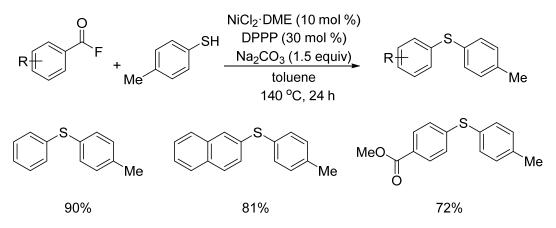
Nickel-Catalyzed Decarbonylative Thioetherification of Acyl Fluorides

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The construction of the C–S bonds is one of the most notable organic transformations. Recent studies have shown that nickel is effective in exploiting less reactive electrophiles, thus enabling the exploration for less toxic and more economic cross-coupling partners. On the other hand, since the reported decarbonylative trifluoromethylation of acid fluorides, acyl fluorides have shown unique reactivity and can be employed in a large number of decarbonylative reactions.¹ Furthermore, acyl fluorides are chemically more stable than the corresponding acyl chlorides and can be readily prepared from the corresponding carboxylic acids. Although recent papers have reported nickel-catalyzed decarbonylative thioetherification of esters and amides successfully,² the method of thioetherification using acyl fluoride is still an unexplored research topic. The present protocol enables the formation of a variety of C-S bonds by a highly efficient decarbonylative process.

Treatment of benzoyl fluoride with 4-methylthiophenol in the presence of NiCl₂·DME (10 mol %) and DPPP (30 mol %) afforded the product, phenyl (p-tolyl) sulfide in 90% yield. This catalyst system allowed the conversion of a series of acyl fluorides containing naphthyl and ester functional groups to the corresponding unsymmetrical diaryl sulfides in moderate to high yields.



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