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# Expedient tandem dehydrogenative alkylation and cyclization reactions under Mn(I)-catalysis†

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Sustainable chemical production requires fundamentally new types of catalysts and catalytic technologies. The development of coherent and robust catalytic systems based on earth-abundant transition metals is essential; however, it is extremely challenging. Herein, an expedient divergence strategy for tandem dehydrogenative alkylation and cyclization reactions of hydrazides is reported under manganese catalysis. Using abundantly available alcohols (including MeOH, EtOH) and earth-abundant metal catalysts with water as a sole by-product makes the present strategy more sustainable and affordable. Interestingly, unsymmetrical selective deuterium incorporation is also presented for the first time. Several selective bond activation/formation reactions occur sequentially *via* amine–amide metal–ligand cooperation.

## Introduction

*N*,*N*-Disubstituted acyl hydrazides and their derivatives are exceptional synthetic scaffolds that have been widely used for the synthesis of agrochemicals, polymers, pharmaceuticals, and bioactive functional materials.[1] In particular, a significant number of *N*,*N*-disubstituted acyl hydrazide analogues having biological activities have been discovered, including antibacterials, antifungals, anthelmintics, antitumors, PG12 agonists, papillomavirus inhibitors, and pesticides (Scheme 1).[2] Notably, cyclic hydrazide organic moieties are highly prominent building blocks and play a significant role in drug synthesis.[3] Consequently, the progress on synthetic strategies that can lead to *N*,*N*-disubstituted and cyclic hydrazide derivatives under an eco-benign approach has gained much more attention in medicinal science.

Typically, the *N*,*N*-disubstitution of acyl hydrazides has been achieved by the direct treatment of acyl hydrazides with alkyl halides in the presence of a stoichiometric amount of base.[4] Substituted acyl hydrazides can also be prepared by the direct reaction of acyl halides with disubstituted hydrazines.[5] In the recent past, *N*-alkylation of hydrazides and *N*-acyl-*N*,*N*-disubstituted hydrazines has also been reported.[6] This approach normally requires multistep synthesis, harsh reaction conditions, and harmful reagents, and generates copious amounts of waste. Thus, the development of an eco-benign, sustainable and affordable method for the synthesis of substituted and cyclized hydrazides is highly desirable.

Recently, the hydrogen auto-transfer (HA) strategy utilizing abundantly available renewable feedstock alcohols for selective C–C or C–N bond formation has been highly sought after.[7] The transition metal-catalyzed C–N coupling of carbonyl compounds *via* alcohol activation through the HA strategy overcomes the limitations of the classical approach.[8,9] Overall, the HA strategy is redox neutral and eliminates water as the only by-product. However, *N*,*N*-dialkylation *via* double borrowing hydrogenation is rarely reported. In 2017, the research group of Zhou reported the nickel/bis(dicyclohexylphosphine)propane (dcpp) and nickel/(*S*)-binapine complex catalyzed simple *N*-alkylation of acyl hydrazides using secondary alcohols under acidic conditions.[10] In 2020, Gunanathan and co-workers developed the first noble-metal catalyzed *N*,*N*-dialkylation of acyl hydrazides with alcohols using a Ru-complex.[11] Very recently, the research group of Renaud and Poater reported a diaminocyclopentadienone ruthenium tricarbonyl complex-catalyzed synthesis of mono- or dialkylated acyl hydrazide compounds using the borrowing hydrogen strategy.[12]

Of late, there have been many massive benefits for studying the progress of catalytic approaches based on earth-abundant base-metal catalysts in sustainable catalysis. Manganese is known to be the third most earth-abundant transition element and found to have manifold applications in dehydrogenation and hydrogenation reactions.[13] To the best of our knowledge, first-row 3d-transition metal catalyzed *N*,*N*-dialkylation (symmetrical and unsymmetrical) and cyclization of acyl hydrazides using alcohols and diols, respectively, have been

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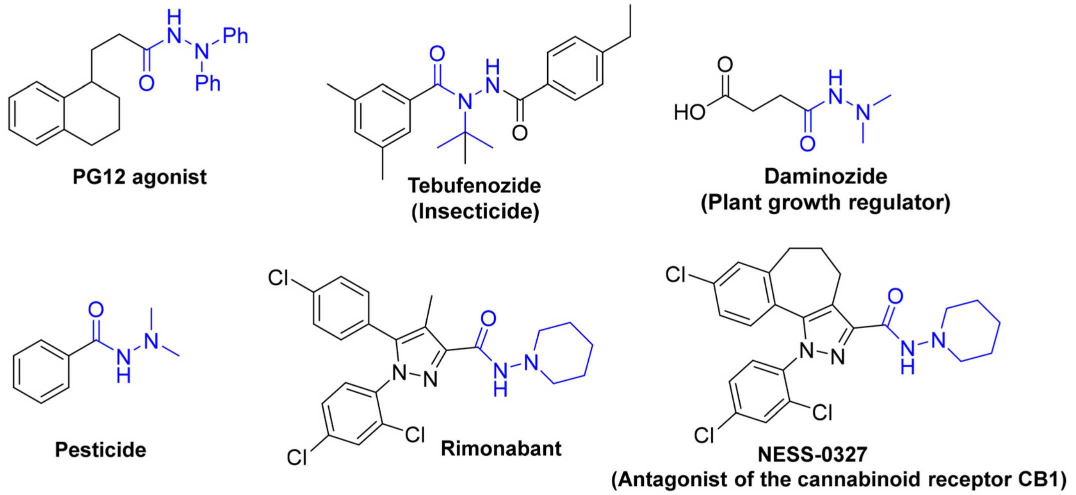
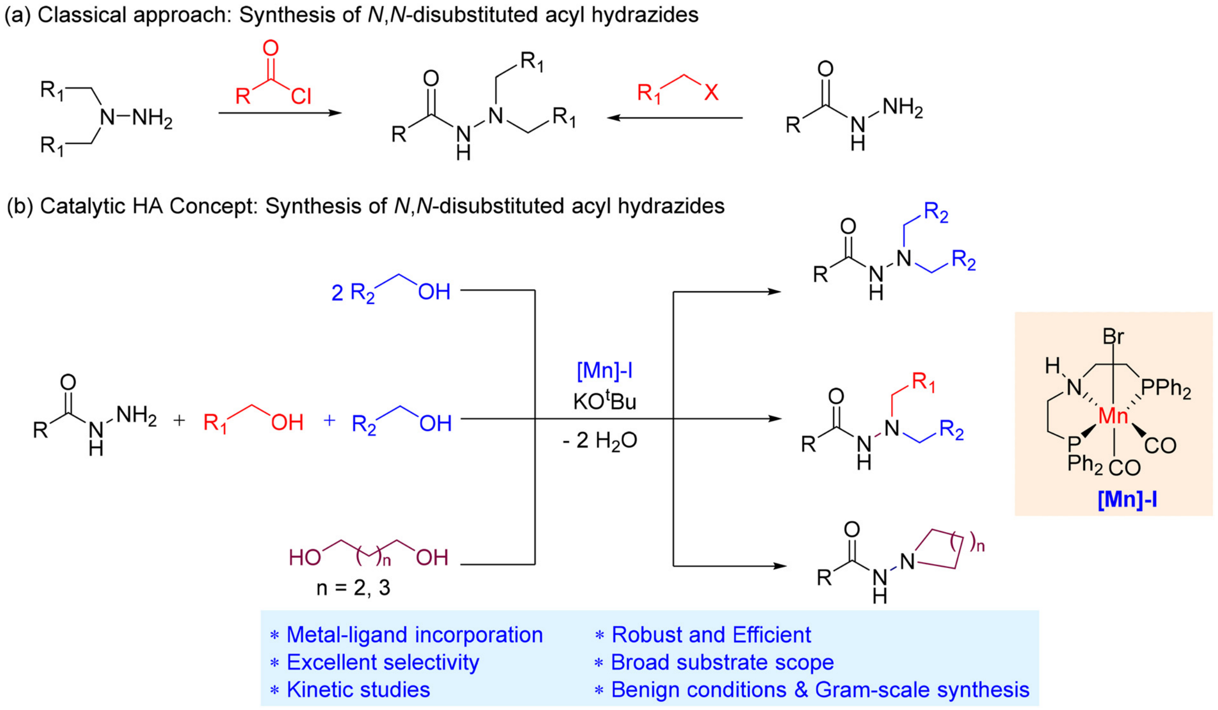


**Scheme 1** Biologically active *N*,*N*-disubstituted hydrazide derivatives (selected examples).

rarely explored. Herein, we report the first earth-abundant base-metal catalyzed direct one-pot *N*,*N*-dialkylation and cyclization of acyl hydrazides using abundantly available alcohols as potential alkylating agents. The reaction is catalyzed by a well-defined Mn(I)-based PNP-pincer complex and it operates *via* the HA strategy. Interestingly, the more challenging intermolecular cyclization of acyl hydrazides with diols was successfully demonstrated. Additionally, diversification of *N*,*N*-dialkylated acyl hydrazides and a study of the kinetics and mechanistic insights into the present Mn-catalysis were performed (Scheme 2).

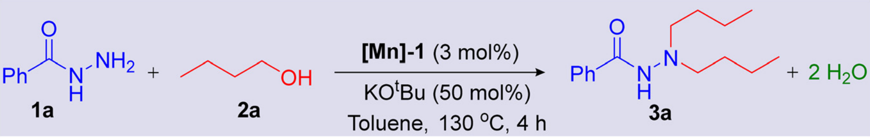
## Results and discussion

Initially, we systematically studied various reaction parameters for the *N*,*N*-dialkylation and cyclization of acyl hydrazides using alcohols as an alkylating agent under Mn-catalysis. Hence, benzohydrazide (**1a**) and 1-butanol (**2a**) were chosen as benchmark substrates. The reaction of **1a** (0.5 mmol) with **2a** (1.25 mmol) in the presence of a catalytic amount of Mn-catalyst (**[Mn]-1** at 5 mol%) and KO$^t$Bu (50 mol%) at 130 °C in toluene for 24 h afforded the desired *N*,*N*-dialkylated product **3a** in 83% isolated yield (Table 1, entry

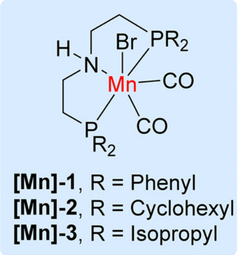


**Scheme 2** Various approaches for the synthesis of *N*,*N*-disubstituted acyl hydrazides.

**Table 1** Optimization of the reaction conditions



| Entry | Deviation from above | Yield of **3a** (%)$^a$ |
|---|---|---|
| 1 | alcohol (2.5 eq.),<br>**[Mn]-1** (5 mol%), 24 h | 83 (>99)$^b$ |
| 2 | alcohol (2.2 eq.),<br>**[Mn]-1** (5 mol%), 24 h | 88 (>99)$^b$ |
| 3 | none | 91 (>99)$^b$ |
| 4 | **[Mn]-2** | 71 (91)$^b$ |
| 5 | **[Mn]-3** | 68 (88)$^b$ |
| 6 | no catalyst | NR |
| 7 | no KO$^t$Bu | trace |
| 8 | 30 mol% KO$^t$Bu | 68 |
| 9 | 110 °C | 84 |
| 10 | NaO$^t$Bu, Cs$_2$CO$_3$, KOH, NaHCO$_3$ as base | <60 |
| 11 | *m*-xylene, n-octane, THF, CH$_3$CN, 1,4-dioxane as solvent | <50 |



Reaction conditions: **1a** (0.5 mmol), **2a** (1.1 mmol), cat. [Mn] (3 mol%), base (50 mol%), and 1 mL of solvent heated at 130 °C (oil-bath temperature) for 4 h. $^a$ Isolated yield. $^b$ GC conversion of benzohydrazide using mesitylene as an internal standard.

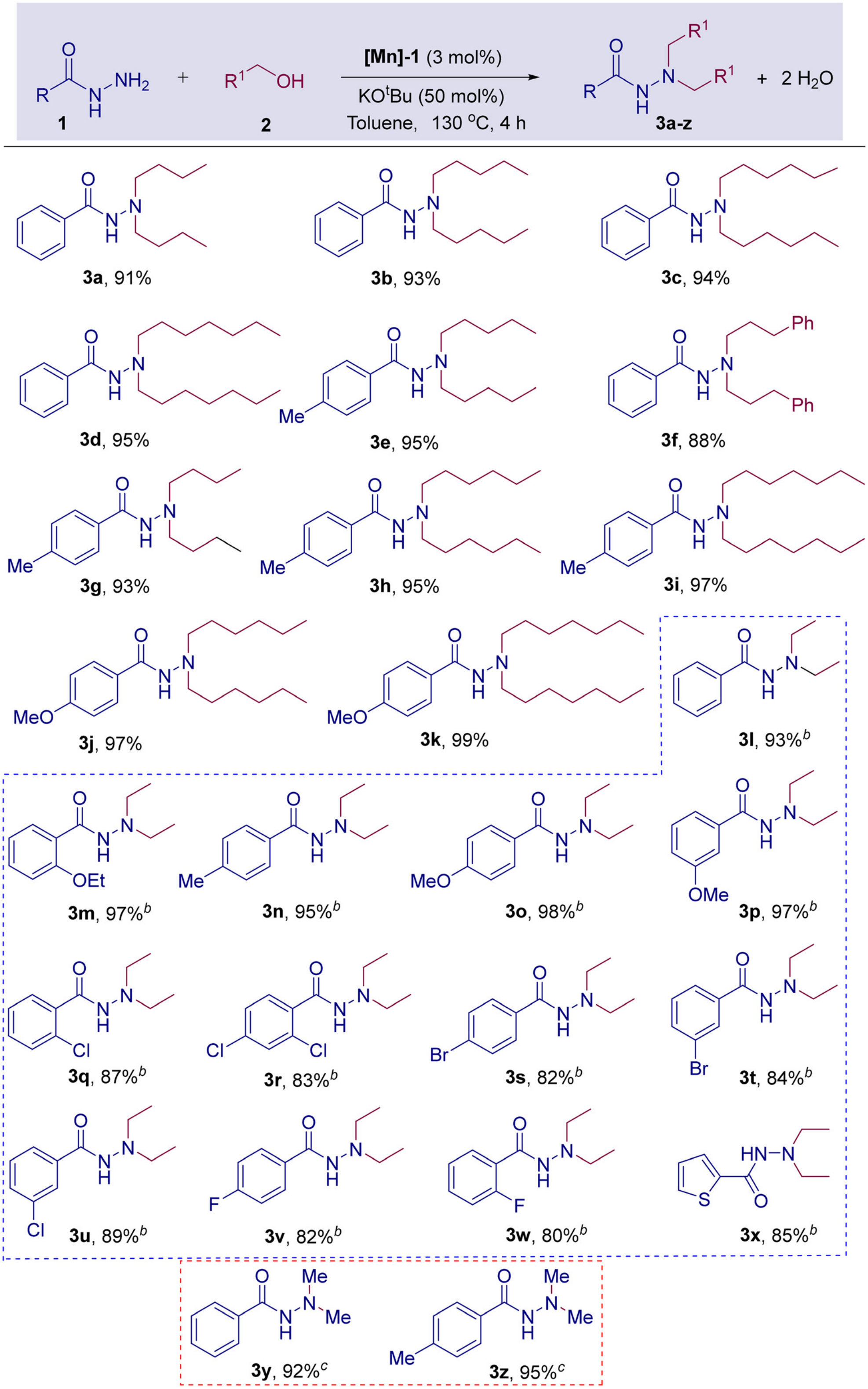
1). Interestingly, the reaction in the presence of 2.2 equiv. of alcohol (**2a**) slightly increased the yield of **3a** (Table 1, entry 2). An excellent outcome was obtained with 3 mol% of the catalyst (**Mn-1**) (Table 1, entry 3). Further changing the catalyst systems to **[Mn]-2** and **[Mn]-3** yielded the desired product **3a** in moderate yield (Table 1, entries 4 and 5; up to 71%). Also, there is no product formation in the absence of either a base or the Mn-catalyst (Table 1, entries 6 and 7). This confirmed that the combination of the base and the present **Mn-1** catalytic system is essential for this *N*,*N*-dialkylation strategy. In particular, decreasing the mole percentage of the base ended up in a low yield of **3a** (Table 1, entry 8). Lowering the temperature from 130 °C to 110 °C afforded 84% **3a** (Table 1, entry 9). Notably, various bases such as NaO$^t$Bu, LiO$^t$Bu, KOH, and NaHCO$_3$ resulted in a lower yield of **3a** under the optimal conditions (Table 1, entry 10, and Table S5†). Under identical conditions, changing the solvents to *m*-xylene, *n*-octane, THF, 1,4-dioxane, and acetonitrile ended with a low yield of **3a** (Table 1, entry 11).

With the optimal reaction conditions in hand, we applied the present catalytic protocol for the *N*,*N*-dialkylation of different acyl hydrazides with alcohols. Initially, we explored the substrate scope of symmetrical *N*,*N*-dialkylation of acyl hydrazides using diverse unactivated alcohols (Table 2). A range of unactivated aliphatic alcohols such as 1-butanol, 1-pentanol, 1-hexanol, and 1-heptanol with acyl hydrazides afforded the corresponding products **3a**–**3e** and **3g**–**3k** in excellent yields. Interestingly, more demanding diethylation and dimethylation reactions of benzohydrazides were performed using an excess amount of ethanol and methanol and **3l** and **3y** were obtained in 93% and 92% yield, respectively, under solventless conditions. Similarly, *p*-toluic hydrazide also smoothly underwent dimethylation with methanol and led to the product **3z** in 95% yield. Notably, 3-phenylpropanol was also reactive under the optimized conditions and yielded **3f** in 88% isolated yield. Next, a series of benzohydrazides having different substituents on the aryl ring was studied for the *N*,*N*-diethylation reactions. Indeed, acyl hydrazides with electron-donating substituents such as methyl, methoxy, and ethyl groups afforded **3m**–**3p** in excellent yields.

Similarly, halide (–Cl, –Br, and –F) substituent containing benzohydrazides successfully underwent *N*,*N*-diethylation reaction with the optimized reaction conditions and yielded the corresponding products **3q**–**3w** in good to excellent yields (80–89% yield). These results suggest that the electronic nature of substituents does not play any significant role in the present Mn-catalysis. Interestingly, 2-thiophenecarboxylic acid hydrazide was well-tolerated and gave **3x** in 85% isolated yield. Further, we extended our synthetic strategy to achieve the challenging unsymmetrical *N*,*N*-dialkylation of acyl hydrazides using two different alcohols (Table 3).

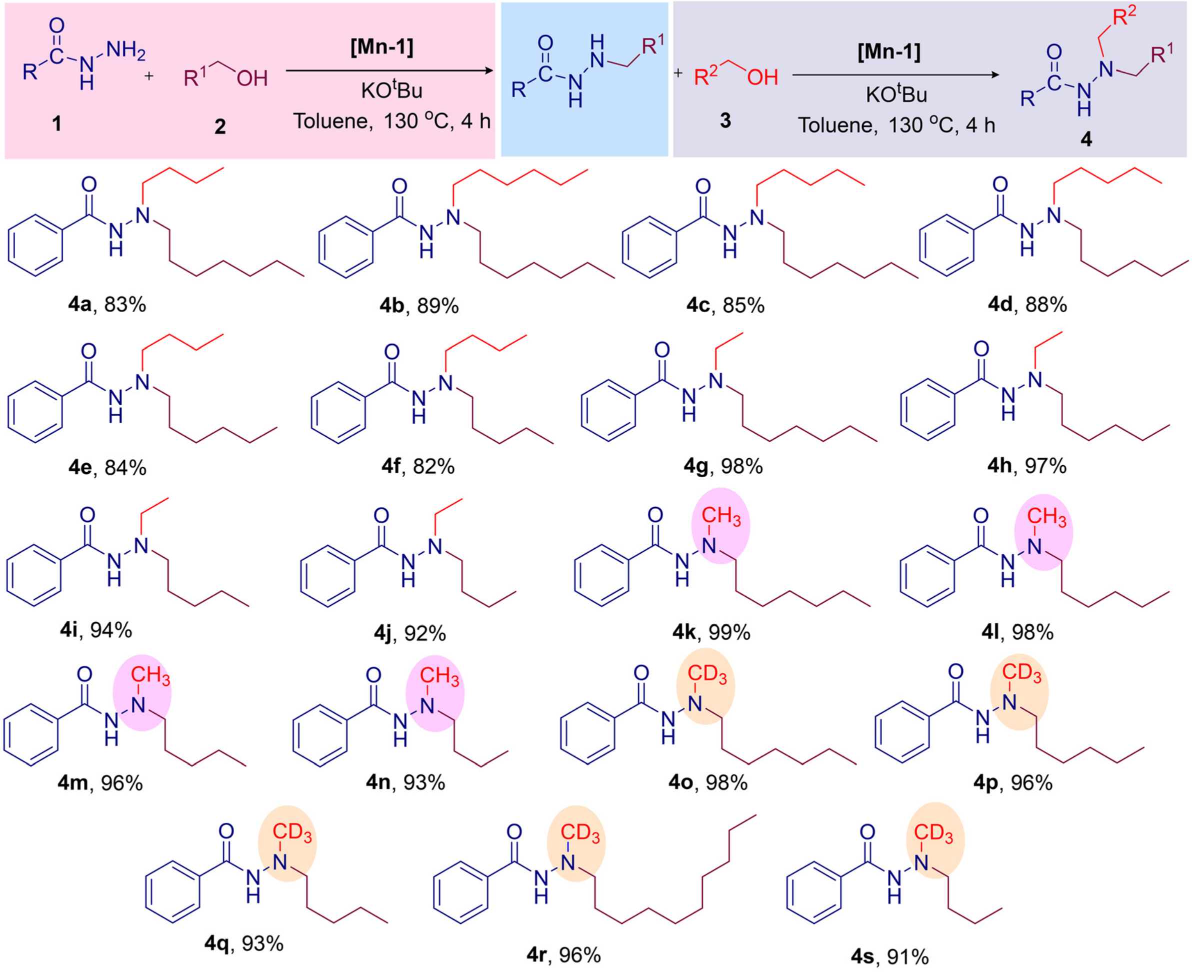
In our initial set of experiments, benzohydrazides were treated with 1.1 equiv. of aliphatic primary alcohols to achieve a monoalkylated product. Further, the reaction was carried out using a different primary aliphatic alcohol to yield the unsymmetrical *N*,*N*-dialkylation products **4a**–**4s** with good to excellent yields (up to 98% isolated yield). Interestingly, more challenging and demanding aliphatic alcohols such as ethanol and methanol underwent highly selective *N*,*N*-

**Table 2** Manganese-catalyzed direct symmetrical *N*,*N*-dialkylation of acyl hydrazides using alcohols[a]



[a] Reaction conditions: **1** (0.5 mmol), 2 (1.1 mmol), **Mn-1** (3 mol%), KO$^t$Bu (0.5 mmol), and 1 mL of toluene heated at 130 °C for 4 h. All the represented yields are isolated yields of the compounds. [b] 10 equiv. of ethanol. [c] 1 mL of methanol.

**Table 3** Manganese-catalyzed selective unsymmetrical *N*,*N*-dialkylation of benzohydrazides[a]



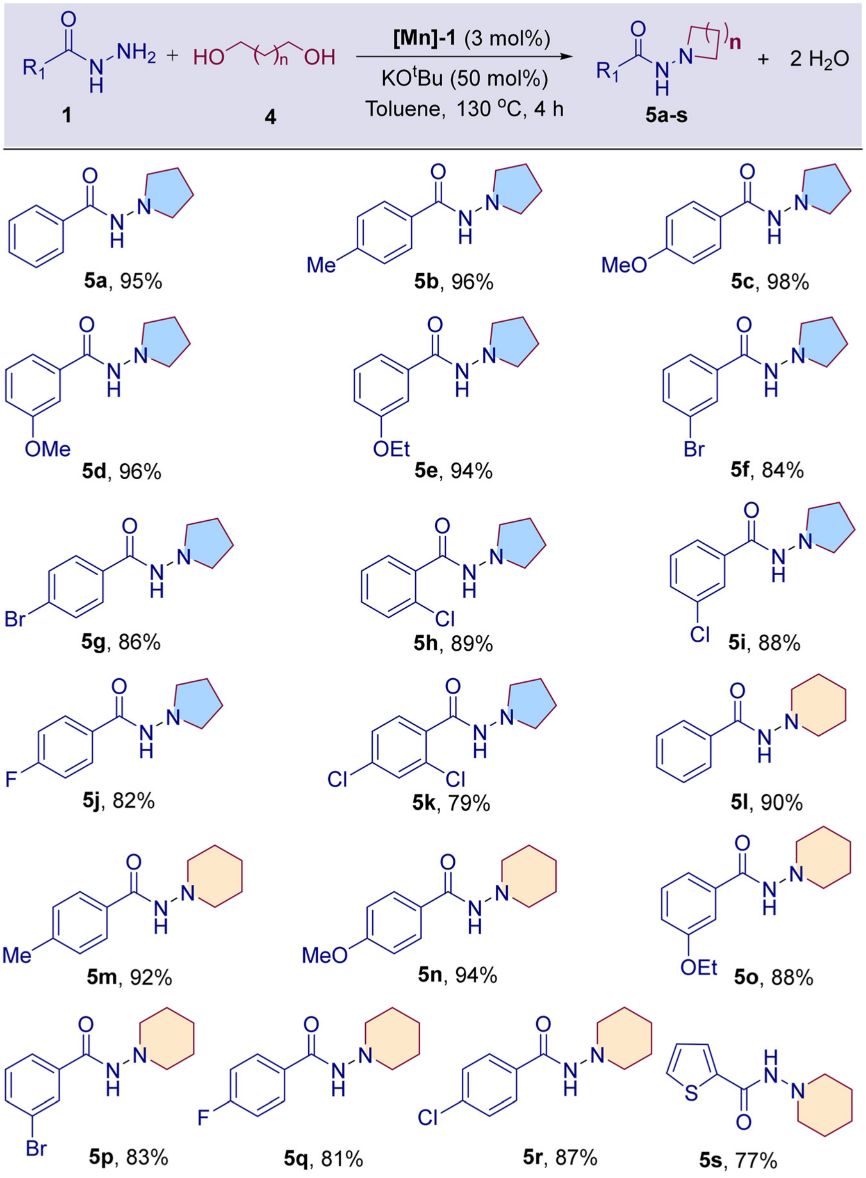
[a] Reaction conditions: **1** (0.5 mmol, 1 equiv), **2** (0.55 mmol, 1.1 equiv), **Mn-1** (3 mol%), KO$^t$Bu (0.5 mmol), and 1 mL of toluene heated at 130 °C under argon flow for 4 h. After 12 h, different alcohol (0.55 mmol, 1.1 equiv), **Mn-1** (3 mol%), base (0.5 mmol), and 1 mL of toluene were added into the reaction mixture and heating continued for another 4 h. All the represented yields are isolated yields of the compounds. For products **4g–4j**: 5 equiv of ethanol was used. For products **4k–4n**: 5 equiv of methanol was used.

dialkylation reactions and gave the corresponding products **4g–4n** in excellent yields (92–98% yield). Interestingly, performing the reaction with deuterated methanol ($CD_3OD$) instead of $CH_3OH$ afforded deuterium incorporation in the methyl α-position and yielded the products **4o–4s** in excellent yields. Impressively, such a kind of unsymmetrical selective deuterium incorporation is unprecedented.

Delightfully, we have explored the intermolecular cyclization of acyl hydrazides using diols. As shown in Table 4, a range of neutral and electron-rich benzohydrazides (*p*-Me, *p*-OMe, *m*-OEt, and *m*-OMe) readily reacted with 1,4-butanediol under optimal conditions and afforded the corresponding five-membered ring acyl hydrazides in excellent yields (products **5a–5e**, up to 98% isolated yield). Under the optimized catalytic conditions, halide (–F, –Cl, and –Br) substituted benzohydrazides yielded the expected products **5f–5k** in good to excellent yields. Further, we extended this strategy for six-membered ring cyclization with 1,5-pentanediol. Under optimal reaction conditions, alkyl, alkoxy, and halide (–Cl, –F, and –Br) substituted acyl hydrazides underwent cyclization reaction *via* double borrowing hydrogenation and gave the respective six-membered ring cyclized products **5m–5r** in 81–94% isolated yields (Table 4). More interestingly, 2-thiophenecarboxylic acid hydrazide also endured the cyclization with 1,5-pentanediol and yielded **5s** in 77% isolated yield.

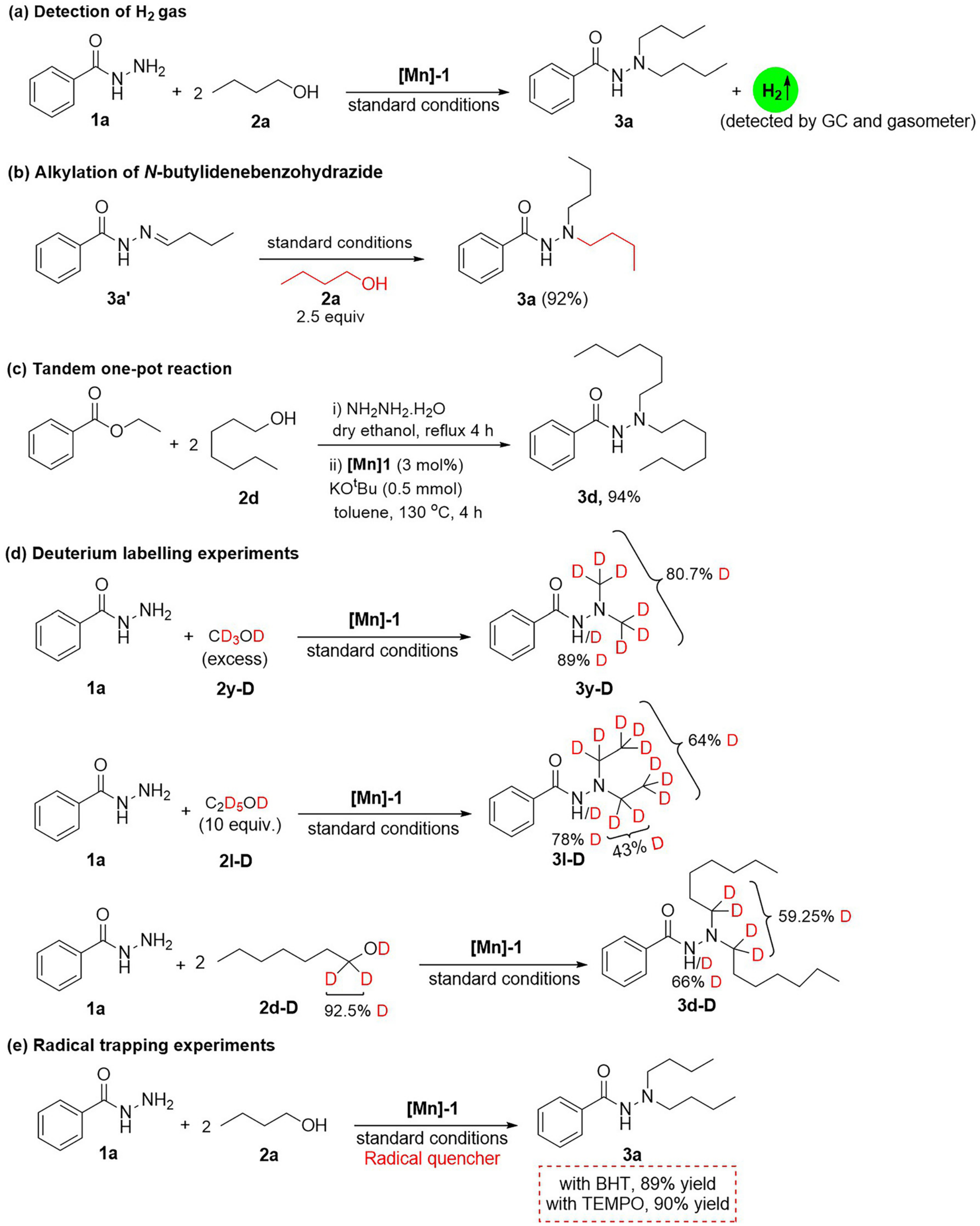
Several control experiments were conducted to gain insights into the reaction mechanism (Scheme 3). The formation of $H_2$ gas was detected from the reaction of **1a** with **2a** under optimal conditions (by using gas chromatography (GC) as well as gasometer analysis; Scheme 3a; see the ESI†). Next, *N*-butylidenebenzohydrazide (**3a′**) was subjected to the present Mn-catalytic alkylation reaction with 1-butanol **2a** and the expected product **3a** was obtained in 92% yield (Scheme 3b). The *in situ* generated *N*-alkylidenebenzohydrazide intermediate undergoes catalytic

**Table 4** Manganese-catalyzed cyclization of acyl hydrazides using diol[a]



[a] Reaction conditions: **1** (0.5 mmol), **4** (1.1 mmol), **Mn-1** (3 mol%), KO$^t$Bu (0.5 mmol), and 1 mL of toluene heated at 130 °C under argon flow for 4 h. All the represented yields are isolated yields of the compounds.

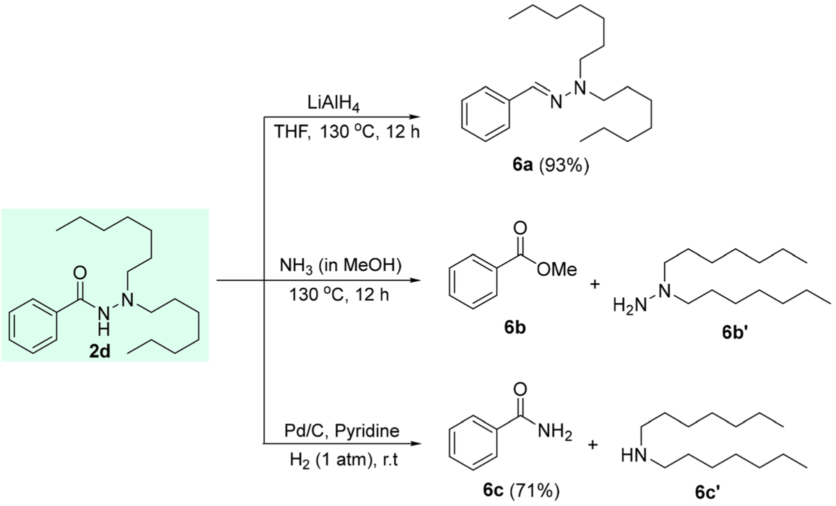
transfer hydrogenation reaction and subsequent *N*-alkylation leads to the desired *N*,*N*-dialkylated product **3a**. This result shows that the reaction proceeds *via* the *N*-alkylidenebenzohydrazide intermediate. We have also performed a tandem one-pot reaction to directly access *N*,*N*-dialkylated products from the corresponding ester derivatives. The reaction of ethyl benzoate with hydrazine hydrate to (*in situ*) generate benzohydrazide, which further reacted with 1-heptanol **2d** in a one-pot manner under the optimal catalytic conditions, afforded the corresponding *N*,*N*-dialkylated product (**3d**) in 94% isolated yield (Scheme 3c). Then, three independent deuterium labeling experiments were carried out; almost 40–80% deuterium incorporated was observed at the α-methylene carbon of the *N*,*N*-dialkylation products **3y-D**, **3l-D**, and **3d-D** under the present catalytic conditions (Scheme 3d). This experiment revealed that the present manganese catalytic cycle follows the borrowing hydrogen strategy. The lower deuterium incorporation may be due to hydrogen–deuterium (H–D) exchange by the presence of formed water molecules during the catalytic process. Finally, to determine the nature of the present Mn-catalysis, we have performed two independent experiments in the presence of mercury and radical scavengers such as (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) and butylated



**Scheme 3** Control experiments (a–e).

hydroxytoluene (BHT). Indeed, performing the reaction in the presence of mercury didn't affect the yield of **3a**. However, performing the reaction in the presence of dibenzo[*a*,*e*]cyclooctatetraene (DCT) significantly affected the yield of **3a** (section 4.5, ESI†). These results confirmed the homogeneous character of the present Mn-catalyst and excluded the involvement of a SET (radical) mechanism (Scheme 3e and section 4.5, ESI†). The kinetic experiments reveal that the consumption of acyl hydrazide follows an exponential decay.[14]

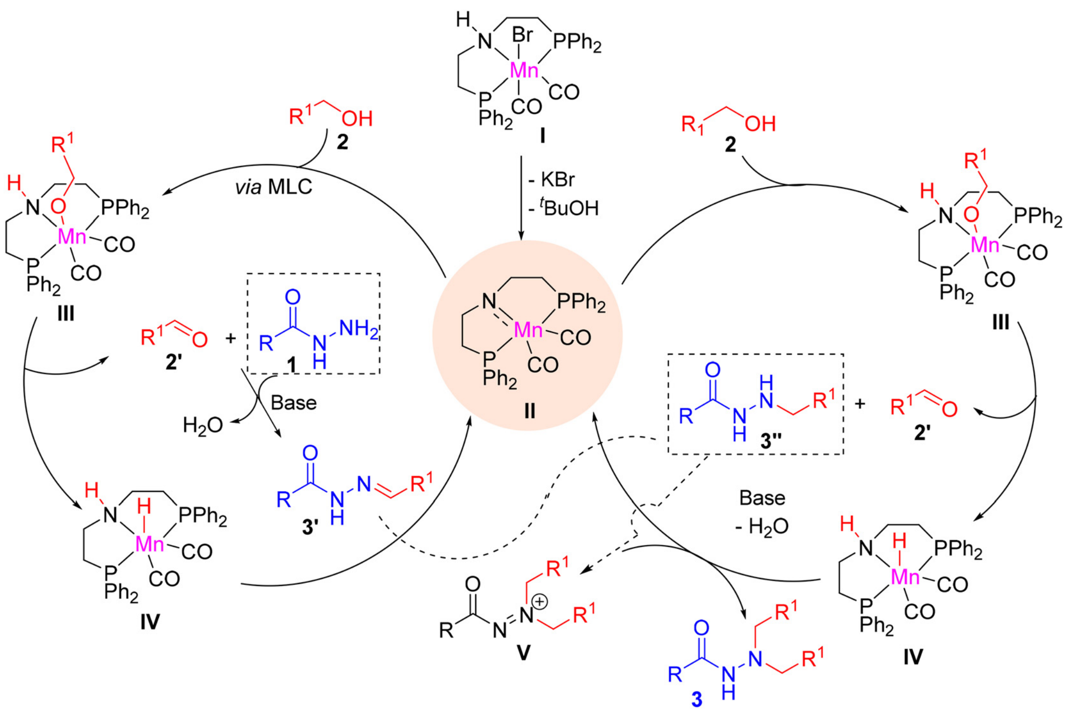
Next, we have successfully demonstrated the diversification of the acquired *N*,*N*-dialkylated product **2d** (Scheme 4a). The reaction of **2d** with lithium aluminum hydride yielded the corresponding reduced product **6a** in 93% isolated yield (Scheme 4a). Then, the reaction of **2d** with methanolic ammonia gave the corresponding ester product **6b** in 32%



**Scheme 4** Diversification of **2d**.

isolated yield (Scheme 4). Performing Pd-catalyzed hydrogenation reaction in the presence of a catalytic amount of pyridine resulted in the corresponding products **6c** and **6c′** in moderate yields.

Based on the experimental results and the literature,[15] a plausible mechanism for the manganese-catalyzed *N*,*N*-dialkylation of acyl hydrazides with alcohols is proposed in Scheme 5. Initially, treatment of the precatalyst **I** with a base leads to the active catalyst **II**, followed by alcohol **2** activation *via* MLC leading to an alkoxy species **III**. Then, the dehydrogenation (of **2**) occurs *via* β-hydride elimination, yielding the corresponding carbonyl compound, and the manganese hydride complex **IV**.[15a,b] However, recent DFT computational studies suggested that the initial dehydrogenation reaction proceeds *via* an outer-sphere mechanism.[15c] Thus, we believe that a blended mechanism may be operative. Further, the base-catalyzed condensation reaction of the *in situ* generated carbonyl compound with acyl hydrazide **1** leads to a hydrazone intermediate **3′**, which undergoes hydrogenation by complex **IV**, yielding monoalkyl acyl hydrazide **3″** with the regeneration of the active catalyst **II**. Subsequently, the monoalkyl acyl hydrazide again undergoes a second condensation with the *in situ* generated aldehyde **2′**, which provides iminium intermediate **V**. Finally,



**Scheme 5** A plausible mechanism for the manganese-catalyzed *N*,*N*-dialkylation of acyl hydrazides using alcohols.

hydrogenation of the iminium intermediate by the manganese complex **IV** yields the expected *N*,*N*-dialkylacylhydrazide **3** with the regeneration of **II**.

In summary, we have disclosed an earth-abundant, Mn-catalyzed, and efficient protocol for the one-pot direct coupling of acyl hydrazides with alcohols to *N*,*N*-dialkylacylhydrazides under mild and benign conditions. The present work was extended to the formation of more challenging five and six-membered heterocyclic acyl hydrazides. Interestingly, demanding diethylation and dimethylation of acyl hydrazides were demonstrated using ethanol and methanol, respectively, as potential alkylating agents. Control and labeling experiments suggest that the reaction proceeds *via* double borrowing hydrogenation.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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