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One-pot preparation of hydroxylated potassium organotrifluoroborates and subsequent Jones oxidation to potassium organocarbonyltrifluoroborates

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ABSTRACT

Alcohol-containing potassium organotrifluoroborates as starting reagents were prepared from their corresponding dibromobenzenes through a sequential one-pot reaction. The oxidation reactions of these substrates, which were carried out using 3.0 equiv of 8 N Jones reagent in acetone at 0 °C, provided a high yield of the desired carbonyl-functionalized compounds. In addition, the cross-coupling reactions of these organocarbonyltrifluoroborates were successfully performed in the presence of 3 mol % of Pd $(PPh_3)_4$ catalyst at 100 °C.

1. Introduction

Carbonyl-substituted compounds have attracted much attention because of their applications as versatile functional groups in synthetic organic chemistry.[1] Thus, a number of methods have been developed for the formation of carbonyl moieties on various pharmaceutical, biological, and industrial compounds. Among them, the method used most widely involves the oxidation of primary and secondary alcohols to the corresponding carbonyl compounds.[2] For example, the selective oxidative transformation of alcohols has been performed routinely using oxidizing agents, such as oxochromium (VI) reagents (PCC, Jones, and Collins reagents), permanganate, active manganese dioxide, activated DMSO with TFAA or oxalyl chloride (Swern oxidation), DessMartin periodinane (DMP), and 2-iodoxybenzoic acid (IBX).[2]

On the other hand, organotrifluoroborate salts have been recognized as useful synthetic reagents in the Suzuki–Miyaura cross-coupling reaction.[3] Recently, methods for the direct functionalization of organotrifluoroborates, using their property of inertness under various reaction conditions, has been developed and used for the preparation of more complex organotrifluoroborates, which may be difficult to prepare by conventional syntheses of organoboron reagents.[3b–d,4]

In 2006, Molander and Petrillo first reported the direct oxidation of hydroxylated organotrifluoroborates using tetra-*n*-propylammonium perruthenate (TPAP), DMP, IBX, and the Swern oxidation.[5] However, depending on the counterions (potassium or tetra-*n*-butylammonium (TBA)) of organotrifluoroborates, this procedure requires long reaction times, high reaction temperatures, and excess oxidizing reagents to obtain satisfactory results. Moreover, pure aldehyde-functionalized potassium organotrifluoroborates could not be prepared from the corresponding primary alcohol-containing organotrifluoroborates because of unisolated IBX byproducts. Therefore, the oxidative transformation of primary and secondary alcohol-containing organotrifluoroborates using a cheap and easily available oxidizing reagent would be very useful for the preparation of various carbonyl-functionalized organoboron compounds.

In a recent paper, Burke and Gillis reported that benzoic acid-containing MIDA (*N*-methyliminodiacetic acid) boronate could be prepared from the corresponding primary alcohol-substituted MIDA boronate via Jones oxidation.[6] However, boronic acid, pinacol boronate ester, 1,8-diaminonaphtalene-masked boronamide, tetra-*n*-butylammoniumtrifluoroborate, and *N*-methyldiethanolamine boronate were all decomposed under the same conditions. Moreover, in their paper, Jones oxidation using potassium organotrifluoroborate as a starting material has not been reported.

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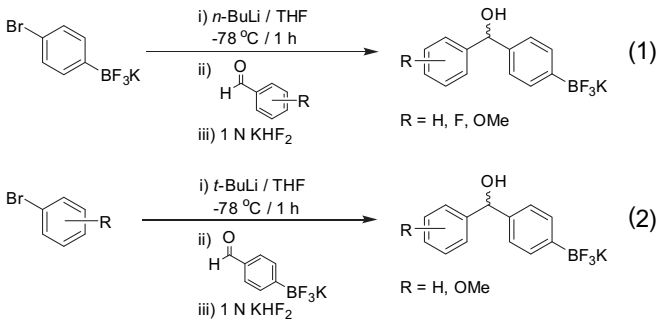
As part of the study to prepare functionalized potassium organotrifluoroborates for use as new coupling reagents in the Suzuki–Miyaura cross-coupling reaction, we discovered that potassium organocarbonyltrifluoroborates are readily obtained from the treatment of primary or secondary alcohol-containing organotrifluoroborates with Jones reagent. The Jones oxidation is generally performed in acetone as a solvent in which potassium organotrifluoroborate salts are soluble. Thus, potassium counterion salts can be used immediately without the need for converting them into TBA salts. Also, we confirmed that these hydroxylated potassium organotrifluoroborates can tolerate under Jones oxidation conditions contrary to other organoboron derivatives.

In this paper, we report a facile one-pot synthesis of secondary alcohol-containing organotrifluoroborates from their corresponding dibromobenzenes, followed by the convenient preparation of potassium organocarbonyltrifluoroborates via Jones oxidation.

2. Results and discussion

As a starting point, we tested two reactions for the preparation of alcohol-containing organotrifluoroborates using potassium 4-bromophenyltrifluoroborate (Scheme 1, Eq. 1) or potassium (4-formylphenyl)trifluoroborate (Scheme 1, Eq. 2).



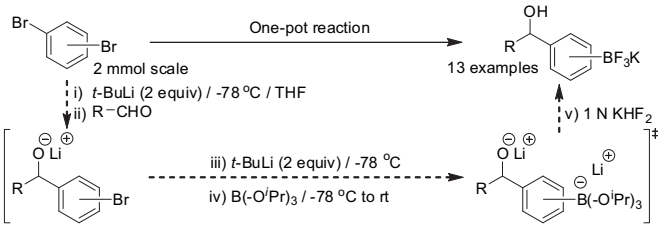
Scheme 1. General preparation of secondary alcohol-substituted potassium organotrifluoroborates.

Although the desired compounds were obtained in the lithium–halogen exchange reaction using potassium 4-bromophenyltrifluoroborate as a starting material (Scheme 1, Eq. 1),[7] all of the products were contaminated with potassium phenyltrifluoroborate as a byproduct, which is not separable (data not shown). When potassium (4-formylphenyl)trifluoroborate was used as the electrophile (Scheme 1, Eq. 2), the target products were produced in much lower yields because of the poor solubility of the electrophile, i.e., trifluoroborate salt, in THF (data not shown). Thus, we discovered the one-pot, sequential reaction for the preparation of various secondary alcohol-containing organotrifluoroborates from the corresponding dibromobenzenes and aldehydes via a lithium–halogen exchange reaction with *t*-BuLi (Table 1).

As expected, when dibromobenzenes were used as starting materials, the yields for the desired products ranged from good to excellent, except when 1,2-dibromobenzene was used (Table 1, entries 1–3). Aliphatic aldehydes as well as benzaldehydes reacted readily to give good yields of corresponding secondary alcohol-containing organotrifluoroborates (Table 1, entries 8–10). However, when conjugated and heterocyclic aldehydes were used as electrophiles, the yields of the target compounds decreased (Table 1, entries 11–13).

Next, we investigated the oxidation of various hydroxylated potassium organotrifluoroborates using 8 N Jones reagent. The various reaction conditions explored are summarized in Table 2. When compound **14** was treated with 1.0 equiv of 8 N Jones reagent at 0 °C for 10 min followed by solvent removal in the absence of a base, product **18** completely decomposed because of residual sulfuric acid in the reaction mixture (Table 2, entry 1). Using K_2CO_3 as a neutralizing agent, we were able to prepare the oxidized product **18** (Table 2, entries 2–5). When 3.0 equiv of Jones reagent

Table 1
Sequential one-pot preparation of secondary alcohol-substituted potassium organotrifluoroborates from dibromobenzenes and aldehydes



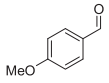
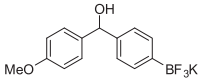
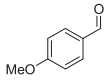
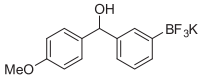
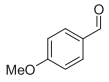
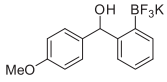
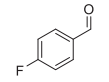
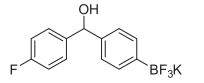
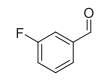
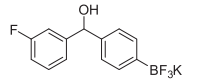
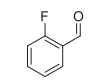
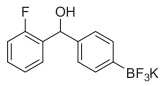
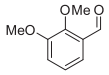
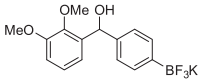
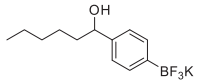
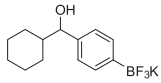
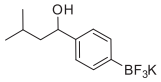
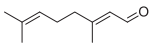
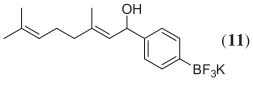
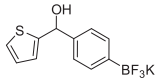
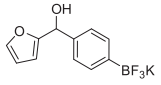
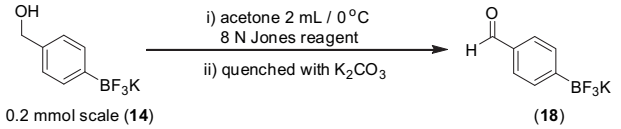
Entry	Aldehyde	HO–RBF$_3$K		Isolated yield (%)
1			(**1**)	83
2			(**2**)	66
3			(**3**)	dec
4			(**4**)	87
5			(**5**)	68
6			(**6**)	65
7			(**7**)	83
8			(**8**)	76
9			(**9**)	78
10			(**10**)	75
11			(**11**)	46
12			(**12**)	52
13			(**13**)	62

Table 2
Optimization of Jones oxidation for the preparation of potassium (4-formylphenyl) trifluoroborate (**18**)



0.2 mmol scale (**14**) (**18**)

Entry	Equiv of 8 N Jones reagent	Equiv of K_2CO_3[a]	Time (min)	Conversion yield (%)[b]
1	1.0	None	10	dec
2	1.0	1.0	10	53
3	1.0	1.0	30	48
4	2.0	2.0	10	81
5	2.0	2.0	30	82
6	3.0	3.0	10	100 (77)[c]

[a] Neutralizing agent.
[b] The conversion yield estimated on the basis of ^{1}H NMR data of crude reaction mixture (4.49 ppm of **14** and 9.94 ppm of **18** in acetone-d_6).
[c] Isolated yield, average of three runs.

was used, the starting material was completely converted to the desired compound **18** (Table 2, entry 6).

However, increasing the reaction times under the same reaction conditions did not improve the conversion yields (Table 2, entries 3 and 5). On the other hand, over-oxidized byproducts, such as potassium (4-carboxyphenyl)trifluoroborate were not generated.

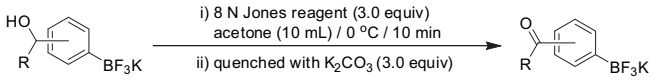
Using the optimized conditions determined in the preparation of **18** (Table 2, entry 6), we carried out the Jones oxidation of various primary and secondary alcohol-containing potassium organotrifluoroborates, and the results are summarized in Table 3.

As expected, all of the carbonyl compounds were quickly prepared from the corresponding alcohols. The yields of the product increased in the order of *para*->*meta*->*ortho*-substituted trifluoroborates (Table 3, entries 1–5). Interestingly, the presence of strong electron-withdrawing group, such as fluorine in the aromatic ring of benzyl alcohol moieties led to the increased yields of oxidized products (Table 3, entries 6–8). Further, the reactions of aliphatic alcohol-containing trifluoroborates produced good yields of their corresponding products (Table 3, entries 10–12). However, the oxidations of allylic- (**13**) and furanyl-substituted (**15**) alcohols were not successful under the same reaction conditions (Table 3, entries 13 and 15). Interestingly, although we could not obtain the aldehyde product under the optimized reaction conditions when potassium 4-(2-hydroxyethyl)phenyltrifluoroborate[8] was used as a starting material, we obtained a moderate yield of the carboxylic acid-containing product **33** in the presence of 9.0 equiv Jones reagent at 0 °C within 30 min (Table 3, entry 16).

Finally, we focused our attention on the optimization of cross-coupling reaction conditions using various potassium organocarbonyltrifluoroborates (Table 4).

In the study of reaction solvents, 20% aqueous 1,4-dioxane was confirmed to be the optimal solvent, whereas methanol[9] and especially 20% aqueous toluene showed lower isolated yields during the same reaction times (Table 4, entries 1, 2, 6, and 7). A number of different Pd catalysts, such as $Pd(OAc)_2/PPh_3$, $Pd(OAc)_2$/XPhos, $PdCl_2(dppf)\cdot CH_2Cl_2$, and $Pd(PPh_3)_4$, were screened for their effectiveness in accomplishing the Suzuki–Miyaura cross-coupling reaction (Table 4, entries 3–6), and it was found that $Pd(PPh_3)_4$ provided the highest isolated yield (Table 4, entry 6). By changing the base from Cs_2CO_3 to K_2CO_3, the product yield declined (Table 4, entry 8). Although attempts to vary the heating source from an oil bath to a microwave did not improve the reaction yield (Table 4,

Table 3
Preparation of carbonyl-containing potassium organotrifluoroborates via Jones oxidation



1.0 mmol scale 16 examples

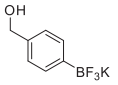
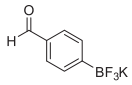
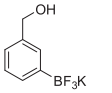
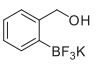
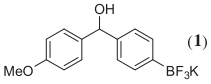
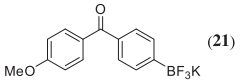
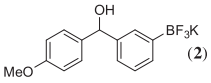
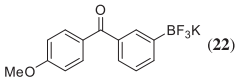
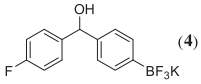
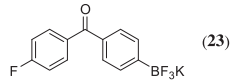
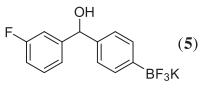
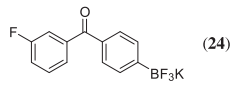
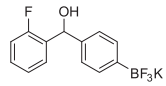
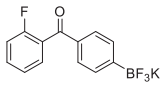
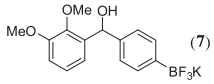
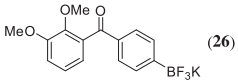
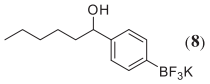
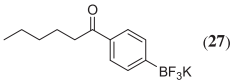
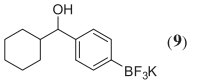
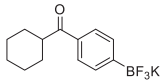
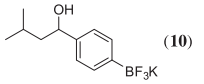
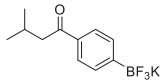
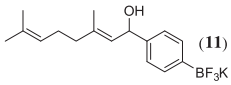
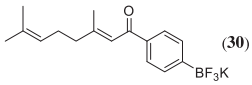
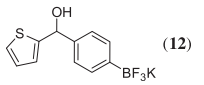
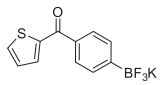
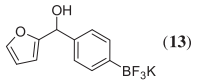
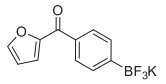
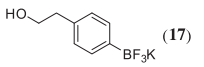
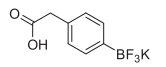
Entry	Aldehyde–BF_3K	Product	Isolated yield (%)
1	 (**14**)	 (**18**)	79
2	 (**15**)	 (**19**)	73
3	 (**16**)	 (**20**)	65
4	 (**1**)	 (**21**)	67
5	 (**2**)	 (**22**)	61
6	 (**4**)	 (**23**)	87
7	 (**5**)	 (**24**)	82

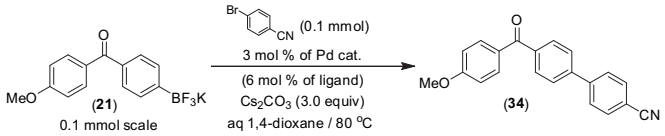
Table 3 (*continued*)

Entry	Aldehyde–BF_3K	Product	Isolated yield (%)
8	 (**6**)	 (**25**)	71
9	 (**7**)	 (**26**)	68
10	 (**8**)	 (**27**)	67
11	 (**9**)	 (**28**)	65
12	 (**10**)	 (**29**)	89
13	 (**11**)	 (**30**)	dec
14	 (**12**)	 (**31**)	87
15	 (**13**)	 (**32**)	dec
16[a]	 (**17**)	 (**33**)	53

[a] Reaction was performed with 9.0 equiv of 8 N Jones reagent at 0 °C for 30 min.

entry 9), a satisfactory cross-coupling product yield of 93% could be achieved by increasing the reaction temperature from 80 °C to 100 °C in an oil bath (Table 4, entry 10).

Table 4
Optimization of cross-coupling reaction conditions[a]



Entry	Pd catalyst/ligand	Time (h)	Isolated yield (%)
1	$Pd(OAc)_2$	2	65
2[b]	$Pd(OAc)_2$	2	42
3	$Pd(OAc)_2/PPh_3$	2	67
4	$Pd(OAc)_2$/XPhos	2	74
5	$PdCl_2(dppf)\cdot CH_2Cl_2$	2	73
6	$Pd(PPh_3)_4$	2	83
7[c]	$Pd(PPh_3)_4$	2	32
8[d]	$Pd(PPh_3)_4$	2	67
9[e]	$Pd(PPh_3)_4$	1	73
10[f]	$Pd(PPh_3)_4$	1	93

[a] All reactions were performed on a 0.1 mmol scale in 1.0 mL of 20% aqueous 1,4-dioxane in an oil bath.
[b] Reaction solvent was MeOH.[9]
[c] Reaction solvent was 20% aqueous toluene.
[d] K_2CO_3 (3.0 equiv) as a base was used instead of Cs_2CO_3.
[e] Initial microwave irradiation of 80 W was used at 80 °C for 1 h.
[f] Reaction temperature was 100 °C in an oil bath.

Under optimal reaction conditions, we also examined the Suzuki–Miyaura cross-coupling reaction of various organocarbonyltrifluoroborates with aryl and alkenyl bromides, and the results are presented in Table 5.

The coupling reactions led to the corresponding products in good to excellent yields. When 4-bromobenzene containing an electron-withdrawing group (CN) was used following the same conditions, a high yield (92%) was obtained (Table 5, entry 1). Also, the coupling reaction using *meta*-substituted organocarbonyltrifluoroborate **22** gave the desired product in 73% yield (Table 5, entry 4). However, attempts to react 4-bromobenzonitrile with electron poor trifluoroborate **23** resulted in low yield of the coupled product (Table 5, entry 5).

3. Conclusion

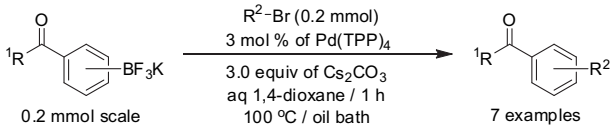
In summary, we have developed a facile one-pot synthesis of secondary alcohol-containing organotrifluoroborates from their corresponding dibromobenzenes and successfully prepared novel potassium organocarbonyltrifluoroborates from the hydroxylated trifluoroborates via the Jones oxidation. Moreover, we found that the potassium organotrifluoroborates can withstand vigorous acidic and oxidative conditions. The Suzuki–Miyaura cross-coupling reaction with these compounds occurs in high yield with carbonyl group tolerance. Further applications and developments of organocarbonyltrifluoroborates are currently under investigation.

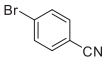
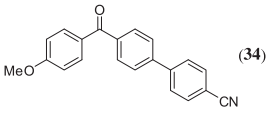
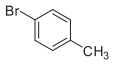
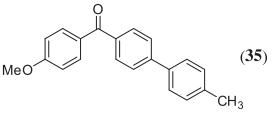
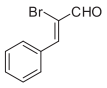
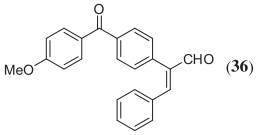
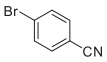
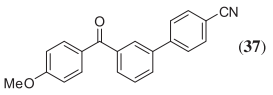
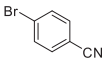
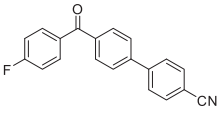
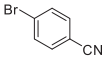
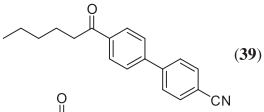
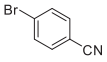
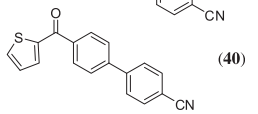
4. Experimental

4.1. General considerations

^1H, ^{13}C, and ^{19}F NMR spectra were recorded at 400, 100, and 376 MHz, respectively. ^{19}F NMR chemical shifts were referenced to external $CFCl_3$ (0.0 ppm). ^{11}B NMR spectra at 128 MHz were obtained on a spectrometer equipped with the appropriate decoupling accessories. All ^{11}B NMR chemical shifts were

Table 5
Cross-coupling reactions



Entry	R^1-BF_3K	R^2-Br	Product	Isolated yield (%)
1	**21**		 (**34**)	92
2	**21**		 (**35**)	74
3	**21**		 (**36**)	84
4	**22**		 (**37**)	73
5	**23**		 (**38**)	72
6	**27**		 (**39**)	81
7	**31**		 (**40**)	87

referenced to external $BF_3 \cdot OEt_2$ (0.0 ppm) with a negative sign indicating an up-field shift. Mass spectra of potassium organotrifluoroborates were performed using negative FAB at the mass spectrometry facilities at the Seoul National University. FTIR spectra were recorded on ATR plate. 1,4-Dioxane and H_2O were distilled and degassed under argon. Commercially available reagents were used without further purification.

4.2. Preparation of secondary alcohol-substituted potassium organotrifluoroborates

*4.2.1. Potassium 4-(hydroxy(4-methoxyphenyl)methyl)phenyltrifluoroborate (**1**).* To a solution of 1,4-dibromobenzene (472 mg, 2.0 mmol) in THF (12 mL) was slowly added *t*-BuLi (1.7 M solution in pentane, 2.4 mL, 4.0 mmol) at −78 °C under N_2. After 1 h, 4-methoxybenzaldehyde (300 mg, 2.2 mmol) was slowly added and then the reaction mixture was slowly warmed to 0 °C for 30 min. The reaction mixture was repeatedly cooled to −78 °C and then *t*-BuLi (1.7 M solution in pentane, 2.4 mL, 4.0 mmol) was slowly added. After 30 min, triisopropyl borate (376 mg, 2 mmol) was added and the reaction mixture was slowly warmed to room temperature for 40 min. After the reaction was completed, 1 N KHF_2 (6.0 mL, 6.0 mmol) was added at room temperature. After stirring for 20 min, the suspension was concentrated and dried in vacuum for 3 h. The residual solid was dissolved in dry acetone (20 mL), and the insoluble salts were filtered off through Celite. The solvent was concentrated on a rotary evaporator and the addition of diethyl ether (8.0 mL) led to precipitation of the product. The product was filtered, collected, and dried in vacuum to obtain the desired pure compound **1** as an ivory solid (532 mg, 83% yield). Mp=68–70 °C. ^{1}H NMR (400 MHz, acetone-d_6) δ 7.42 (d, 2H, J=8.0 Hz), 7.30 (d, 2H, J=8.8 Hz), 7.14 (d, 2H, J=7.6 Hz), 6.84 (d, 2H, J=8.8 Hz), 5.68 (s, 1H), 4.37 (s, 1H), 3.76 (s, 3H). ^{13}C NMR (100 MHz, acetone-d_6) δ 159.4, 143.1, 139.3, 132.2, 128.5, 125.4, 114.0, 76.2, 55.4. ^{19}F NMR (376 MHz, acetone-d_6) δ −142.4. ^{11}B NMR (128 MHz, acetone-d_6) δ 3.62. FTIR (ATR) ν 3418, 3069, 3010, 2950, 2933, 2837, 1610, 1509, 1216, 1170, 953, 802, 579 cm^{-1}. HRFABMS: m/z calcd for $C_{14}H_{13}BF_3O_2$ [M−K$^+$]$^-$ 281.0961, found 281.0965.

*4.2.2. Potassium 3-(hydroxy(4-methoxyphenyl)methyl)phenyltrifluoroborate (**2**).* The title compound was obtained as an ivory solid (423 mg, 66% yield) using 1,3-dibromobenzene (472 mg, 2.0 mmol) and 4-methoxybenzaldehyde (300 mg, 2.2 mmol). Mp=167–170 °C. ^{1}H NMR (400 MHz, acetone-d_6) δ 7.52 (s, 1H), 7.34 (d, 1H, J=7.6 Hz), 7.31 (d, 2H, J=8.4 Hz), 7.10 (dt, 1H, J=5.6, 2.0 Hz), 7.05 (t, 1H, J=7.2 Hz), 6.83 (d, 2H, J=8.8 Hz), 5.68 (d, 1H, J=4.0 Hz), 4.36 (d, 1H, J=4.0 Hz), 3.75 (s, 3H). ^{13}C NMR (100 MHz, acetone-d_6) δ 158.4, 143.0, 138.5130.3, 130.0, 127.5, 125.9, 123.3,

113.0, 75.8, 54.5. ^{19}F NMR (376 MHz, acetone-d_6) δ −142.2. ^{11}B NMR (128 MHz, acetone-d_6) δ 3.75. FTIR (ATR) ν 3526, 3004, 2933, 2835, 1610, 1510, 1234, 1156, 989, 902, 799, 713, 604 cm^{-1}. HRFABMS: m/z calcd for $C_{14}H_{13}BF_3O_2$ $[M-K^+]^-$ 281.0961, found 281.0965.

*4.2.3. Potassium 4-((4-fluorophenyl)hydroxymethyl)phenyltrifluoroborate (**4**).* The title compound was obtained as a white solid (536 mg, 87% yield) using 1,4-dibromobenzene (472 mg, 2.0 mmol) and 4-fluorobenzaldehyde (273 mg, 2.2 mmol). Mp=228–231 °C. ^{1}H NMR (400 MHz, acetone-d_6) δ 7.43 (m, 4H), 7.15 (d, 2H, J=8.0 Hz), 7.04 (t, 2H, J=8.8 Hz), 5.74 (d, 1H, J=4.0 Hz), 4.62 (d, 1H, J=4.0 Hz). ^{13}C NMR (100 MHz, acetone-d_6) δ 161.5 (d, J=240.6 Hz), 142.4 (d, J=2.9 Hz), 141.8, 131.4, 128.1 (d, J=7.9 Hz), 124.6, 114.3 (d, J=21.2 Hz), 75.1. ^{19}F NMR (376 MHz, acetone-d_6) δ −118.5, −142.4. ^{11}B NMR (128 MHz, acetone-d_6) δ 3.72. FTIR (ATR) ν 3527, 3331, 3073, 3029, 2884, 1604, 1506, 1398, 1217, 954, 818, 775, 566 cm^{-1}. HRFABMS: m/z calcd for $C_{13}H_{10}BF_4O$ $[M-K^+]^-$ 269.0761, found 269.0758.

*4.2.4. Potassium 4-((3-fluorophenyl)hydroxymethyl)phenyltrifluoroborate (**5**).* The title compound was obtained as an ivory solid (419 mg, 68% yield) using 1,4-dibromobenzene (472 mg, 2.0 mmol) and 3-fluorobenzaldehyde (273 mg, 2.2 mmol). Mp=228–231 °C. ^{1}H NMR (400 MHz, acetone-d_6) δ 7.44 (d, 2H, J=8.0 Hz), 7.30 (m, 1H), 7.20 (m, 2H), 7.15 (d, 2H, J=7.6 Hz), 6.93 (m, 1H), 5.74 (s, 1H). ^{13}C NMR (100 MHz, acetone-d_6) δ 163.6 (d, J=242.0 Hz), 150.3 (d, J=24.0 Hz), 142.2, 132.4, 130.4 (d, J=8.0 Hz), 125.5, 123.1 (d, J=2.0), 113.8 (d, J=3.0 Hz), 113.6 (d, J=4.0 Hz), 75.9. ^{19}F NMR (376 MHz, acetone-d_6) δ −115.5, −142.4. ^{11}B NMR (128 MHz, acetone-d_6) δ 3.77. FTIR (ATR) ν 3542, 3382, 3074, 2879, 1701, 1589, 1216, 953, 762, 702 cm^{-1}. HRFABMS: m/z calcd for $C_{13}H_{10}BF_4O$ $[M-K^+]^-$ 269.0761, found 269.0764.

*4.2.5. Potassium 4-((2-fluorophenyl)hydroxymethyl)phenyltrifluoroborate (**6**).* The title compound was obtained as an ivory solid (401 mg, 65% yield) using 1,4-dibromobenzene (472 mg, 2.0 mmol) and 2-fluorobenzaldehyde (273 mg, 2.2 mmol). Mp=229–232 °C. ^{1}H NMR (400 MHz, acetone-d_6) δ 7.67 (td, 1H, J=7.6, 1.6 Hz), 7.42 (d, 2H, J=8.0 Hz), 7.25 (m, 1H), 7.17 (td, 1H, J=7.6, 1.2 Hz), 7.16 (d, 2H, J=7.6 Hz), 7.01 (ddd, 1H, J=10.8, 8.4, 1.2 Hz), 6.04 (d, 1H, J=3.2 Hz), 4.65 (d, 1H, J=4.0 Hz). ^{13}C NMR (100 MHz, acetone-d_6) δ 159.6 (d, J=242.7 Hz), 140.6, 133.2 (d, J=13.5 Hz), 131.4, 128.1 (d, J=8.2 Hz), 127.8 (d, J=4.4 Hz), 124.5, 123.9 (d, J=3.3 Hz), 114.6 (d, J=21.9 Hz), 69.1. ^{19}F NMR (376 MHz, acetone-d_6) δ −120.1, −142.4. ^{11}B NMR (128 MHz, acetone-d_6) δ 3.56. FTIR (ATR) ν 3525, 3073, 3045, 2921, 1613, 1486, 1215, 954, 754 cm^{-1}. HRFABMS: m/z calcd for $C_{13}H_{10}BF_4O$ $[M-K^+]^-$ 269.0761, found 269.0765.

*4.2.6. Potassium 4-((2,3-dimethoxyphenyl)hydroxymethyl)phenyltrifluoroborate (**7**).* The title compound was obtained as a white solid (581 mg, 83% yield) using 1,4-dibromobenzene (472 mg, 2.0 mmol) and 2,3-dimethoxybenzaldehyde (366 mg, 2.2 mmol). Mp=207 °C. ^{1}H NMR (400 MHz, acetone-d_6) δ 7.42 (d, 2H, J=8.0 Hz), 7.16 (m, 3H), 7.03 (t, 1H, J=8.0 Hz), 6.89 (dd, 1H, J=8.0, 1.2 Hz), 6.07 (s, 1H), 3.82 (s, 3H), 3.61 (s, 3H). ^{13}C NMR (100 MHz, acetone-d_6) δ 153.4, 146.9, 142.9, 140.5, 132.0, 125.7, 124.2, 120.1, 111.9, 71.0, 60.4, 56.0. ^{19}F NMR (376 MHz, acetone-d_6) δ −142.2. ^{11}B NMR (128 MHz, acetone-d_6) δ 3.76. FTIR (ATR) ν 3500, 3073, 3014, 2939, 2836, 1586, 1478, 1214, 953, 759 cm^{-1}. HRFABMS: m/z calcd for $C_{15}H_{15}BF_3O_3$ $[M-K^+]^-$ 311.1066, found 311.1067.

*4.2.7. Potassium 4-(1-hydroxyhexyl)phenyltrifluoroborate (**8**).* The title compound was obtained as a white solid (432 mg, 76% yield) using 1,4-dibromobenzene (472 mg, 2.0 mmol) and hexanal (220 mg, 2.2 mmol). Mp>250 °C. ^{1}H NMR (400 MHz, acetone-d_6) δ 7.43 (d, 2H, J=7.6 Hz), 7.10 (d, 2H, J=7.6 Hz), 4.52 (t, 1H, J=6.8 Hz), 3.78 (br s, 1H), 1.67 (m, 2H), 1.42 (m, 1H), 1.29 (m, 5H), 0.87 (t, 3H, J=6.8 Hz). ^{13}C NMR (100 MHz, acetone-d_6) δ 142.7, 131.3, 123.9, 73.9, 39.6, 31.8, 25.5, 22.4, 13.4. ^{19}F NMR (376 MHz, acetone-d_6) δ −142.2. ^{11}B NMR (128 MHz, acetone-d_6) δ 3.78. FTIR (ATR) ν 3559, 3399, 3014, 2957, 2928, 2858, 1608, 1228, 964, 914, 826, 745, 576 cm^{-1}. HRFABMS: m/z calcd for $C_{12}H_{17}BF_3O$ $[M-K^+]^-$ 245.1325, found 245.1325.

*4.2.8. Potassium 4-(cyclohexyl(hydroxyl)methyl)phenyltrifluoroborate (**9**)*[7]. The title compound was obtained as a white solid (462 mg, 78% yield) using 1,4-dibromobenzene (472 mg, 2.0 mmol) and cyclohexanecarboxaldehyde (247 mg, 2.2 mmol). Mp>250 °C. ^{1}H NMR (400 MHz, acetone-d_6) δ 7.43 (d, 2H, J=8.0 Hz), 7.06 (d, 2H, J=7.6 Hz), 4.22 (d, 1H, J=7.2 Hz), 3.66 (br s, 1H), 2.02 (m, 1H), 1.73 (m, 1H), 1.62 (m, 2H), 1.53 (m, 1H), 1.40 (m, 1H), 1.18 (m, 3H), 1.05 (m, 1H), 0.92 (m, 1H). ^{13}C NMR (100 MHz, acetone-d_6) δ 142.2, 132.0, 125.6, 79.5, 46.3, 27.4, 27.0, 26.9. ^{19}F NMR (376 MHz, acetone-d_6) δ −142.2. ^{11}B NMR (128 MHz, acetone-d_6) δ 3.76. FTIR (ATR) ν 3342, 3017, 2921, 2850, 1224, 957, 816, 588 cm^{-1}. HRFABMS: m/z calcd for $C_{13}H_{17}BF_3O$ $[M-K^+]^-$ 257.1325, found 257.1320.

*4.2.9. Potassium 4-(1-hydroxy-3-methylbutyl)phenyltrifluoroborate (**10**).* The title compound was obtained as a white solid (405 mg, 75% yield) using 1,4-dibromobenzene (472 mg, 2.0 mmol) and isovaleraldehyde (190 mg, 2.2 mmol). Mp=238–241 °C. ^{1}H NMR (400 MHz, acetone-d_6) δ 7.43 (d, 2H, J=8.0 Hz), 7.11 (d, 2H, J=7.6 Hz), 4.61 (m, 1H), 3.67 (d, 1H, J=4.0 Hz), 1.70 (m, 2H), 1.43 (m, 1H), 0.93 (d, 6H, J=6.4 Hz). ^{13}C NMR (100 MHz, acetone-d_6) δ 143.0, 131.3, 123.8, 72.0, 49.0, 24.5, 22.6, 21.8. ^{19}F NMR (376 MHz, acetone-d_6) δ −142.3. ^{11}B NMR (128 MHz, acetone-d_6) δ 3.81. FTIR (ATR) ν 3554, 3391, 3017, 2956, 2926, 2870, 1608, 1220, 957, 824, 575 cm^{-1}. HRFABMS: m/z calcd for $C_{11}H_{15}BF_3O$ $[M-K^+]^-$ 231.1168, found 231.1165.

*4.2.10. Potassium 4-(1-hydroxy-3,7-dimethylocta-2,6-dienyl)phenyltrifluoroborate (**11**).* The title compound was obtained as an ivory solid (309 mg, 46% yield) using 1,4-dibromobenzene (472 mg, 2.0 mmol) and citral (335 mg, 2.2 mmol). Mp=122–124 °C. ^{1}H NMR (400 MHz, acetone-d_6) δ 7.44 (d, 2H, J=7.6 Hz), 7.19 (d, 2H, J=7.6 Hz), 7.56 (d, 1H, J=16.0 Hz), 6.26 (d, 1H, J=16.0 Hz), 5.15 (m, 1H), 3.53 (s, 1H), 2.09 (m, 2H), 1.65 (s, 3H), 1.62 (m, 2H), 1.59 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (100 MHz, acetone-d_6) δ 134.8, 134.3, 131.8, 130.4, 127.5, 125.0, 124.4, 71.8, 43.1, 27.9, 24.9, 22.7, 16.7. ^{19}F NMR (376 MHz, acetone-d_6) δ −142.4. ^{11}B NMR (128 MHz, acetone-d_6) δ 3.75. FTIR (ATR) ν 3542, 3401, 3017, 2968, 2925, 1606, 1217, 955, 809 cm^{-1}. HRFABMS: m/z calcd for $C_{16}H_{21}BF_3O$ $[M-K^+]^-$ 297.1638, found 297.1640.

*4.2.11. Potassium 4-(hydroxy(thiophen-2-yl)methyl)phenyltrifluoroborate (**12**).* The title compound was obtained as a yellow solid (308 mg, 52% yield) using 1,4-dibromobenzene (472 mg, 2.0 mmol) and 2-thiophenecarboxaldehyde (247 mg, 2.2 mmol) at −78 °C. Mp=219 °C (dec). ^{1}H NMR (400 MHz, acetone-d_6) δ 7.46 (d, 2H, J=8.0 Hz), 7.28 (dd, 1H, J=4.8, 1.2 Hz), 7.21 (d, 2H, J=8.0 Hz), 6.90 (dd, 1H, J=5.2, 3.6 Hz), 6.83 (dt, 1H, J=3.6, 1.2 Hz), 5.94 (d, 1H, J=4.4 Hz), 4.83 (d, 1H, J=4.0 Hz). ^{13}C NMR (100 MHz, acetone-d_6) δ 151.1, 141.2, 131.4, 126.0, 124.3, 124.0, 123.5, 72.3. ^{19}F NMR (376 MHz, acetone-d_6) δ −142.5. ^{11}B NMR (128 MHz, acetone-d_6) δ 3.75. FTIR (ATR) ν 3619, 3520, 3100, 3069, 3021, 2879, 1608, 1221, 955, 707, 602 cm^{-1}. HRFABMS: m/z calcd for $C_{11}H_9BF_3OS$ $[M-K^+]^-$ 257.0419, found 257.0421.

*4.2.12. Potassium 4-(furan-2-yl(hydroxy)methyl)phenyltrifluoroborate (**13**).* The title compound was obtained as a yellow solid (347 mg, 62% yield) using 1,4-dibromobenzene (472 mg, 2.0 mmol) and 2-furaldehyde (211 mg, 2.2 mmol) at −78 °C. Mp=116–120 °C. ^{1}H NMR (400 MHz, acetone-d_6) δ 7.47 (d, 2H, J=8.0 Hz), 7.41 (dd, 1H,

J=2.0, 0.8 Hz), 7.19 (d, 2H, J=8.0 Hz), 6.32 (dd, 1H, J=3.2, 1.6 Hz), 6.11 (dt, 1H, J=3.2, 0.8 Hz), 5.68 (d, 1H, J=4.0 Hz), 4.54 (d, 1H, J=4.4 Hz). ^{13}C NMR (100 MHz, acetone-d_6) δ 158.5, 141.5, 138.9, 131.3, 124.6, 109.8, 105.8, 70.1. ^{19}F NMR (376 MHz, acetone-d_6) δ −142.4. ^{11}B NMR (128 MHz, acetone-d_6) δ 3.67. FTIR (ATR) ν 3518, 3151, 3120, 3072, 3021, 2871, 1610, 1397, 1216, 955, 819, 741, 597 cm^{-1}. HRFABMS: m/z calcd for $C_{11}H_9BF_3O_2$ [M−K$^+$]$^-$ 241.0648, found 241.0651.

4.3. Preparation of 8 N Jones reagent[2b]

Chromium(VI) oxide 10 g (0.1 mol) was dissolved in water (15 mL), and concentrated sulfuric acid (8.6 mL) was slowly added in an ice water bath. The mixture solution was diluted with water up to 37.5 mL.

4.4. Preparation of carbonyl-functionalized potassium organotrifluoroboartes via Jones oxidation

*4.4.1. Potassium 4-formylphenyltrifluoroborate (**18**)[10].* To a solution of 4-(hydroxymethyl)phenyltrifluoroborate[8] (**14**, 214 mg, 1.0 mmol) in acetone (10 mL) was slowly added 8 N Jones reagent (0.38 mL, 3.0 mmol) at 0 °C. The reaction mixture was stirred for 10 min at 0 °C. After 10 min, K_2CO_3 (415 mg, 3.0 mmol) was added. After stirring for 5 min at room temperature, the insoluble salts were filtered off through Celite with charcoal. The solvent was concentrated on a rotary evaporator and then redissolved in a minimal amount of acetone. The addition of diethyl ether (5.0 mL) led to precipitation of the product. The product was filtered, collected, and dried in vacuum to obtain the desired pure compound **18** as a white solid (168 mg, 79% yield). Mp>250 °C. ^{1}H NMR (400 MHz, acetone-d_6) δ 9.94 (s, 1H), 7.69 (d, 2H, J=8.0 Hz), 7.66 (d, 2H, J=8.0 Hz). ^{13}C NMR (100 MHz, acetone-d_6) δ 192.5, 134.5, 132.1, 127.6. ^{19}F NMR (376 MHz, acetone-d_6) δ −143.6. ^{11}B NMR (128 MHz, acetone-d_6) δ 3.02 (q, J=50.2 Hz). FTIR (ATR) ν 3050, 2851, 2762, 1683, 1221, 949, 819, 698, 542 cm^{-1}. HRFABMS: m/z calcd for $C_7H_5BF_3O$ [M−K$^+$]$^-$ 173.0386, found 173.0388.

*4.4.2. Potassium 3-formylphenyltrifluoroborate (**19**)[10].* The title compound was obtained as a white solid (155 mg, 73% yield) using potassium 3-(hydroxymethyl)phenyltrifluoroborate[8] (**15**, 214 mg, 1.0 mmol). Mp=212−214 °C. ^{1}H NMR (400 MHz, acetone-d_6) δ 9.98 (s, 1H), 8.03 (s, 1H), 7.80 (d, 1H, J=7.2 Hz), 7.62 (dt, 1H, J=7.2, 1.6 Hz), 7.32 (t, 1H, J=7.6 Hz). ^{13}C NMR (100 MHz, acetone-d_6) δ 193.3, 138.0, 135.2, 133.7, 126.8, 125.9. ^{19}F NMR (376 MHz, acetone-d_6) δ −143.4. ^{11}B NMR (128 MHz, acetone-d_6) δ 3.24 (q, J=52.2 Hz). FTIR (ATR) ν 3052, 2823, 2726, 1706, 1593, 1245, 1150, 957, 780, 692, 606 cm^{-1}. HRFABMS: m/z calcd for $C_7H_5BF_3O$ [M−K$^+$]$^-$ 173.0386, found 173.0384.

*4.4.3. Potassium 2-formylphenyltrifluoroborate (**20**)[10a,b,11].* The title compound was obtained as a white solid (138 mg, 65% yield) using potassium 2-(hydroxymethyl)phenyltrifluoroborate[8] (**16**, 214 mg, 1.0 mmol). Mp=204−206 °C. ^{1}H NMR (400 MHz, acetone-d_6) δ 10.61 (s, 1H), 7.76, (m, 2H), 7.37 (t, 1H, J=7.2 Hz), 7.20 (t, 1H, J=7.6 Hz). ^{13}C NMR (100 MHz, acetone-d_6) δ 197.0, 140.0, 133.1, 131.4, 125.4, 124.4. ^{19}F NMR (376 MHz, acetone-d_6) δ −135.5. ^{11}B NMR (128 MHz, acetone-d_6) δ 3.33 (q, J=53.4 Hz). FTIR (ATR) ν 3053, 3023, 2897, 2863, 1674, 1592, 1184, 947, 748, 608 cm^{-1}. HRFABMS: m/z calcd for $C_7H_5BF_3O$ [M−K$^+$]$^-$ 173.0386, found 173.0389.

*4.4.4. Potassium 4-(4-methoxybenzoyl)phenyltrifluoroborate (**21**).* The title compound was obtained as an ivory solid (213 mg, 67% yield) using potassium 4-(hydroxy(4-methoxyphenyl)methyl)phenyltrifluoroborate (**1**, 320 mg, 1.0 mmol). Mp=226 °C (dec). ^{1}H NMR (400 MHz, acetone-d_6) δ 7.79 (d, 2H, J=8.8 Hz), 7.63 (d, 2H, J=7.6 Hz), 7.54 (d, 2H, J=8.0 Hz), 7.06 (d, 2H, J=8.8 Hz), 3.91 (s, 3H). ^{13}C NMR (100 MHz, acetone-d_6) δ 195.1, 162.8, 135.1, 131.9, 131.3, 131.1, 127.7, 113.3, 54.9. ^{19}F NMR (376 MHz, acetone-d_6) δ −143.4. ^{11}B NMR (128 MHz, acetone-d_6) δ 3.35. FTIR (ATR) ν 2974, 2903, 2840, 1649, 1595, 1318, 1260, 952, 852, 767, 686, 600 cm^{-1}. HRFABMS: m/z calcd for $C_{14}H_{11}BF_3O_2$ [M−K$^+$]$^-$ 279.0804, found 279.0810.

*4.4.5. Potassium 3-(4-methoxybenzoyl)phenyltrifluoroborate (**22**).* The title compound was obtained as a yellow solid (194 mg, 61% yield) using potassium 3-(hydroxy(4-methoxyphenyl)methyl)phenyltrifluoroborate (**2**, 320 mg, 1.0 mmol). Mp=164−168 °C. ^{1}H NMR (400 MHz, acetone-d_6) δ 7.91 (s, 1H), 7.80 (d, 2H, J=8.8 Hz), 7.74 (d, 1H, J=6.4 Hz), 7.47 (d, 1H, J=7.2 Hz), 7.27 (t, 1H, J=7.2 Hz), 7.05 (d, 2H, J=8.8 Hz), 3.91 (s, 3H). ^{13}C NMR (100 MHz, acetone-d_6) δ 196.0, 162.8, 136.3, 135.5, 133.0, 132.0, 131.1, 126.4, 126.0, 113.3, 54.9. ^{19}F NMR (376 MHz, acetone-d_6) δ −143.3. ^{11}B NMR (128 MHz, acetone-d_6) δ 3.30. FTIR (ATR) ν 3049, 2969, 2930, 2839, 1643, 1597, 1256, 1212, 1168, 1002, 759, 601 cm^{-1}. HRFABMS: m/z calcd for $C_{14}H_{11}BF_3O_2$ [M−K$^+$]$^-$ 279.0804, found 279.0806.

*4.4.6. Potassium 4-(4-fluorobenzoyl)phenyltrifluoroborate (**23**).* The title compound was obtained as a white solid (266 mg, 87% yield) using potassium 4-((4-fluorophenyl)hydroxymethyl)phenyltrifluoroborate (**4**, 308 mg, 1.0 mmol). Mp>250 °C. ^{1}H NMR (400 MHz, acetone-d_6) δ 7.86 (dd, 2H, J=9.2, 5.6 Hz), 7.65 (d, 2H, J=8.0 Hz), 7.56 (d, 2H, J=8.0 Hz), 7.30 (t, 2H, J=8.8 Hz). ^{13}C NMR (100 MHz, acetone-d_6) δ 194.9, 164.8 (d, J=248.8 Hz), 135.1 (d, J=3.2 Hz), 134.4, 132.3 (d, J=8.9 Hz), 131.5, 127.9, 115.0 (d, J=21.8 Hz). ^{19}F NMR (376 MHz, acetone-d_6) δ −109.6, −143.5. ^{11}B NMR (128 MHz, acetone-d_6) δ 3.37. FTIR (ATR) ν 3104, 3071, 3017, 1655, 1596, 1285, 1208, 928, 765, 685 cm^{-1}. HRFABMS: m/z calcd for $C_{13}H_8BF_4O$ [M−K$^+$]$^-$ 267.0604, found 267.0598.

*4.4.7. Potassium 4-(3-fluorobenzoyl)phenyltrifluoroborate (**24**).* The title compound was obtained as an ivory solid (251 mg, 82% yield) using potassium 4-((3-fluorophenyl)hydroxymethyl)phenyltrifluoroborate (**5**, 308 mg, 1.0 mmol). Mp>250 °C. ^{1}H NMR (400 MHz, acetone-d_6) δ 7.66 (d, 2H, J=8.0 Hz), 7.58 (m, 4H), 7.48 (m, 1H), 7.40 (m, 1H). ^{13}C NMR (100 MHz, acetone-d_6) δ 194.9, 162.4 (d, J=244.0), 141.1 (d, J=7.0 Hz), 133.9, 131.5, 130.1 (d, J=7.0 Hz), 128.0, 125.6 (d, J=3.0 Hz), 118.3 (d, J=21.0 Hz), 115.8 (d, J=22.0 Hz). ^{19}F NMR (376 MHz, acetone-d_6) δ −114.2, −143.5. ^{11}B NMR (128 MHz, acetone-d_6) δ 3.18. FTIR (ATR) ν 3075, 3033, 1653, 1205, 948, 759, 715 cm^{-1}. HRFABMS: m/z calcd for $C_{13}H_8BF_4O$ [M−K$^+$]$^-$ 267.0604, found 267.0609.

*4.4.8. Potassium 4-(2-fluorobenzoyl)phenyltrifluoroborate (**25**).* The title compound was obtained as an ivory solid (217 mg, 71% yield) using potassium 4-((2-fluorophenyl)hydroxymethyl)phenyltrifluoroborate (**6**, 308 mg, 1.0 mmol). Mp=243 °C (dec). ^{1}H NMR (400 MHz, acetone-d_6) δ 7.62 (m, 5H), 7.51 (td, 1H, J=7.6, 2.0 Hz), 7.35 (td, 1H, J=7.6, 1.2 Hz), 7.28 (ddd, 1H, J=9.6, 8.4, 0.8 Hz). ^{13}C NMR (100 MHz, acetone-d_6) δ 193.0, 159.6 (d, J=246.7 Hz), 134.4, 132.2 (d, J=8.1 Hz), 131.7, 130.1 (d, J=3.3 Hz), 128.3 (d, J=16.1 Hz), 127.7, 124.5 (d, J=3.6 Hz), 115.8 (d, J=21.7 Hz). ^{19}F NMR (376 MHz, acetone-d_6) δ −114.7, −143.6. ^{11}B NMR (128 MHz, acetone-d_6) δ 3.11. FTIR (ATR) ν 3072, 3029, 1655, 1612, 1217, 956, 844, 753, 657, 545 cm^{-1}. HRFABMS: m/z calcd for $C_{13}H_8BF_4O$ [M−K$^+$]$^-$ 267.0604, found 267.0600.

*4.4.9. Potassium 4-(2,3-dimethoxybenzoyl)phenyltrifluoroborate (**26**).* The title compound was obtained as an ivory solid (237 mg, 68% yield) using potassium 4-((2,3-dimethoxyphenyl)hydroxymethyl)phenyltrifluoroborate (**7**, 350 mg, 1.0 mmol). Mp=142−144 °C. ^{1}H NMR (400 MHz, acetone-d_6) δ 7.61 (d, 2H, J=8.4 Hz), 7.57 (d, 2H, J=8.4 Hz), 7.16 (m, 2H), 6.83 (dd, 1H, J=6.8, 2.0 Hz), 3.92 (s, 3H), 3.66 (s, 3H). ^{13}C NMR (100 MHz, acetone-d_6) δ 195.7, 152.8, 146.5, 135.6, 134.9, 131.4, 127.7, 123.6, 119.7, 113.8, 60.4, 55.3. ^{19}F NMR (376 MHz, acetone-d_6) δ −143.5. ^{11}B NMR (128 MHz, acetone-d_6)

δ 3.26. FTIR (ATR) ν 3072, 3017, 2970, 2938, 2836, 1657, 1474, 1316, 1266, 949, 758, 707, 549 cm^{-1}. HRFABMS: *m*/*z* calcd for $C_{15}H_{13}BF_3O_3$ $[M-K^+]^-$ 309.0910, found 309.0905.

*4.4.10. Potassium 4-(hexanoyl)phenyltrifluoroborate (**27**).* The title compound was obtained as an ivory solid (189 mg, 67% yield) using potassium 4-(1-hydroxyhexyl)phenyltrifluoroborate (**8**, 284 mg, 1.0 mmol). Mp=227–230 °C. ^1H NMR (400 MHz, acetone-d_6) δ 7.77 (d, 2H, *J*=8.0 Hz), 7.60 (d, 2H, *J*=8.0 Hz), 2.95 (t, 2H, *J*=7.2 Hz), 1.69 (m, 2H), 1.37 (m, 4H), 0.91 (t, 3H, *J*=7.2 Hz). ^{13}C NMR (100 MHz, acetone-d_6) δ 199.8, 134.5, 131.6, 125.9, 37.8, 31.4, 24.1, 22.3, 13.3. ^{19}F NMR (376 MHz, acetone-d_6) δ −143.5. ^{11}B NMR (128 MHz, acetone-d_6) δ 3.34. FTIR (ATR) ν 3069, 3029, 2931, 2859, 1672, 1215, 954, 818, 763, 580 cm^{-1}. HRFABMS: *m*/*z* calcd for $C_{12}H_{15}BF_3O$ $[M-K^+]^-$ 243.1168, found 243.1162.

*4.4.11. Potassium 4-(cyclohexanecarbonyl)phenyltrifluoroborate (**28**).* The title compound was obtained as a white solid (191 mg, 65% yield) using potassium 4-(cyclohexyl(hydroxyl)methyl)phenyltrifluoroborate (**9**, 296 mg, 1.0 mmol). Mp>250 °C. ^1H NMR (400 MHz, acetone-d_6) δ 7.76 (d, 2H, *J*=8.0 Hz), 7.60 (d, 2H, *J*=8.0 Hz), 3.36 (m, 1H), 1.83 (m, 4H), 1.72 (m, 1H), 1.45 (m, 4H), 1.26 (m, 1H). ^{13}C NMR (100 MHz, acetone-d_6) δ 203.0, 133.6, 131.7, 126.1, 44.7, 29.5, 25.9, 25.5. ^{19}F NMR (376 MHz, acetone-d_6) δ −143.3. ^{11}B NMR (128 MHz, acetone-d_6) δ 3.32. FTIR (ATR) ν 3072, 3025, 2930, 2853, 1666, 1216, 953, 833, 750 cm^{-1}. HRFABMS: *m*/*z* calcd for $C_{13}H_{15}BF_3O$ $[M-K^+]^-$ 255.1168, found 255.1168.

*4.4.12. Potassium 4-(3-methylbutanoyl)phenyltrifluoroborate (**29**).* The title compound was obtained as an ivory solid (239 mg, 89% yield) using potassium 4-(1-hydroxy-3-methylbutyl)phenyltrifluoroborate (**10**, 270 mg, 1.0 mmol). Mp=133 °C (dec). ^1H NMR (400 MHz, acetone-d_6) δ 7.77 (d, 2H, *J*=8.0 Hz), 7.60 (d, 2H, *J*=8.0 Hz), 2.83 (d, 2H, *J*=6.8 Hz), 2.24 (m, 1H), 0.97 (d, 6H, *J*=6.8 Hz). ^{13}C NMR (100 MHz, acetone-d_6) δ 199.6, 134.9, 131.6, 126.0, 46.8, 25.0, 22.1. ^{19}F NMR (376 MHz, acetone-d_6) δ −143.4. ^{11}B NMR (128 MHz, acetone-d_6) δ 3.36. FTIR (ATR) ν 3072, 3025, 2959, 2930, 2873, 1671, 1221, 944, 816, 705, 584 cm^{-1}. HRFABMS: *m*/*z* calcd for $C_{11}H_{13}BF_3O$ $[M-K^+]^-$ 229.1012, found 229.1012.

*4.4.13. Potassium 4-(thiophene-2-carbonyl)phenyltrifluoroborate (**31**).* The title compound was obtained as an ivory solid (256 mg, 87% yield) using potassium 4-(hydroxy(thiophen-2-yl)methyl) phenyltrifluoroborate (**12**, 296 mg, 1.0 mmol). Mp=117 °C (dec). ^1H NMR (400 MHz, acetone-d_6) δ 7.92 (dd, 1H, *J*=5.2, 1.2 Hz), 7.73 (dd, 1H, *J*=4.0, 1.2 Hz), 7.68 (d, 2H, *J*=8.4 Hz), 7.65 (d, 2H, *J*=8.4 Hz), 7.26 (dd, 1H, *J*=4.8, 3.6 Hz). ^{13}C NMR (100 MHz, acetone-d_6) δ 188.0, 144.3, 135.1, 134.1, 133.3, 131.5, 127.9, 127.1. ^{19}F NMR (376 MHz, acetone-d_6) δ −143.3. ^{11}B NMR (128 MHz, acetone-d_6) δ 3.23. FTIR (ATR) ν 3107, 3069, 3021, 2974, 2927, 2852, 1700, 1623, 1412, 1218, 956, 835, 761, 706 cm^{-1}. HRFABMS: *m*/*z* calcd for $C_{11}H_7BF_3OS$ $[M-K^+]^-$ 255.0263, found 255.0260.

*4.4.14. Potassium 4-(carboxymethyl)phenyltrifluoroborate (**33**).* To a solution of potassium 4-(2-hydroxyethyl)phenyltrifluoroborate[8] (**17**, 228 mg, 1.0 mmol) in acetone (10 mL) was slowly added 8 N Jones reagent (1.13 mL, 9.0 mmol) at 0 °C. The reaction mixture was stirred for 30 min at 0 °C. After 30 min, 3.0 mL of 1 N KHF_2 was added. After stirring for 10 min at room temperature, the suspension was concentrated and dried in vacuum for 3 h. The residual solid was dissolved in dry acetone (10 mL), and the insoluble salts were filtered off through Celite with charcoal. The solvent was concentrated on a rotary evaporator and the addition of CH_2Cl_2 led to precipitation of the product. The product was filtered, collected, and dried in vacuum to obtain the desired pure compound **33** as an ivory solid (128 mg, 53% yield). Mp>250 °C. ^1H NMR (400 MHz, acetone-d_6) δ 7.44 (d, 2H, *J*=7.6 Hz), 7.06 (d, 2H, *J*=7.6 Hz), 3.50 (s, 2H). ^{13}C NMR (100 MHz, acetone-d_6) δ 172.4, 131.7, 130.9, 127.0, 40.7. ^{19}F NMR (376 MHz, acetone-d_6) δ −143.2. ^{11}B NMR (128 MHz, acetone-d_6) δ 3.29. FTIR (ATR) ν 3562, 3076, 3022, 2923, 2646, 2552, 1690, 1610, 1400, 1224, 1185, 958, 804 cm^{-1}. HRFABMS: *m*/*z* calcd for $C_8H_7BF_3O_2$ $[M-K^+]^-$ 203.0491, found 203.0489.

4.5. Suzuki–Miyaura cross-coupling reactions

*4.5.1. 4′-(4-Methoxybenzoyl)biphenyl-4-carbonitrile (**34**).* To a 16× 90 mm glass vessel containing a stirring bar was added the potassium 4-(4-methoxybenzoyl)phenyltrifluoroborate (**21**, 63.6 mg, 0.2 mmol), Cs_2CO_3 (195 mg, 0.6 mmol), $Pd(PPh_3)_4$ (6.9 mg, 3×10^{-3} mmol, 3 mol %), and 4-bromobenzonitrile (36.4 mg, 0.2 mmol). The mixture was dissolved in 20% aqueous 1,4-dioxane (2 mL). The reaction was stirred in an oil bath at 100 °C for 1 h, then cooled to room temperature. The reaction mixture was extracted with diethyl ether and H_2O, and then organic layer was dried over $MgSO_4$. The solvent was filtered off through silica gel. The solvent was concentrated on a rotary evaporator. The crude product was purified by preparative TLC (0.5 mm, elution with hexane/EtOAc=4:1). The pure compound **34** was obtained as a white solid (57.7 mg, 92% yield). Mp=153–154 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, 2H, *J*=8.0 Hz), 7.88 (d, 2H, *J*=8.4 Hz), 7.79 (d, 2H, *J*=10.5 Hz), 7.76 (d, 2H, *J*=10.5 Hz), 7.71 (d, 2H, *J*=8.4 Hz), 7.01 (d, 2H, *J*=8.8 Hz), 3.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8, 163.4, 144.5, 142.4, 138.2, 132.7, 132.5, 130.5, 129.9, 127.9, 127.0, 118.7, 113.7, 111.7, 55.5. FTIR (ATR) ν 3075, 3059, 3036, 2922, 2850, 2231, 1644, 1601, 1313, 1260, 764 cm^{-1}. HRFABMS: *m*/*z* calcd for $C_{21}H_{16}NO_2$ $[M+H]^+$ 314.1181, found 314.1180.

*4.5.2. (4-Methoxyphenyl)(4′-methylbiphenyl-4-yl)methanone (**35**).* The title compound was obtained as a white solid (44.8 mg, 74% yield) using potassium 4-(4-methoxybenzoyl)phenyltrifluoroborate (**21**, 63.6 mg, 0.2 mmol) and 4-bromotoluene (34.2 mg, 0.2 mmol). Mp=171–172 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, 2H, *J*=8.8 Hz), 7.86 (d, 2H, *J*=8.4 Hz), 7.70 (d, 2H, *J*=8.0 Hz), 7.58 (d, 2H, *J*=8.0 Hz), 7.31 (d, 2H, *J*=8.0 Hz), 7.01 (d, 2H, *J*=8.8 Hz), 3.92 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 163.1, 144.7, 138.0, 137.1, 136.6, 132.4, 130.4, 130.3, 129.6, 127.1, 126.6, 113.5, 55.5, 21.1. FTIR (ATR) ν 3070, 3024, 2918, 2852, 1737, 1639, 1600, 1251, 1175, 1029, 932, 763 cm^{-1}. HRFABMS: *m*/*z* calcd for $C_{21}H_{19}O_2$ $[M+H]^+$ 303.1385, found 303.1380.

*4.5.3. (E)-2-(4-(4-Methoxybenzoyl)phenyl)-3-phenylacrylaldehyde (**36**).* The title compound was obtained as a colorless oil (57.5 mg, 84% yield) using potassium 4-(4-methoxybenzoyl)phenyltrifluoroborate (**21**, 63.6 mg, 0.2 mmol) and α-bromocinnamaldehyde (42.2 mg, 0.2 mmol). ^1H NMR (400 MHz, $CDCl_3$) δ 9.82 (s, 1H), 7.89 (d, 2H, *J*=8.8 Hz), 7.85 (d, 2H, *J*=8.4 Hz), 7.49 (s, 1H), 7.34 (m, 3H), 7.26 (m, 4H), 7.00 (d, 2H, *J*=9.2 Hz), 3.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 193.3, 163.3, 151.0, 140.9, 138.0, 137.2, 133.6, 132.6, 130.7, 130.6, 130.2, 130.0, 129.4, 128.7, 113.6, 55.5. FTIR (ATR) ν 3061, 3006, 2958, 2932, 2839, 2713, 1682, 1651, 1604, 1287, 1172, 929, 743 cm^{-1}. HRFABMS: *m*/*z* calcd for $C_{23}H_{19}O_3$ $[M+H]^+$ 343.1334, found 343.1338.

*4.5.4. 3′-(4-Methoxybenzoyl)biphenyl-4-carbonitrile (**37**).* The title compound was obtained as a colorless oil (45.8 mg, 73% yield) using potassium 3-(4-methoxybenzoyl)phenyltrifluoroborate (**22**, 63.6 mg, 0.2 mmol) and 4-bromobenzonitrile (36.4 mg, 0.2 mmol). ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 (t, 1H, *J*=1.6 Hz), 7.88 (d, 2H, *J*=9.2 Hz), 7.82 (m, 1H), 7.80 (m, 1H), 7.77 (d, 2H, *J*=8.4 Hz), 7.74 (d, 2H, *J*=8.8 Hz), 7.61 (t, 1H, *J*=7.6 Hz), 7.01 (d, 2H, *J*=8.8 Hz), 3.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.0, 163.5, 144.6, 139.3, 139.2, 132.7, 132.5, 130.4, 129.8 (2C), 129.0, 128.3, 127.8, 118.7, 113.7, 111.4, 55.5. FTIR

(ATR) ν 3070, 3019, 2917, 2845, 2222, 1736, 1647, 1597, 1509, 1320, 1261, 1174, 1016, 844, 759 cm^{-1}. HRFABMS: m/z calcd for $C_{21}H_{16}NO_2$ $[M+H]^+$ 314.1181, found 314.1175.

*4.5.5. 4′-(4-Fluorobenzoyl)biphenyl-4-carbonitrile (**38**).* The title compound was obtained as a white solid (43.4 mg, 72% yield) using potassium 4-(4-fluorobenzoyl)phenyltrifluoroborate (**23**, 61.2 mg, 0.2 mmol) and 4-bromobenzonitrile (36.4 mg, 0.2 mmol). Mp=177–178 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (m, 4H), 7.81 (d, 2H, J=8.8 Hz), 7.77 (d, 2H, J=8.4 Hz), 7.73 (d, 2H, J=8.4 Hz), 7.21 (t, 2H, J=8.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5, 165.5 (d, J=253.4 Hz), 144.3, 143.0, 137.4, 133.6 (d, J=3.0 Hz), 132.7, 132.6 (d, J=9.3 Hz), 130.6, 127.9, 127.2, 118.6, 115.6 (d, J=21.8 Hz), 111.9. FTIR (ATR) ν 3284, 3061, 2958, 2923, 2852, 2224, 1651, 1592, 1500, 1277, 1151, 929, 854 cm^{-1}. HRFABMS: m/z calcd for $C_{20}H_{13}FNO$ $[M+H]^+$ 302.0981, found 302.0975.

*4.5.6. 4′-Hexanoylbiphenyl-4-carbonitrile (**39**).* The title compound was obtained as a white solid (45.0 mg, 81% yield) using potassium 4-hexanoylphenyltrifluoroborate (**27**, 56.4 mg, 0.2 mmol) and 4-bromobenzonitrile (36.4 mg, 0.2 mmol). Mp=83–85 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, 2H, J=8.8 Hz), 7.78 (d, 2H, J=8.4 Hz), 7.74 (d, 2H, J=8.8 Hz), 7.70 (d, 2H, J=8.4 Hz), 3.01 (t, 2H, J=7.6 Hz), 1.79 (m, 2H), 1.41 (m, 4H), 0.94 (t, 3H, J=6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9, 144.3, 143.2, 136.9, 132.7, 128.8, 127.9, 127.4, 118.6, 111.8, 38.7, 31.5, 24.0, 22.5, 13.9. FTIR (ATR) ν 3059, 2958, 2924, 2863, 2237, 1675, 1602, 1202, 819 cm^{-1}. HRFABMS: m/z calcd for $C_{19}H_{20}NO$ $[M+H]^+$ 278.1545, found 278.1539.

*4.5.7. 4′-(Thiophene-2-carbonyl)biphenyl-4-carbonitrile (**40**).* The title compound was obtained as an ivory solid (50.4 mg, 87% yield) using potassium 4-(thiophene-2-carbonyl)phenyltrifluoroborate (**31**, 58.8 mg, 0.2 mmol) and 4-bromobenzonitrile (36.4 mg, 0.2 mmol). Mp=139 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, 2H, J=8.4 Hz), 7.80 (d, 2H, J=8.8 Hz), 7.75 (m, 5H), 7.71 (dd, 1H, J=3.6, 0.8 Hz), 7.22 (dd, 1H, J=4.8, 4.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.4, 144.4, 143.4, 142.8, 138.0, 134.8, 134.5, 132.7, 130.0, 128.0, 127.9, 127.3, 118.6, 111.8. FTIR (ATR) ν 3106, 2923, 2852, 2225, 1628, 1616, 1600, 1514, 1410, 1292, 826, 717 cm^{-1}. HRFABMS: m/z calcd for $C_{18}H_{12}NOS$ $[M+H]^+$ 290.0640, found 290.0638.

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Supplementary data

Supplementary data (copies of ^1H, ^{13}C, ^{19}F, and ^{11}B NMR spectra of all new compounds). Supplementary data related to this article can be found online at doi:10.1016/j.tet.2010.12.049.

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