

Synthesis of Homoallylic Alcohols in Aqueous Media using Potassium Allyltrifluoroborate

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INTRODUCTION

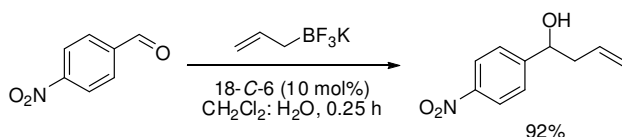
The addition of crotyl and allylorganometallics to carbonyl compounds is of considerable importance in organic synthesis. However, the utility of many of these organometallics is limited by their susceptibility to air and/or moisture.¹

Organotrifluoroborates have proven to be a good option to replace boronic acids and boronate esters providing advantages over the latter reagents in many types of reactions. Among various allylmetal reagents, potassium allyltrifluoroborate is preferred given the recent demand for safe and sustainable organic synthesis, because this reagent is air-stable.²

As part of ongoing studies on the synthesis and reactivity of organotrifluoroborate salts, herein we report the general and convenient 18-C-6 induced allylation of aldehydes by potassium allyltrifluoroborate.

RESULTS AND DISCUSSION

Initially, the effect of the addition of a catalytic amount of 18-C-6 in the allylation reaction was tested using the 4-nitro-benzaldehyde as substrate and potassium allyltrifluoroborate using a biphasic reaction medium (Scheme 1).



Scheme 1

The corresponding homoallylic alcohol was obtained in good yield without the necessity of further purification. In the absence of 18-C-6, the reaction was found to be rather sluggish (15% yield after 15 min at 25°C) and was incomplete after 15 min if less than 10 mol % of 18-C-6 was used.

The scope of the transformation was established with a variety of different aldehydes using 18-C-6 as the PTC. Aliphatic, aromatic, α,β -unsaturated, and heterocyclic aldehydes were efficiently allylated in good yields. The reaction tolerates nitro group (Table 1, entries 1) and, in the case of acrylaldehyde only 1,2-addition was observed (Table 1, entry 6).

Table 1. Addition of potassium allyltrifluoroborate to different aldehydes promoted by 18-C-6

	RCHO	Product	Yield (%) ^a
1			87
2			95
3			98
4			84
5			86
6			48
7			68
8			93

^a isolated yield

CONCLUSION

In summary, we developed a generally green and convenient allylation method to various functionalized aldehydes using potassium allyltrifluoroborate and 18-C-6. The application of the method in the allylation of other compounds as well as the asymmetric version of the reaction is undergoing in our laboratories.

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REFERENCES

- (a) Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, 93, 2207–2293; (b) Denmark, S. E.; Fu, J. *Chem. Rev.* **2003**, 103, 2763–2793.
- Thadani, A. N.; Batey, R. A. *Org. Lett.* **2002**, 4, 3827–3830.