



# Merging photoredox catalysis with allylboration. The photochemical perfluoroalkylation of unsaturated potassium alkyltrifluoroborates and synthesis of fluorinated alcohols

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## ABSTRACT

The development of a visible light-mediated atom transfer radical addition (ATRA) of perfluoroalkyl iodides to potassium 1-penten-5-yl-, vinyl- and allyltrifluoroborates using the reductive quenching of  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$  or  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$  is described. Using an operationally simple and mild protocol, the corresponding potassium trifluoroborates containing perfluoroalkyl groups were obtained in moderate to high yields. In the case of potassium allyltrifluoroborate, the use of acetone as the solvent resulted in allylboration followed by ATRA of perfluoroalkyl iodides to the formed homoallyl alcohol. A one-pot protocol was developed for the synthesis of a series of fluorinated alcohols using potassium allyltrifluoroborate, perfluoroalkyl iodides and selected aliphatic ketones.

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## Introduction

For the last few years, visible light photoredox catalysis has been spreading in organic chemistry impacting the area of boron chemistry.<sup>1</sup> The recent development in photocatalysis has provided support to innovative strategies, such as the oxidative generation of alkyl- and aryl radicals from organoborate derivatives.<sup>2,3</sup> The easy preparation, high stability and convenient redox potentials of trifluoroborate potassium salts made them attractive starting materials in photocatalysis. Much attention has been paid to their use in a photoredox process, to generate alkoxyethyl-,<sup>4</sup> alkyl,<sup>5–9</sup> or aminomethyl radicals,<sup>10</sup> which are utilised in C–C bond formation with electron-deficient olefins. We have established an interest in the development of reactivity of unsaturated trifluoroborates using visible light photoredox catalysis. In this paper, we describe our work on exploiting the reactivity of vinyl-, allyl- and 1-penten-5-yl-BF<sub>3</sub>K reagents with perfluoroalkyl radicals using  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$  or  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$  as the photocatalysts. We initially examined the photocatalytic reaction of potassium vinyltrifluoroborate **1** with perfluoroalkyl iodide (1.33 eq) in the presence of  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$  (0.5 mol%) and sodium ascorbate (0.35 eq) in acetonitrile under visible light irradiation (blue LEDs:

$\lambda_{\text{max}} = 452 \text{ nm}$ ) for 24 h (entry 1 in Table 1). As a result, the ATRA product **1a** was obtained in 88% yield and the C-BF<sub>3</sub>K moiety remained intact.<sup>11</sup> The reaction works well also in more volatile solvents as acetone or methanol, which can be helpful in isolation of the products. The addition order of perfluoroalkane in this reaction is reverse to that observed by the other groups who have found that alkenyltrifluoroborates react with radical species to give alkenylated products (Scheme 1) after spontaneous deboronation.<sup>12,13</sup> The conservation of the C–B bond in this reaction type was only observed for alkylation of vinyl MIDA boronates and vinylboronic acid pinacol boronates.<sup>14,15</sup>

The quantum mechanical calculations performed by Sheikh and coworkers revealed the  $\alpha$ -C atom as the preferred position to be attacked by radicals in vinyltrifluoroborates, owing to the higher spin density and the more favorable reaction enthalpy. We hypothesize that the reverse reactivity of **1** presented in our work is dictated by the formation of a more stable secondary radical (Scheme 2).

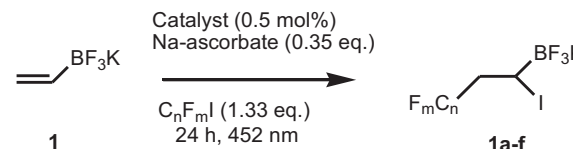
Motivated by the successful application of the ATRA protocol, the reaction scope was broadened using various commercially available perfluoroalkanes (C<sub>6</sub>F<sub>13</sub>I, C<sub>4</sub>F<sub>9</sub>I, (CF<sub>3</sub>)<sub>2</sub>CFI, C<sub>3</sub>F<sub>7</sub>I, CF<sub>3</sub>I) to give the ATRA products **1b–1f** in moderate to good yields (Table 1). Compared to the other transformations, the yield of **1f** was lower presumably due to the high volatility of CF<sub>3</sub>I.

Single crystals of **1a** suitable for X-ray determination were obtained via slow evaporation of its CH<sub>3</sub>CN solution. The crystal

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**Table 1**  
ATRA of various perfluoroalkyl iodides to potassium vinyltrifluoroborate.

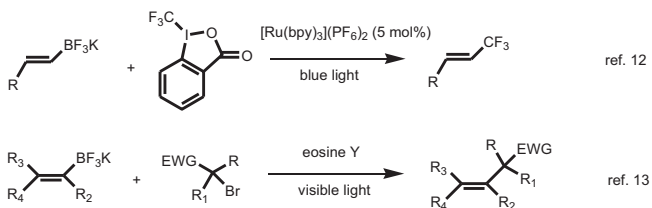


Entry	C <sub>n</sub> F <sub>m</sub> I	Solvent	Catalyst	Product	Yield (%)
1	C <sub>8</sub> F <sub>17</sub> I	CH <sub>3</sub> CN	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	<b>1a</b>	88/85 <sup>a</sup> /80 <sup>b</sup> /0 <sup>c</sup>
2	C <sub>6</sub> F <sub>13</sub> I	Acetone	[Ru(bpy) <sub>3</sub> ](PF <sub>6</sub> ) <sub>2</sub>	<b>1b</b>	73
3	C <sub>4</sub> F <sub>9</sub> I	Acetone	[Ru(bpy) <sub>3</sub> ](PF <sub>6</sub> ) <sub>2</sub>	<b>1c</b>	45
4	C <sub>3</sub> F <sub>7</sub> I	Acetone	[Ru(bpy) <sub>3</sub> ](PF <sub>6</sub> ) <sub>2</sub>	<b>1d</b>	56
5	(CF <sub>3</sub> ) <sub>2</sub> CFI	Acetone	[Ru(bpy) <sub>3</sub> ](PF <sub>6</sub> ) <sub>2</sub>	<b>1e</b>	71
6	CF <sub>3</sub> I	Acetone	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	<b>1f</b>	37

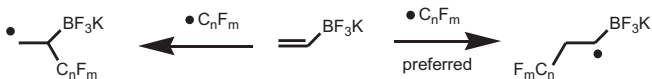
<sup>a</sup> Solvent acetone.

<sup>b</sup> Solvent methanol.

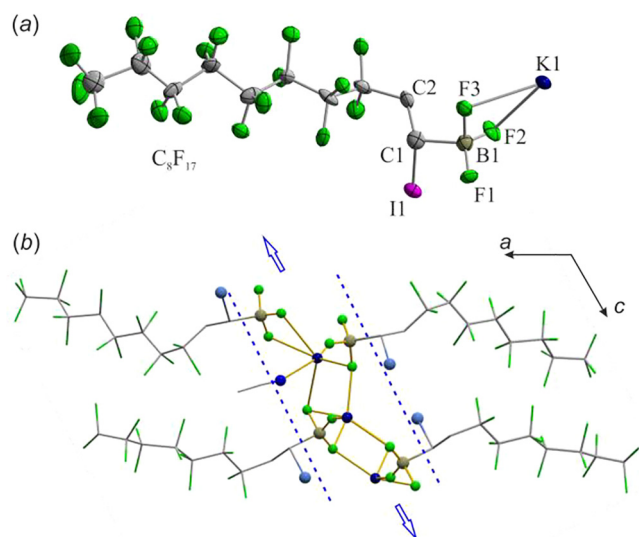
<sup>c</sup> No light.



**Scheme 1.** The known reactivity of potassium alkenyltrifluoroborates in photocatalytic alkylation.



**Scheme 2.** Regioselectivity of the addition of perfluoroalkyl radicals to the vinyltrifluoroborate.



**Fig. 1.** Labeling of atoms and estimation of their atomic thermal motion as Anisotropic Displacement Parameters (50% probability level) for **1a**.

structure revealed that the perfluoroalkyl chain and the boron atom were in the *anti* orientation (Fig. 1). The compound displayed a tetrahedral geometry around the boron centre with C–B and B–F distances in the ranges typical for other organotrifluoroborates.<sup>16</sup> The K<sup>+</sup> ions are stabilised by K–F contacts (distances in the range 2.686–3.029 Å), K–I contacts (distances in the range 3.670–3.831 Å) and by the solvent molecule incorporated into the crystal structure (K–N contact 2.808 Å).

Next we examined if the same conditions could also be applied for perfluoroalkylation of potassium 1-penten-5-yltrifluoroborate **2** and potassium allyltrifluoroborate **3**.

Upon reaction of the corresponding perfluoroiodoalkanes with **2** the ATRA products **2a–f** were generated in yields ranging from 47% to 68% (Table 2).

Allylic boron derivatives have gained a prominent position as a useful class of synthetic reagents. The main use of these reagents is in the synthesis of homoallylic alcohols in the reaction with carbonyl compounds.<sup>17</sup> We expected that upon mixing of perfluoroalkyl iodides with potassium allyltrifluoroborate in the presence of [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> and ketone, the multicomponent allylboration–ATRA process will afford the respective perfluorinated alcohols. Initial experiment with C<sub>8</sub>F<sub>17</sub>I (1.33 eq), [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> (0.5%), light, **3**, sodium ascorbate (0.35 eq) and acetone as the solvent afforded **3a** in 89% yield (Table 3). The reaction was complete after 6 h at room temperature, with conversion not increasing further after 24 h. Subsequent optimization reactions revealed that the product yield was lower when the catalyst loading was decreased to 0.2 mol%, and unchanged when increased to 1%. It should be noted that potassium allyltrifluoroborate is inert to carbonyl compounds, until activated by an external Lewis acid (e.g. BF<sub>3</sub>·Et<sub>2</sub>O), which can be used in catalytic amounts.<sup>18</sup> This method of activation is thought to involve a mechanism whereby the electrophilic BF<sub>3</sub>·Et<sub>2</sub>O strips off a fluoride anion from the trifluoroborate salt affording the highly electrophilic difluoroallylborane. The efficient formation of **3a** can only be achieved when the allylboration of acetone by **3** is faster (*k*<sub>1</sub> ≫ *k*<sub>2</sub>) than the photocatalytic ATRA of C<sub>8</sub>F<sub>17</sub>I to **3** (Scheme 3). These conditions are fulfilled when acetone is used in large excess. The use of acetone in the stoichiometric amount resulted in the formation of **3a** only in 35% yield (Table 3, entry 1). According to the proposed mechanism (Scheme 3) the first step of the reaction involves formation of the homoallyl alcohol **3'**, which is next consumed in the photocatalytic ATRA affording **3a**. This hypothesis was confirmed in the control experiment, where the photocatalytic ATRA of C<sub>8</sub>F<sub>17</sub>I to **3'**

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