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## Oxidation of Organotrifluoroborates via Oxone®

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### Abstract

A method for the oxidation of organotrifluoroborates using Oxone® was developed. A variety of aryl-, heteroaryl-, alkenyl-, and alkyltrifluoroborates were converted into the corresponding oxidized products in excellent yields. This method proved to be tolerant of a broad range of functional groups, and in secondary alkyl substrates it was demonstrated to be completely stereospecific.



### Introduction

Phenols are found in numerous natural products, pharmaceuticals and polymers, and have been widely used as versatile synthetic intermediates.<sup>1</sup> Traditional methods for the synthesis of these compounds include various protocols for substitution of aryl halides. Unfortunately, the harsh reaction conditions required for direct nucleophilic substitution make this approach incompatible with a variety of common functional groups.<sup>2</sup> Copper- and palladium-catalyzed hydroxylation of aryl halides is reported in the literature and offers an alternative to the former method.<sup>3</sup> In this case, however, the use of transition metals with attendant ligands and/or high reaction temperatures leads to processes that are less than ideal. Various boron species can be incorporated into aromatic and heteroaromatic systems in a variety of complementary ways, and recently the oxidation of boronic acids in a copper-catalyzed reaction has been reported.<sup>4</sup> Although perhaps useful on small scale in the laboratory, the use of a copper reagent, ligand and excess base significantly reduces its appeal on a larger scale. As an alternative to this method, several non-metal promoted oxidations of boronic acids and their derivatives have been described.<sup>5</sup> Among the oxidants used for this transformation, hydrogen peroxide,<sup>5a,c,e,f</sup> hydroxylamine<sup>5b</sup> and Oxone®<sup>5d,g</sup> are most often employed. The first two reagents require long reaction times, and the products are obtained in moderate yields for arylboronic acids containing electron withdrawing groups. On the other hand, the use of Oxone® provides an extremely rapid and generally efficient reaction.<sup>5d,g</sup>

Over the past years organotrifluoroborates have been used in many contexts as a valuable alternative to boronic acids and boronate esters.<sup>6</sup> Because of their tetracoordinate nature,

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Supporting Information Available: Copies of <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F spectra for all compounds prepared by the method described. This material is available free of charge *via* the Internet at <http://pubs.acs.org>.

these organoboron species do not undergo undesirable side reactions with commonly employed organic reagents such as bases, organic acids and nucleophiles. Thus, organotrifluoroborates, contrary to most other boron species, can be functionalized to build molecular complexity, while leaving the boron-carbon bond intact (Scheme 1).<sup>7</sup> The organotrifluoroborates can then be conveniently converted in a variety of ways depending on the conditions utilized.<sup>8</sup> Of further importance, heteroaryltrifluoroborates exhibit enhanced stability, and thus they can be prepared and stored for long periods of time, whereas many of the corresponding boronic acids rapidly decompose.<sup>8a,9</sup> Thus, many advantages to using organotrifluoroborates as surrogates for boronic acids are beginning to emerge.

To the best of our knowledge, although organotrifluoroborates present all of the benefits mentioned above, reports of the oxidation of these species into the corresponding phenol, alcohol or related derivatives is currently limited.<sup>4,10</sup> For example, phenyltrifluoroborate has been oxidized to phenol in a copper-catalyzed procedure requiring 8 h at room temperature.<sup>4</sup> In another isolated example, an alkyltrifluoroborate has been oxidized by utilizing an excess of a hypervalent iodonium complex to afford an excellent yield of the desired alcohol in 3 h.<sup>10a</sup> Finally, during the preparation of this manuscript Fensterbank et al. reported the 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) promoted oxidation of several alkyltrifluoroborates, which required high temperatures and long reaction times (120 °C, 20 h) with excess TEMPO (1.2 equiv) and copper salts (1.2 equiv) in DMSO, or 3 equiv of TEMPO in the presence of Dess-Martin periodinane in Et<sub>2</sub>O at room temperature for 1–2 d. The products isolated were the corresponding TEMPO derivatives, which were accessed in modest to good yields depending on the substrates. Importantly, these reactions were demonstrated to proceed via radical intermediates, and thus they would not be expected to be stereospecific for enantiomerically enriched alkyltrifluoroborates, although this latter aspect was not specifically addressed in an unambiguous manner.

The lack of examples detailing a practical method for the oxidation of organotrifluoroborates and the limitations associated with other boron derivatives prompted us to investigate a general, efficient, mild, rapid and convenient method for this transformation. Herein, we report the oxidation of a broad range of aryl-, heteroaryl-, alkenyl-, and alkyltrifluoroborates using Oxone<sup>®</sup> at room temperature.

## Results and Discussion

Based on previous research in which a variety of arylboronic acids and pinacol boronates were transformed to the corresponding phenols,<sup>5d,g</sup> investigations were initiated on the oxidation of potassium naphthalen-1-yltrifluoroborate. Very rapidly it was evident that the protocol developed by Maleczka and Smith for pinacol boronates, using 1 equiv of Oxone<sup>®</sup> (as a 0.2 M solution in H<sub>2</sub>O) in acetone at room temperature, open to the air, was also ideal for the rapid (<5 min) oxidation of organotrifluoroborates. The desired phenol was obtained by an aqueous workup and simple filtration in excellent yield (99%). Because Oxone<sup>®</sup> is an inexpensive,<sup>11</sup> widely available and industrially acceptable reagent, all subsequent reactions were performed using this material.

With optimal conditions in hand, the investigation continued to outline the full scope of this process. The requisite potassium organotrifluoroborates needed for the study were readily prepared by previously reported procedures.<sup>6,12</sup> Initially, a broad range of electron-rich and electron-neutral aryltrifluoroborates were investigated (Table 1). In all cases, quantitative conversion to the desired products was accomplished in only 2 min. The reaction provided excellent yields for all substrates containing para, meta, or ortho substituents (entries 3 to 5). Sterically hindered compounds also afforded the products in high yields (entry 7).

Importantly, we demonstrated that the reaction could be scaled to 55 mmol, providing product **1a** in 96% yield (Table 1, entry 1). Contrary to the metal catalyzed processes utilizing other organoboron species, the use of organotrifluoroborates and Oxone<sup>®</sup> in every case afforded the desired products with little or no formation of organic side products. Therefore, a simple aqueous workup followed, at most, by filtration through a short plug of silica with charcoal afforded the desired products in virtually quantitative yield. *Throughout the course of this study, no chromatography was required to obtain pure products.*

To demonstrate the ability of organotrifluoroborates to serve in the role detailed in Scheme 1, in which a functionalized substrate could be elaborated and then converted into the phenol in a late synthetic stage, potassium (*Z*)-(4-(4-cyanobut-1-en-1-yl)phenyl)trifluoroborate was synthesized through a Wittig reaction of 4-formylphenyltrifluoroborate and the nitrile-containing ylide<sup>12f</sup> (Scheme 2). The organotrifluoroborate was then converted into the phenol, using the oxidation protocol with Oxone<sup>®</sup>. The desired product was obtained in excellent yield in only 2 minutes without affecting either the nitrile or the double bond of the molecule.<sup>13</sup>

Next, attention was turned to electron-poor aryltrifluoroborates. The conditions developed worked equally well for these substrates, providing the phenols in excellent yields (Table 2). Substrates such as aldehyde-, ester-, keto-, nitrile-, and nitro-containing aryltrifluoroborates afforded the hydroxylated product without affecting the pendant functional groups (entries 7 to 11). Halogenated trifluoroborates also provide the corresponding phenol in excellent yields (entries 1 to 6).

To expand the utility of the developed conditions further, heteroaryl systems were investigated, including dibenzothiophenyl-, dibenzofuranyl-, pyridinyl-, benzothiophenyl-, benzofuranyl-, thiophenyl- and furanyl derivatives (Table 3). Heteroaryls, such as dibenzo[b,d]furan-4-yl-, dibenzo[b,d]thiophen-4-yl-, 6-chloropyridin-3-yl- and 6-fluoro-5-methylpyridin-3-yltrifluoroborate, afforded the desired phenol in excellent yields in only 5 min (entries 1 to 4). For substrates where the most stable tautomers are the carbonyl isomer,<sup>14</sup> only the keto-tautomer was observed (entries 5 to 8). 2-Trifluoroborato-furan afforded the  $\beta,\gamma$ -unsaturated lactone (entry 9), along with 10% of the  $\alpha,\beta$ -unsaturated product. Interestingly, under the reaction conditions, no oxidation of the nitrogen or sulfur atom of these heterocycles was observed.<sup>15</sup>

The scope of the general reaction conditions was further extended to alkyl- and alkenyltrifluoroborates (Table 4). We were pleased to find that the desired alcohol was obtained in excellent yields from primary, secondary and benzylic alkyltrifluoroborates (entries 1 to 8). Primary alcohols containing halogens or ester groups were generated without affecting these incorporated functional groups. Alkenyltrifluoroborates were converted into the corresponding aldehydes, also in excellent yields (entries 9 to 11). However, under the reaction conditions, minor amounts of the hydrated aldehyde were observed (entries 9 and 10). Oxidation of both alkyltrifluoroborates and alkenyltrifluoroborates was complete in only 2 minutes.

To investigate the stereochemical integrity of the process, the enantiomerically enriched  $\beta$ -trifluoroboratoamide was prepared from the corresponding  $\alpha,\beta$ -unsaturated amide and bis(pinacolato)diboron in a copper-catalyzed process using (*R*)-(*S*)-Josiphos as the chiral ligand, according to the procedures previously reported by Yun et al. (Scheme 3).<sup>16</sup> With the enantioeriched organotrifluoroborate in hand, this material was subjected to the oxidation conditions with Oxone<sup>®</sup>. We were pleased to observe that the transformation transpired with complete retention of configuration. The desired alcohol was obtained in 97% yield in only 2 minutes, in a 94 : 6 (*R* : *S*) ratio.

In summary, we have successfully developed a general, rapid and efficient method for the oxidation of aryl-, heteroaryl-, alkyl-, and alkenyltrifluoroborates. The reactions were complete in only 2 to 5 minutes at room temperature, affording the desired products in virtually quantitative yield. The use of Oxone<sup>®</sup> as the oxidant makes the process both economical and environmentally sound. Numerous attendant functional groups were tolerated in this process, and no chromatography was required – a simple aqueous workup followed at most by filtration through a plug of silica gel afforded pure material. The oxidation of enantiomerically enriched secondary alkyltrifluoroborates affords the desired alcohols with complete retention of configuration.

## Experimental Section

### General Experimental Procedure for the Preparation of Phenols (55 mmol scale).

#### Preparation of Phenol (1a).<sup>4</sup>

To a 50 mL round bottom flask containing a mixture of potassium phenyltrifluoroborate (10.12 g, 55.0 mmol) and acetone (275 mL, 0.2 M) was added Oxone<sup>®</sup> (275 mL of a 0.2 M solution in H<sub>2</sub>O, 1 equiv) in one portion. The reaction was stirred at rt until <sup>11</sup>B NMR indicated completion of the reaction (~2 min). To the crude mixture was added H<sub>2</sub>O (30 mL) and aqueous HCl (0.1 M, 20 mL), and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 50 mL). The combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>), filtered, concentrated, and dried *in vacuo*. The crude extract was filtered through a small plug of silica topped with charcoal, eluting with CH<sub>2</sub>Cl<sub>2</sub> to afford the desired pure product in 96% yield (5.0 g, 53 mmol) as a light yellow solid, mp 41 – 43 °C (lit. 40 – 42 °C). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.24 (t, *J* = 7.5 Hz, 2H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.83 (d, *J* = 8.5 Hz, 2H), 4.88 (brs, 1H). <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>) δ 155.4, 129.7, 120.8, 115.3.

### General Experimental Procedure for the Preparation of Phenols (1 mmol scale).

#### Preparation of Naphthalen-1-ol (1b).<sup>4</sup>

To a 50 mL round bottom flask containing a mixture of potassium naphthalen-1-yltrifluoroborate (0.23 g, 1.0 mmol) and acetone (5 mL, 0.2 M) was added Oxone<sup>®</sup> (5 mL of a 0.2 M solution in H<sub>2</sub>O, 1 equiv) in one portion. The reaction was stirred at rt until <sup>11</sup>B NMR indicated completion of the reaction (~2 min). To the crude mixture was added H<sub>2</sub>O (5 mL) and aqueous HCl (0.1 M, 3 mL), and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 15 mL). The combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>), filtered, concentrated, and dried *in vacuo*. The crude extract was filtered through a small plug of silica topped with charcoal, eluting with CH<sub>2</sub>Cl<sub>2</sub> to afford the desired pure product in 99% yield (0.14 g, 0.99 mmol) as a white solid, mp 91 – 93 °C (lit.<sup>3a</sup> 92 – 94 °C). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.17 (m, 1H), 7.81 (m, 1H), 7.50–7.48 (m, 2H), 7.44 (d, *J* = 8.5 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 7.5 Hz, 1H), 5.21 (brs, 1H). <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>) δ 151.3, 134.8, 127.7, 126.4, 125.8, 125.2, 124.3, 121.5, 120.7, 108.6.

#### Naphthalen-2-ol (1c).<sup>4</sup>

The general procedure was employed using potassium naphthalen-2-yltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 97% yield (0.14 g, 0.97 mmol) as a white solid, mp 121–123 °C (lit. 122–124 °C). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.75 (t, *J* = 8.9 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.42 (m, 1H), 7.32 (m, 1H), 7.13 (m, 1H), 7.08 (m, 1H), 5.01 (brs, 1H). <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>) δ 134.4, 134.3, 133.1, 130.9, 128.8, 127.9, 126.9, 126.6, 126.0.

#### 4-Methoxyphenol (1d).<sup>4</sup>

The general procedure was employed using potassium 4-methoxyphenyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 98% yield

(0.12 g, 0.98 mmol) as a white solid, mp 57–58 °C (lit 57–58 °C).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.79 – 6.75 (m, 4H), 5.31 (s, 1H), 3.76 (s, 3H).  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{DMSO-d}_6$ )  $\delta$  161.6, 137.6, 136.0, 114.0, 55.8.

### 3-Methoxyphenol (1e).<sup>4</sup>

The general procedure was employed using potassium 3-methoxyphenyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 93% yield (0.11 g, 0.93 mmol) as a light yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.12 (m, 1H), 6.50 (m, 1H), 6.44 – 6.41 (m, 2H), 5.62 (brs, 1H), 3.75 (s, 3H).  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  160.8, 156.6, 130.2, 107.9, 106.5, 101.6, 55.3.

### 2-Methoxyphenol (1f).<sup>4</sup>

The general procedure was employed using potassium 2-methoxyphenyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 97% yield (0.12 g, 0.97 mmol) as a light yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.93 (m, 1H), 6.88 – 6.84 (m, 3H), 5.61 (brs, 1H), 3.89 (s, 3H).  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  146.6, 145.7, 121.5, 120.1, 114.5, 110.7, 55.9.

### 2,4-Dimethoxyphenol (1g).<sup>17</sup>

The general procedure was employed using potassium 2,4-dimethoxyphenyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 95% yield (0.15 g, 0.95 mmol) as a light yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.75 (d,  $J = 9.0$  Hz, 1H), 6.56 (d,  $J = 3.0$  Hz, 1H), 6.37 (m, 1H), 5.78 (brs, 1H), 3.81 (s, 3H), 3.73 (s, 3H).  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  154.5, 146.4, 141.0, 111.5, 104.5, 101.8, 56.5, 55.6.

### 2,6-Dimethylphenol (1h).<sup>4</sup>

The general procedure was employed using potassium 2,6-dimethyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 94% yield (0.11 g, 0.94 mmol) as a white solid, mp 43–45 °C (lit. 42–43 °C).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.96 (d,  $J = 7.5$  Hz, 2H), 6.75 (t,  $J = 7.5$  Hz, 1H), 4.61 (brs, 1H), 2.23 (s, 6H).  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  152.1, 128.6, 123.0, 120.2, 15.8.

### 4-*tert*-Butylphenol (1i).<sup>3d</sup>

The general procedure was employed using potassium 4-*tert*-butylphenyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 99% yield (0.15 g, 0.99 mmol) as a white solid, mp 97–99 °C (lit. 96–99 °C).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25 (d,  $J = 6.5$  Hz, 2H), 7.17 (d,  $J = 6.5$  Hz, 2H), 4.66 (brs, 1H), 1.29 (s, 9H).  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  153.1, 143.6, 126.4, 114.7, 34.1, 31.5.

### 4-(Benzyloxy)phenol (1j).<sup>18</sup>

The general procedure was employed using potassium 4-(benzyloxy)phenyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 97% yield (0.19 g, 0.97 mmol) as a light yellow solid, mp 117–121 °C (lit. 118 – 122 °C).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42–7.36 (m, 4H), 7.32 (m, 1H), 6.85 (d,  $J = 9$  Hz, 2H), 6.75 (d,  $J = 9$  Hz, 2H), 5.00 (s, 2H), 4.46 (brs, 1H).  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  149.6, 137.2, 128.5, 127.9, 127.5, 116.1, 116.0, 70.8.

### (*Z*)-5-(4-Hydroxyphenyl)pent-4-enitrile (1k)

The general procedure was employed using potassium (*Z*)-4-(4-cyanobut-1-enyl)phenyltrifluoroborate, and the reaction was complete in 2 min. The desired pure

product was obtained in 98% yield (0.17 g, 0.98 mmol) as a white solid. mp 67–69 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.12 (d, *J* = 8.5 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 2H), 6.52 (d, *J* = 11.5 Hz, 1H), 5.55 (m, 1H), 5.00 (brs, 1H), 2.69 – 2.65 (m, 2H), 2.44 (t, *J* = 7.0 Hz, 2H). <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>) δ 154.8, 131.6, 130.1, 129.2, 126.0, 119.2, 115.2, 24.4, 17.6. IR (neat) 3325, 2257, 1608, 1514, 1228, 836 cm<sup>-1</sup>. HRMS (ESI) *m/z* calcd. for C<sub>11</sub>H<sub>11</sub>NONa (M+Na)<sup>+</sup> 196.0738, found 196.0741.

#### 4-Iodophenol (2a).<sup>19</sup>

The general procedure was employed using potassium 4-iodophenyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 85% yield (0.19 g, 0.85 mmol) as a light yellow solid mp 90–93 °C (lit. 92–95 °C). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.50 (d, *J* = 9.0 Hz, 2H), 6.61 (d, *J* = 9.0 Hz, 2H), 5.00 (brs, 1H). <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>) δ 155.2, 138.4, 117.8, 82.8.

#### 4-Bromophenol (2b).<sup>20</sup>

The general procedure was employed using potassium 4-bromophenyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 98% yield (0.17 g, 0.98 mmol) as a light yellow solid mp 55–58 °C (lit. 54–64 °C). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.31 (d, *J* = 8.5 Hz, 2H), 6.70 (d, *J* = 9.0 Hz, 2H), 5.64 (brs, 1H). <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>) δ 154.4, 132.5, 117.2, 112.9.

#### 4-Chlorophenol (2c).<sup>4</sup>

The general procedure was employed using potassium 4-chlorophenyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 99% yield (0.13 g, 0.99 mmol) as a white solid, mp 43–46 °C (lit. 44–45 °C). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.18 (d, *J* = 9.0 Hz, 2H), 6.75 (d, *J* = 8.5 Hz, 2H), 5.52 (brs, 1H). <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>) δ 153.9, 129.5, 125.7, 116.7.

#### 4-Fluorophenol (2d).<sup>4</sup>

The general procedure was employed using potassium 4-fluorophenyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 99% yield (0.11 g, 0.99 mmol) as a white solid, mp 45–47 °C (lit. 46–47 °C). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 6.95 – 6.90 (m, 2H), 6.79 – 6.74 (m, 2H), 4.88 (brs, 1H). <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>) δ 157.2 (d, *J* = 235.9 Hz), 151.4, 116.2 (d, *J* = 10.0 Hz, 2C), 116.0 (d, *J* = 22.9, 2C). <sup>19</sup>F NMR (470.8 MHz, CDCl<sub>3</sub>) δ –124.3.

#### 2,4-Difluorophenol (2e).<sup>5f</sup>

The general procedure was employed using potassium 2,4-difluorophenyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 97% yield (0.13 g, 0.97 mmol) as a light yellow oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 6.95 (m, 1H), 6.85 (m, 1H), 6.76 (m, 1H), 5.75 (brs, 1H). <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>) δ 155.9 (dd, *J* = 240.9, 10.3 Hz), 150.4 (dd, *J* = 240.1, 12.2 Hz), 139.9 (dd, *J* = 14.1, 3.5 Hz), 117.3 (d, *J* = 6.4 Hz), 111.7 – 110.6 (m), 104.5 – 103.3 (m). <sup>19</sup>F NMR (470.8 MHz, CDCl<sub>3</sub>) δ –121.0, –135.7.

#### 4-(Trifluoromethyl)phenol (2f).<sup>21</sup>

The general procedure was employed using potassium 4-(trifluoromethyl)phenyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 98% yield (0.16 g, 0.98 mmol) as a light yellow oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.50 (d, *J* = 8.5 Hz, 2H), 6.90 (d, *J* = 9 Hz, 2H), 5.45 (brs, 1H). <sup>13</sup>C

NMR (125.8 MHz, CDCl<sub>3</sub>)  $\delta$  158.1, 127.2 (q,  $J = 3.8$  Hz), 125.4, 123.7 – 122.7 (m), 115.4. <sup>19</sup>F NMR (470.8 MHz, CDCl<sub>3</sub>)  $\delta$  -61.5.

#### 4-Hydroxybenzonitrile (2g).<sup>5f</sup>

The general procedure was employed using potassium 4-cyanophenyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 98% yield (0.12 g, 0.98 mmol) as a light yellow solid mp 107–109 °C (lit. 108–109 °C). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.57 (d,  $J = 9.0$  Hz, 2H), 6.94 (d,  $J = 8.5$  Hz, 2H), (brs, 1H). <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>)  $\delta$  160.0, 134.3, 119.2, 116.4, 103.3.

#### 4-Hydroxybenzaldehyde (2h).<sup>4</sup>

The general procedure was employed using potassium 4-formylphenyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 99% yield (0.12 g, 0.99 mmol) as a white solid, mp 114–117 °C (lit. 114–116 °C). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  9.87 (s, 1H), 7.82 (d,  $J = 8.5$  Hz, 2H), 6.97 (d,  $J = 9.0$  Hz, 2H), 6.73 (brs, 1H). <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>)  $\delta$  191.1, 161.4, 132.4, 129.9, 115.9.

#### Methyl 4-Hydroxybenzoate (2i).<sup>22</sup>

The general procedure was employed using potassium 4-(methoxycarbonyl)phenyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 99% yield (0.15 g, 0.99 mmol) as a white solid, mp 121–123 °C (lit. 127–129 °C). <sup>1</sup>H NMR (500 MHz, acetone-*d*<sub>6</sub>)  $\delta$  9.12 (brs, 1H), 7.89 (d,  $J = 9.0$  Hz, 2H), 6.92 (d,  $J = 9.0$  Hz, 2H), 3.82 (s, 3H). <sup>13</sup>C NMR (125.8 MHz, acetone-*d*<sub>6</sub>)  $\delta$  167.8, 163.4, 133.2, 123.3, 116.8, 52.6.

#### 1-(4-Hydroxyphenyl)ethanone (2j).<sup>20</sup>

The general procedure was employed using potassium 4-acetylphenyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 99% yield (0.13 g, 0.99 mmol) as a white solid, mp 105–107 °C (lit. 108–109 °C). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.24 (brs, 1H), 7.92 (d,  $J = 9.0$  Hz, 2H), 6.97 (d,  $J = 9.0$  Hz, 2H), 2.59 (s, 3H). <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>)  $\delta$  199.0, 161.6, 131.3, 129.4, 115.6, 26.3.

#### 3-Nitrophenol (2k).<sup>4</sup>

The general procedure was employed using potassium 3-nitrophenyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 98% yield (0.14 g, 0.98 mmol) as a light yellow solid mp 96–99 °C (lit. 98–99 °C). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.82 (m, 1H), 7.71 (t,  $J = 2.0$  Hz, 1H), 7.41 (t,  $J = 8.0$  Hz, 1H), 7.19 (m, 1H), 5.61 (brs, 1H). <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>)  $\delta$  156.3, 130.3, 122.0, 115.9, 110.6.

#### Dibenzo[*b,d*]furan-4-ol (3a)

The general procedure was employed using potassium dibenzo[*b,d*]furan-4-yltrifluoroborate, and the reaction was complete in 5 min. The desired pure product was obtained in 97% yield (0.18 g, 0.97 mmol) as a white solid, mp 98–100 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.93 (d,  $J = 7.7$  Hz, 1H), 7.57 (d,  $J = 8.3$  Hz, 1H), 7.51 (d,  $J = 7.7$  Hz, 1H), 7.46 (t,  $J = 7.8$  Hz, 1H), 7.35 (t,  $J = 7.5$  Hz, 1H), 7.23 (m, 1H), 7.02 (d,  $J = 7.9$  Hz, 1H), 5.39 (s, 1H). <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>)  $\delta$  156.1, 144.0, 141.1, 127.3, 125.7, 124.6, 123.7, 123.0, 121.0, 113.6, 112.8, 111.8. IR (neat) 3277, 1603, 1437, 1249, 744 cm<sup>-1</sup>. HRMS (ESI) *m/z* calcd. for C<sub>12</sub>H<sub>7</sub>O<sub>2</sub> (M-H)<sup>-</sup> 183.0446, found 183.0454.

**Dibenzo[*b,d*]thiophen-4-ol (3b)**

The general procedure was employed using potassium dibenzo[*b,d*]thiophen-4-yltrifluoroborate, and the reaction was complete in 5 min. The desired pure product was obtained in 97% yield (0.18 g, 0.97 mmol) as a white solid. mp 158–160 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.13 (m, 1H), 7.89 (m, 1H), 7.78 (d, *J* = 7.9 Hz, 1H), 7.50 – 7.42 (m, 2H), 7.34 (t, *J* = 7.8 Hz, 1H), 6.88 (d, *J* = 7.7 Hz, 1H), 5.35 (s, 1H). <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>) δ 150.5, 139.6, 137.9, 135.9, 126.9, 126.5, 125.7, 124.4, 123.1, 122.0, 114.5, 111.7. IR (neat) 3230, 1569, 1444, 1253, 744 cm<sup>-1</sup>. HRMS (ESI) *m/z* calcd. for C<sub>12</sub>H<sub>7</sub>OS (M-H)<sup>-</sup> 199.0218, found 199.0222.

**6-Chloropyridin-3-ol (3c)**

The general procedure was employed using potassium 6-chloropyridin-3-yltrifluoroborate, and the reaction was complete in 5 min. The desired pure product was obtained in 91% yield (0.12 g, 0.97 mmol) as a white solid, mp 155–157 °C. <sup>1</sup>H NMR (500 MHz, acetone-*d*<sub>6</sub>) δ 9.04 (brs, 1H), 7.99 (d, *J* = 2.9 Hz, 1H), 7.40 – 7.14 (m, 2H). <sup>13</sup>C NMR (125.8 MHz, acetone-*d*<sub>6</sub>) δ 154.9, 142.5, 138.9, 127.6, 126.1. IR (neat) 3004, 1573, 1464, 1278, 1228, 826 cm<sup>-1</sup>. HRMS (ESI) *m/z* calcd. for C<sub>5</sub>H<sub>3</sub>NOCl (M-H)<sup>-</sup> 127.9903, found 127.9902.

**6-Fluoro-5-methylpyridin-3-ol (3d)**

The general procedure was employed using potassium 6-chloropyridin-3-yltrifluoroborate, and the reaction was complete in 5 min. The desired pure product was obtained in 94% yield (0.12 g, 0.94 mmol) as a white solid. mp 120–122 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.69 (brs, 1H), 7.61 (s, 1H), 7.22 (m, 1H), 2.25 (s, 3H). <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>) δ 157.1, 155.2, 151.1, 129.8 (dd, *J* = 44.4, 9.5 Hz), 120.7 (d, *J* = 34.1 Hz), 14.4. <sup>19</sup>F NMR (470.8 MHz, CDCl<sub>3</sub>) δ -83.9. IR (neat) 3048, 1471, 1232, 770 cm<sup>-1</sup>. HRMS (ESI) *m/z* calcd. for C<sub>6</sub>H<sub>7</sub>NOF (M+H)<sup>+</sup> 128.0512, found 128.0510.

**Benzo[*b*]thiophen-2(3*H*)-one (3e).<sup>23</sup>**

The general procedure was employed using potassium benzothiophen-2-yltrifluoroborate, and the reaction was complete in 5 min. The desired pure product was obtained in 99% yield (0.15 g, 0.99 mmol) as a light yellow oil. <sup>1</sup>H NMR (500 MHz, acetone-*d*<sub>6</sub>) δ 7.44 (m, 1H), 7.38 (d, *J* = 7.5 Hz, 1H), 7.33 (m, 1H), 7.25 (m, 1H), 4.09 (s, 2H). <sup>13</sup>C NMR (125.8 MHz, acetone-*d*<sub>6</sub>) δ 203.7, 138.3, 134.7, 129.8, 127.7, 126.7, 124.5, 48.4.

**Benzofuran-2(3*H*)-one (3f).<sup>24</sup>**

The general procedure was employed using potassium benzofuran-2-yltrifluoroborate, and the reaction was complete in 5 min. The desired pure product was obtained in 97% yield (0.13 g, 0.97 mmol) as a light yellow oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.32 – 7.24 (m, 2H), 7.13 (m, 1H), 7.08 (d, *J* = 8.1 Hz, 1H), 3.71 (s, 2H). <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>) δ 174.0, 154.6, 128.8, 124.5, 123.9, 123.0, 110.6, 32.8.

**5-Bromobenzo[*b*]thiophen-2(3*H*)-one (3g)**

The general procedure was employed using potassium 5-bromobenzo[*b*]thiophen-2-yltrifluoroborate, and the reaction was complete in 5 min. The desired pure product was obtained in 94% yield (0.21 g, 0.94 mmol) as a light yellow solid. mp 117–120 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.49 – 7.37 (m, 2H), 7.21 (d, *J* = 8.9 Hz, 1H), 3.97 (s, 2H). <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>) δ 201.5, 136.1, 133.9, 131.4, 127.9, 124.3, 119.7, 47.1. FT-IR (neat) 1711, 1017, 819 cm<sup>-1</sup>. HRMS (ESI) *m/z* calcd. for C<sub>8</sub>H<sub>4</sub>OSBr (M-H)<sup>-</sup> 226.9166, found 226.9158.



**4-Methylthiophen-2(3H)-one (3h)**

The general procedure was employed using potassium 4-methylthiophen-2-yltrifluoroborate, and the reaction was complete in 5 min. The desired pure product was obtained in 89% yield (0.10 g, 0.89 mmol) as a light yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.09 (m, 1H), 3.97 (s, 2H), 2.21 (s, 3H).  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  199.7, 167.7, 129.0, 40.8, 18.9. FT-IR (neat) 2918, 1676, 1096, 653  $\text{cm}^{-1}$ . HRMS (ESI)  $m/z$  calcd. for  $\text{C}_5\text{H}_7\text{OS}$  (M+H) $^+$  115.0218, found 115.0215.

**Furan-2(3H)-one (3i).<sup>25</sup>**

The general procedure was employed using potassium thiophen-3-yltrifluoroborate, and the reaction was complete in 5 min. The desired pure product was obtained in 98% yield (0.10 g, 0.98 mmol) as a light yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.77 (m, 1H), 5.55 (m, 1H), 3.14 (s, 2H).  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  176.5, 143.8, 105.4, 32.3.

**4-Hydroxybutyl Benzoate (4a).<sup>26</sup>**

The general procedure was employed using potassium 4-(benzoyloxy)butyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 99% yield (0.19 g, 0.99 mmol) as a colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 – 8.02 (m, 2H), 7.53 (m, 1H), 7.44 – 7.40 (m, 2H), 4.35 (t,  $J = 6.5$  Hz, 2H), 3.70 (t,  $J = 6.5$  Hz, 2H), 2.60 (brs, 1H), 1.88 – 1.83 (m, 2H), 1.74 – 1.69 (m, 2H).  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  166.7, 132.8, 130.2, 129.4, 128.3, 64.8, 62.0, 29.1, 25.1.

**6-Hydroxyhexyl Benzoate (4b).<sup>27</sup>**

The general procedure was employed using potassium 7-(benzoyloxy)hexyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 99% yield (0.23 g, 0.99 mmol) as a colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05 – 8.03 (m, 2H), 7.53 (m, 1H), 7.44 – 7.41 (m, 2H), 4.31 (t,  $J = 6.5$  Hz, 2H), 3.63 (t,  $J = 6.5$  Hz, 2H), 2.38 (brs, 1H), 1.80 – 1.75 (m, 2H), 1.62 – 1.56 (m, 2H), 1.48 – 1.43 (m, 4H).  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  166.6, 132.7, 130.2, 129.4, 128.2, 64.8, 62.4, 32.4, 28.5, 25.7, 25.3.

**3-Bromopropan-1-ol (4c).<sup>28</sup>**

The general procedure was employed using potassium 3-bromopropyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 98% yield (0.14 g, 0.98 mmol) as a colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.78 (t,  $J = 6.0$  Hz, 2H), 3.54 (t,  $J = 6.5$  Hz, 2H), 2.69 (brs, 1H), 2.11 – 2.07 (m, 2H).  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  60.1, 34.9, 30.3.

**Cyclopentanol (4d).<sup>29</sup>**

The general procedure was employed using potassium cyclopentyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 99% yield (0.09 g, 0.99 mmol) as a colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  4.33 (m, 1H), 1.78 – 1.76 (m, 4H), 1.59 (brs, 1H), 1.58 – 1.56 (m, 4H).  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  74.0, 35.5, 23.2.

**2-Methylcyclohexanol (4e).<sup>30</sup>**

The general procedure was employed using potassium 2-methylcyclohexyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 96% yield (0.11 g, 0.96 mmol) as a colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.11 (m, 1H), 1.95 – 1.93 (m, 1H), 1.75 – 1.59 (m, 4H), 1.36 – 1.18 (m, 4H), 1.01 (d,  $J = 6.5$  Hz, 3H).  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  76.5, 40.2, 35.5, 33.6, 25.7, 25.2, 18.5.

**3,6,6-Trimethylbicyclo[3.1.1]heptan-2-ol (4f).<sup>31</sup>**

The general procedure was employed using potassium 3,6,6-trimethylbicyclo[3.1.1]heptan-2-yltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 98% yield (0.15 g, 0.98 mmol) as a white solid, mp 49 – 52 °C (lit. 51–53 °C). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 4.05 (m, 1H), 2.64 (brs, 1H), 2.50 (m, 1H), 2.37 (m, 1H), 2.00 – 1.90 (m, 2H), 1.79 (m, 1H), 1.73 (m, 1H), 1.21 (s, 3H), 1.13 (d, *J* = 7.4 Hz, 3H), 1.06 (d, *J* = 9.7 Hz, 1H), 0.92 (s, 3H). <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>) δ 71.3, 47.7, 47.4, 41.67, 38.8, 38.1, 34.2, 27.6, 23.6, 20.6. IR (neat) 3260, 2905, 1469, 1043, 1006, 923 cm<sup>-1</sup>. HRMS (ESI) *m/z* calcd. for C<sub>10</sub>H<sub>17</sub> (M-OH)<sup>+</sup> 137.1330, found 137.1326.

**2-Phenylethanol (4g).<sup>27</sup>**

The general procedure was employed using potassium phenethyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 99% yield (0.12 g, 0.99 mmol) as a colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.30 – 7.27 (m, 2H), 7.21 – 7.18 (m, 3H), 3.78 (t, *J* = 6.5 Hz, 2H), 2.81 (t, *J* = 6.5 Hz, 2H), 2.20 (brs, 1H). <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>) δ 138.6, 129.0, 128.5, 126.4, 63.5, 39.1.

**Phenylmethanol (4h).<sup>32</sup>**

The general procedure was employed using potassium benzyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 99% yield (0.11 g, 0.99 mmol) as a colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.32 – 7.25 (m, 5H), 4.56 (s, 2H), 2.90 (brs, 1H). <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>) δ 140.8, 128.4, 127.4, 126.9, 64.9.

**11-Hydroxydodecanal (4i).<sup>33</sup>**

The general procedure was employed using potassium (*E*)-11-hydroxydodec-1-en-1-yltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 99% yield (0.2 g, 0.99 mmol) as a colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.76 (t, *J* = 1.9 Hz, 1H), 3.79 (m, 1H), 2.44 – 2.40 (m, 2H), 1.69 – 1.50 (m, 2H), 1.41 (d, *J* = 14.2 Hz, 2H), 1.29 (s, 12H), 1.19 (d, *J* = 6.2 Hz, 3H). <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>) δ 68.2, 43.9, 39.3, 29.6, 29.3, 29.1, 25.7, 22.1.

**Methyl 6-Oxohexanoate (4j).<sup>34</sup>**

The general procedure was employed using potassium (*E*)-6-methoxy-6-oxohex-1-en-1-yltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 99% yield (0.14 g, 0.99 mmol) as a colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.77 (t, *J* = 1.2 Hz, 1H), 3.67 (s, 3H), 2.55 – 2.25 (m, 4H), 1.67 (m, 4H). <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>) δ 202.0, 174.0, 173.7, 51.5, 43.5, 33.7, 24.3, 21.5.

**2-(2,2-Dimethyl-4-oxo-4*H*-benzo[*d*][1,3]dioxin-5-yl)acetaldehyde (4k)**

The general procedure was employed using potassium (*E*)-(2-(2,2-dimethyl-4-oxo-4*H*-benzo[*d*][1,3]dioxin-5-yl)vinyl)trifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 99% yield (0.22 g, 0.99 mmol) as a light yellow solid, mp 55 – 57 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.84 (s, 1H), 7.50 (t, *J* = 8 Hz, 1H), 6.96 (d, *J* = 8.3 Hz, 1H), 6.91 (d, *J* = 7.5 Hz, 1H), 4.22 (s, 2H), 1.75 (s, 6H). <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>) δ 198.1, 160.8, 157.1, 137.0, 135.6, 126.4, 117.0, 112.6, 105.7, 49.0, 25.6. IR (neat) 1722, 1292, 1052 cm<sup>-1</sup>. HRMS (ESI) *m/z* calcd. for C<sub>12</sub>H<sub>12</sub>O<sub>4</sub>Na (M+Na)<sup>+</sup> 243.0633, found 243.0633.

**(R)-3-hydroxy-N-(4-methoxyphenyl)butanamide (5).**<sup>35</sup>

The general procedure was employed using 0.1 mmol of potassium (*R*)-(4-((4-methoxyphenyl)amino)-4-oxobutan-2-yl)trifluoroborate (*R* : *S*) (97 : 3), and the reaction was complete in 2 min. The desired pure product was obtained in 97% yield (0.020 g, 0.097 mmol) as a white solid, mp 136–138 °C (lit. 135 °C). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.75 (brs, 1H), 7.39 (d, *J* = 9.0 Hz, 2H), 6.85 (d, *J* = 9.0 Hz, 2H), 4.28 (m, 1H), 3.78 (s, 3H), 3.43 (d, *J* = 2.9 Hz, 1H), 2.52 – 2.41 (m, 2H), 1.27 (d, *J* = 6.5 Hz, 3H). <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>) δ 170.3, 156.5, 130.5, 122.0, 114.1, 64.9, 55.5, 44.8, 22.9.

**Supplementary Material**

Refer to Web version on PubMed Central for supplementary material.

**Acknowledgments**

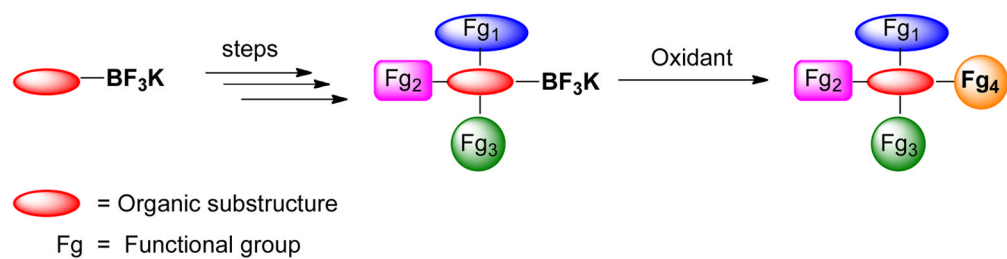
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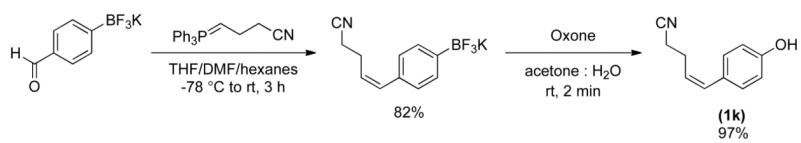
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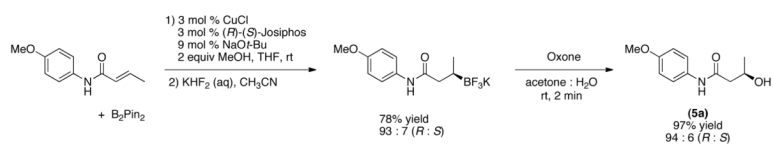
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SCHEME 1.



SCHEME 2.



SCHEME 3.



TABLE 1

Oxidation of Electron-rich and Electron-neutral Potassium Aryltrifluoroborates<sup>a</sup>

entry	substrate	product	isolated yield (%)	
1			<b>1a</b>	96 <sup>b</sup>
2			<b>1b</b>	99
3			<b>1c</b>	97
4			<b>1d</b>	98
5			<b>1e</b>	93
6			<b>1f</b>	97
7			<b>1g</b>	95
8			<b>1h</b>	94
9			<b>1i</b>	99
10			<b>1j</b>	97

<sup>a</sup> All reactions were carried out using 1 mmol of aryltrifluoroborate and Oxone (5 mL, 0.2 M in H<sub>2</sub>O) in 5 mL of acetone for 2 min at rt.<sup>b</sup> 55 mmol scale.

TABLE 2

Oxidation of Electron-poor Potassium Aryltrifluoroborates<sup>a</sup>

entry	substrate	product	isolated yield (%)	
1			<b>2a</b>	85
2			<b>2b</b>	98
3			<b>2c</b>	99
4			<b>2d</b>	99
5			<b>2e</b>	97
6			<b>2f</b>	98
7			<b>2g</b>	98
8			<b>2h</b>	99
9			<b>2i</b>	99
10			<b>2j</b>	99
11			<b>2k</b>	98

<sup>a</sup>All reactions were carried out using 1 mmol of aryltrifluoroborate and Oxone (5 mL, 0.2 M in H<sub>2</sub>O) in 5 mL of acetone for 2 min at rt.

TABLE 3

Hydroxylation of Potassium Heteroaryltrifluoroborates<sup>a</sup>

entry	substrate	product	isolated yield (%)
1			<b>3a</b> 97
2			<b>3b</b> 95
3			<b>3c</b> 91
4			<b>3d</b> 94
5			<b>3e</b> 99
6			<b>3f</b> 97
7			<b>3g</b> 94
8			<b>3h</b> 89
9			<b>3i</b> 97

<sup>a</sup> All reactions were carried out using 1 mmol of aryltrifluoroborate and Oxone (5 mL, 0.2 M in H<sub>2</sub>O) in 5 mL of acetone for 2 min at rt.

TABLE 4

Hydroxylation of Potassium Alkyl- and Alkenyltrifluoroborates<sup>a</sup>

entry	substrate	product	isolated yield (%)
1			<b>4a</b> 99
2			<b>4b</b> 99
3			<b>4c</b> 98
4			<b>4d</b> 95
5			<b>4e</b> 96
6			<b>4f</b> 98
7			<b>4g</b> 99
8			<b>4h</b> 99
9			<b>4i</b> 99
10			<b>4j</b> 99
11			<b>4k</b> 99

<sup>a</sup>All reactions were carried out using 1 mmol of aryltrifluoroborate and Oxone (5 mL, 0.2 M in H<sub>2</sub>O) in 5 mL of acetone for 2 min at rt.