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## Defluorohydrogenation of Acyl Fluorides by Secondary Phosphine Oxide as a Hydride Donor

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Acyl fluorides are a class of compounds containing a carbonyl–fluorine bond. They are more stable than other acyl halides, but more reactive than the corresponding esters and amides. This moderate reactivity has recently attracted attention and opened up new fields to utilize acyl fluorides as easy-to-handle electrophiles.<sup>1</sup> Another synthetically useful feature is two possible reaction modes: acyl coupling (RCOF as the RCO source) and decarbonylative coupling (RCOF as the R source). Late transition metal catalysts are especially suitable for controlling selectivity and expanding the variation of transformations.

Following our reports on the transformation of acyl fluorides,<sup>2</sup> we this time employed secondary phosphine oxide as a nucleophile under nickel catalysis. However, unlike the reported decarbonylative phosphorylation of amides,<sup>3</sup> only a trace amount of the expected tertiary phosphine oxide was obtained. Instead, we observed clear formation of the corresponding aldehyde and phosphinic fluoride resulting from the exchange of hydrogen with fluorine. After optimizing the reaction conditions, the defluorohydrogenation of *p*-toluic fluoride by diphenylphosiphine oxide was found to be efficiently catalyzed by NiCl<sub>2</sub>/DPEphos system in the presence of a base (eq. 1(A)). Moreover, the same reaction turned out to be also promoted by use of a base alone. Utilizing the proper base, aldehydes were formed in yields comparable to those obtained under nickel-catalyzed conditions (eq. 1(B)).



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