

Iridium-Catalyzed sp^3 C–H Borylation in Hydrocarbon Solvent Enabled by 2,2'-Dipyridylarylmethane Ligands

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I. General Information

General Considerations. Syntheses and manipulations with organometallic reagents were carried out using standard vacuum, Schlenk, cannula, or glovebox techniques under N_2 in oven- or flame-dried glassware unless otherwise specified. Tetrahydrofuran, dichloromethane, toluene, pentane, and diethyl ether were degassed with argon and dried over activated alumina using a solvent purification system.

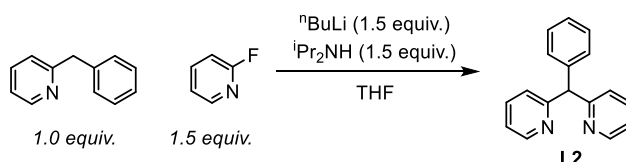
Spectroscopy. ^1H , $^{13}\text{C}\{^1\text{H}\}$, ^{11}B , and ^{19}F NMR spectra were recorded on Bruker NMR spectrometers at ambient temperatures unless otherwise noted. ^1H and $^{13}\text{C}\{^1\text{H}\}$ chemical shifts are referenced to residual solvent signals, ^{19}F chemical shifts are referenced to an external C_6F_6 standard. $^{13}\text{C}\{^1\text{H}\}$ resonances for boron-attached carbon atoms are not observed and are not included in the listings of spectral data.

II. Synthesis and Characterization

Organometallic starting materials. Bis(1,5-cyclooctadiene)diiridium(I) dichloride [(cod)IrCl]₂,¹ Bis(1,5-cyclooctadiene)diiridium(I) dimethoxide [(cod)IrOMe]₂,² [(cod)RhOMe]₂,² (η^5 -indenyl)(1,5-cyclooctadiene)iridium [(Ind)Ir(cod)],³ and (η^6 -mesitylene)(tris-pinacolboryl)iridium [(Mes)Ir(Bpin)₃],⁴ were prepared according to published procedures. IrCl₃·3H₂O, pinacolborane and bispinacolatodiboron were purchased from chemical vendors and used as received.

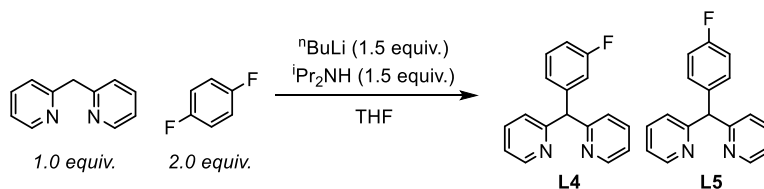
Substrate syntheses. *n*-octane, cyclohexane, cyclooctane, isooctane, di-*n*-butyl ether, triethylamine, cyclopentyl methyl ether, mesitylene, ethyl *n*-butyl ether, methyl butanoate, 3,5-dibromotoluene, dimethoxy ethane, and 5-butyl-4-methyldihydro-2(3*H*)-furanone (1.3:1 *cis:trans*) were purchased from chemical vendors and used as received. Diethylpivalamide,⁵ *n*-butyl pivalate,⁶ and butoxytriisopropylsilane⁷⁻⁸ were prepared and characterized by reported literature procedures.

Ligand syntheses. Di(2-pyridyl)methane (**L1**)⁹ and di(2-pyridyl)(phenyl)fluoromethane (**L3**)¹⁰ were prepared according to published procedures. Tetramethylphenanthroline, 2-fluoropyridine, 2-benzylpyridine, 1,4-difluorobenzene, 2,2-dipyridyl ketone, phenyl magnesium bromide, diethylaminosulfur trifluoride, 2,6-difluorobromobenzene, and pyridine-2-carboxaldehyde were purchased from chemical vendors and used as received.

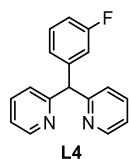


Di(2-pyridyl)(phenyl)methane (L2**).** This compound was synthesized according to a reported procedure¹¹ with the following modifications: A 50 mL Schlenk flask was charged with 6 mL THF and iPr₂NH (1.25 mL, 8.86 mmol) under an atmosphere of nitrogen and was cooled to -78 °C. ⁿBuLi (4 mL, 2.2 M in hexanes) was added dropwise over 15 min. The resulting solution was allowed to warm to 0 °C while stirring for 1 hr. 12 mL THF and 2-benzylpyridine (1.0 g, 5.9 mmol) were added to a separate 100 mL Schlenk flask, placed under an atmosphere of nitrogen, and cooled to 0 °C. The LDA solution in the 50 mL Schlenk flask was transferred dropwise via cannula to the 2-benzylpyridine solution, and the resulting mixture allowed to warm to ambient temperature while stirring for 30 min. 2-Fluoropyridine (0.76 mL, 8.86 mmol) in THF (12 mL) was then added dropwise via syringe over 15 min, and the reaction was allowed to stir at room temperature for 3 hr. The mixture was quenched by slow addition of deionized water and the organic layer extracted. The aqueous phase was washed with three portions of dichloromethane and the combined organic layers were

washed with brine and dried over Na₂SO₄ followed by concentration *in vacuo*. The resulting mixture was purified by column chromatography (60% EtOAc in hexanes, and flushed with 10% MeOH in CH₂Cl₂) to give the product **L2** as an off-white crystalline solid. Yield: 1.2 g (83%).



Di(2-pyridyl)(3/4-fluorophenyl)methane (L4 and L5). A 250 mL 3-necked round bottom flask was fitted with addition funnel and placed under an atmosphere of nitrogen. 15 mL THF and iPr₂NH (3.7 mL, 26.4 mmol) were added and the solution was cooled to -78 °C. ⁿBuLi (12 mL, 2.2 M in hexanes) was then added dropwise over 15 min. The resulting solution was allowed to warm to 0 °C while stirring for 1 hr. To the addition funnel was added dipyridylmethane (3.0 g, 17.6 mmol) and 30 mL THF; the solution was added dropwise over 20 min and allowed to stir for 30 min upon completion of the addition while warming to room temperature. At this point a solution of 1,4-difluorobenzene (3.6 mL, 35.2 mmol) in 35 mL THF was added and the resulting solution was allowed to stir at room temperature for 18 hr. The mixture was quenched by slow addition of deionized water and the organic layer extracted. The aqueous phase was washed with three portions of dichloromethane and the combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated *in vacuo*. The resulting mixture was purified by column chromatography (75 → 100% EtOAc in hexanes, and flushed with 10% MeOH in CH₂Cl₂) to give **L4** and **L5** as pure, separated products.



Di(2-pyridyl)(3-fluorophenyl)methane (L4). This product from the procedure above as a red-brown solid. Yield: 0.71 g (15%); mp 90-92 °C.

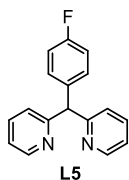
Alternatively, **L4** can be prepared by a variation of the procedure used for **L2** using 2-(3-fluorobenzyl)pyridine¹²⁻¹³ (0.10 g, 0.53 mmol) to give **L4**. Yield: 0.094 g (67%).

¹H NMR (CDCl₃, 400 MHz): δ 8.60 (d, *J* = 4.8 Hz, 2H), 7.64 (td, *J* = 7.7, 1.9 Hz, 2H), 7.28 (dd, *J* = 8.0, 6.2 Hz, 1H), 7.25 (d, *J* = 7.1 Hz, 2H), 7.16 (dd, *J* = 7.6, 4.7 Hz, 2H), 7.06 (d, *J* = 7.9 Hz, 1H), 7.01 (dt, *J* = 10.1, 2.2 Hz, 1H), 6.93 (td, *J* = 8.4, 2.5 Hz, 1H), 5.81 (s, 1H)

¹³C{¹H} NMR (CDCl₃, 151 MHz): δ 162.8 (d, *J*_{CF} = 245 Hz), 161.4, 149.5, 144.2 (d, *J*_{CF} = 7.1 Hz), 136.6, 129.8 (d, *J*_{CF} = 8.4 Hz), 124.9 (d, *J*_{CF} = 2.5 Hz), 123.9, 121.7, 116.3 (d, *J*_{CF} = 21.6 Hz), 113.6 (d, *J*_{CF} = 21.1 Hz), 61.2.

$^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3 , 376 MHz): δ -113.0

HRMS $[\text{M}+\text{H}]^+$ Calc. 265.1063, Found 265.1109



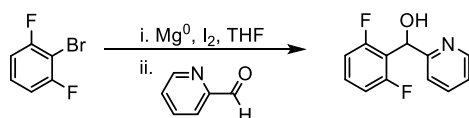
Di(2-pyridyl)(4-fluorophenyl)methane (L5). This product was obtained as a red-brown solid. Yield: 0.89 g (19%); mp 88-90 °C.

^1H NMR (CDCl_3 , 400 MHz): δ 8.58 (d, J = 4.9 Hz, 2H), 7.62 (td, J = 7.7, 1.9 Hz, 2H), 7.26 (td, J = 5.6, 2.6 Hz, 2H), 7.23 (d, J = 6.9 Hz, 2H), 7.14 (dd, J = 7.6, 4.9 Hz, 2H), 6.99 (t, J = 8.7 Hz, 2H), 5.79 (s, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 151 MHz): δ 161.7 (d, J_{CF} = 245 Hz), 161.8, 149.4, 137.3 (d, J_{CF} = 30.4 Hz), 136.5, 130.7 (d, J_{CF} = 7.7 Hz), 123.9, 121.6, 115.3 (d, J_{CF} = 21.5 Hz), 60.8.

$^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3 , 376 MHz): δ -118.0

HRMS $[\text{M}+\text{H}]^+$ Calc. 265.1063, Found 265.1109



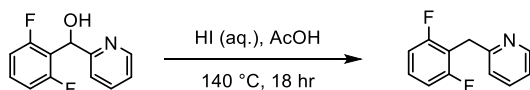
(2,6-difluorophenyl)(2-pyridyl)methanol. A flame-dried 250 mL 3-neck round bottom flask fitted with an addition funnel was charged with magnesium turnings (0.175 g, 7.2 mmol) and two iodine crystals under an atmosphere of nitrogen. The flask was heated briefly until iodine vapor was observed. Upon cooling to room temperature, 5 mL dry, degassed THF was added. A solution of 2,6-difluorobromobenzene (1.20 g, 6.24 mmol) in 3 mL THF was added dropwise over 20 min. After initiation, the solution was stirred at ambient temperature for 1 hr. At this point the mixture was cooled to 0 °C, and a solution of pyridine-2-carboxaldehyde (0.456 mL, 4.8 mmol) in 10 mL THF was added dropwise over 30 min. Upon completion of the addition, the reaction was allowed to warm to room temperature and was stirred for 2 hours. The mixture was quenched by slow addition of saturated aqueous NH_4Cl and the organic layer separated. The aqueous phase was washed with three portions of dichloromethane and the combined organic layers were washed with brine, dried over Na_2SO_4 , and concentrated *in vacuo*. The resulting mixture was passed through a plug of silica with ethyl acetate, concentrated on a rotary evaporator, and dried under vacuum to give the alcohol as a pale yellow crystalline solid. Yield: 0.980 g (92%).

^1H NMR (CDCl_3 , 600 MHz): δ 8.60 (d, J = 4.7 Hz, 1H), 7.65 (td, J = 7.7, 1.7 Hz, 1H), 7.28 – 7.21 (m, 2H), 7.15 (d, J = 7.9 Hz, 1H), 6.87 (t, J = 8.3, 2H), 6.20 (d, J = 5.1 Hz, 1H), 5.45 (d, J = 5.3 Hz, 1H)

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 151 MHz): δ 161.6 (dd, $J_{\text{CF}} = 250.4$, 8.0 Hz), 159.1, 147.9, 137.1, 130.0 (t, $J_{\text{CF}} = 10.6$ Hz), 122.7, 120.6, 119.1 (t, $J_{\text{CF}} = 16.1$ Hz), 111.9 (dd, $J_{\text{CF}} = 4.7$ Hz, 21.4 Hz), 65.7 (t, $J_{\text{CF}} = 3.3$ Hz)

$^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3 , 376 MHz): δ -114.7

HRMS $[\text{M}+\text{H}]^+$ Calc. 222.0725, Found 222.0727



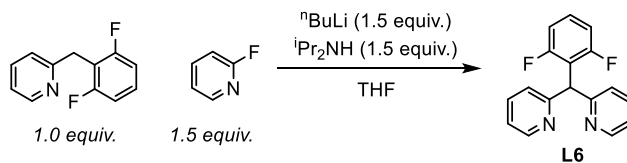
2-(2,6-difluorobenzyl)pyridine. This product was synthesized by a variation of a reported procedure.¹² A 100 mL round bottom flask fitted with a condenser was charged with (2,6-difluorophenyl)(2-pyridyl)methanol (0.626 g, 2.83 mmol) under an atmosphere of N_2 . To the flask was added acetic acid (12 mL), followed by careful addition of concentrated aqueous HI (2.0 mL, 15 mmol). The mixture was heated to 140 °C and stirred for 20 hr. The flask was then cooled to room temperature and diluted with 50 mL deionized water. The mixture was neutralized by the addition of saturated aqueous NaHCO_3 , made basic with Na_2CO_3 , and extracted twice with 50 mL portions of ethyl acetate. The combined organic fractions were dried over Na_2SO_4 , concentrated under vacuum, and purified by column chromatography on silica gel (10% - 20% EtOAc in hexane). The product was obtained as a pale yellow oil. Yield: 0.087 g (14%); Recovered (2,6-difluorophenyl)(2-pyridyl)methanol: 0.520 g (83%).

^1H NMR (CDCl_3 , 400 MHz): δ 8.54 (d, $J = 4.6$ Hz, 1H), 7.58 (dt, $J = 1.8$, 7.7 Hz, 1H), 7.21 (m, 1H), 7.11 (m, 2H), 6.90 (t, $J = 7.7$ Hz, 2H), 4.23 (s, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 151 MHz): δ 161.85 (dd, $J = 247.8$, 8.4 Hz), 159.0, 149.6, 136.8, 128.5 (t, $J = 10.2$ Hz), 122.6, 121.7, 115.3, (t, $J = 20.2$), 111.5 (dd, $J = 20.9$, 5.3 Hz), 31.3 (t, $J = 2.5$ Hz).

$^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3 , 376 MHz): δ -114.3

HRMS $[\text{M}+\text{H}]^+$ Calc. 206.0776, Found 206.0771



Di(2-pyridyl)(2,6-difluorophenyl)methane (L6). This product was prepared and purified according to the procedure used for **L2** using 2-(2,6-difluorobenzyl)pyridine (0.050 g, 0.244 mmol). The product was obtained as a red-brown solid. Yield: 0.036 g (52%); mp 98-100 °C.

^1H NMR (CDCl_3 , 600 MHz): δ 8.59 (d, J = 4.2 Hz, 2H), 7.62 (td, J = 7.7, 1.8 Hz, 2H), 7.26 – 7.21 (m, 1H), 7.16 (dd, J = 7.2, 5.0 Hz, 2H), 7.11 (d, J = 7.9 Hz, 2H) 6.90 (t, J = 8.2, 2H), 6.20 (s, 1H)

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 151 MHz): δ 161.6 (dd, J_{CF} = 248.9, 8.0 Hz), 160.3, 149.6, 136.6, 129.1 (t, J_{CF} = 10.5 Hz), 123.4, 121.9, 118.2 (t, J_{CF} = 17.3 Hz), 111.9 (dd, J_{CF} = 4.3 Hz, J_{CF} = 21.3 Hz), 51.4.

$^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3 , 376 MHz): δ -111.6

HRMS $[\text{M}+\text{H}]^+$ Calc. 283.1041, Found 283.1049

III. General procedures

Procedure for ligand comparisons (Figure 2). In an inert-atmosphere glove box, a 4 mL vial was charged with $[\text{Ir}(\text{COD})\text{OMe}]_2$ (0.0030 g, 0.010 mmol (Ir basis), 10 mol % Ir) and B_2pin_2 (0.026 g, 0.10 mmol). *n*-octane (1.0 mL, 200 mM) was added and the solution stirred for 3 min. The resulting solution was transferred to a separate 4 mL vial charged with ligand (0.010 mmol, 10 mol %). The vial was sealed with a PTFE-lined cap, removed from the glove box, and heated to 120 °C in an oil bath with stirring for 24 hr. At this point the reaction was cooled to room temperature and the crude mixture analyzed by GC-FID. Yields were obtained using a calibrated dodecane internal standard.

Procedure for catalytic borylation of neat substrate (Figure 4). In an inert-atmosphere glove box, a 4 mL vial equipped with magnetic stirbar was charged with $[(\text{Mes})\text{Ir}(\text{Bpin})_3]$ (0.0021 g, 3.0 μmol , 1 mol %), **L4** (0.0008 g, 3.0 μmol , 1 mol %), and B_2pin_2 (0.076 g, 300 μmol). Substrate (3 mL) was then added to give a pale yellow-orange solution. The vial was sealed with a PTFE-lined cap, removed from the glove box and was heated in a 120 °C oil bath with stirring for 24 hr, giving a deep red solution. The crude mixture was cooled to room temperature, concentrated *in vacuo*, and analyzed by ^1H NMR with a tetrachloroethane standard to obtain NMR yields. Isolated yields were obtained by conversion to the trifluoroborate salt according to the general procedure given below.

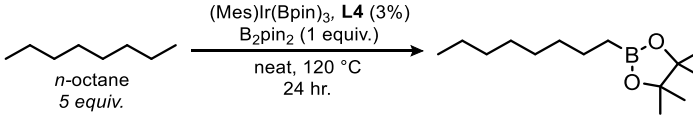
Procedure for catalytic borylation of substrate in cyclohexane solvent (Figure 5). In an inert-atmosphere glove box, a 15 mL Schlenk bomb flask equipped with a magnetic stirbar was charged with $[(\text{Mes})\text{Ir}(\text{Bpin})_3]$ (0.0062 g, 9 μmol , 3 mol %), **L4** (0.0024 g, 9 μmol , 3 mol %), and B_2pin_2 (0.076 g, 300 μmol). The mixture was taken up in 2.7 mL cyclohexane and allowed to stir for 2-3 min at room temperature to give a pale yellow-orange solution, followed by the addition of substrate (1.5 mmol, 5.0 equiv.). The reaction flask was sealed with a PTFE plug, was removed from the glove box and was heated in a 120 °C oil bath for 48 hours to give a deep red solution. The crude mixture was cooled to room temperature, concentrated *in vacuo*, and analyzed by ^1H NMR with a tetrachloroethane standard to obtain NMR yields. Isolated yields were obtained by conversion to the trifluoroborate salt according to the general procedure given below.

Procedure for conversion of boronate esters to potassium trifluoroborates for isolation. In air, the crude boronate ester was taken up in 2 mL MeOH and transferred to a 20 mL glass vial equipped with a magnetic stirbar. To this solution was added aqueous KHF_2 (0.287 mL of a 4.7 M solution, 1.35 mmol, 4.5 equiv.), and the mixture was allowed to stir at ambient temperature for 3 hr. The resulting mixture was concentrated on a rotary evaporator. A 5 mL portion of methanol was added followed

by evaporation again. This process was repeated two additional times to remove free pinacol. The mixture was then triturated with three, 3 mL portions of acetone and the extracts were filtered and evaporated to dryness. The crude residue was washed with 2 mL diethyl ether and dried *in vacuo* to give the pure alkyl trifluoroborate.

Procedure for ^{11}B NMR monitoring of the borylation of neat *n*-octane (Figure 6). In an inert-atmosphere glove box, a 4 mL vial was charged with $[(\text{Mes})\text{Ir}(\text{Bpin})_3]$ (0.0021 g, 3.0 μmol , 3 mol %), **L4** (0.0008 g, 3.0 μmol , 3 mol %), and B_2pin_2 (0.026 g, 100 μmol). The mixture was then taken up in 1 mL of *n*-octane, stirred briefly, and 0.5 mL of the resulting solution was added to a J. Young NMR tube equipped with a sealed C_6D_6 capillary. The sealed tube was then removed from the glove box and an initial ^{11}B NMR spectrum was collected at room temperature. The J. Young tube was then heated in a 120 $^\circ\text{C}$ oil bath. The tube was removed from heat after 1, 3, 5, and 18 hours for analysis by ^{11}B NMR. NMR spectra were collected at 23 $^\circ\text{C}$ after which the tube was returned to the oil bath. ^{11}B integrations were calculated by fitting to Lorentzian functions using Fityk¹⁴ and normalized to give the data presented in Figure 6. The *y*-axis is presented as $2 \times (\text{normalized peak area})$.

Table S1. Survey of solvents for catalytic C–H borylation.

			
Entry	Solvent	Octyl-Bpin ^a	Solvent-Bpin ^a
1	Cyclooctane	57%	< 5%
2	THF	8%	24%
3	1,4-dioxane	< 5%	21%
4	Isooctane	63%	< 1%
5	Cyclohexane	79%	< 5%
6 ^b	Cyclohexane	103%	< 5%

^aYields determined by GC-FID with a dodecane standard; based on 1 equiv. B_2pin_2 . ^b48 hr.

IV. Synthesis and Characterization of Borylated Products

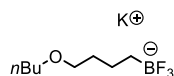


4,4,5,5-tetramethyl-2-octyl-1,3,2-dioxaborolane. This product was synthesized according to the general procedure for borylation under neat conditions. The crude boronate ester was isolated by column chromatography (5% EtOAc in hexane) to give the product as a pale yellow oil. Yield: 0.113 g (156%).

This product was also synthesized according to the general procedure for borylation in cyclohexane solvent using 0.244 mL *n*-octane. The crude boronate ester was isolated by column chromatography (5% EtOAc in hexane) to give the product as a pale yellow oil. Yield: 0.055 g (76%).

This product has been previously characterized.¹⁵

¹H NMR (CDCl₃, 400 MHz): δ 1.43-1.18 (m, 12H), 1.23 (s, 12H), 0.86 (t, J = 6.8 Hz, 3H), 0.75 (t, J = 7.7 Hz, 2H).



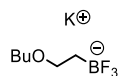
Potassium 4-(*n*-butoxy)*n*-butyltrifluoroborate. This product was synthesized according to the general procedure for borylation under neat conditions using 3 mL di-*n*-butyl ether. The crude boronate ester was then converted to the trifluoroborate according to the general procedure. The product was isolated as a white solid. Yield: 0.118 g (167%).

This product was also synthesized according to the general procedure for borylation in cyclohexane solvent using 0.254 mL di-*n*-butyl ether. The crude boronate ester was then converted to the trifluoroborate according to the general procedure. The product was isolated as a white solid. Yield: 0.056 g (79%).

This product has been previously characterized.¹⁶

¹H NMR (acetone-*d*₆, 400 MHz): δ 3.34 (t, J = 6.35 Hz, 2H), 3.32 (t, J = 7.28 Hz, 2H), 1.23-1.54 (m, 8H), 0.89 (t, J = 7.3 Hz, 3H), 0.12 (m, 2H)

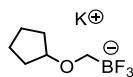
¹³C{¹H} NMR (acetone-*d*₆, 151 MHz): δ 72.4, 71.0, 34.6, 32.9, 23.2 (q, J = 2.6 Hz), 20.2, 14.3
HRMS [M-K]⁺ Calc. 197.1330, Found 197.1317



Potassium 2-butoxyethyltrifluoroborate. This product was synthesized according to the general procedure for borylation under neat conditions using 3 mL butyl methyl ether. The crude boronate ester was then converted to the trifluoroborate according to the general procedure. The product was isolated as a white solid. Yield: 0.084 g (134%).

This product has been previously characterized.¹⁶

¹H NMR (acetone-*d*₆, 400 MHz): δ 3.40 (q, J = 6.9 Hz, 2H), 3.09 (m, 2H), 1.32 – 1.26 (m, 2H), 1.15 – 1.07 (m, 2H), 0.87 (t, J = 7.4 Hz, 3H), 0.44 (br m, 2H)



Potassium (cyclopentyloxy)methyltrifluoroborate. This product was synthesized according to the general procedure for borylation under neat conditions using 3 mL cyclopentyl methyl ether. The crude boronate ester was then converted to the trifluoroborate according to the general procedure. The product was isolated as a white solid. Yield: 0.048 g (81%).

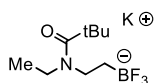
This product was also synthesized according to the general procedure for borylation in cyclohexane solvent using 0.175 mL cyclopentyl methyl ether. The crude boronate ester was then converted to the trifluoroborate according to the general procedure. The product was isolated as a white solid. Yield: 0.051 g (83%).

This product has been previously characterized.¹⁷

¹H NMR (acetone-*d*₆, 400 MHz): δ 3.56 (m, 1H), 2.50 (q, *J* = 5.4 Hz, 2H) 1.42-1.58 (m, 6H), 1.28-1.36 (m, 2H)

¹³C{¹H} NMR (acetone-*d*₆, 151 MHz): δ 84.5, 32.6, 24.2

HRMS [M-K]⁺ Calc. 167.0861, Found 167.0853



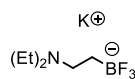
Potassium (2-(N-ethylpivalamido)ethyl)trifluoroborate. This product was synthesized according to the general procedure for borylation in cyclohexane solvent using 0.236 g N,N-diethylpivalamide. The crude boronate ester was then converted to the trifluoroborate according to the general procedure. The product was isolated as a white solid. Yield: 0.051 g (64%).

N,N-diethylpivalamide does not undergo efficient borylation following the general procedure for borylation under neat conditions. Analysis of the crude reaction mixture by ¹H NMR with a tetrachloroethane internal standard shows the formation of the corresponding boronate ester in low yield. Yield: 2%.

¹H NMR (acetone-*d*₆, 400 MHz): δ 3.19-3.45 (m, 4H), 1.20 (s, 9H), 1.02 (t, *J* = 6.7 Hz, 3H), 0.45 (m, 2H)

¹³C{¹H} NMR (acetone-*d*₆, 151 MHz): δ 175.8, 41.2 (br), 39.2, 29.0, 13.3 (br)

HRMS [M-K]⁺ Calc. 224.1439, Found 224.1431

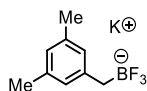


Potassium 2-(diethylamino)ethyltrifluoroborate. This product was synthesized according to the general procedure for borylation under neat conditions using 3 mL triethylamine. The crude boronate ester was then converted to the trifluoroborate according to the general procedure. The product was isolated as a white solid. Yield: 0.078 g (126%).

This product was also synthesized according to the general procedure for borylation in cyclohexane solvent using 0.208 mL triethylamine. The crude boronate ester was then converted to the trifluoroborate according to the general procedure. The product was isolated as a white solid. Yield: 0.046 g (74%).

This compound has been previously characterized.¹⁶

¹H NMR (acetone-*d*₆, 400 MHz): δ 3.21 (q, *J* = 7.3, 4H), 3.13 (m, 2H), 1.31 (t, *J* = 7.3 Hz, 6H), 0.47 (m, 2H)



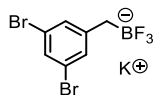
Potassium (3,5-dimethylbenzyl)trifluoroborate. This product was synthesized according to the general procedure for borylation under neat conditions using 3 mL mesitylene. The crude boronate ester was then converted to the trifluoroborate according to the general procedure. The product was isolated as a white solid. Yield: 0.106 g (166%).

This product was also synthesized according to the general procedure for borylation in cyclohexane solvent using 0.209 mL mesitylene. The crude boronate ester was then converted to the trifluoroborate according to the general procedure. The product was isolated as a white solid. Yield: 0.059 g (94%).

¹H NMR (acetone-*d*₆, 400 MHz): δ 6.59 (s, 2H), 6.37 (s, 1H), 2.02 (s, 6H), 1.43 (br, 2H)

¹³C{¹H} NMR (acetone-*d*₆, 151 MHz): δ 147.9, 136.5, 127.8, 124.7, 21.6

HRMS [M-K]⁺ Calc. 187.0911, Found 187.0905

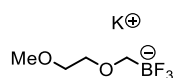


Potassium (3,5-dibromobenzyl)trifluoroborate. This product was synthesized according to the general procedure for borylation in cyclohexane solvent using 0.372 g 3,5-dibromotoluene. The crude boronate ester was purified by column chromatography (5→15% EtOAc in hexanes) and concentrated *in vacuo*. The boronate ester was then converted to the trifluoroborate according to the general procedure. The product was isolated as a white solid. Yield: 0.073 g (68%).

¹H NMR (acetone-*d*₆, 400 MHz): δ 7.09-7.13 (m, 3H), 1.49 (br, 2H)

$^{13}\text{C}\{^1\text{H}\}$ NMR (acetone- d_6 , 151 MHz): δ 154.1, 131.4, 127.9, 122.1

HRMS $[\text{M-K}]^-$ Calc. 314.8809, Found 314.8798



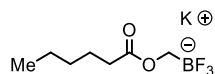
Potassium (2-methoxyethoxy)methyltrifluoroborate. This product was synthesized according to the general procedure for borylation under neat conditions using 3 mL dimethoxyethane. The crude boronate ester was then converted to the trifluoroborate according to the general procedure. The product was isolated as a white solid. Yield: 0.047 g (80%).

This product was also synthesized according to the general procedure for borylation in cyclohexane solvent using 0.156 mL dimethoxyethane. The crude boronate ester was then converted to the trifluoroborate according to the general procedure. The product was isolated as a white solid. Yield: 0.041 g (70%).

^1H NMR (acetone- d_6 , 400 MHz): δ 3.46 (m, 4H), 3.33 (s, 3H), 2.71 (q, J = 5.3 Hz, 2H)

$^{13}\text{C}\{^1\text{H}\}$ NMR (acetone- d_6 , 151 MHz): δ 73.2, 72.6, 58.7

HRMS $[\text{M-K}]^-$ Calc. 157.0653, Found 157.0647



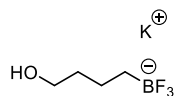
Potassium Methyltrifluoroborate hexanoate. This product was synthesized according to the general procedure for borylation under neat conditions using 3 mL methyl hexanoate. The crude boronate ester was then converted to the trifluoroborate according to the general procedure with the following modifications to the workup: After conversion to the trifluoroborate, the crude reaction mixture was reduced to a volume of 1 mL. To prevent hydrolysis, 2 mL toluene was added to the mixture and the solution reduced in volume, this was repeated three times. After evaporation to dryness, the residue was extracted with acetone and the extracts were filtered and evaporated to dryness. The product was isolated as a white solid. Yield: 0.063 g (89%).

This product was also synthesized according to the general procedure for borylation in cyclohexane solvent using 0.220 mL methyl hexanoate. The crude boronate ester was then converted to the trifluoroborate according to the general procedure with the same modifications as above. The product was isolated as a white solid. Yield: 0.044 g (62%).

^1H NMR (acetone- d_6 , 400 MHz): δ 3.16 (q, J = 5.3 Hz, 2H), 2.06 (t, J = 7.3 Hz, 2H), 1.42 (quintet, 7.4 Hz, 2H), 1.11-1.21 (m, 4H), 0.74 (t, 7.1 Hz, 3H)

$^{13}\text{C}\{^1\text{H}\}$ NMR (acetone- d_6 , 151 MHz): δ 175.2, 35.1, 32.2, 25.8, 23.2, 14.3

HRMS $[\text{M-K}]^-$ Calc. 197.0966, Found 197.0957



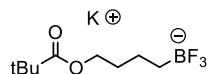
Potassium (4-hydroxybutyl)trifluoroborate. This product was synthesized according to the general procedure for borylation under neat conditions using 3 mL butoxytriisopropylsilane. The crude boronate ester was then converted to the trifluoroborate according to the general procedure with the following modifications: 10 equiv. KHF_2 was used and the reaction was carried out at 65 °C for 18 hr. The crude reaction mixture was evaporated to dryness *in vacuo*. The residue was washed with ice cold acetone, and the solid extracted with five, 3 mL portions of acetone. The combined acetone extracts were concentrated to 3 mL and precipitated with Et_2O to yield the product as a colorless solid. Yield: 0.034 g (63%).

This product was also synthesized according to the general procedure for borylation in cyclohexane solvent using 0.346 g butoxytriisopropylsilane. The crude mixture was cooled to room temperature, concentrated *in vacuo*, and analyzed by ^1H NMR with a tetrachloroethane standard to obtain an NMR yield of 4-(triisopropylsiloxy)butyl-pinacolborane. (51%)

^1H NMR (D_2O , 400 MHz): δ 3.36 (t, J = 6.7 Hz, 2H), 1.30 (quintet, J = 7.3 Hz, 2H), 0.96-1.07 (m, 2H), 0.01 (q, J = 8.1 Hz, 2H)

$^{13}\text{C}\{^1\text{H}\}$ NMR (D_2O , 101 MHz): δ 61.8, 34.4, 20.2

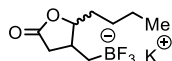
HRMS $[\text{M-K}]^-$ Calc. 141.0704, Found 141.0704



Potassium ((4-pivaloyloxy)butyl)trifluoroborate. This product was synthesized according to the general procedure for borylation in cyclohexane solvent using 0.277 mL butyl pivalate. The crude boronate ester was concentrated *in vacuo*, and analyzed by ^1H NMR with a tetrachloroethane standard to obtain an NMR yield. (44%). The crude boronate ester was then converted to the known trifluoroborate according to the general procedure. The identity of the product was confirmed by comparison of ^1H NMR spectra to reported data.¹⁸

^1H NMR (acetone- d_6 , 400 MHz): δ 3.98 (t, J = 6.9 Hz, 2H), 1.55 (p, J = 6.8 Hz, 2H), 1.31 (m, 2H), 1.14 (s, 9H), 0.10-0.15 (br m, 2H),

HRMS $[\text{M-K}]^-$ Calc. 225.1279, Found 225.1272



Potassium 4-methyl-5-(4-(trifluoroboranyl)butyl)dihydrofuran-2-one. This product was synthesized according to the general procedure for borylation in cyclohexane solvent using 0.246 mL 5-butyl-4-methyldihydrofuran-2(3*H*)-one (1:1.3 *cis:trans*). The crude boronate ester was then converted to the trifluoroborate according to the general procedure. The product was isolated as a white solid (1:2 *cis:trans*). Yield: 0.038 g (48%).

5-butyl-4-methyldihydrofuran-2(3*H*)-one does not undergo borylation following the general procedure for borylation under neat conditions. Analysis of the crude reaction mixture by ^1H NMR or GC-FID shows no evidence for formation of the corresponding boronate ester.

Assignment of the site of borylation was made on the basis of 1D and 2D NMR spectra and the observation of a major mass fragment at $m/z = 282$ (M-Bu) in the GC-MS (EI) spectrum of the boronate ester prior to fluorination.

^1H NMR (acetone- d_6 , 400 MHz): *cis* isomer: δ 4.33 (ddd, $J = 9.6$ Hz, 6.3 Hz, 4.2 Hz, 1H), 2.51 (m, 1H), 2.40 (dd, $J = 7.7$ Hz, 17.0 Hz, 1H), 2.31 (dd, $J = 7.5$ Hz, 17.1 Hz, 1H), 1.60 (m, 1H), 1.48-1.53 (m, 1H), 1.41-1.48 (m, 1H) 1.30-1.38 (m, 3H), 0.90 (t, $J = 7.1$ Hz, 3H), 0.28 (m, 1H), 0.07 (m, 1H) *trans* isomer: δ 3.96 (dt, $J = 3.4$ Hz, 8.0 Hz, 1H), 2.51 (dd, $J = 7.9$ Hz, 17.4 Hz, 1H), 2.16 (dd, $J = 10.0$ Hz, 17.3 Hz, 1H), 2.08, (m, 1H) 1.72 (m, 1H), 1.41-1.48 (m, 2H) 1.30-1.38 (m, 3H), 0.90 (t, $J = 7.1$ Hz, 3H), 0.43 (m, 1H), 0.15 (m, 1H)

$^{13}\text{C}\{^1\text{H}\}$ NMR (acetone- d_6 , 151 MHz): *cis* isomer: δ 178.7, 85.9, 37.2, 36.9, 30.3, 29.0, 23.4, 14.3, *trans* isomer: δ 178.4, 89.5, 40.1, 38.1, 34.3, 29.1, 23.3, 14.3.

HRMS [M-K] $^-$ Calc. 223.1123, Found 223.1110

V. NMR Spectra

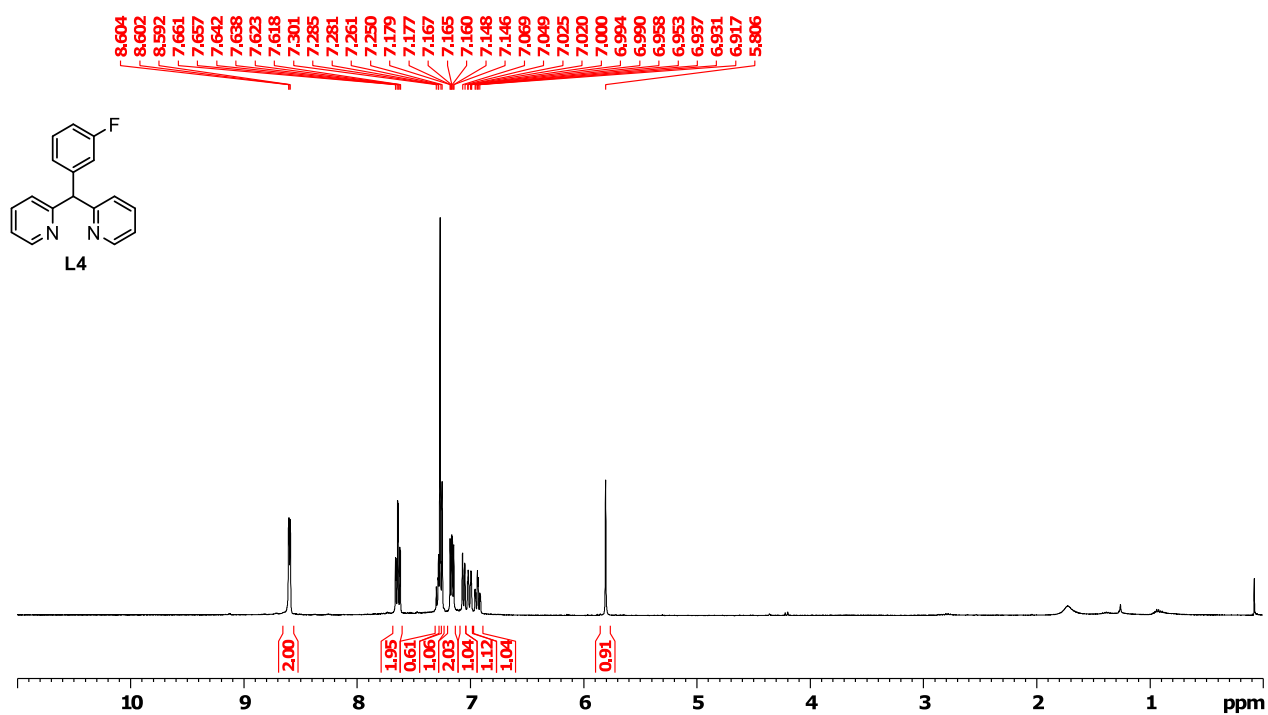


Figure S1. ¹H NMR of di(2-pyridyl)(3-fluorophenyl)methane (L4)

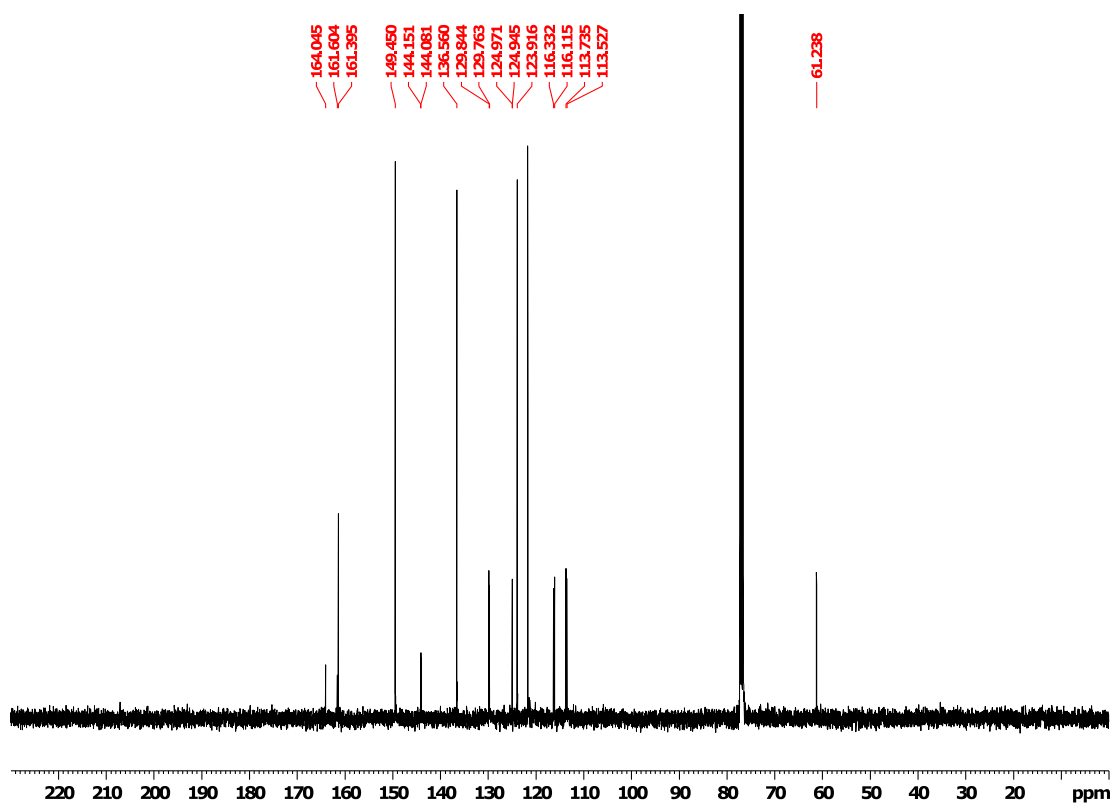


Figure S2. ¹³C{¹H} NMR of di(2-pyridyl)(3-fluorophenyl)methane (L4)

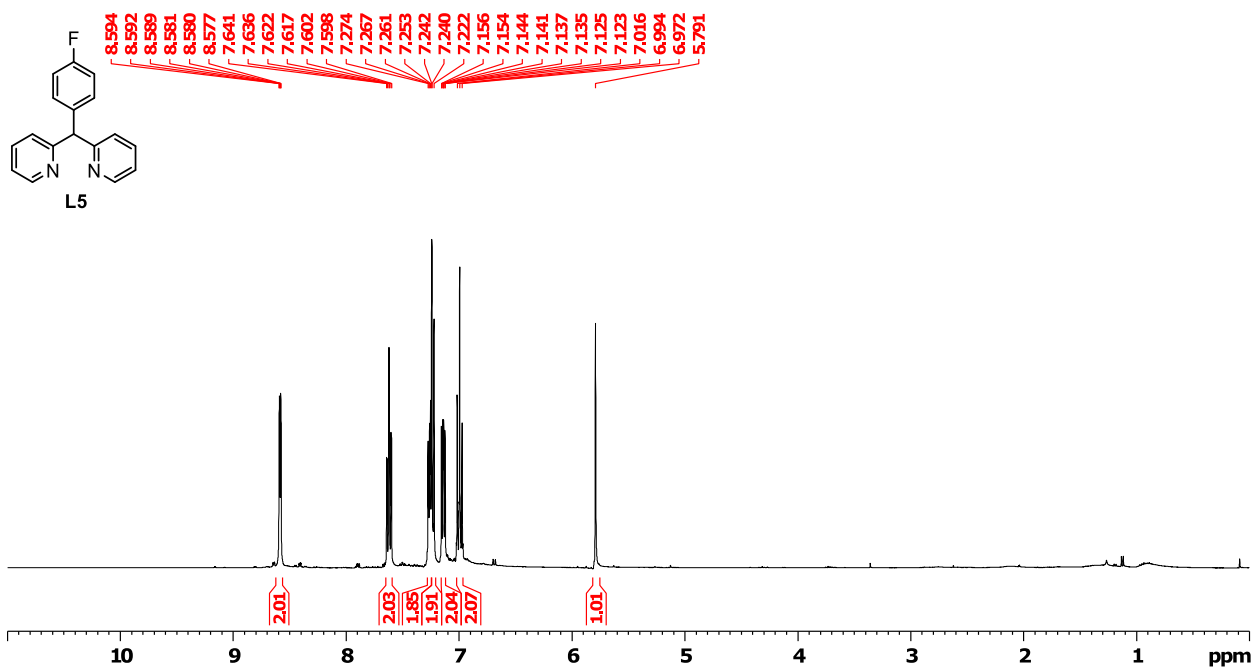


Figure S3. ¹H NMR of di(2-pyridyl)(4-fluorophenyl)methane (L5)

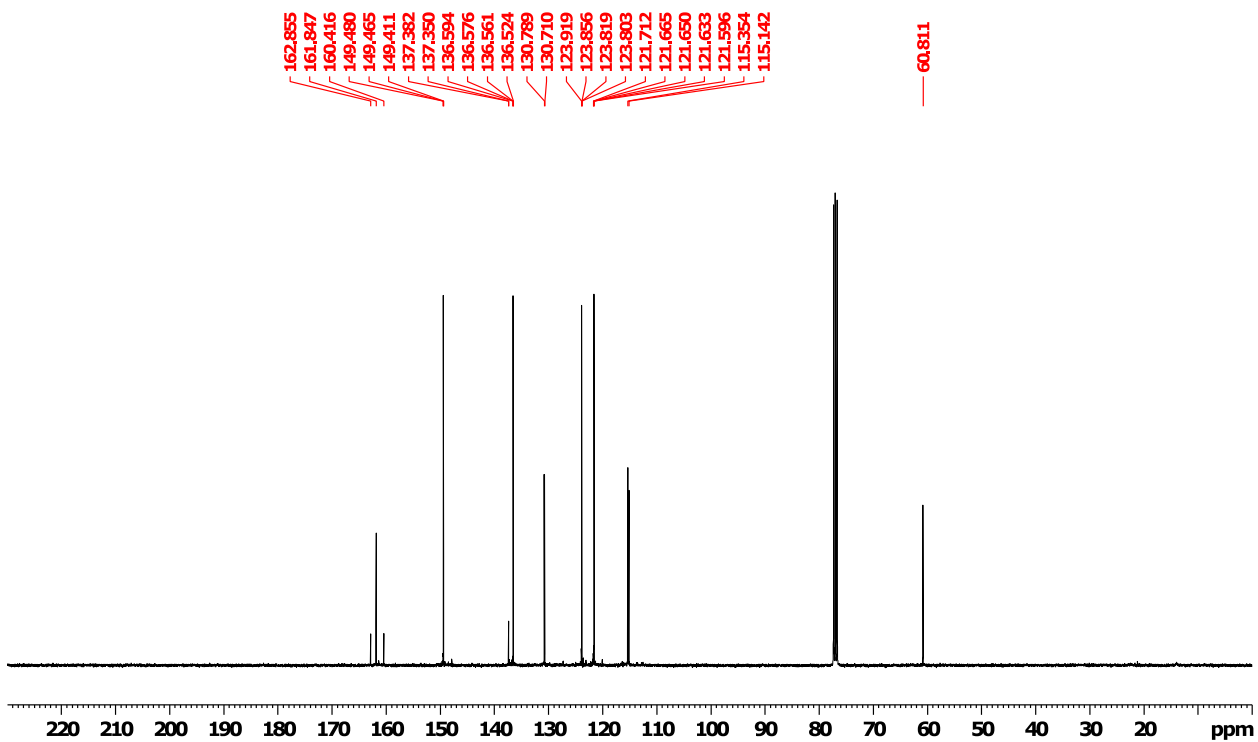


Figure S4. ¹³C{¹H} NMR of di(2-pyridyl)(4-fluorophenyl)methane (L5)

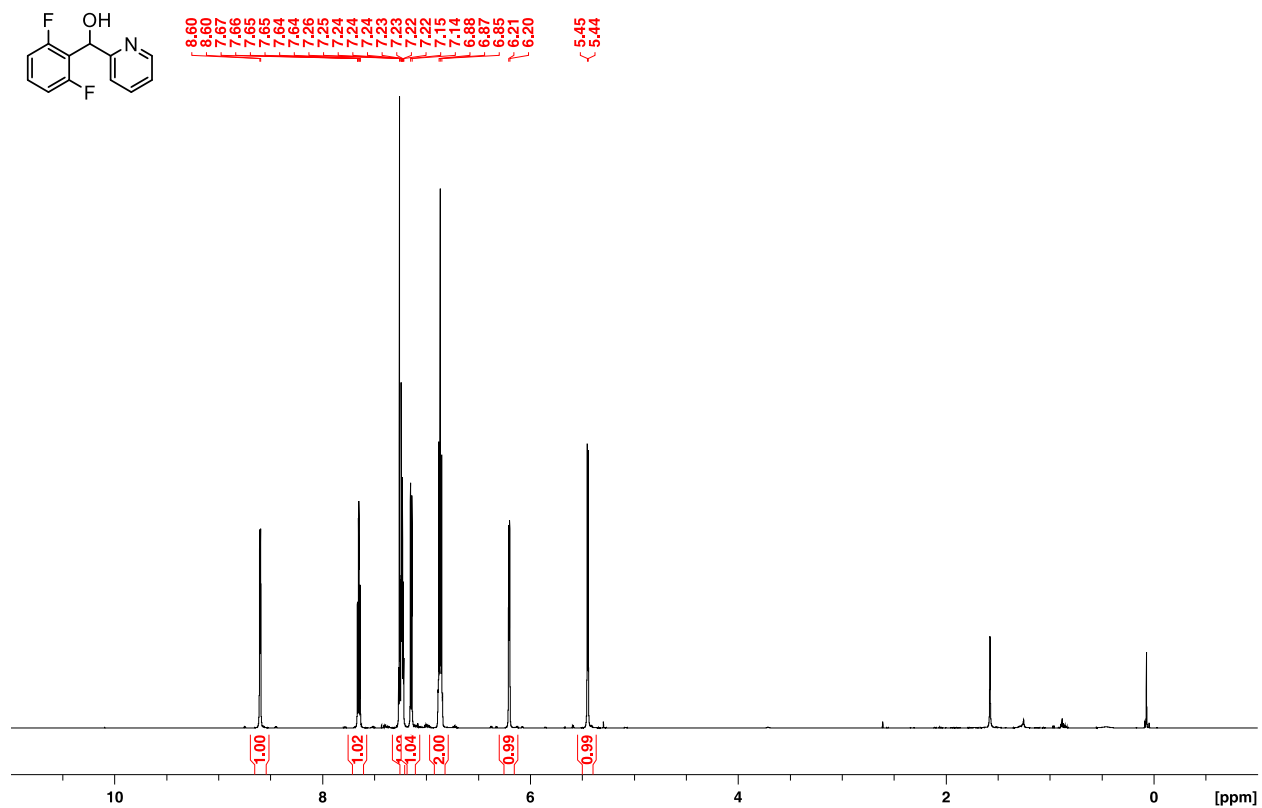


Figure S5. ¹H NMR of (2,6-difluorophenyl)(2-pyridyl)methanol

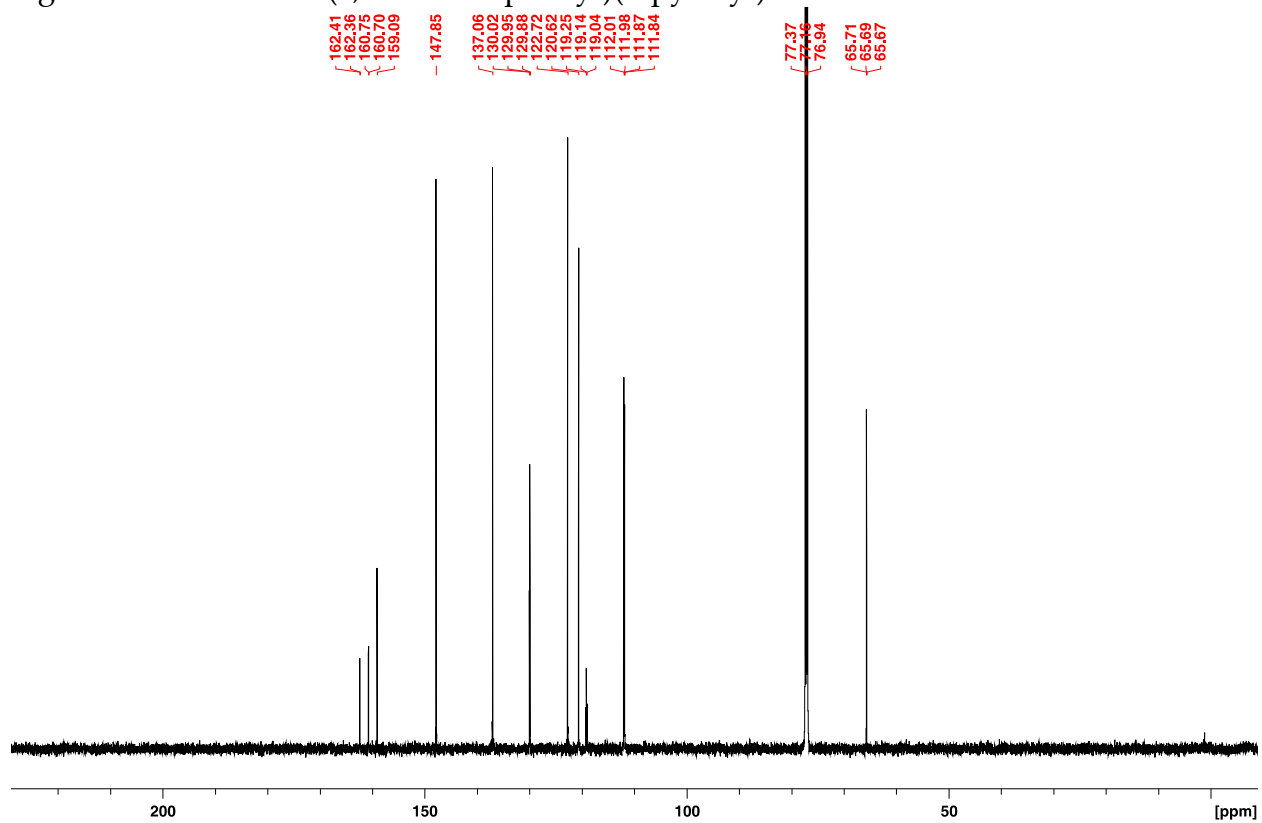


Figure S6. ¹³C{¹H} NMR of (2,6-difluorophenyl)(2-pyridyl)methanol

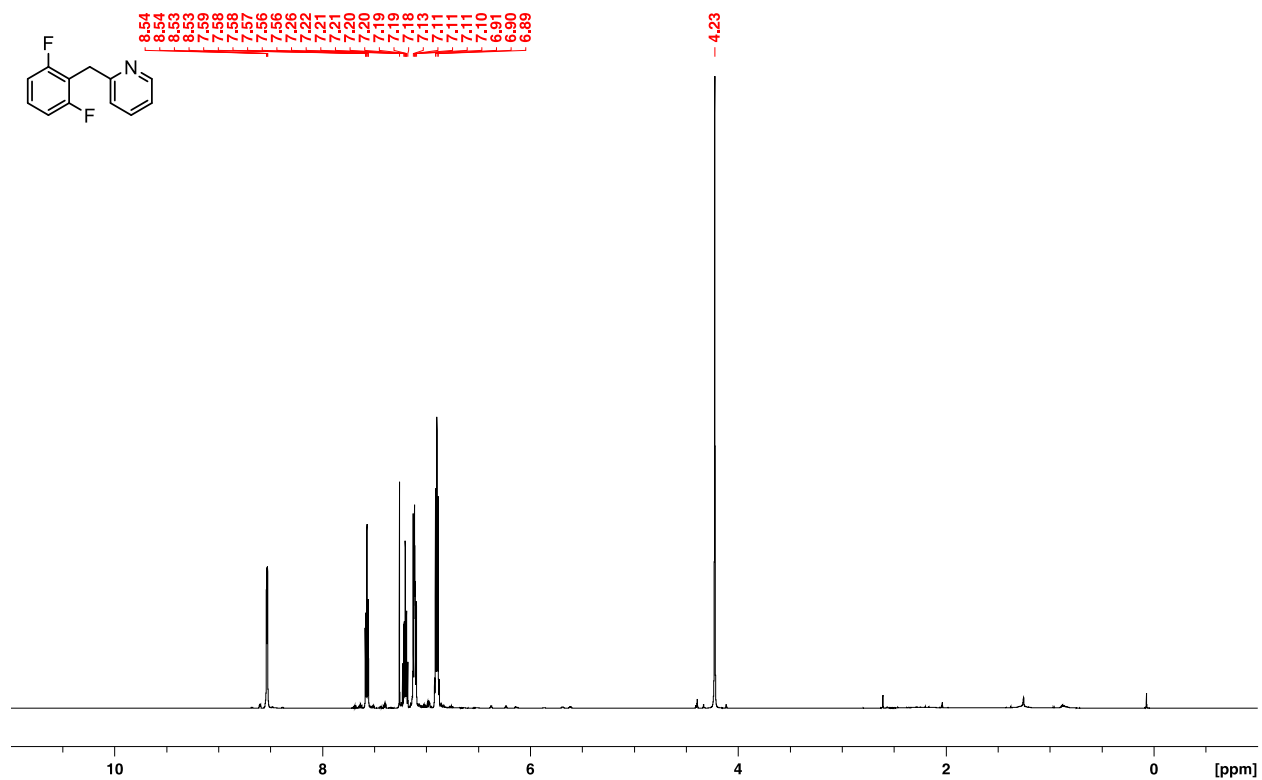


Figure S7. ¹H NMR of 2-(2,6-difluorobenzyl)pyridine

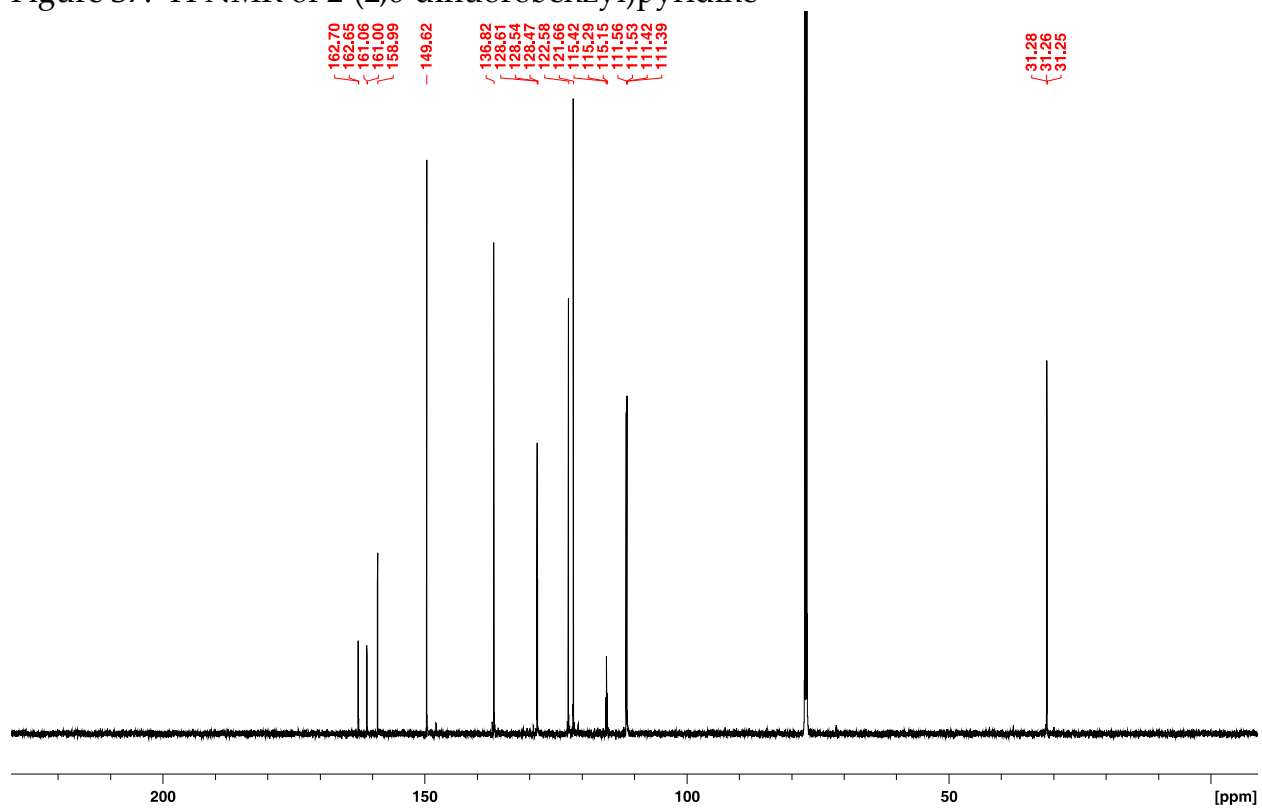


Figure S8. ¹³C{¹H} NMR of 2-(2,6-difluorobenzyl)pyridine

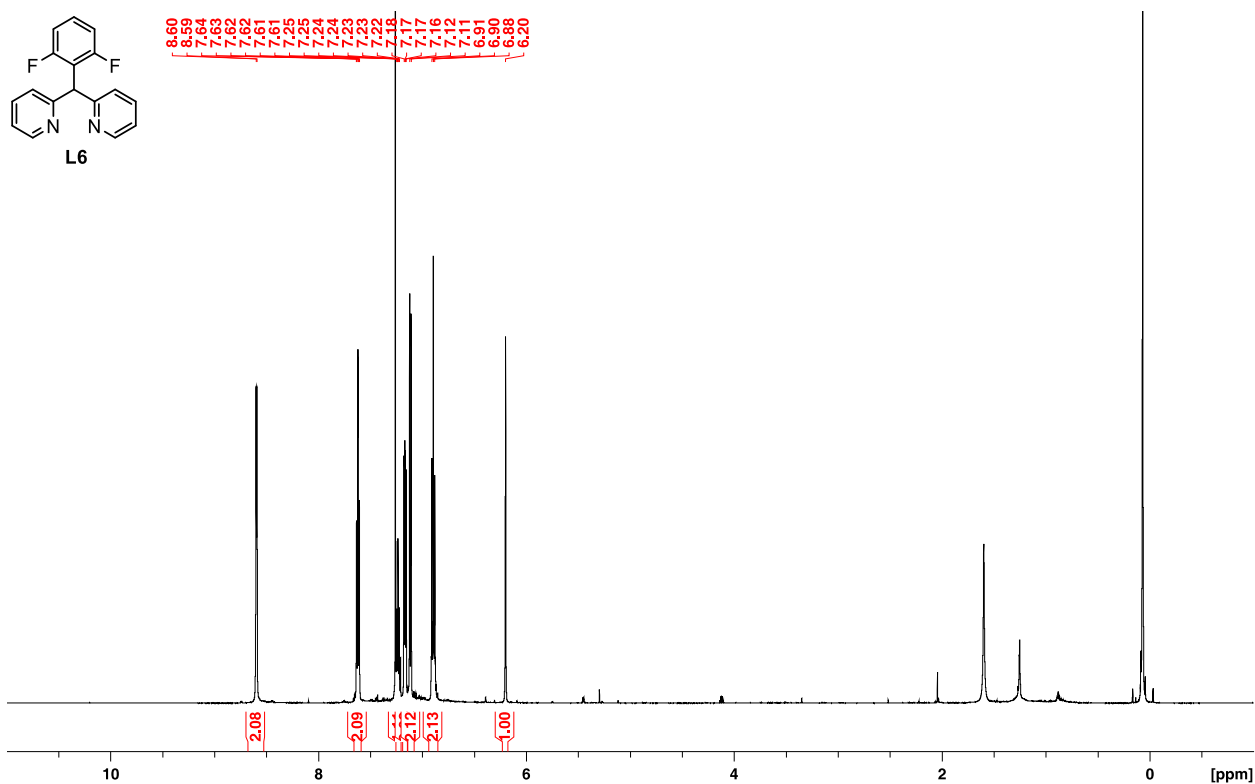


Figure S9. ¹H NMR of di(2-pyridyl)(2,6-difluorophenyl)methane (L6)

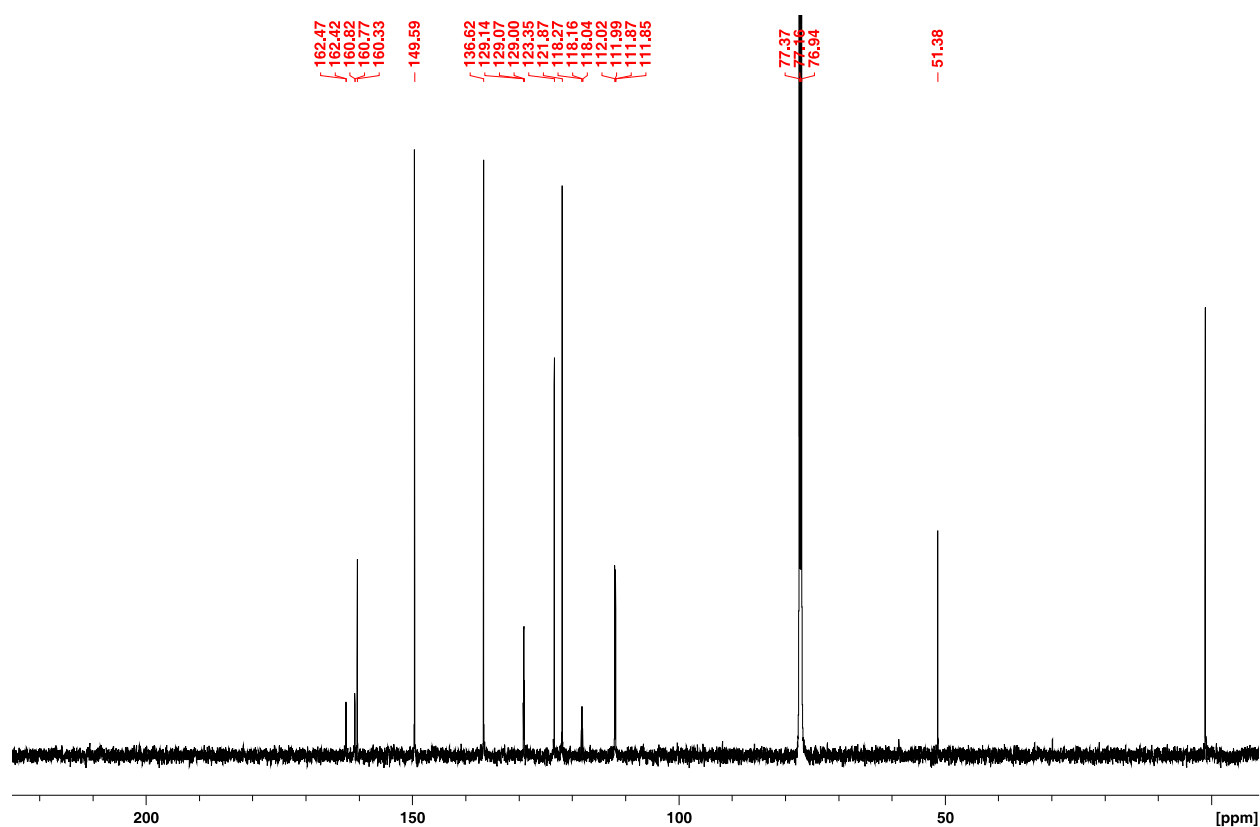


Figure S10. ¹³C{¹H} NMR of di(2-pyridyl)(2,6-difluorophenyl)methane (L6)

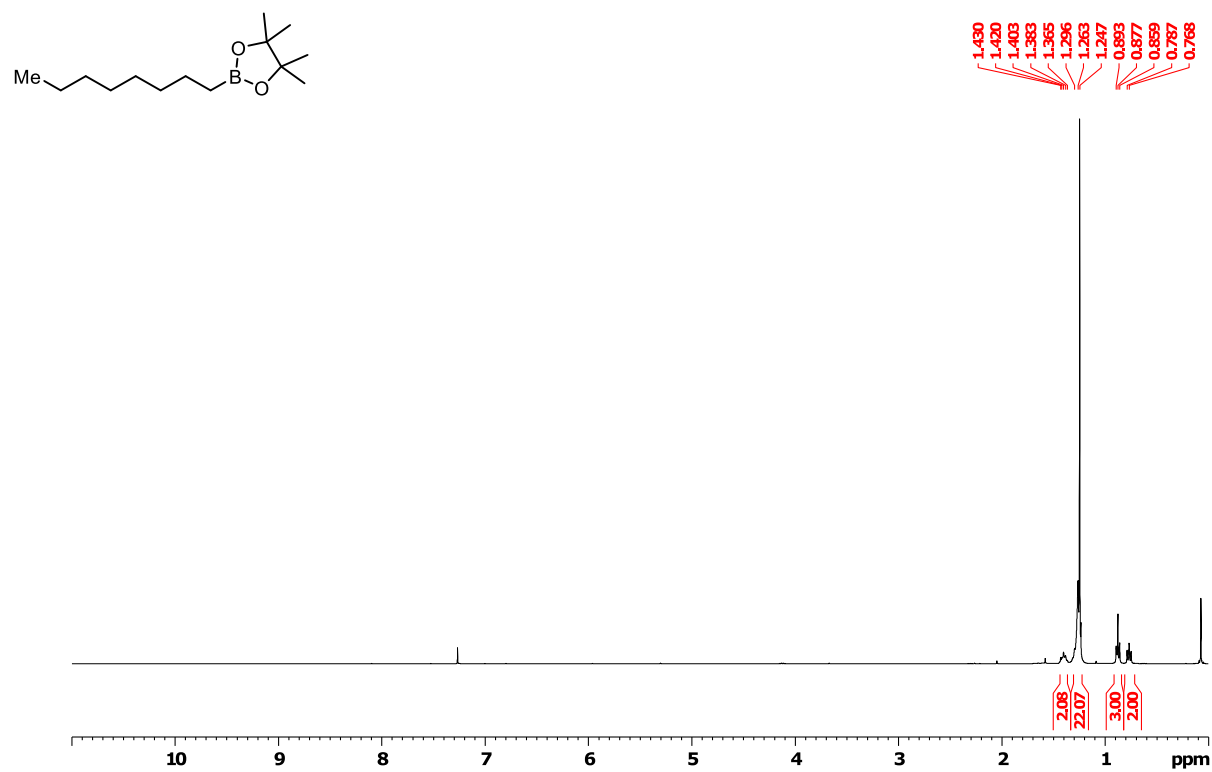


Figure S11. ¹H NMR of 4,4,5,5-tetramethyl-2-octyl-1,3,2-dioxaborolane

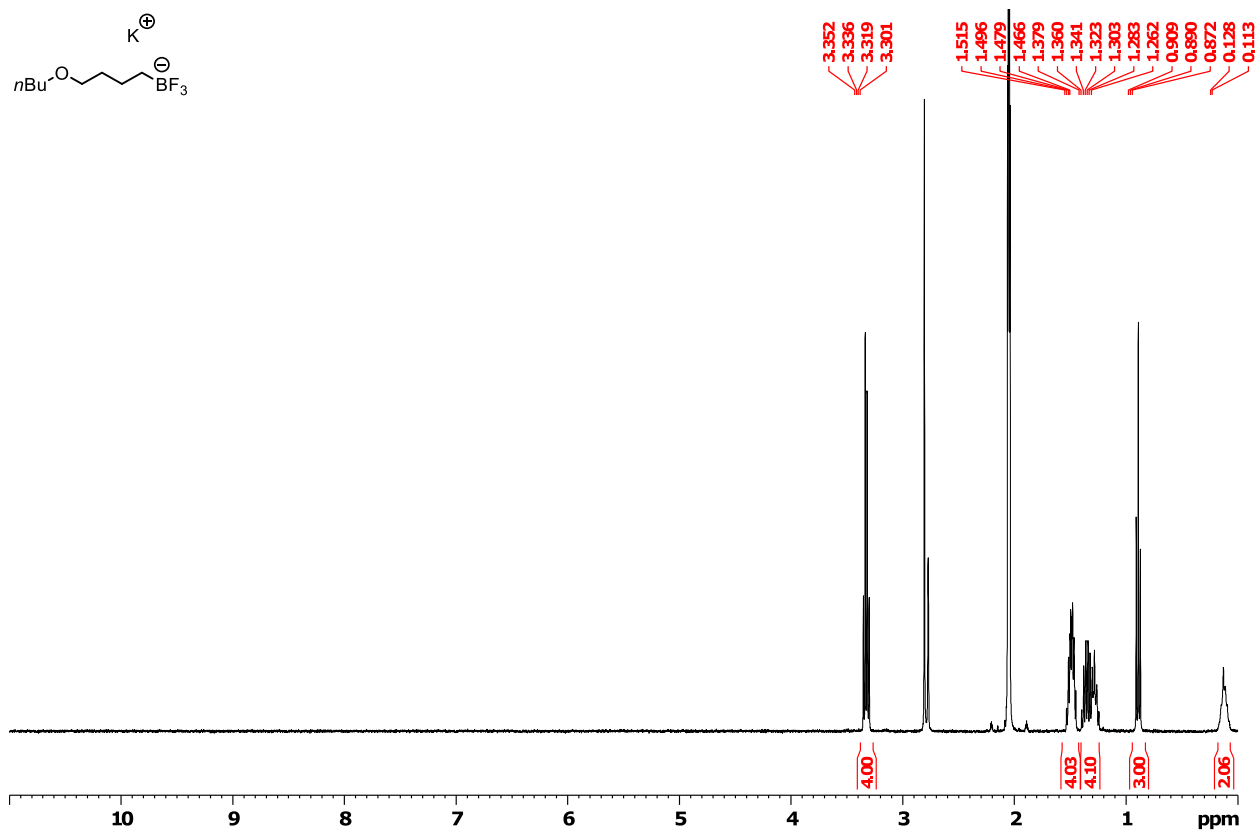


Figure S12. ^1H NMR of potassium 4-(*n*-butoxy)*n*-butyltrifluoroborate

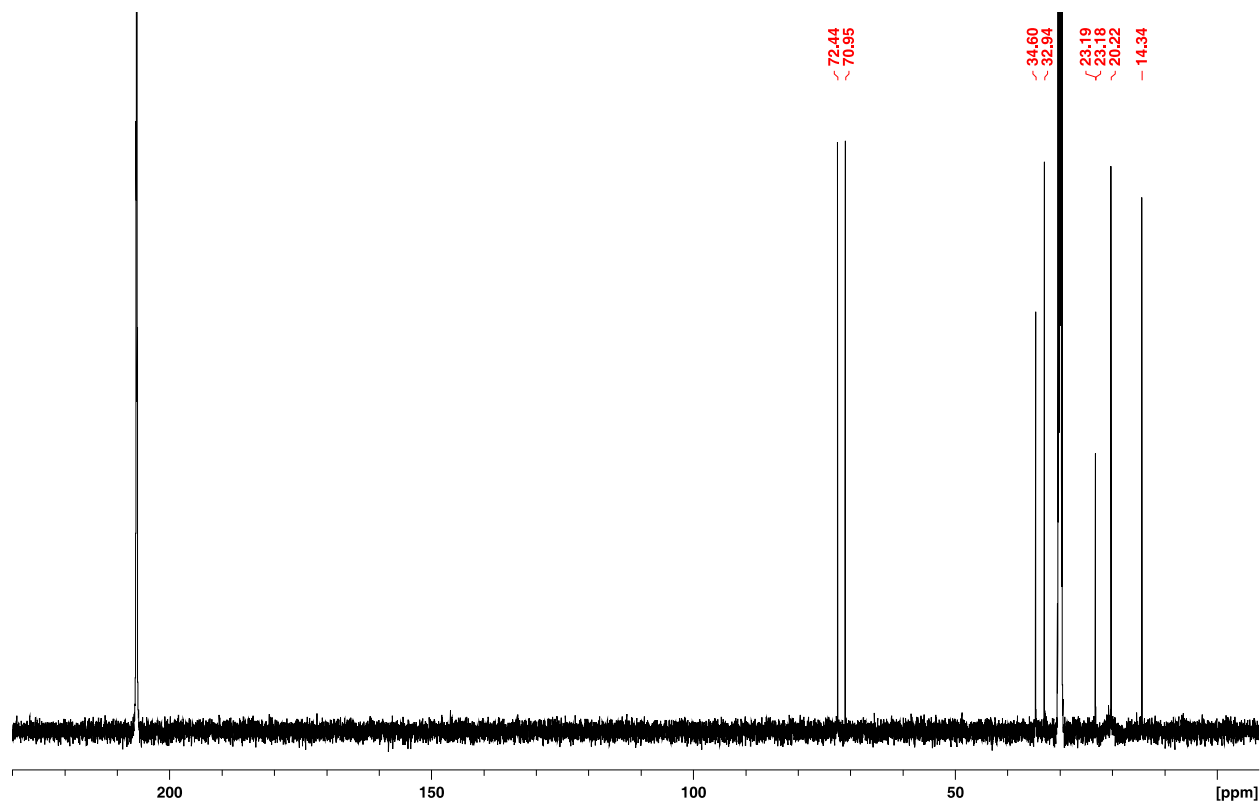


Figure S13. $^{13}\text{C}\{^1\text{H}\}$ NMR of potassium 4-(*n*-butoxy)*n*-butyltrifluoroborate

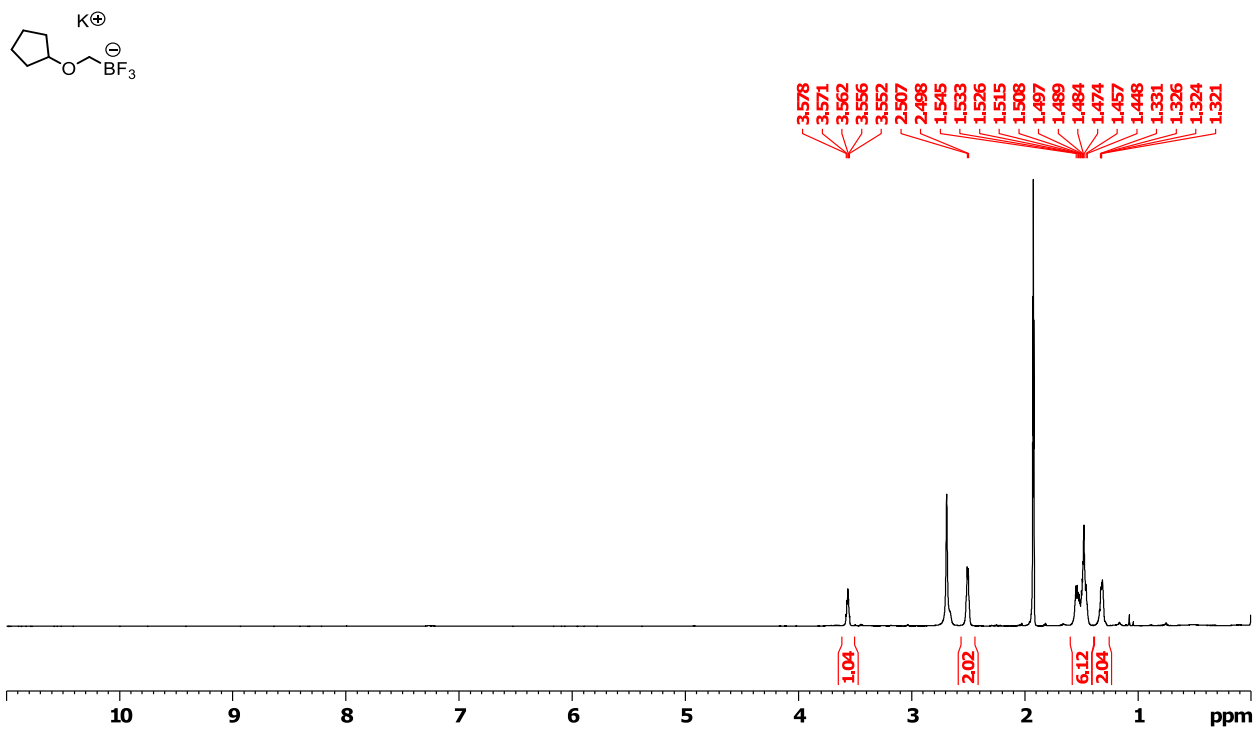


Figure S14. ¹H NMR of potassium (cyclopentyloxy)methyltrifluoroborate

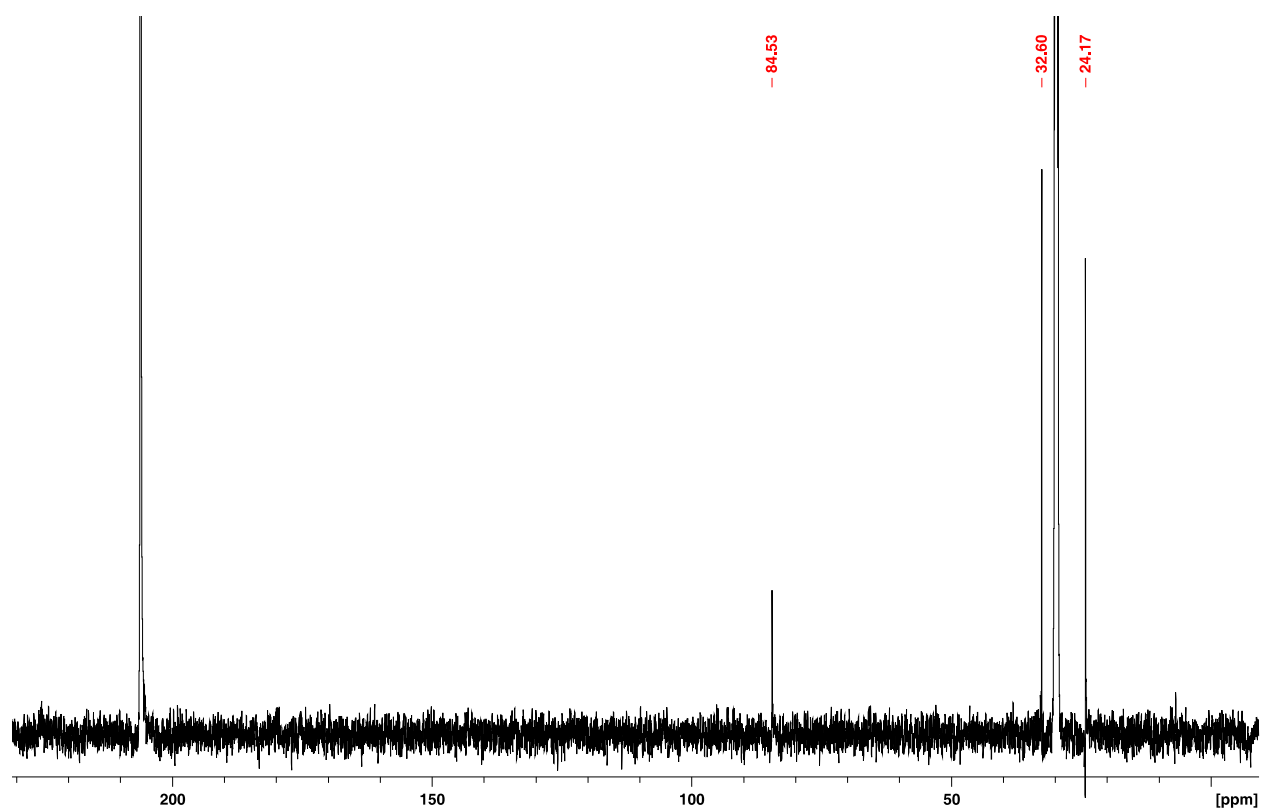


Figure S15. ¹³C{¹H} NMR of potassium (cyclopentyloxy)methyltrifluoroborate

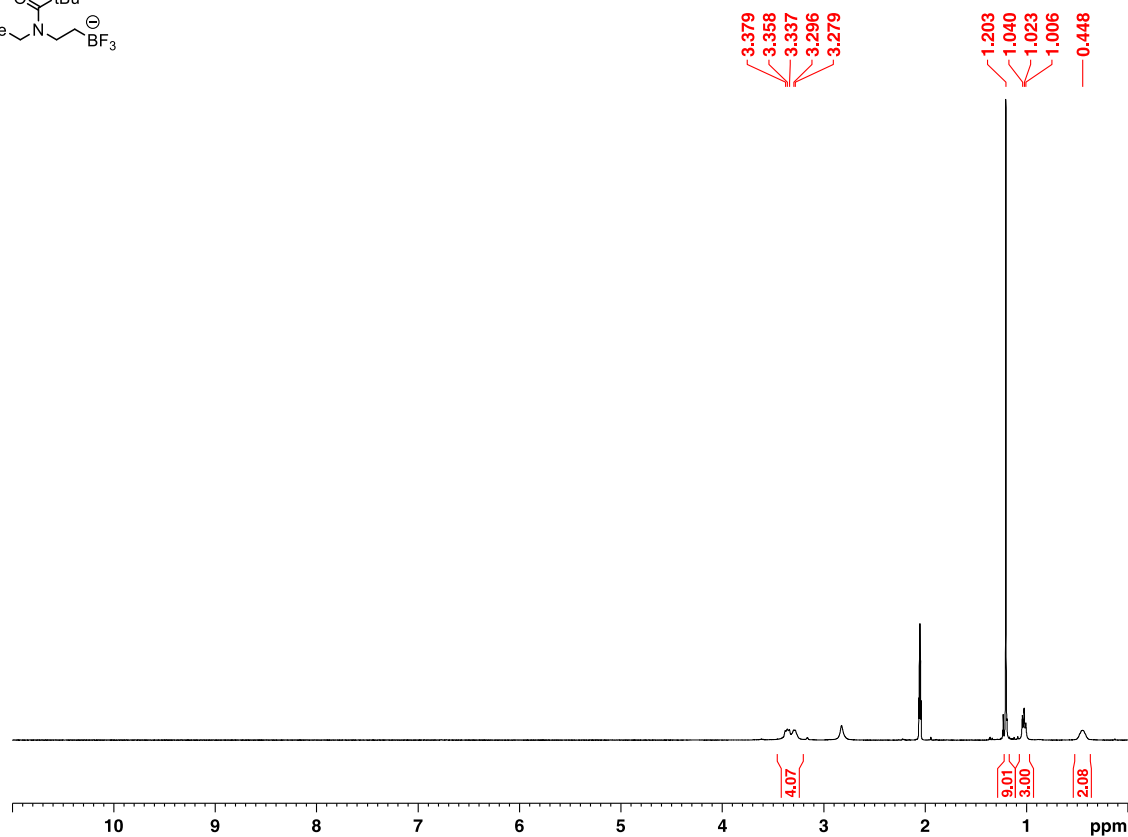
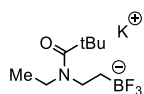


Figure S16. ¹H NMR of potassium (2-(N-ethylpivalamido)ethyl)trifluoroborate

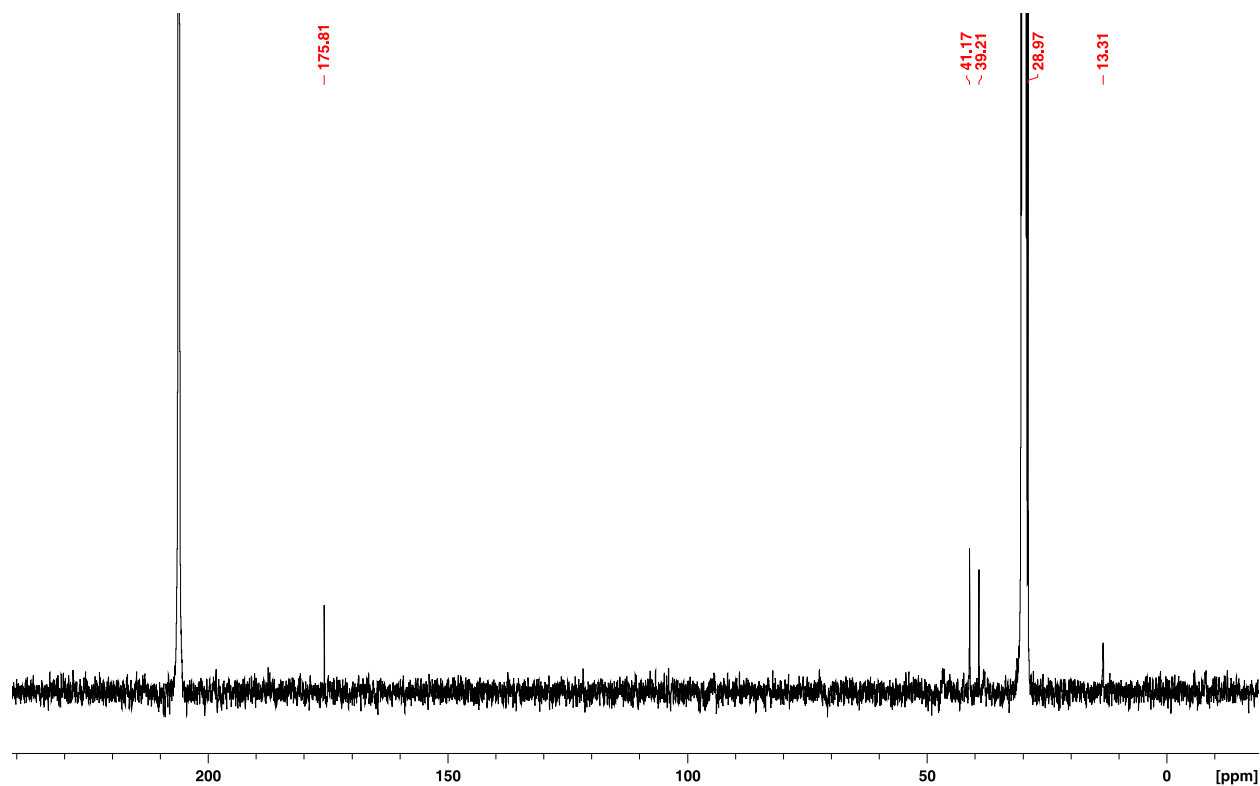


Figure S17. ¹³C{¹H} NMR of potassium (2-(N-ethylpivalamido)ethyl)trifluoroborate

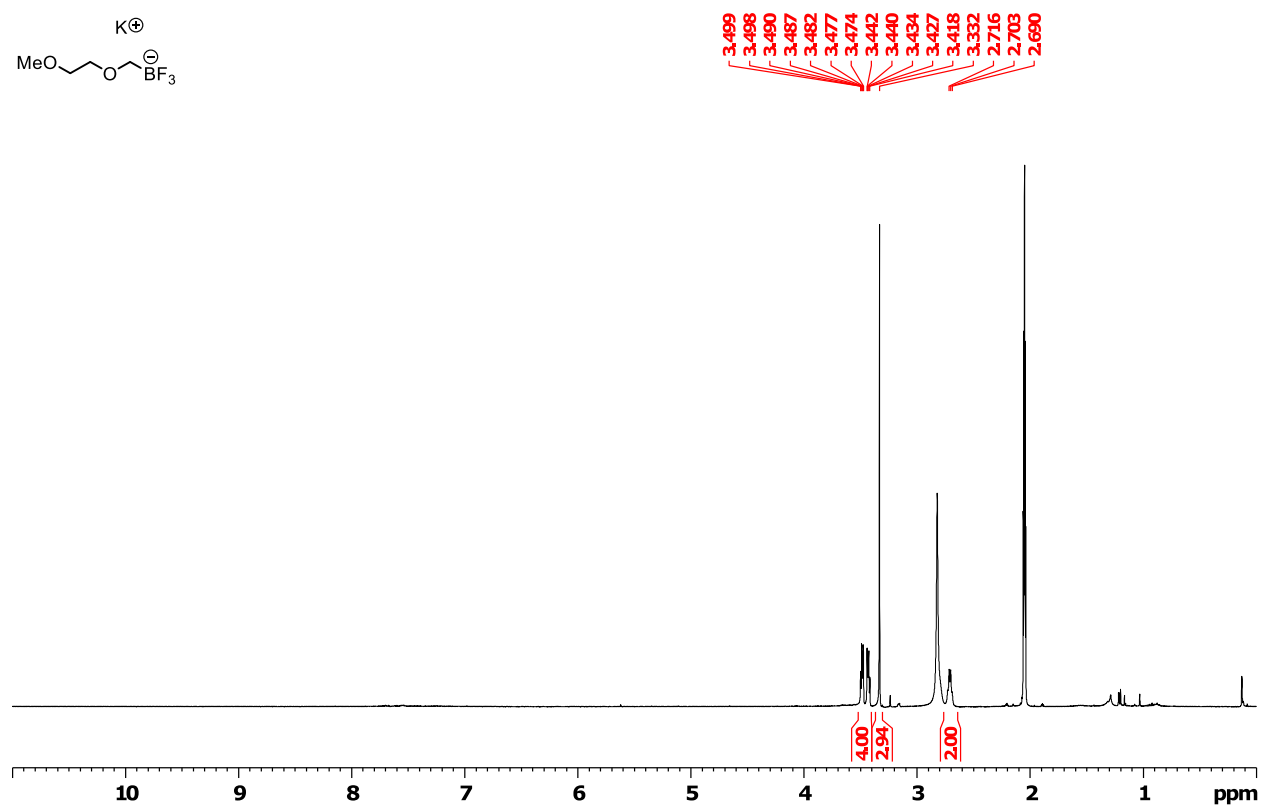
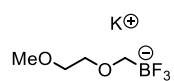


Figure S18. ^1H NMR of potassium (2-methoxyethoxy)methyltrifluoroborate

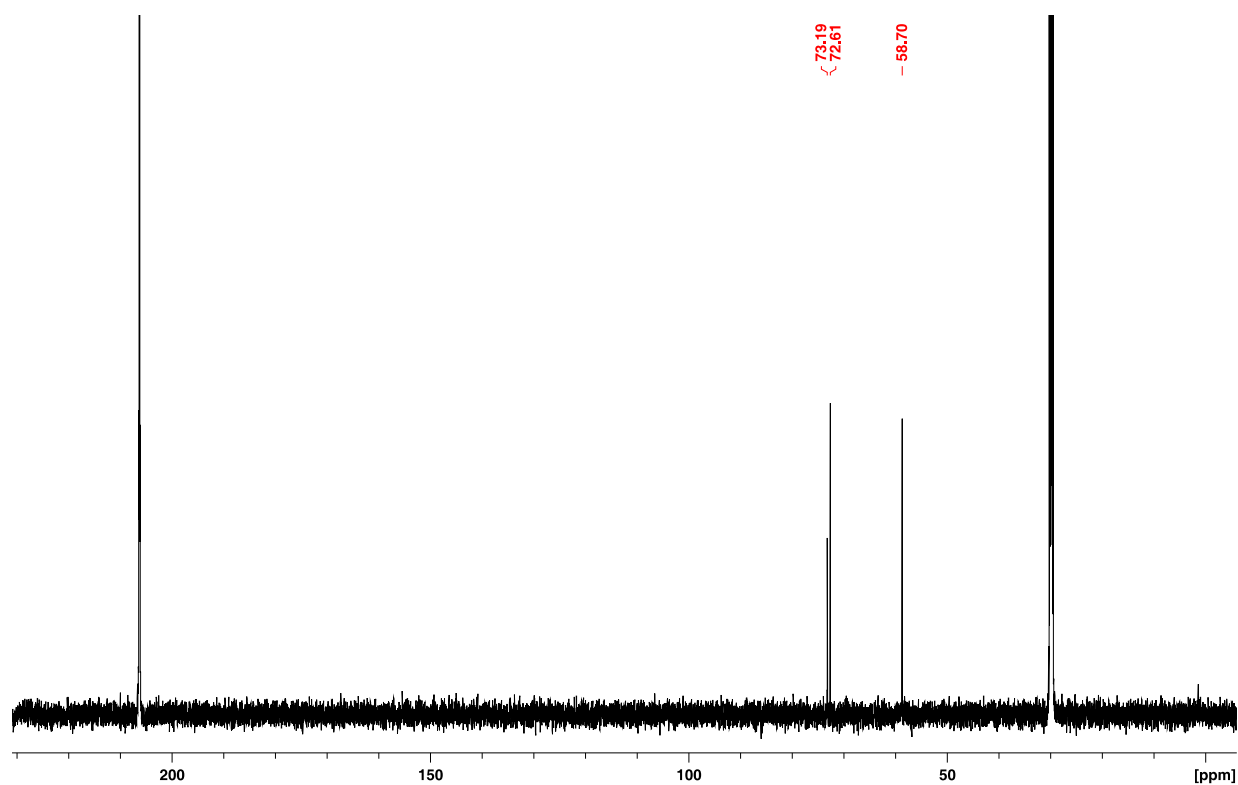


Figure S19. $^{13}\text{C}\{^1\text{H}\}$ NMR of potassium (2-methoxyethoxy)methyltrifluoroborate

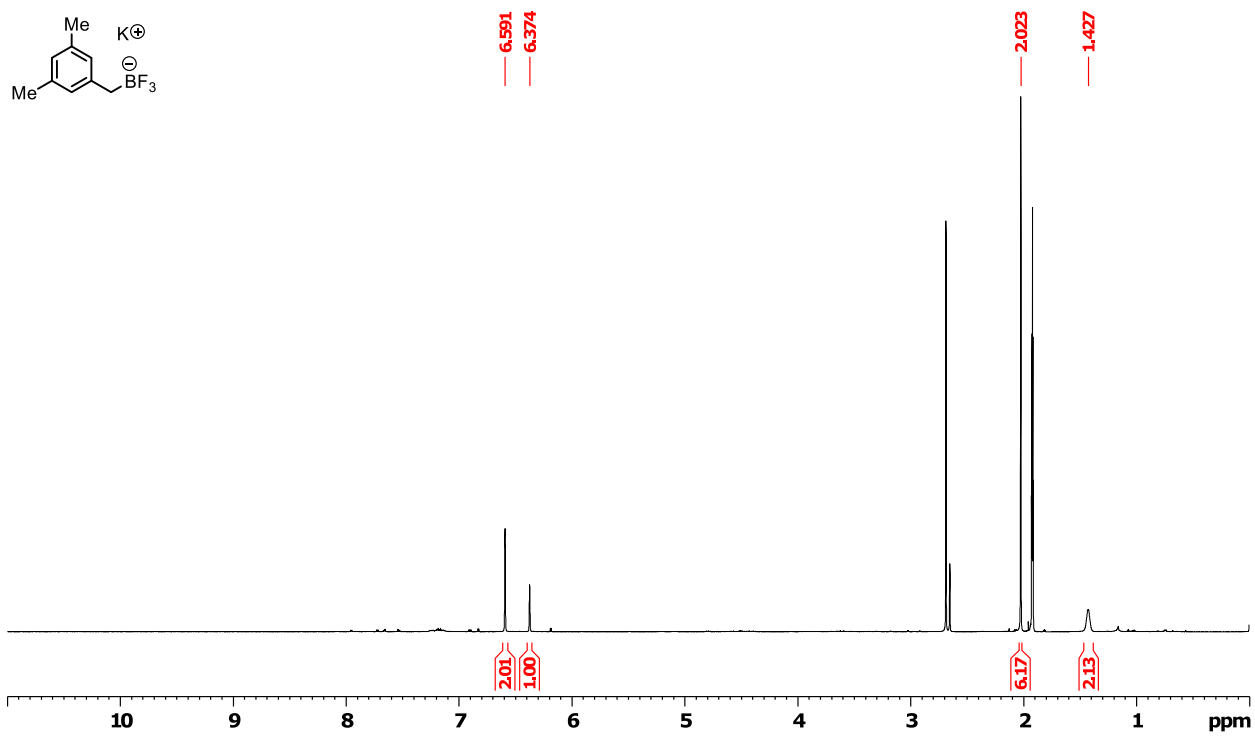


Figure S20. ¹H NMR of potassium (3,5-dimethylbenzyl)trifluoroborate

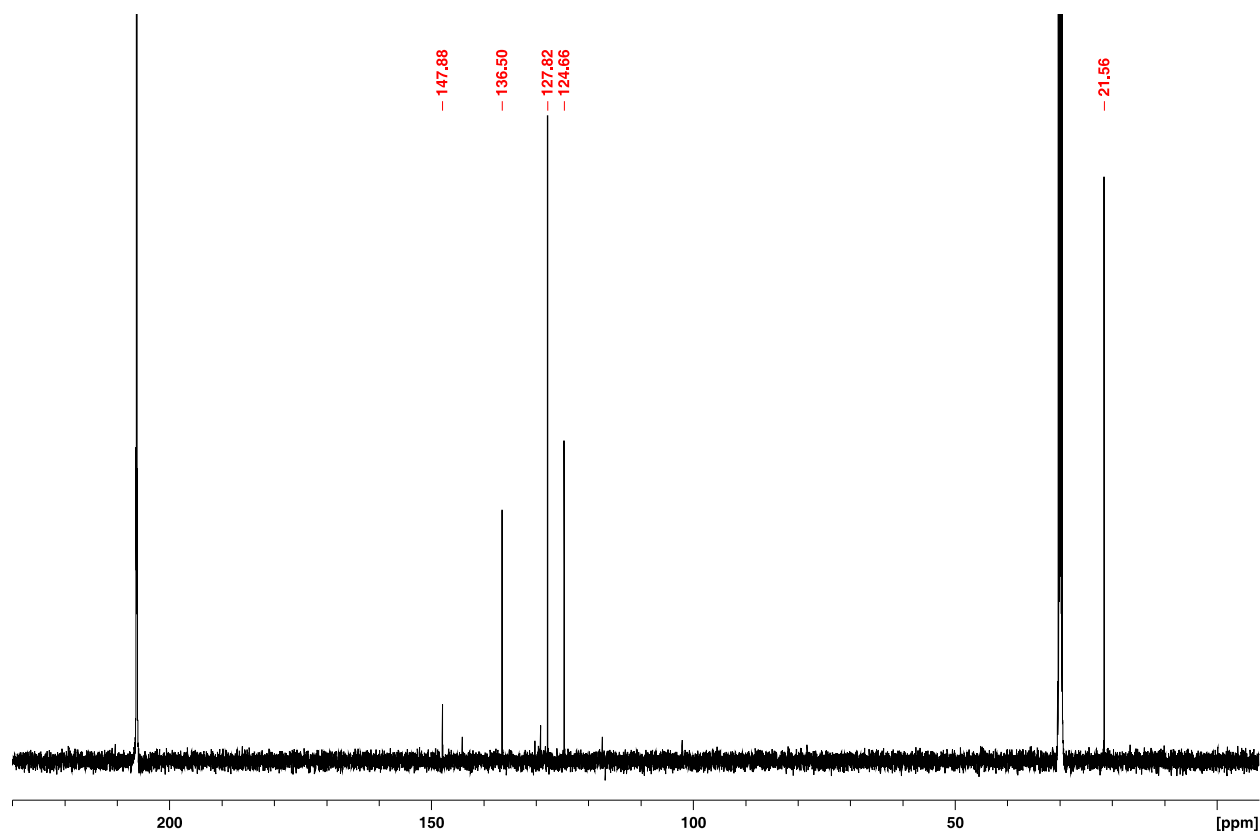


Figure S21. ¹³C{¹H} NMR of potassium (3,5-dimethylbenzyl)trifluoroborate

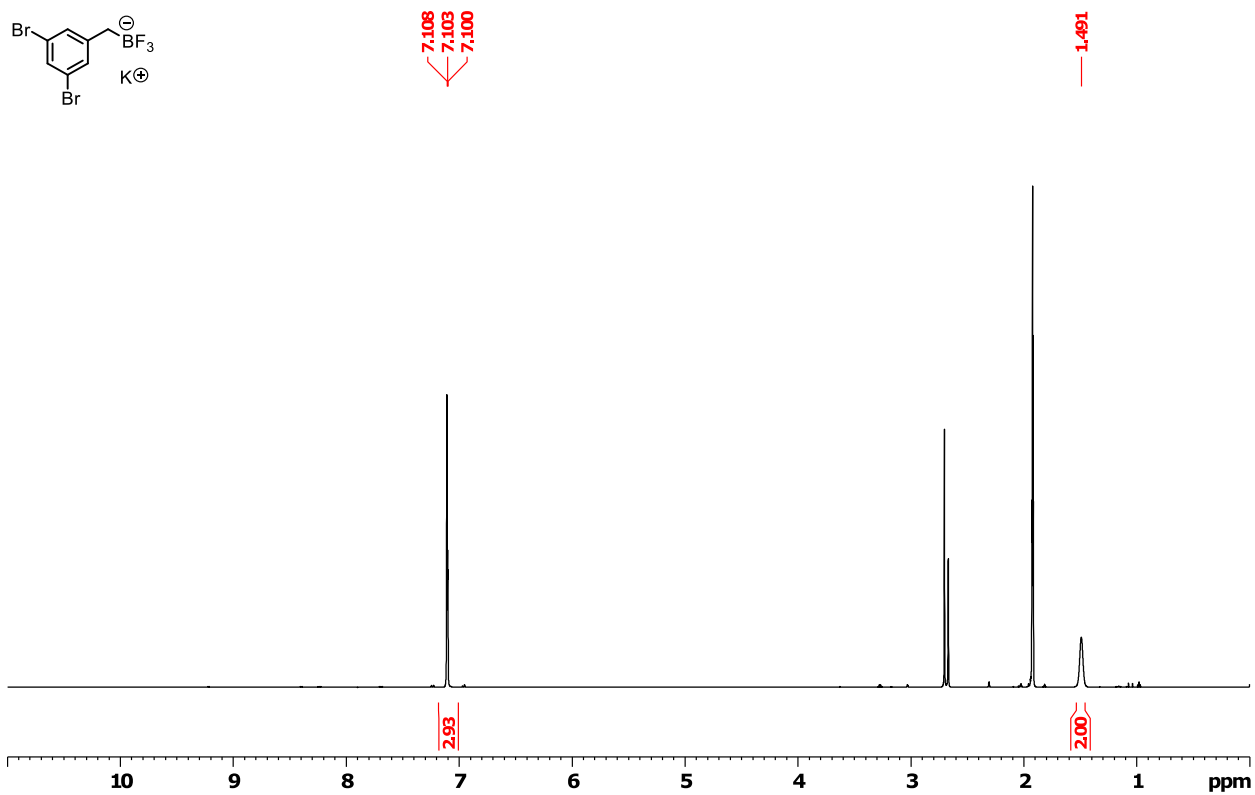


Figure S22. ¹H NMR of potassium (3,5-dibromobenzyl)trifluoroborate

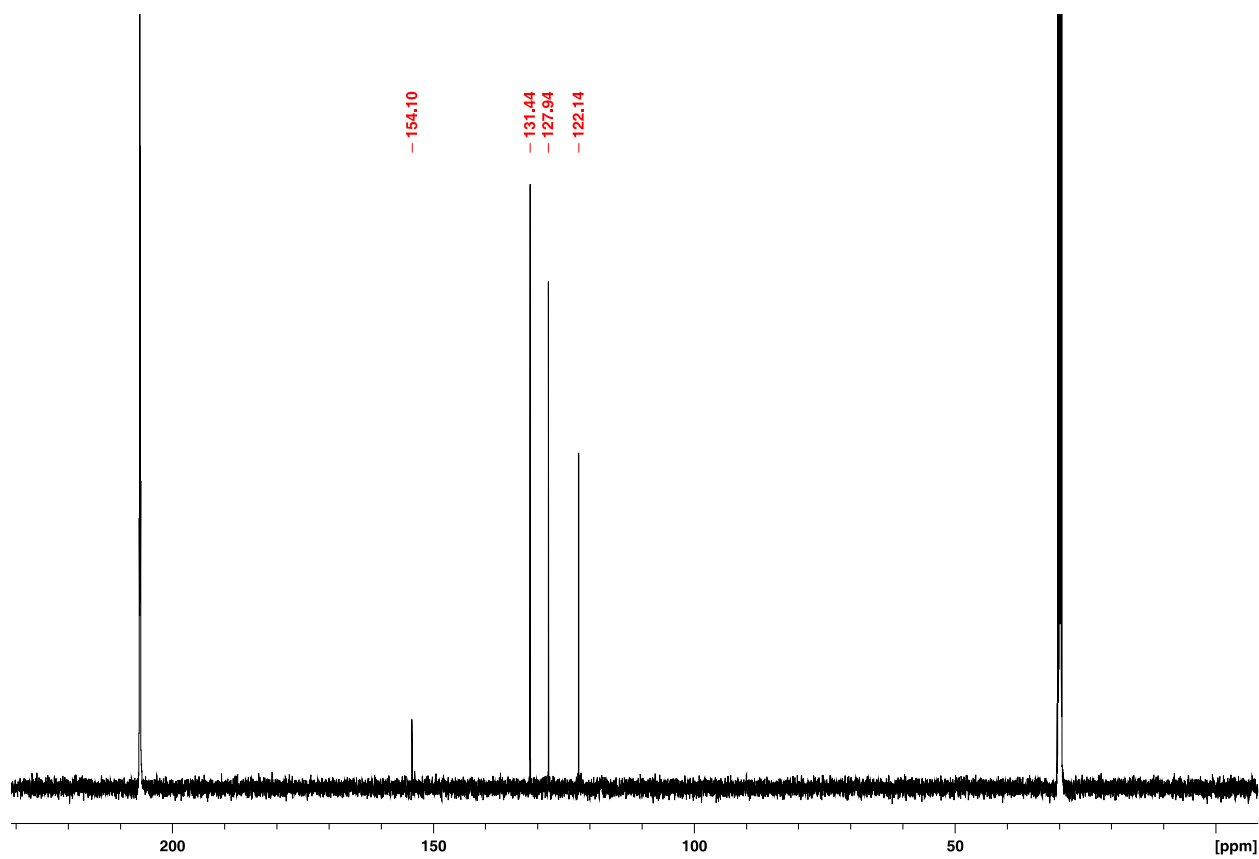


Figure S23. ¹³C{¹H} NMR of potassium (3,5-dibromobenzyl)trifluoroborate

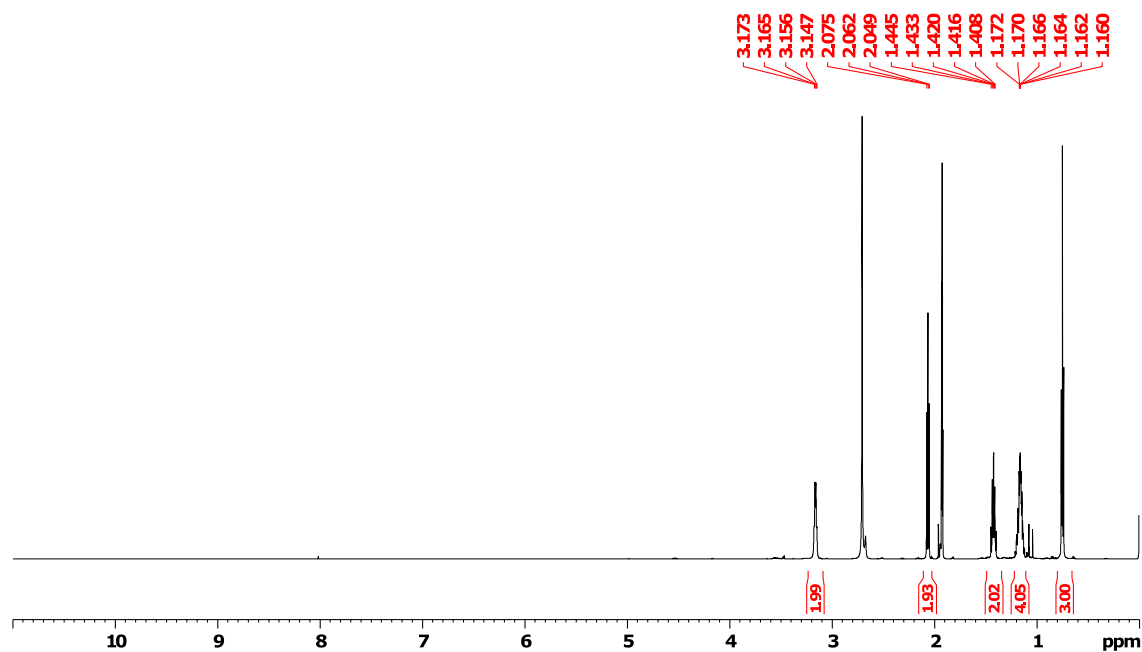
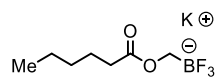


Figure S24. ¹H NMR of potassium methyltrifluoroborate hexanoate

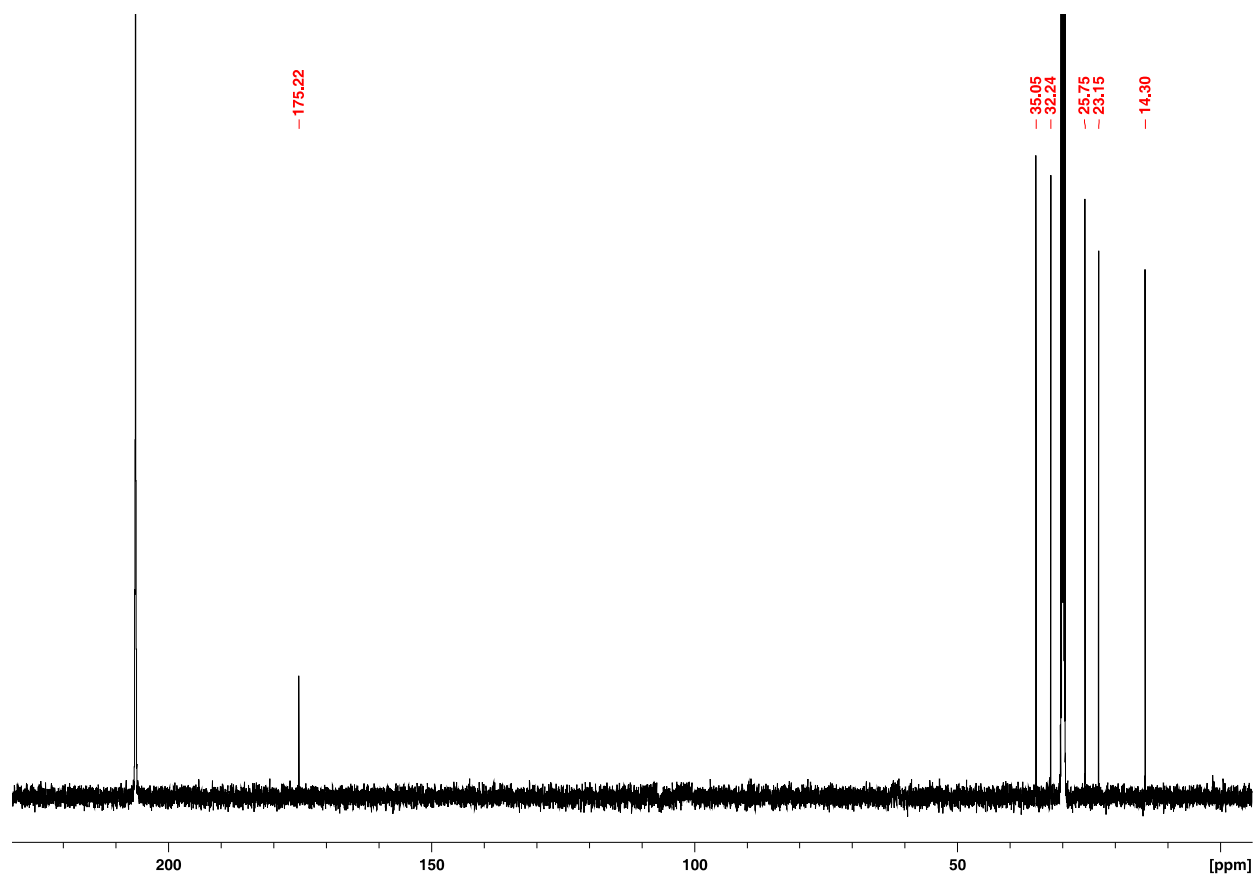


Figure S25. ¹³C{¹H} NMR of potassium methyltrifluoroborate hexanoate

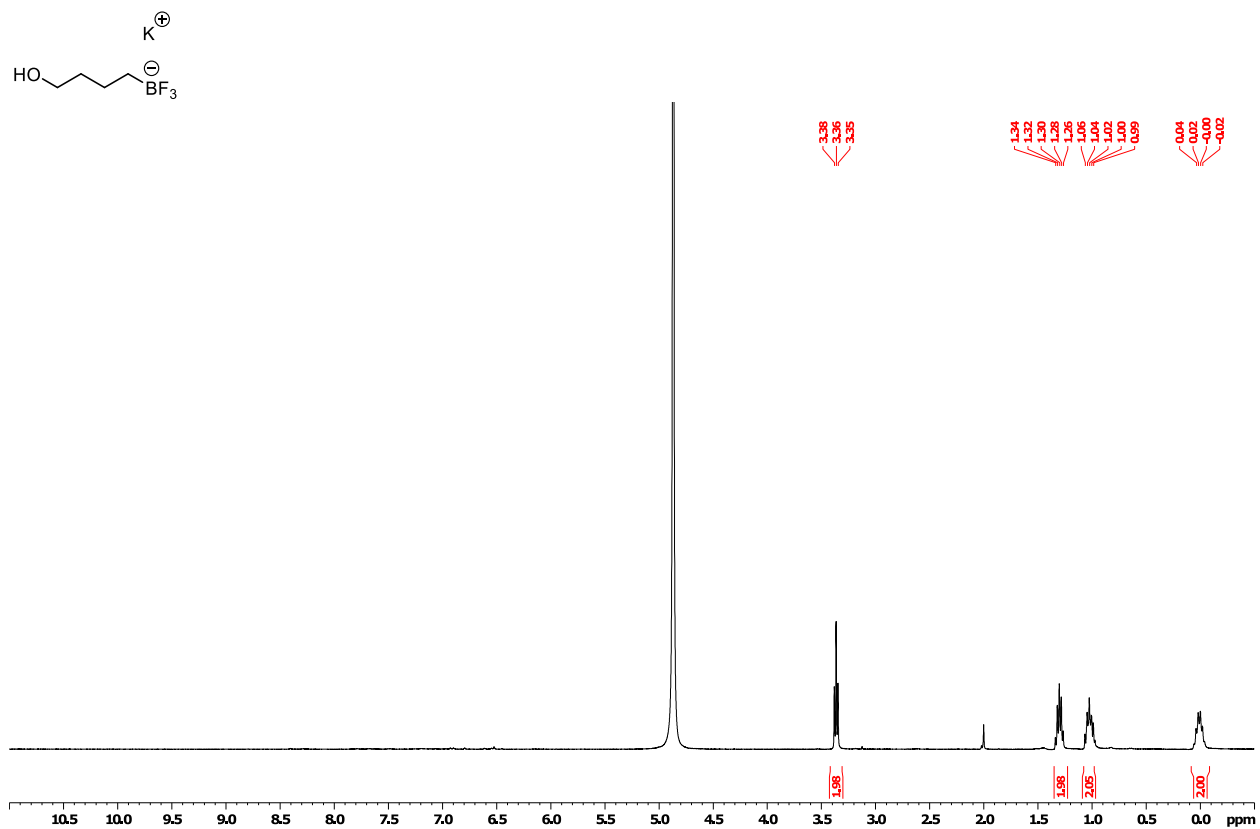


Figure S26. ¹H NMR of potassium (4-hydroxybutyl)trifluoroborate

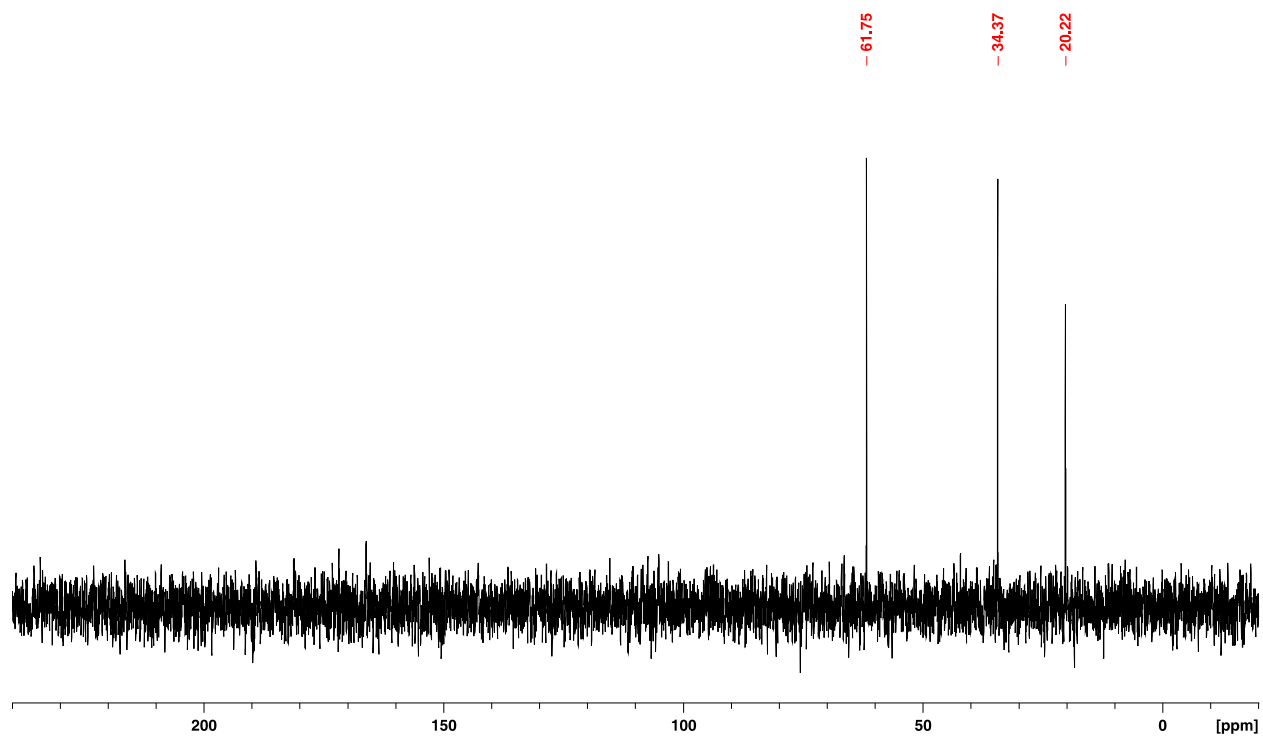


Figure S27. ¹³C{¹H} NMR of potassium (4-hydroxybutyl)trifluoroborate

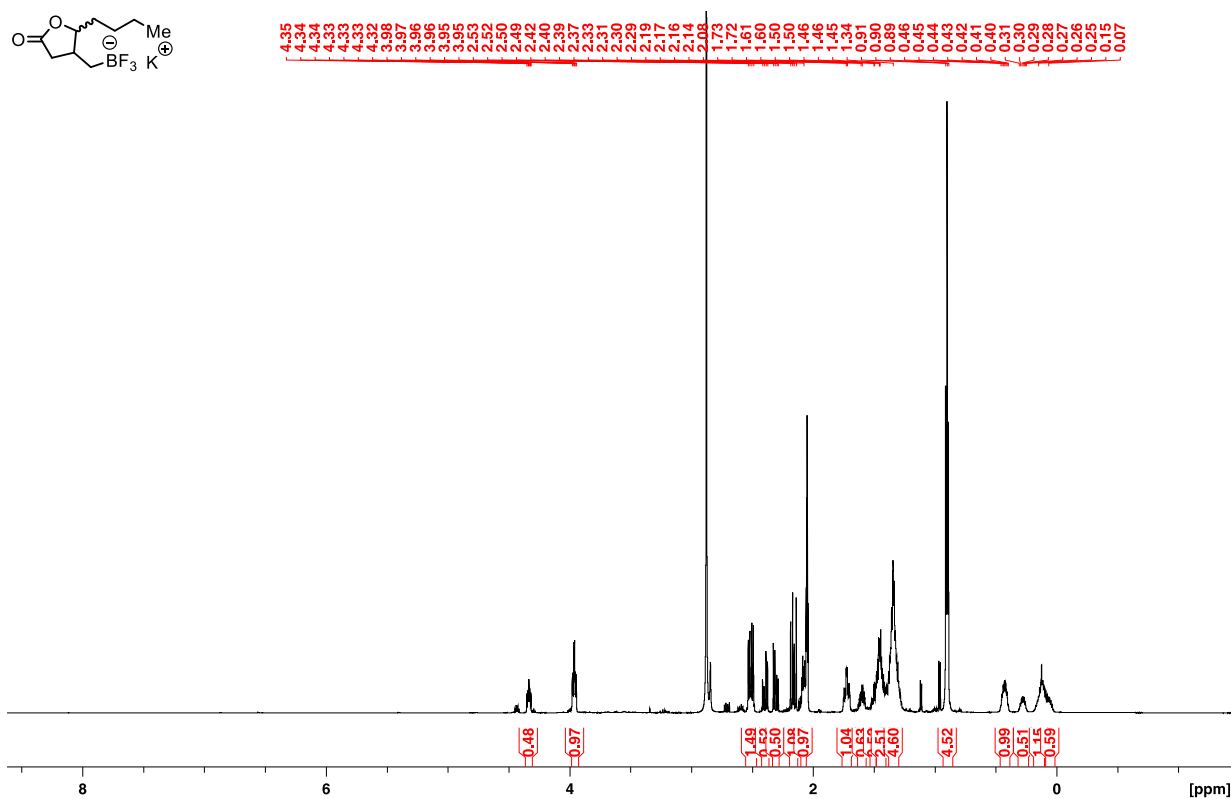


Figure S28. ¹H NMR of K[4-methyl-5-(4-(trifluoroboranyl)butyl)dihydrofuran-2-one]

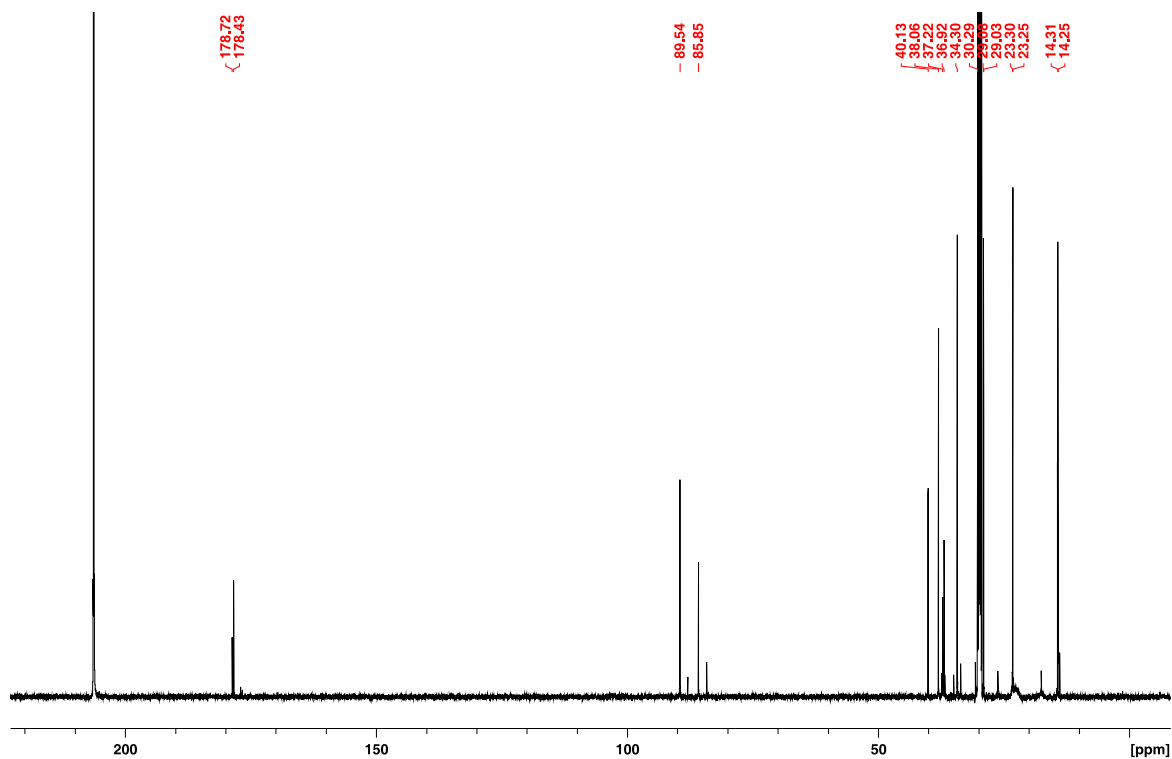


Figure S29. ¹³C{¹H} NMR of K[4-methyl-5-(4-(trifluoroboranyl)butyl)dihydrofuran-2-one]

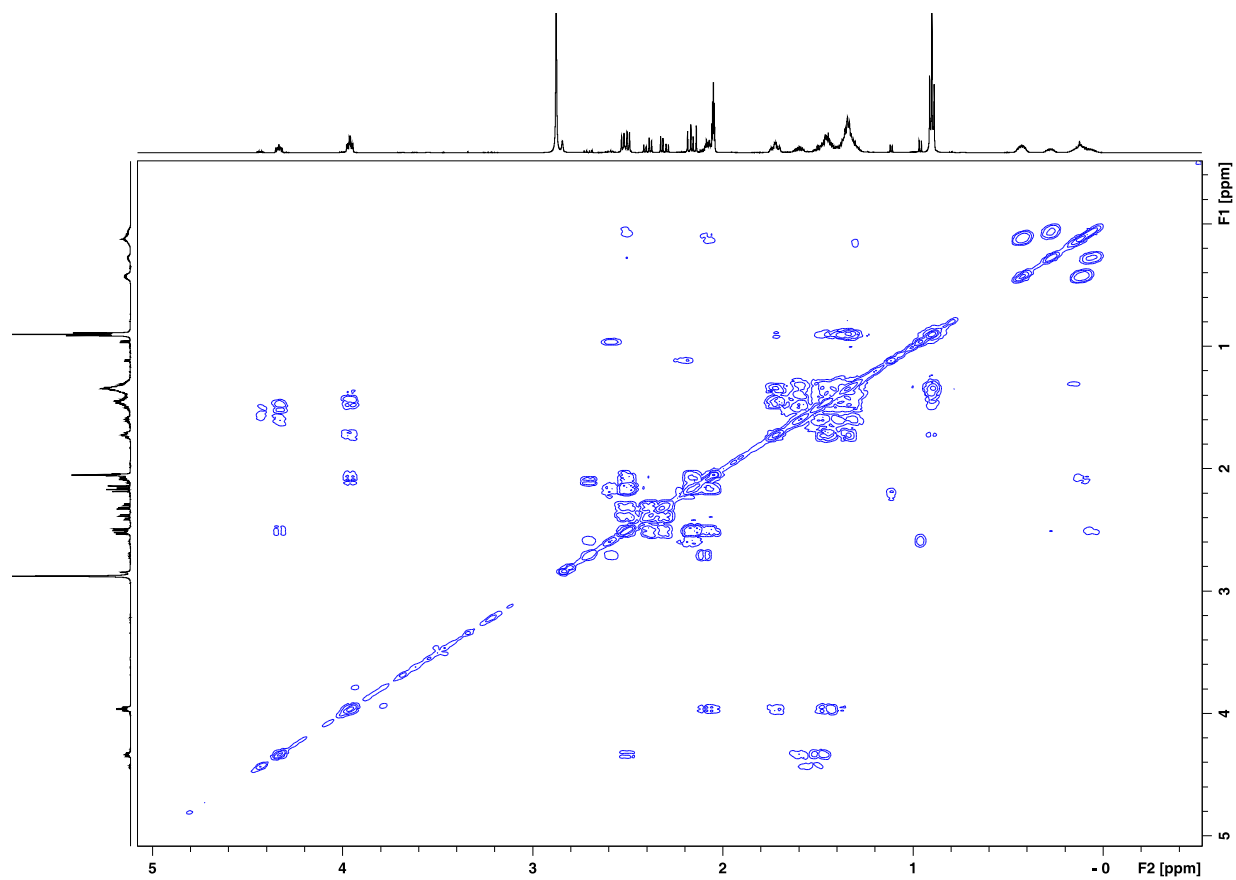


Figure S30. ^1H COSY of K[4-methyl-5-(4-(trifluoroboranyl)butyl)dihydrofuran-2-one]

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