Figure S1 Spectra obtained when referencing a C$_2$H$_3$D$_2$-Si(111) sample to a C$_2$H$_2$D$_3$-Si(111) sample. The shoulder and the two prominent peaks, at 2960 cm$^{-1}$, 2931 cm$^{-1}$, and 2877 cm$^{-1}$, in the p-polarized spectrum must originate from the CH$_3$ group thus further supporting the assignment of those peaks.
Figure S2 Spectrum a shows the p-polarized Si-H peak of a C\textsubscript{2}H\textsubscript{5}-Si(111) surface; spectrum b being the subtraction result of spectrum c and d; spectrum c showing the p-polarized C-D stretch region for a C\textsubscript{2}D\textsubscript{5}-Si(111) surface synthesized using all deuterated solvents; and spectrum d showing the p-polarized C-D stretch region for a C\textsubscript{2}D\textsubscript{5}-Si(111) surface synthesized using all protic solvents. Note that no residual signal attributable to the Si-H stretch is detectable in spectrum b.
Figure S3 The bottom spectrum (b) shows the subtraction result of a p-polarized spectrum from a C$_2$D$_5$-Si(111) surface synthesized using all protic solvents, and a p-polarized spectrum from a C$_2$D$_5$-Si(111) surface synthesized using all deuterated solvents. The top spectrum (a) is the p-polarized spectrum of a C$_2$H$_5$-Si(111) surface included as a scale reference. Note that no signal attributable to C-H stretching is present in the bottom spectrum suggesting that no side reactions involving the solvents took place, to the limit of detection.