

New Chiral *N*-heterocyclic Carbene Borane Complexes: Synthesis and Structural Analysis

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1. General

Experiments were carried out under nitrogen atmosphere using standard Schlenk technique. Solvents were dried with a Solvtek[®] system. For the synthesis of NHC-boranes, dry THF was degassed by two pump-freeze-thaw cycles. All commercially available compounds were used as received. Deuterated solvents were obtained from Cambridge Isotope Laboratories. NMR spectra were recorded on Bruker AMX 500 and AMX 400 spectrometers at ambient probe temperature. IR spectra were recorded using a Perkin-Elmer Spectrum One spectrometer. Melting points were measured using a Büchi 510 apparatus. $[\alpha]_D$ values were recorded on a Perkin-Elmer 241 polarimeter using a quartz cell ($l = 10$ cm) and a Na high-pressure lamp ($\lambda = 589$ nm).

As we have already discussed in the article, the carbene carbons coupling with the borons were identified as broad multiples due to the coupling with the quadrupolar nuclei boron. Boron has two isomers B^{10} ($I = 3$) and B^{11} ($I = 3/2$) with a abundance of about 1 : 4. This could be the possible reason of not observing a quartet but a multiplet. However, analysis of the proton carbon correlation spectra i.e. HMBC, we can clearly see the 3J (C,H) coupling between the carbene carbon and the vinylic protons and the protons at the stereogenic centers.

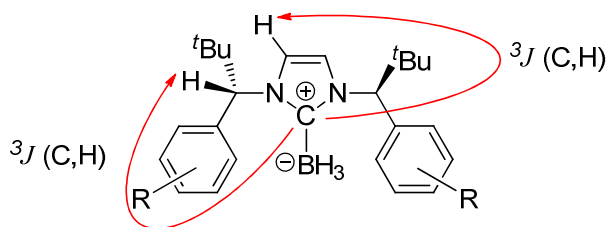
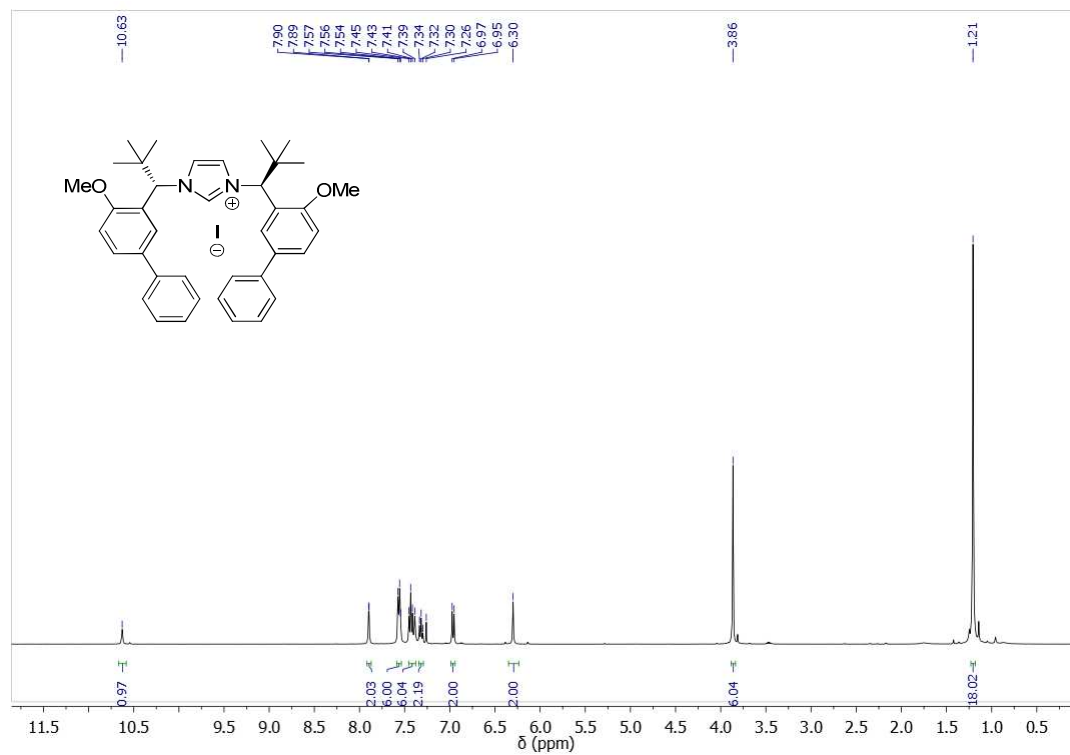


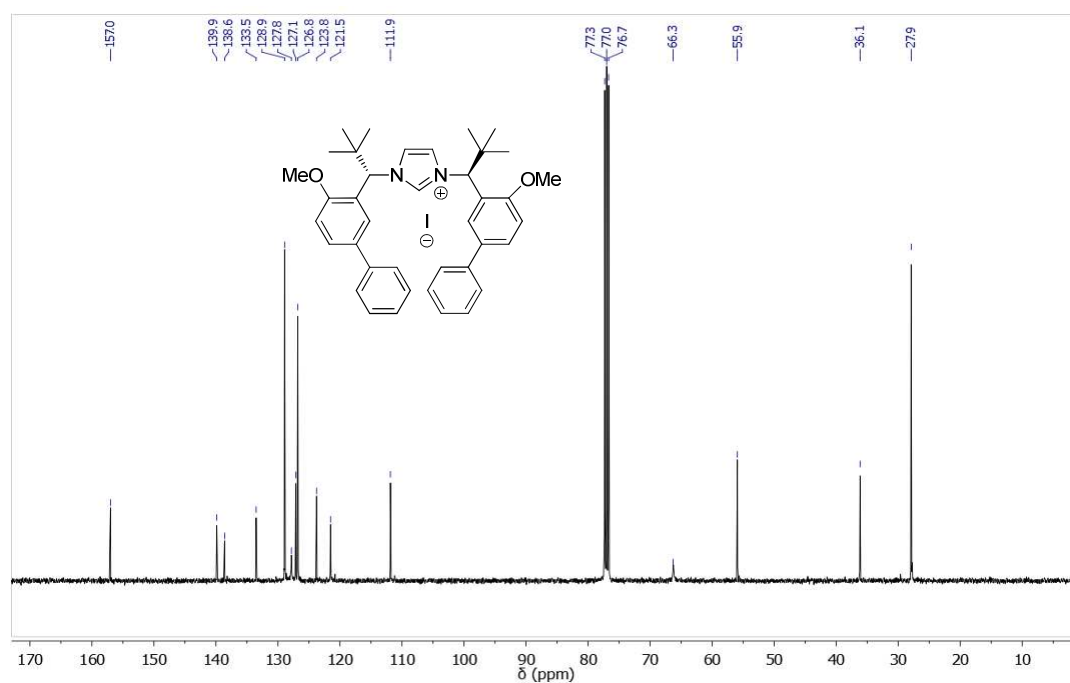
Figure 1: HMBC correlation between carbon and protons

2. NMR spectra of 1,3-bis((S)-1-(4-methoxy-[1,1'-biphenyl]-3-yl)-2,2-dimethylpropyl)-1H-imidazol-3-ium iodide (3):

^1H NMR spectrum:

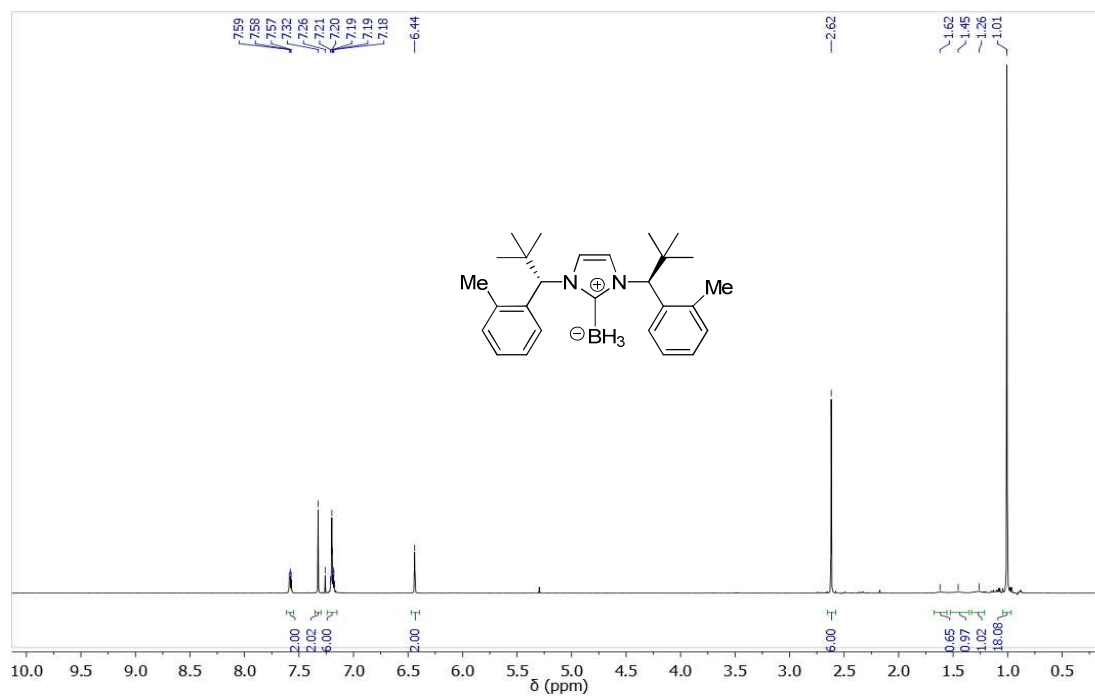


^{13}C NMR spectrum:

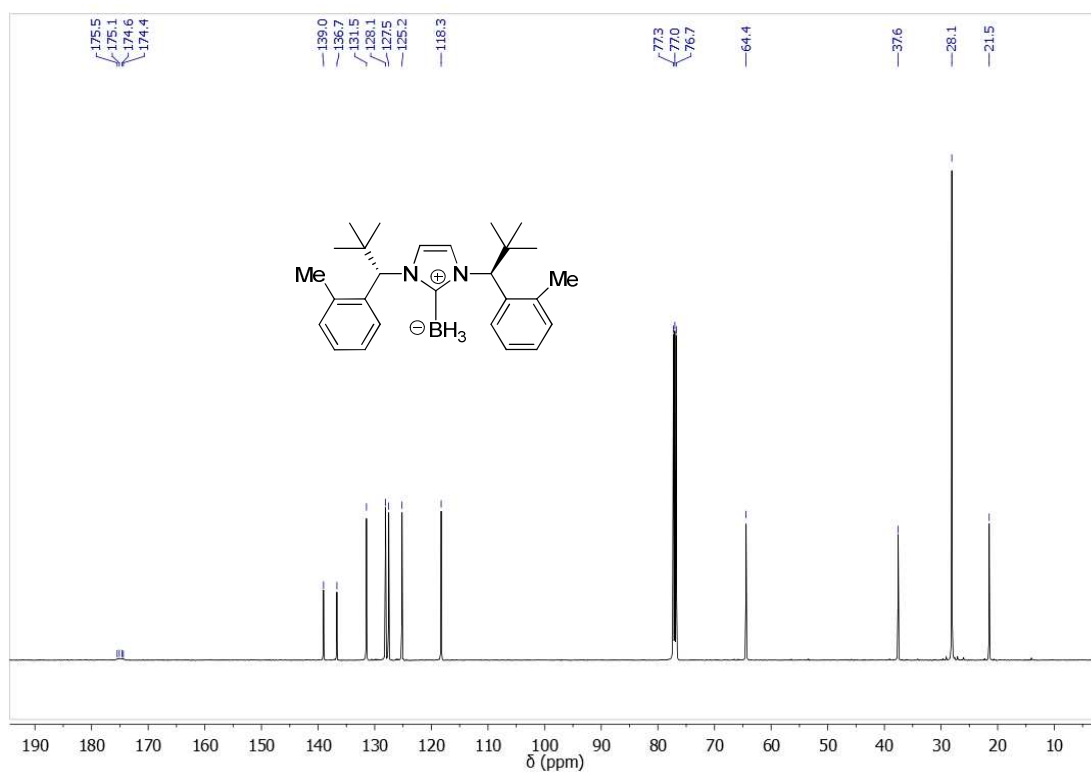


3. NMR spectra of (1,3-bis((*S*)-2,2-dimethyl-1-(*o*-tolyl)propyl-1*H*-imidazol-3-ium-2-yl)trihydroborate (5):

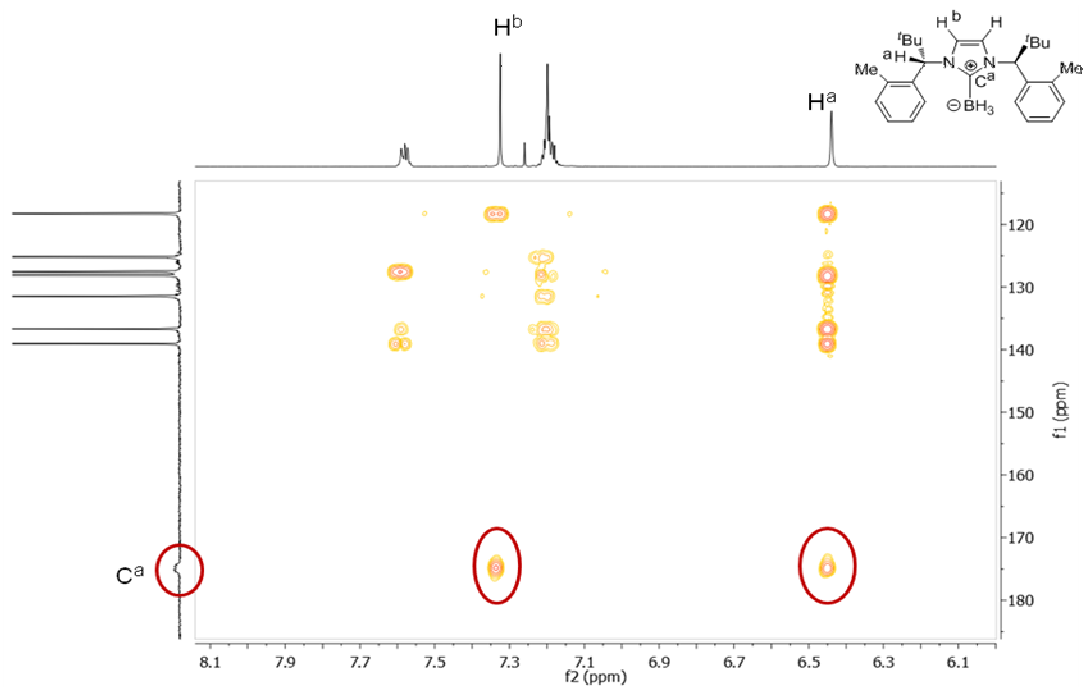
¹H NMR spectrum:



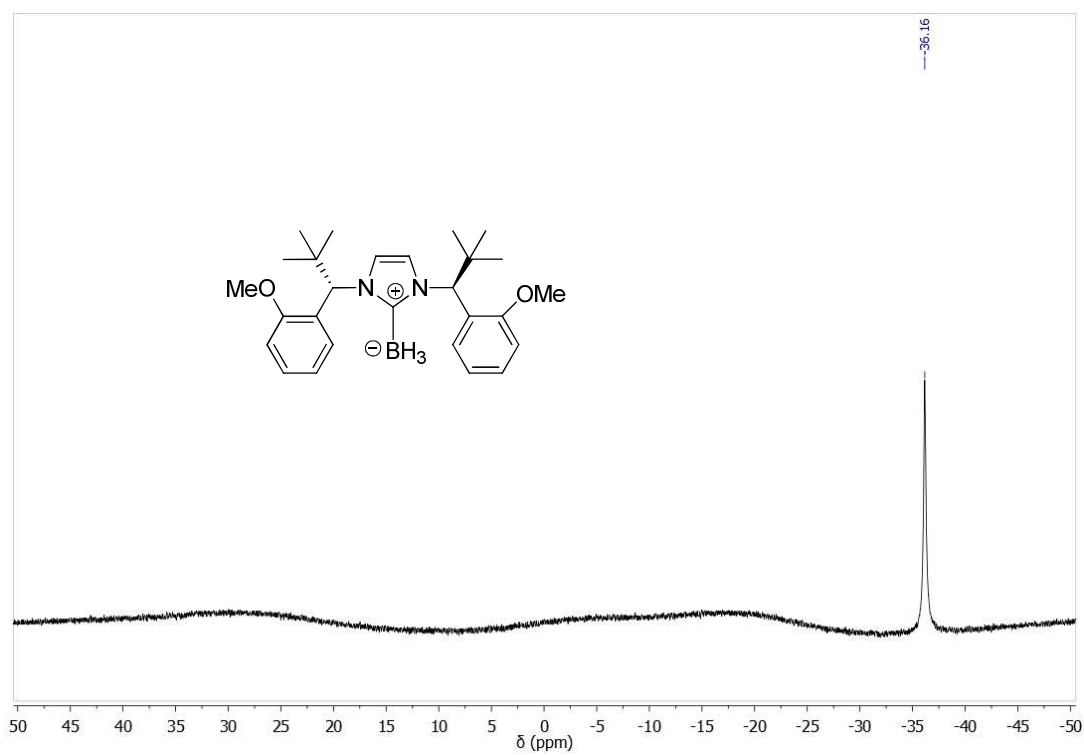
¹³C NMR spectrum:



Magnified proton carbon correlation spectrum (HMBC):

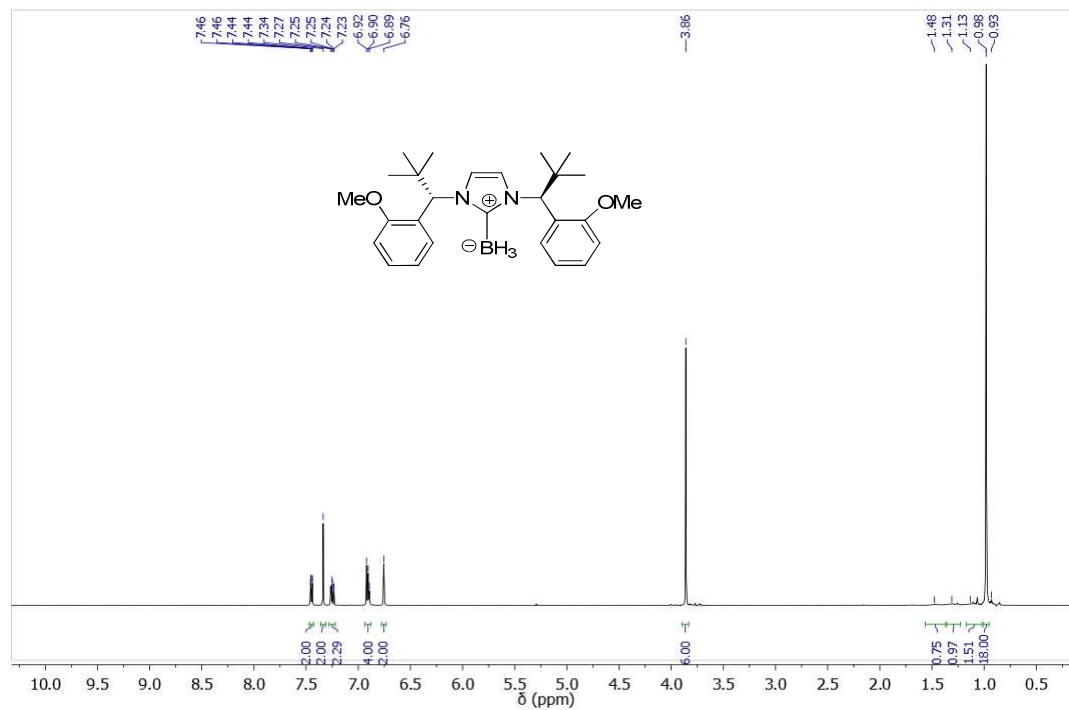


^{11}B NMR spectrum:

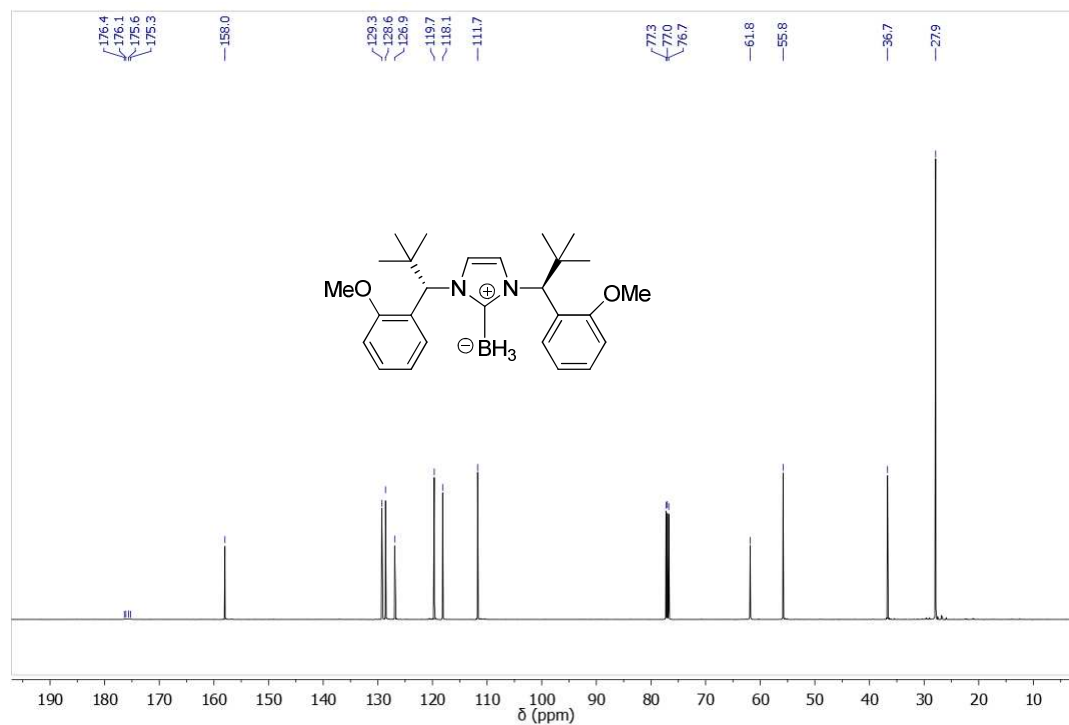


4. NMR spectra of (1,3-bis((*S*)-1-(2-methoxyphenyl)-2,2-dimethylpropyl)-1*H*-imidazol-3-ium-2-yl) trihydroborate (6):

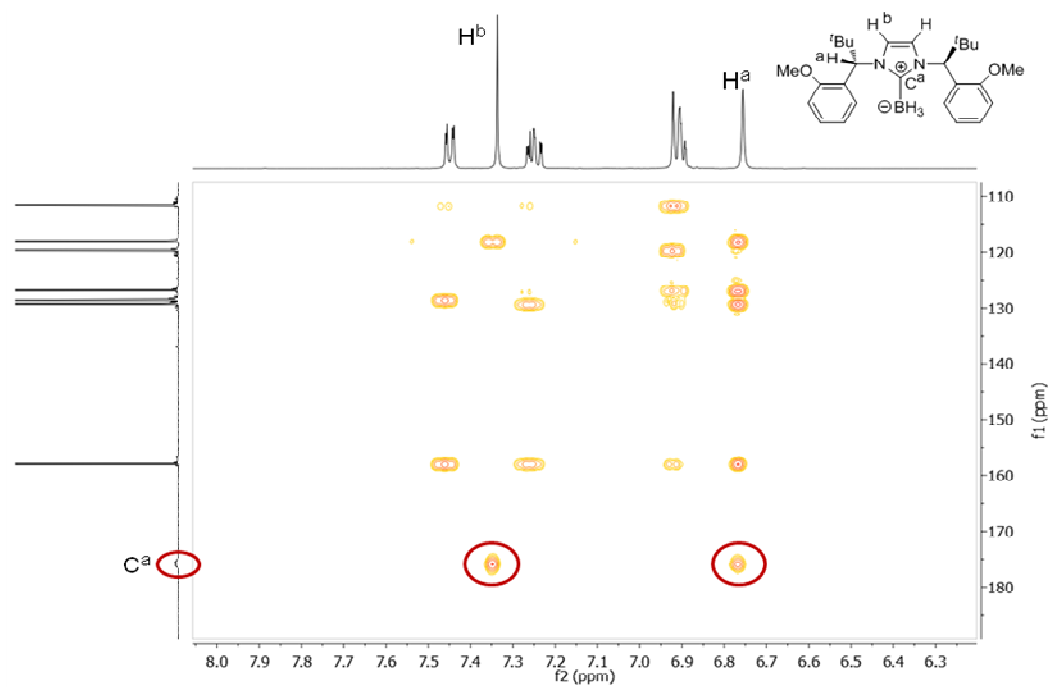
^1H NMR spectrum:



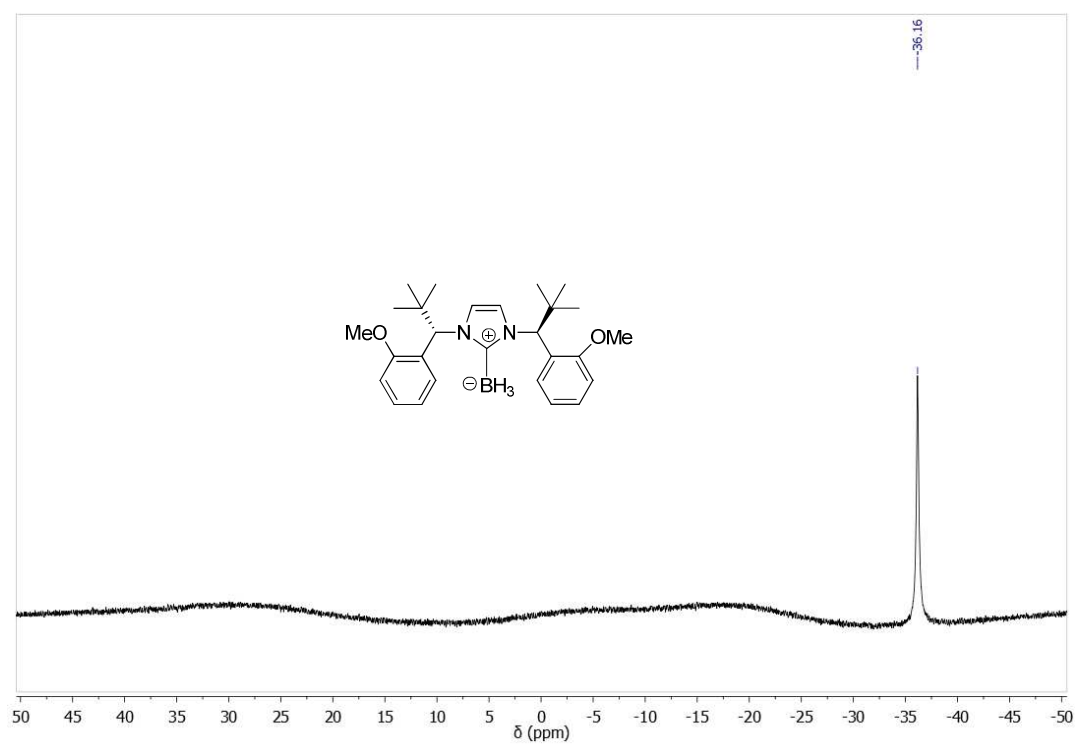
^{13}C NMR spectrum:



Magnified proton carbon correlation spectrum (HMBC):

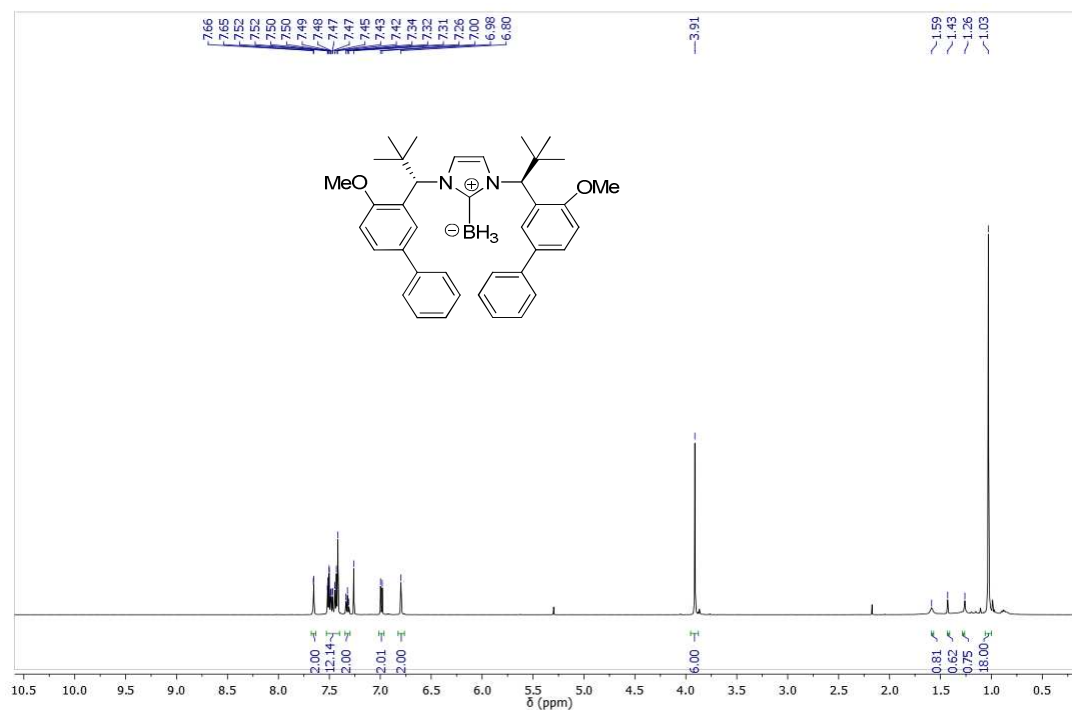


^{11}B NMR spectrum:

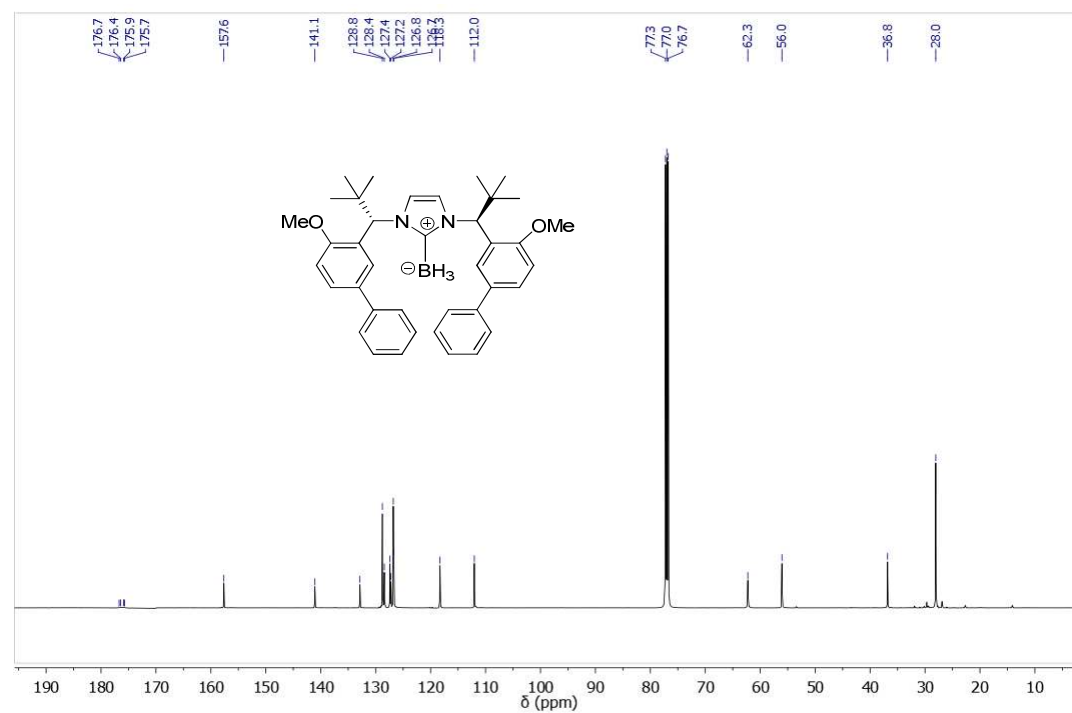


5. NMR spectra of (1,3-bis((S)-1-(4-methoxy-[1,1'-biphenyl]-3-yl)-2,2-dimethylpropyl)-1H-imidazol-3-ium-2-yl) trihydroborate (7):

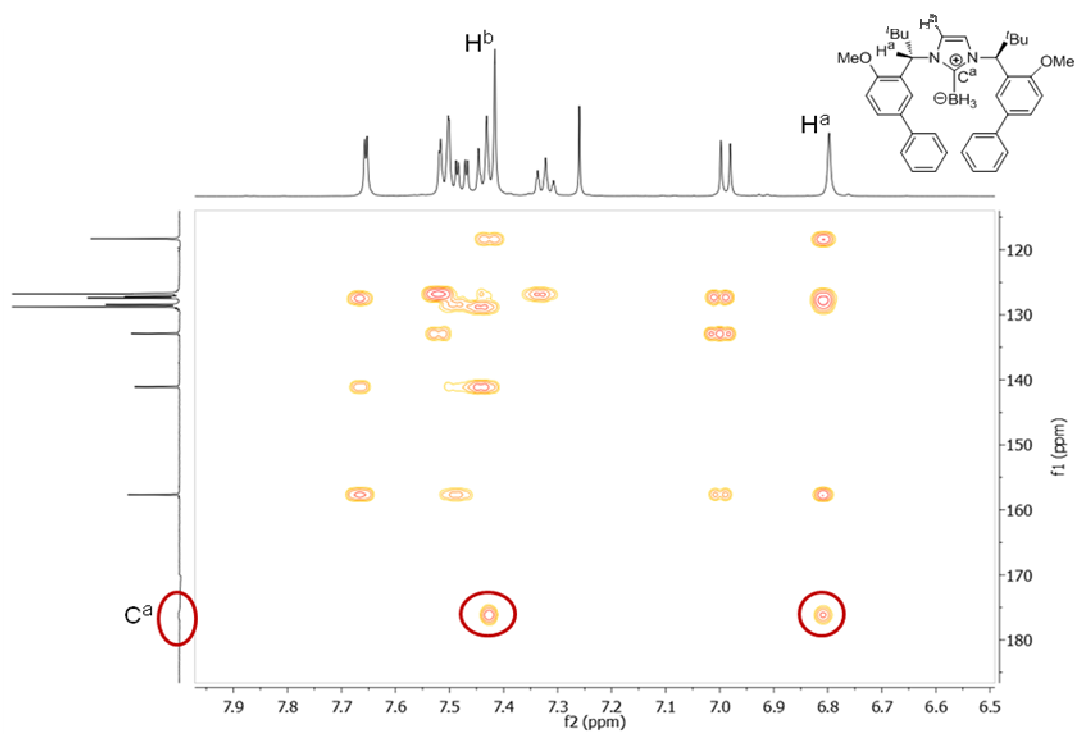
¹H NMR spectrum:



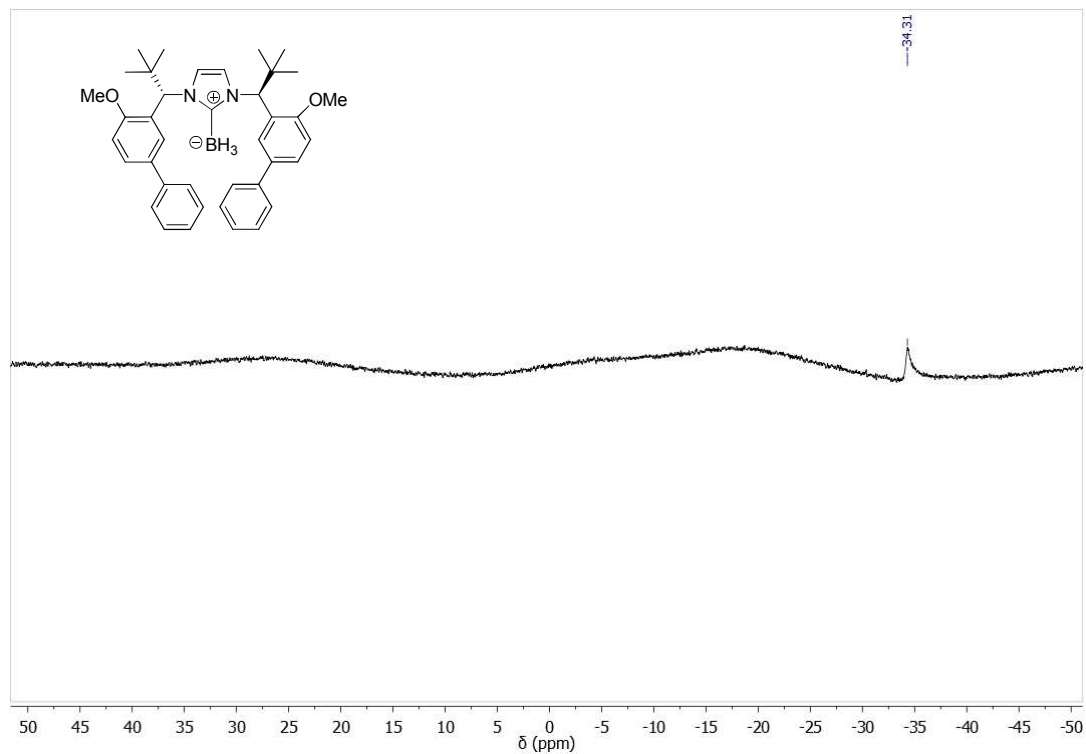
¹³C NMR spectrum:



Magnified proton carbon correlation spectrum (HMBC):

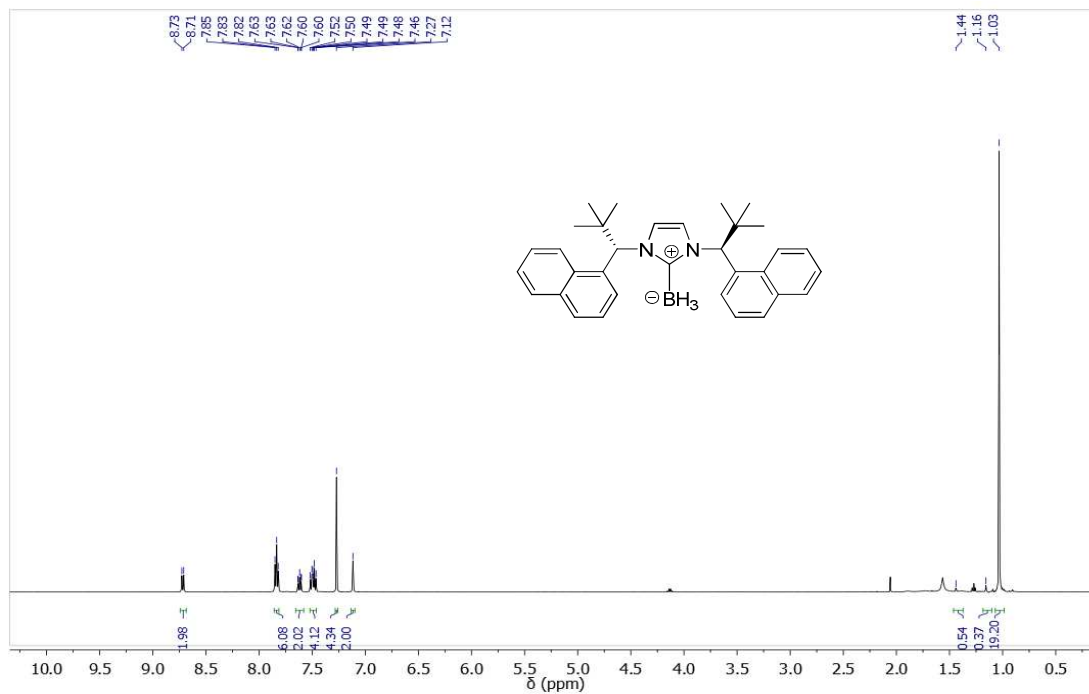


^{11}B NMR spectrum:

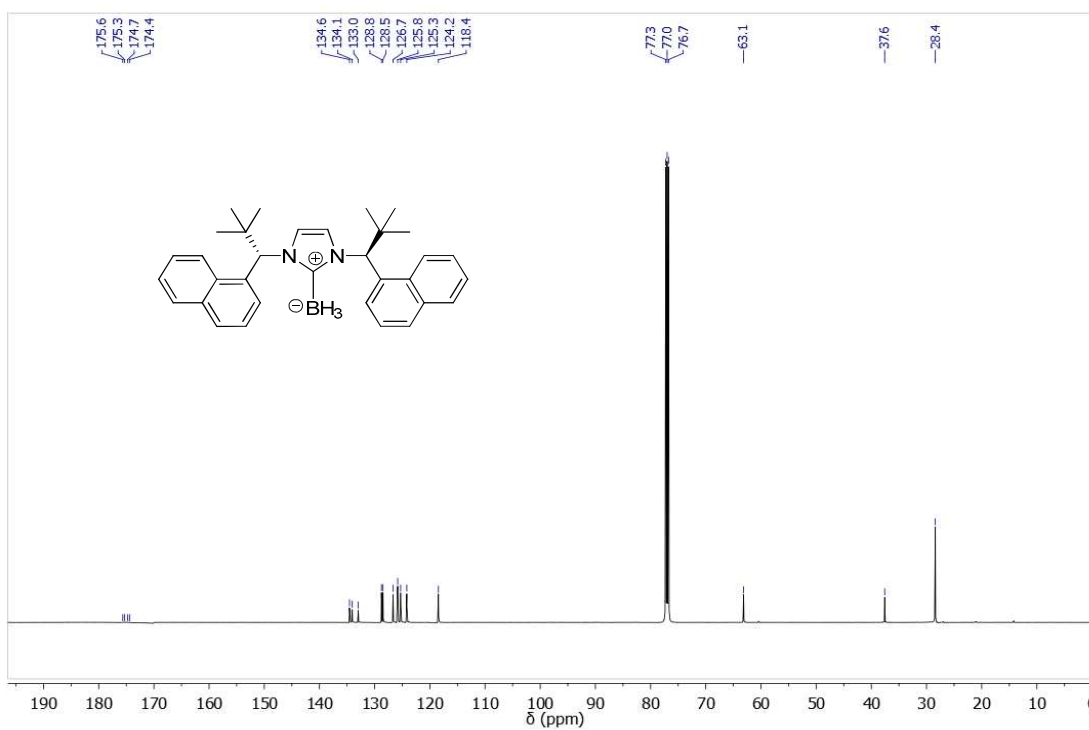


6. NMR spectra of (1,3-bis((*S*)-2,2-dimethyl-1-(naphthalene-1-yl)propyl)-1*H*-imidazol-3-ium-2-yl) trihydroborate (8):

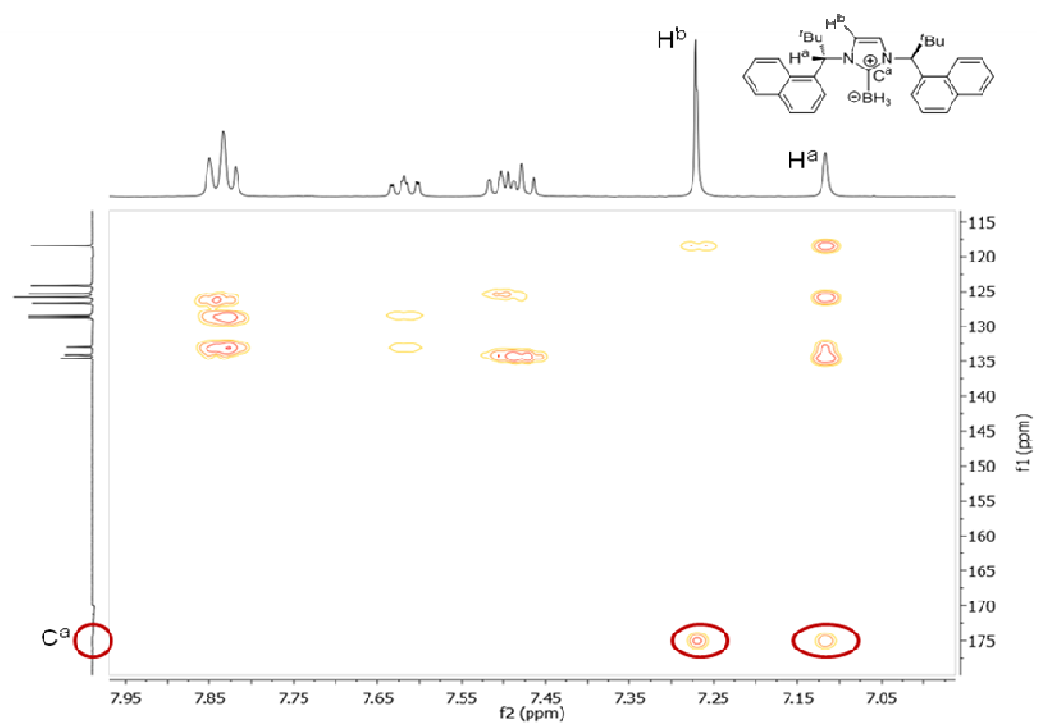
¹H NMR spectrum:



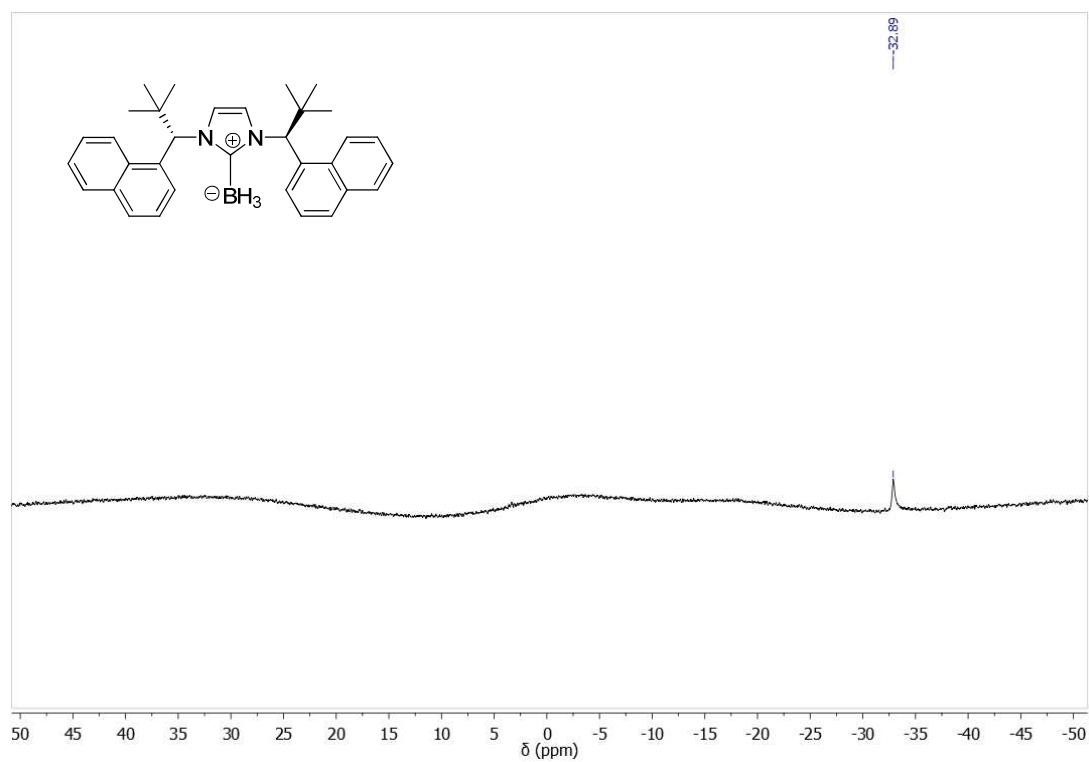
¹³C NMR spectrum:



Magnified proton carbon correlation spectrum (HMBC):

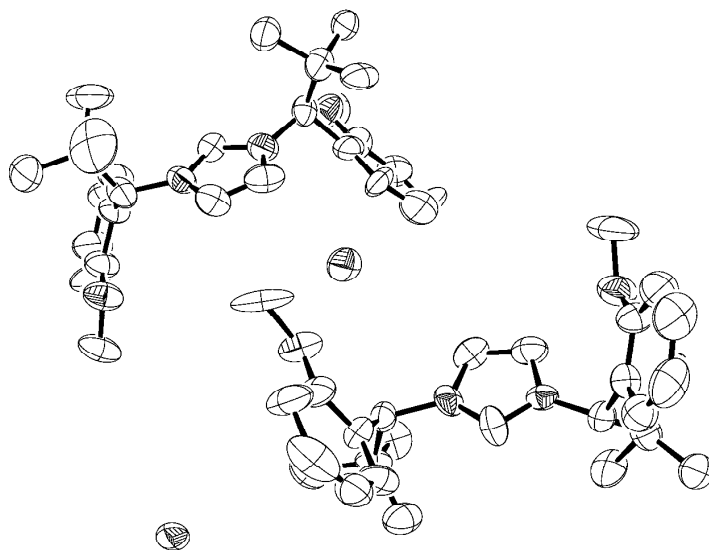


¹¹B NMR spectrum:



7. X-ray structure determination of imidazolium salt 2:

Crystals suitable for X-ray diffraction were grown from a saturated solution of the sample in benzene. However, due to the disordered solvent, the quality of the structure is not optimal.



There are two independent molecules per asymmetric unit that differ by the position of the o-methyl groups.

Crystallographic data:

Empirical formula $C_{72}H_{92}I_2N_4O_4$; **Formula weight** 1331.35; **Temperature** 220 K; **Crystal system** monoclinic; **Space group** $P2_1$; **Unit-cell parameters** $a=12.9999(12)$ Å, $b=13.6228(9)$ Å, $c=20.590(2)$ Å, β 104.234(7); **Volume** 3534.5(5) Å³; **Z**=2; $\rho_{\text{calc}}=1.2515$ mg.mm⁻³ $\mu=0.938$ mm⁻¹ ; **F(000)** 1375 ; **Crystal size**(mm³) $0.3 \times 0.25 \times 0.1$; **2 θ range for data collection** 2.98 to 56.52°; **Index ranges** $-15 \leq h \leq 14$, $-16 \leq k \leq 16$, $0 \leq l \leq 24$; **Reflections collected** 26238, **Independent reflections** 16596 [$R(\text{int}) = 0.0628$]; **Data/restraints/parameters** 16596/1/594 ; **Goodness-of-fit on F^2** 1.053; **Final R indexes [$I > 2\sigma(I)$]** $R_1 = 0.0622$, $wR_2 = 0.1634$; **Final R indexes [all data]** $R_1 = 0.0793$, $wR_2 = 0.1783$; **Largest diff. peak/hole/e Å⁻³** 0.944/-0.945

Details of the crystal structure determination:

The data was collected using Mo radiation on a STOE image plate diffractometer. The structure was solved using direct methods in SIR 92 and refinement was carried out in the SHELXL program.

Very disordered benzene solvent molecules appeared in the Fourier difference map on three different positions (0.07 0.73 0.57, 0.44 0.77 0.57, 0.81 0.51 0.63). A satisfactory disordered model for these molecules was not found so that the bypass procedure was used inside the OLEX2 program. In the void, 226 electrons were found, which roughly correspond to 6 benzene molecules per asymmetric unit that were added to the formula. The use of this approximate solvent model hampered the quality of the structure determination. This is reflected in the thermal ellipsoids of the structure that are elongated for some of the atoms.