

Supporting information

Borylation of Fluorinated Arenes with the Boron-centred Nucleophile $\text{B}(\text{CN})_3^{2-}$
– a Unique and Convenient Access to Aryltricyanoborates

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1. General Synthetic Aspects

Reactions involving air-sensitive compounds were performed either in round bottom flasks or in glass tubes equipped with valves with PTFE stems (Rettberg, Göttingen and Young, London) under argon using standard Schlenk line techniques.

2. Analytical Instruments and Details, DFT Calculations

^1H , ^{11}B and ^{13}C NMR spectra were recorded at 25 °C in $(\text{CD}_3)_2\text{CO}$ on a Bruker Avance 500 or on a Bruker Avance III HD 300 spectrometer. NMR signals were referenced against TMS (^1H and ^{13}C ; $\Xi(^{13}\text{C}) = 25.145020$ MHz) and $\text{BF}_3 \cdot \text{OEt}_2$ in CDCl_3 ($\Xi(^{11}\text{B}) = 32.083974$ MHz).¹ Chemical shifts were calibrated against the residual solvent signal and the solvent signal, respectively ($\delta(^1\text{H})$: $(\text{CD}_2\text{H})(\text{CD}_3)\text{CO}$ 2.05 ppm; $\delta(^{13}\text{C})$: $(\text{CD}_3)_2\text{CO}$ 206.26 and 29.84 ppm.² The labeling of the nuclei according to Figure S1.

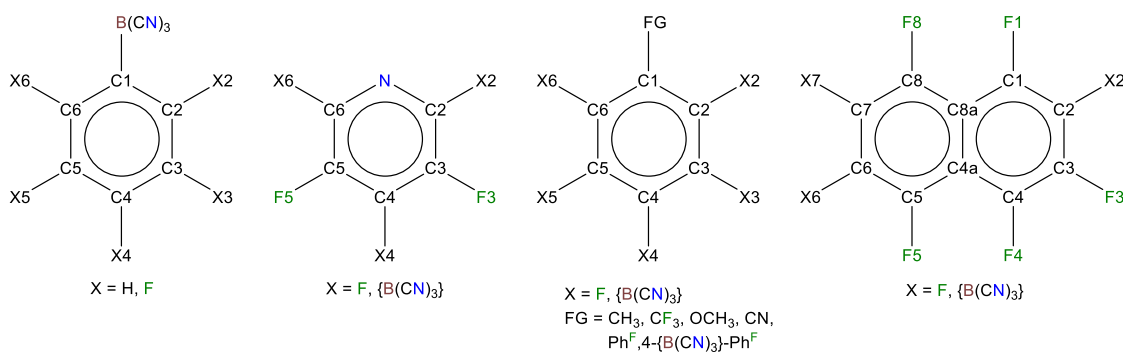


Figure S1. Labeling of the nuclei and positions of the borate anions.

The assignment of the NMR signals is aided by chemical shifts derived from DFT calculations.³ DFT-GIAO⁴ NMR shielding constants $\sigma(^{11}\text{B})$, $\sigma(^{13}\text{C})$, $\sigma(^1\text{H})$ and $\sigma(^{19}\text{F})$ were calculated at the B3LYP/6-311++G(2d,p) level of theory using the geometries computed at the B3LYP/6-311++G(d,p) level of theory. The ^{11}B , ^{13}C , ^1H and ^{19}F NMR shielding constants were calibrated to the respective chemical shift scale $\delta(^{11}\text{B})$, $\delta(^{13}\text{C})$, $\delta(^1\text{H})$ and $\delta(^{19}\text{F})$ using predictions on diborane(6), Me_4Si , and CFCl_3 with chemical shifts of 16.6 ppm for B_2H_6 ⁵ and 0 ppm for Me_4Si and CFCl_3 .⁶ All calculations were performed using the Gaussian09 program suite.⁷

Elemental analyses (C, H, N) were performed either with a Euro EA3000 instrument (HEKA-Tech, Germany) or with an Elementar Vario MICRO cube instrument (Elementar Analysensysteme, Germany).

3. Chemicals

All standard chemicals were obtained from commercial sources and used without further purification. Solvents were dried according to standard protocols⁸ and stored in flasks equipped with valves with PTFE stems (Young, London) under an argon atmosphere. $K_2B(CN)_3$ (**K₂1**) was synthesized according to known procedures.⁹

4. Syntheses

General procedures for the syntheses of the borates.

If not stated otherwise, the synthesis of the borate anions were performed according to method A (without LiCl) or method B (in the presence of LiCl). The work-up procedure described for method B was applied for the removal of $[BH(CN)_3]^-$, in general.

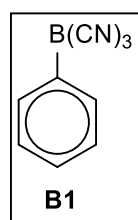
Method A: $K_2B(CN)_3$ (**K₂1**) was suspended in THF (5–8 mL). The fluoroarene was added in a single portion at room temperature either as neat compound (liquid fluoroarenes) or as a solution in THF (solid fluoroarenes) using a syringe. The end of the reaction was either evident from decolorization of **1** (yellow compound) or by ^{19}F and ^{11}B NMR spectroscopy. For the NMR spectroscopic control experiments, a small sample of the suspension was taken while stirring and dissolved in H_2O to give a clear solution. Residual solid **1** was converted into $[BH(CN)_3]^-$ and the hydridoborate anion was detected by ^{11}B NMR spectroscopy. If necessary, the reaction mixture was stirred at elevated temperatures.

All solid material that had formed (mainly KF) was separated by filtration through a plug of Celite. The Celite plug was washed with THF (3×5 – 10 mL), the solvent of the combined THF layers was removed, and the residue was dried in a vacuum (removal of excess arene). The residue was dissolved in THF (5 mL) again and the product was precipitated by slow addition of CH_2Cl_2 . Fractional precipitation allowed the separation of by- and/or side products. The off-white to colourless solids were dried in a vacuum.

Method B: In contrast to method A, LiCl (ca. 1.5 equivalents) was added to the reaction mixture. After completion of the reaction (see method A) the combined THF layers were dried in a vacuum. The residue was dissolved in slightly acidified H_2O (ca. 20 mL) and an aqueous solution of an excess of $[Me_3NH]Cl$ or $[Et_3NH]Cl$ was slowly added, which resulted in the precipitation of the respective organic salt either as a solid that was filtered off or the formation of an oily material. In the latter case the mixture was extracted with CH_2Cl_2 (3×15

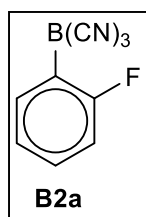
mL) and the combined organic layers were washed with H₂O (5 × 2 mL). After removal of all volatiles the oily remainder of the CH₂Cl₂ phases, H₂O (25 mL) and an excess of K₂CO₃ was added in several portions. After dissolution, the mixture was concentrated under reduced pressure until K₂CO₃ began to precipitate. The mixture was extracted with THF (3 × 20 mL), the combined organic layers were dried with K₂CO₃, filtered and concentrated to a volume of ~5 mL. CH₂Cl₂ (20 mL) was added and an off-white to colourless precipitate formed that was collected by filtration and dried in a vacuum.

K[1-{(NC)₃B}-C₆H₅] (KB1): Method B was employed for the preparation of **KB1**, using



fluorobenzene (ca. 0.5 mL, 5.4 mmol), K₂1 (200 mg, 1.20 mmol) and LiCl (150 mg, 3.54 mmol). The reaction mixture was heated to 80 °C for 2 days. Yield: 110 mg (0.536 mmol, 45%). ¹¹B NMR (160.5 MHz, (CD₃)₂CO): δ = -28.9 ppm (s, 1B). ¹H NMR (500.1 MHz, (CD₃)₂CO): δ = 7.54–7.49 (m, 2H, H2/6), 7.28–7.24 (m, 2H, H3/5), 7.21–7.16 ppm (m, 1H, H4). ¹H{¹¹B} NMR (500.1 MHz, (CD₃)₂CO): δ = 7.54–7.49 (m, 2H, H2/6), 7.28–7.24 (m, 2H, H3/5), 7.21–7.16 ppm (m, 1H, H4). ¹³C{¹H} NMR (125.8 MHz, (CD₃)₂CO): δ = 140.6 (q, 1C, ¹J(¹³C, ¹¹B) = 56 Hz, C1), 133.3 (s, 2C, C2/6), 129.7 (q, 3C, ¹J(¹³C, ¹¹B) = 64 Hz, CN), 128.3 (s, 2C, C3/5), 127.2 ppm (s, 1C, C4). Elemental analysis: calculated (%) for C₉H₅BKN₃, C 52.71, H 2.46, N 20.49; found, C 51.89, H 2.55, N 20.77. (-)-ESI-MS, m/z, [(C₆H₅)B(CN)₃]⁻: calculated 166.06 (100.0%), 165.06 (24.8%), 167.06 (9.7%); found 166.06 (100.0%), 165.06 (25.5%), 167.06 (9.7%).

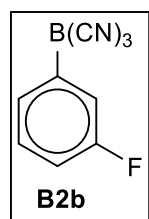
K[1-{(NC)₃B}-2-F-C₆H₄] (KB2a): Method B was employed for the preparation of **KB2a**,



using 1,2-difluorobenzene (0.5 mL, 5.1 mmol), K₂1 (350 mg, 2.10 mmol) and LiCl (150 mg, 3.54 mmol). The reaction mixture was stirred at room temperature overnight. Yield: 270 mg (1.21 mmol, 58%). ¹¹B NMR (160.5 MHz, (CD₃)₂CO): δ = -30.8 ppm (s, 1B). ¹¹B{¹H} NMR (160.5 MHz, (CD₃)₂CO): δ = -30.8 ppm (d, 1B, ³J(¹⁹F, ¹¹B) ≈ 8 Hz). ¹H NMR (500.1 MHz, (CD₃)₂CO): δ = 7.54 (s, br, 1H, H6), 7.30–7.25 (m, 1H, H4), 7.09 (dddd, 1H, J = 7.4 Hz (2×), 1.1 Hz, 0.4 Hz, H5), 6.96 ppm (ddd, br, 1H, J = 9.4 Hz, 8.2 Hz, 1.1 Hz, H3). ¹H{¹¹B} NMR (500.1 MHz, (CD₃)₂CO): δ = 7.54 (dddd, 1H, J = 7.4 Hz, 6.8 Hz, 1.9 Hz, 0.3 Hz, H6) [other signals as stated for the ¹H NMR spectrum]. ¹⁹F NMR (470.6 MHz, (CD₃)₂CO): δ = -105.1 ppm (s, 1F). ¹³C{¹H} NMR (125.8 MHz, (CD₃)₂CO): δ = 166.3 (d, 1C, ¹J(¹⁹F, ¹³C) = 243 Hz, C2), 135.4 (d, 1C, ³J(¹⁹F, ¹³C) = 8.8 Hz, C6), 130.0 (d, 1C, ³J(¹⁹F, ¹³C) = 8.3 Hz, C4), 128.5 (q, 3C, ¹J(¹³C, ¹¹B) = 65 Hz, CN),

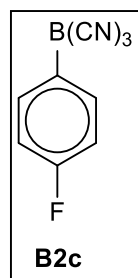
126.2 (qd, 1C, $^1J(^{13}\text{C}, ^{11}\text{B}) = 56$ Hz, $^2J(^{19}\text{F}, ^{13}\text{C}) \approx 23$ Hz, C1), 124.4 (s, 1C, C5), 115.1 ppm (d, 1C, $^2J(^{19}\text{F}, ^{13}\text{C}) \approx 24$ Hz, C3). $^{13}\text{C}\{^{19}\text{F}\}$ NMR (125.8 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 166.3$ (dddd, 1C, $J(^{13}\text{C}, ^1\text{H}) = 11$ Hz ($2\times$), 4.5 Hz, 1.7 Hz, C2), 135.4 (ddd, 1C, $^1J(^{13}\text{C}, ^1\text{H}) = 159$ Hz, $J(^{13}\text{C}, ^1\text{H}) = 8.7$ Hz, 2.1 Hz, C6), 130.7–129.3 (m, 1C, C4), 128.5 (q, 3C, $^1J(^{13}\text{C}, ^{11}\text{B}) = 65$ Hz, CN), 126.2 (q, 1C, $^1J(^{13}\text{C}, ^{11}\text{B}) = 56$ Hz, C1), 124.4 (dm, 1C, $^1J(^{13}\text{C}, ^1\text{H}) = 159$ Hz, C5), 115.1 ppm (dd, 1C, $^1J(^{13}\text{C}, ^1\text{H}) = 161$ Hz, $^2J(^{13}\text{C}, ^1\text{H}) = 8.1$ Hz, C3). Elemental analysis: calculated (%) for $\text{C}_9\text{H}_4\text{BFKN}_3$, C 48.46, H 1.81, N 18.84; found, C 48.17, H 1.62, N 18.72. (–)-ESI-MS, m/z , $[(\text{C}_6\text{FH}_4)\text{B}(\text{CN})_3]^-$: calculated 184.05 (100.0%), 183.05 (24.8%), 185.05 (9.7%); found 184.05 (100.0%), 183.05 (25.2%), 185.05 (9.6%). Crystals of **KB2a** suitable for an X-ray diffraction study were obtained from an acetone solution by slow evaporation of the solvent.

K[1- $\{(\text{NC})_3\text{B}\}$ -3-F- C_6H_4] (KB2b): Method B was employed for the preparation of **KB2b**,



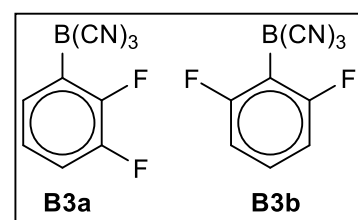
using 1,3-difluorobenzene (0.4 mL, 4.1 mmol), **K₂1** (300 mg, 1.80 mmol) and LiCl (115 mg, 2.71 mmol). The reaction mixture was stirred at room temperature for 3 days. Yield: 280 mg (1.26 mmol, 70%). ^{11}B NMR (160.5 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = -29.1$ ppm (s, 1B). ^1H NMR (500.1 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 7.36$ – 7.28 (m, 2H), 7.19 (d, br, 1H, $^2J(^{19}\text{F}, ^1\text{H}) \approx 10$ Hz), 6.97–6.92 ppm (m, 1H) [A definite assignment even with the aid of calculated chemical shifts was not possible]. ^{19}F NMR (470.6 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = -116.1$ ppm (m, 1F). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 163.4$ (d, 1C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 244$ Hz, C3), 144.1 (q, 1C, $^1J(^{13}\text{C}, ^{11}\text{B}) \approx 56$ Hz, C1), 130.2 (d, 1C, $^3J(^{19}\text{F}, ^{13}\text{C}) = 7.4$ Hz, C5), 129.1 (d, 1C, $^4J(^{19}\text{F}, ^{13}\text{C}) = 2.7$ Hz, C6), 129.1 (q, 3C, $^1J(^{13}\text{C}, ^{11}\text{B}) \approx 64$ Hz, CN), 119.3 (d, 1C, $^2J(^{19}\text{F}, ^{13}\text{C}) = 19.3$ Hz, C2), 113.9 ppm (d, 1C, $^2J(^{19}\text{F}, ^{13}\text{C}) = 21.1$ Hz, C4). $^{13}\text{C}\{^{19}\text{F}\}$ NMR (125.8 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 163.4$ (s, 1C, C3), 144.1 (q, 1C, $^1J(^{13}\text{C}, ^{11}\text{B}) \approx 56$ Hz, C1), 130.2 (d, 1C, $^1J(^{13}\text{C}, ^1\text{H}) = 161$ Hz, C5), 129.1 (ddd, 1C, $^1J(^{13}\text{C}, ^1\text{H}) = 159$ Hz, $^3J(^{13}\text{C}, ^1\text{H}) = 7.7$ Hz ($2\times$), C6), 129.1 (q, 3C, $^1J(^{13}\text{C}, ^{11}\text{B}) \approx 64$ Hz, CN), 119.3 (dm, 1C, $^1J(^{13}\text{C}, ^1\text{H}) = 159$ Hz, C2), 113.9 ppm (dm, 1C, $^1J(^{13}\text{C}, ^1\text{H}) = 162$ Hz, C4). Elemental analysis: calculated (%) for $\text{C}_9\text{H}_4\text{BFKN}_3$, C 48.46, H 1.81, N 18.84; found, C 47.90, H 1.73, N 18.51. (–)-ESI-MS, m/z , $[(\text{C}_6\text{FH}_4)\text{B}(\text{CN})_3]^-$: calculated 184.05 (100.0%), 183.05 (24.8%), 185.05 (9.7%); found 184.05 (100.0%), 183.05 (24.9%), 185.05 (9.4%). Crystals of **KB2b** suitable for an X-ray diffraction study were obtained from an *isopropanol* solution by slow evaporation of the solvent.

K[1-{(NC)₃B}-4-F-C₆H₄] (KB2c): Method B was employed for the preparation of **KB2c**,



using 1,4-difluorobenzene (0.4 mL, 3.9 mmol), **K₂1** (300 mg, 1.80 mmol) and LiCl (115 mg, 2.71 mmol). The reaction mixture was stirred at 75 °C for 30 hrs. Yield: 180 mg (0.807 mmol, 45%). The product is a mixture of **KB2c** and **KB2b** (ratio 7:3) and additionally contained 11% K[BH(CN)₃]. The NMR spectroscopic data for **KB2b** match with those given above. NMR data of **KB2c**: ¹¹B NMR (160.5 MHz, (CD₃)₂CO): δ = -29.1 ppm (s, 1B). ¹H NMR (500.1 MHz, (CD₃)₂CO): δ = 7.50 (dd, br, 2H, ³J(¹H,¹H) ≈ 8.6 Hz, ⁴J(¹⁹F,¹H) ≈ 6.1 Hz, H2/6), 7.01 ppm (ddd, 2H, ³J(¹⁹F,¹H) = 9.5 Hz, ³J(¹H,¹H) = 8.6 Hz, H3/5). ¹⁹F NMR (470.6 MHz, (CD₃)₂CO): δ = -118.6 ppm (tt, 1F, ³J(¹⁹F,¹H) = 9.4 Hz, ⁴J(¹⁹F,¹H) = 6.1 Hz). ¹³C{¹H} NMR (125.8 MHz, (CD₃)₂CO): δ = 162.9 (d, 1C, ¹J(¹⁹F,¹³C) = 243 Hz, C4), 136.5 (q, 1C, ¹J(¹³C,¹¹B) ≈ 56 Hz, C1), 135.0 (d, 2C, ³J(¹⁹F,¹³C) = 7.4 Hz, C2/6), 129.5 (q, 3C, ¹J(¹³C,¹¹B) ≈ 64 Hz, CN), 115.0 ppm (d, 2C, ²J(¹⁹F,¹³C) = 20.0 Hz, C3/5). ¹³C{¹⁹F} NMR (125.8 MHz, (CD₃)₂CO): δ = 162.9 (tt, 1C, ²J(¹³C,¹H) = 10.9 Hz, ³J(¹³C,¹H) = 4.7 Hz, C4), 136.5 (m, 1C, C1), 135.0 (dd, 2C, ¹J(¹³C,¹H) = 159 Hz, ⁿJ(¹³C,¹H) = 8.9 Hz, C2/6), 129.5 (q, 3C, ¹J(¹³C,¹¹B) ≈ 64 Hz, CN), 115.0 ppm (d, 2C, ¹J(¹³C,¹H) = 162 Hz, C3/5). (-)-ESI-MS, m/z, [(C₆FH₄)B(CN)₃]⁻: calculated 184.05 (100.0%), 183.05 (24.8%), 185.05 (9.7%); found 184.05 (100.0%), 183.05 (25.2%), 185.05 (9.4%).

K[1-{(NC)₃B}-2,3-F₂-C₆H₃] (KB3a): Method B was employed for the preparation of **KB3a**,

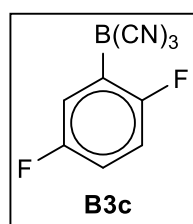


using 1,2,3-trifluorobenzene (0.4 mL, 3.9 mmol), **K₂1** (300 mg, 1.80 mmol) and LiCl (115 mg, 2.71 mmol). The reaction mixture was stirred at room temperature for 3 days. Yield: 285 mg (1.18 mmol, 66%). The product is a mixture of **KB3a** and

K[1-{(NC)₃B}-2,6-F₂-C₆H₃] (KB3b) (ratio 4:1). NMR spectroscopic data of the main product **KB3a**: ¹¹B NMR (160.5 MHz, (CD₃)₂CO): δ = -31.0 ppm (s, br, 1B). ¹¹B{¹H} NMR (160.5 MHz, (CD₃)₂CO): δ = -31.0 ppm (dd, 1B, ³J(¹⁹F,¹¹B) = 8.4 Hz, ⁴J(¹⁹F,¹¹B) = 3.5 Hz). ¹H NMR (500.1 MHz, (CD₃)₂CO): δ = 7.34–7.27 (m, br, 1H, H6), 7.20–7.06 ppm (m, 2H, H4/5). ¹⁹F NMR (470.6 MHz, (CD₃)₂CO): δ = -132.5 (m, 1F, F2), -142.3 ppm (m, 1F, F3). ¹³C{¹H} NMR (125.8 MHz, (CD₃)₂CO): δ = 153.5 (dd, 1C, ¹J(¹⁹F,¹³C) = 244 Hz, ²J(¹⁹F,¹³C) = 11.3 Hz, C2), 151.1 (dd, br, 1C, ¹J(¹⁹F,¹³C) = 246 Hz, ²J(¹⁹F,¹³C) = 14.9 Hz, C3), 130.2 (dd, 1C, ¹J(¹⁹F,¹³C) = 7.6 Hz, 3.6 Hz, C6), 129.8 (qd, 1C, overlapped, C1), 128.1 (q, 3C, ¹J(¹³C,¹¹B) ≈ 66 Hz, CN), 125.0 (s, br, 1C, C5), 116.9 ppm (d, 1C, ²J(¹⁹F,¹³C) = 17.2 Hz, C4). ¹³C{¹⁹F}

NMR (125.8 MHz, (CD₃)₂CO): δ = 153.5 (dd, 1C, $^3J(^{13}\text{C}, ^1\text{H}) = 11.9$ Hz, 7.2 Hz, C2), 151.1 (s, br, 1C, C3), 130.2 (dd, 1C, $^1J(^{13}\text{C}, ^1\text{H}) = 162$ Hz, $^2J(^{13}\text{C}, ^1\text{H}) \approx 9$ Hz, C6), 129.8 (q, 1C, overlapped, C1), 128.1 (q, 3C, $^1J(^{13}\text{C}, ^{11}\text{B}) \approx 66$ Hz, CN), 125.0 (d, 1C, $^1J(^{13}\text{C}, ^1\text{H}) = 163$ Hz, C5), 116.9 ppm (dd, 1C, $^1J(^{13}\text{C}, ^1\text{H}) = 164$ Hz, $^2J(^{13}\text{C}, ^1\text{H}) \approx 9.5$ Hz, C4). NMR spectroscopic data of the side product **KB3b**: ^{11}B NMR (160.5 MHz, (CD₃)₂CO): δ = -33.6 ppm (t, 1B $^3J(^{19}\text{F}, ^{11}\text{B}) = 7.8$ Hz). ^1H NMR (500.1 MHz, (CD₃)₂CO): δ = 7.31–7.25 (m, 1H, H4), 6.86–6.80 ppm (m, 2H, H3/5). ^{19}F NMR (470.6 MHz, (CD₃)₂CO): δ = -101.4 ppm (m, 2F, F2/6). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, (CD₃)₂CO): δ = 166.1 (dd, 2C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 246$ Hz, $^2J(^{19}\text{F}, ^{13}\text{C}) = 13.0$ Hz, C2/6), 130.5 (t, 1C, $^3J(^{19}\text{F}, ^{13}\text{C}) = 10.8$ Hz, C4), 128.2 (q, 3C, $^1J(^{13}\text{C}, ^{11}\text{B}) \approx 66$ Hz, CN), 111.6 ppm (m, 2C, C3/5) [the signal of the C1 atom was not identified]. $^{13}\text{C}\{^{19}\text{F}\}$ NMR (125.8 MHz, (CD₃)₂CO): δ = 166.1 (d, 2C, $^2J(^{13}\text{C}, ^1\text{H}) = 12.6$ Hz, C2/6), 130.5 (d, 1C, $^1J(^{13}\text{C}, ^1\text{H}) = 164$ Hz, C4), 128.2 (q, 3C, $^1J(^{13}\text{C}, ^{11}\text{B}) \approx 66$ Hz, CN), 111.6 (dd, 2C, $^1J(^{13}\text{C}, ^1\text{H}) = 164$ Hz, $^2J(^{13}\text{C}, ^1\text{H}) = 7.8$ Hz, C3/5) [the signal of the C1 atom was not identified]. Elemental analysis: calculated (%) for C₉H₃BF₂KN₃, C 44.85, H 1.25, N 17.43; found, C 44.89, H 1.22, N 17.42. (-)-ESI-MS, m/z, [(C₆F₂H₃)B(CN)₃]⁻: calculated 202.04 (100.0%), 201.04 (24.8%), 203.04 (9.7%); found 202.04 (100.0%), 201.04 (24.5%), 203.04 (9.8%). Further purification of **KB3a** was achieved by crystallization from a solution in ethyl acetate by slow evaporation of the solvent. The single crystals obtained, were suitable for an X-ray diffraction study.

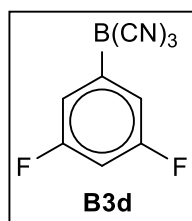
K[1-{(NC)₃B}-2,5-F₂-C₆H₃] (KB3c): Method B was employed for the preparation of **KB3c**,



using 1,2,4-trifluorobenzene (0.4 mL, 3.8 mmol), **K₂1** (300 mg, 1.80 mmol) and LiCl (115 mg, 2.71 mmol). The reaction mixture was stirred at room temperature for 2 hrs. Yield: 330 mg (1.37 mmol, 76%). ^{11}B NMR (160.5 MHz, (CD₃)₂CO): δ = -31.0 ppm (s, 1B). ^1H NMR (500.1 MHz, (CD₃)₂CO): δ = 7.20 (d, br, 1H, H6), 7.04–6.98 ppm (m, 2H, H3/4). $^1\text{H}\{^{11}\text{B}\}$ NMR (500.1 MHz, (CD₃)₂CO): δ = 7.22–7.18 (m, 1H, H6), 7.04–6.98 ppm (m, 2H, H3/4). ^{19}F NMR (470.6 MHz, (CD₃)₂CO): δ = -111.7 (s, br, 1F, F2), -122.1 (m, 1F, F5). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, (CD₃)₂CO): δ = 162.1 (dd, 1C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 239$ Hz, $^4J(^{19}\text{F}, ^{13}\text{C}) = 1.9$ Hz, C2), 159.4 (d, br, 1C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 240$ Hz, C5), 128.8 (qd, 1C, $^1J(^{13}\text{C}, ^{11}\text{B}) \approx 56$ Hz, $^2J(^{19}\text{F}, ^{13}\text{C}) \approx 25$ Hz, C1), 128.0 (q, 3C, $^1J(^{13}\text{C}, ^{11}\text{B}) = 66$ Hz, CN), 120.9 (dd, 1C, $^2J(^{19}\text{F}, ^{13}\text{C}) = 23.0$ Hz, $^3J(^{19}\text{F}, ^{13}\text{C}) = 9.5$ Hz, C6), 116.6 (dd, 1C, $^2J(^{19}\text{F}, ^{13}\text{C}) = 27.7$ Hz, $^3J(^{19}\text{F}, ^{13}\text{C}) = 8.3$ Hz, C3), 115.9 ppm (dd, 1C, $^2J(^{19}\text{F}, ^{13}\text{C}) = 24.4$ Hz, $^3J(^{19}\text{F}, ^{13}\text{C}) = 9.1$ Hz, C4). $^{13}\text{C}\{^{19}\text{F}\}$ NMR (125.8 MHz, (CD₃)₂CO): δ = 162.3–162.0 (m, 1C, C2), 159.4 (s, br, 1C, C5), 128.8 (q, 1C, $^1J(^{13}\text{C}, ^{11}\text{B}) \approx 57$ Hz, C1), 128.0

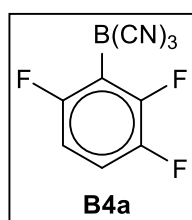
(q, 3C, $^1J(^{13}\text{C}, ^{11}\text{B}) = 66$ Hz, CN), 120.9 (d, 1C, $^1J(^{13}\text{C}, ^1\text{H}) = 162$ Hz, C6), 116.6 (d, 1C, $^1J(^{13}\text{C}, ^1\text{H}) = 165$ Hz, C3), 115.9 ppm (dd, 1C, $^1J(^{13}\text{C}, ^1\text{H}) = 166$ Hz, $^3J(^{13}\text{C}, ^1\text{H}) \approx 5$ Hz, C4). Elemental analysis: calculated (%) for $\text{C}_9\text{H}_3\text{BF}_2\text{KN}_3$, C 44.85, H 1.25, N 17.43; found, C 44.15, H 1.27, N 16.52. (-)-ESI-MS, m/z, $[(\text{C}_6\text{F}_2\text{H}_3)\text{B}(\text{CN})_3]^-$: calculated 202.04 (100.0%), 201.04 (24.8%), 203.04 (9.7%); found 202.04 (100.0%), 201.04 (25.3%), 203.04 (9.5%). Crystals of **KB3c** suitable for an X-ray diffraction study were obtained from an aqueous solution by slow evaporation of the solvent.

K[1- $\{(\text{NC})_3\text{B}\}$ -3,5- F_2 - C_6H_3] (KB3d): Method B was employed for the preparation of **KB3d**,



using 1,3,5-trifluorobenzene (0.3 mL, 2.9 mmol), **K21** (300 mg, 1.80 mmol) and LiCl (115 mg, 2.71 mmol). The reaction mixture was stirred at room temperature overnight. Yield: 275 mg (1.14 mmol, 63%). ^{11}B NMR (160.5 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = -29.3$ ppm (s, 1B). ^1H NMR (500.1 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 7.04$ (m, 2H, H2/6), 6.81 ppm (tt, 1H, $^3J(^{19}\text{F}, ^1\text{H}) = 9.3$ Hz, $^4J(^1\text{H}, ^1\text{H}) = 2.4$ Hz, H4). ^{19}F NMR (470.6 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = -112.7$ ppm (m, 2F). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 163.6$ (d, 2C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 248$ Hz, C3/5), 146.4 (q, 1C, $^1J(^{13}\text{C}, ^{11}\text{B}) = 56$ Hz, C1), 128.6 (q, 3C, $^1J(^{13}\text{C}, ^{11}\text{B}) = 65$ Hz, CN), 115.4 (m, 2C, C2/6), 102.4 (t, 1C, $^2J(^{19}\text{F}, ^{13}\text{C}) = 25.6$ Hz, C4). $^{13}\text{C}\{^{19}\text{F}\}$ NMR (125.8 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 163.6$ (s, 2C, C3/5), 146.4 (q, 1C, $^1J(^{13}\text{C}, ^{11}\text{B}) = 56$ Hz, C1), 128.6 (q, 3C, $^1J(^{13}\text{C}, ^{11}\text{B}) = 65$ Hz, CN), 115.4 (dq, 2C, $^1J(^{13}\text{C}, ^1\text{H}) = 163$ Hz, $^2J(^{13}\text{C}, ^{11}\text{B}) \approx 4$ Hz, C2/6), 102.4 (dt, 1C, $^1J(^{13}\text{C}, ^1\text{H}) = 166$ Hz, $^3J(^{13}\text{C}, ^1\text{H}) = 4.5$ Hz, C4). $^{13}\text{C}\{^{13}\text{B}, ^1\text{H}\}$ NMR (75.5 Hz, $(\text{CD}_3)_2\text{CO}$): $\delta = 163.6$ (dd, 2C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 248$ Hz, $^3J(^{19}\text{F}, ^{13}\text{C}) = 11.6$ Hz, C3/5), 146.4 (t, 1C, $^3J(^{19}\text{F}, ^{13}\text{C}) = 6.2$ Hz, C1), 128.6 (s, 3C, CN), 115.4 (m, 2C, C2/6), 102.4 (t, 1C, $^2J(^{19}\text{F}, ^{13}\text{C}) = 25.6$ Hz, C4). Elemental analysis: calculated (%) for $\text{C}_9\text{H}_3\text{BF}_2\text{KN}_3$, C 44.85, H 1.25, N 17.43; found, C 45.09, H 1.12, N 17.51. (-)-ESI-MS, m/z, $[(\text{C}_6\text{F}_2\text{H}_3)\text{B}(\text{CN})_3]^-$: calculated 202.04 (100.0%), 201.04 (24.8%), 203.04 (9.7%); found 202.04 (100.0%), 201.04 (24.6%), 203.04 (9.5%). Crystals of **KB3d** suitable for an X-ray diffraction study were obtained from an acetone solution by slow evaporation of the solvent.

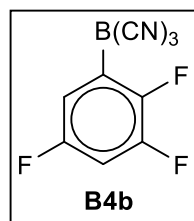
K[1- $\{(\text{NC})_3\text{B}\}$ -2,3,6- F_3 - C_6H_2] (KB4a): Method B was employed for the preparation of



KB4a, using 1,2,3,4-tetrafluorobenzene (0.3 mL, 2.8 mmol), **K21** (225 mg, 1.35 mmol) and LiCl (85 mg, 2.01 mmol). The reaction mixture was stirred at room temperature for several minutes. Yield: 270 mg (1.04 mmol, 77%). ^{11}B NMR (160.5 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = -33.7$ ppm (dd, 1B, $^3J(^{19}\text{F}, ^{11}\text{B}) \approx 8$ Hz (2 \times)). ^1H NMR (500.1 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 7.21$ (dddd, 1H, $^3J(^1\text{H}, ^1\text{H}) = 9.1$ Hz,

$^{3/4}J(^{19}\text{F}, ^1\text{H}) = 9.9 \text{ Hz}, 9.1 \text{ Hz}, 5.0 \text{ Hz}, \text{H4}), 6.85 \text{ ppm (m, 1H, H5)}$. $^1\text{H}\{^{11}\text{B}\}$ NMR (500.1 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 6.85 \text{ ppm (dddd, 1H, } ^3J(^1\text{H}, ^1\text{H}) = 9.1 \text{ Hz, } ^{3/4/5}J(^{19}\text{F}, ^1\text{H}) = 9.1 \text{ Hz}, 8.8 \text{ Hz}, 3.6 \text{ Hz}, 2.2 \text{ Hz, H5)}$ [other signal as stated for the ^1H NMR spectrum]. ^{19}F NMR (470.6 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = -106.8 \text{ (s, br, 1F, F6), -127.1 (s, br, 1F, F2), -145.6 ppm (m, 1F, F3)}$. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 160.8 \text{ (ddd, 1C, } ^1J(^{19}\text{F}, ^{13}\text{C}) = 243 \text{ Hz, } ^3J(^{19}\text{F}, ^{13}\text{C}) = 10.6 \text{ Hz, } ^4J(^{19}\text{F}, ^{13}\text{C}) = 2.3 \text{ Hz, C6), 152.6 (ddd, 1C, } ^1J(^{19}\text{F}, ^{13}\text{C}) = 247 \text{ Hz, } ^{2/3}J(^{19}\text{F}, ^{13}\text{C}) = 13.4 \text{ Hz (2}\times\text{), C2), 147.9 (dd, br, 1C, } ^1J(^{19}\text{F}, ^{13}\text{C}) = 242 \text{ Hz, } ^2J(^{19}\text{F}, ^{13}\text{C}) \approx 15 \text{ Hz, C3), 127.5 (q, 3C, } ^1J(^{13}\text{C}, ^{11}\text{B}) = 67 \text{ Hz, CN), 117.2 (ddd, 1C, } ^2J(^{19}\text{F}, ^{13}\text{C}) = 19.6 \text{ Hz, } ^3J(^{19}\text{F}, ^{13}\text{C}) = 10.8 \text{ Hz, } ^4J(^{19}\text{F}, ^{13}\text{C}) = 1.6 \text{ Hz, C4), 116.4 (m, 1C, C1), 111.5 ppm (ddd, br, 1C, } ^3J(^{19}\text{F}, ^{13}\text{C}) = 28.2 \text{ Hz, 6.3 Hz, } ^4J(^{19}\text{F}, ^{13}\text{C}) = 4.0 \text{ Hz, C5)}$. $^{13}\text{C}\{^{13}\text{B}, ^1\text{H}\}$ NMR (75.5 Hz, $(\text{CD}_3)_2\text{CO}$): $\delta = 147.9 \text{ (ddd, 1C, } ^1J(^{19}\text{F}, ^{13}\text{C}) = 242 \text{ Hz, } ^2J(^{19}\text{F}, ^{13}\text{C}) = 15.5 \text{ Hz, } ^4J(^{19}\text{F}, ^{13}\text{C}) = 3.7 \text{ Hz, C3), 127.5 (dd, 3C, } ^4J(^{19}\text{F}, ^{13}\text{C}) = 1.4 \text{ Hz (2}\times\text{), CN), 116.4 (ddd, } ^2J(^{19}\text{F}, ^{13}\text{C}) = 28.0 \text{ Hz, 21.6 Hz, } ^3J(^{19}\text{F}, ^{13}\text{C}) = 1.6 \text{ Hz, C1)}$ [other signals as stated for the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum]. Elemental analysis: calculated (%) for $\text{C}_9\text{H}_2\text{BF}_3\text{KN}_3$, C 41.73, H 0.78, N 16.22; found, C 41.80, H 0.84, N 16.08. (–)-ESI-MS, m/z , $[(\text{C}_6\text{F}_3\text{H}_2)\text{B}(\text{CN})_3]^-$: calculated 220.03 (100.0%), 219.03 (24.8%), 221.03 (9.7%); found 220.03 (100.0%), 219.03 (24.0%), 221.03 (9.5%). Crystals of **KB4a** suitable for an X-ray diffraction study were obtained from an acetone/water solution by slow evaporation of acetone.

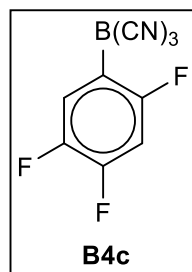
K[1-{(NC)₃B}-2,3,5-F₃-C₆H₂] (KB4b): 1. Entry: Method B was employed for the



preparation of **KB4b**, using 1,2,3,5-tetrafluorobenzene (0.4 mL, 2.8 mmol), **K₂1** (200 mg, 1.20 mmol) and LiCl (80.0 mg, 1.89 mmol). The reaction mixture was stirred at room temperature for 2 hrs. Yield: 195 mg (0.753 mmol, 63%). **2. Entry:** Method B was employed for the preparation of **KB4b**, using 1,2,3,5-tetrafluorobenzene (ca. 0.4 mL, 3.7 mmol) and **K₂1** (300 mg, 1.80 mmol) but without addition of LiCl. The reaction mixture was stirred at room temperature for 3 days and then at 75 °C for 30 hrs. Yield: 240 mg (0.926 mmol, 51%). The product contained 8% of other isomers. ^{11}B NMR (160.5 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = -31.2 \text{ ppm (s, 1B)}$. ^1H NMR (500.1 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 7.10\text{--}7.04 \text{ (m, 1H, H4), 7.05\text{--}6.99 \text{ ppm (m, br, 1H, H6)}$. ^{19}F NMR (470.6 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = -117.8 \text{ (m, 1F, F5), -136.7 (m, 1F, F3), -137.2 ppm (m, 1F, F2)}$. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 158.3 \text{ (dm, 1C, } ^1J(^{19}\text{F}, ^{13}\text{C}) = 244 \text{ Hz, C5), 150.6 (dm, 1C, } ^1J(^{19}\text{F}, ^{13}\text{C}) = 248 \text{ Hz, C3), 149.7 (ddd, 1C, } ^1J(^{19}\text{F}, ^{13}\text{C}) = 239 \text{ Hz, } ^2J(^{19}\text{F}, ^{13}\text{C}) = 10.6 \text{ Hz, } ^4J(^{19}\text{F}, ^{13}\text{C}) = 3.4 \text{ Hz, C2), 131.0 (qd, 1C, } ^1J(^{13}\text{C}, ^{11}\text{B}) = 55 \text{ Hz, } ^2J(^{19}\text{F}, ^{13}\text{C}) \approx 22 \text{ Hz, C1), 127.5 (q, 3C, } ^1J(^{13}\text{C}, ^{11}\text{B}) = 66 \text{ Hz, CN), 115.6 (ddd, 1C, } ^2J(^{19}\text{F}, ^{13}\text{C}) = 22.4 \text{ Hz, } ^3J(^{19}\text{F}, ^{13}\text{C})$

= 7.5 Hz, $^4J(^{19}\text{F}, ^{13}\text{C}) = 3.5$ Hz, C6), 105.0 ppm (ddd, 1C, $^2J(^{19}\text{F}, ^{13}\text{C}) = 28.0$ Hz, 21.4 Hz, C4). $^{13}\text{C}\{^{13}\text{B}, ^1\text{H}\}$ NMR (75.5 Hz, $(\text{CD}_3)_2\text{CO}$): $\delta = 158.3$ (ddd, $^1J(^{19}\text{F}, ^{13}\text{C}) = 244$ Hz, $^3J(^{19}\text{F}, ^{13}\text{C}) = 9.4$ Hz, $^4J(^{19}\text{F}, ^{13}\text{C}) = 2.5$ Hz, C5), 150.6 (m, 1C, C3), 149.7 (m, 1C, C2), 131.1 (dd, 1C, $^2J(^{19}\text{F}, ^{13}\text{C}) = 21.7$ Hz, $^3J(^{19}\text{F}, ^{13}\text{C}) = 6.2$ Hz, C1), 127.5 ppm (s, 3C, CN) [Signals for C4 and C6 as stated for the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum]. Elemental analysis: calculated (%) for $\text{C}_9\text{H}_2\text{BF}_3\text{KN}_3$, C 41.73, H 0.78, N 16.22; found, C 41.41, H 0.91, N 15.28. (–)-ESI-MS, m/z , $[(\text{C}_6\text{F}_3\text{H}_2)\text{B}(\text{CN})_3]^-$: calculated 220.03 (100.0%), 219.03 (24.8%), 221.03 (9.7%); found 220.03 (100.0%), 219.03 (24.9%), 221.03 (9.4%). Crystals of **KB4b** suitable for an X-ray diffraction study were obtained from an acetone/water solution by slow evaporation of acetone.

K[1-{(NC)₃B}-2,4,5-F₃-C₆H₂] (KB4c) and [Me₃NH][1-{(NC)₃B}-2,4,5-F₃-C₆H₂] ([Me₃NH]-

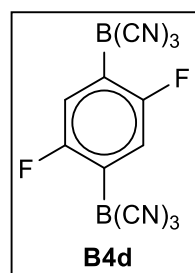


B4c): 1. Entry: Method B was employed for the preparation of **KB4c**, using 1,2,4,5-tetrafluorobenzene (0.3 mL, 2.7 mmol), **K₂1** (200 mg, 1.20 mmol) and LiCl (80.0 mg, 1.89 mmol). The reaction mixture was stirred at room temperature for 30 min. Yield: 155 mg (0.598 mmol, 50%). **2. Entry:** **[Me₃NH]B4c:** Method B (modified) was employed for the preparation of

[Me₃NH]B4c, using 1,2,4,5-tetrafluorobenzene (0.6 mL, 5.4 mmol), **K₂1** (310 mg, 1.86 mmol) and LiCl (120 mg, 2.83 mmol). The reaction mixture was stirred at room temperature for 2 hrs. The product was precipitated with slightly acidified aqueous solution of excess **[Me₃NH]Cl**, filtrated and dried in a vacuum. Yield: 260 mg (0.928 mmol, 50%). NMR spectroscopic data for **KB4c**: ^{11}B NMR (160.5 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = -31.2$ ppm (s, 1B). ^1H NMR (500.1 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 7.31$ (m, br, 1H, H6), 7.05 ppm (ddd, 1H, $^{3/4}J(^{19}\text{F}, ^1\text{H}) = 10.8$ Hz, 8.6 Hz, 6.3 Hz, H3). $^1\text{H}\{^{11}\text{B}\}$ NMR (500.1 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 7.31$ (ddd, 1H, $^{3/4}J(^{19}\text{F}, ^1\text{H}) = 11.0$ Hz, 9.6 Hz, 5.8 Hz, H6) [signal for H3 as stated for the ^1H NMR spectrum]. ^{19}F NMR (470.6 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = -106.7$ (s, br, 1F, F2), -137.8 (m, 1F, F4), -146.5 ppm (m, 1F, F5). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 160.9$ (ddd, 1C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 243$ Hz, $^3J(^{19}\text{F}, ^{13}\text{C}) = 9.4$ Hz, $^4J(^{19}\text{F}, ^{13}\text{C}) = 2.2$ Hz, C2), 150.1 (ddd, 1C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 248$ Hz, $^2J(^{19}\text{F}, ^{13}\text{C}) = 14.5$ Hz, $^3J(^{19}\text{F}, ^{13}\text{C}) = 13.1$ Hz, C4), 147.2 (dm, br, 1C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 242$ Hz, C5), 127.8 (qd, 3C, $^1J(^{13}\text{C}, ^{11}\text{B}) = 66$ Hz, $^4J(^{19}\text{F}, ^{13}\text{C}) \approx 11$ Hz, CN), 123.4 (qd, 1C, $^1J(^{13}\text{C}, ^{11}\text{B}) \approx 56$ Hz, $^2J(^{19}\text{F}, ^{13}\text{C}) = 27$ Hz, C1), 122.1 (dd, 1C, $^{2/3}J(^{19}\text{F}, ^{13}\text{C}) = 18.1$ Hz, 10.9 Hz, C6), 105.6 ppm (dd, 1C, $^{2/3}J(^{19}\text{F}, ^{13}\text{C}) = 31.2$ Hz, 20.3 Hz, C3). $^{13}\text{C}\{^{19}\text{F}\}$ NMR (125.8 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 160.9$ (dd, 1C, $^{2/3}J(^{13}\text{C}, ^1\text{H}) = 13.8$ Hz, 6.3 Hz, C2), 150.1 (dd, 1C, $^{2/3}J(^{13}\text{C}, ^1\text{H}) = 9.3$ Hz, 6.5 Hz, C4), 147.1 (s, br, 1C, C5), 127.1 (q, 3C, $^1J(^{13}\text{C}, ^{11}\text{B}) = 66$ Hz,

CN), 123.4 (q, 1C, $^1J(^{13}\text{C}, ^{11}\text{B}) \approx 56$ Hz, C1), 122.1 (d, 1C, $^1J(^{13}\text{C}, ^1\text{H}) = 164$ Hz, C6), 105.6 ppm (d, 1C, $^1J(^{13}\text{C}, ^1\text{H}) = 166$ Hz, C3). Elemental analysis: calculated (%) for $\text{C}_{12}\text{H}_{12}\text{BF}_3\text{N}_4$, C 51.46, H 4.32, N 20.01; found, C 51.59, H 4.04, N 20.54. (–)-ESI-MS, m/z , $[(\text{C}_6\text{F}_3\text{H}_2)\text{B}(\text{CN})_3]^-$: calculated 220.03 (100.0%), 219.03 (24.8%), 221.03 (9.7%); found 220.03 (100.0%), 219.03 (24.4%), 221.03 (9.4%). Crystals of $[\text{Me}_3\text{NH}]\text{B4c}$ suitable for an X-ray diffraction study were obtained from an acetone/water solution by slow evaporation of acetone.

$[\text{Et}_3\text{NH}]_2[1,4\text{-}\{(\text{NC})_3\text{B}\}_2\text{-}2,5\text{-F}_2\text{-C}_6\text{H}_2]$ ($[\text{Et}_3\text{NH}]_2\text{B4d}$): $\text{K}_2\text{B}(\text{CN})_3$ (**K21**, 300 mg, 1.80 mmol)

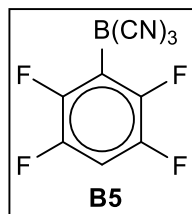


and LiCl (115 mg, 2.71 mmol) was suspended in THF (7 mL). 1,2,4,5-tetrafluorobenzene (0.100 mL, 0.896 mmol) was added with a syringe in one portion. The reaction mixture was stirred at room temperature overnight. All solid materials that had formed were separated by filtration through a plug of Celite and washed with THF (2×5 mL). The Celite plug was washed with

H_2O and upon addition of an aqueous solution with an excess of $[\text{Et}_3\text{NH}]\text{Cl}$ to the aqueous layers ($\text{pH} < 7$) the main product precipitated. $[\text{Et}_3\text{NH}]_2\text{B4d}$ was separated by filtration and dried in a vacuum. Yield: 185 mg (0.374 mmol, 42%, calculated for the fluoroarene). A second product crop was obtained from the combined THF layers: The solvent was removed first, the residue was dissolved in H_2O and the addition of an aqueous solution of $[\text{Et}_3\text{NH}]\text{Cl}$ yielded 100 mg of a mixture of $[\text{Et}_3\text{NH}]_2\text{B4d}$ and $[\text{Et}_3\text{NH}]\text{B4c}$ (ratio according to ^{19}F NMR spectroscopy: 55:45). The NMR spectroscopic data for $[\text{Et}_3\text{NH}]\text{B4c}$ match with those given above. ^{11}B NMR (160.5 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = -31.1$ ppm (s, 1B). ^1H NMR (500.1 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 7.76$ (t, br, 2H, $^1J(^{14}\text{N}, ^1\text{H}) = 49$ Hz, NH), 7.10 (dd, 2H, $^3J(^{19}\text{F}, ^1\text{H}) = ^4J(^{19}\text{F}, ^1\text{H}) = 7.2$ Hz, H3/6), 3.41 (qd, 12H, $^3J(^1\text{H}, ^1\text{H}) = 7.3$ Hz, 4.1 Hz, CH_2), 1.37 ppm (t, 18H, $^3J(^1\text{H}, ^1\text{H}) = 7.3$ Hz, CH_3). ^{19}F NMR (470.6 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = -113.4$ ppm (t, 2F, $^3J(^{19}\text{F}, ^1\text{H}) = 7.2$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 162.2$ (dd, 2C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 241$ Hz, $^4J(^{19}\text{F}, ^{13}\text{C}) = 3.5$ Hz, C2/5), 128.3 (q, 6C, $^1J(^{13}\text{C}, ^{11}\text{B}) \approx 64$ Hz, CN), 127.5 (m, br, 2C, C1/4), 120.6 (m, 2C, C3/5), 48.0 (s, 6C, CH_2), 9.2 (s, 6C, CH_3). $^{13}\text{C}\{^{19}\text{F}\}$ NMR (125.8 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 162.2$ (dd, 2C, $^{2/3}J(^{13}\text{C}, ^1\text{H}) = 11.1$ Hz, 4.4 Hz, C2/5), 128.3 (q, 6C, $^1J(^{13}\text{C}, ^{11}\text{B}) \approx 64$ Hz, CN), 127.5 (m, br, 2C, C1), 120.6 (d, 2C, $^1J(^{13}\text{C}, ^1\text{H}) = 161$ Hz, C3/5), 48.0 (t, 6C, $^1J(^{13}\text{C}, ^1\text{H}) = 145$ Hz, CH_2), 9.2 (qt, 6C, $^1J(^{13}\text{C}, ^1\text{H}) = 128$ Hz, $^2J(^{13}\text{C}, ^1\text{H}) = 3.7$ Hz, CH_3). Elemental analysis: calculated (%) for $\text{C}_{24}\text{H}_{34}\text{B}_2\text{F}_2\text{N}_8$, C 58.33, H 6.93, N 22.67; found, C 57.95, H 6.80, N 21.14. (–)-ESI-MS, m/z , $[(\text{C}_6\text{F}_2\text{H}_2)\{(\text{CN})_3\text{B}\}_2]^{2-}$: calculated 145.02 (100.0%), 144.53 (49.7%), 145.53 (13.0%); found 145.02 (100.0%), 144.53 (48.9%), 145.53

(12.1%). Crystals of $[\text{Et}_3\text{NH}]_2\text{B4d}$ suitable for an X-ray diffraction study were obtained from an acetone/water solution by slow evaporation of acetone.

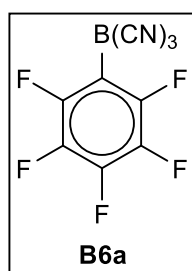
K[1-{(NC)₃B}-2,3,5,6-F₄-C₆H] (KB5): 1. Entry: Method B was employed for the preparation



of **KB5**, using pentafluorobenzene (0.3 mL, 2.7 mmol), **K₂1** (200 mg, 1.20 mmol) and LiCl (80.0 mg, 1.89 mmol). The arene was added at $-78\text{ }^\circ\text{C}$, warmed up to room temperature, and the reaction mixture was stirred for 10 minutes. Yield: 205 mg (0.740 mmol, 62%). The product contained ca. 6% of

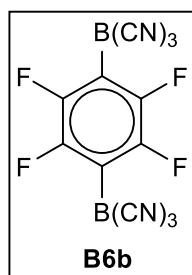
another isomer. **2. Entry:** Method B was employed for the preparation of **KB5**, using pentafluorobenzene (0.5 mL, 4.5 mmol) and **K₂1** (350 mg, 2.08 mmol) without addition of LiCl. The arene was added at $-78\text{ }^\circ\text{C}$, warmed up to room temperature, and the reaction mixture was stirred for 2 days. Yield: 225 mg (0.812 mmol, 39%). The product contained ca. 20% of other isomers and $[\text{BH}(\text{CN})_3]^-$. ^{11}B NMR (160.5 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = -33.7$ ppm (tt, 1B, $^3J(^{19}\text{F}, ^{11}\text{B}) = 7.6$ Hz, $^4J(^{19}\text{F}, ^{11}\text{B}) = 3.1$ Hz). ^1H NMR (500.1 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 7.33$ (tt, 1H, $^3J(^{19}\text{F}, ^1\text{H}) = 10.1$ Hz, $^4J(^{19}\text{F}, ^1\text{H}) = 7.5$ Hz). ^{19}F NMR (470.6 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = -132.7$ (m, 2F, F2/6), -141.8 ppm (m, 2F, F3/5). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 148.3$ (dddd, 2C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 244$ Hz, $^{3/4}J(^{19}\text{F}, ^{13}\text{C}) \approx 13$ Hz, 11 Hz, $^5J(^{19}\text{F}, ^{13}\text{C}) \approx 4$ Hz, C2/6), 146.5 (dm, 2C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 247$ Hz, C3/5), 127.0 (q, 3C, $^1J(^{13}\text{C}, ^{11}\text{B}) = 67$ Hz, CN), 118.3 (qt, 1C, $^1J(^{13}\text{C}, ^{11}\text{B}) = 56$ Hz, $^2J(^{19}\text{F}, ^{13}\text{C}) = 24$ Hz, C1), 106.1 ppm (tt, 1C, $^2J(^{19}\text{F}, ^{13}\text{C}) = 23.2$ Hz, $^3J(^{19}\text{F}, ^{13}\text{C}) = 1.4$ Hz, C4). $^{13}\text{C}\{^{19}\text{F}\}$ NMR (125.8 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 148.3$ (d, 2C, $^3J(^{13}\text{C}, ^1\text{H}) = 9.0$ Hz, C2/6), 146.5 (m, 2C, C3/5), 127.0 (q, 3C, $^1J(^{13}\text{C}, ^{11}\text{B}) = 67$ Hz, CN), 118.3 (q, 1C, $^1J(^{13}\text{C}, ^{11}\text{B}) = 56$ Hz, C1), 106.1 ppm (d, 1C, $^1J(^{13}\text{C}, ^1\text{H}) = 169$ Hz, C4). Elemental analysis: calculated (%) for $\text{C}_9\text{HBF}_4\text{KN}_3$, C 39.02, H 0.36, N 15.17; found, C 40.02, H 0.42, N 14.12. (-)-ESI-MS, m/z, $[(\text{C}_6\text{F}_4\text{H})\text{B}(\text{CN})_3]^-$: calculated 238.02 (100.0%), 237.02 (24.8%), 239.02 (9.7%); found 238.02 (100.0%), 237.02 (24.1%), 239.02 (9.3%).

K[1-{(NC)₃B}-C₆F₅] (KB6a): The preparation of **KB6a** was performed as described in the



literature and the NMR spectroscopic data are consistent to the published ones.¹⁰ (-)-ESI-MS, m/z, $[(\text{C}_6\text{F}_5)\text{B}(\text{CN})_3]^-$: calculated 256.01 (100.0%), 255.01 (24.8%), 257.01 (9.7%), found 256.01 (100.0%), 255.01 (24.7%), 257.01 (9.5%).

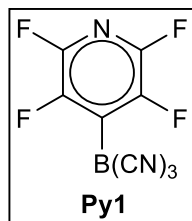
K₂[1,4-{(NC)₃B}₂-C₆F₄] (**K₂B6b**): Method A was employed for the preparation of **K₂B6b**



using hexafluorobenzene (2.30 mL, 19.9 mmol), **K₂1** (7.20 g, 43.1 mmol) and THF (50 mL). The reaction mixture was heated to reflux for 20 hrs. The Celite plug was extracted with THF (2 × 50 mL) and CH₃CN (200 mL) due to the low solubility of **K₂B6b** in THF. Yield: 5.95 g (14.7 mmol, 74%, calculated for C₆F₆). The following analytical data were obtained for

[Et₄N]₂[**B6b**] which was precipitated from an aqueous solution of **K₂B6b** with aqueous [Et₄N]OH, filtered off and dried in a vacuum. ¹¹B NMR (160.5 MHz, (CD₃)₂CO): δ = -34.7 ppm (s, 2B). ¹⁹F NMR (470.6 MHz, (CD₃)₂CO): δ = -133.8 ppm (s, 4F). ¹³C{¹H} NMR (125.8 MHz, (CD₃)₂CO): δ = 148.2 (dm, 4C, ¹J(¹⁹F, ¹³C) ≈ 250 Hz, C2/3/5/6), 127.4 (q, 6C, ¹J(¹³C, ¹¹B) = 67 Hz, CN), 116.7 ppm (m, 2C, C1/C4). ¹³C{¹³B, ¹H} NMR (75.5 Hz, (CD₃)₂CO): δ = 148.2 (dm, 4C, ¹J(¹⁹F, ¹³C) = 247 Hz, C2/3/5/6), 127.4 (s, 6C, CN), 116.6 ppm (m, 2C, C1/C4). Elemental analysis: calculated (%) for C₂₈H₄₀B₂F₄N₈, C 57.36, H 6.88, N 19.11; found, C 57.36, H 6.97, N 18.35. (-)-ESI-MS, m/z, [(C₆F₄){B(CN)₃}₂]²⁻: calculated 163.02 (100.0%), 162.52 (49.7%), 163.52 (13.0%); found 163.02 (100.0%), 162.52 (47.3%), 163.52 (11.9%). Crystals of [Et₄N]₂[**B6b**] suitable for an X-ray diffraction study were obtained from an acetone solution by slow evaporation of the solvent.

K[4-{(NC)₃B}-C₅F₄N] (**KPy1**): Method A was employed for the preparation of **KPy1** using

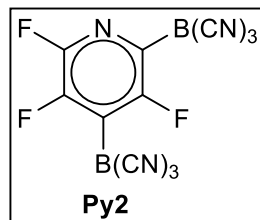


pentafluoropyridine (ca. 0.8 mL, 7.3 mmol), **K₂1** (400 mg, 2.39 mmol) and THF (15 mL). The pyridine was added at -40 °C and the reaction mixture was stirred at room temperature for 12 hrs. Yield: 575 mg (1.94 mmol, 81%; contained ca. 15% of other tricyano(fluoropyridinyl)borates). ¹¹B NMR

(160.5 MHz, (CD₃)₂CO): δ = -33.9 ppm (tt, 1B, ³J(¹⁹F, ¹¹B) = 6.2 Hz, ⁴J(¹⁹F, ¹¹B) ≈ 2.5 Hz). ¹⁹F NMR (470.6 MHz, (CD₃)₂CO): δ = -96.0 (m, 2F, F2/6), -134.7 ppm (m, 2F, F3/5). ¹³C{¹H} NMR (125.8 MHz, (CD₃)₂CO): δ = 145.2–142.8 (m, 4C, C2/3/5/6), 133.5 (m, 1C, C4), 125.8 ppm (q, 3C, ¹J(¹³C, ¹¹B) ≈ 68 Hz, CN). ¹³C{¹⁹F} NMR (125.8 MHz, (CD₃)₂CO): δ = 144.1 (s, 2C, C3/5), 144.0 (s, 2C, C2/6), 133.7 (q, 1C, ¹J(¹³C, ¹¹B) = 54 Hz, C4), 125.9 ppm (q, 3C, ¹J(¹³C, ¹¹B) = 68 Hz, CN). ¹³C{¹³B, ¹H} NMR (75.5 Hz, (CD₃)₂CO): δ = 145.6–141.7 (m, 4C, C2/3/5/6), 132.5 (tt, 1C, ²J(¹⁹F, ¹³C) = 21.7 Hz, ³J(¹⁹F, ¹³C) = 1.1 Hz, C4), 125.6 ppm (t, 3C, ⁴J(¹⁹F, ¹³C) = 1.1 Hz, CN). (-)-ESI-MS, m/z, [(NC₅F₄)B(CN)₃]⁻: calculated 239.02 (100.0%), 238.02 (24.8%), 240.02 (8.7%); found 239.02 (100.0%), 238.02 (24.4%), 240.02

(8.6%). Crystals of **KPy1** suitable for an X-ray diffraction study were obtained by slow diffusion of dichloromethane into an acetone solution.

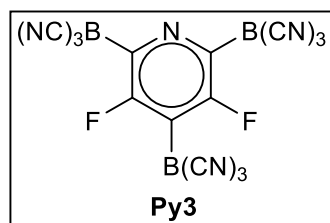
K₂[2,4-{(NC)₃B}₂-C₅F₃N] (**K₂Py2**): Method A was employed for the preparation of **K₂Py2**



using pentafluoropyridine (0.160 mL, 1.46 mmol), **K₂1** (500 mg, 2.99 mmol) and THF (15 mL). The pyridine was added at $-60\text{ }^{\circ}\text{C}$ and the reaction mixture was stirred for 4 days. Addition of CH_2Cl_2 to the combined THF layers resulted in two fractions. The first fraction was pure **K₃Py3** (85.0 mg, 0.171 mmol, 12%; for the analytical data see the

following experiment). Yield (2. fraction, only): 335 mg (0.866 mmol, 59%; calculated for $\text{C}_5\text{F}_5\text{N}$; contained 15% of **K₃Py3** and 10% of another tricyano(fluoropyridinyl)borate). ^{11}B NMR (160.5 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = -30.9$ (s, 1B, B2), -33.9 ppm (s, 1B, B4). ^{19}F NMR (470.6 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = -94.7$ (dd, 1F, $^{3/5}J(^{19}\text{F}, ^{19}\text{F}) = 30.0$ Hz, 32.3 Hz, F6), -108.3 (m, 1F, F3), -132.4 ppm (m, 1F, F5). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 161.9$ (d, 1C, $^1J(^{19}\text{F}, ^{13}\text{C}) \approx 253$ Hz, C3), 147.9 (dm, 1C, $^1J(^{19}\text{F}, ^{13}\text{C}) \approx 230$ Hz, C6), 146.3 (ddd, 1C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 259$ Hz, $^{2/3}J(^{19}\text{F}, ^{13}\text{C}) = 32.0$ Hz, 8.6 Hz, C5), 142.8 (m, br, 1C, C2), 130.4–125.7 ppm (m, 7C, C4/CN). (–)-ESI-MS, m/z , $[(\text{NC}_5\text{F}_3)\{\text{B}(\text{CN})_3\}_2]^{2-}$: calculated 154.52 (100.0%), 154.02 (49.7%), 155.02 (11.9%); found 154.52 (100.0%), 154.02 (47.9%), 155.02 (11.2%). Crystals of **K₂Py2**· $\text{OC}(\text{CH}_3)_2$ suitable for an X-ray diffraction study were obtained from an acetone solution by slow evaporation of the solvent.

K₃[2,4,6-{(NC)₃B}₃-C₅F₂N] (**K₃Py3**): Method A was employed for the preparation of **K₃Py3**

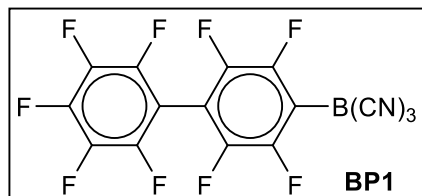


using pentafluoropyridine (0.108 mL, 0.988 mmol), **K₂1** (500 mg, 2.99 mmol) and THF (10 mL). The pyridine was added at $-78\text{ }^{\circ}\text{C}$ and the reaction mixture was stirred at room temperature for four days. Upon addition of CH_2Cl_2 to the combined THF layers two

fractions were obtained. The first fraction was pure **K₃Py3** and the second fraction was a mixture of **K₃Py3** and **K₂Py2** (4:6; 150 mg, 0.340 mmol, 34%). Yield (1. fraction, only): 150 mg (0.302 mmol, 31%, calculated for $\text{C}_5\text{F}_5\text{N}$). ^{11}B NMR (160.5 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = -30.0$ (s, br, 2B, B2/6), -33.9 ppm (s, 1B, B4). ^{19}F NMR (470.6 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = -107.5$ ppm (s, 2F). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 164.7$ (dd, 2C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 258$ Hz, $^3J(^{19}\text{F}, ^{13}\text{C}) = 5.7$ Hz, C3/5), 146.4 (m, 2C, C2/6), 128.3 (m, 9C, CN), 118.4 ppm (m, 1C, C4). (–)-ESI-MS, m/z , $[(\text{NC}_5\text{F}_2)\{\text{B}(\text{CN})_3\}_3]^{3-}$: calculated 126.35 (100.0%), 126.02 (66.9%), 125.69 (16.6%), 126.69 (13.6%); found 126.35 (100.0%), 126.02 (69.6%), 125.69 (16.7%),

126.69 (13.7%). Crystals of $K_3\text{Py}3 \cdot 3\text{THF} \cdot 1.04\text{H}_2\text{O}$ suitable for an X-ray diffraction study were obtained by slow diffusion of hexane in a THF solution.

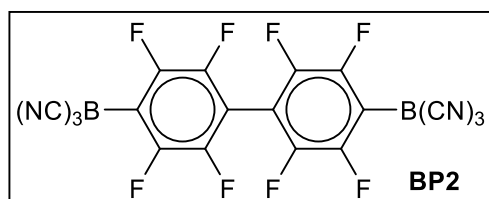
K[4- $\{(\text{NC})_3\text{B}\}_2\text{-C}_{12}\text{F}_9$] (KBP1): Method A was employed for the preparation of **KBP1** using



decafluorobiphenyl (750 mg, 2.24 mmol), $K_2\text{I}$ (300 mg, 1.80 mmol) and THF (15 mL). The reaction mixture was stirred at room temperature for 2 hrs. Upon addition of CH_2Cl_2 to the combined THF layers two fractions were

obtained. The first fraction contained impurities (mainly $K_2\text{BP}2$, see next example) and was neglected. Yield (2. fraction, only): 390 mg (0.880 mmol, 49%). ^{11}B NMR (160.5 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = -33.7$ ppm (s, 1B). ^{19}F NMR (470.6 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = -131.4$ (m, 2F, F3/5), -139.8 (m, 2F, F2'/6'), -141.6 (m, 2F, F2/6), -153.2 (tt, 1F, $^3J(^{19}\text{F}, ^{19}\text{F}) = 20.5$ Hz, $^4J(^{19}\text{F}, ^{19}\text{F}) = 3.0$ Hz, F4'), -163.3 ppm (m, 2F, F3'/5'). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 148.6$ (ddd, 2C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 245$ Hz, $^{2/3}J(^{19}\text{F}, ^{13}\text{C}) = 12$ Hz, 4 Hz, C3/5), 145.4 (dm, 2C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 250$ Hz, C2'/6'), 144.6 (dm, br, 2C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 251$ Hz, C2/6), 143.3 (tt, 1C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 254$ Hz, $^2J(^{19}\text{F}, ^{13}\text{C}) = 13.5$ Hz, $^3J(^{19}\text{F}, ^{13}\text{C}) = 5.2$ Hz, C4'), 138.9 (dm, 2C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 250$ Hz, C3'/C5'), 126.7 (q, 3C, $^1J(^{13}\text{C}, ^{11}\text{B}) = 68$ Hz, CN), 121.1 (qt, 1C, $^1J(^{13}\text{C}, ^{11}\text{B}) \approx 55$ Hz, $^2J(^{19}\text{F}, ^{13}\text{C}) \approx 25$ Hz, C4), 105.8 (t, 1C, $^2J(^{19}\text{F}, ^{13}\text{C}) = 18$ Hz, C1'), 103.6 ppm (t, 1C, $^2J(^{19}\text{F}, ^{13}\text{C}) = 19$ Hz, C1). $^{13}\text{C}\{^{19}\text{F}\}$ NMR (125.8 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 148.6$ (s, 2C, C3/5), 145.4 (s, 2C, C2'/6'), 144.6 (s, br, 2C, C2/6), 143.3 (s, 1C, C4'), 138.9 (s, 2C, C3'/C5'), 126.7 (q, 3C, $^1J(^{13}\text{C}, ^{11}\text{B}) = 68$ Hz, CN), 121.1 (q, 1C, $^1J(^{13}\text{C}, ^{11}\text{B}) = 55$ Hz, C4), 105.8 (s, 1C, C1'), 103.6 ppm (s, 1C, C1). Elemental analysis: calculated (%) for $\text{C}_{15}\text{BF}_9\text{KN}_3$, C 40.66, N 9.48; found, C 40.81, N 9.81. (-)-ESI-MS, m/z , $[(\text{C}_{12}\text{F}_9)\text{B}(\text{CN})_3]^-$: calculated 404.00 (100.0%), 403.01 (24.8%), 405.01 (16.2%); found 404.00 (100.0%), 403.01 (25.0%), 405.01 (16.3%).

K₂[4,4'- $\{(\text{NC})_3\text{B}\}_2\text{-C}_{12}\text{F}_8$] (K₂BP2): Method A was employed for the preparation of **K₂BP2**

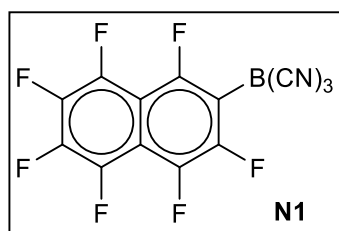


using decafluorobiphenyl (450 mg, 1.35 mmol), $K_2\text{I}$ (500 mg, 2.99 mmol) and THF (10 mL). The reaction mixture was stirred at 50 °C for 1 hr. Yield: 675 mg (1.22 mmol, 90%, calculated for $\text{C}_{10}\text{F}_{10}$).

^{11}B NMR (160.5 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = -33.7$ ppm (s, 2B). ^{19}F NMR (470.6 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = -131.7$ (s, br, 4F, F3/5), -141.7 ppm (m, 4F, F2/6). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 148.5$ (dm, 4C, $^1J(^{19}\text{F}, ^{13}\text{C}) \approx 245$ Hz, C3/5), 144.6 (dd, 4C, $^1J(^{19}\text{F}, ^{13}\text{C}) \approx 250$ Hz, $^2J(^{19}\text{F}, ^{13}\text{C})$

≈ 18 Hz, C2/6), 126.7 (q, 6C, $^1J(^{13}\text{C}, ^{11}\text{B}) = 67$ Hz, CN), 120.3 (m, 2C, C4), 107.1 ppm (m, 2C, C1). $^{13}\text{C}\{^{19}\text{F}\}$ NMR (125.8 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 148.5$ (s, 4C, C3/5), 144.5 (s, 4C, C2/6), 126.7 (q, 6C, $^1J(^{13}\text{C}, ^{11}\text{B}) \approx 66$ Hz, CN), 120.3 (q, br, 2C, $^1J(^{13}\text{C}, ^{11}\text{B}) \approx 53$ Hz, C4), 107.1 ppm (s, 2C, C1). $^{13}\text{C}\{^{13}\text{B}, ^1\text{H}\}$ NMR (75.5 Hz, $(\text{CD}_3)_2\text{CO}$): $\delta = 148.5$ (dm, 4C, $^1J(^{19}\text{F}, ^{13}\text{C}) \approx 246$ Hz, C3/5), 144.6 (dd, 4C, $^1J(^{19}\text{F}, ^{13}\text{C}) \approx 250$ Hz, $^2J(^{19}\text{F}, ^{13}\text{C}) \approx 18$ Hz, C2/6), 126.7 (t, 6C, $^4J(^{19}\text{F}, ^{13}\text{C}) = 1.3$ Hz, CN), 120.3 (t, 2C, $^2J(^{19}\text{F}, ^{13}\text{C}) = 23.8$ Hz, C4), 107.1 ppm (m, 2C, C1). Elemental analysis: calculated (%) for $\text{C}_{18}\text{B}_2\text{F}_8\text{K}_2\text{N}_6$, C 39.16, N 15.22; found, C 39.05, N 14.62. (-)-ESI-MS, m/z , $[(\text{C}_{12}\text{F}_8)\{\text{B}(\text{CN})_3\}_2]^{2-}$: calculated 237.01 (100.0%), 236.51 (49.7%), 237.51 (19.5%), 237.02 (9.7%); found 237.01 (100.0%), 236.51 (44.9%), 237.51 (17.2%). Crystals of $\text{K}_2\text{BP2}\cdot\text{THF}$ suitable for an X-ray diffraction study were obtained by slow diffusion of hexane into a THF solution.

K[2- $\{(\text{NC})_3\text{B}\}$ - C_{10}F_7] (KN1): Method A was employed for the preparation of KN1 using

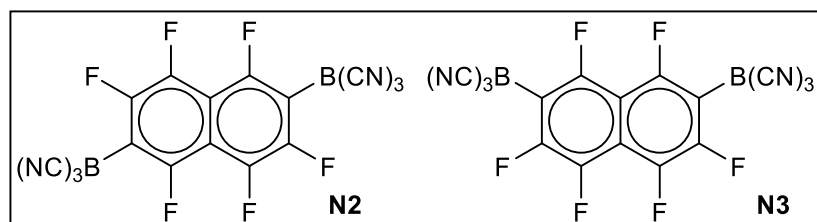


octafluoronaphthalene (650 mg, 2.39 mmol) and $\text{K}_2\mathbf{1}$ (200 mg, 1.20 mmol). The reaction mixture was stirred at room temperature for 3 days. The crude product was washed with CH_2Cl_2 (100 mL) and then dissolved in THF (10 mL) again. Addition of CH_2Cl_2 resulted in solid KN1. Yield: 250 mg (0.656

mmol, 55%). ^{11}B NMR (160.5 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = -33.6$ ppm (dd, 1B, $^2J(^{19}\text{F}, ^{11}\text{B}) \approx 8$ Hz ($2\times$)). ^{19}F NMR (470.6 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = -107.3$ (d, 1F, $^4J(^{19}\text{F}, ^{19}\text{F}) = 74$ Hz, F1), -127.3 (s, 1F, F3), -146.3 (dddm, 1F, $^4J(^{19}\text{F}, ^{19}\text{F}) = 74$ Hz, $^3J(^{19}\text{F}, ^{19}\text{F}) \approx ^5J(^{19}\text{F}, ^{19}\text{F}) \approx 17$ Hz, F8), -149.4 (dddd, 1F, $^4J(^{19}\text{F}, ^{19}\text{F}) = 56$ Hz, $^3J(^{19}\text{F}, ^{19}\text{F}) \approx ^5J(^{19}\text{F}, ^{19}\text{F}) \approx 16$ Hz, $J(^{19}\text{F}, ^{19}\text{F}) = 5$ Hz, F5), -153.3 (dddm, 1F, $^4J(^{19}\text{F}, ^{19}\text{F}) = 56$ Hz, $^3J(^{19}\text{F}, ^{19}\text{F}) \approx ^5J(^{19}\text{F}, ^{19}\text{F}) \approx 18$ Hz, F4), -157.3 (ddm, 1F, $^3J(^{19}\text{F}, ^{19}\text{F}) \approx ^3J(^{19}\text{F}, ^{19}\text{F}) \approx 18$ Hz, F6), -159.6 ppm (ddm, 1F, $^3J(^{19}\text{F}, ^{19}\text{F}) \approx ^3J(^{19}\text{F}, ^{19}\text{F}) \approx 18$ Hz, F7). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 154.4$ (d, 1C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 255$ Hz, C3), 150.5 (ddd, 1C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 248$ Hz, $J(^{19}\text{F}, ^{13}\text{C}) \approx 12$ Hz ($2\times$)), 142.2 (dm, 1C, $^1J(^{19}\text{F}, ^{13}\text{C}) \approx 255$ Hz), 141.7 (dm, 1C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 255$ Hz), 140.9 (dm, 1C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 252$ Hz), 140.2 (ddd, br, 1C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 252$ Hz, $J(^{19}\text{F}, ^{13}\text{C}) \approx 15$ Hz ($2\times$)), 139.1 (ddd, br, 1C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 250$ Hz, $J(^{19}\text{F}, ^{13}\text{C}) \approx 15$ Hz ($2\times$)), 127.0 (q, 3C, $^1J(^{13}\text{C}, ^{11}\text{B}) \approx 67$ Hz, CN), 116.8 (qd, 1C, $^1J(^{13}\text{C}, ^{11}\text{B}) \approx 56$ Hz, $^2J(^{19}\text{F}, ^{13}\text{C}) \approx 28$ Hz, C2), 112.2 (dd, 1C, $J(^{19}\text{F}, ^{13}\text{C}) \approx 12$ Hz ($2\times$), C4a), 108.9 ppm (dd, 1C, $J(^{19}\text{F}, ^{13}\text{C}) \approx 19$ Hz, 12 Hz, C8a) [A definite assignment even with the aid of calculated chemical shifts was not possible]. $^{13}\text{C}\{^{19}\text{F}\}$ NMR (125.8 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 154.4$ (s, 1C), 150.5 (s, 1C), 142.2 (s, 1C), 141.7 (s, 1C), 140.2 (s, 1C), 140.9 (s, br, 1C), 139.1 (s, 1C), 127.0 (q, 3C, $^1J(^{13}\text{C}, ^{11}\text{B}) \approx 67$ Hz, CN), 116.8 (q, 1C, $^1J(^{13}\text{C}, ^{11}\text{B}) \approx 56$ Hz, C2),

112.2 (s, 1C, C4a), 108.9 ppm (s, 1C, C8a) [A definite assignment even with the aid of calculated chemical shifts was not possible]. Elemental analysis: calculated (%) for $C_{13}BF_7KN_3$, C 40.98, N 11.03; found, C 40.81, N 11.01. (-)-ESI-MS, m/z, $[(C_{10}F_7)B(CN)_3]^-$: calculated 342.01 (100.0%), 341.01 (24.8%), 343.01 (14.1%); found 342.01 (100.0%), 341.01 (23.2%), 343.01 (13.3%).

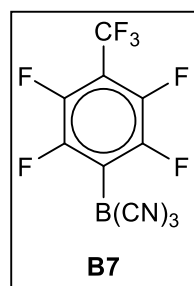
K₂[2,6- $\{(NC)_3B\}_2-C_{10}F_6]$ (K₂N2): Modified Method A was employed for the preparation of



K₂N2 using octafluoro-naphthalene (163 mg, 0.599 mmol), K₂1 (200 mg, 1.20 mmol) and THF (5 mL).

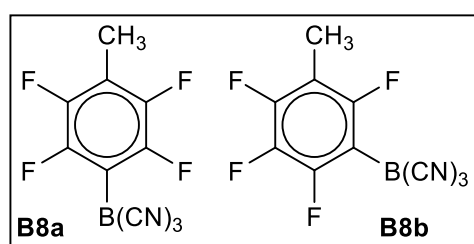
The reaction mixture was stirred at 60 °C for 16 hrs. All solids that had formed were separated by filtration through a plug of Celite and washed with cold THF (3 × 1.5 mL). Then, the plug was washed with H₂O (10 mL), and after reducing the volume and cooling to 0 °C small colourless needles had formed. These were decanted and dried in a vacuum. Yield: 70.0 mg (0.143 mmol, 24%; calculated for C₁₀F₈). The combined THF layers contained additional product which could not be separated from other isomers formed. The total ratio of the borates formed was 0.4:1.0:0.7 (KN1:K₂N2:K₂N3; N3 = [2,7- $\{(NC)_3B\}_2-C_{10}F_6]^{2-}$). NMR spectroscopic data for K₂N2: ¹¹B NMR (160.5 MHz, (CD₃)₂CO): δ = -33.6 ppm (dd, 1B, ²J(¹⁹F, ¹¹B) ≈ 8 Hz (2×)). ¹⁹F NMR (470.6 MHz, (CD₃)₂CO): δ = -108.8 (m, 2F, F1/5), -130.1 (s, 2F, F3/7), -152.1 ppm (m, 2F, F4/8). ¹³C{¹⁹F} NMR (125.8 MHz, (CD₃)₂CO): δ = 154.2 (s, 2C, C1/5), 149.7 (s, 2C, C3/7), 140.9 (s, 2C, C4/8), 127.3 (q, 6C, ¹J(¹³C, ¹¹B) = 67 Hz, CN), 116.7 (q, 2C, ¹J(¹³C, ¹¹B) = 55 Hz, C2/6), 112.9 ppm (s, 2C, C4a/8a). Elemental analysis (the salt used contained one equivalent of H₂O): calculated (%) for C₁₆H₂B₂F₆K₂N₆O, C 37.83, H 0.40, N 16.54; found, C 37.65, H 0.25, N 15.38. (-)-ESI-MS, m/z, $[(C_{10}F_6)\{B(CN)_3\}_2]^{2-}$: calculated 206.01 (100.0%), 205.52 (49.7%), 206.52 (17.3%); found 206.01 (100.0%), 205.52 (48.9%), 206.51 (16.0%). Crystals of K₂N2·2EtOAc suitable for an X-ray diffraction study were obtained from an ethyl acetate solution by slow evaporation of the solvent. NMR spectroscopic data for K₂N3: ¹¹B NMR (160.5 MHz, (CD₃)₂CO): δ = ¹¹B NMR (160.5 MHz, (CD₃)₂CO): [the signal is covered by the signal of anion N2]. ¹⁹F NMR (470.6 MHz, (CD₃)₂CO): δ = -104.6 (m, 2F, F1/8), -127.6 (m, 2F, F3/6), -154.5 ppm (m, 2F, F4/5). [In the ¹³C NMR spectra the signals of anion N3 were not observed.]

K[1-F₃C-4-{(NC)₃B}-C₆F₄] (KB7): Method A was employed for the preparation of **KB7**



using octafluorotoluene (ca. 0.3 mL, 2.1 mmol) and **K₂1** (150 mg, 0.898 mmol). The reaction mixture was stirred at room temperature for 3 hrs. Yield: 210 mg (0.609 mmol, 68%). ¹¹B NMR (160.5 MHz, (CD₃)₂CO): δ = -33.8 ppm (tt, 1B, ³J(¹⁹F, ¹¹B) = 7.3 Hz, ⁴J(¹⁹F, ¹¹B) = 2.8 Hz). ¹⁹F NMR (470.6 MHz, (CD₃)₂CO): δ = -57.2 (tt, 3F, ⁴J(¹⁹F, ¹⁹F) = 22 Hz, ⁵J(¹⁹F, ¹⁹F) = 0.6 Hz, CF₃), -130.4 (m, 2F, C3/5), -144.3 ppm (m, 2F, C2/6). ¹³C{¹H} NMR (125.8 MHz, (CD₃)₂CO): δ = 148.8 (dm, 2C, ¹J(¹⁹F, ¹³C) = 246 Hz, C3/5), 144.5 (dm, 2C, ¹J(¹⁹F, ¹³C) = 257 Hz, C2/6), 126.4 (q, 3C, ¹J(¹³C, ¹¹B) = 68 Hz, CN), 123.6 (qm, 1C, ¹J(¹³C, ¹¹B) = 55 Hz, C4), 122.1 (qm, 1C, ¹J(¹⁹F, ¹³C) = 273 Hz, CF₃), 108.8 ppm (qt, 1C, ²J(¹⁹F, ¹³C) = 34 Hz, ²J(¹⁹F, ¹³C) = 13 Hz, C1). ¹³C{¹³B, ¹H} NMR (75.5 Hz, (CD₃)₂CO): δ = 148.8 (dm, 2C, ¹J(¹⁹F, ¹³C) = 246 Hz, C3/5), 144.5 (dm, 2C ¹J(¹⁹F, ¹³C) = 257 Hz, C2/6), 126.3 (t, 3C, ⁴J(¹⁹F, ¹³C) = 1.4 Hz, CN), 123.5 (t, 1C, ²J(¹⁹F, ¹³C) ≈ 24 Hz, C4), 122.1 (qtt, 1C, ¹J(¹⁹F, ¹³C) = 273 Hz, ³J(¹⁹F, ¹³C) ≈ 3.5 Hz, ⁴J(¹⁹F, ¹³C) ≈ 1.5 Hz, CF₃), 108.8 ppm (qt, 1C, ²J(¹⁹F, ¹³C) = 34 Hz, ²J(¹⁹F, ¹³C) = 13 Hz, C1). Elemental analysis: calculated (%) for C₁₀BF₇KN₃, C 34.81, N 12.18; found, C 34.41, N 12.41. (-)-ESI-MS, m/z, [(CF₃C₆F₄){B(CN)₃}]⁻: calculated 306.01 (100.0%), 305.01 (24.8%), 307.01 (10.8%); found 306.01 (100.0%), 305.01 (23.4%), 307.01 (10.5%). Crystals of **KB7**·THF suitable for an X-ray diffraction study were obtained from a THF solution by slow evaporation of the solvent.

K[1-H₃C-4-{(NC)₃B}-C₆F₄] (KB8a): Method A was employed for the preparation of **KB8a**

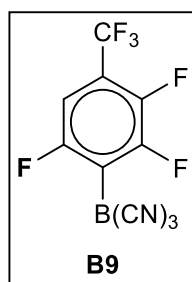


using 2,3,4,5,6-pentafluorotoluene (ca. 0.18 mL, 1.4 mmol) and **K₂1** (200 mg, 1.20 mmol). The reaction mixture was stirred at 90 °C for 3 days. Yield: not determined. The product contained ca. 10% of **K[1-H₃C-4-{(NC)₃B}-C₆F₄] (KB8b)**. NMR spectroscopic

data for **KB8a**: ¹¹B NMR (160.5 MHz, (CD₃)₂CO): δ = -33.8 ppm (tt, 1B, ³J(¹⁹F, ¹¹B) = 7.5 Hz, ⁴J(¹⁹F, ¹¹B) = 3.2 Hz). ¹⁹F NMR (470.6 MHz, (CD₃)₂CO): δ = -134.1 (m, 2F, F3/5), -146.7 ppm (dd, 2F, ^{2/3}J(¹⁹F, ¹⁹F) = 22 Hz, 14 Hz, F2/6). ¹H NMR (500.1 MHz, (CD₃)₂CO): δ = 2.23 ppm (t, 3H, ⁴J(¹⁹F, ¹H) = 2.1 Hz). ¹³C{¹H} NMR (125.8 MHz, (CD₃)₂CO): δ = 148.1 (dddd, 2C, ¹J(¹⁹F, ¹³C) = 243 Hz, ^{2/3}J(¹⁹F, ¹³C) ≈ 14 Hz, 12 Hz, ⁴J(¹⁹F, ¹³C) ≈ 4 Hz, C3/5), 145.6 (dm, br, 2C, ¹J(¹⁹F, ¹³C) = 243 Hz, C2/6), 127.3 (q, 3C, ¹J(¹³C, ¹¹B) = 67 Hz, CN), 116.0 (t, 1C, ²J(¹⁹F, ¹³C) = 19.4 Hz, C1), 115.3–113.6 (m, 1C, C4), 7.3 ppm (tt, 1C, ³J(¹⁹F, ¹³C) = 3.5 Hz,

$J(^{19}\text{F}, ^{13}\text{C}) = 2.2$ Hz, CH_3). $^{13}\text{C}\{^{19}\text{F}\}$ NMR (125.8 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 148.1$ (s, 2C, C3/5), 145.6 (s, br, 2C, C2/6), 127.3 (q, 3C, $^1J(^{13}\text{C}, ^{11}\text{B}) = 67$ Hz, CN), 116.0 (q, 1C, $^2J(^{13}\text{C}, ^1\text{H}) = 6.3$ Hz, C1), 114.4 (q, 1C, $^1J(^{13}\text{C}, ^{11}\text{B}) = 56$ Hz, C4), 7.3 ppm (q, 1C, $^1J(^{13}\text{C}, ^1\text{H}) = 131$ Hz, CH_3). $^{13}\text{C}\{^{13}\text{B}, ^1\text{H}\}$ NMR (75.5 Hz, $(\text{CD}_3)_2\text{CO}$): $\delta = 148.1$ (dddd, 2C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 243$ Hz, $^{2/3}J(^{19}\text{F}, ^{13}\text{C}) = 13.6$ Hz, 11.6 Hz, $^4J(^{19}\text{F}, ^{13}\text{C}) = 3.8$ Hz, C3/5), 145.6 (dddd, 2C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 243$ Hz, $^{2/3/4}J(^{19}\text{F}, ^{13}\text{C}) = 16.9$ Hz, 6.5 Hz, 3.5 Hz, C2/6), 127.3 (t, 3C, $^4J(^{19}\text{F}, ^{13}\text{C}) = 1.3$ Hz, CN), 116.0 (tt, 1C, $^2J(^{19}\text{F}, ^{13}\text{C}) = 19.4$ Hz, $^3J(^{19}\text{F}, ^{13}\text{C}) = 1.2$ Hz, C1), 114.4 (tt, 1C, $^2J(^{19}\text{F}, ^{13}\text{C}) = 23.9$ Hz, $^3J(^{19}\text{F}, ^{13}\text{C}) = 1.7$ Hz, C4), 7.3 ppm (tt, 1C, $^3J(^{19}\text{F}, ^{13}\text{C}) = 3.5$ Hz, $^4J(^{19}\text{F}, ^{13}\text{C}) = 2.2$ Hz, CH_3). NMR spectroscopic data for the side product **KB8b**: ^{11}B NMR (160.5 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = -33.8$ ppm (s, 1B). ^{19}F NMR (470.6 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = -109.2$ (s, 1F, F2), -130.4 (m, 1F, F4), -140.5 (d, 1F, $^{2/3}J(^{19}\text{F}, ^{19}\text{F}) = 20.6$ Hz, F6), -169.6 ppm (ddd, 1F, $^{2/3}J(^{19}\text{F}, ^{19}\text{F}) = 21.0$ Hz (2 \times), 11.9 Hz, F5). ^1H NMR (500.1 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 2.14$ ppm (dd, 3H, $^4J(^{19}\text{F}, ^1\text{H}) = 2.2$ Hz, 1.3 Hz). $^{13}\text{C}\{^{19}\text{F}\}$ NMR (125.8 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 158.0$ (m, 1C, C2), 151.1 (s, 1C, C4), 149.6 (q, 1C, $^3J(^{13}\text{C}, ^1\text{H}) = 4.3$ Hz, C6), 137.5 (s, 1C, C5), 127.5 (q, 3C, $^1J(^{13}\text{C}, ^{11}\text{B}) = 67$ Hz, CN), 110.7 (m, 1C, C1), 7.0 ppm (q, 1C, $^1J(^{13}\text{C}, ^1\text{H}) = 131$ Hz, CH_3) [the signal of C3 was not observed]. [In the $^{13}\text{C}\{^{13}\text{B}, ^1\text{H}\}$ and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra the signals of anion **B8b** were not observed.] Elemental analysis: calculated (%) for $\text{C}_{10}\text{H}_3\text{BF}_4\text{KN}_3$, C 41.27, H 1.04, N 14.44; found, C 40.88, H 1.11, N 14.10. (–)-ESI-MS, m/z , $[(\text{CH}_3\text{C}_6\text{F}_4)\{\text{B}(\text{CN})_3\}]^-$: calculated 252.04 (100.0%), 251.04 (24.8%), 253.04 (10.8%); found 252.04 (100.0%), 251.04 (23.8%), 253.04 (10.3%).

K[1-F₃C-4-{(NC)₃B}-2,3,5-F₃-C₆H] (**KB9**): Method A was employed for the preparation of

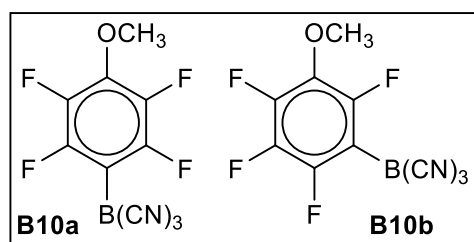


KB9 using 2,3,4,5-tetrafluorobenzotrifluoride (ca. 0.5 mL, 3.4 mmol) and **K₂1** (300 mg, 1.80 mmol). The reaction mixture was stirred at room temperature for 4 days. Yield: 460 mg (1.41 mmol, 78%). The product contained ca. 7% of other isomers. ^{11}B NMR (160.5 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = -33.8$ ppm (s, 1B). ^1H NMR (500.1 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 7.24$ ppm (m, 1H).

$^1\text{H}\{^{11}\text{B}\}$ NMR (500.1 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 7.24$ ppm (dddq, 1H, $J(^{19}\text{F}, ^1\text{H}) = 8.7$ Hz, 4.9 Hz, 2.3 Hz, 0.6 Hz). ^{19}F NMR (470.6 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = -61.9$ (dm, 3F, $^4J(^{19}\text{F}, ^1\text{H}) = 12.8$ Hz, CF_3), -103.7 (s, 1F, F5), -124.1 (s, 1F, F3), -147.5 ppm (m, 1F, F2). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 160.1$ (ddd, 1C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 246$ Hz, $^{3/4}J(^{19}\text{F}, ^{13}\text{C}) \approx 11.5$ Hz, 3.5 Hz, C5), 153.3 (ddd, 1C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 249$ Hz, $^2J(^{19}\text{F}, ^{13}\text{C}) \approx ^2J(^{19}\text{F}, ^{13}\text{C}) \approx 12$ Hz, C3), 145.4 (dm,

br, 1C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 253$ Hz, C2), 126.8 (q, 3C, $^1J(^{13}\text{C}, ^{11}\text{B}) = 68$ Hz, CN), 122.7 (qddd, 1C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 272$ Hz, $^{3/4}J(^{19}\text{F}, ^{13}\text{C}) = 4.3$ Hz, 2.7 Hz, 0.9 Hz, CF_3), 122.5 (m, 1C, C4), 119.3 (qddd, 1C, $^2J(^{19}\text{F}, ^{13}\text{C}) = 34.5$ Hz, $^{2/3}J(^{19}\text{F}, ^{13}\text{C}) = 11.1$ Hz, 10.5 Hz, 1.9 Hz, C1), 109.3 ppm (dm, 1C, $^2J(^{19}\text{F}, ^{13}\text{C}) = 31.7$ Hz, C6). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 Hz, $(\text{CD}_3)_2\text{CO}$): $\delta = 160.2$ (ddd, 1C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 246$ Hz, $^{3/4}J(^{19}\text{F}, ^{13}\text{C}) \approx 11.3$ Hz, 3.3 Hz, C5), 153.3 (ddd, 1C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 249$ Hz, $^2J(^{19}\text{F}, ^{13}\text{C}) \approx 13.3$ Hz, 12.2 Hz, C3), 145.4 (ddm, 1C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 253$ Hz, $^2J(^{19}\text{F}, ^{13}\text{C}) \approx 18$ Hz, C2), 126.8 (s, 3C, CN), 122.7 (qm, 1C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 272$ Hz, CF_3), 122.4 (ddm, 1C, $^2J(^{19}\text{F}, ^{13}\text{C}) = 27.7$ Hz, 22.0 Hz, C4), 119.3 (qddd, 1C, $^2J(^{19}\text{F}, ^{13}\text{C}) = 34.5$ Hz, $^{2/3}J(^{19}\text{F}, ^{13}\text{C}) \approx 10.8$ Hz (2 \times), 1.9 Hz, C1), 109.3 ppm (ddq, 1C, $^2J(^{19}\text{F}, ^{13}\text{C}) = 31.7$ Hz, $^3J(^{19}\text{F}, ^{13}\text{C}) \approx 4.5$ Hz (2 \times), C6). Elemental analysis: calculated (%) for $\text{C}_{10}\text{HBF}_6\text{KN}_3$, C 36.73, H 0.31, N 12.85; found, C 36.71, H 0.36, N 13.06. (-)-ESI-MS, m/z , $[(\text{CF}_3\text{C}_6\text{F}_3\text{H})\text{B}(\text{CN})_3]^-$: calculated 288.02 (100.0%), 287.02 (24.8%), 289.02 (10.8%); found 288.02 (100.0%), 287.02 (24.7%), 289.02 (10.4%).

K[1-CH₃O-4-{(NC)₃B}-C₆F₄] (KB10a) and **K[1-CH₃O-3-{(NC)₃B}-C₆F₄] (KB10b)**:

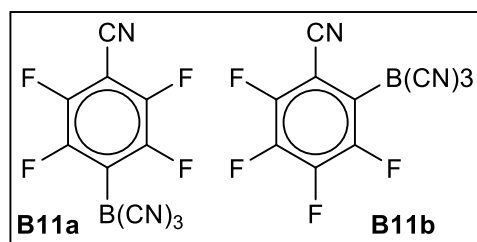


Method A was employed for the preparation of **KB10a** and **KB10b** using 2,3,4,5,6-pentafluoroaniline (ca. 0.6 mL, 4.2 mmol) and **K₂1** (300 mg, 1.80 mmol). The reaction mixture was stirred at 60 °C overnight. Yield: 450 mg (1.47 mmol, 82%). The product was a mixture

of **KB10a** and **KB10b** (ratio 1:1). NMR spectroscopic data for **KB10a**: ^{11}B NMR (160.5 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = -33.8$ ppm (s, 1B). ^{19}F NMR (470.6 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = -133.8$ (m, 2F, F3/5), -160.2 ppm (dd, 2F, $^{2/3}J(^{19}\text{F}, ^{19}\text{F}) = 21.0$ Hz, 9.9 Hz, F2/6). ^1H NMR (500.1 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 4.05$ ppm (m, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 148.7$ (dddd, 2C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 242$ Hz, $^{3/4}J(^{19}\text{F}, ^{13}\text{C}) = 14$ Hz, 11 Hz, 4 Hz, C3/5), 141.4 (dm, br, 2C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 246$ Hz, C2/6), 138.3 (tt, 1C, $^2J(^{19}\text{F}, ^{13}\text{C}) = 12.2$ Hz, $^3J(^{19}\text{F}, ^{13}\text{C}) = 8.1$ Hz, C1), 127.1 (q, 3C, $^1J(^{13}\text{C}, ^{11}\text{B}) = 67$ Hz, CN), 111.1 (m, 1C, C4), 62.7 ppm (t, 1C, $^4J(^{19}\text{F}, ^{13}\text{C}) = 3$ Hz, OCH_3). $^{13}\text{C}\{^{19}\text{F}\}$ NMR (125.8 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 148.7$ (s, 2C, C3/5), 141.4 (s, br, 2C, C2/6), 138.3 (s, 1C, C1), 127.1 (q, 3C, $^1J(^{13}\text{C}, ^{11}\text{B}) = 67$ Hz, CN), 111.1 (q, 1C, $^1J(^{13}\text{C}, ^{11}\text{B}) = 57$ Hz, C4), 62.6 ppm (q, 1C, $^1J(^{13}\text{C}, ^1\text{H}) = 146$ Hz, OCH_3). NMR spectroscopic data for **KB10b**: ^{11}B NMR (160.5 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = -33.8$ ppm (s, 1B). ^{19}F NMR (470.6 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = -124.6$ (s, 1F, F2), -133.6 (m, 1F, F4), -153.1 (dm, 1F, $^3J(^{19}\text{F}, ^{19}\text{F}) \approx 20$ Hz, F6), -167.0 ppm (ddd, 1F, $^{3/5}J(^{19}\text{F}, ^{19}\text{F}) \approx 22$ Hz, 20 Hz, 10 Hz, F5). ^1H NMR (500.1 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 3.93$ ppm (m, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 153.3$ (ddm,

1C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 244$ Hz, $^{3/4}J(^{19}\text{F}, ^{13}\text{C}) = 13.5$ Hz, C2), 148.2 (dm, 1C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 242$ Hz, C4), 145.3 (dddd, 1C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 247$ Hz, $^{2/3}J(^{19}\text{F}, ^{13}\text{C}) = 11.7$ Hz, 7.9 Hz, 5.9 Hz, C6), 137.8 (dm, br, $^1J(^{19}\text{F}, ^{13}\text{C}) \approx 247$ Hz, 1C, C5), 134.5 (m, 1C, C1), 127.2 (q, 3C, $^1J(^{13}\text{C}, ^{11}\text{B}) = 67$ Hz, CN), 109.9 (m, 1C, C3), 62.3 ppm (q, 1C, $^4J(^{19}\text{F}, ^{13}\text{C}) = 3.6$ Hz, OCH₃). $^{13}\text{C}\{^{19}\text{F}\}$ NMR (125.8 MHz, (CD₃)₂CO): $\delta = 153.3$ (s, 1C, C2), 148.2 (s, br, 1C, C4), 145.3 (s, 1C, C6), 137.8 (s, 1C, C5), 134.5 (s, 1C, C1), 127.2 (q, 3C, $^1J(^{13}\text{C}, ^{11}\text{B}) = 67$ Hz, CN), 109.9 (q, 1C, $^1J(^{13}\text{C}, ^{11}\text{B}) = 56$ Hz, C3), 62.3 ppm (q, 1C, $^1J(^{13}\text{C}, ^1\text{H}) = 147$ Hz, OCH₃). Elemental analysis: calculated (%) for C₁₀H₃BF₄KN₃O, C 39.12, H 0.98, N 13.69; found, C 38.59, H 0.89, N 15.15. (-)-ESI-MS, m/z, [(CH₃OC₆F₄)B(CN)₃]⁻: calculated 268.03 (100.0%), 267.03 (24.8%), 269.03 (10.8%); found 268.03 (100.0%), 267.03 (25.5%), 269.03 (10.9%). Crystals of **KB10a** suitable for an X-ray diffraction study were obtained from an *isopropanol* solution by slow evaporation of the solvent.

K[1-NC-4-{(NC)₃B}-C₆F₄] (KB11a): Method A was employed for the preparation of **KB11a**



using 2,3,4,5,6-pentafluorobenzonitrile (ca. 0.45 mL, 3.6 mmol) and **K21** (300 mg, 1.80 mmol). The arene was added at -100 °C and slowly warmed up to room temperature. The dark raw product was a mixture of **KB11a**, **K[1-NC-2-{(NC)₃B}-C₆F₄] (KB11b)** and

K[B(CN)₄] (ratio 2.5:1.5:1.0). Yield: ca. 350 mg. Upon slow addition of CH₂Cl₂ to the THF layers several fractions were obtained which resulted in an enrichment of the main and the side product, respectively. NMR spectroscopic data for **KB11a**: ^{11}B NMR (160.5 MHz, (CD₃)₂CO): $\delta = -33.8$ ppm (tt, 1B, $^3J(^{19}\text{F}, ^{11}\text{B}) = 7.4$ Hz, $^4J(^{19}\text{F}, ^{11}\text{B}) = 2.7$ Hz). ^{19}F NMR (470.6 MHz, (CD₃)₂CO): $\delta = -129.8$ (m, 2F, F3/5), -136.8 (m, 2F, F2/6). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, (CD₃)₂CO): $\delta = 148.2$ (dddd, 2C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 246$ Hz, $^{2/3/4}J(^{19}\text{F}, ^{13}\text{C}) \approx 11$ Hz (2×), 4 Hz, C3/5), 147.6 (dm, 2C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 259$ Hz, 2/6), 126.0 (q, 3C, $^1J(^{13}\text{C}, ^{11}\text{B}) = 68$ Hz, B-CN), 108.6 (t, 1C, $^3J(^{19}\text{F}, ^{13}\text{C}) = 3.9$ Hz, Ph-CN), 93.8 ppm (tt, 1C, $^2J(^{19}\text{F}, ^{13}\text{C}) = 17.4$ Hz, $^3J(^{19}\text{F}, ^{13}\text{C}) = 3.2$ Hz, C1) [the signal of C4 is covered by the signal of the B(CN)₃ group]. $^{13}\text{C}\{^{19}\text{F}\}$ NMR (125.8 MHz, (CD₃)₂CO): $\delta = 148.2$ (s, 2C, C3/5), 147.6 (m, 2C, C2/6), 126.0 (q, 3C, $^1J(^{13}\text{C}, ^{11}\text{B}) = 68$ Hz, B-CN), 108.7 (s, 1C, Ph-CN), 93.8 ppm (s, 1C, C1) [the signal of C4 is covered by the signal of the B(CN)₃ group]. NMR spectroscopic data for the side product **KB11b**: ^{11}B NMR (160.5 MHz, (CD₃)₂CO): $\delta = -32.4$ ppm (dm, 1B, $^3J(^{19}\text{F}, ^{11}\text{B}) \approx 7.2$ Hz). ^{19}F NMR (470.6 MHz, (CD₃)₂CO): $\delta = -127.9$ (m, 1F, F3), -133.8 (m, 1F, F6), -149.0 (m, 1F, F4), -156.8 ppm (ddd, 1F, $^3J(^{19}\text{F}, ^{19}\text{F}) = 19.8$ Hz (2×), $^4J(^{19}\text{F}, ^{19}\text{F}) = 5.6$ Hz, F5).

$^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, $(\text{CD}_3)_2\text{CO}$): δ = 151.2 (dm, 1C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 258$ Hz, C6), 149.9 (ddm, 1C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 246$ Hz, $^2J(^{19}\text{F}, ^{13}\text{C}) = 10.0$ Hz, C3), 144.4 (dm, 1C, $^1J(^{19}\text{F}, ^{13}\text{C}) \approx 262$ Hz, C4), 140.5 (ddd, 1C, $^1J(^{19}\text{F}, ^{13}\text{C}) = 253$ Hz, $^2J(^{19}\text{F}, ^{13}\text{C}) = 15.9$ Hz, 13.1 Hz, $^3J(^{19}\text{F}, ^{13}\text{C}) = 4.4$ Hz, C5), 126.4 (q, 3C, $^1J(^{13}\text{C}, ^{11}\text{B}) = 68$ Hz, B–CN), 111.6 (s, br, 1C, Ph–CN), 101.9 ppm (dd, 1C, $^2J(^{19}\text{F}, ^{13}\text{C}) \approx 11$ Hz (2 \times), C1) [the signal of C2 is covered by the signal of the $\text{B}(\text{CN})_3$ group]. $^{13}\text{C}\{^{19}\text{F}\}$ NMR (125.8 MHz, $(\text{CD}_3)_2\text{CO}$): δ = 151.2 (s, br, 1C, C6), 149.9 (s, 1C, C3), 144.4 (s, br, 1C, C4), 140.5 (s, 1C, C5), 126.4 (q, 3C, $^1J(^{13}\text{C}, ^{11}\text{B}) = 68$ Hz, B–CN), 111.6 (s, br, 1C, Ph–CN), 101.9 ppm (s, 1C, C1) [the signal of C2 is covered by the signal of the $\text{B}(\text{CN})_3$ group]. (–)-ESI-MS, m/z , $[(\text{NCC}_6\text{F}_4)\text{B}(\text{CN})_3]^-$: calculated 263.02 (100.0%), 262.02 (24.8%), 264.02 (10.8%); found 263.02 (100.0%), 262.02 (24.7%), 264.02 (10.6%). Crystals of **KB11a** suitable for an X-ray diffraction study were obtained by slow diffusion of hexane in an ethyl acetate solution.

5. Table of Experimental and Calculated Chemical Shifts

Table S1. Selected experimental and calculated^a chemical shifts^b of the tricyanoborates.

anion		B1	B2a	B2b	B2c	B3a	B3b	B3c	B3d	B4a	B4b	B4c	B5	B4d	B6a ^c	B6b
$\delta(^{11}\text{B})$	B	-28.9	-30.8	-29.1	-29.1	-31.0	-33.6	-31.0	-29.3	-33.7	-31.2	-31.2	-33.7	-31.1	-33.9	-34.7
		<i>-33.1</i>	<i>-34.9</i>	<i>-33.6</i>	<i>-33.4</i>	<i>-35.0</i>	<i>-37.6</i>	<i>-35.1</i>	<i>-33.5</i>	<i>-37.6</i>	<i>-35.1</i>	<i>-35.3</i>	<i>-37.6</i>	<i>-34.7</i>	<i>-37.8</i>	<i>-37.8</i>
$\delta(^{19}\text{F}/^1\text{H})$	X2	7.5	-105.1	^d	7.5	-132.5	-101.4	-111.7	7.0	-127.1	-137.2	-106.7	-132.7	-113.4	-132.1	-133.8
		<i>8.1</i>	<i>-119.7</i>	<i>7.8</i>	<i>8.0</i>	<i>-146.8</i>	<i>-113.7</i>	<i>-127.9</i>	<i>7.5</i>	<i>-141.5</i>	<i>-153.2</i>	<i>-122.5</i>	<i>-146.6</i>	<i>-136.3</i>	<i>-146.0</i>	<i>-157.7</i>
	X3	7.3	7.0	-116.1	7.0	-142.3	6.8	7.0	-112.7	-145.6	-136.7	7.1	-141.8	7.1	-165.4	-133.8
		<i>7.2</i>	<i>6.9</i>	<i>-141.9</i>	<i>6.9</i>	<i>-167.5</i>	<i>6.6</i>	<i>6.7</i>	<i>-139.4</i>	<i>-171.3</i>	<i>-162.8</i>	<i>6.6</i>	<i>-168.5</i>	<i>7.3</i>	<i>-192.9</i>	<i>-152.7</i>
	X4	7.2	7.3	6.9	-118.6	7.1	7.3	7.0	6.8	7.2	7.1	-137.8	7.3	-	-158.5	-
		<i>7.1</i>	<i>7.1</i>	<i>6.7</i>	<i>-147.6</i>	<i>6.8</i>	<i>7.0</i>	<i>6.7</i>	<i>6.4</i>	<i>6.7</i>	<i>6.5</i>	<i>-167.5</i>	<i>6.6</i>	<i>-</i>	<i>-188.7</i>	<i>-</i>
	X5	7.3	7.1	^d	7.0	7.1	6.8	-122.1	-112.7	6.9	-117.8	-146.5	-141.8	-113.4	-165.4	-133.8
		<i>7.2</i>	<i>7.0</i>	<i>7.2</i>	<i>6.9</i>	<i>6.9</i>	<i>6.6</i>	<i>-148.9</i>	<i>139.4</i>	<i>6.5</i>	<i>-145.1</i>	<i>-173.7</i>	<i>-168.5</i>	<i>-136.3</i>	<i>-192.9</i>	<i>-157.7</i>
	X6	7.5	7.5	^d	7.5	7.3	-101.4	7.2	7.0	-106.8	7.0	7.3	-132.7	7.1	-132.1	-133.8
		<i>8.1</i>	<i>8.1</i>	<i>7.7</i>	<i>8.0</i>	<i>7.8</i>	<i>-113.7</i>	<i>7.8</i>	<i>7.5</i>	<i>-118.2</i>	<i>7.6</i>	<i>7.8</i>	<i>-146.6</i>	<i>7.3</i>	<i>-146.0</i>	<i>-152.7</i>
$\delta(^{13}\text{C})$	CN	129.6	128.5	129.1	129.5	128.1	128.2	128.0	128.6	127.5	127.5	127.8	127.0	128.3	126.7	127.4
		<i>134.0</i>	<i>132.4</i>	<i>133.4</i>	<i>133.8</i>	<i>130.4</i>	<i>131.9</i>	<i>131.9</i>	<i>132.9</i>	<i>131.3</i>	<i>131.4</i>	<i>131.7</i>	<i>130.8</i>	<i>134.6</i>	<i>130.7</i>	<i>133.2</i>
	C1	140.6	126.2	144.1	136.5	n.d.	n.d.	128.8	146.4	116.4	131.0	123.4	118.3	127.5	111.6	116.7
		<i>155.2</i>	<i>140.4</i>	<i>158.9</i>	<i>150.1</i>	<i>144</i>	<i>128.3</i>	<i>143.3</i>	<i>161.1</i>	<i>131.0</i>	<i>145.8</i>	<i>137.0</i>	<i>133.2</i>	<i>134.1</i>	<i>125.5</i>	<i>123.6</i>
	C2	133.3	166.3	119.3	135.0	153.5	166.1	162.2	115.4	152.6	149.7	160.9	148.3	162.2	148.4	148.2
		<i>139.6</i>	<i>176.6</i>	<i>124.5</i>	<i>140.7</i>	<i>163.2</i>	<i>176.2</i>	<i>171.9</i>	<i>120.1</i>	<i>161.4</i>	<i>158.8</i>	<i>170.3</i>	<i>157.2</i>	<i>171.5</i>	<i>157.2</i>	<i>156.9</i>
	C3	128.3	115.1	163.4	115.0	151.1	111.6	116.6	163.6	147.9	150.6	105.6	146.5	120.6	137.9	148.2
		<i>130.0</i>	<i>117.1</i>	<i>172.2</i>	<i>115.9</i>	<i>159.8</i>	<i>112.9</i>	<i>117.2</i>	<i>171.7</i>	<i>156.3</i>	<i>158.6</i>	<i>106.0</i>	<i>154.1</i>	<i>124.5</i>	<i>145.1</i>	<i>156.9</i>
	C4	127.2	130.0	113.9	162.9	116.9	130.5	115.9	102.4	117.2	105.0	150.1	106.1	127.5	141.1	116.7
		<i>127.0</i>	<i>129.0</i>	<i>112.9</i>	<i>170.9</i>	<i>116.1</i>	<i>128.8</i>	<i>114.6</i>	<i>101.3</i>	<i>115.3</i>	<i>103.5</i>	<i>157.0</i>	<i>104.2</i>	<i>134.1</i>	<i>147.5</i>	<i>123.6</i>
	C5	128.3	124.4	130.2	115.0	125.0	111.6	159.4	163.6	111.5	158.3	147.2	146.5	162.2	137.9	148.2
		<i>130.0</i>	<i>125.2</i>	<i>130.4</i>	<i>115.9</i>	<i>124.6</i>	<i>112.9</i>	<i>167.8</i>	<i>171.7</i>	<i>111.2</i>	<i>166.0</i>	<i>154.6</i>	<i>154.1</i>	<i>171.5</i>	<i>145.1</i>	<i>156.9</i>
	C6	133.3	135.4	129.1	135.0	130.2	166.1	120.9	115.4	160.8	115.6	122.1	148.3	120.6	148.4	148.2
		<i>139.6</i>	<i>141.9</i>	<i>135.8</i>	<i>140.7</i>	<i>135.8</i>	<i>176.2</i>	<i>126.9</i>	<i>120.1</i>	<i>171.5</i>	<i>120.7</i>	<i>128.3</i>	<i>157.2</i>	<i>124.5</i>	<i>157.2</i>	<i>156.9</i>

^a B3LYP/6-311++G(2d,p) using geometries calculated at the B3LYP/6-311++G(2,p) level of theory; calculated values in italics; mean values where applicable. ^b Chemical shifts in ppm. ^c Literature values.¹⁰ ^d A definite assignment even with the aid of calculated chemical shifts was not possible.

Table S1 continued.

anion		B11a	B7	B8a	B10a	B11b	B11c ^e	B8b	B10b	B9	BP2	BP1	Py1	Py2	Py3	
$\delta(^{11}\text{B})$	B	-33.8	-33.8	-33.8	-33.8	-32.4		-33.8	-33.8	-33.8	-33.7	-33.7	B4	-33.9	-33.9	-33.9
		-37.6	-37.6	-37.7	-37.7	-36.5	-37.9	-37.8	-37.8	-37.7	-37.4	-37.6		-37.7	-37.4	-37.1
													B2/6	-	-30.9	-30.0
														-	-34.2	-33.3
$\delta(^{19}\text{F})^e$	X2	-136.8	-144.3	-146.7	-160.2	-		-109.2	-124.6	-147.5	-141.7	-141.6		-96.0	-	-
		-158.6	-166.7	-173.7	-186.4	-	-109.4	-118.3	-134.7	-169.1	-165.4	-167.1		-118.0	-	-
	X3	-129.8	-130.4	-134.1	-133.8	-127.9	-	-	-	-124.1	-131.7	-131.4		-134.7	-108.3	-107.5
		-143.2	-144.5	-148.2	-149.5	-143.6	-	-	-	-133.5	-150.8	-145.3		-149.3	-123.6	-125.2
	X4	-	-	-	-	-149.0		-130.4	-133.6	-	-	-		-	-	-
		-	-	-	-	-174.9	-119.4	-144.8	-148.5	-	-	-		-	-	-
	X5	-129.8	-130.4	-134.1	-133.8	-156.8		-169.6	-167.0	-103.7	-131.7	-131.4		-134.7	-132.4	-107.5
		-143.2	-144.5	-148.2	-146.0	-187.7	-192.6	-195.9	-193.3	-121.0	-150.8	-145.3		-149.3	-152.6	-125.2
	X6	-136.8	-144.3	-146.7	-160.2	-133.8		-140.5	-153.1	7.24	-141.7	-141.6		-96.0	-94.7	-
		-158.6	-166.7	-173.7	-186.4	-156.4	-155.7	-172.1	-182.6	6.9	-165.4	-167.1		-118.0	-121.2	-
$\delta(^{13}\text{C})$	CN	126.0	126.4	127.3	127.1	126.4		127.5	127.2	126.8	126.7	126.7	B4-CN	125.8	^d	128.3
		129.6	130.0	131.1	131.0	130.0	130.0	131.4	131.2	130.5	131.7	130.3		129.8	132.6	135.2
													B2/6-CN	-	^d	128.3
														-	133.1	135.7
	C1	93.8	108.8	116.0	138.3	101.9		110.7	134.5	119.3	107.1	103.6		-	-	-
		93.4	110.7	115.2	141.3	108.8	91.1	111.9	138.3	121.4	112.5	106.0		-	-	-
	C2	147.6	144.5	145.6	141.4	n.d.		158.0	153.3	145.4	144.6	144.6		144.0	142.8	146.4
		156.2	152.0	153.0	150.1	144.1	170.1	168.5	164.5	153.5	152.7	151.8		150.9	153.6	154.2
	C3	148.2	148.8	148.1	148.7	149.9		n.d.	109.3	153.3	148.5	148.6		144.0	161.9	164.7
		157.0	157.4	157.2	157.5	157.0	127.1	123.9	124.1	163.6	157.2	157.5		152.6	170.7	173.6
	C4	n.d.	123.6	114.4	111.1	144.4		151.1	148.2	122.5	120.3	121.1		133.5	^d	118.4
		141.6	138.3	129.3	126.2	151.3	167.3	159.9	157.0	137.1	129.9	136.7		147.3	134.8	123.2
	C5	148.2	148.8	148.1	148.7	140.5		137.5	137.8	160.1	148.5	148.6		144.0	146.3	164.7
		157.0	157.4	157.2	157.5	146.2	144.9	145.3	145.5	168.0	157.2	157.5		152.6	154.8	173.6
	C6	147.6	144.5	145.6	141.4	151.2		149.6	145.3	109.3	144.6	144.6		144.0	147.9	146.4
		156.2	152.0	153.0	150.1	159.3	159.9	155.7	151.8	110.5	152.7	151.8		150.9	153.9	154.2
	C _{Gr}	108.6	122.1	7.3	62.6	111.6		7.0	62.3	122.7	-	^f		-	-	-
		114.2	135.2	7.8	62.1	115.4	114.2	7.4	61.7	135.8	-	^f		-	-	-

^e B11c = [1-H₃C-3-((NC)₂B)-C₆F₄]⁻. ^f Data of the second Ph-ring: C1': 105.8 (114.4), C2'/6': 145.4 (154.1), C3'/C5': 138.9 (146.0), C4': 143.3 (149.5); F2'/6': -139.8 (-155.4), F3'/5': -163.3 (-188.7), F4': -153.2 (-180.6).

Table S1 continued.

anion		N1	N2	N3	
$\delta(^{11}\text{B})$	B	-33.6	-33.6	-33.6	
		-37.5	-37.2	-37.2	
$\delta(^{19}\text{F})$	F1	-107.3	-108.8	-104.6	
		-120.9	-127.6	-118.4	
	F3	-127.3	-130.1	-127.6	
		-131.7	-147.0	-143.1	
	F4	-153.3	-152.1	-154.5	
		-177.3	-175.9	-182.8	
	F5	-149.4	-108.8	-154.5	
		-171.5	-127.6	-182.8	
	F6	-157.3	-	-127.6	
		-186.5	-	-143.1	
	F7	-159.6	-130.1	-	
		-189.1	-147.0	-	
	F8	-146.3	-152.1	-104.6	
		-163.0	-175.9	-118.4	
	$\delta(^{13}\text{C})$	CN	127.0	127.3	n.d.
			130.4	132.6	132.6
C1		^d	154.2	n.d.	
		162.3	161.9	163.6	
C2		116.8	116.7	n.d.	
		132.4	125.1	122.9	
C3		^d	149.7	n.d.	
		162.5	159.4	160.6	
C4		^d	140.9	n.d.	
		148.4	149.5	148.4	
C4a		112.2	112.9	n.d.	
		115.4	117.1	119.6	
C5		^d	154.2	n.d.	
		149.4	161.9	148.4	
C6		^d	116.7	n.d.	
		146.5	125.1	160.6	
C7		^d	149.7	n.d.	
		145.1	159.4	122.9	
C8		^d	140.9	n.d.	
		151.3	149.5	163.6	
C8a		108.9	112.9	n.d.	
		112.9	117.1	115.0	

6. Crystal Structure Determination

All crystal data were collected on a Bruker X8-Apex II diffractometer with a CCD area detector and multi-layer mirror or graphite monochromated $\text{Mo}_{K\alpha}$ radiation. The structures were solved by intrinsic phasing methods (SHELXT).¹¹⁻¹² Refinement is based on full-matrix least-squares calculations on F^2 (SHELXL).¹²⁻¹³ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to the phenyl rings of the anions were refined without any restraints. For all remaining CH moieties idealized bond lengths and angles were used and their isotropic displacement parameters were fixed to the equivalent isotropic displacement parameters of the respective parent carbon atom. The crystal of $\text{K}_2\text{N}_2 \cdot 2\text{EtOAc}$ was a pseudo-merohedral twin with domains rotated by 179.9° around the real axis $[-0.001 \ 0.000 \ 1.000]$. The BASF parameter was refined to 50%. Calculations were carried out using the ShelXle graphical interface.¹⁴ Molecular structure diagrams were drawn with the program Diamond 4.3.2.¹⁵

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre. Experimental details, crystal data, and CCDC numbers are collected in Table S2. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S2. Crystal data and structure refinement details of the tricyanoborates.

compound	KB2a	KB2b	KB3a	KB3c	KB3d	[Et₃NH]₂B4d	KB4b	KB4a	[Me₃NH]B4c	[Et₄N]₂B6b
empirical formula	C ₁₈ H ₈ B ₂ F ₂ K ₂ N ₆	C ₉ H ₄ BFKN ₃	C ₉ H ₃ BF ₂ KN ₃	C ₉ H ₃ BF ₂ KN ₃	C ₉ H ₃ BF ₂ KN ₃	C ₂₄ H ₃₄ B ₂ F ₂ N ₈	C ₉ H ₂ BF ₃ KN ₃	C ₉ H ₂ BF ₃ KN ₃	C ₁₂ H ₁₃ BF ₃ N ₄	C ₂₈ H ₄₀ B ₂ F ₄ N ₈
<i>M</i> _w [g mol ⁻¹]	446.12	223.06	241.05	241.05	241.05	494.21	259.05	259.05	281.07	586.30
colour	colourless	colourless	colourless	colourless	colourless	colourless	colourless	colourless	colourless	colourless
<i>T</i> [K]	100	100	100	100	100	100	100	100	100	100
crystal system	triclinic	monoclinic	triclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	orthorhombic	triclinic
space group	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>Ima</i> 2	<i>P</i> -1
<i>a</i> [Å]	9.0844(6)	11.3175(10)	7.2218(4)	7.3664(11)	11.1415(11)	7.2310(18)	7.1368(4)	7.4212(4)	7.7462(5)	9.2925(5)
<i>b</i> [Å]	9.8593(6)	12.5441(11)	7.3375(4)	21.174(3)	12.3048(12)	10.113(3)	21.0081(11)	21.5366(12)	16.7938(10)	13.9870(7)
<i>c</i> [Å]	12.0751(8)	7.3312(6)	11.5902(7)	7.3900(11)	7.4382(7)	10.502(3)	6.8083(3)	7.4276(4)	10.8073(7)	19.7322(10)
α [°]	91.429(2)		100.165(2)			98.148(9)				103.804(2)
β [°]	109.254(2)	100.954(4)	95.640(2)	117.188(4)	99.762(3)	105.678(9)	90.830(2)	118.496(2)		92.966(2)
γ [°]	90.945(2)		116.645(2)			106.755(8)				107.242(2)
<i>V</i> [Å ³]	1020.35(11)	1021.83(15)	529.22(5)	1025.3(3)	1004.97(17)	687.6(3)	1020.67(9)	1043.31(10)	1405.90(15)	2357.8(2)
<i>Z</i>	2	4	2	4	4	1	4	4	4	3
ρ_{calcd} [Mg m ⁻³]	1.452	1.450	1.513	1.562	1.593	1.194	1.686	1.649	1.328	1.239
μ [mm ⁻¹]	0.499	0.498	0.500	0.516	0.527	0.083	0.539	0.527	0.110	0.092
<i>F</i> (000) [e]	448	448	240	480	480	262	512	512	580	930
θ range [°]	2.376–26.372	1.833–26.791	1.822–26.798	1.924–26.802	1.855–26.811	2.166–26.973	1.939–26.815	1.891–26.798	2.241–26.756	1.072–26.886
reflections collected	13952	13906	7270	8062	9084	9798	13961	14316	4838	31095
independent reflections [<i>I</i> > 2 σ (<i>I</i>)]	3639	1792	2100	1765	1779	1980	1886	2035	1477	6261
<i>R</i> (int)	0.0311	0.0495	0.0195	0.0373	0.0481	0.0646	0.0367	0.0324	0.0250	0.0509
data / restraints / parameters	4180 / 0 / 303	2185 / 0 / 152	2258 / 0 / 145	2198 / 0 / 157	2139 / 0 / 157	2926 / 0 / 231	2183 / 0 / 162	2236 / 0 / 162	1597 / 1 / 140	10150 / 131 / 771
<i>R</i> 1 [<i>I</i> > 2 σ (<i>I</i>)]	0.0272	0.0369	0.0389	0.0336	0.0317	0.0458	0.0284	0.0272	0.0287	0.0624
<i>wR</i> 2 (all data)	0.0677	0.0876	0.1059	0.0784	0.0835	0.1260	0.0647	0.0657	0.0686	0.1745
GOF on <i>F</i> ²	1.037	1.063	1.078	1.053	1.055	0.984	1.051	1.087	1.030	1.030
largest diff. peak / hole [e Å ⁻³]	0.327 / -0.252	0.329 / -0.324	1.575 / -0.429	0.315 / -0.238	0.374 / -0.355	0.325 / -0.328	0.399 / -0.202	0.382 / -0.219	0.179 / -0.136	0.746 / -0.312
CCDC number	1548900	1548901	1548902	1548903	1548904	1548893	1548906	1548905	1548895	1548894

Table S2 continued.

compound	K ₂ BP2·THF	KPy1	K ₂ Py2·OC(CH ₃) ₂	K ₃ Py3·3THF·1.04H ₂ O	KB7·THF	KB10a	KB11a	K ₂ N2·2EtOAc
empirical formula	C ₂₆ H ₁₆ B ₂ F ₈ K ₂ N ₆ O ₂	C ₁₆ B ₂ F ₈ K ₂ N ₈	C ₁₄ H ₆ B ₂ F ₃ K ₂ N ₇ O	C ₅₂ H _{52.17} B ₆ F ₄ K ₆ N ₂₀ O _{8.01}	C ₅₆ H ₃₂ B ₄ F ₂₈ K ₄ N ₁₂ O ₄	C ₁₀ H ₃ BF ₄ KN ₃ O	C ₂₀ B ₂ F ₈ K ₂ N ₈	C ₁₂ H ₈ BF ₃ KN ₃ O ₂
<i>M</i> _w [g mol ⁻¹]	696.27	556.06	445.08	1460.91	1668.57	307.06	604.10	333.12
colour	colourless	colourless	colourless	colourless	colourless	colourless	colourless	colourless
<i>T</i> [K]	100	100	100	100	100	100	100	100
crystal system	monoclinic	orthorhombic	tetragonal	monoclinic	monoclinic	orthorhombic	triclinic	monoclinic
space group	<i>C2</i>	<i>Pbca</i>	<i>I4₁/a</i>	<i>C2/c</i>	<i>P2₁/c</i>	<i>Pnma</i>	<i>P-1</i>	<i>P2₁/c</i>
<i>a</i> [Å]	28.487(4)	10.0487(6)	25.5118(15)	41.3012(11)	12.5972(7)	10.9629(9)	9.8453(7)	12.9371(9)
<i>b</i> [Å]	12.3676(16)	18.9832(12)	25.5118(15)	8.4531(2)	32.4417(17)	8.0873(7)	10.0627(7)	7.5514(5)
<i>c</i> [Å]	8.8225(11)	22.2949(13)	12.1914(8)	46.0735(11)	16.9137(9)	14.1771(10)	13.4136(10)	14.3323(10)
<i>α</i> [°]							87.223(3)	
<i>β</i> [°]	94.050(5)			113.7870(10)	92.820(3)		87.467(3)	93.205(3)
<i>γ</i> [°]							66.895(2)	
<i>V</i> [Å ³]	3100.6(7)	4252.9(4)	7934.8(11)	14718.9(6)	6903.8(6)	1256.95(17)	1220.40(15)	1397.98(17)
<i>Z</i>	4	8	16	8	4	4	2	4
<i>ρ</i> _{calcd} [Mg m ⁻³]	1.492	1.737	1.490	1.319	1.605	1.623	1.644	1.583
<i>μ</i> [mm ⁻¹]	0.389	0.539	0.525	0.425	0.388	0.468	0.477	0.423
<i>F</i> (000) [e]	1400	2176	3552	5986	3328	608	592	672
<i>θ</i> range [°]	1.433–26.785	1.827–26.727	1.596–26.030	1.120–26.373	1.255–26.372	2.348–26.791	2.202–26.372	2.847–26.372
reflections collected	21628	28164	31833	44601	89364	10502	16011	17851
independent reflections [<i>I</i> > 2σ(<i>I</i>)]	5996	3993	3088	11477	7469	1158	3659	2516
<i>R</i> (int)	0.0318	0.0258	0.0442	0.0285	0.1395	0.0522	0.0465	0.0751
data / restraints / parameters	6608 / 1 / 415	4508 / 0 / 325	3902 / 12 / 322	15069 / 33 / 944	14119 / 218 / 1047	1439 / 0 / 104	5004 / 0 / 361	2857 / 0 / 202
<i>R</i> 1 [<i>I</i> > 2σ(<i>I</i>)]	0.0301	0.0575	0.0734	0.0457	0.0552	0.0362	0.0400	0.0500
<i>wR</i> 2 (all data)	0.0611	0.1509	0.1519	0.1377	0.1311	0.0984	0.0802	0.1260
GOF on <i>F</i> ²	1.038	1.134	1.272	1.052	1.009	1.072	1.009	1.087
largest diff. peak / hole [e Å ⁻³]	0.272 / -0.172	1.293 / -0.546	1.210 / -0.857	1.075 / -0.505	0.544 / -0.435	0.495 / -0.270	0.355 / -0.278	0.920 / -0.478
CCDC number	1548896	1548910	1548898	1548899	1548907	1548908	1548909	1548897

7. Experimental and Calculated Bond Lengths

Table S3. Experimental and calculated^a bond lengths^b of the tricyanoborate anions.

anion	B2a	B2b	B3a	B3c	B3d	B4a	B4b	B4c	B4d	B6a ¹⁰	B6b ^c
<i>d</i> (B–CN)	1.605(3)	1.601(3)	1.598(3)	1.598(3)	1.600(3)	1.600(2)	1.602(2)	1.601(3)	1.601(3)	1.607(2)	1.588(5)
	1.597(2)	1.604(3)	1.606(3)	1.615(3)	1.601(2)	1.604(2)	1.605(2)	1.601(3)	1.600(2)	1.605(2)	1.578(4)
	1.605(2)	1.607(3)	1.605(3)	1.600(3)	1.608(3)	1.606(2)	1.599(2)	1.598(4)	1.603(3)	1.599(2)	1.602(4)
	<i>1.599</i>	<i>1.599</i>	<i>1.598</i>	<i>1.598</i>	<i>1.598</i>	<i>1.599</i>	<i>1.597</i>	<i>1.598</i>	<i>1.604</i>	<i>1.597</i>	<i>1.603</i>
<i>d</i> (C–N)	1.145(2)	1.144(3)	1.142(3)	1.147(2)	1.145(2)	1.141(2)	1.143(2)	1.143(3)	1.145(2)	1.141(2)	1.128(4)
	1.146(2)	1.147(2)	1.145(3)	1.144(3)	1.144(2)	1.141(2)	1.142(2)	1.143(3)	1.146(2)	1.142(2)	1.143(4)
	1.147(2)	1.145(2)	1.145(3)	1.145(2)	1.148(2)	1.143(2)	1.145(2)	1.141(4)	1.144(2)	1.147(2)	1.145(4)
	<i>1.157</i>	<i>1.157</i>	<i>1.156</i>	<i>1.156</i>	<i>1.157</i>	<i>1.156</i>	<i>1.156</i>	<i>1.156</i>	<i>1.157</i>	<i>1.156</i>	<i>1.157</i>
<i>d</i> (B–C1)	1.612(2)	1.614(3)	1.606(3)	1.611(3)	1.616(2)	1.613(2)	1.618(2)	1.618(4)	1.612(3)	1.626(2)	1.623(3)
	<i>1.638</i>	<i>1.637</i>	<i>1.640</i>	<i>1.639</i>	<i>1.638</i>	<i>1.648</i>	<i>1.642</i>	<i>1.639</i>	<i>1.634</i>	<i>1.652</i>	<i>1.644</i>
<i>d</i> (C2–F2)	1.378(2)	-	1.352(3)	1.365(2)	-	1.346(2)	1.360(2)	1.364(3)	1.370(2)	1.345(2)	1.356(3)
	<i>1.361</i>	-	<i>1.351</i>	<i>1.360</i>	-	<i>1.346</i>	<i>1.350</i>	<i>1.356</i>	<i>1.370</i>	<i>1.344</i>	<i>1.354</i>
<i>d</i> (C3–F3)	-	1.373(2)	1.335(3)	-	1.361(2)	1.360(2)	1.352(2)	-	-	1.348(2)	1.350(3)
	-	<i>1.369</i>	<i>1.358</i>	-	<i>1.365</i>	<i>1.358</i>	<i>1.354</i>	-	-	<i>1.346</i>	<i>1.356</i>
<i>d</i> (C4–F4)	-	-	-	-	-	-	-	1.351(4)	-	1.343(2)	1.616(3) ^d
	-	-	-	-	-	-	-	<i>1.355</i>	-	<i>1.344</i>	<i>1.644</i>
<i>d</i> (C5–F5)	-	-	-	1.372(2)	1.372(2)	-	1.364(2)	1.353(4)	-	1.344(2)	1.352(3)
	-	-	-	<i>1.368</i>	<i>1.365</i>	-	<i>1.364</i>	<i>1.357</i>	-	<i>1.345</i>	<i>1.354</i>
<i>d</i> (C6–F6)	-	-	-	-	-	1.360(2)	-	-	-	1.351(2)	1.349(3)
	-	-	-	-	-	<i>1.356</i>	-	-	-	<i>1.344</i>	<i>1.356</i>
<i>d</i> (C1–C2)	1.381(2)	1.392(3)	1.383(3)	1.391(3)	1.399(2)	1.385(2)	1.385(2)	1.387(4)	1.374(3)	1.385(2)	1.373(4)
	<i>1.394</i>	<i>1.401</i>	<i>1.393</i>	<i>1.395</i>	<i>1.403</i>	<i>1.394</i>	<i>1.394</i>	<i>1.394</i>	<i>1.392</i>	<i>1.394</i>	<i>1.394</i>
<i>d</i> (C2–C3)	1.377(2)	1.385(3)	1.383(3)	1.378(3)	1.374(2)	1.381(2)	1.377(2)	1.379(5)	1.377(3)	1.383(2)	1.376(3)
	<i>1.388</i>	<i>1.386</i>	<i>1.390</i>	<i>1.387</i>	<i>1.384</i>	<i>1.394</i>	<i>1.389</i>	<i>1.389</i>	<i>1.387</i>	<i>1.393</i>	<i>1.391</i>
<i>d</i> (C3–C4)	1.389(3)	1.361(3)	1.371(4)	1.384(3)	1.377(3)	1.370(2)	1.376(2)	1.376(4)	1.396(2)	1.374(3)	1.380(4)
	<i>1.394</i>	<i>1.383</i>	<i>1.384</i>	<i>1.394</i>	<i>1.386</i>	<i>1.380</i>	<i>1.385</i>	<i>1.384</i>	<i>1.402</i>	<i>1.385</i>	<i>1.394</i>
<i>d</i> (C4–C5)	1.384(3)	1.375(3)	1.379(4)	1.374(4)	1.379(3)	1.388(2)	1.375(2)	1.380(5)	1.374(3)	1.370(3)	1.382(4)
	<i>1.393</i>	<i>1.397</i>	<i>1.394</i>	<i>1.383</i>	<i>1.386</i>	<i>1.393</i>	<i>1.385</i>	<i>1.386</i>	<i>1.392</i>	<i>1.387</i>	<i>1.394</i>
<i>d</i> (C5–C6)	1.388(2)	1.379(3)	1.387(3)	1.377(3)	1.380(3)	1.372(2)	1.377(2)	1.372(5)	1.377(3)	1.386(2)	1.374(3)
	<i>1.396</i>	<i>1.392</i>	<i>1.394</i>	<i>1.386</i>	<i>1.384</i>	<i>1.385</i>	<i>1.384</i>	<i>1.386</i>	<i>1.387</i>	<i>1.389</i>	<i>1.391</i>
<i>d</i> (C6–C1)	1.398(2)	1.397(3)	1.403(4)	1.397(3)	1.399(2)	1.393(2)	1.402(2)	1.396(4)	1.396(2)	1.387(3)	1.385(4)
	<i>1.403</i>	<i>1.405</i>	<i>1.403</i>	<i>1.402</i>	<i>1.403</i>	<i>1.399</i>	<i>1.403</i>	<i>1.402</i>	<i>1.402</i>	<i>1.397</i>	<i>1.394</i>

^a B3LYP/6-311++G(d,p); calculated values in italics; mean values where applicable. ^b Bond lengths in Å. ^c Data of the second {B(CN)₃} moiety: *d*(B–CN) = 1.589(4), 1.603(4), 1.597(4) Å [*calc.*: 1.603 Å]; *d*(C–N) = 1.134(4), 1.136(4), 1.145(3) Å [*calc.*: 1.157 Å]; ^d *d*(C4–B).

Table S3 continued.

anion	B11a	B7	B10a	BP2 ^f		Py1	Py2	Py3	
<i>d</i> (B–CN)	1.597(4)	1.602(5)	1.604(3)	1.595(4)	<i>d</i> (B–CN)	at C2	-	1.597(7)	1.590(3)
	1.609(4)	1.590(5)	1.589(3)	1.604(5)		-	1.590(7)	1.596(4)	
	1.601(4)	1.586(5)	1.604(3)	1.599(5)		-	1.601(6)	1.600(4)	
	1.600	1.596	1.598	1.600		-	1.601	1.607	
<i>d</i> (C–N)	1.140(4)	1.137(5)	1.139(3)	1.138(4)	at C4	1.591(4)	1.580(37)	1.591(4)	
	1.142(3)	1.141(5)	1.139(3)	1.138(4)		1.597(4)	1.594(31)	1.604(3)	
	1.146(3)	1.138(5)	1.139(3)	1.142(4)		1.594(4)	1.593(32)	1.596(3)	
	1.155	1.156	1.156	1.156		1.596	1.602	1.606	
	at C6					-	-	1.589(3)	
						-	-	1.597(3)	
						-	-	1.597(3)	
						-	-	1.606	
<i>d</i> (C–N)						at C2	-	1.144(7)	1.148(2)
						-	1.135(7)	1.144(4)	
						-	1.139(6)	1.137(4)	
						-	1.157	1.158	
at C4					1.140(4)	1.139(31)	1.142(3)		
					1.144(4)	1.137(27)	1.137(3)		
					1.144(4)	1.133(24)	1.142(3)		
					1.156	1.157	1.157		
at C6					-	-	1.140(3)		
					-	-	1.146(3)		
					-	-	1.144(2)		
					-	-	1.158		
<i>d</i> (C2–F2)	1.343(3)	1.342(5)	1.349(3)	1.343(3)	<i>d</i> (C2–X2) ^e	1.340(4)	1.627(6)	1.620(4)	
	1.342	1.343	1.349	1.349		1.345	1.639	1.639	
<i>d</i> (C3–F3)	1.353(3)	1.344(4)	1.346(3)	1.350(3)	<i>d</i> (C3–F3)	1.335(4)	1.366(5)	1.356(3)	
	1.342	1.344	1.346	1.348		1.343	1.353	1.363	
<i>d</i> (C4–B)	1.626(3)	1.618(6)	1.621(4)	1.627(4)	<i>d</i> (C4–B)	1.631(4)	1.728(26)	1.620(3)	
	1.654	1.653	1.650	1.649		1.651	1.646	1.642	
<i>d</i> (C5–F5)	1.349(3)	1.348(4)	1.346(3)	1.351(3)	<i>d</i> (C5–F5)	1.345(4)	1.328(5)	1.374(3)	
	1.341	1.345	1.347	1.349		1.343	1.353	1.362	
<i>d</i> (C6–F6)	1.341(3)	1.344(4)	1.349(3)	1.346(3)	<i>d</i> (C6–X6) ^e	1.337(4)	1.352(5)	1.617(4)	
	1.342	1.343	1.352	1.348		1.346	1.361	1.640	
<i>d</i> (C1–C2)	1.386(4)	1.374(6)	1.368(3)	1.389(4)	<i>d</i> (N–C2)	1.310(4)	1.352(5)	1.3445(3)	
	1.395	1.391	1.392	1.392		1.312	1.349	1.347	
<i>d</i> (C2–C3)	1.374(3)	1.368(6)	1.391(3)	1.378(4)	<i>d</i> (C2–C3)	1.377(5)	1.374(5)	1.390(2)	
	1.389	1.395	1.393	1.392		1.387	1.400	1.397	
<i>d</i> (C3–C4)	1.387(4)	1.370(5)	1.386(3)	1.384	<i>d</i> (C3–C4)	1.385(4)	1.385(6)	1.382(3)	
	1.397	1.394	1.393	1.393		1.397	1.401	1.396	
<i>d</i> (C4–C5)	1.391(4)	1.382(5)	1.386(3)	1.391(4)	<i>d</i> (C4–C5)	1.387(4)	1.368(6)	1.386(4)	
	1.399	1.398	1.397	1.396		1.394	1.391	1.393	
<i>d</i> (C5–C6)	1.371(3)	1.372(6)	1.391(3)	1.380(4)	<i>d</i> (C5–C6)	1.376(4)	1.378(5)	1.380(2)	
	1.385	1.385	1.387	1.388		1.392	1.387	1.400	
<i>d</i> (C6–C1)	1.384(4)	1.377(6)	1.368(3)	1.386(4)	<i>d</i> (C6–N)	1.314(4)	1.296(5)	1.347(3)	
	1.398	1.397	1.395	1.394		1.309	1.300	1.345	
<i>d</i> (C1–Gr.)	1.425(3)	1.504(6)	1.373(4)	1.481(4)					
	1.423	1.506	1.367	1.485					

^e X = F or B; ^f data for the second Ph ring: *d*(B–CN) = 1.601(4), 1.592(4), 1.612(4) Å [calc.: 1.600 Å]; *d*(C–N) = 1.143(3), 1.142(4), 1.136(4) Å [calc.: 1.156 Å]; *d*(C2–F2) = 1.343(3) Å [calc.: 1.348 Å]; *d*(C3–F3) = 1.350(3) Å [calc.: 1.349 Å]; *d*(C4–B) = 1.625(4) Å [calc.: 1.649 Å]; *d*(C5–F5) = 1.349(3) Å [calc.: 1.348 Å]; *d*(C6–F6) = 1.341(3) Å [calc.: 1.349 Å]; *d*(C1–C2) = 1.389(4) Å [calc.: 1.394 Å]; *d*(C2–C3) = 1.383(4) Å [calc.: 1.388 Å]; *d*(C3–C4) = 1.394(4) Å [calc.: 1.396 Å]; *d*(C4–C5) = 1.380(4) Å [calc.: 1.393 Å]; *d*(C5–C6) = 1.385(4) Å [calc.: 1.392 Å]; *d*(C6–C1) = 1.386(4) Å [calc.: 1.392 Å].

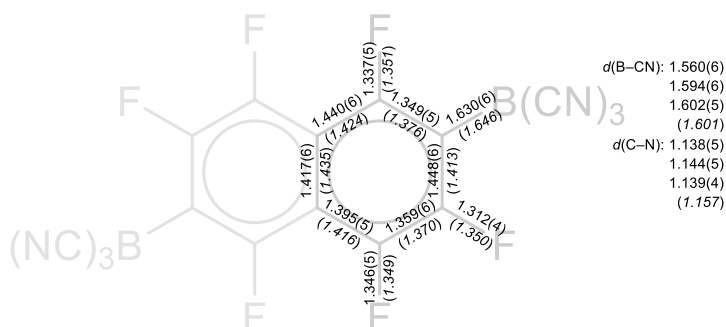


Figure S2: Experimental and calculated bond lengths [Å] of anion N2.

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