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Promising route to aryl(polyfluoroorganyl)borates: aryltris(pentafluorophenyl)borates

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Experimental part

The NMR spectra were acquired using a Bruker Avance 300 (^{1}H at 300.13 MHz, ^{19}F at 282.40 MHz) and an Avance 400 (^{1}H, 400.13 MHz; ^{11}B, 128.37 MHz; ^{19}F, 376.49 MHz). spectrometers. The chemical shifts were referenced to TMS (^{1}H), $BF_3{\cdot}OEt_2$ (^{11}B) and CCl_3F (^{19}F, with C_6F_6 as secondary reference (−162.9 ppm)), respectively. Ether was refluxed with sodium, distilled and stored over sodium pieces. Bromopentafluorobenzene (P&M Invest), butyl bromide (Reachem) and magnesium (Acros) were used as supplied. Borates $K[C_6F_5BF_3]$, $K[C_6H_5BF_3]$, $K[4\text{-}CF_3C_6H_4BF_3]$, $K[4\text{-}FC_6H_4BF_3]$ and $K[\beta\text{-}C_{10}F_7BF_3]$[S1], $K[4\text{-}MeC_6H_4BF_3]$, $K[4\text{-}MeOC_6H_4BF_3]$[S2] were prepared as described. All manipulations with organomagnesium compounds were performed under an atmosphere of dry argon. Products **3** and **4** were identified on their ^{1}H and ^{11}B NMR spectra,[S3,S4] borate **1** was identified on ^{19}F and ^{11}B NMR spectra.[S5]

Optimization of reaction conditions

Pentafluorophenylmagnesium bromide in ether

Method a. A three-necked flask (50 ml volume) equipped with magnetic stir bar, thermometer, dropping funnel and reflux condenser topped with T-adapter for argon inlet/outlet was charged with magnesium (219 mg, 9.0 mmol), a few crystals of iodine and filled with argon. After cooling to room temperature, a solution of BuBr (0.17 ml, 1.6 mmol) in ether (20 ml) was added, and the mixture was stirred till discoloration. Then a solution of bromopentafluorobenzene (1.0 ml, 8.0 mmol) in ether (15 ml) was added dropwise keeping gentle reflux. Finally, the reaction mixture was refluxed for an additional 4 h.

Method b. A three-necked flask (50 ml) equipped with magnetic stir bar, thermometer, dropping funnel and reflux condenser topped with T-adapter for argon inlet/outlet was charged with magnesium (219 mg, 9.0 mmol), a few crystals of iodine and filled with argon. After cooling to room temperature, a solution of BuBr (0.17 ml, 1.6 mmol) in ether (20 ml) was added, and the mixture was stirred till discoloration. Then reactor was cooled in ice bath and a solution of bromopentafluorobenzene (1.0 ml, 8.0 mmol) in ether (15 ml) was added dropwise keeping temperature below 10 °C. Finally, the reaction mixture was stirred in ice bath for an additional 4.5 h.

Potassium 4-tolyltris(pentafluorophenyl)borate (**2**)

Experiment 1. K[4-MeC$_6$H$_4$BF$_3$] **1** (396 mg, 2.0 mmol) was added in small portions to a solution of C$_6$F$_5$MgBr (prepared by method *a*) without allowing the solution to boil. The suspension was refluxed for 1 h, cooled to room temperature and poured to stirred saturated solution of K$_2$CO$_3$ in water (10 ml). The suspension was filtered, the cake was washed with ether (2x15 ml). The organic phase of filtrate was separated, the aqueous one was extracted with ether (2x10 ml). The combined washings and extracts were dried with MgSO$_4$ and evaporated to dryness to yield brown residue (64 mg).

Experiment 2. Two-necked flask (100 ml) equipped with magnetic stir bar and reflux condenser topped with T-adapter for argon inlet/outlet was charged with K[4-MeC$_6$H$_4$BF$_3$] **1** (396 mg, 2.0 mmol) and filled with argon. After addition of ether (20 ml), the solution of C$_6$F$_5$MgBr (prepared by method *a*) was siphoned under argon without allowing solvent to boil. The suspension was refluxed for 1 h, cooled and treated as above to yield brown residue (90 mg).

Experiment 3. Salt K[4-MeC$_6$H$_4$BF$_3$] **1** (396 mg, 2.0 mmol) was added in small portions to a cold solution of C$_6$F$_5$MgBr (prepared by method *b*) without allowing the solvent to boil. The suspension was stirred at room temperature for 5 h, and treated as above to yield brown residue (45 mg).

Experiment 4. Three-necked flask (100 ml in volume) equipped with magnetic stir bar, thermometer and reflux condenser topped with T-adapter for argon inlet/outlet was charged with K[4-MeC$_6$H$_4$BF$_3$] **1** (396 mg, 2.0 mmol) and filled with argon. After addition of ether (20 ml), the suspension was cooled in ice bath, and cold solution of C$_6$F$_5$MgBr (prepared by method *b*) was siphoned under argon to keep temperature at 7-10°C. Finally the reaction mixture was stirred at room temperature over a period of 5 h and treated as above to yield brown solid (161 mg).

Experiment 5. The reaction was performed similarly to *Experiment 4*, but the reaction mixture was stirred at room temperature over a period of 30 h to yield after treatment brown solid (276 mg).

Experiment 6. The reaction was performed similarly to *Experiment 5*, but finally the reaction mixture was refluxed for 4 h to yield after treatment brown solid (430 mg).

Experiment 7. The reaction was performed similarly to *Experiment 5*, but finally the reaction mixture was refluxed for 12 h to yield after treatment brown solid (462 mg).

Table S1. Optimization of reaction conditions for synthesis of K[4-$MeC_6H_4B(C_6F_5)_3$] **2**

Entry	C_6F_5MgBr, method	Reaction conditions			Yield, % [a]	Ratio **2:3:4** [b]
		Mixing order	Temperature	Time, h		
1	a	direct	reflux	1	10	10:184:6
2	a	reverse	reflux	1	14	10:127:6
3	b	direct	RT	5	7	10:85:5
4	b	reverse	RT	5	25	10:10:3
5	b	reverse	RT	30	43	10:4:1
6	b	reverse	reflux	4	67	10:2:0
7	b	reverse	reflux	12	72	10:1:0

[a] In % based on K[4-$MeC_6H_4BF_3$] **1** (396 mg, 2.0 mmol). [b] ^{1}H NMR data.

Preparation of potassium aryltris(pentafluorophenyl)borates (general procedure)

A three-necked flask (50 ml in volume) equipped with magnetic stir bar, thermometer, dropping funnel and reflux condenser topped with T-adapter for argon inlet/outlet was charged with magnesium (219 mg, 9.0 mmol), a few crystals of iodine and filled with argon. After cooling to room temperature, a solution of BuBr (0.17 ml, 1.6 mmol) in ether (20 ml) was added, and the mixture was stirred till discoloration. The reactor was cooled in an ice bath, and the solution of bromopentafluorobenzene (1.0 ml, 8.0 mmol) in ether (15 ml) was added dropwise keeping temperature below 10 °C. Finally, the reaction mixture was stirred in ice bath for an additional 4.5 h.

Another three-necked flask (100 ml) equipped with magnetic stir bar, thermometer and reflux condenser topped with T-adapter for argon inlet/outlet was charged with potassium aryltrifluoroborate (2.0 mmol) and filled with argon. After addition of ether (20 ml), the suspension was cooled in ice bath, and cold solution of C_6F_5MgBr was siphoned under argon to keep temperature at 7-10°C. The reaction mixture was warmed to room temperature, refluxed over a period of 12-18 h and after cooling was poured into a saturated solution of potassium carbonate (10 ml). The suspension was filtered. The organic phase was separated, the aqueous one was extracted with ether (2x10 ml), and the cake was washed with ether (2x15 ml). The combined extract was dried with $MgSO_4$ and the solvent was removed on evaporator. The residue was dissolved in hot water (25 ml) and boiled with charcoal (1-1.5 g) for 20-30 min. After filtration, the aqueous solution was evaporated under reduced pressure to yield white or pale yellow solid.

Potassium (4-methoxyphenyl)tris(pentafluorophenyl)borate **5** (527 mg, 40%). Reflux time was 15 h.

^{1}H NMR (DMSO-d$_6$) δ: 3.61 (s, 3H, OCH_3), 6.54 (m, 2H), 7.01 (m, 2H). ^{11}B NMR (DMSO-d$_6$) δ: -12.9 (br. s). ^{19}F NMR (DMSO-d$_6$) δ: -128.9 (m, 6F, F^{2,6}), -162.2 (t, $^{3}J_{FF}$ 19.8 Hz, 3F, F^{3}), -165.4 (m, 6F, F^{3,5}).

Calc., %: C 45.62 H 1.07 F 43.30. $C_{25}H_7OF_{15}BK$ (658.21). Found, %: C 45.6, H 1.06, F 43.4.

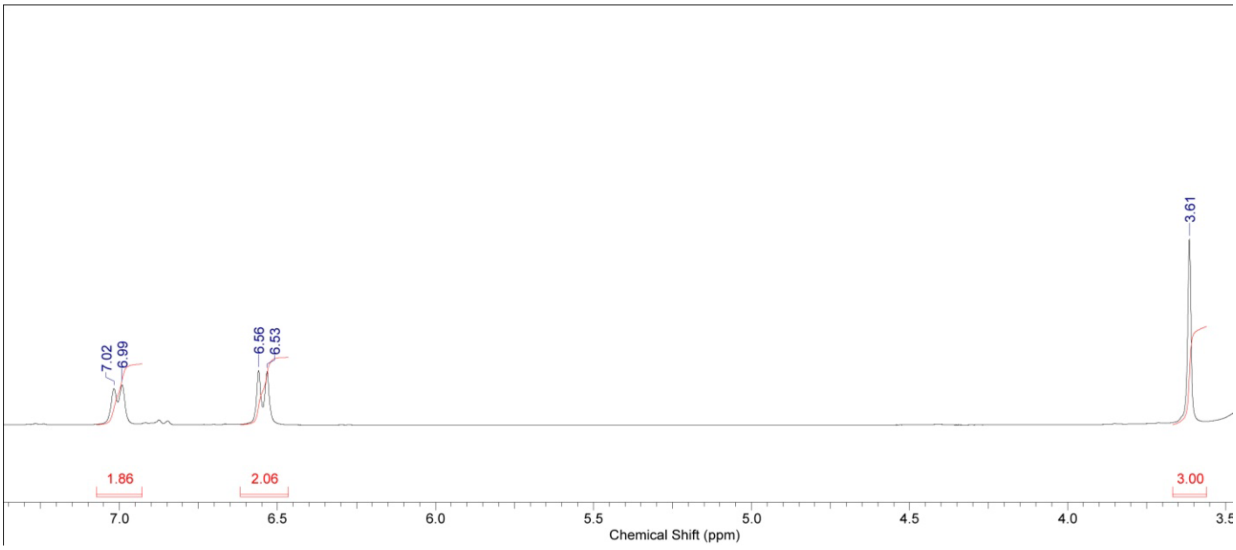

Figure S1. ^{1}H NMR spectrum of potassium (4-methoxyphenyl)tris(pentafluorophenyl)borate **5**.

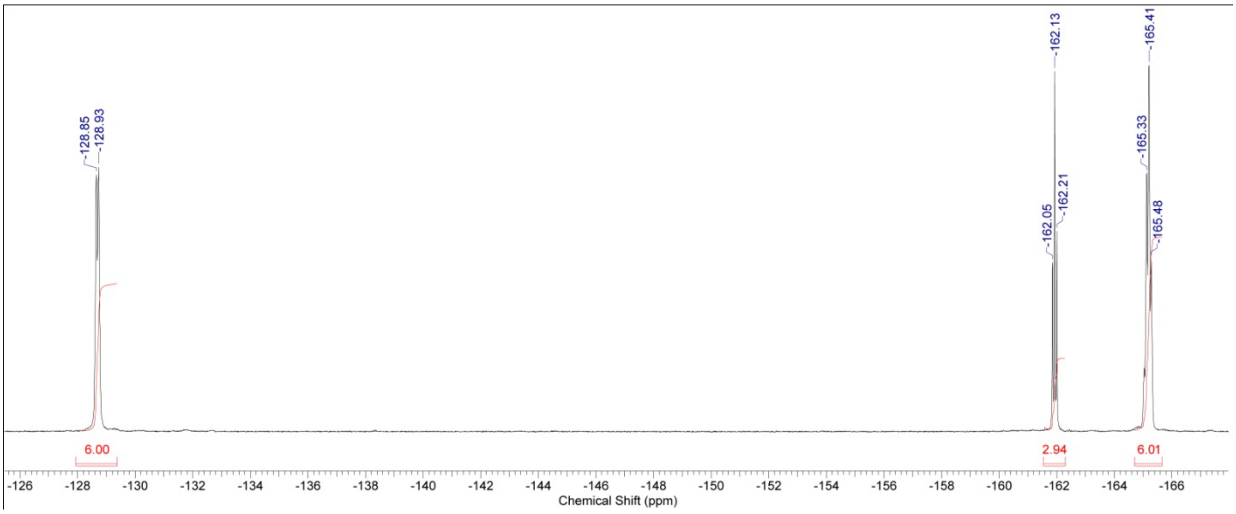

Figure S2. ^{19}F NMR spectrum of potassium (4-methoxyphenyl)tris(pentafluorophenyl)borate **5**.

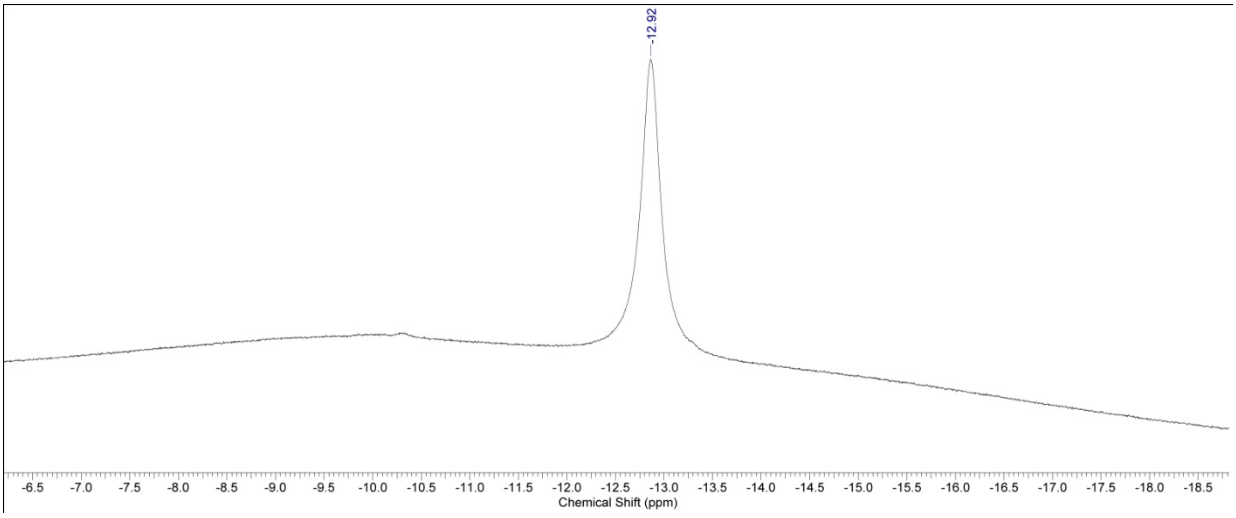

Figure S3. ^{11}B NMR spectrum of potassium (4-methoxyphenyl)tris(pentafluorophenyl)borate **5**.

Potassium (4-methylphenyl)tris(pentafluorophenyl)borate **2** (520 mg, 37%). Reflux time was 14 h.

^{1}H NMR (DMSO-d$_6$) δ: 2.14 (s, 3H, CH_3), 6.78 (d, $^3J_{HH}$ 7.6 Hz, 2H, H^{2,6}), 7.01 (d, $^3J_{HH}$ 7.3 Hz, 2H, H^{3,5}). ^{11}B NMR (DMSO-d$_6$) δ: -13.0 (br. s). ^{19}F NMR (DMSO-d$_6$) δ: -128.0 (m, 6F, F^{2,6}), -161.5 (t, $^3J_{FF}$ 21.6 Hz, 3F, F^4), -164.8 (m, 6F, F^{3,5}).

Calc., %: C 46.76 H 1.10 F 44.37. $C_{25}H_7F_{15}BK$ (642.21). Found, %: C 46.8, H 1.11, F 44.3.

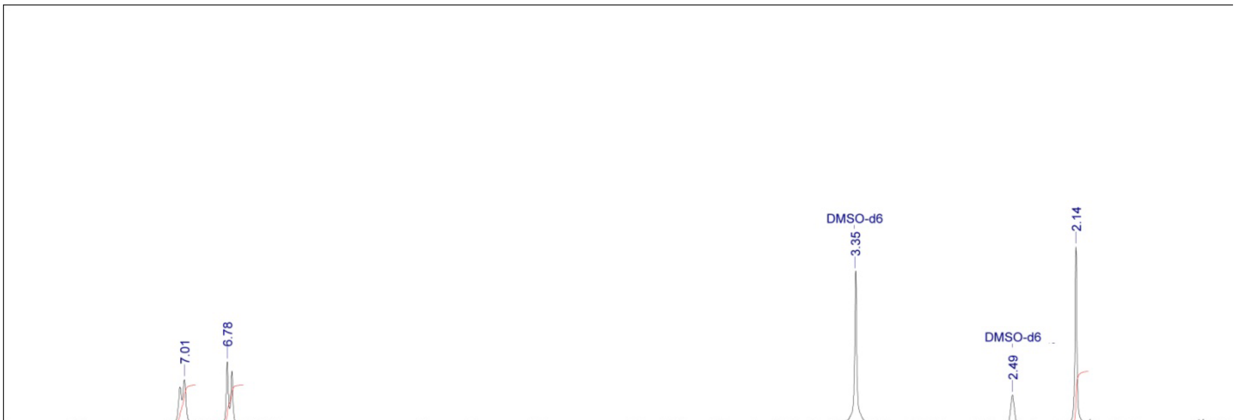

Figure S4. ^{1}H NMR spectrum of potassium (4-methylphenyl)tris(pentafluorophenyl)borate **2**.

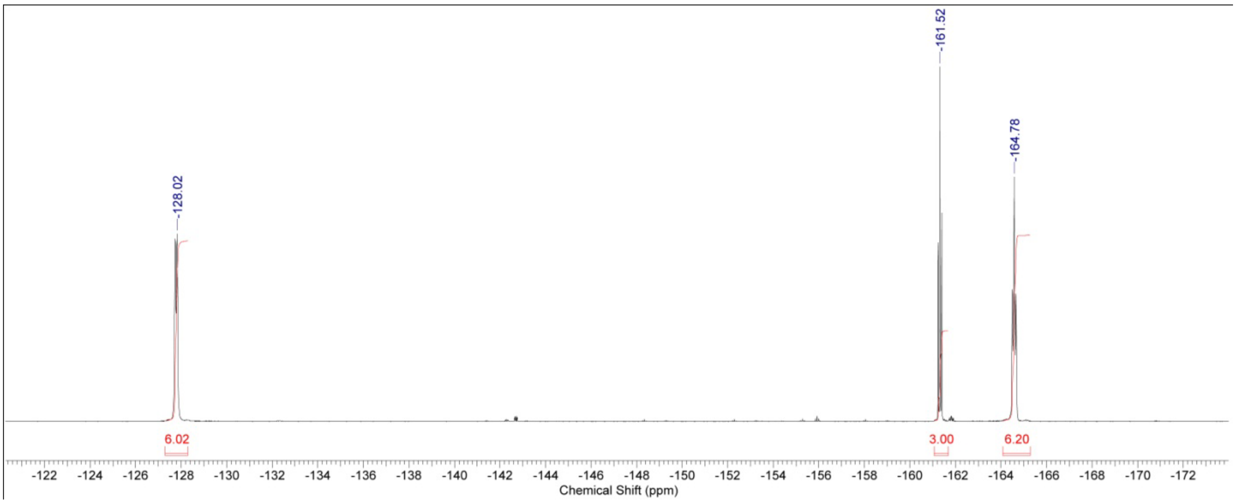

Figure S5. ^{19}F NMR spectrum of potassium (4-methylphenyl)tris(pentafluorophenyl)borate **2**.

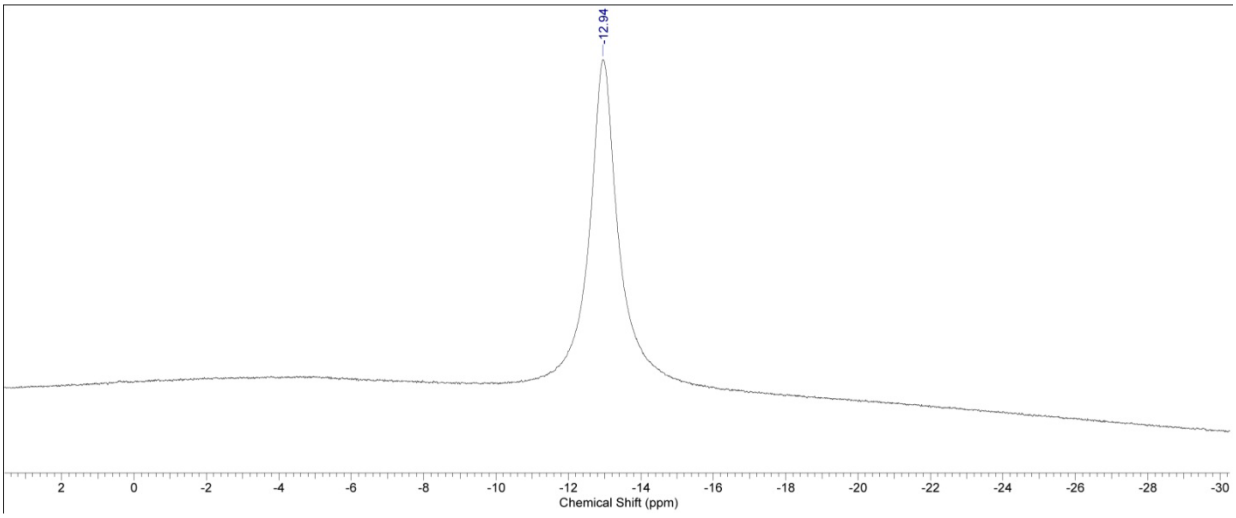

Figure S6. ^{11}B NMR spectrum of potassium (4-methylphenyl)tris(pentafluorophenyl)borate **2**.

Potassium phenyltris(pentafluorophenyl)borate **6** (515 mg, 41%). Reflux time was 12 h. ^{1}H NMR (DMSO-d$_6$) δ: 6.84-6.88 (m, 1H, H^4), 6.94-6.99 (m, 2H, H^{3,5}), 7,15-7.17 (m, 2H, H^{2,,6}). ^{11}B NMR (DMSO-d$_6$) δ: -12.9 (s). ^{19}F NMR (DMSO-d$_6$) δ: -128.1 (m, 6F, F^{2,6}), -161.5 (t, $^3J_{FF}$ 21.6 Hz, 3F, F^4), -164.9 (m, 6F, F^{3,5}).

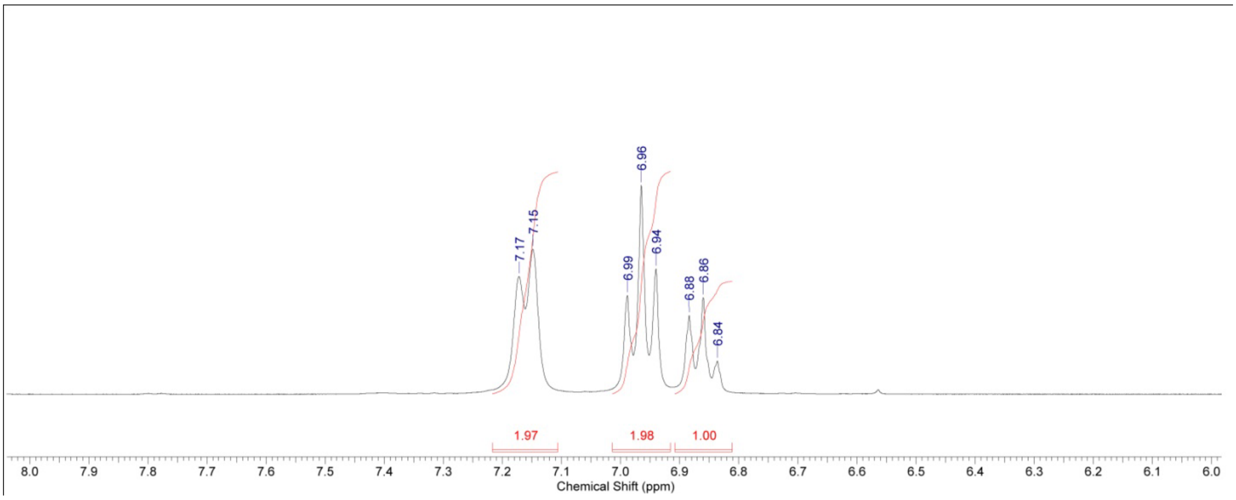

Figure S7. ^{1}H NMR spectrum of potassium phenyltris(pentafluorophenyl)borate **6**.

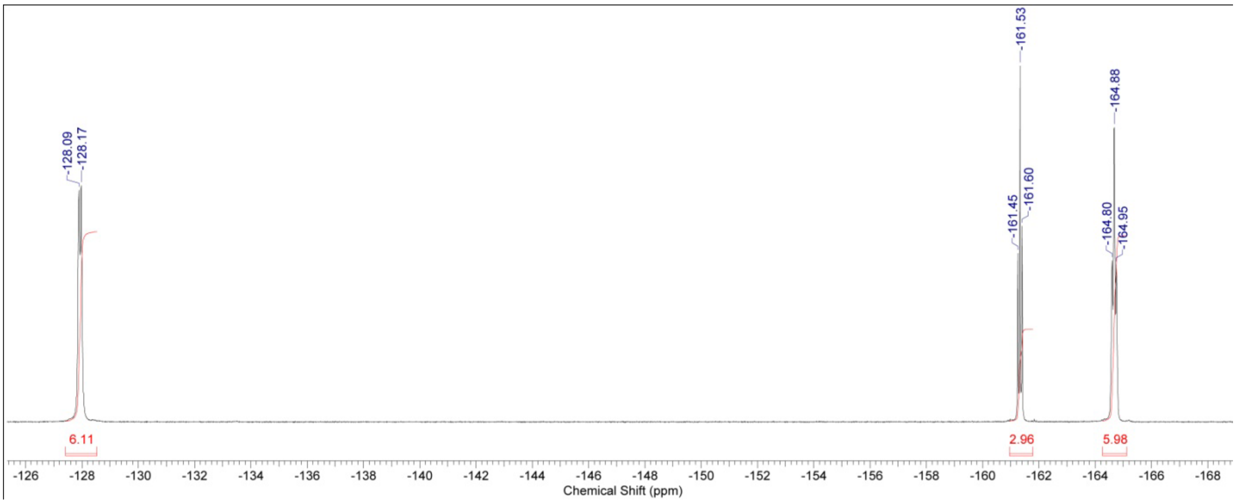

Figure S8. ^{19}F NMR spectrum of potassium phenyltris(pentafluorophenyl)borate **6**.

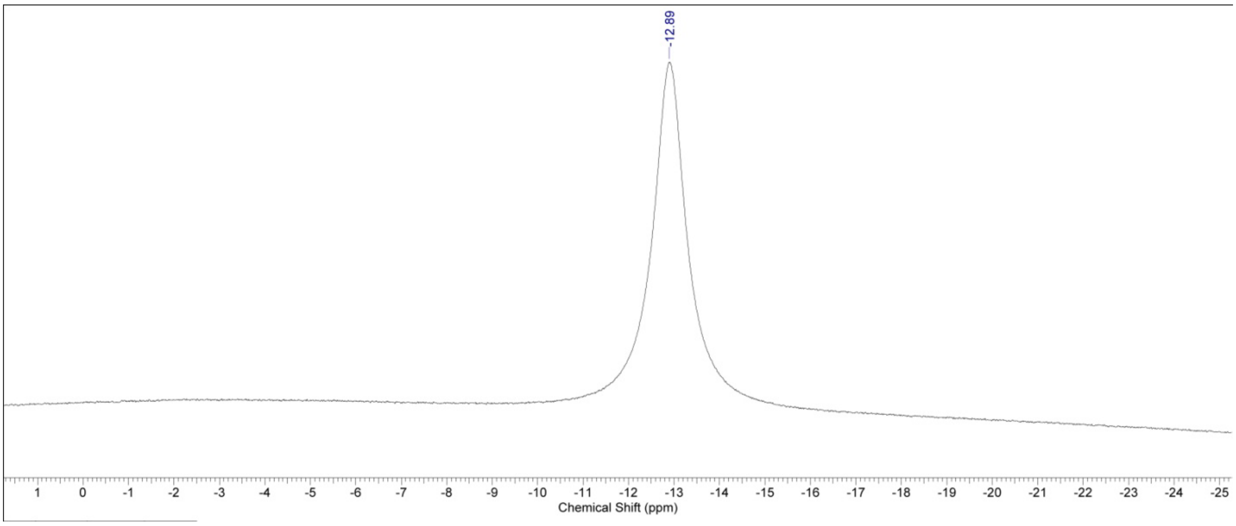

Figure S9. ^{11}B NMR spectrum of potassium phenyltris(pentafluorophenyl)borate **6**.

Potassium (4-fluorophenyl)tris(pentafluorophenyl)borate **7** (465 mg, 36%). Reflux time was 15 h. ^{1}H NMR (DMSO-d$_6$) δ: 6.77 (m, 2H), 7.14 (m, 2H). ^{11}B NMR (DMSO-d$_6$) δ: -13.1 (br. s). ^{19}F NMR (DMSO-d$_6$) δ: -119.9 (m, 1F, FC$_6$H$_4$), -128.4 (m, 6F, F^{2,6}), -161.3 (t, $^{3}J_{\mathrm{FF}}$ 21.7 Hz, 3F, F^{4}), -164.7 (m, 6F, F^{3,5}).

Calc., %: C 44.61 H 0.62 F 47.04. C$_{24}$H$_4$F$_{16}$BK (646.17). Found, %: C 44.6, H 0.65, F 47.0.

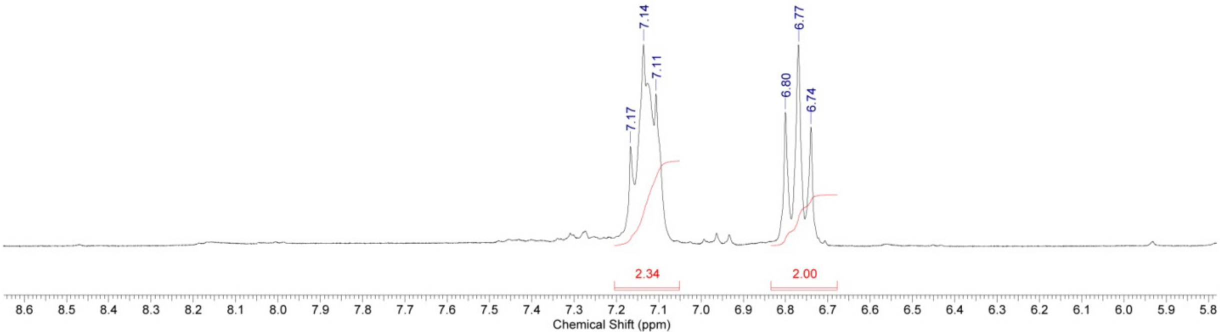

Figure S10. ^{1}H NMR spectrum of potassium (4-fluorophenyl)tris(pentafluorophenyl)borate **7**.

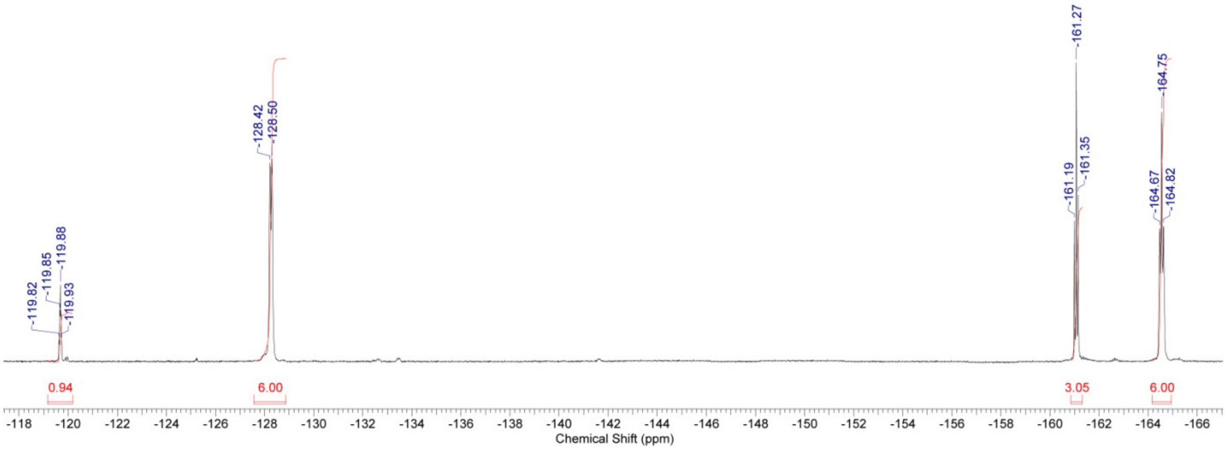

Figure S11. ^{19}F NMR spectrum of potassium (4-fluorophenyl)tris(pentafluorophenyl)borate **7**.

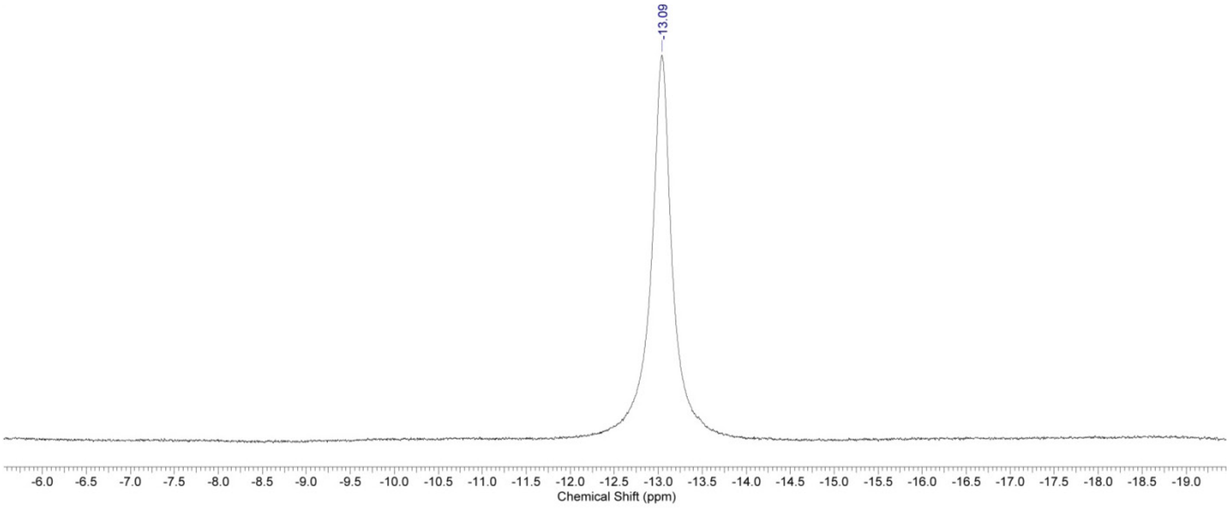

Figure S12. ^{11}B NMR spectrum of potassium (4-fluorophenyl)tris(pentafluorophenyl)borate **7**.

Potassium (4-trifluoromethylphenyl)tris(pentafluorophenyl)borate **8** (459 mg, 33%). Reflux time was 15 h.

^{1}H NMR (DMSO-d$_6$) δ: 7.32 (m, 2H), 7.59 (m, 2H). ^{11}B NMR (DMSO-d$_6$) δ: -13.1 (br. s). ^{19}F NMR (DMSO-d$_6$) δ: -58.0 (s, 3F, C*F*$_3$), -127.1 (m, 6F, F^{2,6}), -159.6 (m, 3F, F^4), -163.3 (m, 6F, F^{3,5}).

Calc., %: C 43.13 H 0.58 F 49.12. $C_{25}H_4F_{18}BK$ (696.18). Found, %: C 43.1, H 0.57 F 49.1.

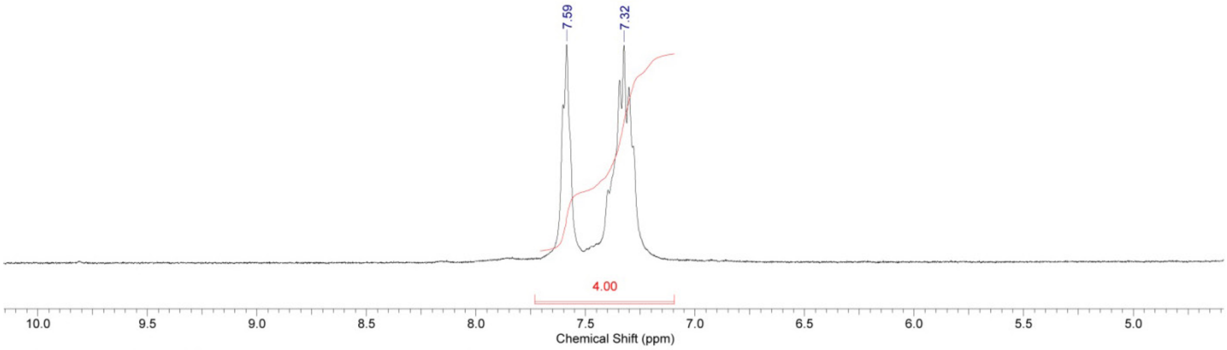

Figure S13. ^{1}H NMR spectrum of potassium (4-trifluoromethylphenyl)-tris(pentafluorophenyl)borate **8**.

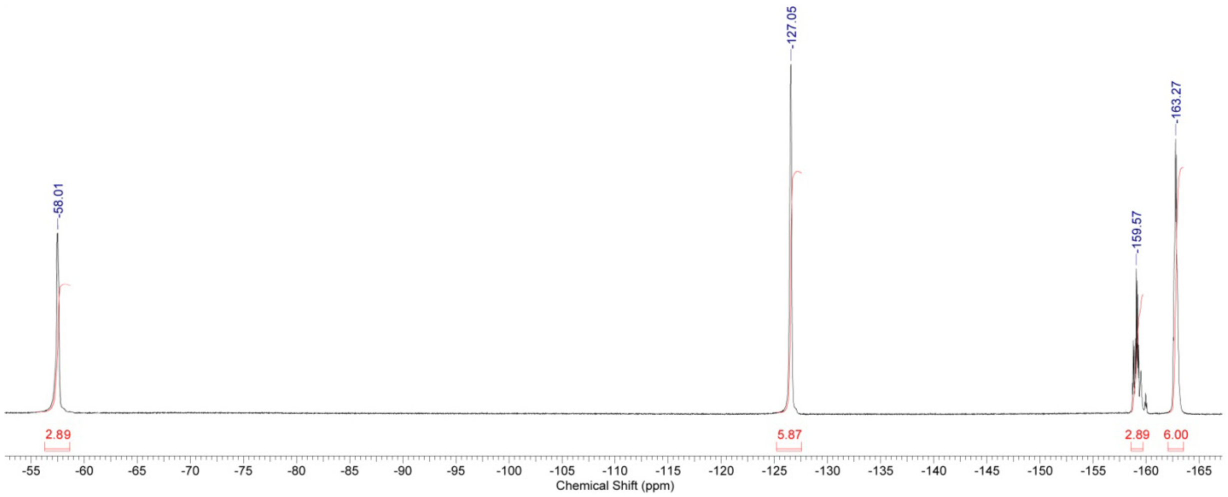

Figure S14. ^{19}F NMR spectrum of potassium (4-trifluoromethylphenyl)-tris(pentafluorophenyl)borate **8**.

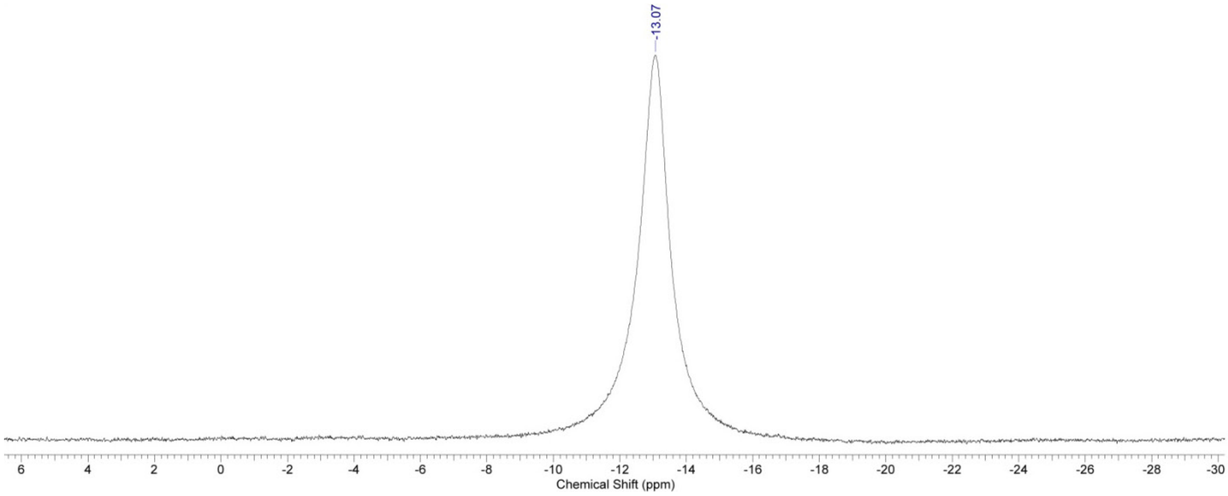

Figure S15. ^{11}B NMR spectrum of potassium (4-trifluoromethylphenyl)-tris(pentafluorophenyl)borate **8**.

Potassium tetrakis(pentafluorophenyl)borate **9** (474 mg, 33%). Reflux time was 18 h.
^{11}B NMR (DMSO-d_6) δ: -16.8 (s). ^{19}F NMR (DMSO-d_6) δ: -132.8 (m, 8F, $F^{2,6}$), -161.8 (t, $^3J_{FF}$ 21.7 Hz, 4F, F^4), -166.4 (m, 8F, $F^{3,5}$).

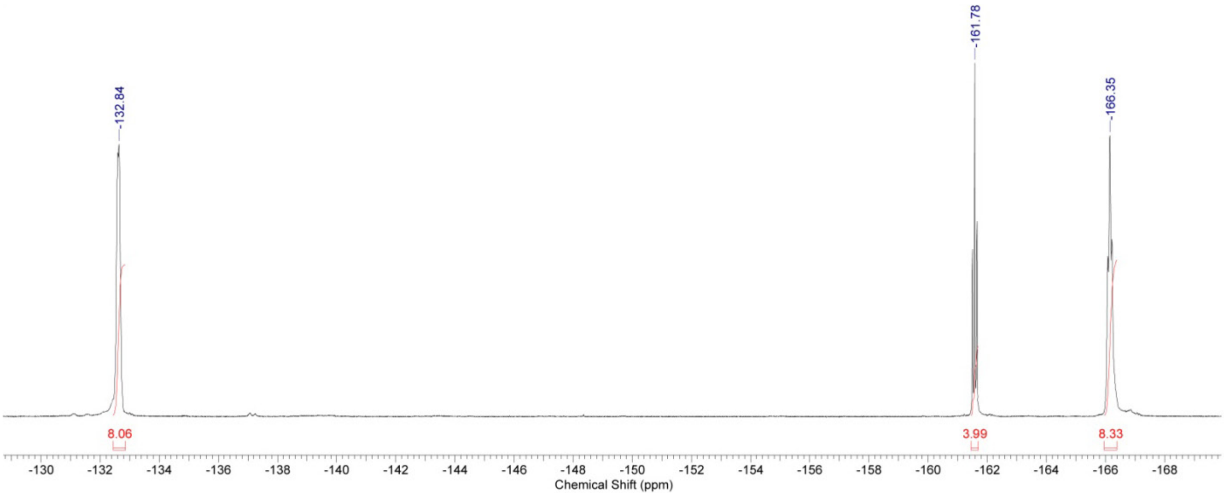

Figure S16. ^{19}F NMR spectrum of potassium tetrakis(pentafluorophenyl)borate **9**.

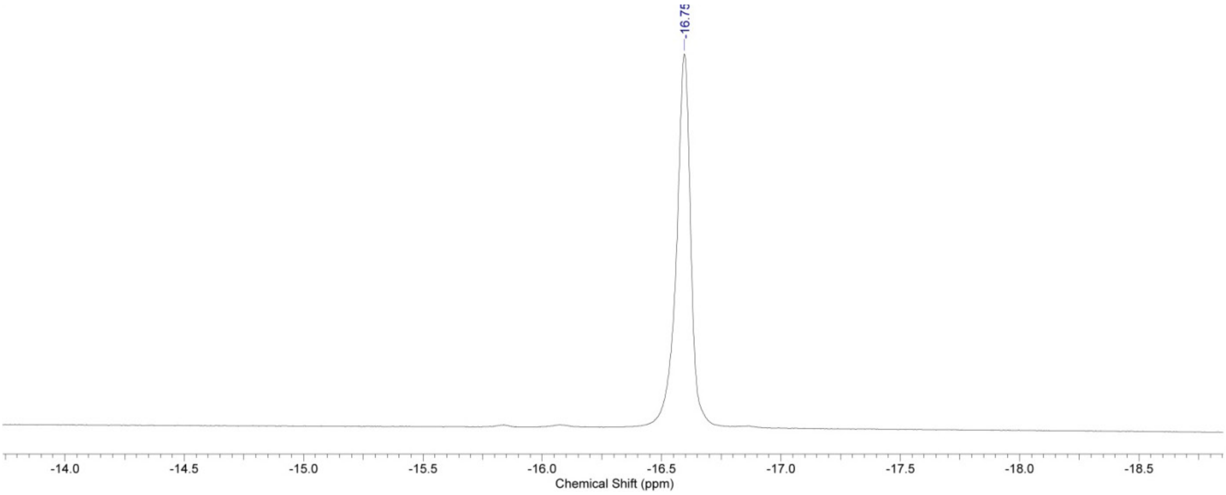

Figure S17. ^{11}B NMR spectrum of potassium tetrakis(pentafluorophenyl)borate **9**.

Potassium (heptafluoronaphthalen-2-yl)tris(pentafluorophenyl)borate **10** (466 mg, 29%). Reflux time was 18 h.

^{11}B NMR (DMSO-d$_6$) δ: -16.5 (s). ^{19}F NMR (DMSO-d$_6$) δ: -108.3 (dm, ^4J(F^1, F^8) 75.7 Hz, 1F, F^1), -124.9 (s, 1F, F^3), -145.2 (ddd, ^4J(F^8, F^1) 75.1 Hz, ^3J(F^8, F^7) 16.8 Hz, ^5J(F^8, F^5) 16.8 Hz, 1F, F^8), -148.3 (ddd, ^4J(F^5, F^4) = 52.9 Hz, ^3J(F^5, F^6) 16.2 Hz, ^3J(F^5, F^8) 16.2 Hz, 1F, F^5), -153.8 (ddd, ^4J(F^4, F^5) 52.5 Hz, ^3J(F^4, F^3) 18.6 Hz, ^5J(F^4, F^1) 18.6 Hz, 1F, F^4), -156.8 (dd, ^3J(F^6, F^5) 19.8 Hz, ^3J(F^6, F^7) 19.8 Hz, 1F, F^6), -158.0 (dd, ^3J(F^7, F^6) 19.5 Hz, ^3J(F^7, F^8) 19.5 Hz, 1F, F^7) (***2-$C_{10}F_7$***); -130.28 (m, 1F, F-*ortho*), -130.62 (m, 1F, F-*ortho*), -130.91 (m, 1F, F-*ortho*), -131.38 (m, 1F, F-*ortho*), -131.83 (m, 1F, F-*ortho*), -132.09 (m, 1F, F-*ortho*), -160.33 (t, ^3J(F-*para*, F-*meta*) 22.5 Hz, 1F, F-*para*), -160.49 (t, ^3J(F-*para*, F-*meta*) 21.3 Hz, 1F, F-*para*), -160.56 (t, ^3J(F-*para*, F-*meta*) 21.0 Hz, 1F, F-*para*), -165.0 (m, 6F, F-*meta*) (3 ***C_6F_5***).

Calc., %: C 41.82 F 51.97. $C_{28}F_{22}BK$ (804.17). Found, %: C 41.8, F 51.9.

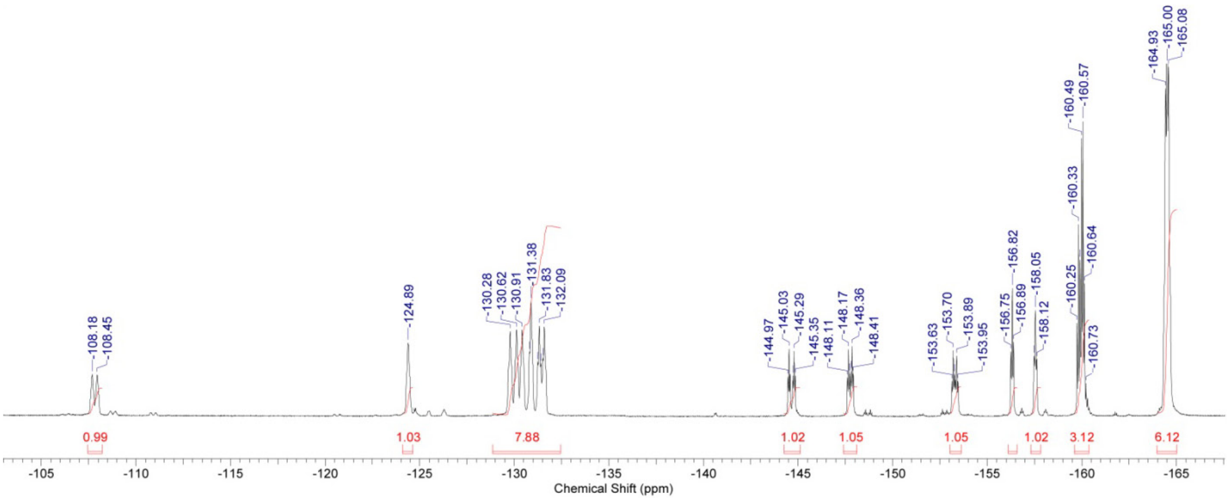

Figure S18. ^{19}F NMR spectrum of potassium (heptafluoronaphthalen-2-yl)-tris(pentafluorophenyl)borate **10**.

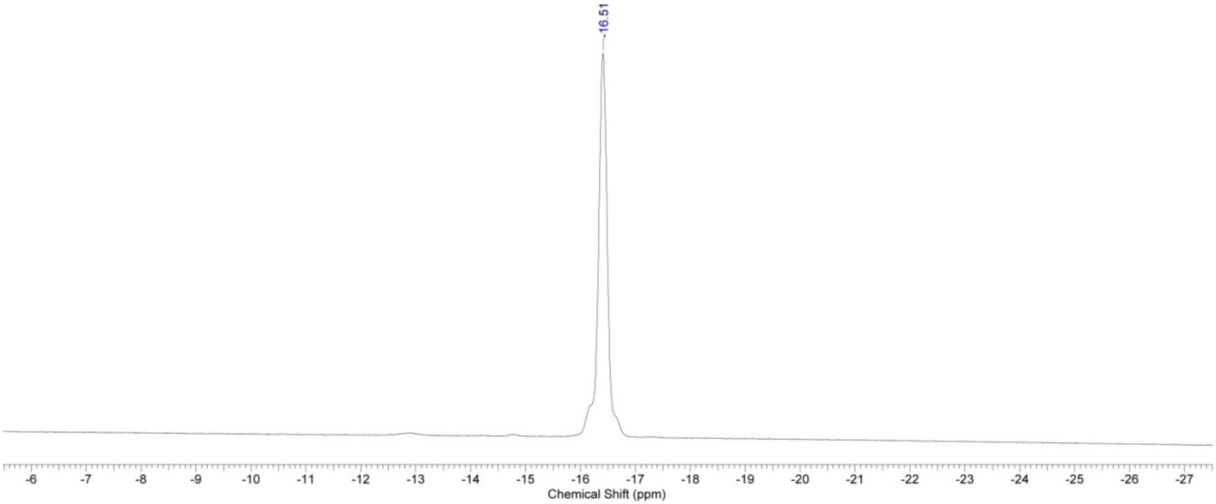

Figure S19. ^{11}B NMR spectrum of potassium (heptafluoronaphthalen-2-yl)-tris(pentafluorophenyl)borate **10**.

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