. Next, alkyl aryl sulfoxides were studied. Not only could unsubstituted methyl phenyl sulfoxide (**1 d**) be effectively deoxygenated, but substrates with sensitive bromine (**1 e**) and iodine (**1 j**) atoms at different positions were also well tolerated, as was the electron-withdrawing and potentially reducible nitro group (**1 f**), which remained unaffected under the reaction conditions. Notably, sulfoxides containing different carbonyl groups were reduced selectively in high yields, maintaining unaltered aldehyde (**1 g**), ester (**1 h**), and carboxylic acid (**1 i**) functional groups. Furthermore, the reduction of heteroaromatic substrates **1 k** and **1 l** led to the formation of dibenzothiophene **2 k** and thianthrene **2 l** in good yields. In addition, benzylic sulfoxide **1 m** was efficiently reduced by γ-terpinene, and a free hydroxyl group was tolerated in the sulfoxide scaffold, although leading to a moderate yield of **2 n**. Furthermore, di-*n*-octyl sulfide (**2 o**) was obtained from the reduction of dialkyl sulfoxide **1 o** in high yield. Finally, indole- functionalized trifluoromethyl sulfoxide **1 p** was efficiently deoxygenated in high yield. Interestingly, very high yields (>90% by ^{1}H NMR) were obtained in most cases for the crude sulfoxides, which were isolated in nearly pure form following the removal of excess γ-terpinene.[23]

Furthermore, this process could be scaled up for the multigram preparation of sulfides. As an example, bis(*p*-tolyl)sulfoxide (**1 a**) (4.61 g, 20 mmol) was efficiently deoxygenated with γ-terpinene (20 mL) yielding **2 a** (4.03 g, 94%). In addition, the catalyst loading could be lowered to 1 mol%.

Considering that only one equiv. of the reducing agent, γ-terpinene, is required for the complete deoxygenation of sulfoxides **1**, producing the corresponding sulfides **2** and *p*-cymene as the oxidized byproduct, the sustainability of this catalytic process could be improved by reusing the remaining γ-terpinene/*p*-cymene mixture in subsequent catalytic cycles. We carried out a recycling study with model substrate **1 a** (Scheme 3). After completion of the first reaction under the reported conditions at 0.5 M, the remaining solvent mixture of γ-terpinene and *p*-cymene was distilled under reduced pressure and reused as a reducing agent in a second experiment, achieving an excellent yield (>95%) of the target sulfide **2 a**. The



Scheme 2. Scope of sulfoxide reduction. Reaction conditions: **1** (0.5-1 mmol) in γ-terpinene (1 M); under air; yields of the almost pure crude sulfides determined by ^{1}H-NMR analysis using internal standards after removal of excess γ-terpinene; isolated yields of pure sulfides after column chromatography in brackets. [a] 94% (4.03 g) of **2 a** was obtained from 20 mmol of **1 a** with 1 mol% of catalyst. [b] Reaction time = 5 h.



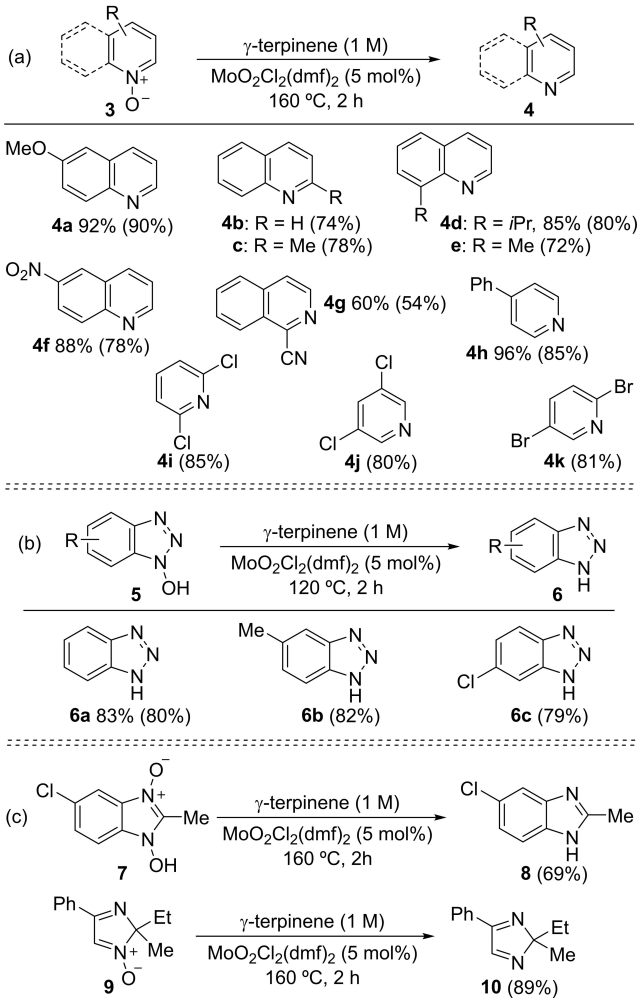
Scheme 3. Recyclability of the reducing agent (γ-terpinene) and usefulness of γ-terpinene/*p*-cymene mixtures as reductant.

process was repeated once more with the same efficiency.[24] The limit of the utility of γ-terpinene/*p*-cymene mixtures was established by independently testing various mixtures. Complete conversions and nearly quantitative yields of **2 a** were obtained until a 5/1 γ-terpinene/*p*-cymene ratio was used. In this case, trace amounts of bis(*p*-tolyl)sulfone (**S1a**) were observed, thus determining the limit of the γ-terpinene/*p*-cymene ratio that can be efficiently employed for the deoxygenation of sulfoxides.[24]

Deoxygenation of *N*-oxides and *N*-hydroxybenzotriazoles

Taking into account the excellent directing effect of *N*-oxides in C-H functionalization reactions,[25] the development of suitable chemoselective protocols for the removal of oxygen from *N*-oxides continues to be an active area of research.[26] To expand the scope and demonstrate the applicability of our Mo(VI)-catalyzed reduction of sulfoxides **1** with γ-terpinene, we decided to apply this methodology to the deoxygenation of *N*-oxides and related *N*-hydroxybenzotriazoles (Scheme 4). Based on the conditions previously developed for sulfoxides, several experiments were performed with 6-methoxyquinoline *N*-oxide (**3 a**), achieving complete deoxygenation after 2 h of heating at 160 °C in γ-terpinene (1 M), used as both solvent and reducing agent. After optimizing the reaction, various quinoline *N*-oxides bearing different functional groups were tested, resulting in good to high isolated yields of the desired quinolines, including those functionalized with methoxy (**4 a**), alkyl (**4 c-e**), and electron-withdrawing groups such as nitro (**4 f**) and cyano (**4 g**). Additionally, pyridine *N*-oxides with phenyl (**3 h**), as well as chlorine and bromine substituents (**3 i-k**), also proved to be suitable substrates for this reduction process, yielding the corresponding pyridines **4 h-k** in high yields (Scheme 4a).

In addition, a few experiments were carried out using *N*-hydroxybenzotriazoles **5**, considering that their prototropy could lead to an *N*-oxide tautomer (Scheme 4b).[27] Accordingly, a brief optimization of the reduction of *N*-hydroxybenzotriazole (**5 a**) demonstrated that heating at 120 °C for 2 h was sufficient to achieve complete N-OH→N-H reduction of the starting material. We carried out the deoxygenation not only for the model substrate **5 a** but also for compounds containing a methyl group (**5 b**) and a chlorine substituent (**5 c**), which yielded the corresponding benzotriazoles **6 a-c** in very high yields. These results are noteworthy because it is known that the position of the *N*-oxide/*N*-hydroxy tautomeric equilibrium is more shifted toward the less polar *N*-oxide in polar solvents, whereas γ-terpinene is highly apolar.[28] Finally, we explored the reduction of other heterocycles containing the $^{+}$N-O^{-} unit using the developed procedure (Scheme 4c). For example, 1-hydroxy-1*H*-benzimidazole derivative **7** was doubly reduced to the corresponding benzimidazole **8** with good yield, and the efficient deoxygenation of 2*H*-imidazole 1-oxide **9** to 2*H*-imidazole **10** was also achieved.



Scheme 4. Deoxygenation of *N*-oxides and *N*-hydroxybenzotriazoles. Reaction conditions: **3**, **5**, **7** or **9** (0.5-0.7 mmol) in γ-terpinene (1 M); under air; yields of the almost pure crude products determined by ^{1}H-NMR analysis using internal standards after removal of excess γ-terpinene; isolated yields of pure compounds after column chromatography in brackets.

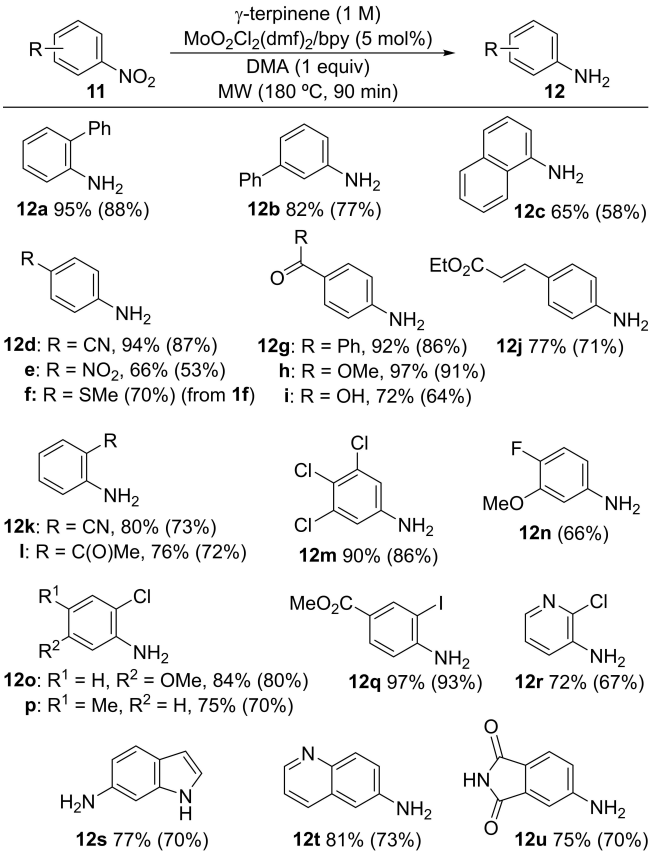
Reduction of Nitroarenes

On the other hand, the development of general and efficient methods for synthesizing aromatic amines from nitroarenes, which are abundant and cheap chemical raw materials, is an active area of research. In this context, the chemoselective reduction of nitro(hetero)arenes is a significant challenge due to the

harsh reaction conditions often required, which lead to selectivity and functional group tolerance issues.[29]

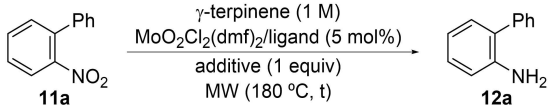
To address this goal, 2-nitrobiphenyl (**11 a**) was selected as the model substrate for the optimization process (Table 2). Under the same conditions employed for the reduction of sulfoxides **1**, but using microwave irradiation to accelerate the process, only a low conversion of the nitroarene was observed (entry 1). Considering the potential positive effect of adding an external ligand such as 2,2'-bipyridine, in related transformations,[15c] we decided to run the reaction in its presence. However, low conversion was again observed, likely due to the low solubility of the starting material in γ-terpinene (entry 2). Increasing the amount of terpene did not improve the result (entry 3). To enhance the polarity of the reaction medium, 1 equiv. of DMA was added as an additive, resulting in a significant improvement in both conversion and yield of the desired aniline **12 a** (entry 4). Gratifyingly, complete conversion and an excellent yield of **12 a** were achieved by extending the reaction time to 90 min (entry 5). The crucial role of the external ligand was confirmed, as an experiment without bpy under the same conditions resulted in only moderate conversion (entry 6). Finally, other alternatives were evaluated as potential additives instead of DMA, but none of them led to complete reactions (entries 7-9).

With these optimal conditions established (Table 2, entry 5), we proceeded to study the substrate scope for this nitroarene reduction (Scheme 5). The reaction worked efficiently for nitrobiphenyls **11 a,b**, as well as for nitronaphthalene **11 c**. Notably, sensitive and potentially reducible electron-withdrawing functional groups, such as cyano, ketone, ester and even free carboxylic acid, were well tolerated as demonstrated



Scheme 5. Nitroarene scope. Reaction conditions: **11** (1 mmol) and DMA (93 µL, 1 mmol) in γ-terpinene (1 M), under microwave irradiation; under air; yields of the almost pure crude products determined by ^{1}H-NMR analysis using internal standards after removal of excess γ-terpinene; isolated yields of pure compounds after column chromatography in brackets.

Table 2. Optimization of the Mo-catalyzed reduction of 2-nitrobiphenyl (**11 a**) with γ-terpinene.[a]



Entry	Ligand	Additive	t (min)	Conversion [%][b]	**2 a** [%][b]
1	–	–	60	42	38
2	bpy	–	60	45	35
3[c]	bpy	–	60	48	39
4	bpy	DMA	60	73	67
5	bpy	DMA	90	100	95
6	–	DMA	90	49	41
7	bpy	Dimethyl isosorbide	90	40	38
8	bpy	cyrene	90	55	35
9	bpy	γ-valerolactone	90	72	70

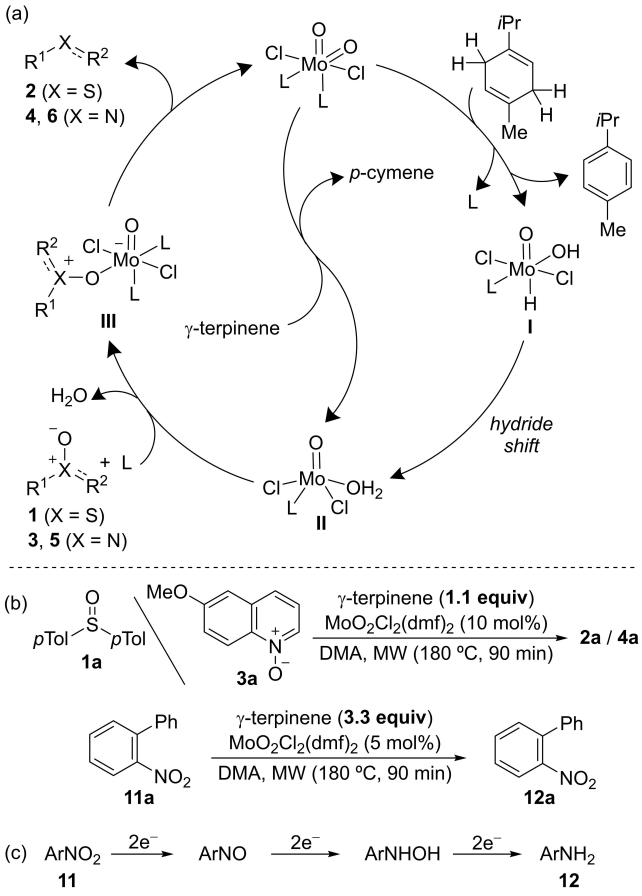
[a] Reaction conditions: **11 a** (0.3 mmol), under air.
[b] Determined by ^{1}H-NMR analysis using 1,3,5-trimethoxybenzene as internal standard.
[c] 12 equiv. of γ-terpinene (0.5 M) were used.

by the high-yielding reductions of **11 d,g-i**. Remarkably, selective monoreduction of 1,4-dinitrobenzene **11 e** was achieved, affording a moderate isolated yield of 4-nitroaniline **12 e**. Interestingly, whereas the sulfoxide group in methyl 4-nitrophenyl sulfoxide (**1f**) could be chemoselectively reduced to thioether **2f**, under the conditions reported in Scheme 2, its treatment under the present conditions led to both functional groups (sulfoxide and nitro) reduction, yielding 4-methylthioaniline (**12f**) in good yield. Additionally, the nitro group on ethyl 4-nitrocinnamate (**11j**) was also selectively reduced. These EWG groups were also tolerated in the *ortho*-position (**11k,l**) without significantly interfering in the reduction process. The method was also compatible with halide-functionalized nitroaromatics, regardless of the halide substituent's location, leading to haloanilines **12m-q** in high to excellent yields. Electron-donating groups were also well-tolerated, as demonstrated with nitroarenes **12n-p**. Finally, nitroheteroaromatics were tested, and the corresponding aromatic amines containing pyridine (**12r**), indole (**12s**), quinoline (**12t**), and phthalimide (**12u**) scaffolds were isolated in good yields. These results further enhance the applicability of γ-terpinene as a reducing agent under molybdenum-catalysis.[30]

Mechanistic Proposal

A plausible mechanistic proposal for this catalytic reaction sequence is depicted in Scheme 6a. First, $MoO_2Cl_2(dmf)_2$ would react with γ-terpinene. After the abstraction of a hydrogen atom by one of the oxo ligands of the catalyst, accompanied by the corresponding electron movement and hydride donation to the molybdenum center, intermediate **I** would be generated, along with the release of the oxidized byproduct, *p*-cymene. Based on previous work by Royo and co-workers,[19] we propose the formation of this transient species considering the tendency of MoO_2Cl_2 complexes to experience [2 + 2] addition reaction with H_2, generating metal hydrides similar to **I**, which were proposed as intermediates in related processes using H_2 as reductant. Following the hydride shift, intermediate **II**, containing a Mo(IV) metal center, would form. Alternatively, this reduced species could be accessed without involving the hydride intermediate.[31] The oxomolybdenum(IV) species **II** could then coordinate with an *O*-atom donor, such as sulfoxides, giving rise to intermediate **III** (X = S) and releasing a water molecule. Finally, the deoxygenation of sulfoxide **1** to the corresponding thioether **2** would regenerate the Mo(VI) catalyst. Similarly, *N*-oxides **3** and **5** would be deoxygenated to yield pyridines **4** and benzotriazoles **6** via the corresponding intermediate **III** (X = N).

On the other hand, we have confirmed the equivalents of reductant needed for these reductions with γ-terpinene (Scheme 6b) using DMA as solvent and microwave irradiation. So, as expected, both sulfoxide **1a** and *N*-oxide **3a** were reduced with 1 equiv of γ-terpinene, whereas the reduction of nitroarene **11 a** requires 3 equiv. of γ-terpinene, producing the corresponding aromatic amine **12 a**, again with *p*-cymene and water as byproducts. DFT studies previously conducted on the reduction of nitroaromatics **11** with pinacol[32] confirmed that the three reductive steps needed to produce **12** would involve nitrosoarenes and *N*-arylhydroxylamines as intermediates (Scheme 6c).



Scheme 6. Proposed mechanism.

Conclusions

In summary, we have described for the first time the use of γ-terpinene as a novel biorenewable hydrogen surrogate for the reduction of sulfoxides, *N*-oxides, *N*-hydroxybenzotriazoles and even the more challenging nitroarenes in a reduction reaction catalyzed by a dichlorodioxomolybdenum(VI) complex. This represents one of the scarcely reported applications where monoterpenes are used as sustainable and low-cost reagents for promoting an organic transformation, rather than as building block intermediates. Furthermore, no additional solvent is required to achieve

deoxygenation in high yields. Remarkably, this methodology offers several key advantages, including generally high isolated yields, excellent chemoselectivity, tolerance to potentially reducible functional groups, and compatibility with the presence of air and water, all within short reaction times.

Experimental Section

Mo-catalyzed Reduction of Sulfoxides 1 with γ-Terpinene

In a 10 mL reaction vessel, the corresponding sulfoxide **1** (0.5-1 mmol), γ-terpinene (0.5-1 mL, 1 M), and $MoO_2Cl_2(dmf)_2$ (8.6-17.3 mg, 5 mol%) were combined. The vessel was sealed with a septum, and the reaction mixture was stirred at 160 °C for 2 h under conventional heating. After cooling to RT, the mixture was concentrated under reduced pressure. Although most sulfides were obtained in nearly pure form following the almost complete removal of γ-terpinene and *p*-cymene, they were further purified using a silica pad or column chromatography on silica gel (eluent hexane/EtOAc) to isolate them in a pure form and ensure proper characterization.

Mo-catalyzed Reduction of N-Oxides 3, 9 and N-hydroxides 5, 7 with γ-Terpinene

In a 10 mL reaction vessel, the corresponding heteroaromatic *N*-oxide or *N*-hydroxide **3**, **5**, **7** or **9** (0.5-0.7 mmol), γ-terpinene (0.5-0.7 mL, 1 M), and $MoO_2Cl_2(dmf)_2$ (8.6-12.1 mg, 5 mol%) were combined. The vessel was sealed with a septum and the reaction mixture was stirred at 160 °C (for *N*-oxides and *N*-hydroxides **3**, **7** and **9**) or 120 °C (for *N*-hydroxides **5**) for 2 h under conventional heating. The mixture was then cooled to RT and concentrated under reduced pressure. The residue was purified either by a silica pad or flash column chromatography on silica gel (eluent: hexane/EtOAc) yielding the desired deoxygenated *N*-heterocycles **4**, **6**, **8** or **10**.

Mo-catalyzed Reduction of Nitroarenes 11 with γ-Terpinene

In a 10 mL reaction vessel, the corresponding nitroarene **11** (1 mmol), γ-terpinene (1 mL, 1 M), bpy (7.8 mg, 5 mol%), $MoO_2Cl_2(dmf)_2$ (17.3 mg, 5 mol%) and DMA (93 µL, 1 mmol) were combined. The vessel was sealed with a septum and the reaction mixture was stirred at 180 °C for 90 min under microwave irradiation. After cooling to RT, the mixture was concentrated under reduced pressure. Although most of the anilines **12** were obtained in nearly pure form after the removal of γ-terpinene, *p*-cymene, and DMA, they were further purified using a silica pad or column chromatography on silica gel (eluent: hexane/EtOAc) to isolate them in a pure state for characterization.

Supporting Information

The authors have cited additional references within the Supporting Information.[33-35]

Acknowledgements

Financial support from Junta de Castilla y León and FEDER (BU028P23) and Ministerio de Ciencia, Innovación y Universidades (PID2020-115789GB–C21, PID2023-148198NB–C21, and PDC2021-115789GB–C21) is gratefully acknowledged. R.H.-R. thanks Ministerio de Ciencia, Innovación y Universidades for a FPU predoctoral contract. M.S. thanks Junta de Castilla y León and FEDER for a postdoctoral contract. S.S.-P. thanks Ministerio de Ciencia, Innovación y Universidades and "NextGenerationEU"/PRTR EU for a Ramón y Cajal contract (RYC2021-031533-I).

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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