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^1H , ^{13}C , ^{19}F and ^{11}B NMR spectral reference data of some potassium organotrifluoroborates

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Abstract

Complete ^1H , ^{13}C , ^{19}F and ^{11}B NMR spectral data for 28 potassium organotrifluoroborates are described. The resonance for the carbon bearing the boron atom is described for most of the studied compounds. A modified ^{11}B NMR pulse sequence was used and better resolution was observed allowing the observation of ^{11}B – ^{19}F coupling constants for some of the studied compounds.

Keywords

1D NMR; ^{19}F NMR; ^{11}B NMR; potassium organotrifluoroborates

Introduction

Since the discovery of the Suzuki–Miyaura reaction,[1] organoboron have become important reagents in transition-metal-catalyzed reactions, particularly in palladium-catalyzed reactions, producing new carbon–carbon bonds. The large number of applications of tricoordinate boron compounds, particularly boronic acids and esters, can also be explained by the fact that these compounds are easily synthesized via transmetalation or hydroboration reactions.[2]

Organotrifluoroborates have proven to be a good option to replace boronic acids and boronate esters providing advantages over the latter reagents in many Suzuki type coupling reactions,[3] 1,2-[4] and 1,4-additions[5] to carbonyl compounds, Mannich type reactions,[6] synthesis of alcohols,[7] amines,[8] and iodides,[9] and Heck type reactions,[10] among other transformations.[11] (For an extensive review about synthesis and applications of organotrifluoroborate salts see Ref. [11].)

One of the major benefits is the ability to elaborate upon the structure of a simple, functionalized organotrifluoroborate, increasing its molecular complexity while maintaining the valuable carbon–boron bond for subsequent transformation. Organotrifluoroborates may

also act as serine protease inhibitors[12] and, more recently, the pharmacological and toxicological properties of potassium thiophene-3-trifluoroborate were investigated.[13]

This paper describes the complete spectral reference data of 28 potassium organotrifluoroborates, including hetero-nuclei analysis of ^{11}B and ^{19}F . The selected list of organotrifluoroborates includes compounds with different functional groups and structures that allowed an analysis of the neighboring influence in the hetero-nuclei shifts. The structural and spectroscopic assignments were also made through the combined use of 1D and heteronuclear nuclear magnetic resonance (NMR) experiments.

Results and Discussion

Compounds **1**,[14] **2**,[15] **3–4**,[16] **27**,[17] and **28**[18] were prepared according to literature procedures. The potassium organotrifluoroborates **5–26** were prepared from the corresponding boronic acids using KHF_2 in $\text{MeOH}:\text{H}_2\text{O}$ in good yields[19] and submitted to ^1H , ^{13}C , ^{11}B , and ^{19}F NMR analyses.

In some of the studied compounds the $J(^{11}\text{B}-^{19}\text{F})$ in the ^{11}B NMR spectra and $J(^{19}\text{F}-^{11}\text{B})$ in the ^{19}F NMR spectra were observed (Fig. 1a and b). The relative rapid ^{11}B relaxation often hinders or excludes the observation of ^{11}B coupling constants $J(^{11}\text{B}-\text{X})$ in spectra of both ^{11}B and other nuclei by line broadening.[20] A modified ^{11}B NMR pulse sequence was used and better resolution was observed, allowing the observation of $^{11}\text{B}-^{19}\text{F}$ coupling constants for some compounds. A comparison between the spectrum obtained using standard acquisition parameters (Fig. 2a) and the spectrum obtained using a different pulse sequence (Fig. 2b) is shown in Fig. 2. Because of the better resolution on the spectrum, it was possible to observe the coupling constant more clearly.

Considering that nuclear spins of ^{11}B and ^{19}F nuclei are equal to $3/2$ and $1/2$, respectively and that the lines number on the spectrum is determined by the term $2nI+1$, where I is the nuclear spin value and n is number of neighbor nucleus, the spectra show different lines due to scalar coupling. ^{19}F NMR spectrum of compound **1** (Fig. 1a) shows four lines of approximately the same intensity (1 : 1 : 1 : 1) because there is only one nucleus of ^{11}B coupling with the ^{19}F nucleus; in the Fig. 1b, it is possible to observe a quartet (1 : 3 : 3 : 1) due to scalar coupling with three ^{19}F nucleus. The resonances corresponding to the carbon bearing the boron atom were observed to be broad due to the quadrupolar relaxation mechanism of ^{11}B nucleus. This effect can be observed in Fig. 1c where the ^{13}C spectrum shows two signals being the signal at $\delta 96.98$ ppm broad because of the quadrupole moment of ^{11}B nuclei. Notably, this resonance is not described for potassium organotrifluoroborates. [21]

By using line-narrowing techniques or less viscous solvents and/or higher temperatures it is possible to improve the resolution. As predicted, different coupling constants values were observed in both ^{11}B and ^{19}F spectra of potassium ethynyltrifluoroborate at 25°C when the solvent was changed (Table 1). In the expectation that the relation between the variation of magnitude of J with temperature, we also obtained the spectra of potassium ethynyltrifluoroborate at 25°C , and 50°C in different solvents. The temperature dependence of the coupling constants is also given in Table 1. The chemical shifts practically do not change with temperature.

Good resolution was obtained for the ^{19}F spectra of potassium organotrifluoroborates. The ^{19}F nucleus has a zero quadrupolar moment, it is only 20% less sensitive than ^1H , and has a high sensitivity because of a high-magnetogyric ratio.[22] These factors support the idea that ^{19}F nucleus is the appropriate choice to analyze potassium organotrifluoroborates by NMR.

The chemical shifts in the ^{19}F spectrum generally decrease from a neutral molecule to an anion. In this way, it would be expected the more fluorines attached to any given atom, the less shielded would be the ^{19}F nucleus.[23] This effect was also observed for the studied organotrifluoroborates where the fluorines attached to the boron atom presented chemical shifts in the range of -129 to -141 ppm (Table 2).

It was also known that the J (^{19}F - ^{11}B) varies by changing the solvent.[24] In fact, the observed coupling constants for **1** in protic solvents were significantly smaller than the ones observed in nonprotic solvents. The coupling constants did not appear to be dependent on the temperature on the analyzed compound (Table 1).[25]

In spite of being salts, potassium organotrifluoroborates are slightly soluble in water, with some exceptions. Generally these compounds show high solubility in polar solvents such as methanol, acetonitrile, acetone, dimethylfumarate (DMF), and dimethyl sulphoxide (DMSO). It is also known from literature that electron-donating groups enhance the rate of hydrolysis of these compounds into the corresponding boronic acids.[26] These factors together with the small changes in the coupling constants and chemical shifts (Table 1), make DMSO- d_6 the appropriate choice for the analysis of potassium organotrifluoroborates.

Experimental

Standard bench top techniques were employed for handling air-sensitive reagents. tetrahydrofuran (THF) was distilled from Na/benzophenone ketyl. Methanol was distilled from magnesium methoxide. Distilled H_2O was degassed by sparging with $\text{Ar}(\text{g})$ for >30 min. All other solvents were high-performance liquid chromatographic (HPLC) grade and used as received. Boronic acids **5** and **6** were purchased from Aldrich Chemical Company. Boronic acids **7–26** were purchased from Frontier Chemicals and used as received. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. (CIL).

Potassium ethynyltrifluoroborate (**1**)

To a solution of ethynylmagnesium bromide in THF (10.0 mmol, 20 ml of a 0.5 M THF solution) trimethyl borate was added (1.59 g, 15.3 mmol) at -78 °C. The solution was stirred for 1 h at this temperature, and then warmed up to -20 °C and stirred for an additional hour. To the resultant white suspension a solution of KHF_2 was added (4.71 g, 60.3 mmol) in water (15 ml) and the solution was stirred at this temperature for 1 h and at room temperature for 1 h. The obtained reaction mixture was concentrated *in vacuo* and the residue was dissolved in hot acetone. The residue was removed by filtration and the filtrate was concentrated to yield 1.05 g (80%) of the title compound as a white solid (mp 210 – 212 °C decomp.).

Potassium vinyltrifluoroborate (**2**)

To a solution of trimethyl borate (3.4 ml, 30 mmol) in THF (20 ml) at -78 °C under argon was added dropwise vinyl magnesium bromide (20 ml, 20 mmol of a 1 M solution in THF). The mixture was stirred for 0.5 h at this temperature and at room temperature for 0.5 h. KHF_2 (9.4 g, 120 mmol) was added in one portion at 0 °C followed by water (20 ml). The resulting suspension was stirred for 0.5 h at room temperature, and the solvents were removed and the resulting white solid was dried under high vacuum for 2 h. The solid was then washed with acetone and with hot acetone. The resulting organic solution was filtered, and the solvent was removed to yield a white solid, which was dissolved in hot acetone and precipitated with diethyl ether to yield 2.20 g (80%) of the title compound as a white solid.

Potassium alkynyltrifluoroborates (3 and 4)

To a solution of the appropriate alkyne (10 mmol, 1 equiv) in THF (20 ml) at $-78\text{ }^{\circ}\text{C}$ under argon dropwise *n*-BuLi (6.25 ml, 1.6 M in hexane, 10 mmol, 1 equiv) was added. The solution was stirred for 1 h at this temperature, then trimethyl borate (1.56 g, 15 mmol, 1.5 equiv) was added dropwise. The solution was stirred at $-78\text{ }^{\circ}\text{C}$ for 1.5 h and allowed to warm to $-20\text{ }^{\circ}\text{C}$. A saturated aqueous solution of KHF_2 (4.7 g, 60 mmol, 6.0 equiv) was added to the vigorously stirred solution. The resulting mixture was stirred for 1 h at $-20\text{ }^{\circ}\text{C}$ and at room temperature for 1 h. The solvent was removed *in vacuo*, and the resulting white solid was dried under high vacuum for 2 h. The solid was then washed with acetone and with hot acetone. The resulting organic solution was filtered, and the solvent was removed to yield a white solid, which was dissolved in hot acetone and precipitated with diethyl ether. Potassium phenylethynyltrifluoroborate (**3**) 1.41 g (68%); potassium hex-1-ynyltrifluoroborate (**4**) 1.39 g (74%).

General procedure for preparation of potassium organotrifluoroborates (5–26)

To the boronic acid (5 mmol) in MeOH (10 ml) a solution of KHF_2 was added dropwise (1.56 g, 20 mmol) in H_2O (8 ml) using an addition funnel. The mixture was stirred for 30 min and concentrated under high vacuum. The residual solids were extracted with four portions of 20% MeOH in acetone. The combined extracts were concentrated close to the saturation point and Et_2O was added until no more precipitation was observed. The solids were collected, washed with two portions of Et_2O , and dried under high vacuum to give the corresponding products. Potassium phenyltrifluoroborate (**5**) 0.73 g, 80%; potassium perfluorotrifluoroborate (**6**) 0.82 g (60%); potassium 4-methoxyphenyltrifluoroborate (**7**) 0.92 g (82%); potassium 4-(trifluoromethyl)phenyltrifluoroborate (**8**) 1.00 g (80%); potassium 4-formyl-phenyltrifluoroborate (**9**) 0.97 g (92%); potassium 3-formyl-phenyltrifluoroborate (**10**) 0.95 g (90%); potassium 2-formyl-phenyltrifluoroborate (**11**) 0.90 g (85%); potassium *o*-tolyl-trifluoroborate (**12**) 0.84 g (85%); potassium 2,6-dimethyltrifluoroborate (**13**) 0.84 g (80%); potassium 4-fluoro-phenyltrifluoroborate (**14**) 0.80 g (80%); potassium 3-nitro-phenyltrifluoroborate (**15**) 0.93 g (82%); potassium 2,6-difluorophenyltrifluoroborate (**16**) 0.93 g (85%); potassium phenylethyltrifluoroborate (**17**) 0.85 g (81%); potassium 5-formyl-2-methoxyphenyltrifluoroborate (**18**) 1.08 g (90%); potassium 3,5-bis(trifluoromethyl)phenyltrifluoroborate (**19**) 1.36 g (85%); potassium *p*-tolyl-trifluoroborate (**20**) 0.79 g (80%); potassium 5-formylthiophen-2-yl-trifluoroborate (**21**) 0.89 g (82%); potassium 5-formylthiophen-3-yl-trifluoroborate (**22**) 0.87 g (80%); potassium pyridin-3-yltrifluoroborate (**23**) 0.76 g (83%); potassium 2-thienyltrifluoroborate (**24**) 0.77 g (82%); potassium 3-thienyltrifluoroborate (**25**) 0.80 g (85%); potassium cyclopropyl trifluoroborate (**26**) 0.59 g (80%);

Potassium 4-oxopentyltrifluoroborate (27)

To a solution of potassium 4-methylpent-4-enyltrifluoroborate [$\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2\text{BF}_3\text{K}$] (0.202 g, 1.28 mmol) in an acetone/ H_2O mixture (30% H_2O in acetone, 14 ml) at $-70\text{ }^{\circ}\text{C}$ was applied a flow of ozone for 14 min. The solution was then degassed with N_2 for 15 min followed by the addition of H_2O (2 ml). This was allowed to warm to r.t. while stirring. Following solvent removal, the resulting white solid was purified by dissolving in hot acetone and precipitating with Et_2O , affording **27** (0.14 g, 70%) as a white solid.

Potassium iodomethyltrifluoroborate (28)

To a solution of potassium bromomethyltrifluoroborate (2.0 g, 10 mmol) in acetone (150 ml) NaI was added (1.5 g, 10 mmol) in one portion. After stirring at $25\text{ }^{\circ}\text{C}$ for 2 h, the suspension was filtered through a Celite pad and then the solvent was evaporated under

reduced pressure to give the crude product, which was purified by dissolving in a minimal amount of dry acetone and precipitating with Et₂O to yield a 2.38 g(96%) of the title compound as a white solid.

NMR measurements—¹H (300 MHz), ¹³C (75MHz), ¹¹B (96MHz), and ¹⁹F (282 MHz) NMR spectra were obtained on a Varian UNITY PLUS 300 spectrometer. Spectra were recorded in dimethylsulfoxide (DMSO-*d*₆), using DMSO residual peak as the ¹H internal reference (2.5 ppm); and the central peak of DMSO-*d*₆ at 39.5 ppm for ¹³C NMR. ¹¹B NMR spectra were calibrated using BF₃ Et₂O (0.0 ppm) as external reference. All ¹⁹F NMR chemical shifts were referenced to external CF₃CO₂H (0.0 ppm).

Typical parameters were as follows: ¹H NMR: Pulse angle of 45°, acquisition time of 3.6 s, 16 repetitions and, spectral width of 15 ppm. ¹³C NMR: Pulse angle of 90°, delay of 2.3s, acquisition time of 1.7 s, 1024 repetitions, and, spectral width of 250 ppm. ¹⁹F NMR: Pulse angle of 45°, delay of 1.0 s, acquisition time of 0.3 s, 80 repetitions, line broadening of 0.3 Hz and, a spectral width of 177 ppm. All ¹¹B NMR spectra were obtained using a S2PUL pulse sequence (VARIAN) which consists in a first pulse of 90°, a delay of 0.5 s, and a second pulse of 180°, followed by an acquisition time of 1.0 s. The spectra were recorded as 128 repetitions, spectral width of 171 ppm, and processed with line broadening of 5 Hz. For all nuclei spectra the temperature was maintained within ± 1 °C by using a Varian temperature unit.

The parameters to obtain standard ¹¹B NMR spectra (128 MHz) using a Bruker spectrometer were as follows: *zpg30* pulse sequence (Bruker) which consists in a single pulse sequence with p1 = 7 μs (90°) and a two level Waltz decoupling scheme with lower power during 1 s recycle delay and higher power during pulse and acquisition. The delay was 1.0 s and the spectrum was recorded using 128 repetitions, with 5 Hz line broadening and 1 Hz.

Conclusion

In this study, complete ¹H, ¹³C, ¹⁹F, and ¹¹B NMR spectral data for 28 potassium organotrifluoroborates were described. The resonance for the carbon bearing the boron atom is described for the first time for most of the studied compounds. In addition, a modified ¹¹B NMR pulse sequence was used and better resolution was observed, allowing the observation of ¹¹B–¹⁹F coupling constants for some compounds.

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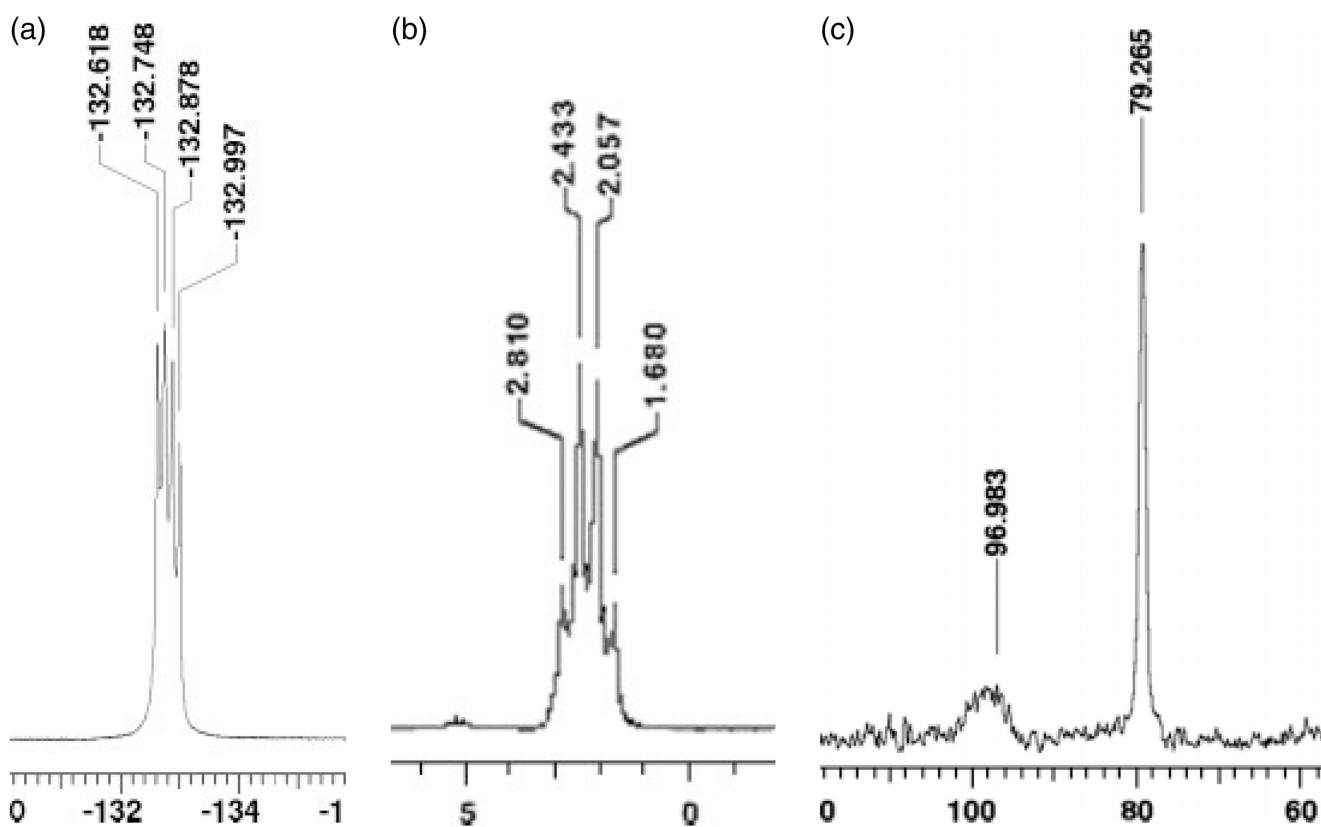


Figure 1. NMR spectra of compound **1**, parts (a) ^{19}F NMR spectrum (282 MHz, $\text{DMSO-}d_6$) showing the $^{19}\text{F-}^{11}\text{B}$ coupling; (b) ^{11}B NMR spectrum (96 MHz, $\text{DMSO-}d_6$) showing the $^{11}\text{B-}^{19}\text{F}$ coupling; (c) ^{13}C NMR spectrum (75 MHz, $\text{DMSO-}d_6$) showing the resonance from the carbon bearing the boron nuclei (broad).

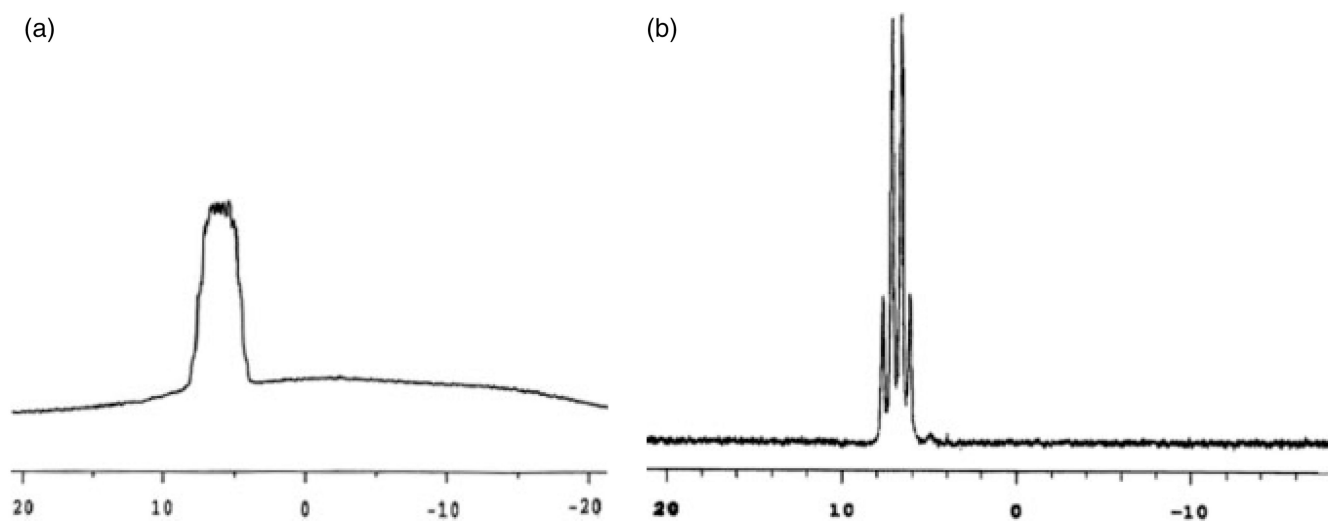


Figure 2.
(a) ^{11}B NMR (128 MHz, $\text{DMSO-}d_6$) spectra of **28** using standard acquisition parameters and; (b) ^{11}B NMR (96 MHz, $\text{DMSO-}d_6$) using a different pulse sequence.

Table 1


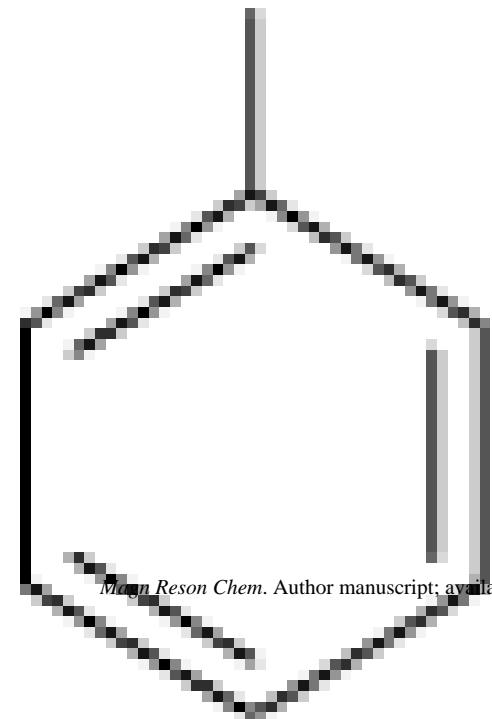
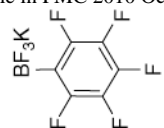
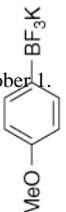
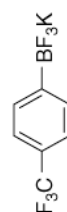
Effect of solvent and temperature on the ^{11}B and ^{19}F chemical shifts and coupling constants for **1**

Compound	Solvent	Temp. (°C)	$\delta^{11}\text{B}$ (ppm)	$\delta^{19}\text{F}$ (ppm)	$J(^{11}\text{B}-^{19}\text{F})$ (Hz)
1	D ₂ O	25	2.62	-144.2	15.1
	D ₂ O	50	2.86	-143.8	14.6
	Acetone- <i>d</i> ₆	25	2.96	-135.8	32.8
	Acetone- <i>d</i> ₆	50	2.97	-136.0	36.2
	CD ₃ OD	25	4.00	-155.7	11.6
	CD ₃ OD	50	4.03	-155.7	11.5
	CD ₃ CN	25	2.89	-135.7	35.9
	CD ₃ CN	50	2.92	-135.8	35.9
	DMSO- <i>d</i> ₆	25	2.20	-132.8	36.6
	DMSO- <i>d</i> ₆	50	2.23	-132.9	36.1

Table 2

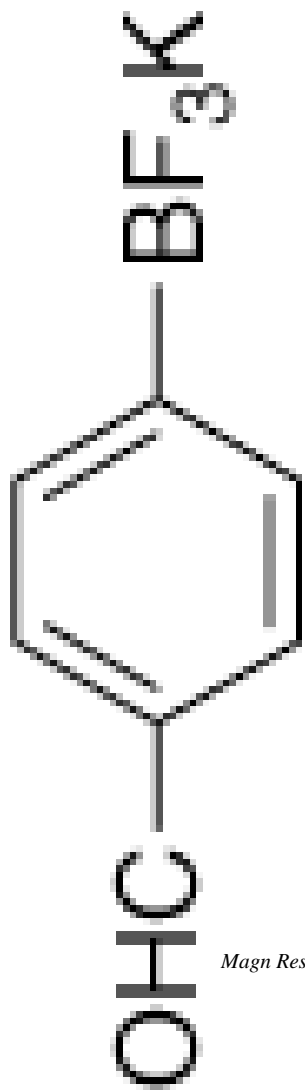
¹H, ¹³C, ¹¹B, and ¹⁹F chemical shifts of selected potassium organotrifluoroborates

Compound	$\delta(^1\text{H})$ (ppm)	$\delta(^{13}\text{C})$ (ppm)	$\delta(^{11}\text{B})$ (ppm)	$\delta(^{19}\text{F})$ (ppm)
1	1.93 (s, 1H)	97.6 (br); 79.1	2.20 ($J = 36.6$ Hz)	-132.8
2	5.84–5.69 (m, 1H); 5.22–2.13 (m, 2H)	146.2 (br); 121.6	6.87 ($J = 51$ Hz)	-139.5
3	7.28–7.25 (m, 5H)	130.9; 128.3; 126.9; 125.4; 104.3 (br); 89.5	2.92 ($J = 19$ Hz)	-132.0

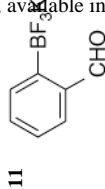
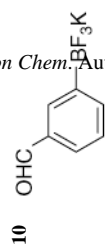
Compound	$\delta(^1\text{H})$ (ppm)	$\delta(^{13}\text{C})$ (ppm)	$\delta(^{19}\text{F})$ (ppm)	$\delta(^{19}\text{F})$ (ppm)
4 	1.97 (t, $J = 5.1$ Hz, 2H); 1.34–1.29 (m, 4H); 0.83 (t, $J = 7.2$ Hz, 3H)	90.8; 56.9; 31.5; 22.0; 18.7; 14.0	2.65	-131.5
5 	7.43 (d, $J = 6.6$ Hz, 2H); 7.19–7.10 (m, 3H)	149.1 (br); 131.6; 126.8; 125.8	7.94	-139.3
6 	–	147.9 (d, $J = 247$ Hz); 139.0 (d, $J = 240$ Hz); 136.6 (d, $J = 247$ Hz); 119.1 (br)	6.01 ($J = 42$ Hz)	-132.8; (-135.0)– (-135.1) (m); -160.7 (t, $J = 19$ Hz); (-165.3)– (-165.7) (m)
7 	7.73 (d, $J = 7.8$ Hz, 2H); 7.49 (d, $J = 7.8$ Hz, 2H); 2.51 (s, 3H)	157.9; 141.5 (br); 132.8; 112.6; 55.1	7.39	-140.1
8 	7.58–7.50 (m, 2H); 7.43–7.35 (m, 2H)	155.9 (br); 132.0; 126.2 (qua, $J = 30$ Hz); 125.2 (qua, $J = 272$ Hz); 122.8	7.44	-135.4; -140.2

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Compound	δ (¹ H) (ppm)	δ (¹³ C) (ppm)	δ (¹¹ B) (ppm)	δ (¹⁹ F) (ppm)
9	9.90 (s, 1H); 7.66 (d, <i>J</i> = 7.5 Hz, 2H); 7.55 (d, <i>J</i> = 7.5 Hz, 2H)	193.3; 159.5(br); 133.8; 131.6; 127.7	7.12	-140.2
10	9.95 (s, 1H); 7.89 (s, 1H); 7.68 (ddd, <i>J</i> ^β = 7.5 Hz, Hz, <i>J</i> ^α = 1.5, 1H); 7.61 (ddd, <i>J</i> ^β = 7.5 Hz, <i>J</i> ^α = 1.5, 1H); 7.34 (dd, <i>J</i> ^β = 7.5 Hz, 1H)	195.0; 150.3 (br); 138.4; 135.1; 133.4; 127.7; 127.2	7.44	-139.9
11	10.45 (s, 1H); 7.69 (d, <i>J</i> = 7.5 Hz, 1H); 7.63 (d, <i>J</i> = 7.2 Hz, 1H); 7.40 (dd, <i>J</i> = 7.5 Hz, <i>J</i> = 7.2 Hz, 1H); 7.24 (dd, <i>J</i> = 7.2 Hz, <i>J</i> = 7.5 Hz, 1H)	197.1; 156.0 (br); 139.2; 132.9; 132.1; 126.0; 124.6	7.59 (<i>J</i> = 51 Hz)	-132.5

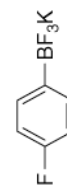
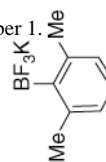


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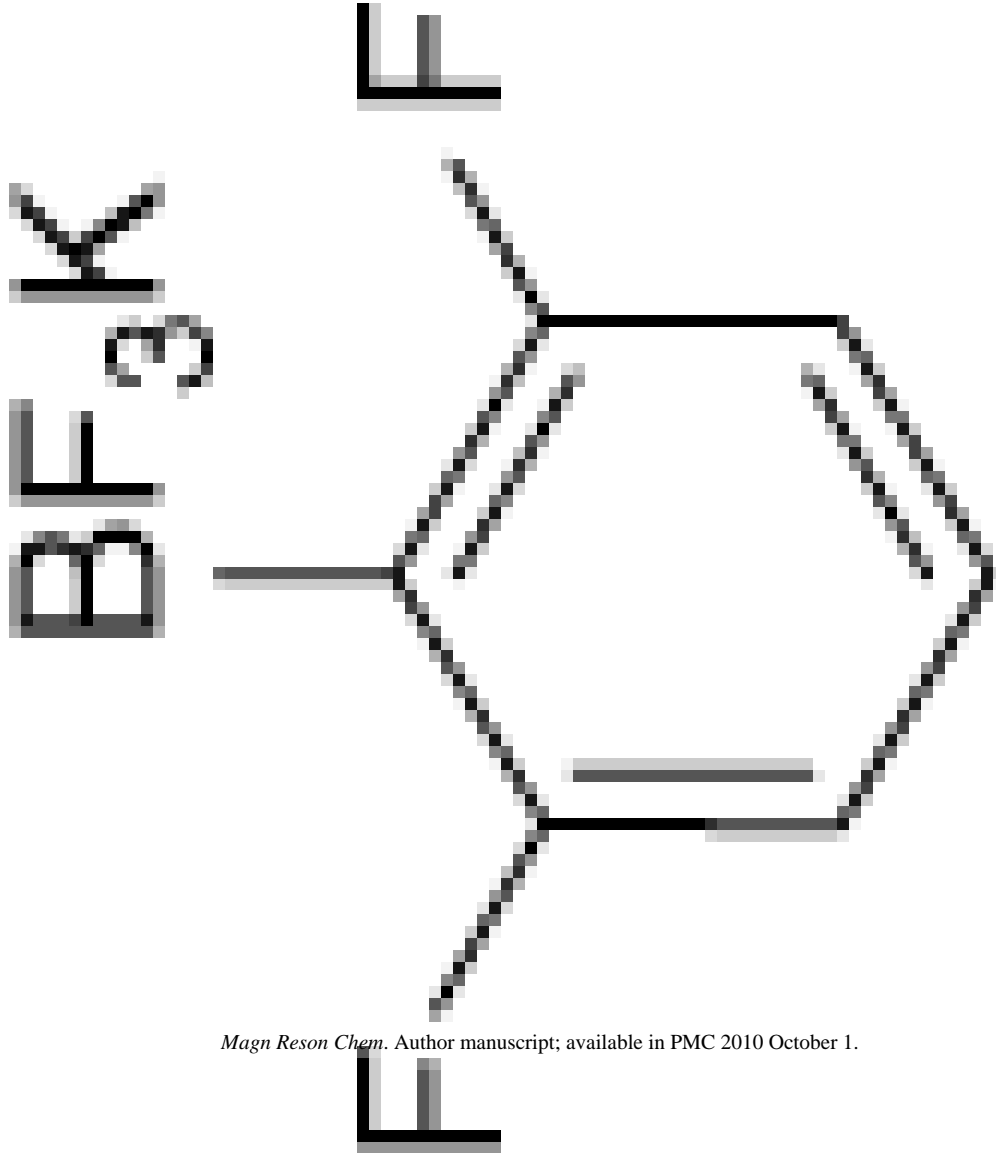


Compound	$\delta(^1\text{H})$ (ppm)	$\delta(^{13}\text{C})$ (ppm)	$\delta(^{11}\text{B})$ (ppm)	$\delta(^{19}\text{F})$ (ppm)
12	7.30 (d, $J = 6.0$ Hz, 1H); 6.85–6.87 (m, 3H); 2.27 (s, 3H)	148.9 (bp); 140.5; 131.6; 128.2; 125.1; 123.4; 21.7	7.74 ($J = 52$ Hz)	-137.7
13	6.81–6.76 (m, 1H); 6.69 (d, $J = 7.2$ Hz; 2H); 2.31 (s, 6H)	141.0; 126.6; 126.0 (bp); 124.7; 23.4	8.23 ($J = 53$ Hz)	-129.6
14	7.40–7.36 (m, 2H); 6.93–6.87 (m, 2H)	161.7 (d, $J^1 = 240$ Hz); 145.2 (bp); 133.4; 113.5 (d, $J^2 = 15$ Hz)	7.77	-118.6; -139.1

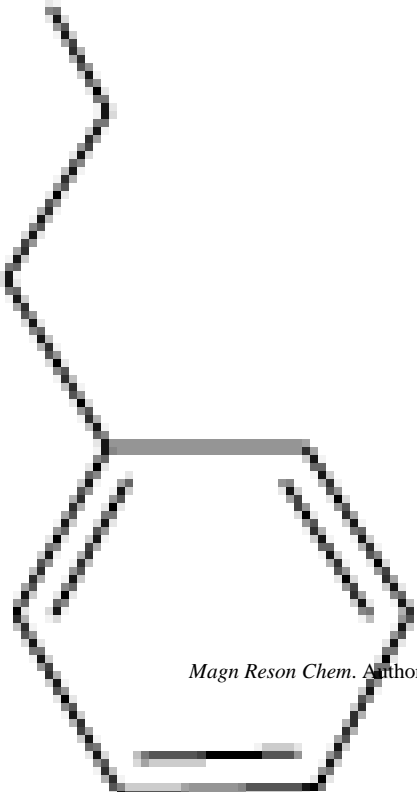
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Compound	δ (¹ H) (ppm)	δ (¹³ C) (ppm)	δ (¹⁹ F) (ppm)
15 	8.18 (s, 1H); 7.96 (dd, $J^3 = 8.1$ Hz, $J^4 = 2.0$ Hz, 1H); 7.80 (dd, $J = 7.2$ Hz, $J^4 = 2.0$ Hz, 1H); 7.43 (dd, $J^3 = 7.8$ Hz, $J^3 = 7.2$ Hz, 1H)	152.4 (bp); 147.4; 138.7; 128.5; 125.7; 121.1	7.24 -140.5

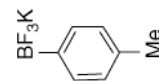
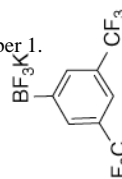
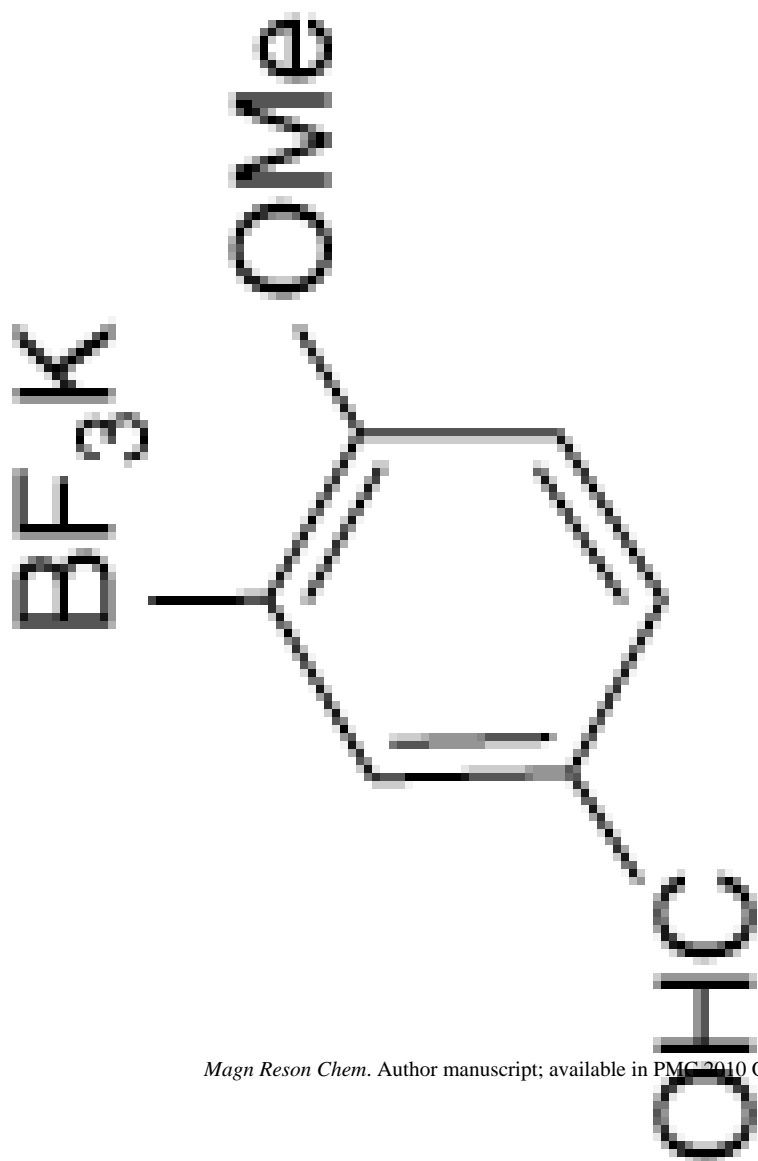
Compound	δ (¹ H) (ppm)	δ (¹³ C) (ppm)	δ (¹⁹ F) (ppm)
	7.16–7.06 (m, 1H); 6.69 (t, J = 9.0 Hz, 2H)	166.1 (dd, J ¹ = 240 Hz, J ² = 17 Hz); 128.0; 121.3 (br); 110.3 (d, J ² = 29 Hz)	6.57 (J = 45 Hz) -103.0; -132.5

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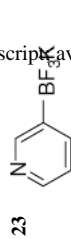
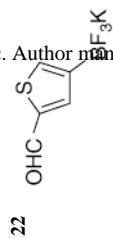
Compound	δ (¹ H) (ppm)	δ (¹³ C) (ppm)	δ (¹⁹ F) (ppm)
 <chem>CC(F)(F)CCc1ccccc1</chem>	7.21–7.02 (m, 5H); 2.48–2.42 (m, 2H); 0.40–0.28 (m, 2H)	148.0; 127.9; 127.7; 124.5; 32.1; 22.3 (br)	5.19 (J = 18 Hz) –138.3

Compound	$\delta(^1\text{H})$ (ppm)	$\delta(^{13}\text{C})$ (ppm)	$\delta(^{11}\text{B})$ (ppm)	$\delta(^{19}\text{F})$ (ppm)
18	9.78 (s, 1H); 7.87 (d, $J^4 = 2.5$ Hz, 1H); 7.66 (dd, $J^3 = 8.7$ Hz, $J^4 = 2.5$ Hz, 1H); 6.91 (d, $J^3 = 8.7$ Hz, 1H); 3.74 (s, 3H)	192.2; 168.1; 137.8 (br); 135.1; 131.0; 128.5; 109.6; 55.1	7.23	-138.2
19	7.88 (s, 2H); 7.72 (s, 1H)	131.3; 128.2(br); 126.0; 122.4; 118.8	6.94	-61.7; -141.2
20	7.22 (d, $J = 7.2$ Hz, 2H); 6.91 (d, $J = 7.2$ Hz, 2H); 2.21 (s, 3H)	146.0 (br); 133.6; 131.5; 127.2; 21.2	7.88	-138.8

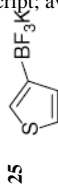
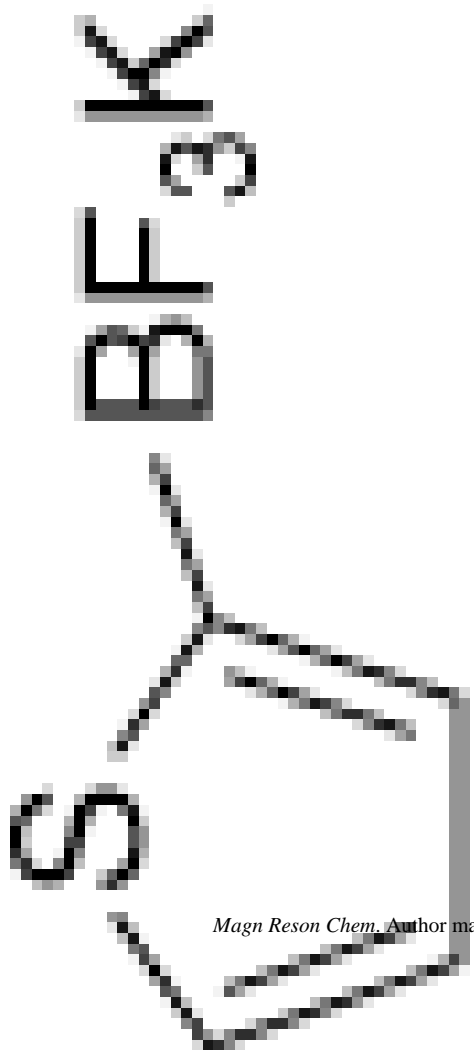
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Compound	$\delta(^1\text{H})$ (ppm)	$\delta(^{13}\text{C})$ (ppm)	$\delta(^{19}\text{F})$ (ppm)	$\delta(^{31}\text{P})$ (ppm)
21	9.87 (s, 1H); 7.84 (s, 1H); 7.64 (s, 1H)	185.3; 153.7 (br); 144.0; 143.1; 136.9		6.41
22	9.86 (s, 1H); 7.85 (s, 1H); 7.65 (s, 1H)	185.1; 153.6 (br); 143.9; 143.0; 136.7		6.60
23	8.54 (s, 1H); 8.29 (d, $J = 4.8$ Hz, 1H); 7.67 (d, $J = 9.0$ Hz, 1H); 7.12 (dd, $J^2 = 9.0$, $J^3 = 4.8$, 1H)	152.6; 147.0; 142.2 (br); 139.6; 123.2		7.66



Compound	$\delta(^1\text{H})$ (ppm)	$\delta(^{13}\text{C})$ (ppm)	$\delta(^{19}\text{F})$ (ppm)	$\delta(^{41}\text{K})$ (ppm)
24	7.23 (<i>dd</i> , $J^3 = 3.9$, $J^5 = 3.8$, 1H); 6.93 (<i>dd</i> , $J^3 = 3.8$, $J^5 = 3.8$, 1H); 1.2, 1H); 6.87 (<i>br</i>)	150.6 (<i>br</i>); 127.5; 126.9; 124.4	6.87 ($J = 46$ Hz)	-134.1
25	7.22 (<i>d</i> , $J^3 = 3.0$ Hz, 1H); 7.10 (<i>s</i> , 1H); 7.06 (<i>d</i> , $J^3 = 3.0$ Hz, 1H)	151.3 (<i>br</i>); 132.0; 124.7; 123.0	7.20	-135.8
26	(-0.02)–(-0.151) (<i>m</i> , 4H); (-0.71)–(-0.84) (<i>m</i> , 1H)	1.2; -0.4(<i>br</i>)	8.77	-141.2



Compound	δ (¹ H) (ppm)	δ (¹³ C) (ppm)	δ (¹¹ B) (ppm)	δ (¹⁹ F) (ppm)
27	2.28 (t, <i>J</i> = 7.5 Hz, 2H); 2.03 (s, 3H); 1.37 (qui., <i>J</i> = 7.5 Hz, 2H); 1.07 (qui., <i>J</i> = 7.5 Hz, 2H); -0.06 (m, 2H)	210.8; 43.9; 30.0; 27.7; 25.5	9.36	-137.2
28 	1.80 (s, 2H).	*	6.85 (<i>J</i> = 50 Hz)	-140.7

No peak was observed for this compound.