Supplementary Information

Experimental

Materials and Methods. *Tris*(pentafluorophenyl)borane (BCF) was obtained from Boulder Scientific and purified by sublimation under reduced pressure at 90°C. Bromobenzene was purified by distillation over CaH_2 prior to use. Pyridine and 2,6-Lutidine (Lut) and N-methyl, 2,2,6,6- tetramethyl piperidine (MeTMP) were obtained from Aldrich and used as received. 2,2,6,6-tetramethylpiperidine (TMP) also was obtained from Aldrich and purified by distillation.

Instrumentation. Sample preparation was carried out in an inert (nitrogen) atmosphere glove box. All NMR spectra were recorded on a 500 MHz Varian INOVA spectrometer equipped with a boron-free 5-mm dual broadband gradient probe. ^{11}B NMR spectra were referenced externally to $BF_3 \bullet Et_2O$ ($\delta = 0$) and were acquired in boron-free quartz NMR tubes. C_6D_5Br was used as an internal reference for ^1H and ^{13}C NMR measurements. Calorimetric measurements were performed on a Calvet calorimeter, C80, operating in isothermal mode. Calorimetric measurements were conducted in a modified Hastealloy® reversal mixing cell. The commercial mixing vessels were modified to include an inlet with 1/16 inch OD PEEK tubing that allowed gases to be introduced.

Calorimetry measurements. Bromobenzene solutions of the Lewis acid (2.0 mL, 0.1 M) and Lewis base (2.0 mL, 0.11 M) were placed in separate chambers of a sample calorimeter cell while bromobenzene (4.0 mL) was placed in the reference calorimeter cell. Both cells were charged in a glove box under ambient nitrogen atmosphere. The cells were placed in the C80 and then pressurized with ~ 6.89 bars of hydrogen pressure. Then, the cells were allowed to equilibrate before being mixed, and the heat of hydrogenation determined. Calorimetric trace in all cases indicates completion of the hydrogenation event within 1 h. ^{11}B NMR spectra of the hydrogenated FLP solutions were acquired to determine the extent of conversion and identify the hydrogenated product. The instrument response was determined by measuring the heat of dissolving potassium chloride in aqueous media providing an additional test of the instrument calibration relative to the accepted literature value for $\Delta H_{diss}(KCl/H_2O)$. The return of q(t) to baseline takes ca. 300 s for this reaction assumed to be instantaneous. In our experiments, the integrated heat flow, q(t), was collected at 1.5-s intervals until the heat signal returned to baseline, thus providing thousands of data points to be used in processing the reaction conversion.

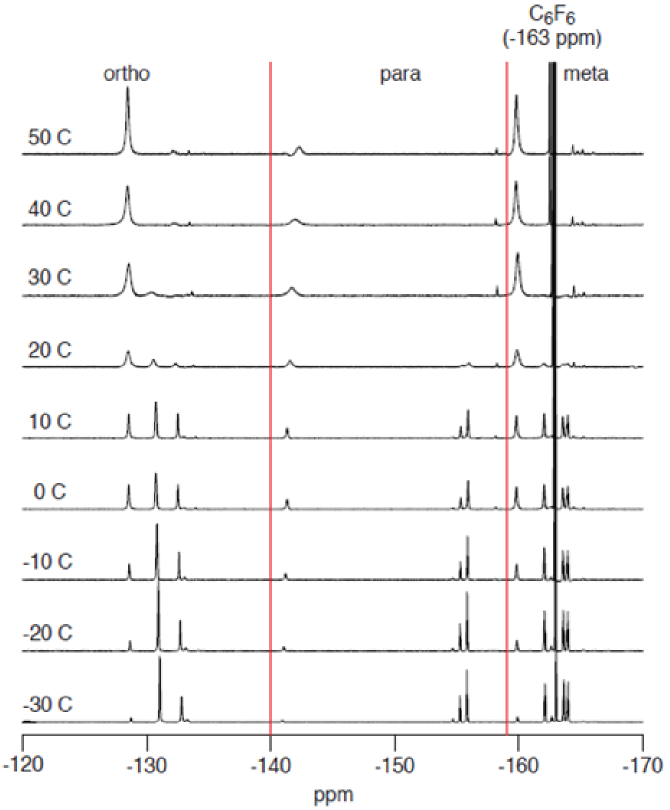

Figure S.1. ^{19}F NMR of Lut + BCF ↔ Lut—BCF (eq 7)

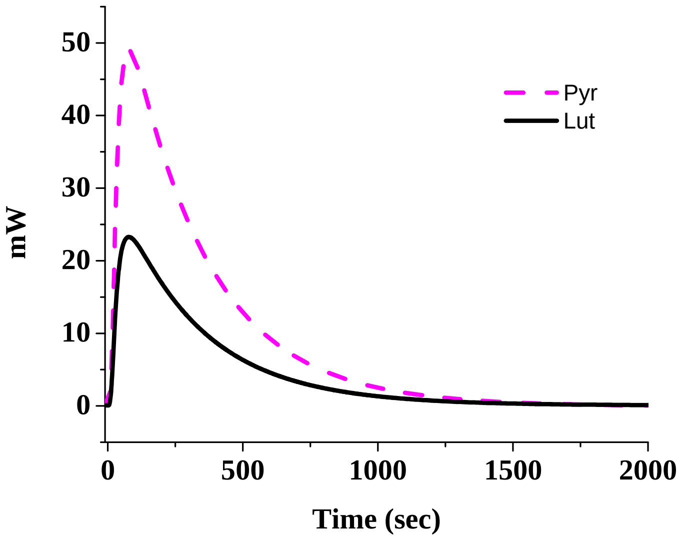

Figure S.2. Comparison of Heat Released from Mixing the Lewis Acid BCF with the Lewis Base Pyridine to the Heat Released from Mixing BCF with Lut (eq 7) in C_6H_5Br

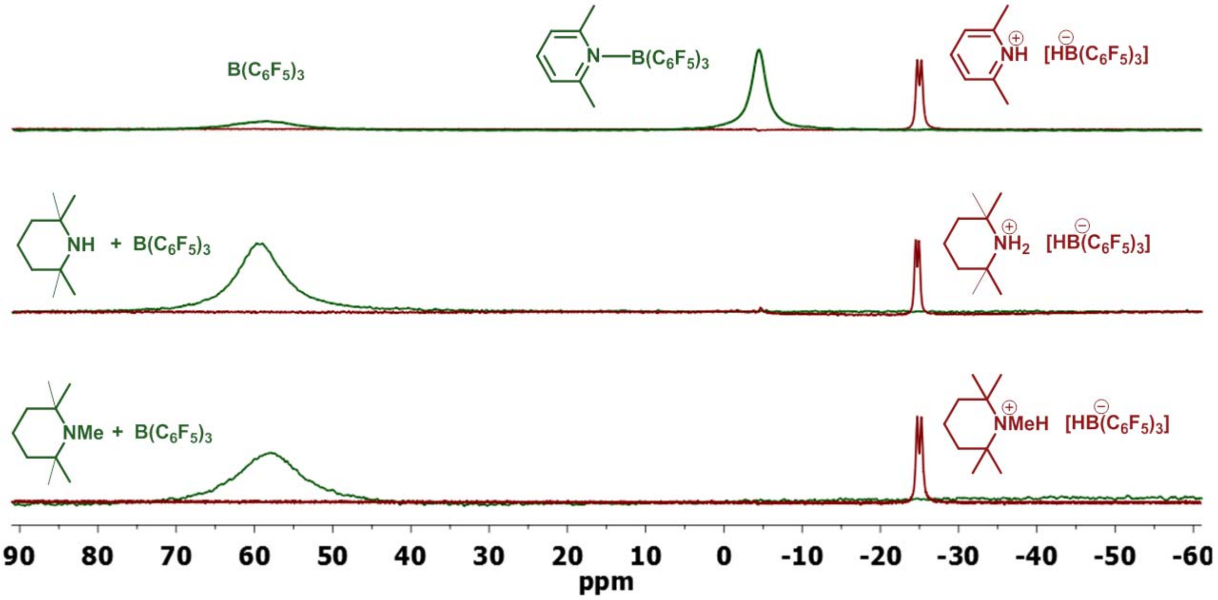

Figure S.3. ^{11}B NMR Spectra of the FLP's before Hydrogenation (green trace) and Ionic Products Formed (red trace) from Calorimetry

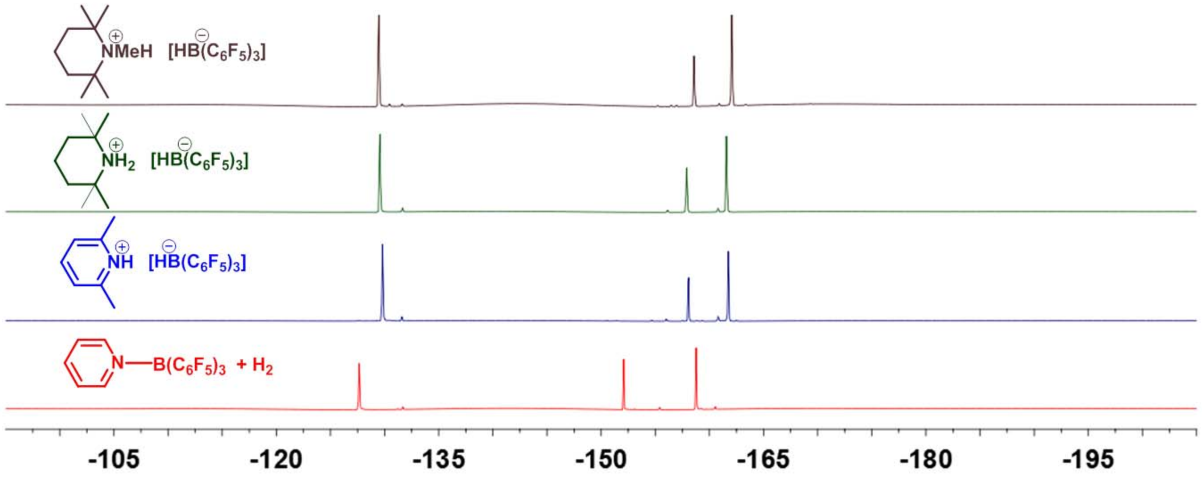

Figure S.4. ^{19}F NMR Spectra of the Products Formed in the Calorimetry shows only the Presence of the Ionic Products, [Lewis baseH]$^{+}$[HBCF]$^{-}$