

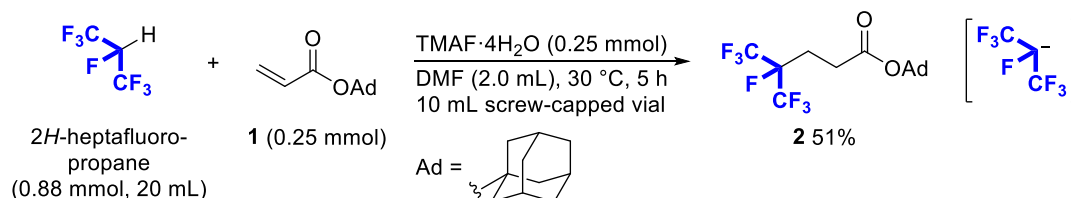
1,4-Addition of 2*H*-Heptafluoropropane to Unsaturated C-C Bond

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Perfluoroalkyl-containing organic compounds are often found in a wide range of fields, including pharmaceuticals, pesticide, electronic materials and polymer materials.¹ Although many researchers have developed synthetic methods for such compounds, most of them involve the introduction of primary fluoroalkyl groups, such as CF₃ and C₂F₅, and few methods have been developed to introduce secondary or tertiary perfluoroalkyl groups. Even in the case of the introduction of the simplest secondary perfluoroalkyl group, only some reactions have been reported for the introduction of (CF₃)₂FC groups from hexafluoropropene, CF₃CF=CF₂, or 2-iodoheptafluoropropane, (CF₃)₂CFI. In all of these methods, the radical species, (CF₃)₂FC•, is involved in the reaction as an important intermediate, but considering the electronic properties of the (CF₃)₂FC group, synthetic transformation via the anion species, (CF₃)₂FC[−], also have potential to become an effective method for the introduction of the (CF₃)₂FC group. Herein, we report a new synthetic reaction which proceeds via the generation of anion species from 2*H*-heptafluoropropane, (CF₃)₂FCH.

The reaction of (CF₃)₂FC-H with 1-adamantyl acrylate (**1**) in the presence of Me₄N⁺F[−]·4H₂O (TMAF·4H₂O) in anhydrous DMF at 30 °C for 5 h afforded 1-adamantyl 3-heptafluoropropylpropanoate (**2**), in which (CF₃)₂FC group is introduced at the terminus of conjugated system, in 50% yield (Scheme).² In this reaction, the fluoride ion acts as a strong base under nonaqueous conditions, deprotonating from (CF₃)₂FC-H to generate the anionic species, (CF₃)₂FC[−], which forms a bond with the β-position carbon of the α,β-unsaturated ester in the manner of 1,4-addition. Also, it was found that DMF not only acts as a solvent, but also, contributes to the stabilization of (CF₃)₂FC[−] generated in situ, as in the other fluoroalkyl anion such as [−]CF₃ and [−]C₂F₅. This represents the first reaction in which (CF₃)₂FC group is introduced into an aliphatic chain using (CF₃)₂FC-H as the raw material. Furthermore, it was found that the present method is applicable to the 1,4-addition reaction into a wide variety of electron-deficient alkenes to yield the corresponding 1,4-adducts in moderate to high yields.



1) N. Shibata *et al.* *ASC Omega* **2020**, 5, 10633-10640. 2) T. Morimoto *et al.* JP2021-188866; PCT/JP2022-118114.