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# Nickel-Catalyzed Deoxygenative Deuteration of Aryl Sulfamates

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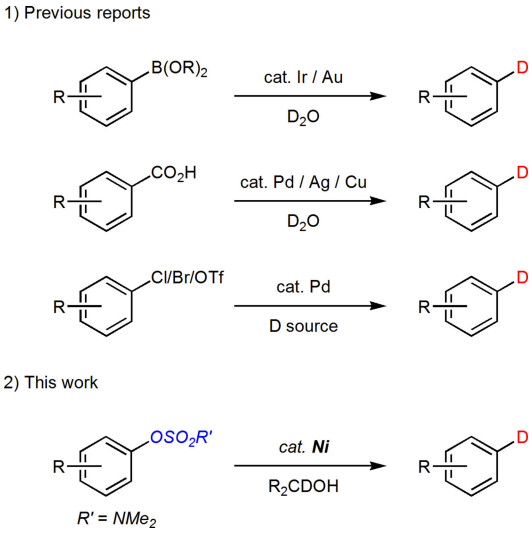
**Abstract:** The nickel-catalyzed deoxygenative deuteration of aryl/heteroaryl sulfamates has been developed, and the effective incorporation of deuterium into a variety of aromatic compounds was achieved with sufficient catalytic efficiency and high deuteration degree. This process tolerated reducible functional moieties and heterocyclic structures. Additionally, a double introduction of deuterium also successfully gave a desired product with a high yield and deuterium content.

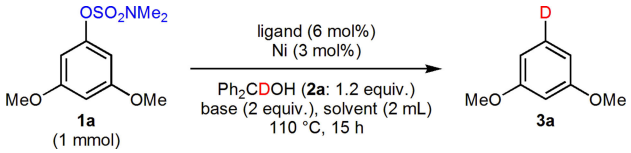
**Keywords:** Arenes; Deoxygenation; Deuteration; Nickel; Sulfamates

Catalytic deuteration of organic molecules is a key process because deuterated compounds are used in extensive investigation such as the metabolic analysis of bioactive agents as well as the mechanistic study of various reactions.[1] In addition, increasing interest has been recently focused on the site-specific introduction of deuterium into pharmaceutical molecules owing to its beneficial effects to improve their therapeutic profiles.[2] In particular, the catalytic deuteration methods for aryl groups are highly important on the ground of their ubiquity in pharmaceutical and bioactive agents.[3] As a typical deuterium incorporation into aromatic compounds, metal-catalyzed H/D exchange has made rapid strides, in which multiple deuteration in a molecule is basically promoted by precious metal catalysts depending on the respective reactivity of reactive sites.[4,5,6] On the other hand, deuterodefunctionalization is also known as a powerful transformation,[7] and a few kinds of the catalytic methods for aromatics have been developed, such as deborylative[8], decarboxylative[9], deoxygenative[10], and dehalogenative[11,12] deuteration. In these processes, precious metals were principally used as catalysts, such as palladium, silver, iridium, and gold, although a copper-catalyzed deuterodecarboxylation[9b] was reported as an exceptional and developing approach (Scheme 1). In recent years, focus has shifted to first-row transition metals as promising catalysts because of their advantageous features, such as a lower level of costs and high natural abundance.[13,14] Among these base metals, nickel has played a significant role in industrial applications,[15] and the distinctive homogeneous catalysis has contributed to the progress of catalytic transformation.[16,17] Meanwhile, phenol derivatives are less expensive, easily available, and highly diverse compounds, while the ingenuity for phenolic hydroxyl groups is often required for the deoxygenative transformation.[18] Aryl sulfamates have attracted much interest by reason of their facile preparation, pronounced stability, and easy functionalization via ortho or para metalation.[19] Therefore, we envisaged that an attractive deuteration system would be given by the combined use of nickel catalysts and sulfamoylated phenols.[20] Herein, we report the nickel-catalyzed deoxygenative deuteration of aryl sulfamates employing an unsymmetrical NHC ligand.




**Scheme 1.** Metal-catalyzed deuterodefunctionalization for aromatic compounds.

**Table 1.** Optimization of Reaction Conditions.[a]




| Entry | Ligand | Ni | Base | Solvent | Yield [%] | D content [%] |
|---|---|---|---|---|---|---|
| 1 | none | Ni(1-naph)Cl($PPh_3$)$_2$ | $K_3PO_4$ | toluene | 0 | ND |
| 2 | **L1** | Ni(1-naph)Cl($PPh_3$)$_2$ | $K_3PO_4$ | toluene | 59 | 98 |
| 3 | **L2** | Ni(1-naph)Cl($PPh_3$)$_2$ | $K_3PO_4$ | toluene | 63 | 99 |
| 4 | **L3** | Ni(1-naph)Cl($PPh_3$)$_2$ | $K_3PO_4$ | toluene | 75 | >99 |
| 5 | **L4** | Ni(1-naph)Cl($PPh_3$)$_2$ | $K_3PO_4$ | toluene | 63 | >99 |
| 6 | **L5** | Ni(1-naph)Cl($PPh_3$)$_2$ | $K_3PO_4$ | toluene | 86 | >99 |
| 7 | **L6** | Ni(1-naph)Cl($PPh_3$)$_2$ | $K_3PO_4$ | toluene | 64 | >99 |
| 8 | **L7** | Ni(1-naph)Cl($PPh_3$)$_2$ | $K_3PO_4$ | toluene | 84 | >99 |
| 9 | $Cy_3P{\cdot}HBF_4$ | Ni(1-naph)Cl($PPh_3$)$_2$ | $K_3PO_4$ | toluene | 4 | 87 |
| 10 | $t$-$Bu_3P{\cdot}HBF_4$ | Ni(1-naph)Cl($PPh_3$)$_2$ | $K_3PO_4$ | toluene | 0 | ND |
| 11 | **L5** | $NiCl_2$ | $K_3PO_4$ | toluene | 0 | ND |
| 12 | **L5** | $Ni(OTf)_2$ | $K_3PO_4$ | toluene | 1 | 88 |
| 13 | **L5** | $Ni(COD)_2$ | $K_3PO_4$ | toluene | 27 | 93 |
| 14 | **L5** | $Ni[P(OPh)_3]_2$ | $K_3PO_4$ | toluene | trace | ND |
| 15 | **L5** | Ni(1-naph)Cl($PPh_3$)$_2$ | $Na_3PO_4$ | toluene | trace | ND |
| 16 | **L5** | Ni(1-naph)Cl($PPh_3$)$_2$ | $Cs_2CO_3$ | toluene | 14 | >99 |
| 17 | **L5** | Ni(1-naph)Cl($PPh_3$)$_2$ | $K_2CO_3$ | toluene | 0 | ND |
| 18 | **L5** | Ni(1-naph)Cl($PPh_3$)$_2$ | $Na_2CO_3$ | toluene | trace | ND |
| 19 | **L5** | Ni(1-naph)Cl($PPh_3$)$_2$ | KF | toluene | trace | ND |
| 20 | **L5** | Ni(1-naph)Cl($PPh_3$)$_2$ | $K_3PO_4$ | dioxane | 74 | >99 |
| 21 | **L5** | Ni(1-naph)Cl($PPh_3$)$_2$ | $K_3PO_4$ | DMA | 39 | 60 |
| 22 | **L5** | Ni(1-naph)Cl($PPh_3$)$_2$ | $K_3PO_4$ | DMSO | 0 | ND |

[a] Reaction conditions: **1a** (1 mmol), **2a** (1.2 equiv.), ligand (6 mol%), Ni (3 mol%), base (2 equiv.), solvent (2 mL), 110 °C, 15 h. D content was determined by $^1$H-NMR (500 MHz).

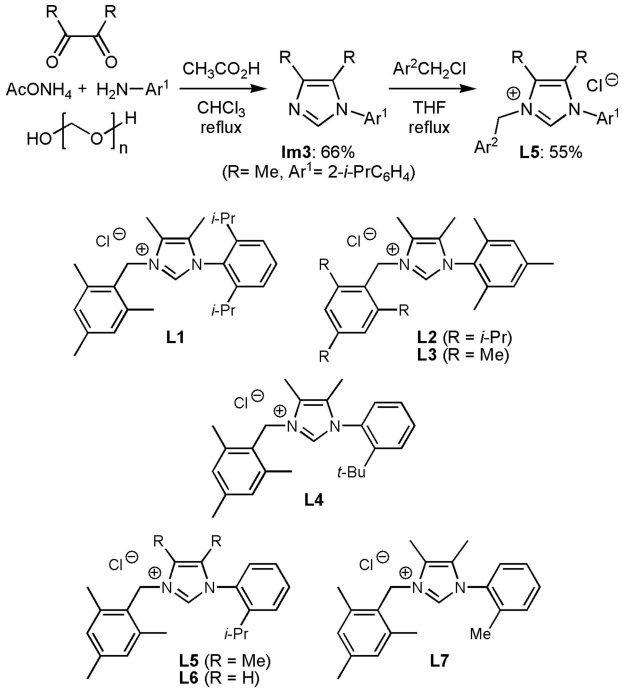
Initially, optimization of reaction conditions for deoxygenative deuteration was conducted in the presence of a nickel catalyst (3 mol%) with sulfamate **1a** (1 mmol) and D source **2a** (1.2 equiv.) as model substrates (Table 1). The nickel-catalyzed deoxygenative deuteration with no additional ligand never proceeded (entry 1). Unsymmetrical NHC ligand precursors (Scheme 2), which were readily prepared as stable solids with a simple two-step procedure, were examined (entries 2–8), because we recently found that this type of NHC ligand design showed positive effects in transition metal-catalyzed reactions.[11d,21] Compared with NHC precursors bearing a di- or triisopropylated phenyl moiety (entries 2–3), less bulky ligand precursor **L3** gave a better result in yield and D content (entry 4). Therefore, a series of NHC precursors with a monoalkylated phenyl ring were applied (entries 5–8). Basically, ligand precursors with a less bulky substituent led to higher yields, and imidazolium salt **L5** proved to be a superior NHC ligand precursor to afford the desired product **3a** in 86% yield and >99% D, in which the formation of benzophenone was observed (entry 6). In addition, methyl groups at the 4- and 5-position in this kind of ligand precursors were found to be necessary for high catalyst performance (entries 6–7). The evaluation of phosphine ligands unexpectedly revealed that the use of $Cy_3P{\cdot}HBF_4$ and $t$-$Bu_3P{\cdot}HBF_4$ gave a highly significant decrease in yield (entries 9–10), which are known as effective ligands for nickel-catalyzed reactions with sulfamates.[20] In the screening of nickel sources, most of zero- and divalent nickel complexes did not provide sufficient catalytic activity (entries 11–14), although Ni(1-naph)Cl($PPh_3$)$_2$[22] was exceptionally suitable for this transformation (entry 6). Subsequently, the examination of a series of bases also afforded fewer options. Inorganic carbonates as well as sodium phosphate tribasic and potassium fluoride were almost ineffective (entries 15–19), and potassium phosphate tribasic proved to be a reagent of choice (entry 6). Some kinds of solvents such as toluene, 1,4-dioxane, DMA, DMSO were examined (entries 6 and 20–22), and toluene led to better results in terms of both yield and D content.

Influence of sulfonate leaving groups and α-deuterioalcohols as D sources in the nickel-catalyzed deoxygenative deuteration was investigated (Table 2). In comparison with an aryl sulfamate (entry 3), the

deuteration reaction with an aryl tosylate gave a relatively lower yield (entry 2), whereas the use of an aryl mesylate resulted in a significant decrease in yield (entry 1). In the examination of α-deuterioalcohols **2a–d**, the lower reactivity of D sources was observed as the number of alkyl substituents at the α-position increased (entries 4 and 6). In the case of α-trifluoromethylated D source **2c**, no desired deuterated product was obtained (entry 5).

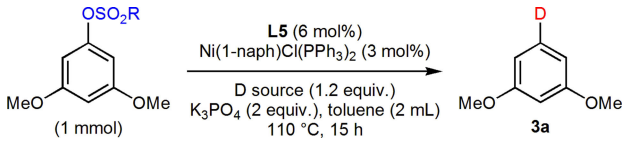
Investigation of varying aryl/heteroaryl sulfamates in the nickel-catalyzed deoxygenative introduction of deuterium was conducted (Table 3). An electron-rich aryl sulfamate bearing benzyloxy moiety showed high reactivity without reductive deprotection of a benzyl group (**3b**). In the presence of a coordinating amino group, a high yield was observed with enhanced reaction conditions (**3c**), while the use of a substrate with a thioether moiety led to 57% yield (**3d**). Steric hindrance close to a reactive site did not give a significant decrease in yield, and the desired product **3e** was obtained in 75% yield. Electron-withdrawing functional groups such as acetyl and cyano group proved to be suitable to this deuteration method without reductive side reactions (**3f** and **3g**). An aryl sulfamate with a reducible alkenyl moiety was also tried out to provide 76% yield (**3h**). The deuteration with substrates including an ester group efficiently proceeded even in gram-scale despite the concern about transesterification (**3i**), and a double incorporation of deuterium was also achieved (**3j**). In addition to a tertiary amide group (**3k**), a secondary amide moiety was acceptable even in the presence of a free NH group (**3l**). Subsequently, some kinds of the heterocycle-containing sulfamates were examined (**3m–o**). A substrate with a piperazine moiety was deuterated with adequate efficiency, giving the desired product in a high yield (**3m**). A *N*,*N*-dimethylsulfamoyloxy group on a quinoline core was smoothly replaced with a deuterium atom (**3n**). A dihydrobenzofuran derivative was additionally found to be a good reaction partner (**3o**). The deuterium introduction for a sulfamoylated compound **1p** derived from estrone was carried out to lead to 81% yield (**3p**). In these examinations, almost quantitative D-incorporations were observed as well as high selectivity and functional group tolerance as distinctive features.

The deuterium introduction for **1i** also proceeded readily in the presence of a radical scavenger, such as 2,6-di-*tert*-butyl-4-methylphenol (BHT) (Scheme 3), which suggested that this reaction might not include a single electron transfer process. On the basis of the observation of deuterium transfer from **2a** with the formation of benzophenone in addition to the result of a radical trapping experiment, a tentative reaction mechanism for this nickel-catalyzed deoxygenative deuteration of aryl sulfamates is shown in Scheme 4. In the first step, oxidative addition of an aryl sulfamate to a Ni(0) complex proceeds, leading to an arylnickel intermediate. After the displacement of a *N*,*N*-dimethylsulfamate anion is promoted by a base, an α-deuterioalkoxy-nickel species is converted to an arylnickel-deuteride complex through β-deuterium elimination with the formation of benzophenone. Finally, reductive elimination gives a deuterated product, and a Ni(0) catalyst is regenerated. A similar reaction mechanism was recently proposed for a palladium-catalyzed reductive cleavage of tosylated arene.[23]




**Scheme 2.** Unsymmetrical NHC ligand precursors.

**Table 2.** Influence of leaving groups and D sources.




| Entry | R | D source | Yield [%] | D content [%] |
|---|---|---|---|---|
| 1 | Me | **2a** | 36 | 99 |
| 2 | *p*-Tol | **2a** | 77 | >99 |
| 3 | $NMe_2$ | **2a** | 86 | >99 |
| 4 | $NMe_2$ | **2b** | 67 | >99 |
| 5 | $NMe_2$ | **2c** | 0 | ND |
| 6 | $NMe_2$ | **2d** | 37 | >99 |

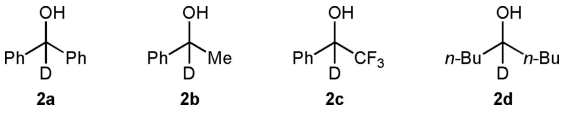
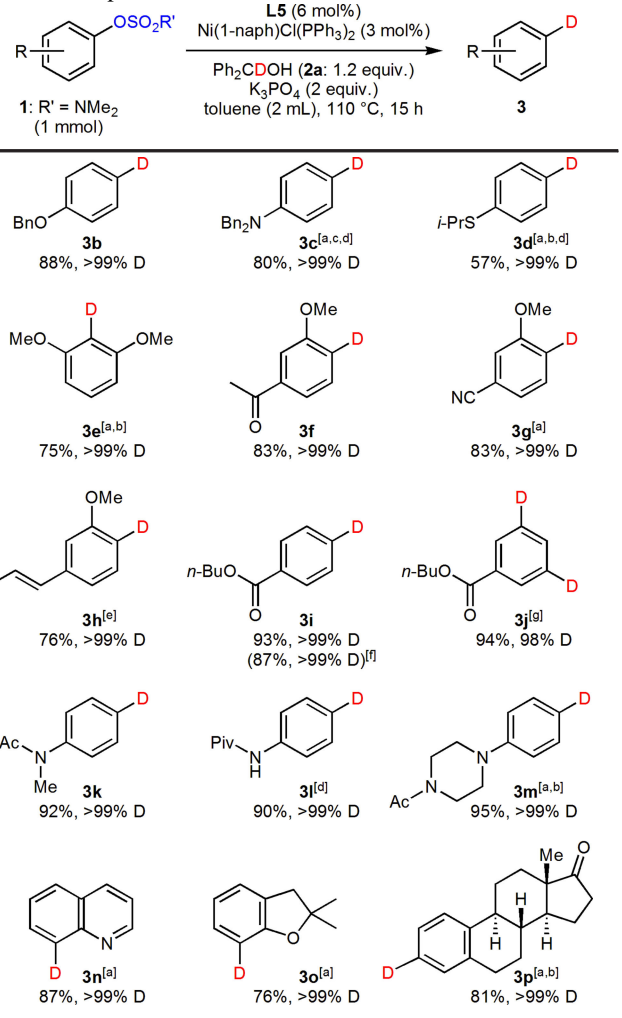
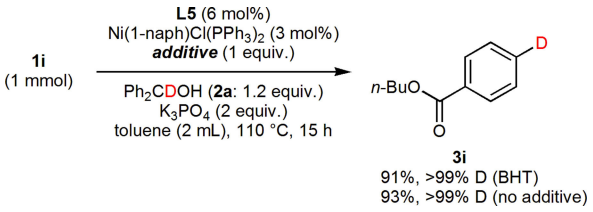


**Table 3.** Scope of substrates.

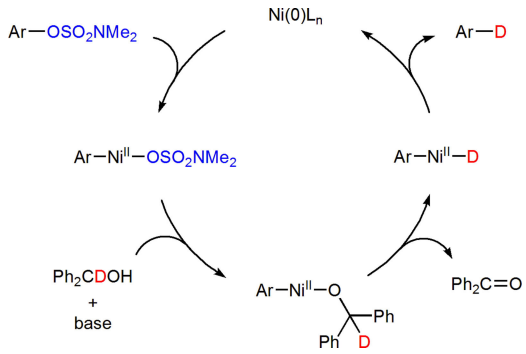



[a] Catalyst (5 mol%).
[b] $K_3PO_4$ (2.5 equiv.).
[c] $K_3PO_4$ (3.5 equiv.).
[d] **2a** (1.5 equiv.).
[e] 8 h.
[f] Gram-scale reaction (**1i**: 8 mmol).
[g] Catalyst (5 mol%), $K_3PO_4$ (3.0 equiv.), **2a** (2.4 equiv.).




**Scheme 3.** Deuteration in the presence of BHT.

In summary, a catalytic deoxygenative deuteration of aryl sulfamates was achieved with an NHC-ligated nickel catalyst. The deuterium introduction proceeded with sufficient catalytic activity, and a variety of deutertated aromatics were obtained with high D contents. In this process, reducible functional groups were well tolerated, and a double deuteration was also successfully attained. Moreover, heterocycle-containing substrates in addition to a sulfamoylated estrone were transformed with adequate efficiency. We believe this method would contribute to the progress of the precisely-controlled introduction of deuterium required in drug development.




**Scheme 4.** Plausible reaction mechanism.

## Experimental Section

### General Procedure for Nickel-Catalyzed Deoxygenative Deuteration of Aryl Sulfamates

Under an argon atmosphere, a reaction tube was charged with **L5** (23.0 mg, 0.06 mmol), Ni(1-naph)Cl($PPh_3$)$_2$ (22.4 mg, 0.03 mmol), and $K_3PO_4$ (425 mg, 2.0 mmol). After toluene (2.0 mL) was added, the mixture was stirred for 15 min at 80 °C. Then, aryl sulfamate **1** (1.0 mmol) and α-deuteriobenzhydrol **2a** (222 mg, 1.2 mmol) were added at room temperature. The reaction mixture was stirred for 15 h at 110 °C, and then cooled to room temperature. After water was added, the resulting mixture was extracted with AcOEt. The combined organic layers were dried over $MgSO_4$. Concentration and purification through silica gel column chromatography gave a desired product.

## Acknowledgements

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## Nickel-Catalyzed Deoxygenative Deuteration of Aryl Sulfamates

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