



Ni-Catalyzed Silylation of Inert C-O Bonds under Mild Conditions

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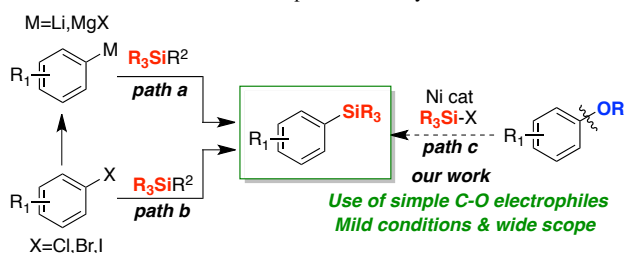
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C-O activation; silylation; Nickel-Catalyzed

INTRODUCTION

Scheme 1. Preparation of Aryl Silanes.

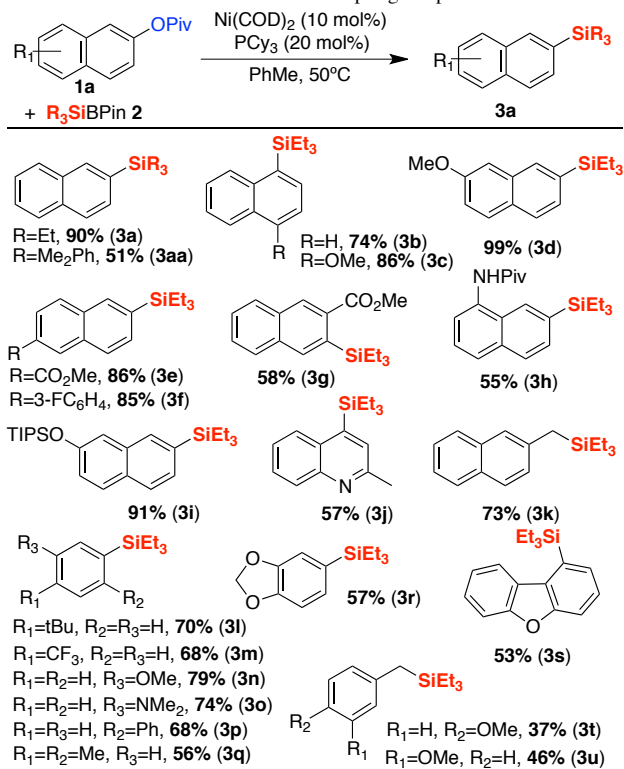


The pivotal role of arylsilanes as synthetic intermediates together with their use in medicinal chemistry and material science has attracted the attention and interest of the synthetic community. The synthesis of arylsilanes is typically accomplished via the reaction of stoichiometric and highly reactive organolithium or Grignard reagents with activated silicon sources (*path a*).¹ Alternatively, aryl halides can be used as coupling partners (*path b*);² however, the need for organic halides and the use of strongly reducing trialkylsilanes still constitute serious drawbacks when preparing backbones with sensitive functional groups. In recent years, the utilization of C-O electrophiles as coupling partners has received a great deal of attention due to their lack of toxicity and the readily availability of phenol as compared to commonly employed aryl halides as counterparts. While formidable advances have been realized in this area of expertise,³ to the best of our knowledge, the development of a catalytic C-Si bond-forming event using simple and inert C-O bonds has no precedents in the literature. Herein, we report the success of this approach via Ni-catalyzed silylation of unactivated aryl esters via C-O bond-activation (*path c*).

RESULTS AND DISCUSSION

The Ni-catalyzed C-O cleavage/C-Si bond-formation protocol presented in this work is characterized by its mild conditions and wide scope, including challenging substrate combinations such as heteroaryl and *ortho*-substituted pivalates, tertiary amines or nitrogen containing heterocycles (*Table 1*). Notably, C(sp³)-O bonds can also be coupled under the same optimized reaction conditions and, unlike other methodologies reported in the C-O bond-cleavage area, both simple arenes and extended Π -systems could equally be employed, thus showing the robustness of our methodology.

Table 1. C-Si Coupling Scope.



CONCLUSION

In summary, we have discovered the first silylation reaction of aryl esters with a silicon electrophile via Ni-catalyzed C-O cleavage. This catalytic silylation under mild conditions is feasible for electron-rich, -neutral, and -deficient naphthyl, phenyl and benzyl pivalates, affording the desired silylated product in good to excellent yields and constituting an alternative to existing methodologies for the preparation of aryl silanes (*a* & *b*).

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