Supporting Information

for

Synthesis of tetraarylborates via tetralithio intermediates and the effect of polar functional groups and cation on their crystal structures

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^{1}H and ^{13}C NMR spectra of new compounds

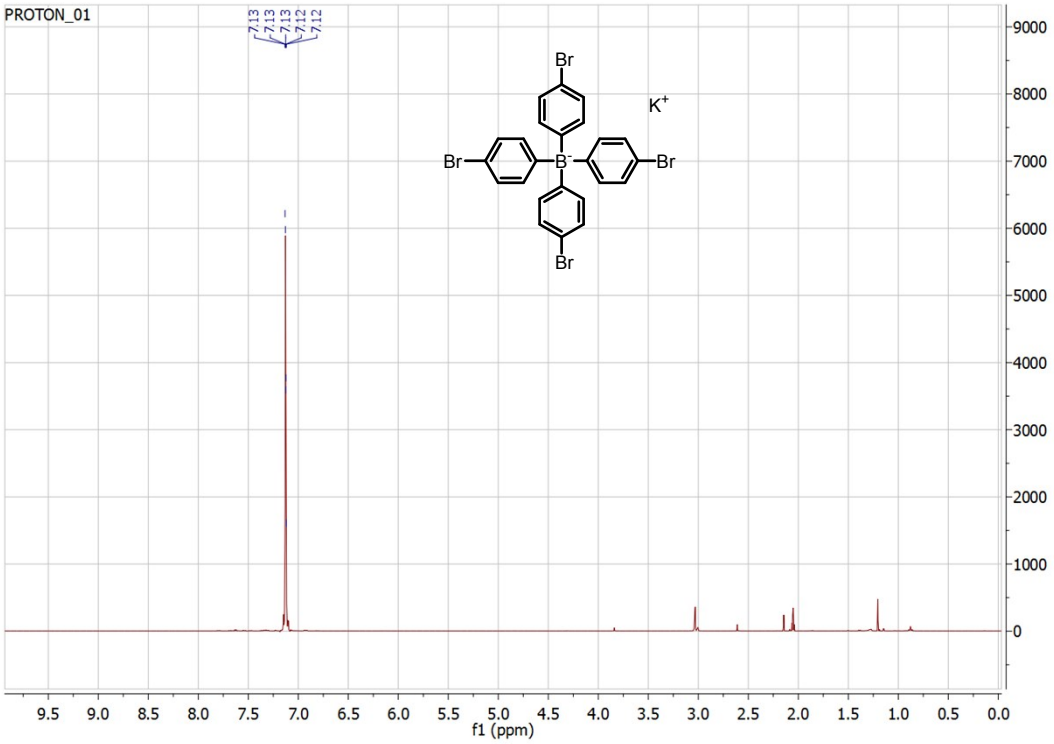

Fig. S1. ^{1}H NMR spectrum (400 MHz, acetone-d_6) of potassium tetrakis(4-bromophenyl)borate (**1**)

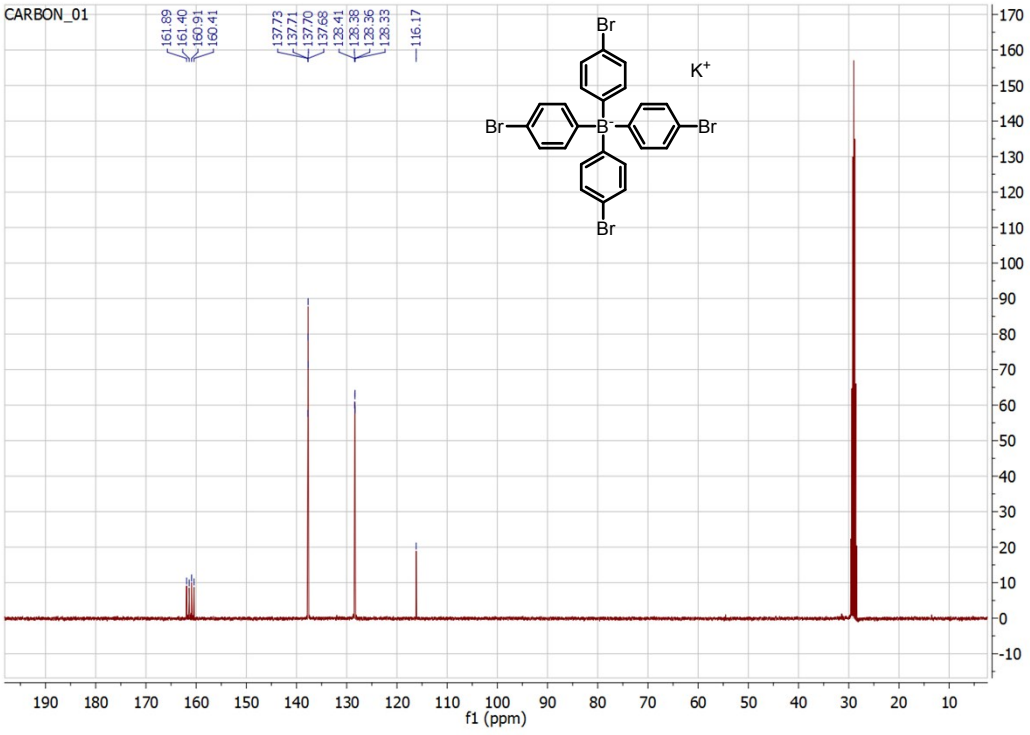

Fig. S2. ^{13}C NMR spectrum (101 MHz, acetone-d_6) of potassium tetrakis(4-bromophenyl)borate (**1**).

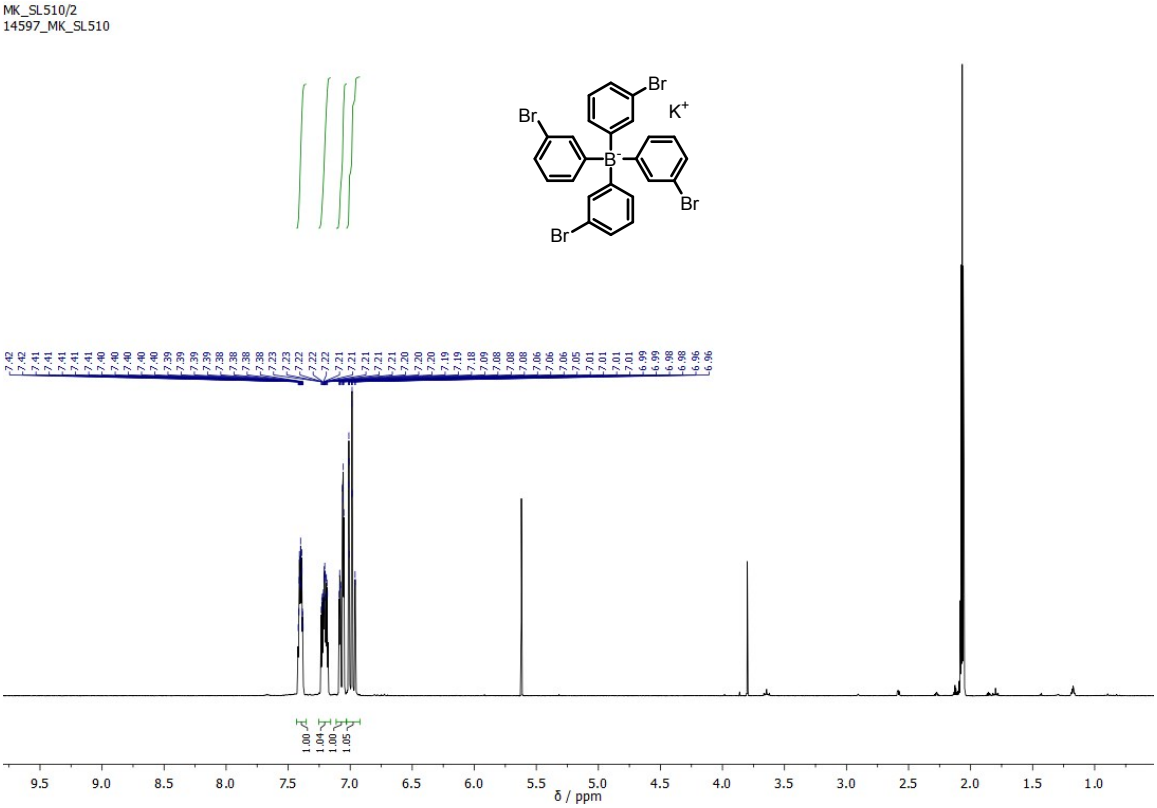

Fig. S3. ^{1}H NMR spectrum (400 MHz, acetone-d_6) of potassium tetrakis(3-bromophenyl)borate (**2**).

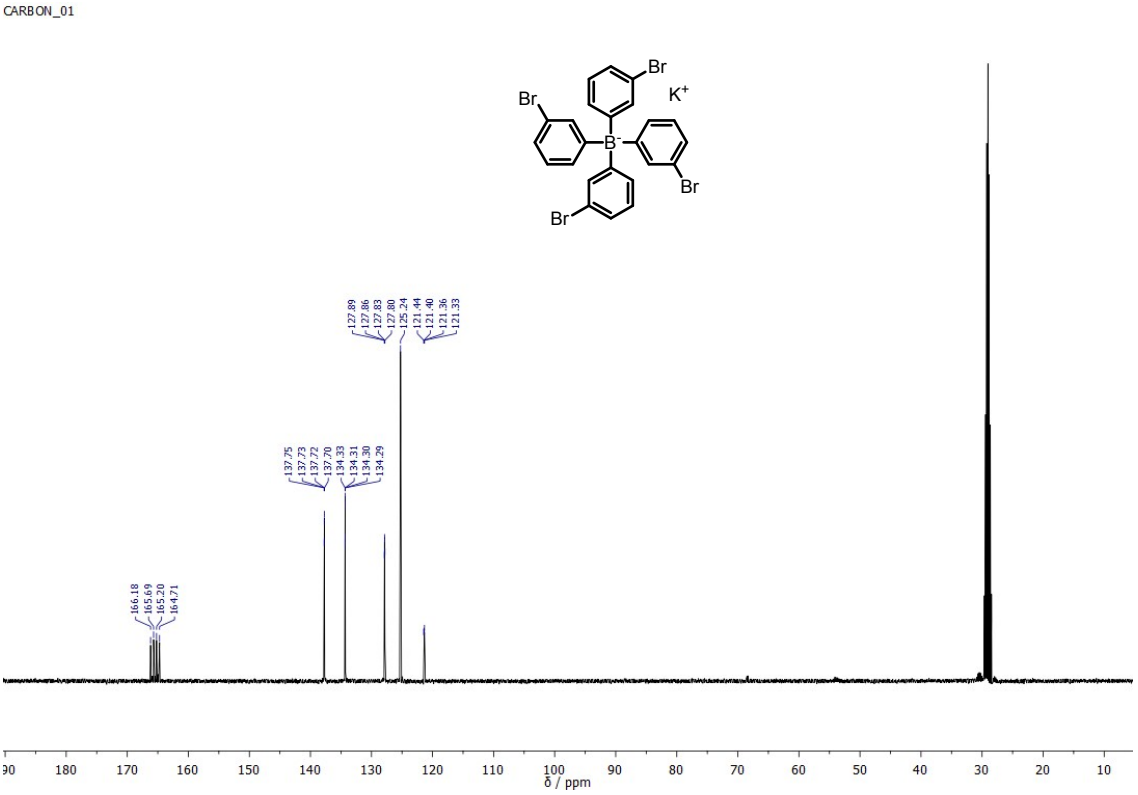

Fig. S4. ^{13}C NMR spectrum (101 MHz, acetone-d_6) of potassium tetrakis(3-bromophenyl)borate (**2**).

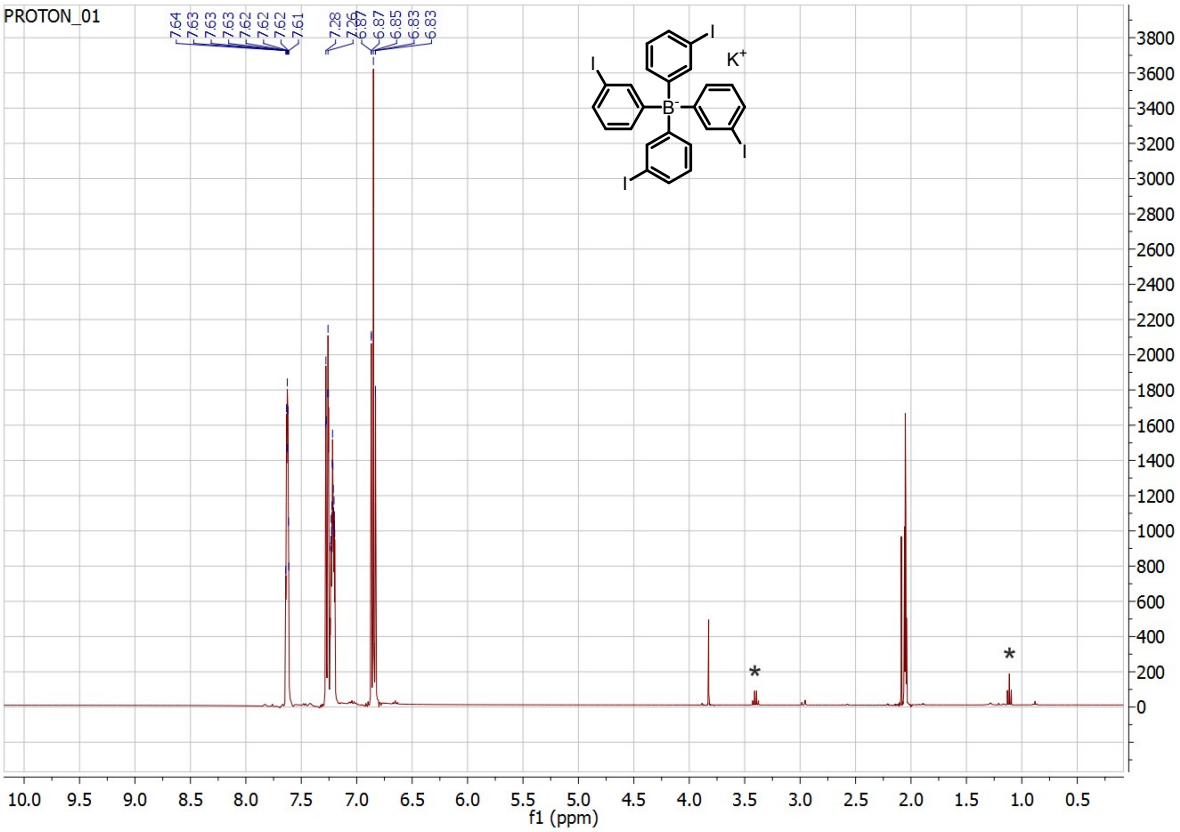

Fig. S5. ^{1}H NMR spectrum (101 MHz, acetone-d_6) of potassium tetrakis(3-iodophenyl)borate (**4**). Signals of residual solvent (Et_2O) are marked with asterisks (*).

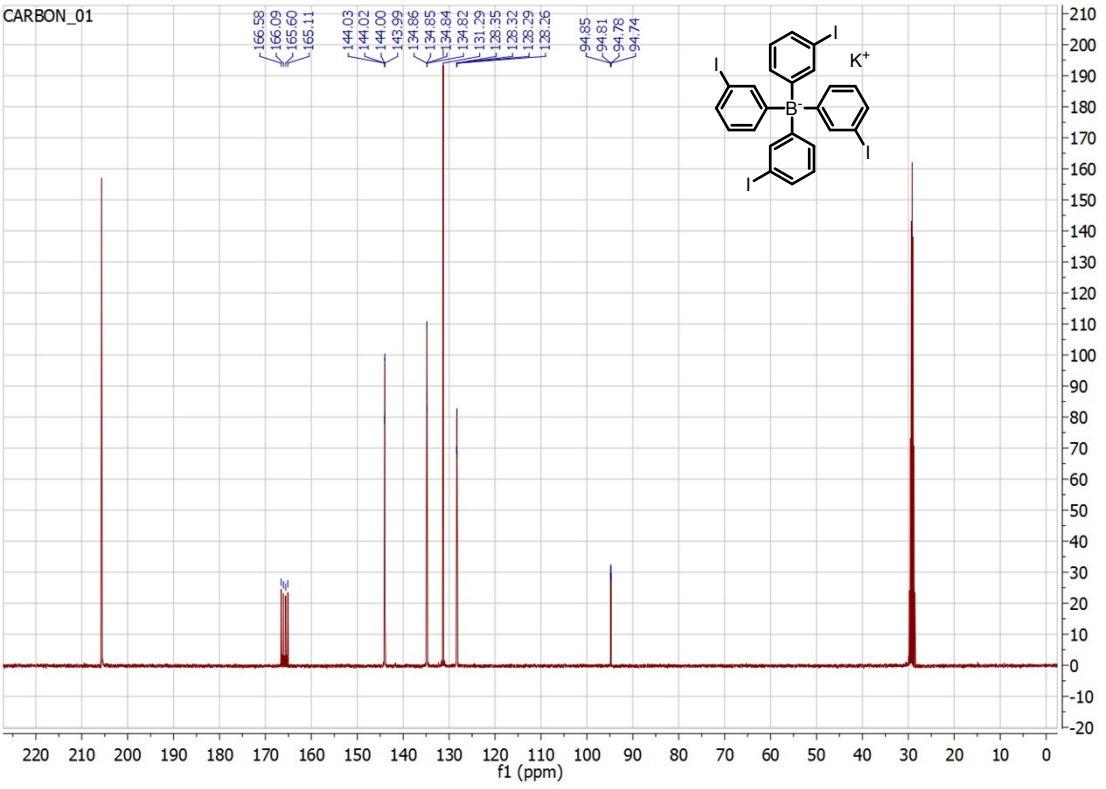

Fig. S6. ^{13}C NMR spectrum (101 MHz, acetone-d_6) of potassium tetrakis(3-iodophenyl)borate (**4**).

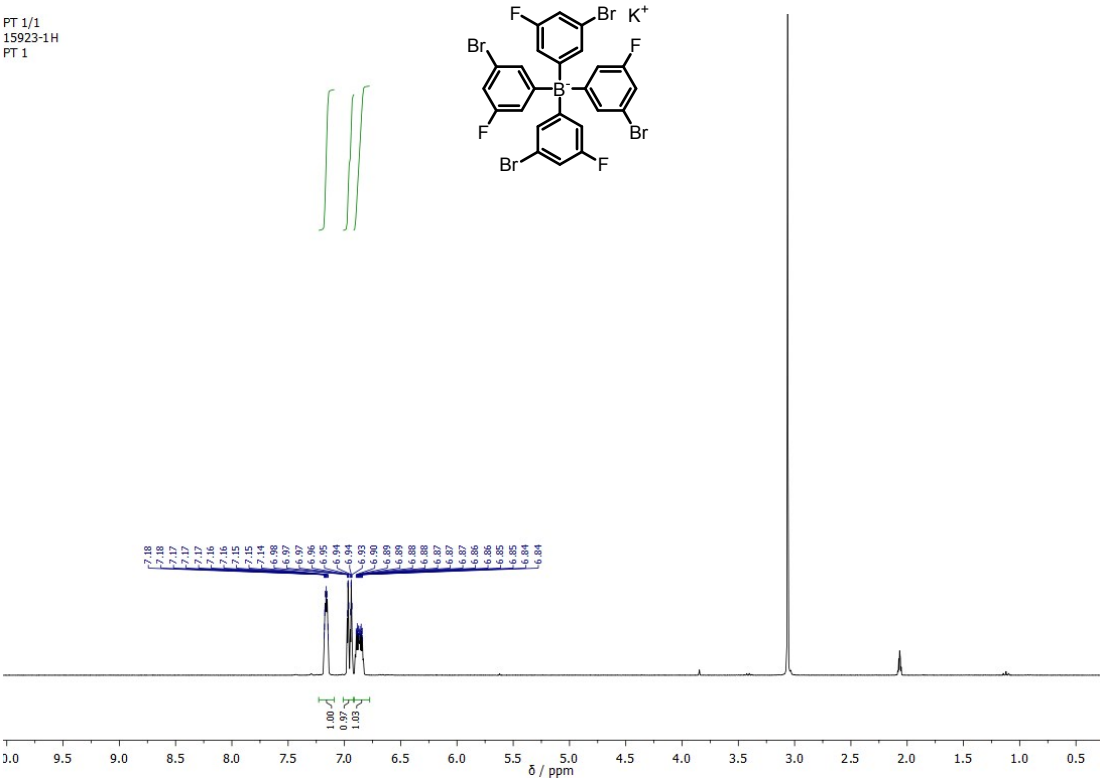

Fig. S7. ^{1}H NMR spectrum (400 MHz, acetone-d_6) of potassium tetrakis(3-bromo-5-fluorophenyl)borate (**5**)

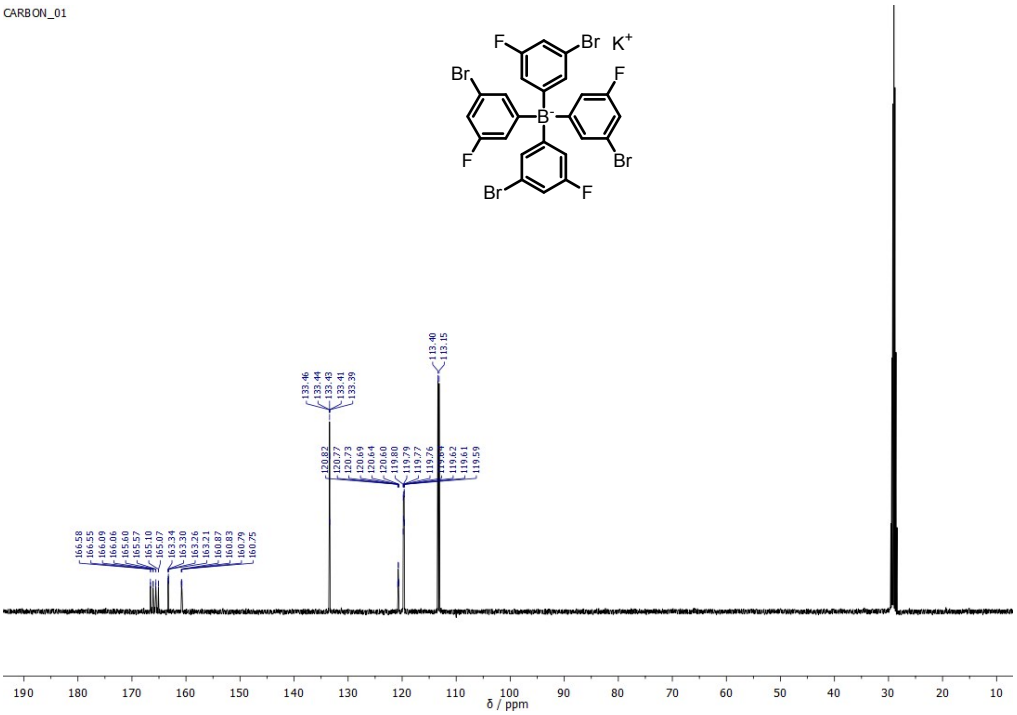

Fig. S8. ^{13}C NMR spectrum (400 MHz, acetone-d_6) of potassium tetrakis(3-bromo-5-fluorophenyl)borate (**5**)

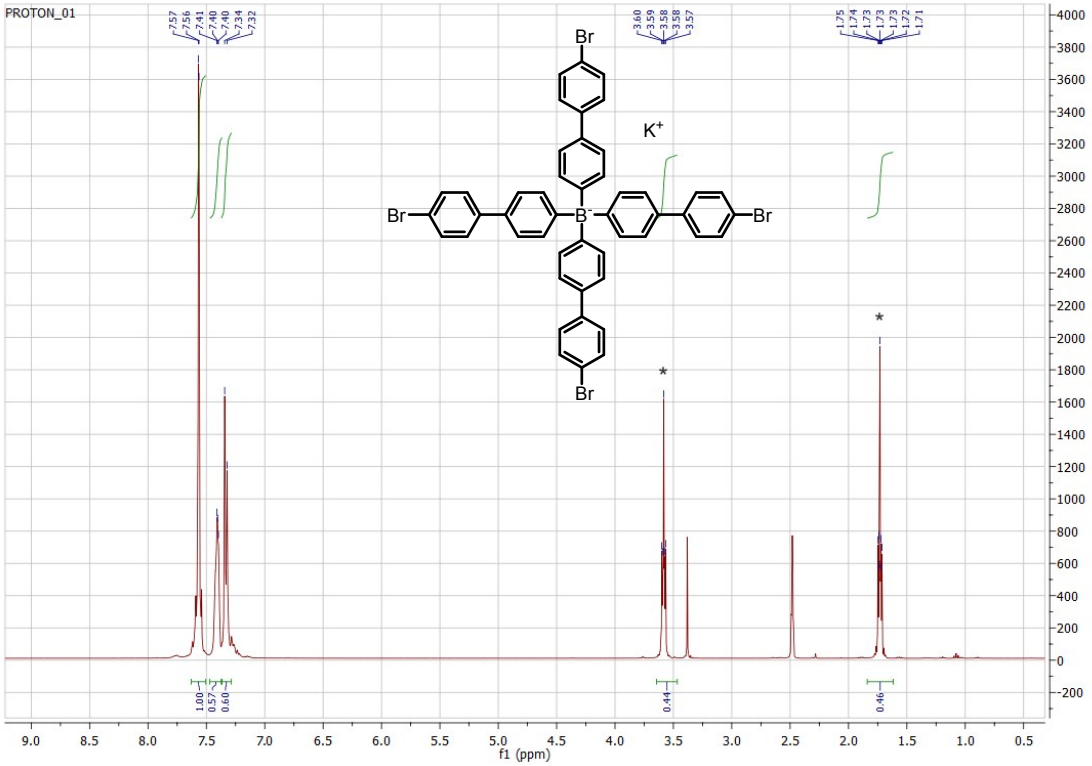

Fig. S9. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of potassium tetrakis(4'-bromobiphenylyl)borate (**6·THF**). Signals of residual solvent (THF) are marked with asterisks (*).

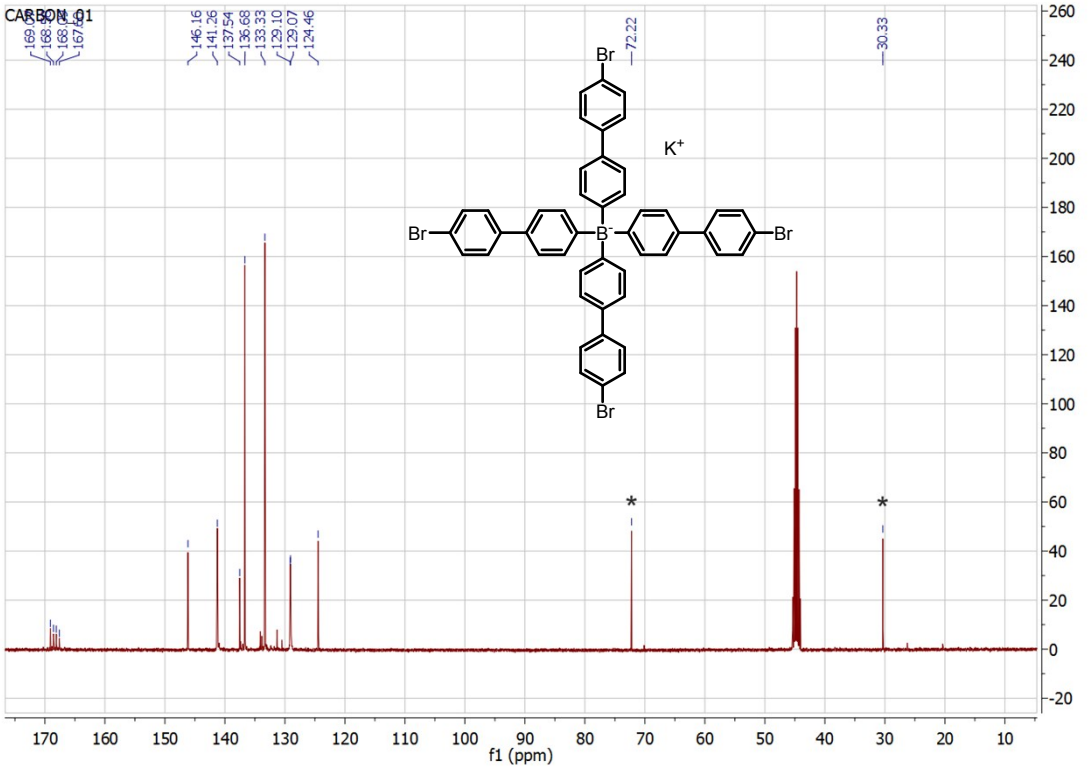

Fig. S10. ^{13}C NMR spectrum (101 MHz, DMSO-d_6) of potassium tetrakis(4'-bromobiphenylyl)borate (**6·THF**). Signals of residual solvent (THF) are marked with asterisks (*).

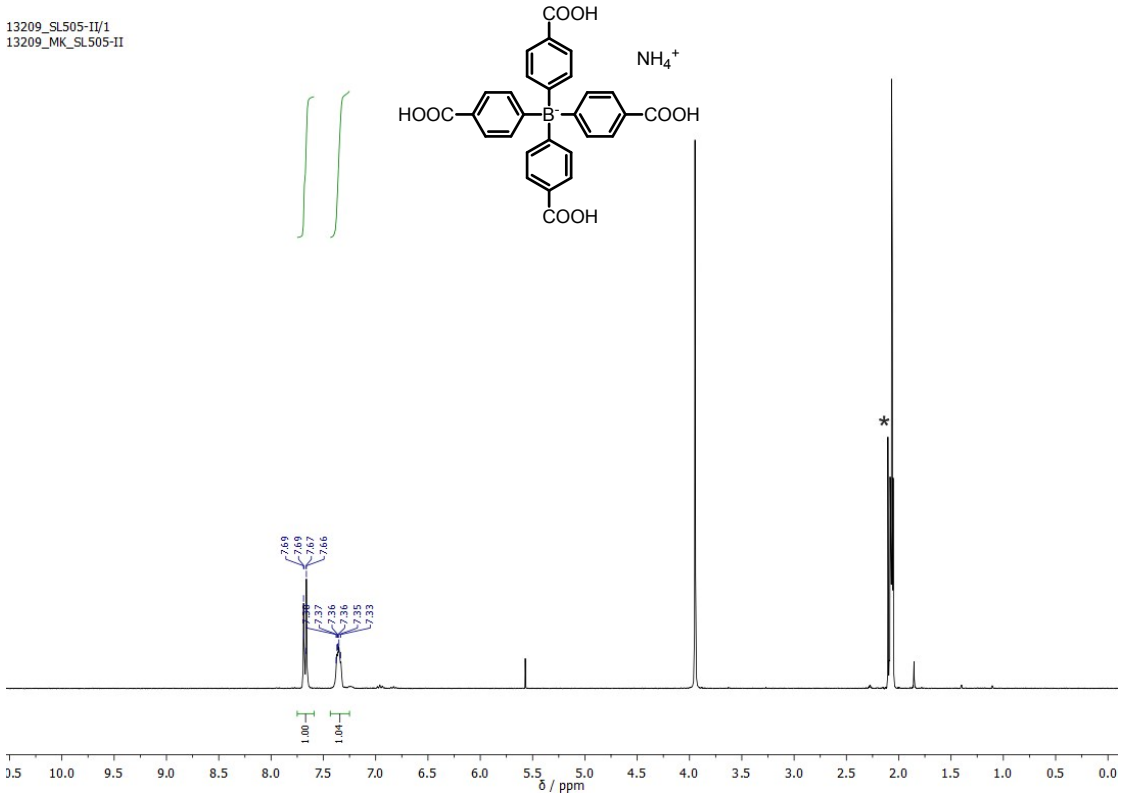

Fig. S11. ^{1}H NMR spectrum (400 MHz, acetone-d_6) of ammonium tetrakis[4-carboxyphenyl]borate (**3a**). Signal of residual solvent (acetone) is marked with an asterisk (*).

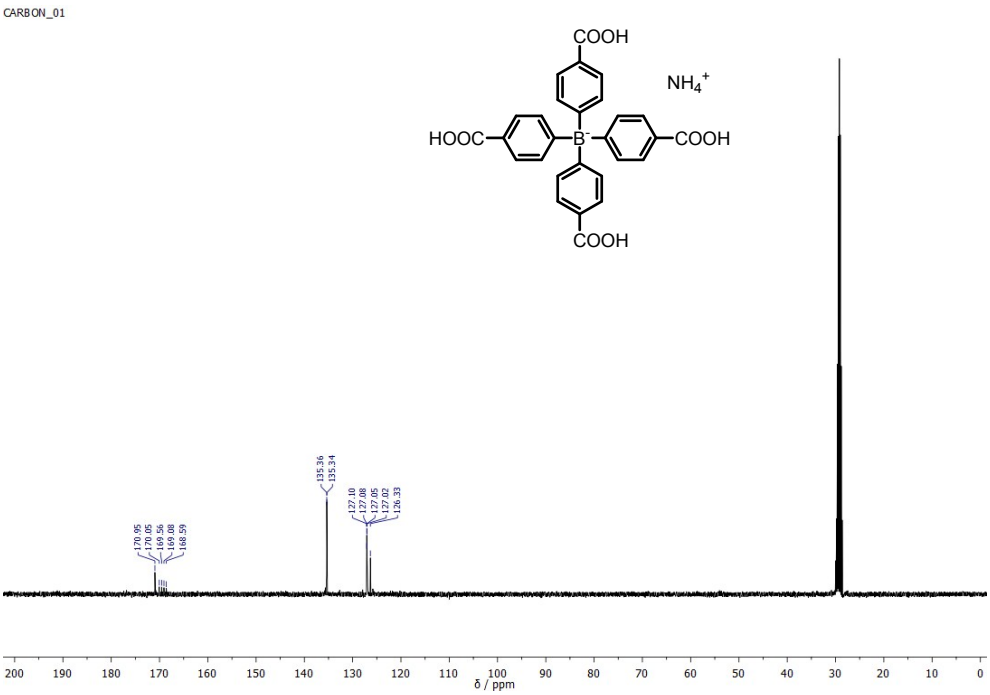

Fig. S12. ^{13}C NMR spectrum (101 MHz, acetone-d_6) of ammonium tetrakis[4-carboxyphenyl]borate (**3a**).

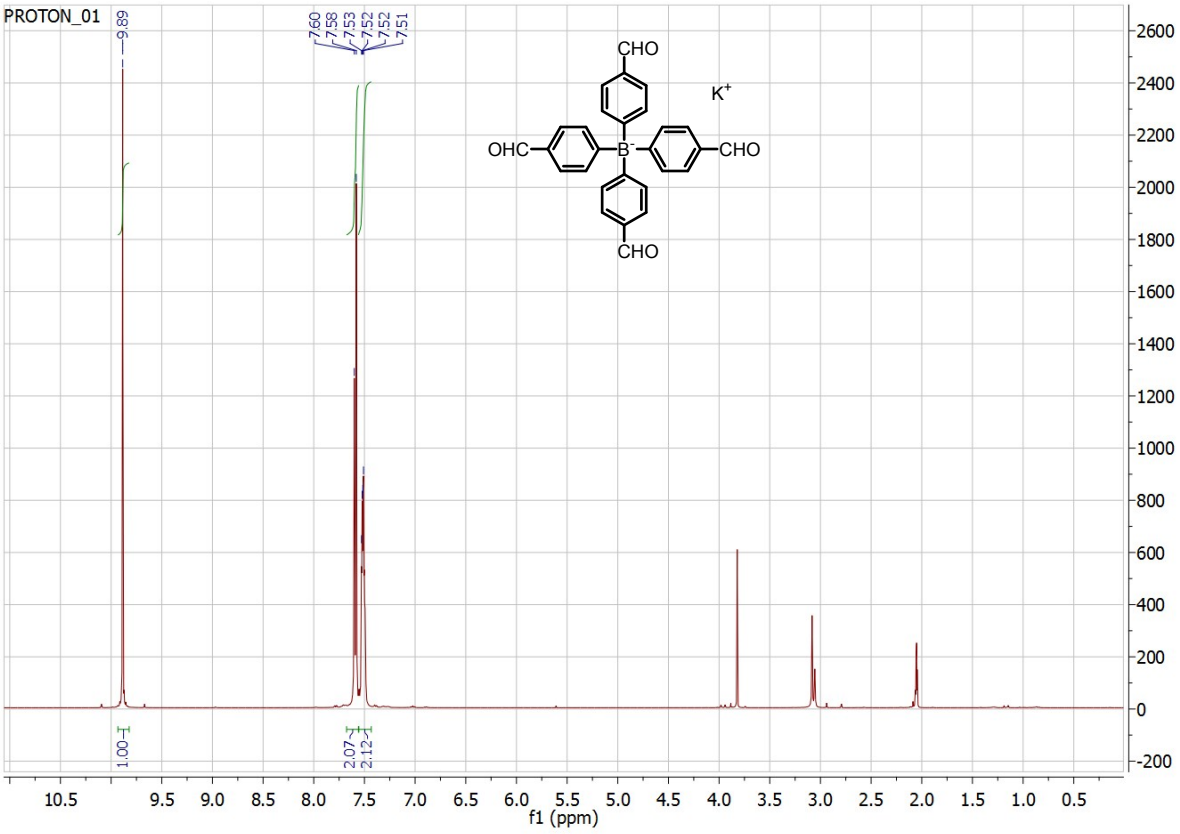

Fig. S13. ^{1}H NMR spectrum (400 MHz, acetone-d_6) of potassium tetrakis[4-formylphenyl]borate (**3b**).

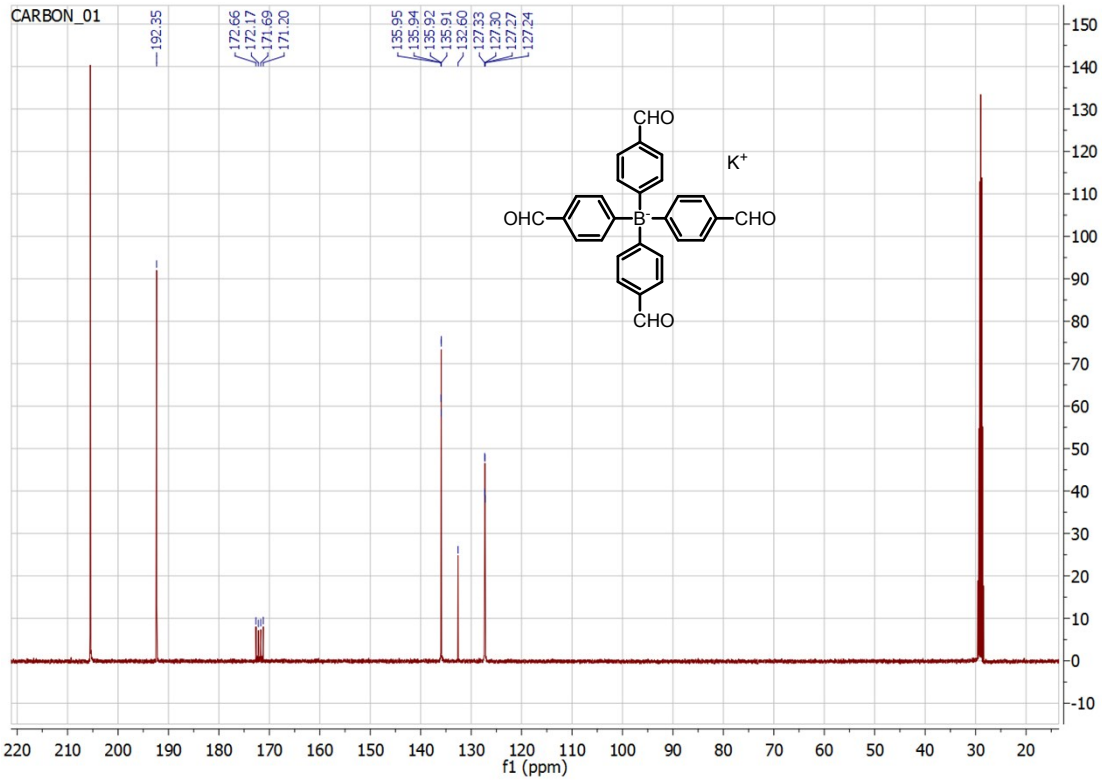

Fig. S14. ^{13}C NMR spectrum (101 MHz, acetone-d_6) of potassium tetrakis[4-formylphenyl]borate (**3b**).

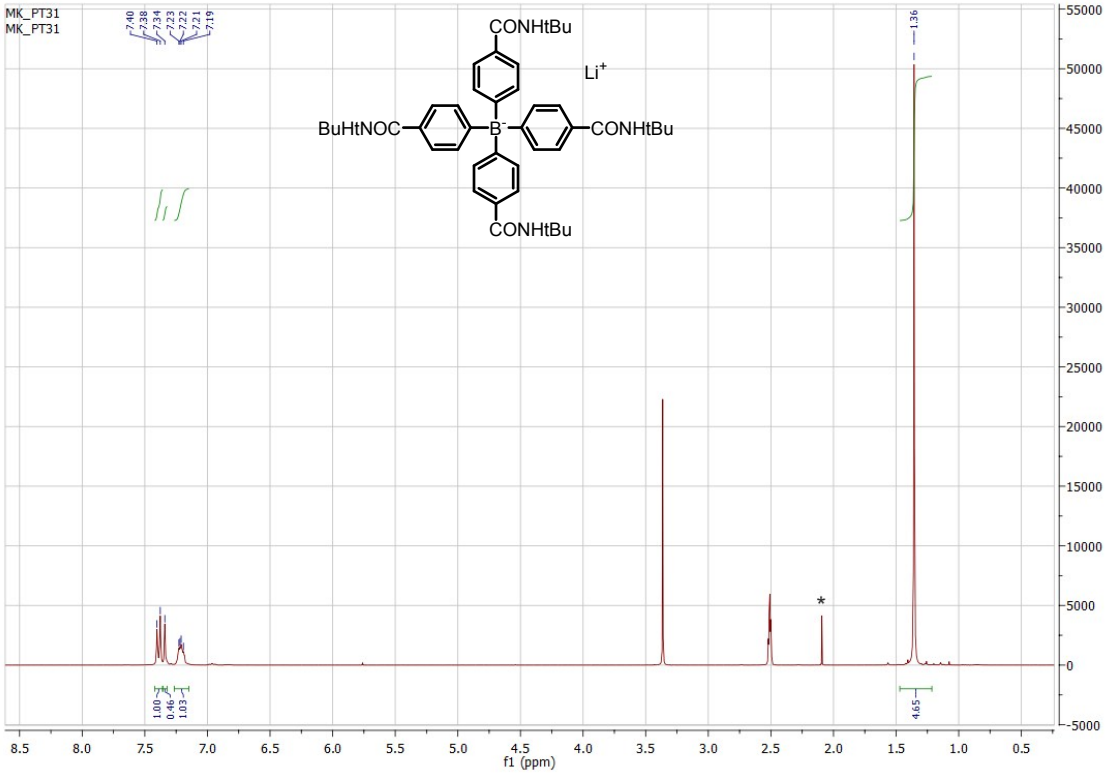

Fig. S15. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of lithium tetrakis[4-(*N*-tert-butylcarbamoyl)phenyl]borate (**3c**). Signal of residual solvent (acetone) is marked with an asterisk (*).

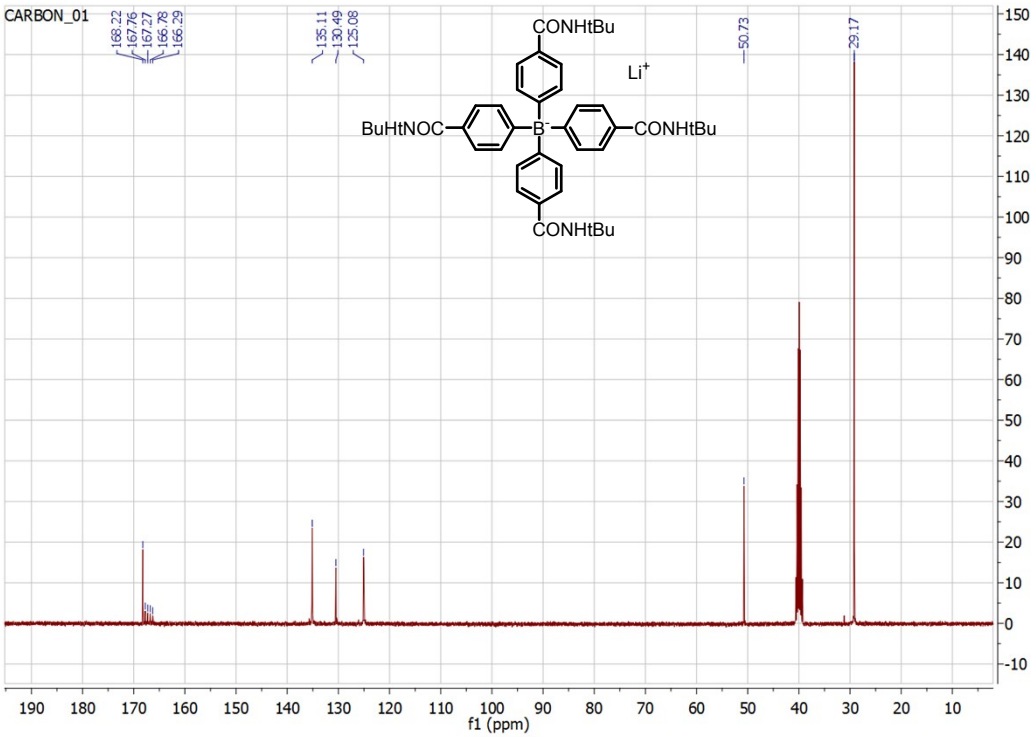

Fig. S16. ^{13}C NMR spectrum (101 MHz, DMSO-d_6) of lithium tetrakis[4-(*N*-tert-butylcarbamoyl)phenyl]borate (**3c**).

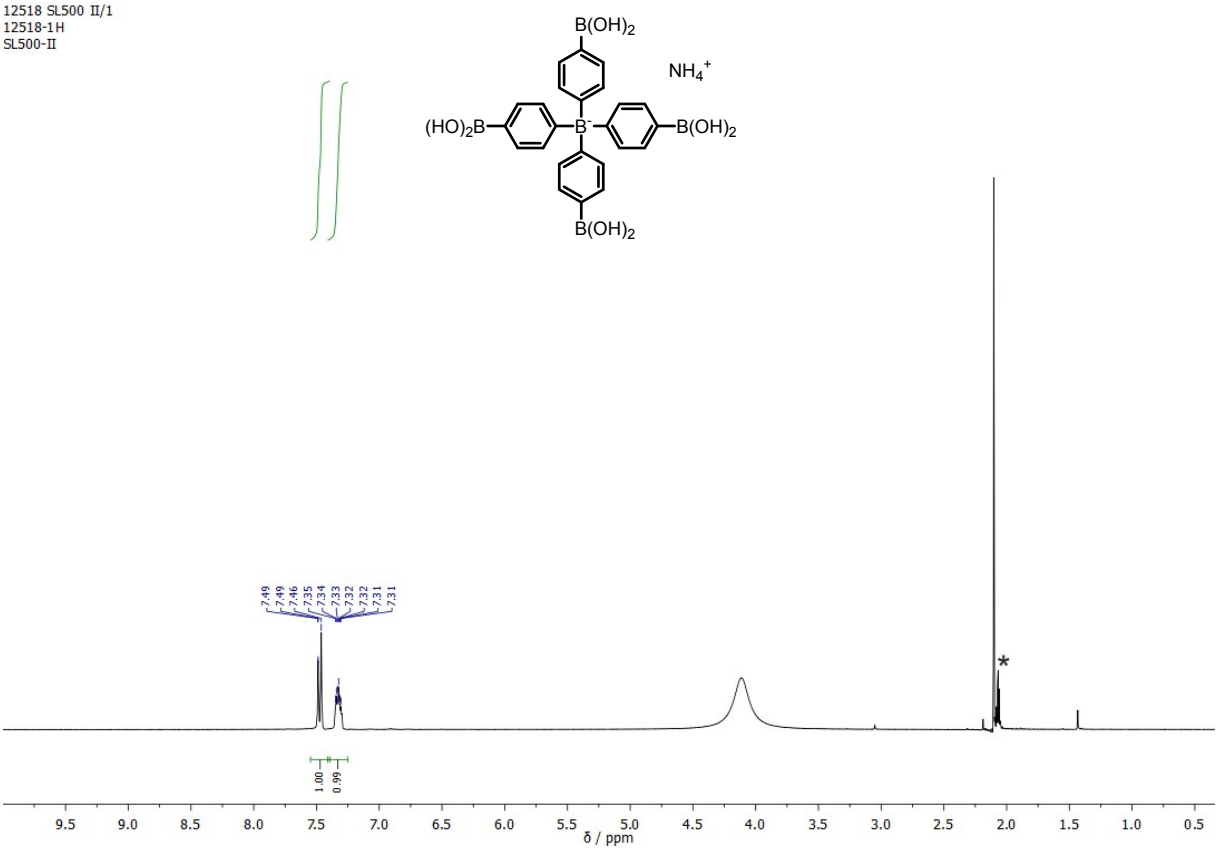

Fig. S17. ^{1}H NMR spectrum (400 MHz, acetone-d_6) of ammonium tetrakis[4-(dihydroxyboryl)phenyl]borate (**3d**). Signal of residual solvent (acetone) is marked with an asterisk (*).

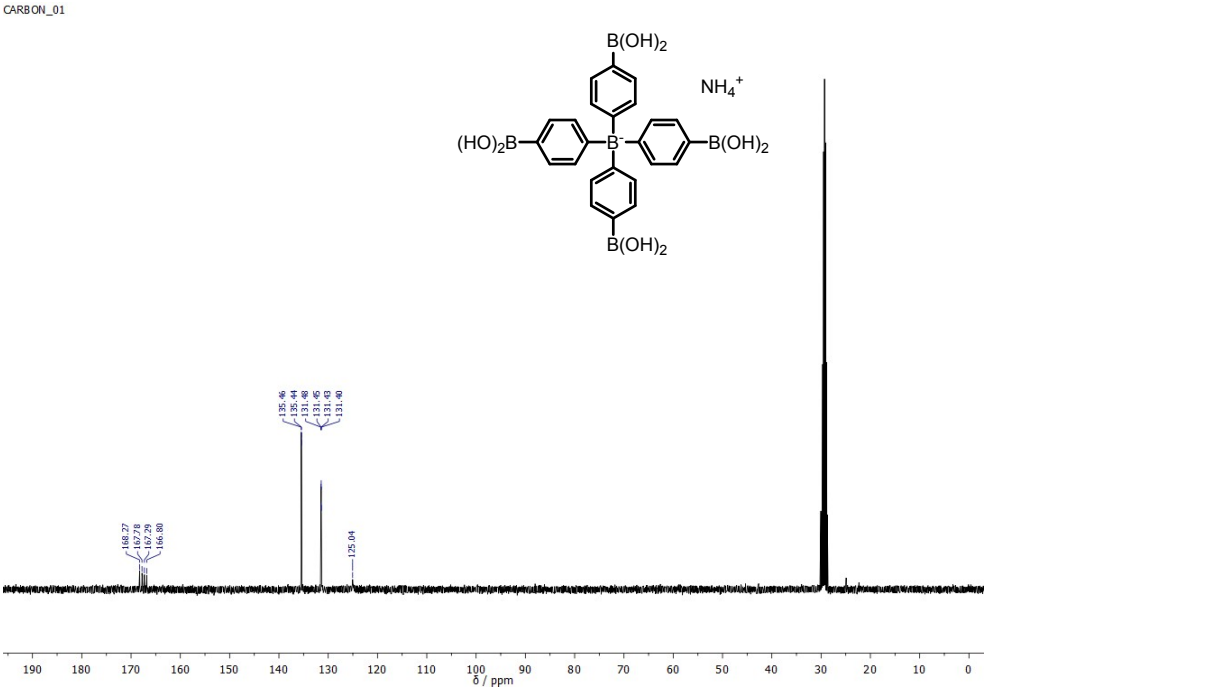

Fig. S18. ^{13}C NMR spectrum (101 MHz, acetone-d_6) of ammonium tetrakis[4-(dihydroxyboryl)phenyl]borate (**3d**).

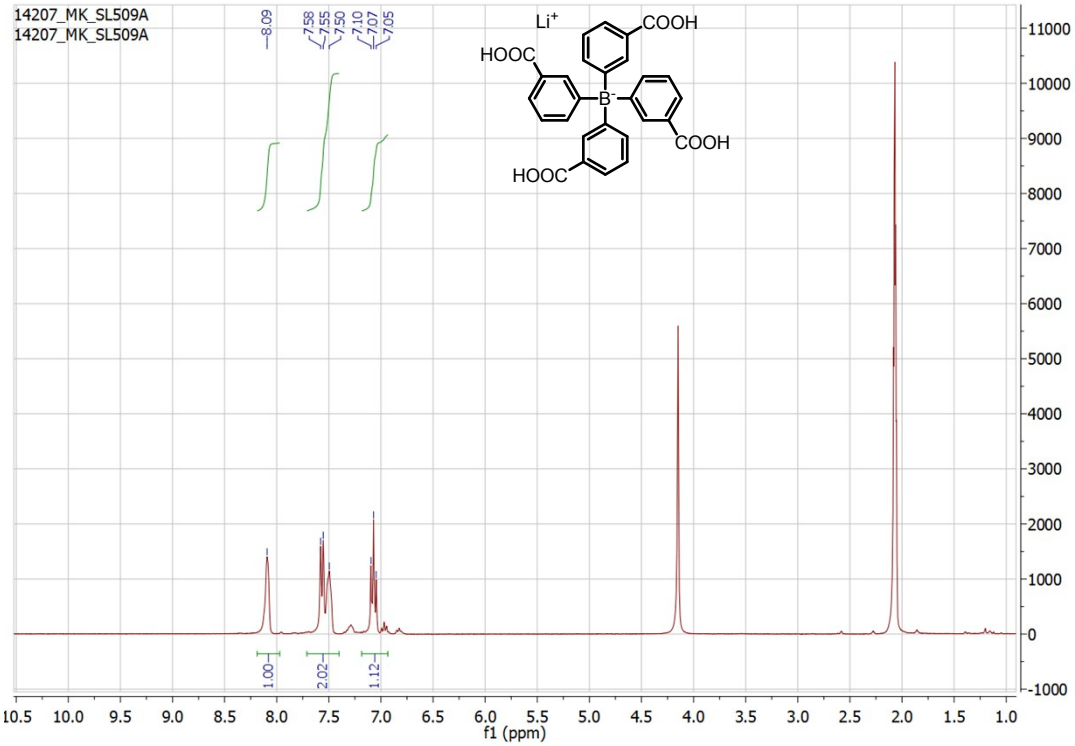

Fig. S19. ^{1}H NMR spectrum (400 MHz, acetone-d_6) of lithium tetrakis[3-carboxyphenyl]borate (**4a**).

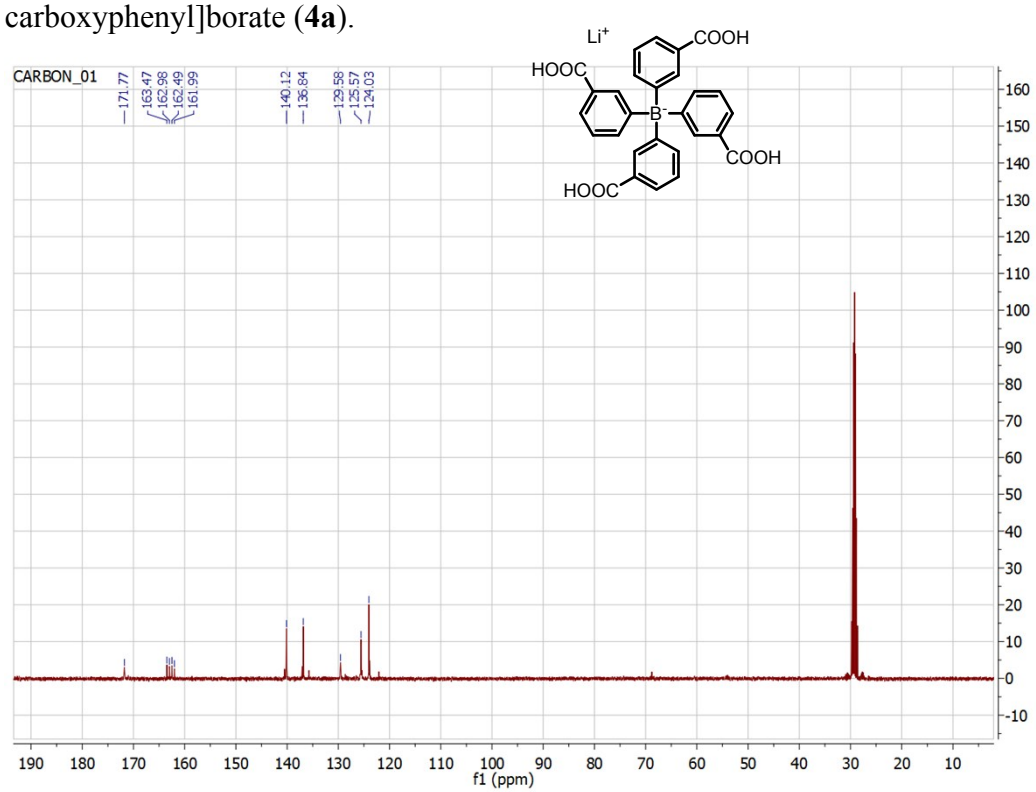

Fig. S20. ^{13}C NMR spectrum (101 MHz, DMSO-d_6) of lithium tetrakis[3-carboxyphenyl]borate (**4a**).

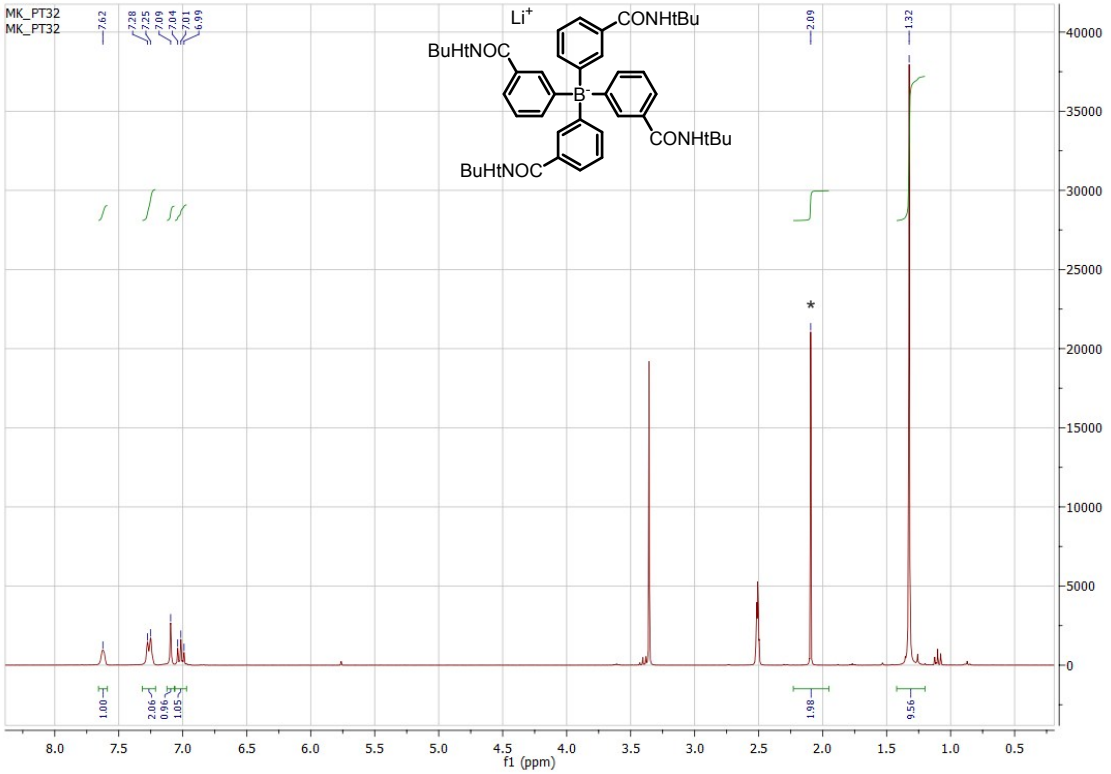

Fig. S21. [1]H NMR spectrum (400 MHz, DMSO-d_6) of lithium tetrakis[3-(*N*-tert-butylcarbamoyl)phenyl]borate (**4b**). Signal of residual solvent (acetone) is marked with an asterisk (*).

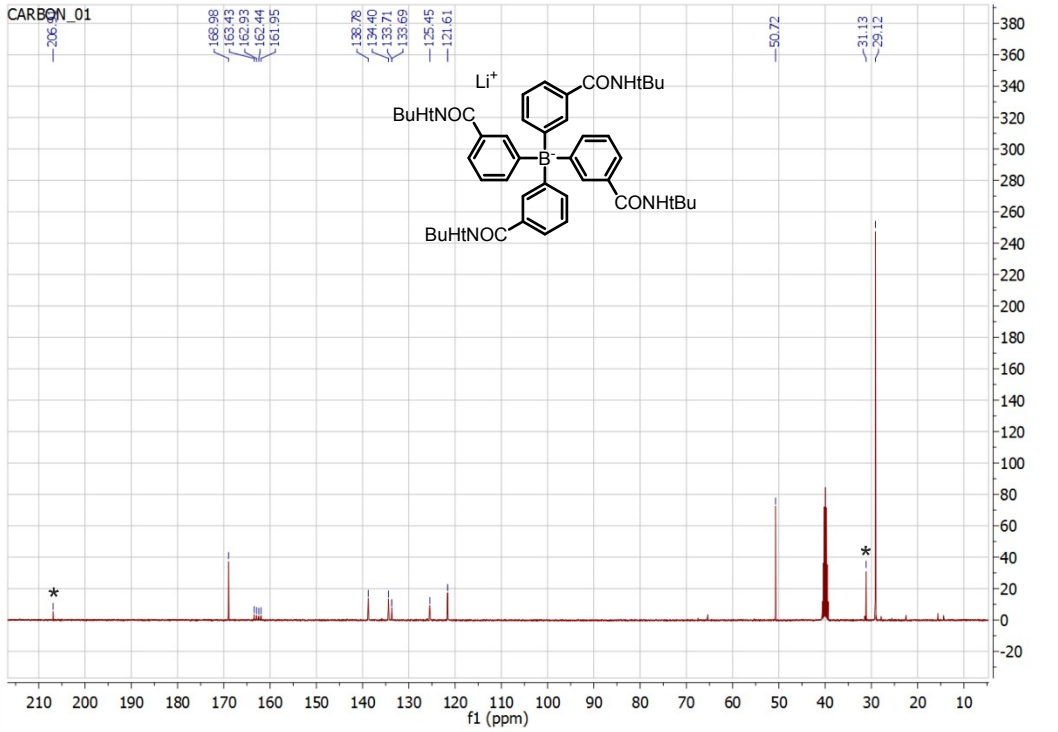

Fig. S22. [13]C NMR spectrum (101 MHz, DMSO-d_6) of lithium tetrakis[3-(*N*-tert-butylcarbamoyl)phenyl]borate (**4b**). Signals of residual solvent (acetone) are marked with asterisks (*).

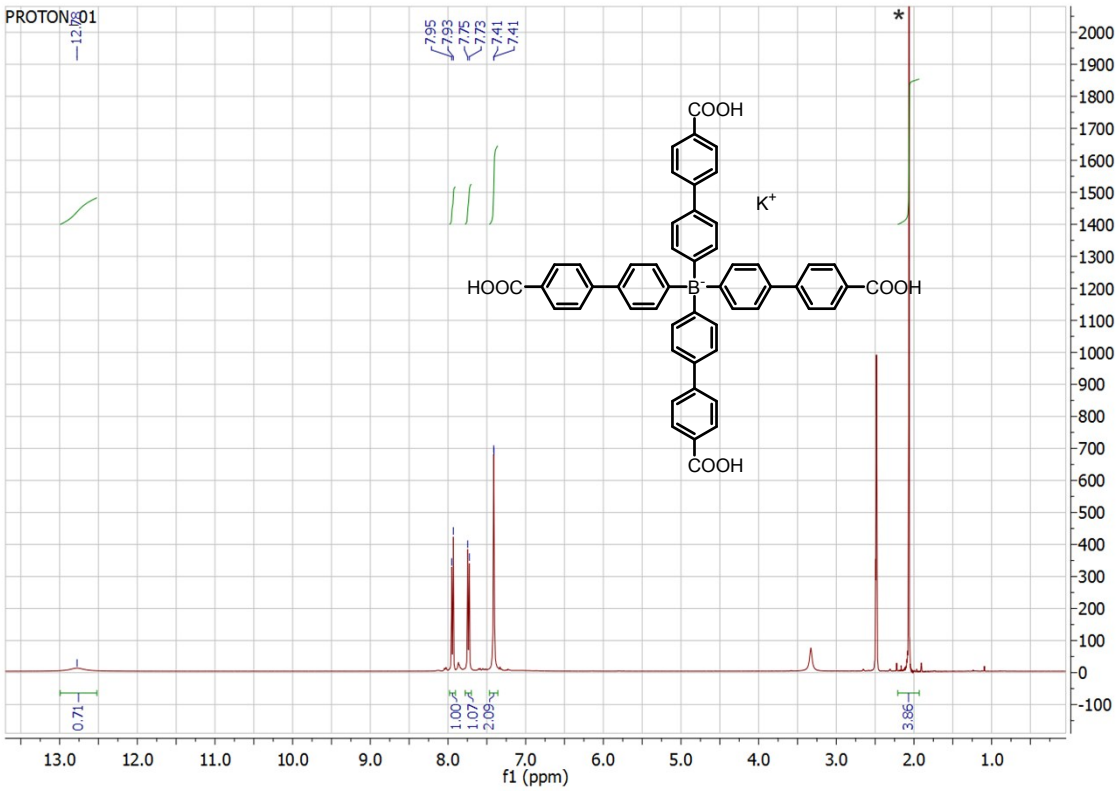

Fig. S23. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of ammonium tetrakis[4'-carboxybiphenylyl]borate (**6a**). Signals of residual solvent (acetone) is marked with an asterisk (*).

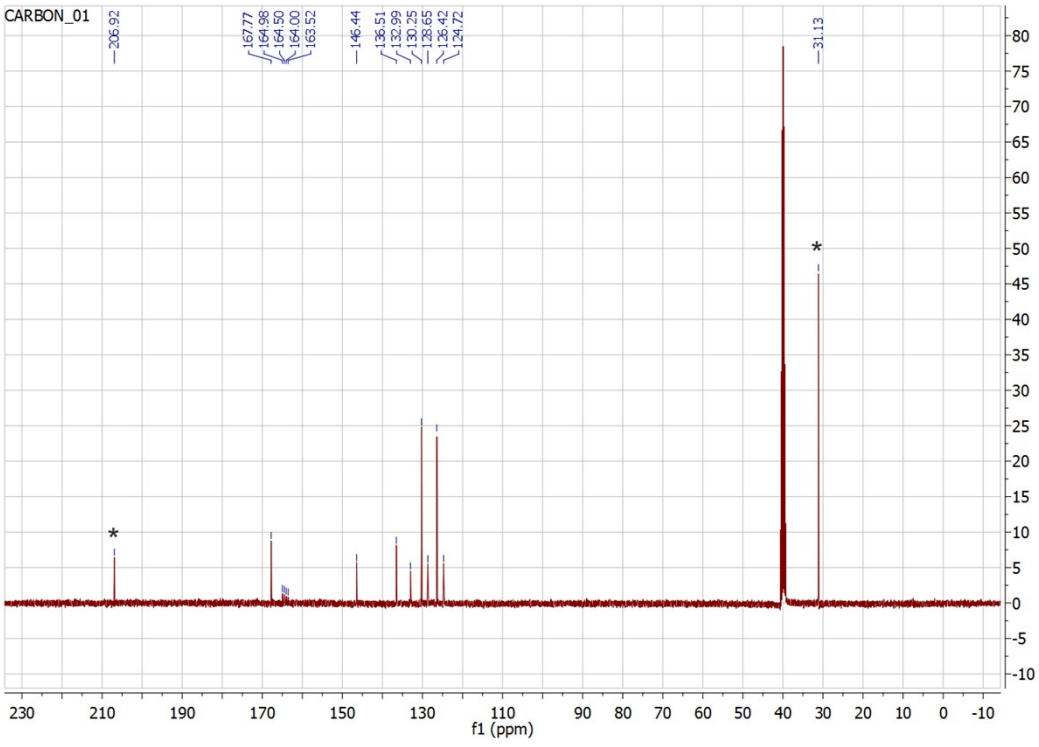

Fig. S24. ^{13}C NMR spectrum (101 MHz, DMSO-d_6) of ammonium tetrakis[4'-carboxybiphenylyl]borate (**6a**). Signals of residual solvent (acetone) are marked with asterisks (*).

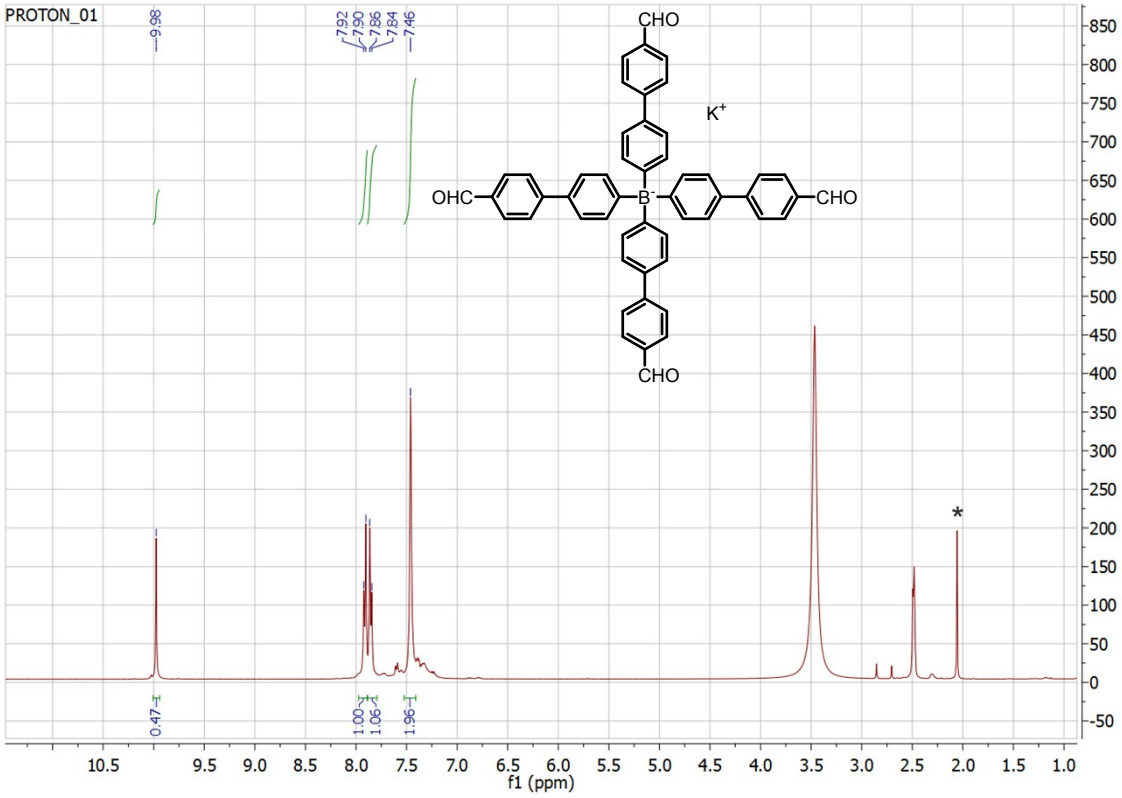

Fig. S25. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of potassium tetrakis[4'-formylbiphenylyl]borate (**6b**). Signal of residual solvent (acetone) is marked with an asterisk (*).

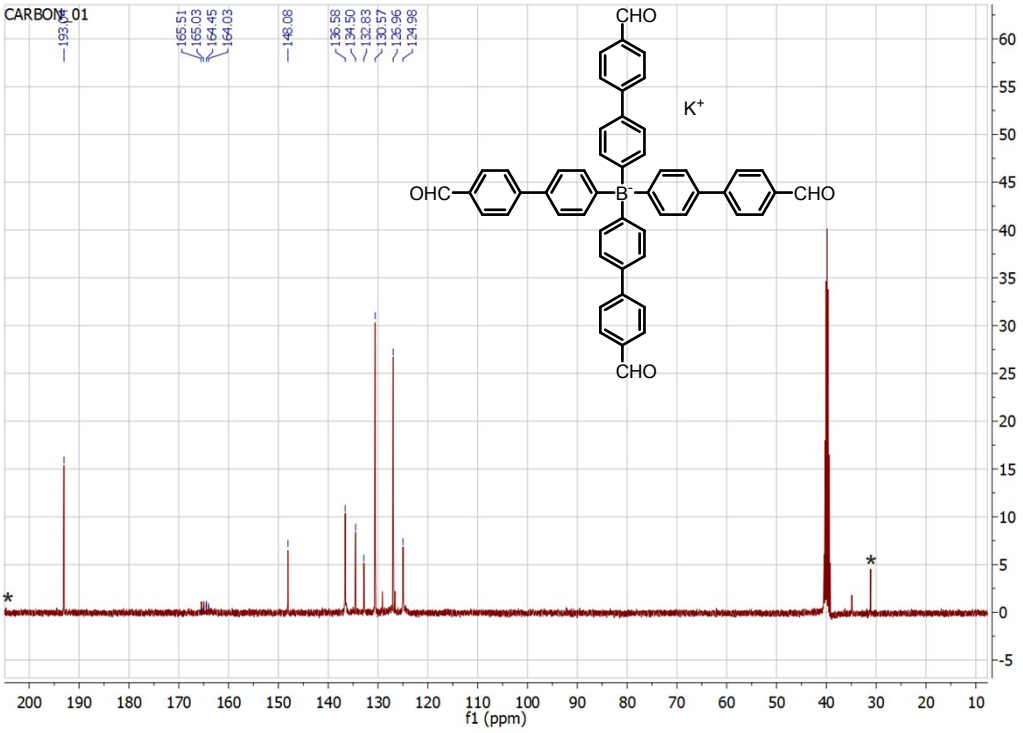

Fig. S26. ^{13}C NMR spectrum (101 MHz, DMSO-d_6) of potassium tetrakis[4'-formylbiphenylyl]borate (**6b**). Signal of residual solvent (acetone) are marked with asterisks (*).

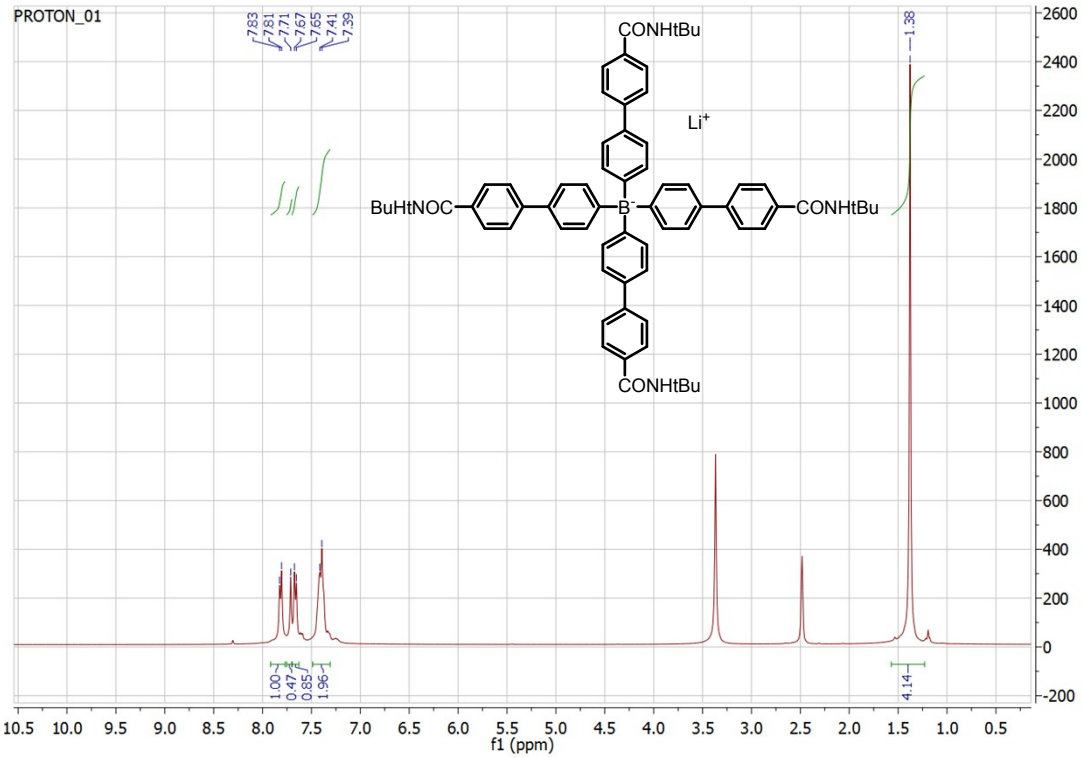

Fig. S27. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of lithium tetrakis[4'-(*N*-tert-butylcarbamoyl)biphenylyl]borate (**6c**).

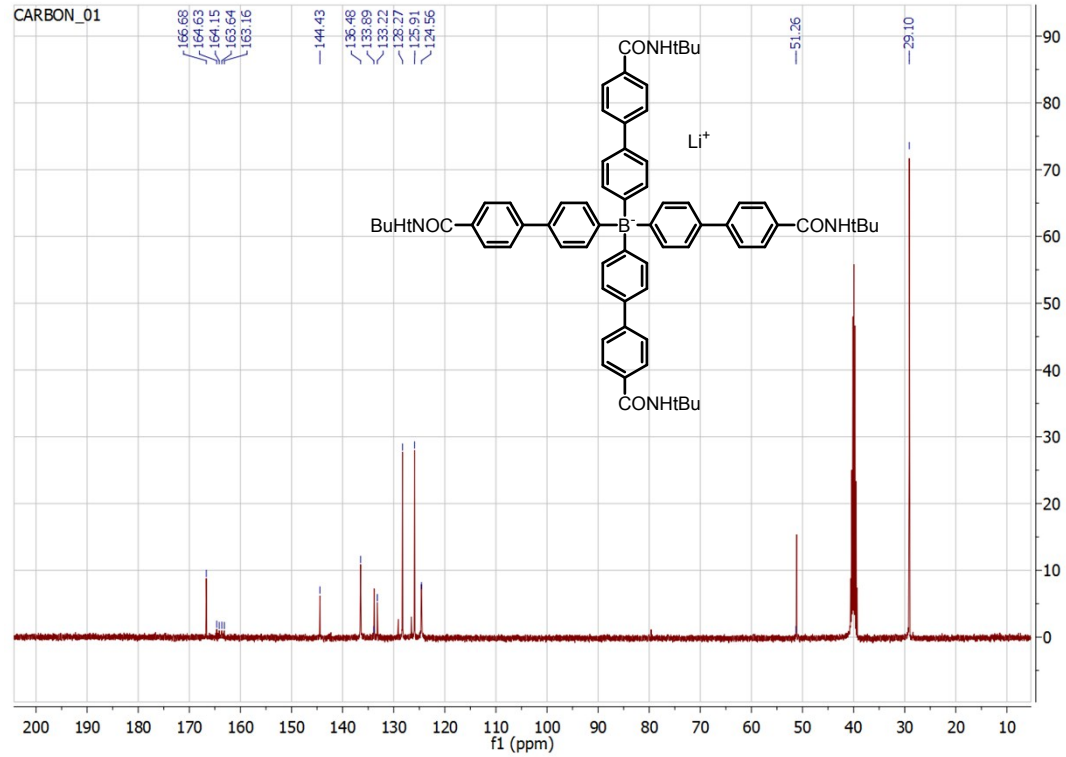

Fig. S28. ^{13}C NMR spectrum (101 MHz, DMSO-d_6) of lithium tetrakis[4'-(*N*-tert-butylcarbamoyl)biphenylyl]borate (**6c**).

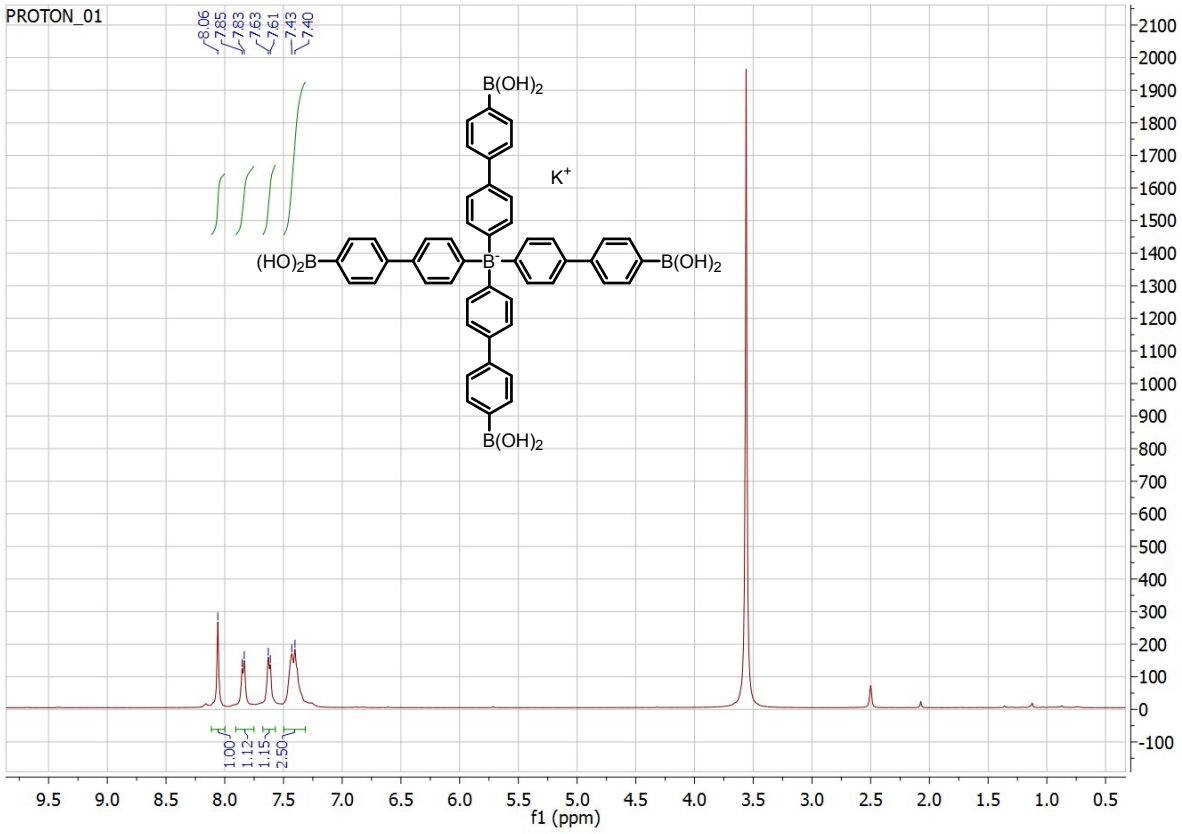

Fig. S29. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of potassium tetrakis[4'-(dihydroxyboryl)biphenylyl]borate (**6d**).

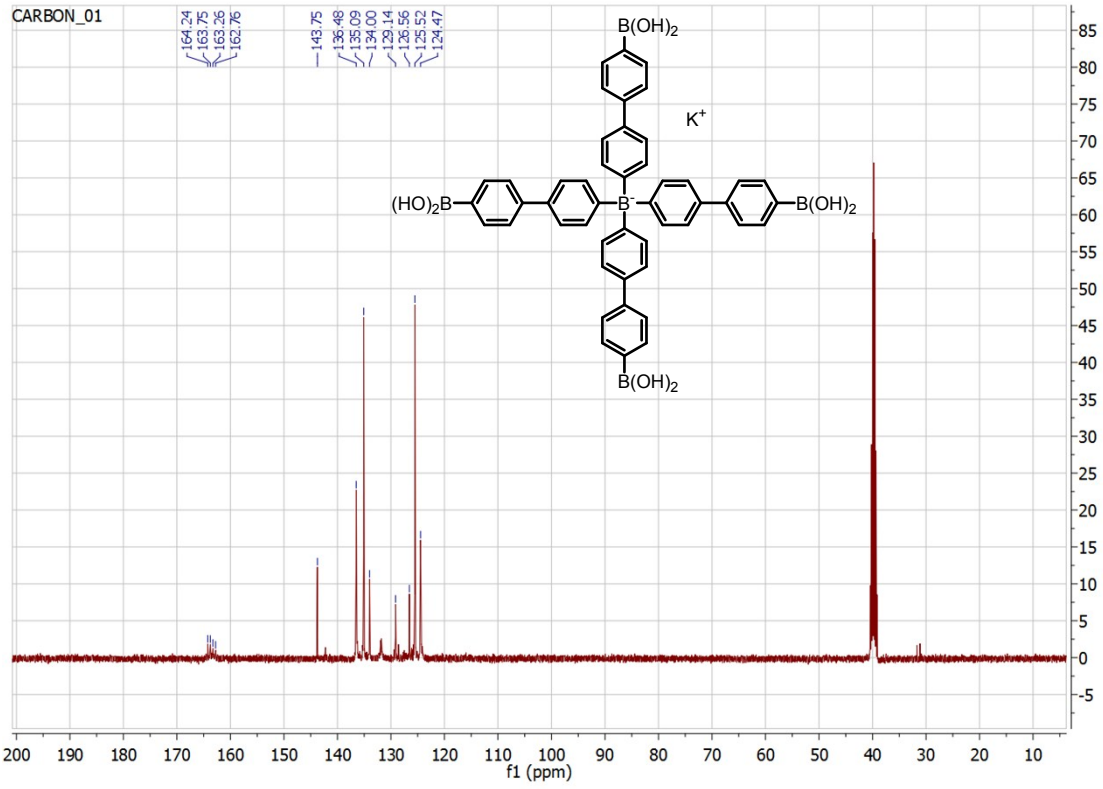

Fig. S30. ^{13}C NMR (101 MHz, DMSO-d_6) spectrum of potassium tetrakis[4'-(dihydroxyboryl)biphenylyl]borate (**6d**).

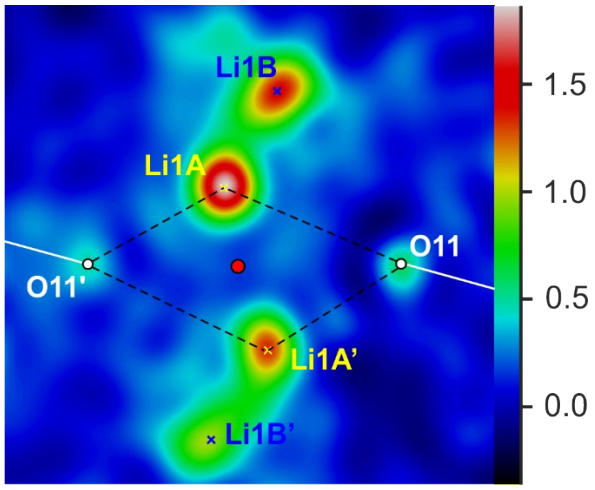

Figure S31. Difference-Fourier maps from datasets collected for compound **4a** reconstructed in the plane defined O11, Li1A and Li1B atoms with Lithium atoms omitted in the refinement procedure. Note that atoms (O11', Li1A' and Li1B') generated through the centre of symmetry operation (marked as red point) are aligned slightly above the given plane. Map was generated with MAPVIEW program within WinGX [L. J. Farrugia, *J Appl. Cryst.,* **2012**, *45*, 849-854].