Contents:

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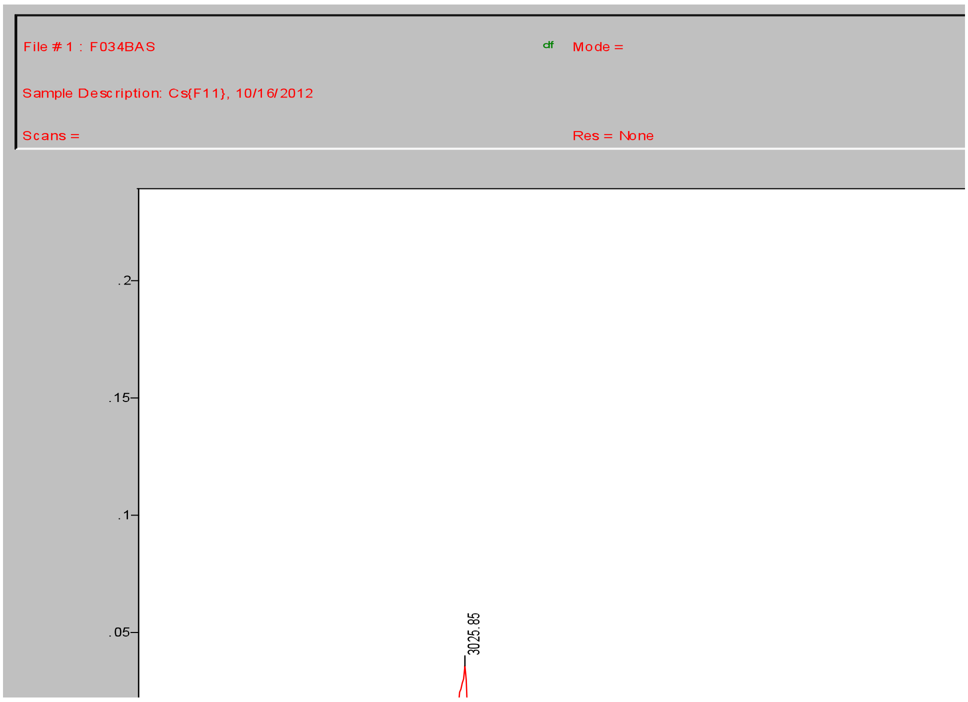
Fig. S1. ATR-IR spectrum of $Cs(CHB_{11}F_{11})$:



File # 1 : F034BAS

df

Mode =

Sample Description: Cs(F11), 10/16/2012

Scans =

Res = None

Fig. S2. ^{19}F NMR $Cs(CHB_{11}F_{11})$ in acetone-d_6:

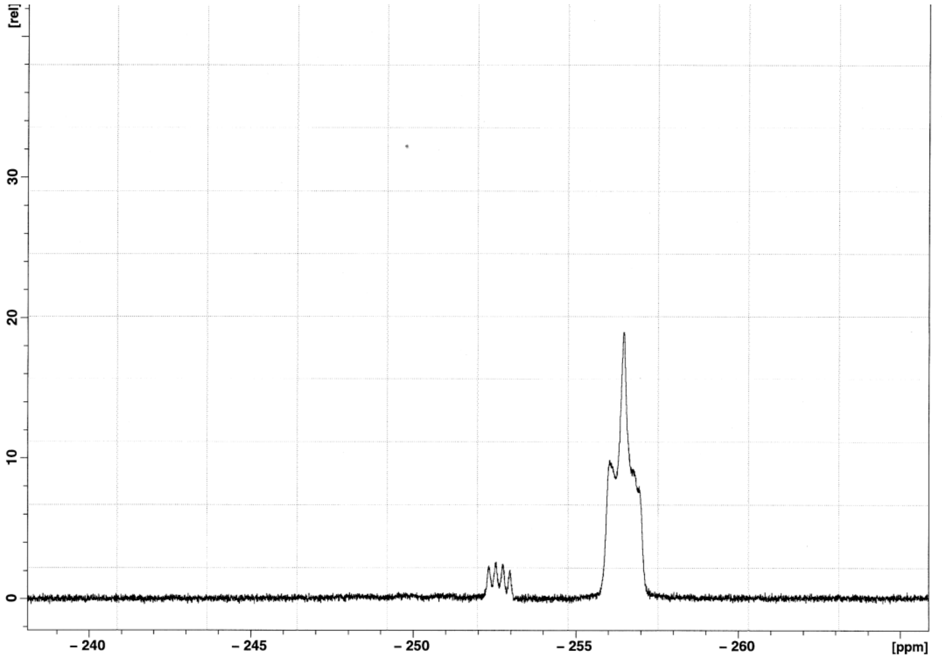


Fig. S3. ^{11}B NMR Cs($CHB_{11}F_{11}$) in acetone-d_6:

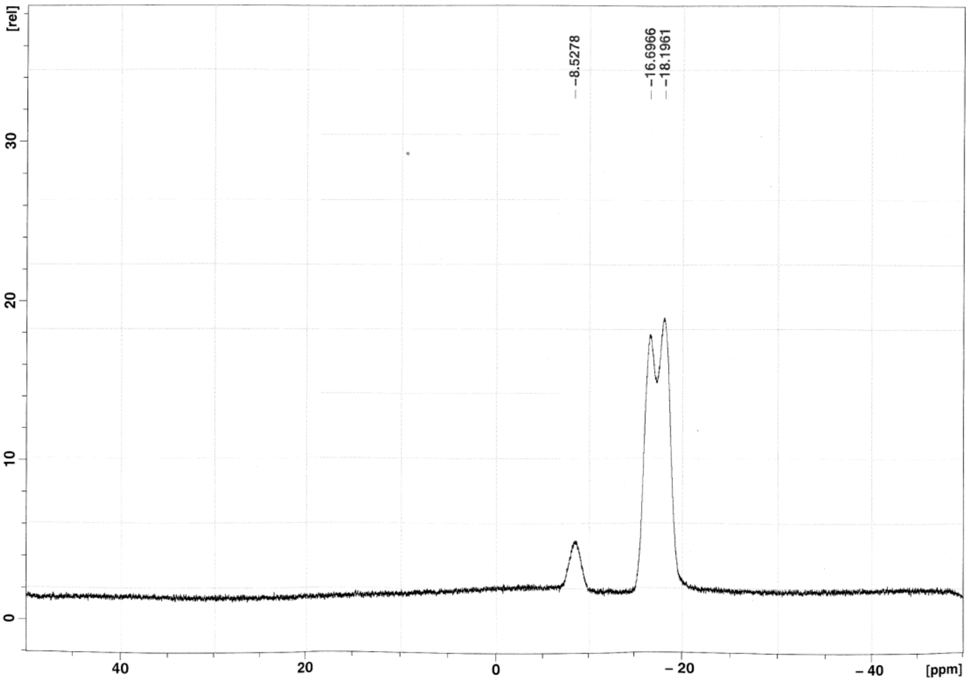


Fig. S4. Negative ion electrospray ionization mass spectrum of Cs($CHB_{11}F_{11}$):

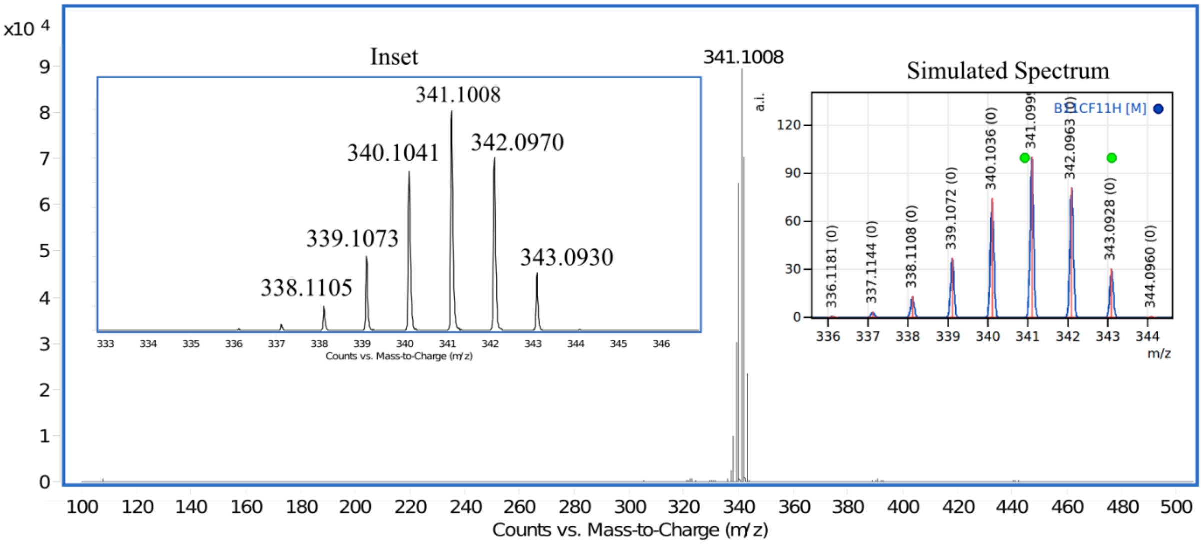
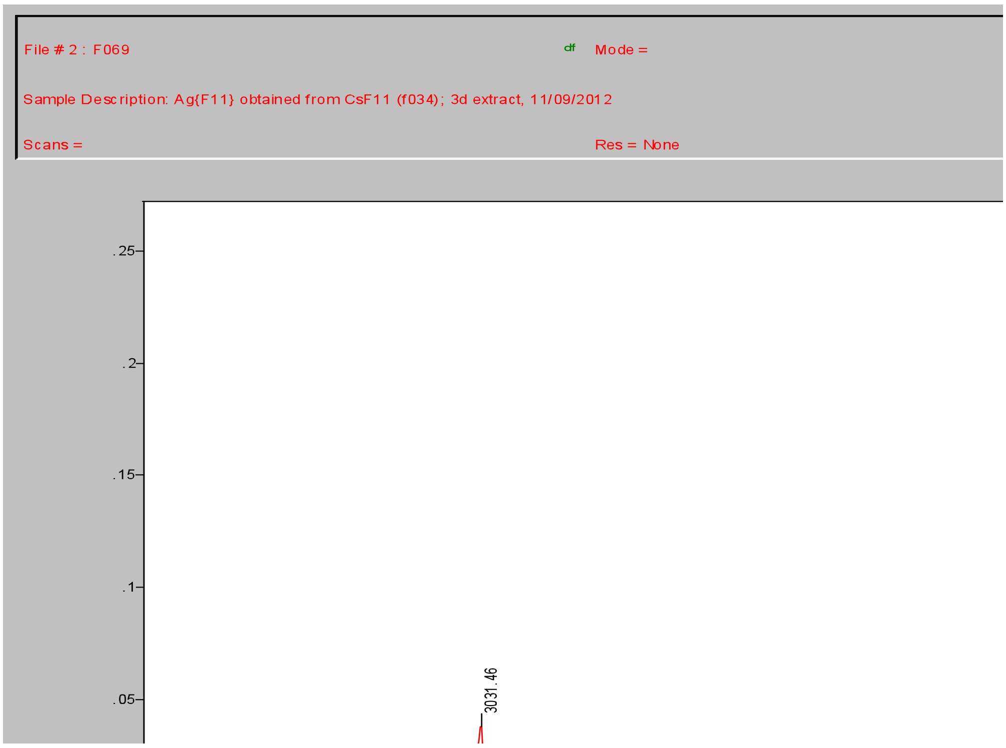


Fig. S5. ATR IR spectrum of $Ag(CHB_{11}F_{11})\cdot 2C_6H_6$:


File # 2 : F069 df Mode =

Sample Description: Ag{F11} obtained from CsF11 (f034); 3d extract, 11/09/2012

Scans = Res = None

Fig. S6. ^1H NMR spectrum of $Ag(CHB_{11}F_{11})\cdot 2C_6H_6$:

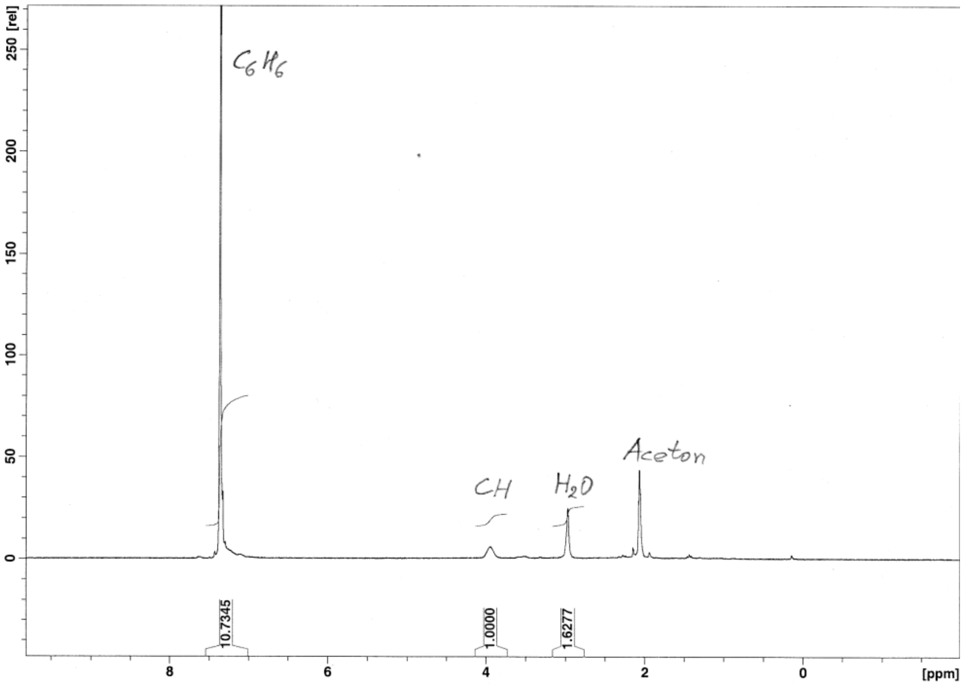
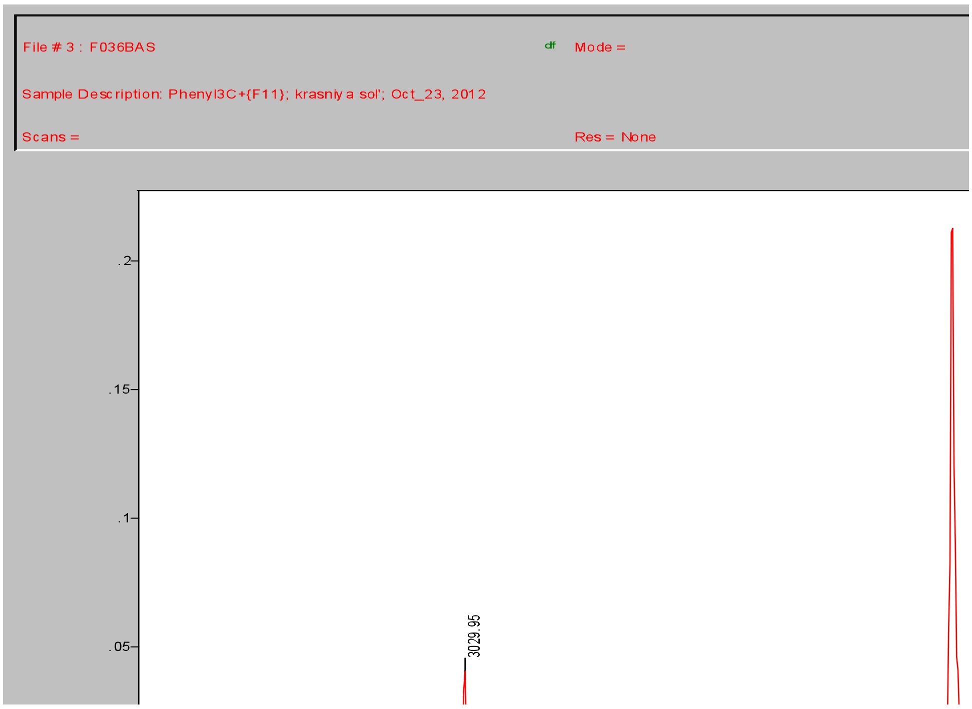


Fig. S7. ATR IR spectrum of [$(C_6H_5)_3C$][$CHB_{11}F_{11}$]:



File # 3 : F036BAS

Mode =

Sample Description: Phenyl3C+{F11}; krasniya sol'; Oct_23, 2012

Scans =

Res = None

Fig. S8. ^{1}H NMR [$(C_6H_5)_3C$][$CHB_{11}F_{11}$] in CD_2Cl_2.

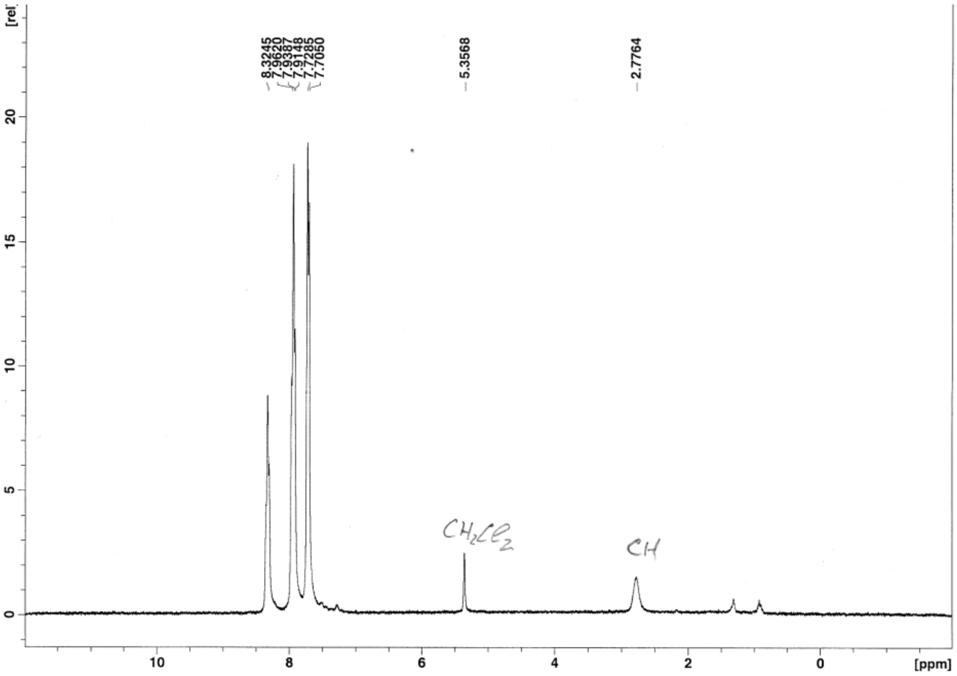


Fig. S9. ATR IR spectrum of [(Et$_3$Si)$_2$H][(CHB$_{11}$F$_{11}$]. Note the diagnostic νSiHSi band at 1873 cm^{-1}.[25]

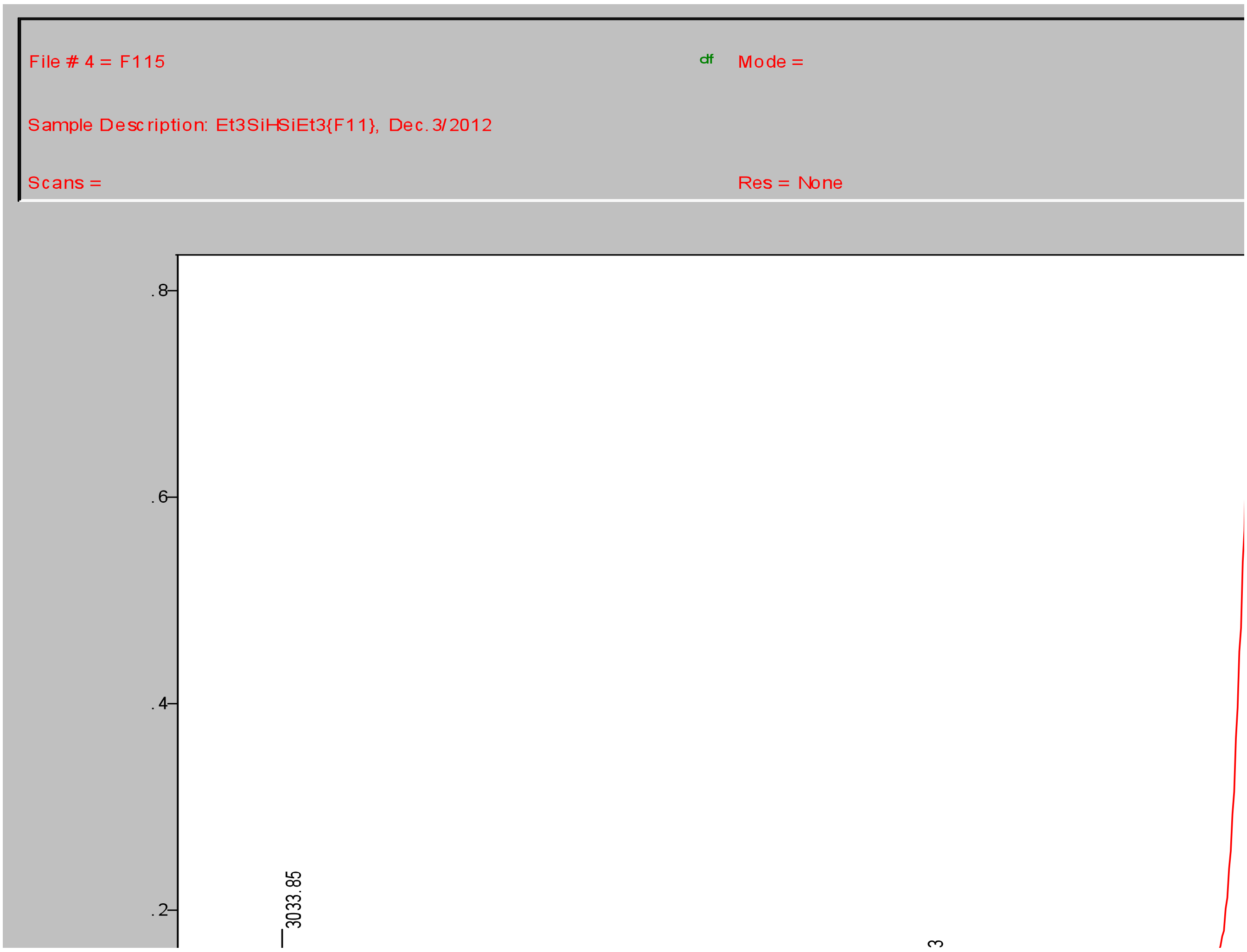


Fig. S10. Comparison of IR spectra of protio (blue) and deuterio (red) H(CHB$_{11}$F$_{11}$) with assignments indicated below. Unaffected peaks (black font in assignments given below) are νCH of the anion at 3029 cm^{-1}, νBB at ca. 1200 cm^{-1} (which happens to coincide with νFDF) and four relatively sharp νBF bands in the 700 cm^{-1} region. Complexity in the region below 1000 cm^{-1} indicates that δFHF and/or δFDF are broad and either anharmonic or subject to distortions from resonance effects leading to transparent windows (Evans holes), an effect commonly observed in strongly H-bonded systems. See discussion in ref. 14, p13872.

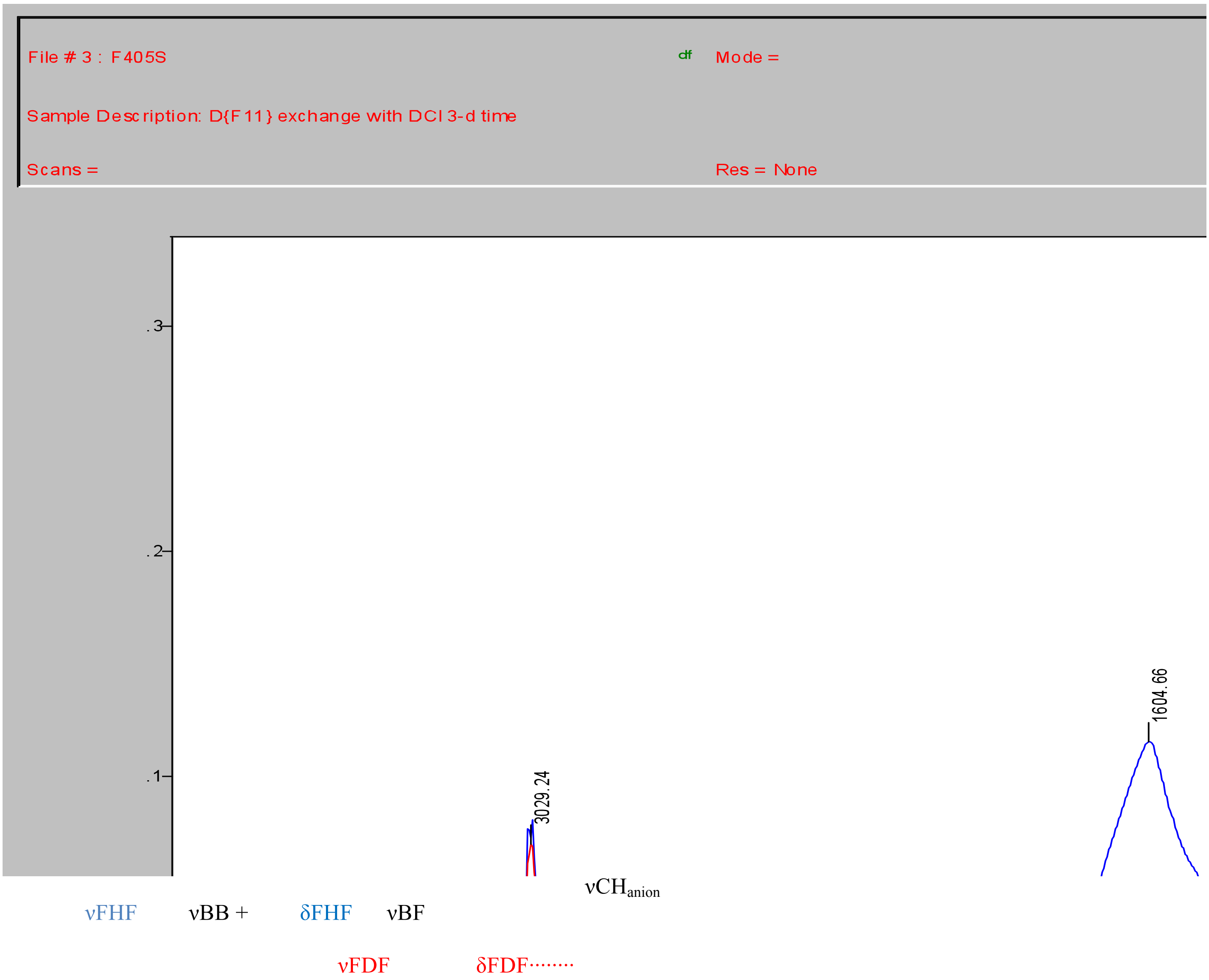
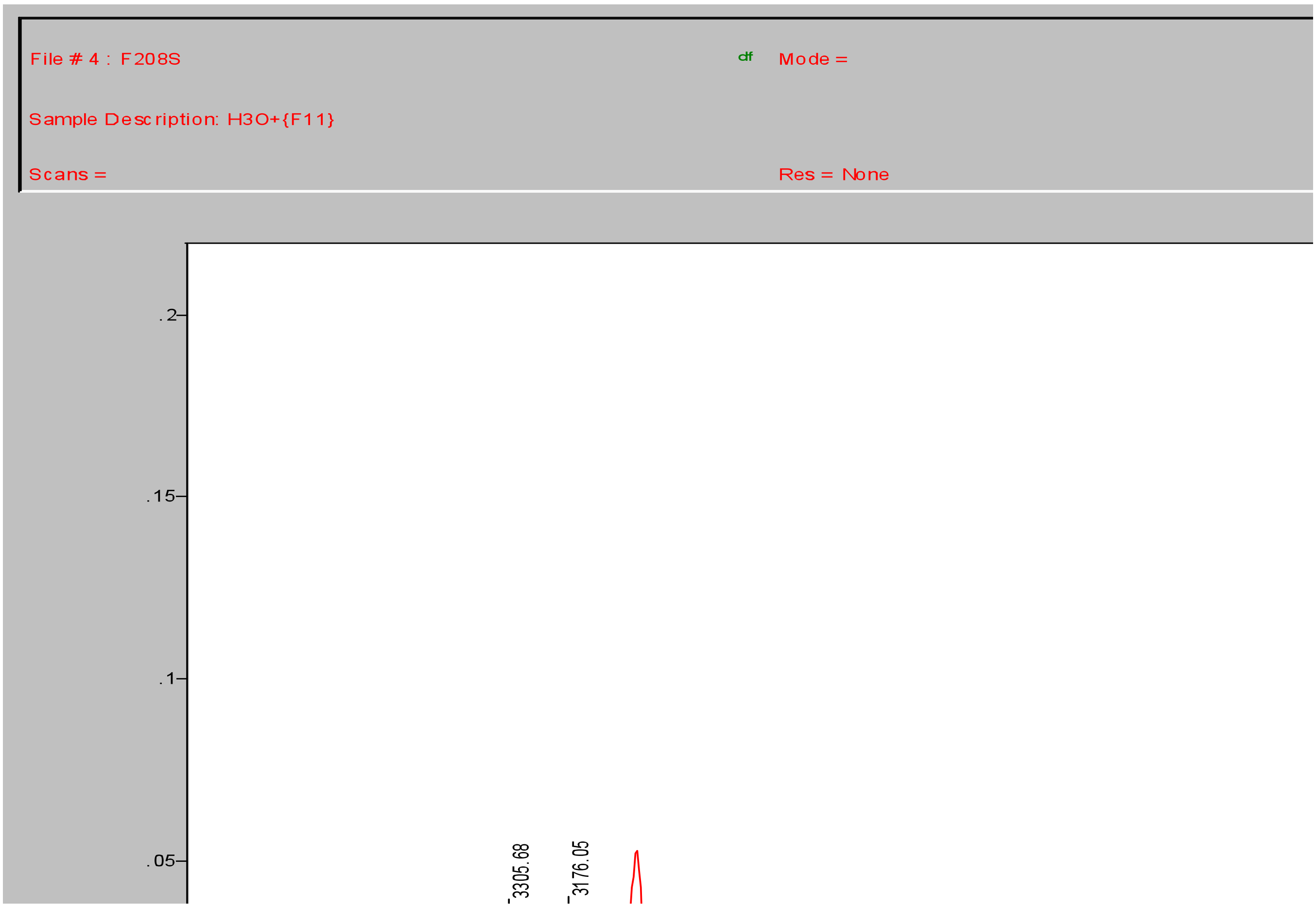


Fig. S11. IR spectrum of $[H_3O][CHB_{11}F_{11}]$ from minimal exposure of $H(CHB_{11}F_{11})$ to moist air:



File # 4 : F208S

Mode =

Sample Description: H3O+{F11}

Scans =

Res = None

Fig. S12. IR spectra of the benzenium ion salt $[C_6H_7][CHB_{11}F_{11}]$ from contact of $H(CHB_{11}F_{11})_{(s)}$ with dry benzene (red) compared with that of known $[C_6H_7][CHB_{11}Cl_{11}]$ (blue). The ring νCC bands near 1500 cm^{-1} coincide but the νCH bands vary with anion because of H-bonding. The νCH bands are assigned as follows: *sp*^{2} aromatic ca. 3100 cm^{-1}, carborane anion 3029 cm^{-1} and *sp*^{3} 2700-2820 cm^{-1}.

File # 4 : F404BAS

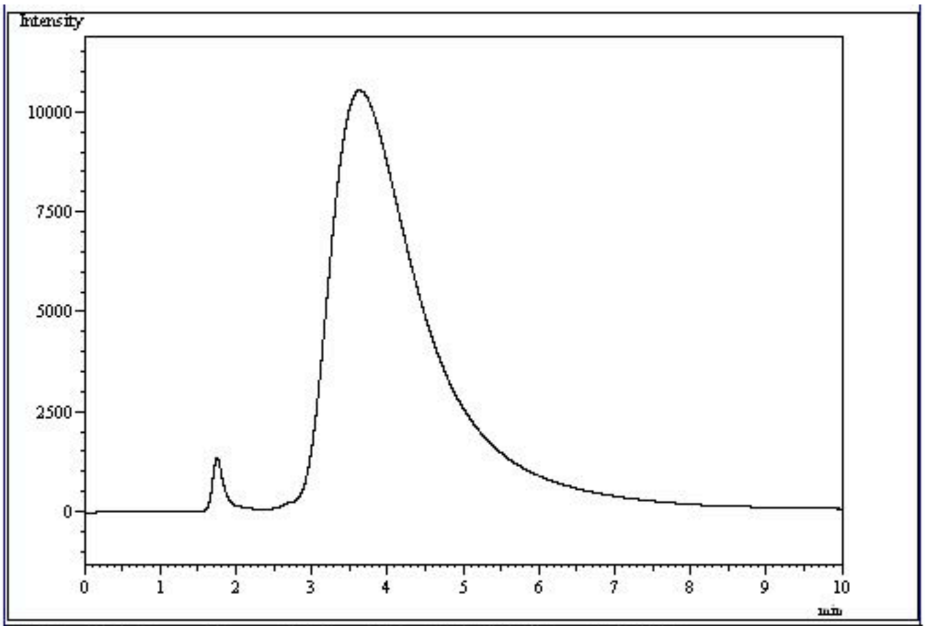
Mode =

Sample Description: to f404 added drop of C6H6

Scans =

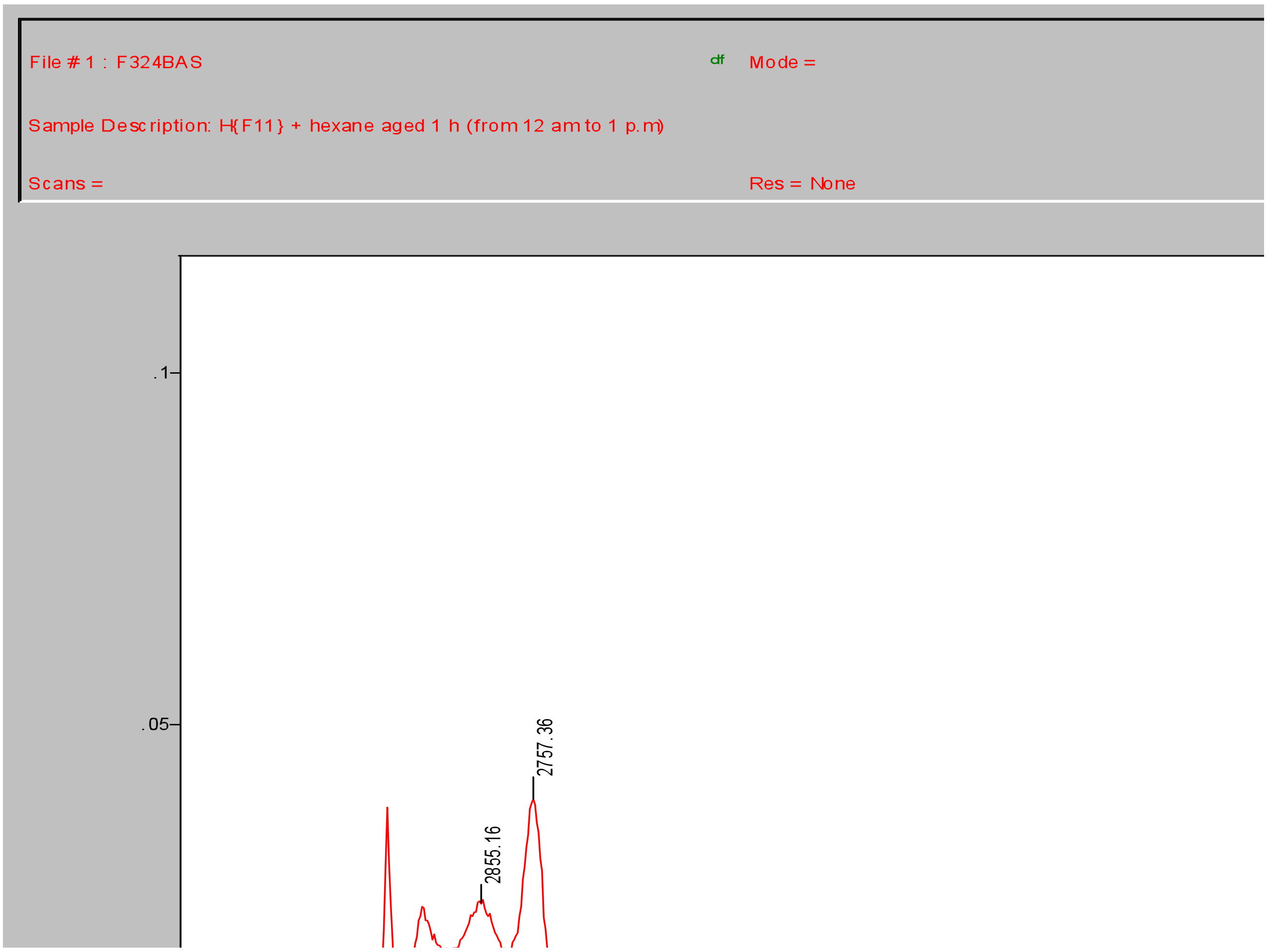
Res = None

Fig. S13. Gas Chromatographic trace for detection of H_2 (1.7 min) from the reaction of $H(CHB_{11}F_{11})$ with hexane under N_2 (3.7 min). About 50 mg of $H(CHB_{11}F_{11})$ was placed in a Schlenk tube under an N_2 atmosphere inside a glove box and 0.5 ml of *n*-hexane was added. After 8 h, when ca. 75% of acid was converted to carbocation salt(s), the gaseous phase was analyzed. Prior to this analysis, the gc was calibrated with a gas sample known to contain dihydrogen in dinitrogen.



Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	17.604	5817	616	0.696				
2	19.688	830215	8953	99.304				
Total		836032	9569					

Fig. S14. IR spectrum of carbocation salt(s) resulting from the reaction of H($CHB_{11}F_{11}$) with *n*-hexane. The spectrum of remnant unreacted acid has been subtracted.



File # 1 : F324BAS

Mode =

Sample Description: H{F11} + hexane aged 1 h (from 12 am to 1 p.m)

Scans =

Res = None

Fig. S15. IR spectrum of the *t*-butyl cation salt resulting from the reaction of $H(CHB_{11}F_{11})$ with *n*-butane. The spectrum of a small amount of unreacted acid has been subtracted.

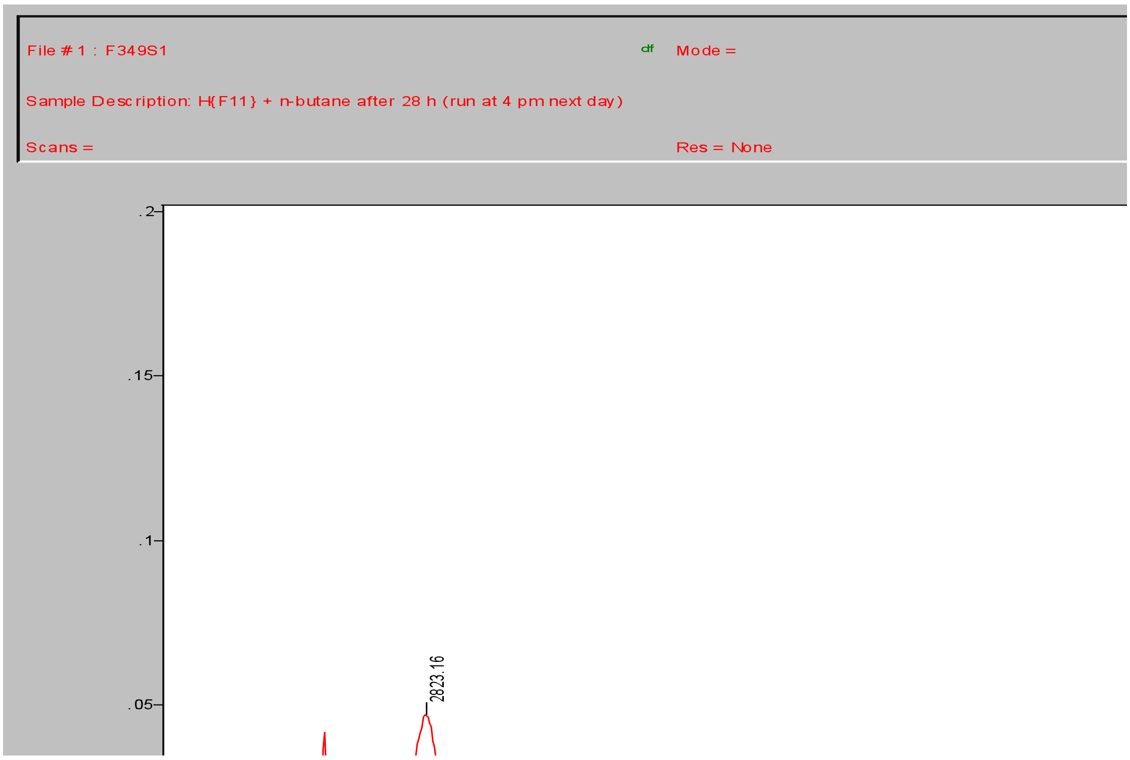


Fig. S16. IR spectrum of known $[t\text{-}Bu^+][CHB_{11}Cl_{11}^-]$ for comparison to Fig. S15 above. Note the similarity in the shape of the broad νCH band near 2800 cm^{-1}. Attempts to subtract the respective anions from S15 and S16 only partially helps to reveal the identity of the cation because (a) the cation spectra are not expected to be identical -- due to differences in CH hydrogen bonding with basicity of anion, and (b) cation-anion interactions in the solid state change the *anion* spectra as well, so finding the correct anion spectrum to subtract is problematic. Nevertheless, see Fig. S17 on following page.

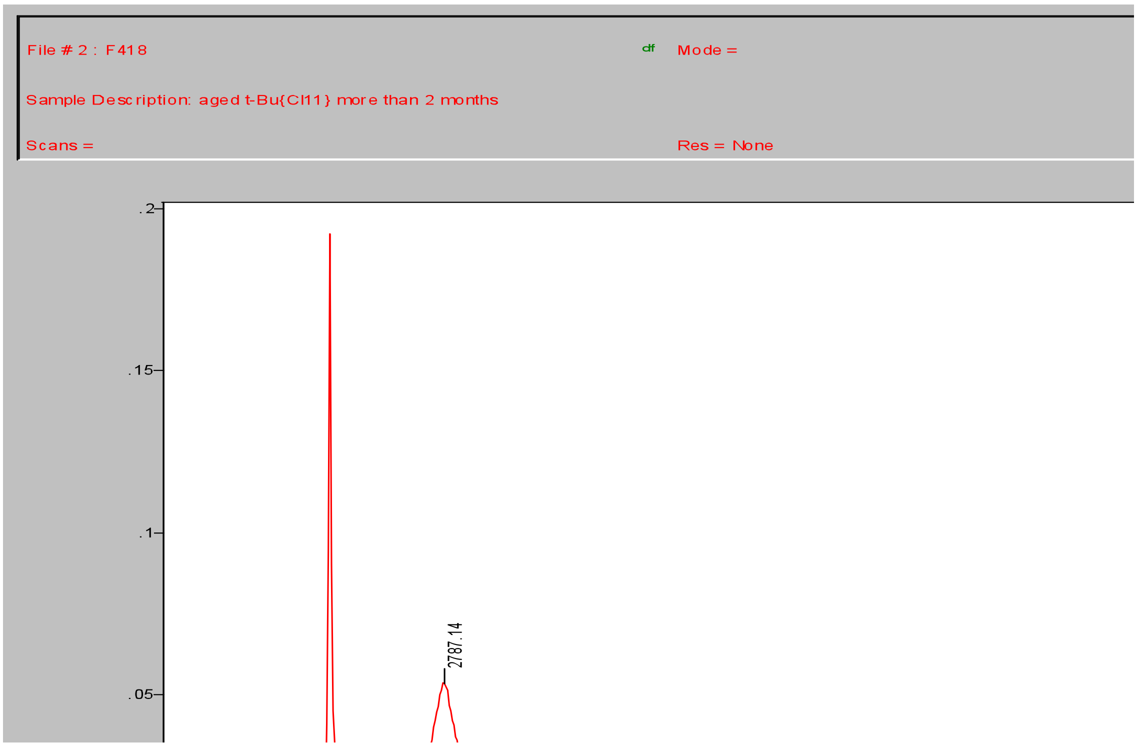


Fig. S17. Comparison of Figs. S15 (red) and S16 (black) showing coincidence of the two broad bands in the 1280-1400 cm^{-1} region arising from δCH of *t*-Bu^{+} and inexact subtraction of the anion below 1400 cm^{-1} (using the anion spectrum of [Et_2Cl][$CHB_{11}Cl_{11}$]).

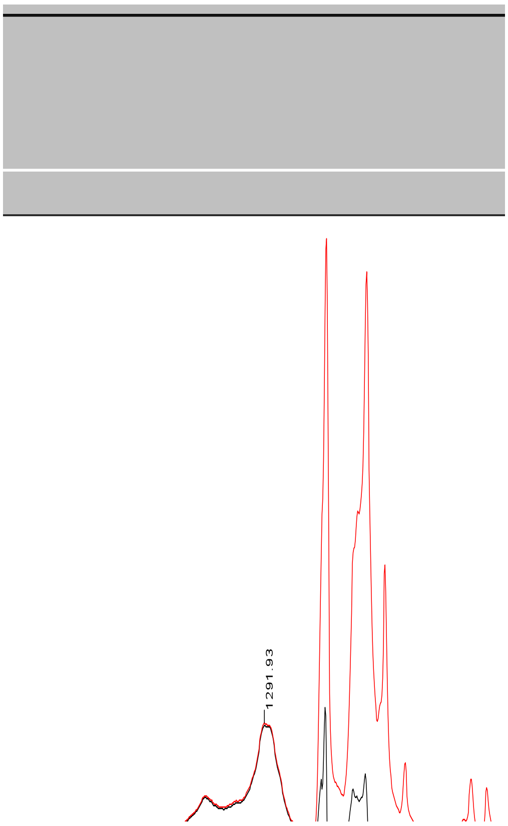


Fig. S18. Gas chromatographic trace of evolved hydrocarbon (hexene) from the reaction of C_6 carbocation $CHB_{11}F_{11}^-$ salt with NaH in $SO_{2(l)}$. Retention time (compound): 1.82 (Ar), 1.90 (SO_2), 3.62 (reference compound), 4.38 (hexene). The sample was prepared by dissolving NaH (excess) and the C_6 carbocation $CHB_{11}F_{11}^-$ salt in dry liquid SO_2 and stirring overnight at room temperature. After cooling to ca. -5 °C, SO_2 was allowed to boil off for several seconds and then, after warming the vessel to ca. 30 °C, a 30 µL sample of the remaining head gas was taken by syringe for gc/ms measurement.

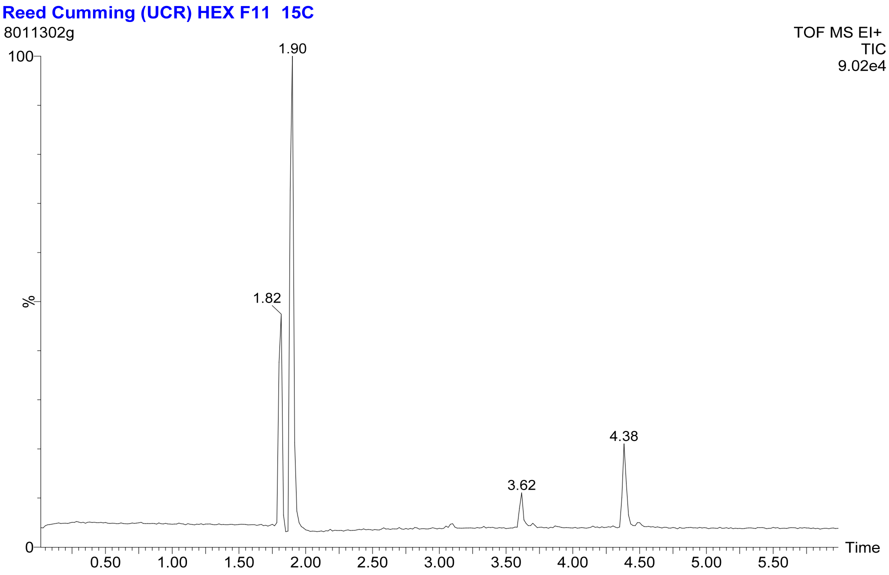


Fig. S19. Time of flight electron impact mass spectrum of hexene arising from deprotonation of C_6 carbocation $CHB_{11}F_{11}^-$ salt with NaH in liquid SO_2.

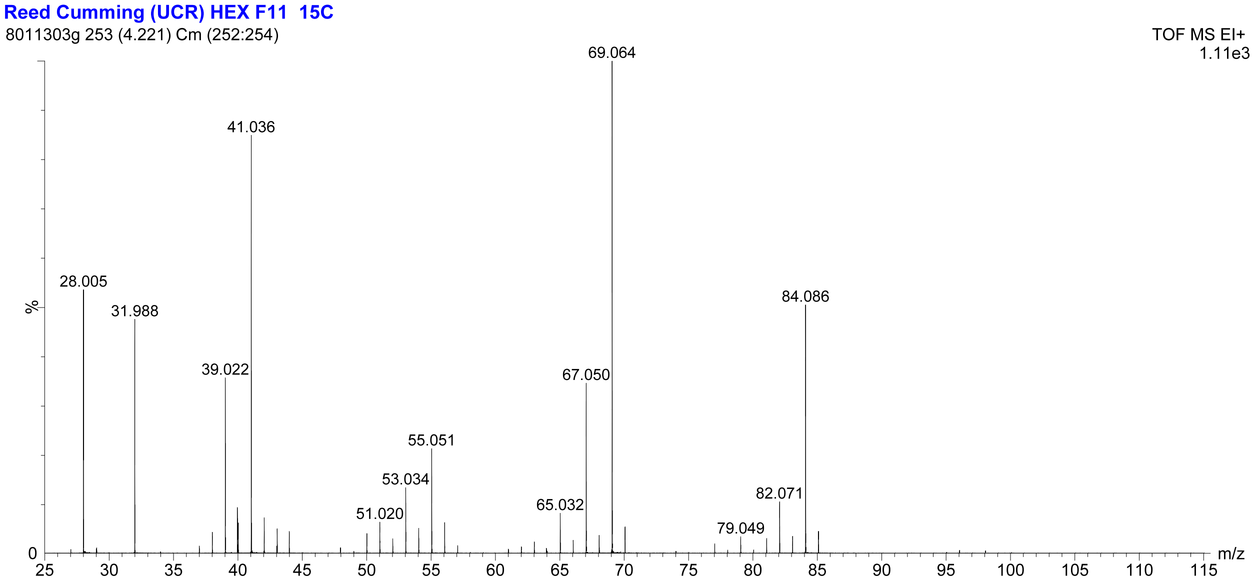
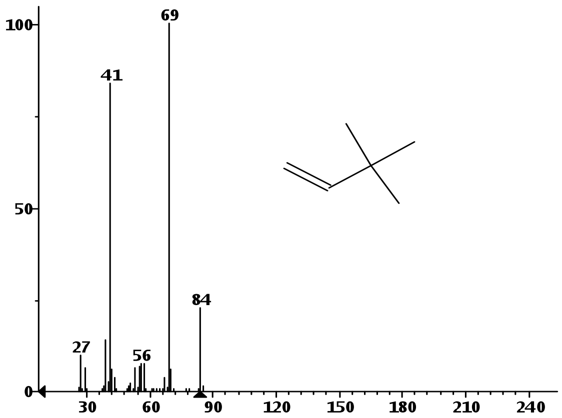
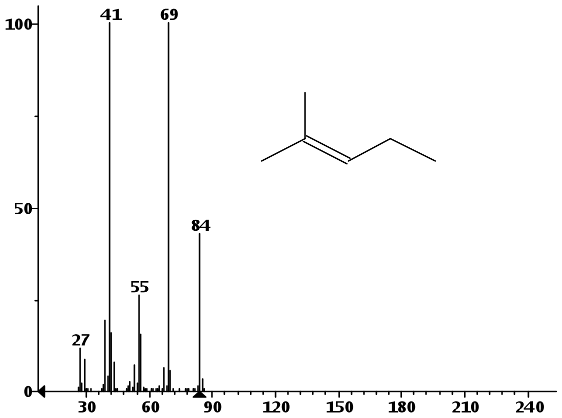


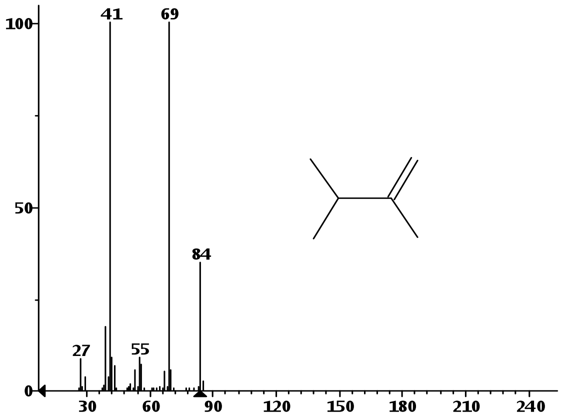
Fig. S20. Published electron impact mass spectra of various C_6 alkenes (as well as methyl-*cyclo*-pentane) with formula C_6H_{12} for comparison to Fig. S19.



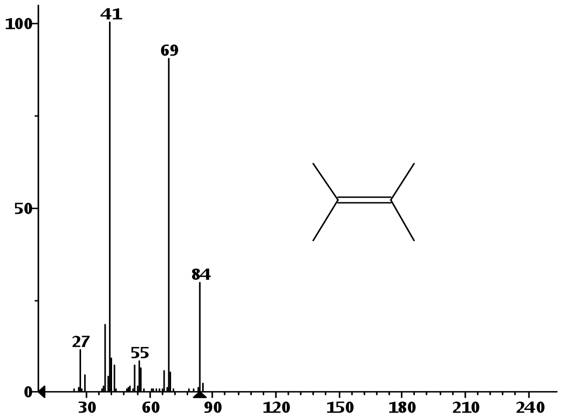
(mainlib) 1-Butene, 3,3-dimeth



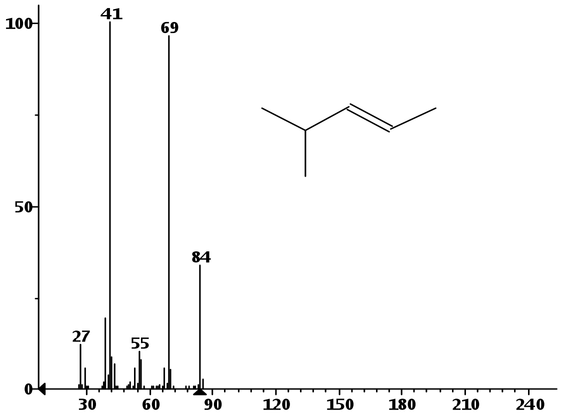
(mainlib) 2-Pentene, 2-meth



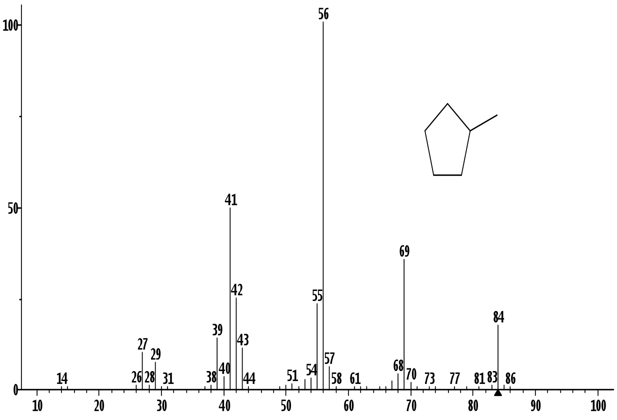
(mainlib) 1-Butene, 2,3-dimeth



(mainlib) 2-Butene, 2,3-dimeth



(mainlib) 2-Pentene, 4-meth



(mainlib) Cyclopentane, methyl

Fig. S21. Gas chromatograph of vapors above an intimately ground mixture of $NaH_{(s)}$ and C_6 carbocation salt isolated from the reaction of $H(CHB_{11}F_{11})$ with *n*-hexane. Retention time (compound): 1.80 (CO_2), 1.92 (*iso*-butane), 2.17 ref. compd., 2.23 (C_5H_{12} hydrocarbon), 2.28 ref. compd., 2.42 ref. compd., 2.67 (2,2-dimethylbutane), 2.80 ref. compd., 2.97 (2,3-dimethylbutane), 3.07 (2-methylpentane); 3.28 (3-methylpentane).

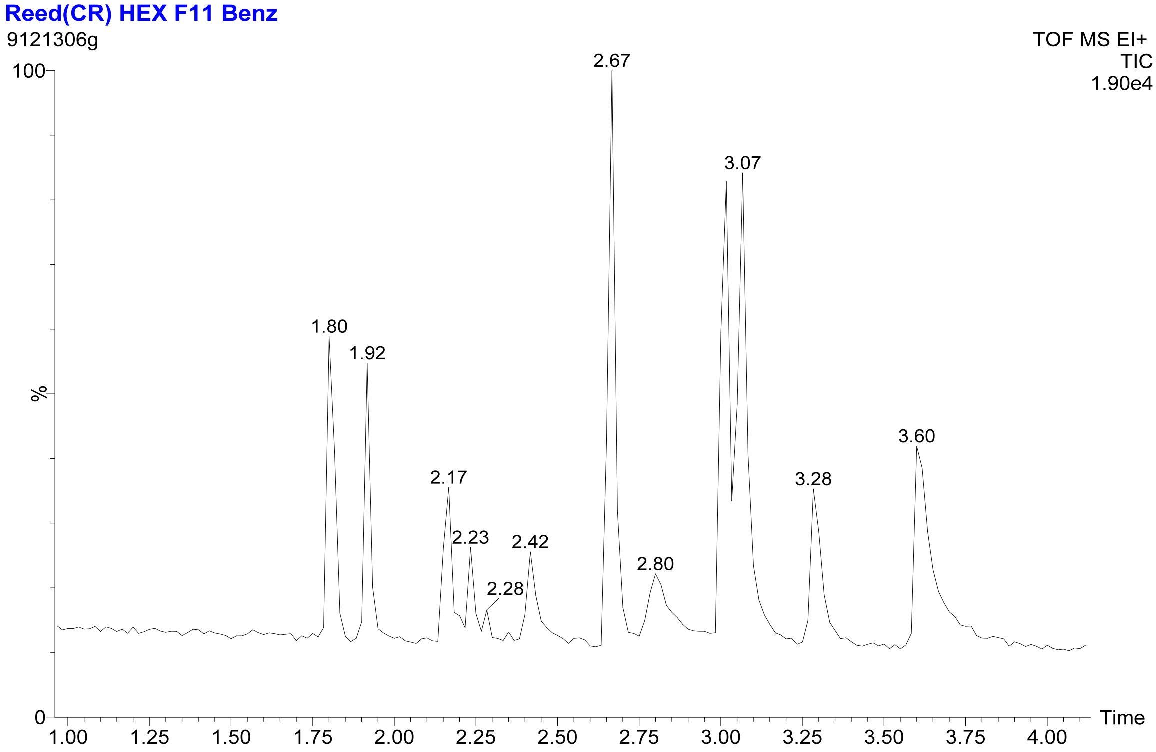


Fig. S22. Gas chromatogram of the head space vapors above an intimately ground mixture of $NaH_{(s)}$ and t-$Bu^+[CHB_{11}F_{11}^-]_{(s)}$ obtained from protonation of *n*-butane with $H(CHB_{11}F_{11})$ showing *iso*-butane as the major product (1.92). Retention time (compound): 1.82 (CO_2), 1.92 (*iso*-butane), 2.17, 2.42, 2.80 (reference compounds). Minor peaks at 2.05 and 2.25 correspond to traces of *n*-butane and a C_5H_{12} hydrocarbon, respectively, whose origin is uncertain.