Supporting Information

for

Triethylsilyl Perfluoro-Tetraphenylborate, $[Et_3Si^+][F_{20}\text{-}BPh_4^-]$, a widely used Non-Existent Compound

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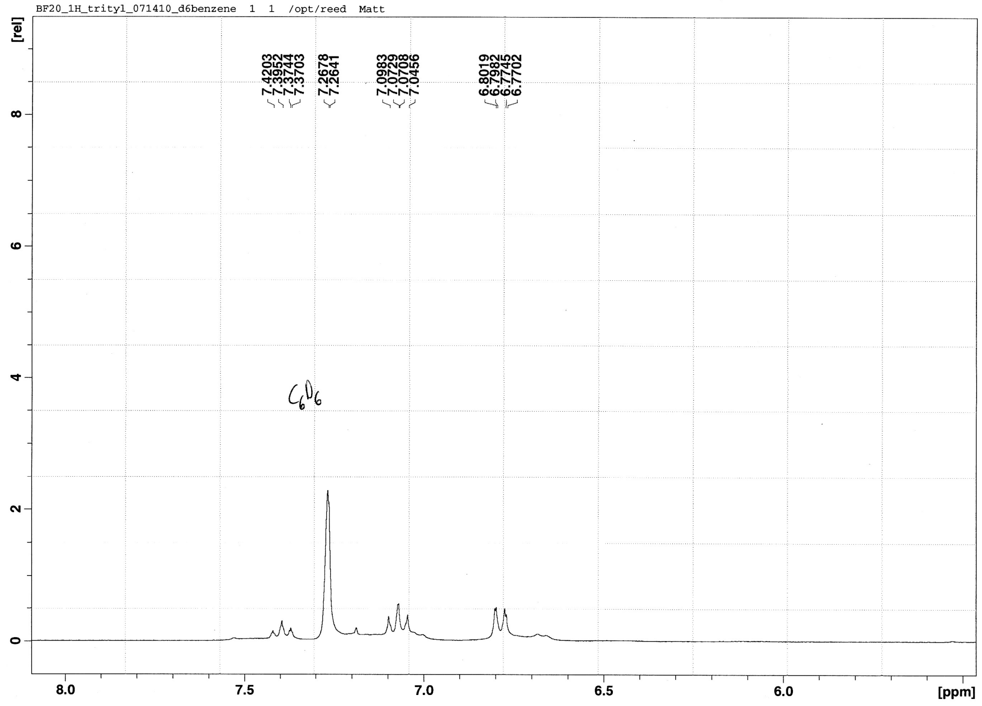
11 pages

General Considerations:

All reactions were carried out in a helium atmosphere glovebox with O_2 < 1ppm or utilizing standard Schlenk and vacuum line techniques. Hexane, diethylether and isooctane were distilled from sodium/benzophenone. Dichloromethane was distilled from P_2O_5. Triethylsilane and triisopropylsilane were degassed and stored over 4A molecular sieves 1 week prior to use. n-Butyl lithium, boron trichloride, potassium chloride and triphenylmethylbromide were purchased from Acros and used as received. Bromopentafluorobenzene and triethylsilane were purchased from Oakwood Products. NMR spectra were obtained on a Bruker Avance 300 MHZ and referenced to the solvent signal. IR spectra were obtained on a Perkin Elmer Spectrum 100 FT-IR with ATR capabilities in a nitrogen filled glovebox. Elemental analyses were performed by Desert Analytical Services, Tucson, AZ.

Synthesis of $[Ph_3C][F_{20}\text{-}BPh_4]$, 1. This was prepared according to Romanato, P.; Duttwyler, S.; Linden, A.; Baldridge, K. K.; and Siegel, J. S. *J. Am. Chem. Soc.*, 2010, *132*, 7828–7829 except for two changes. The synthesis of the precursor $K[F_{20}\text{-}BPh_4]$ was performed on a 20g scale with respect to bromopentafluorobenzene and isooctane was used instead of cyclohexanone for washing **1**. Identical yields were obtained.

^1H NMR (C_6D_6 25 ºC): 6.79 (d, 1H, p, J = 8.22 Hz), 7.07 (t, 2H, m, J = 7.62 Hz), 7.39 (t, 2H, o, J = 7.53 Hz)

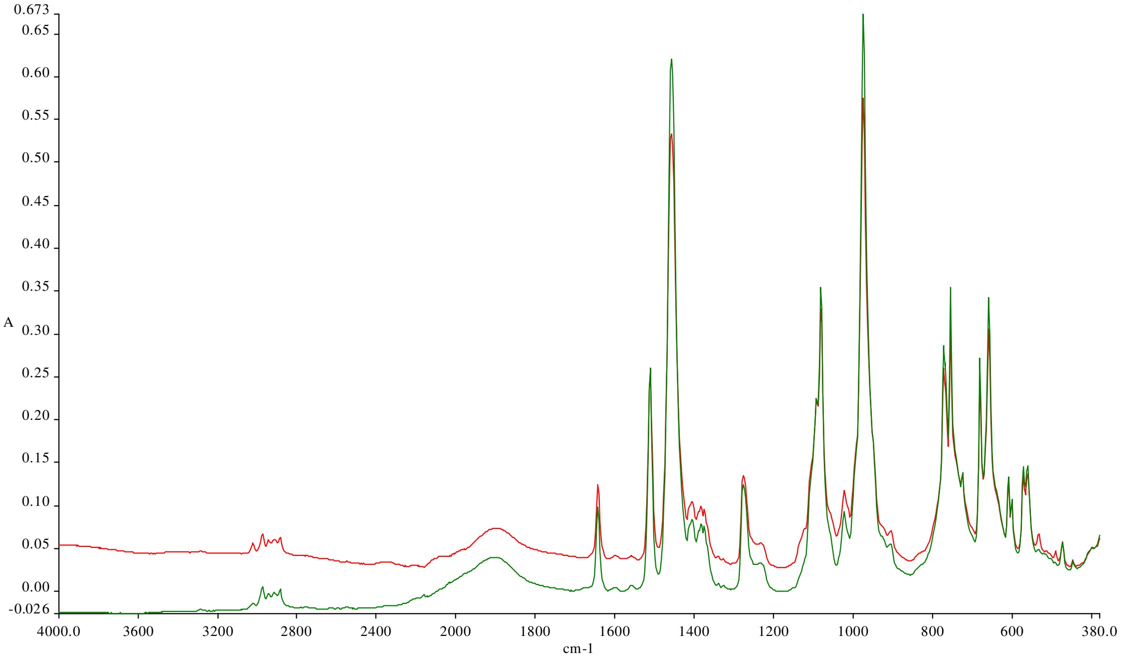


Synthesis of [$R_3SiHSiR_3$][F_{20}-BPh_4], R=Et, 2; R = i-Pr, 3. In a 12 mL glass vial with a teflon stirbar and screw cap, 500mg of **1** was layered with 2mL of hexane. 1.5 mL of the appropriate silane was added via pipette and the reaction was allowed to stir for 36 (for **2**) or 48 (for **3**) hours yielding a faintly brown, white suspension. The solid was collected on a medium filter frit and washed with 1 mL of dry hexane before being transferred to a small Schlenk tube and dried under vacuum. After 5 minutes of drying, the solid was returned to the same filter frit, washed with 2 mL of hexane and redried for 10 minutes.

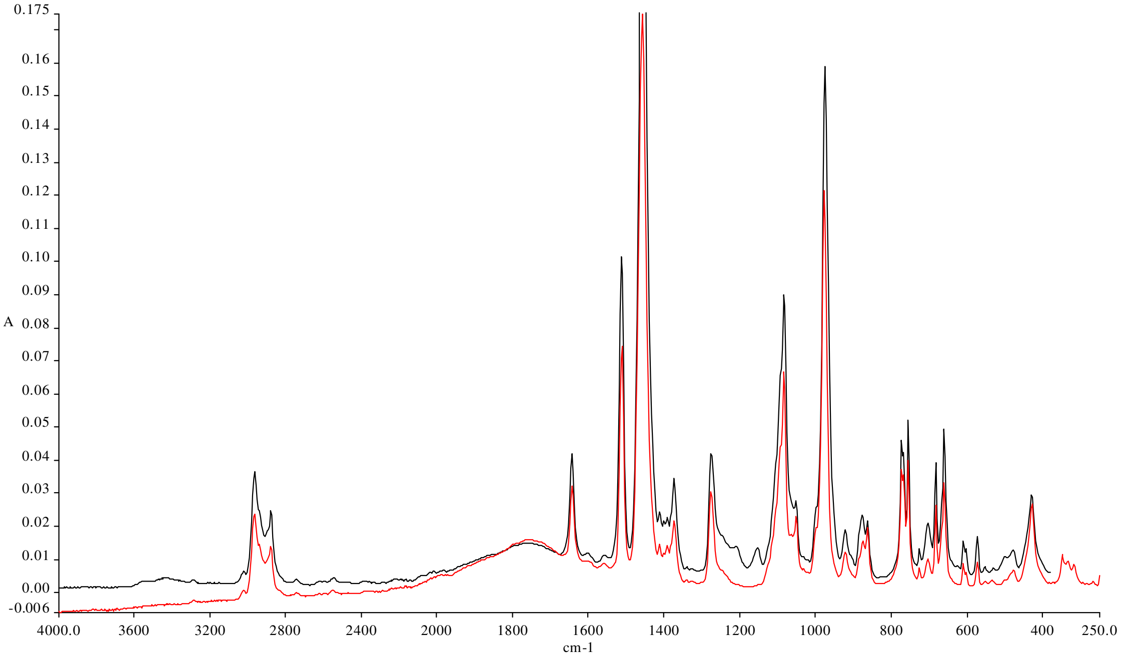
Anal calcd for **2**, $C_{36}H_{31}F_{20}BSi_2$: C, 47.48; H, 3.43. Found: C, 47.24; H, 3.42. IR(ATR): 3024, 2975, 2946, 2917, 2886 cm^{-1}(weak, ethyl group), 1899 cm^{-1} (medium, broad, Si-H-Si). ^1H NMR (C_6D_6 25 ºC): 0.50 (m, 6H, α ethyl, *J = 7.98 Hz*), 0.94 (m, 9H, β ethyl, *J = 7.83 Hz*).

Anal calcd for **3**, $C_{42}H_{43}F_{20}BSi_2$: C, 50.71; H, 4.35. Found: C, 50.01; H, 4.32. IR(ATR): 3022, 2965, 2942, 2879 cm^{-1} (medium, i-Pr group), 1750 cm^{-1} (weak, broad, Si-H-Si).

IR [$Et_3SiHSiEt_3$][F_{20}-BPh_4] **2**. Red before diffusion pumping; green after pumping for 6 hrs.



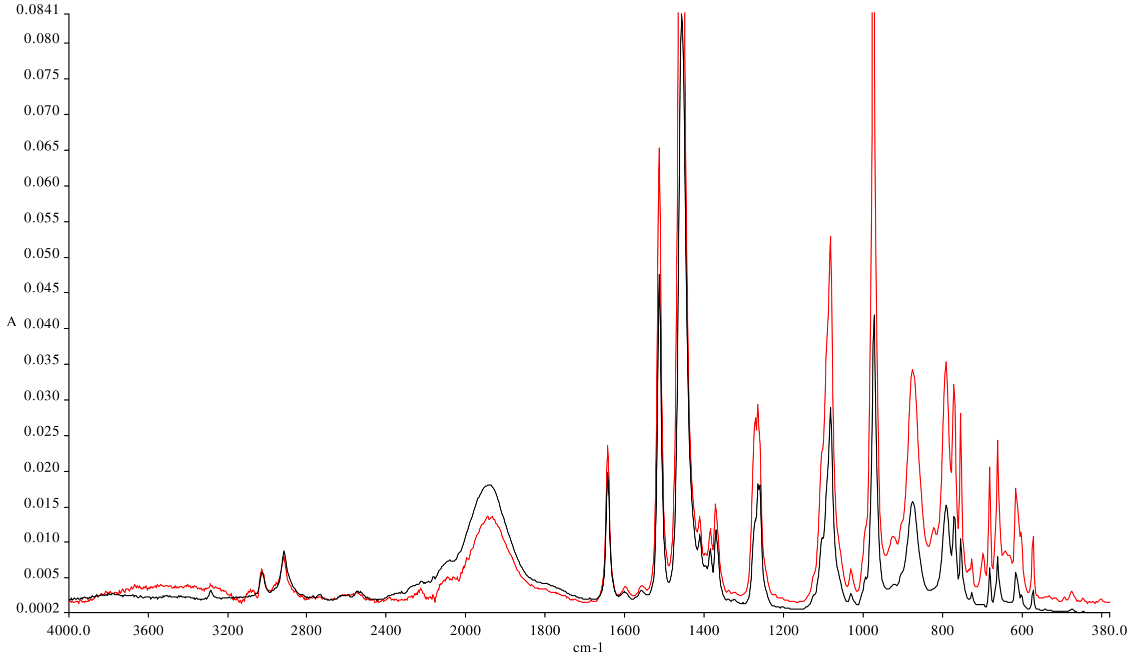
IR [i-Pr_3SiHSii-Pr_3][F_{20}-BPh_4] **3**. Black before diffusion pumping; red after pumping for 6 hrs.



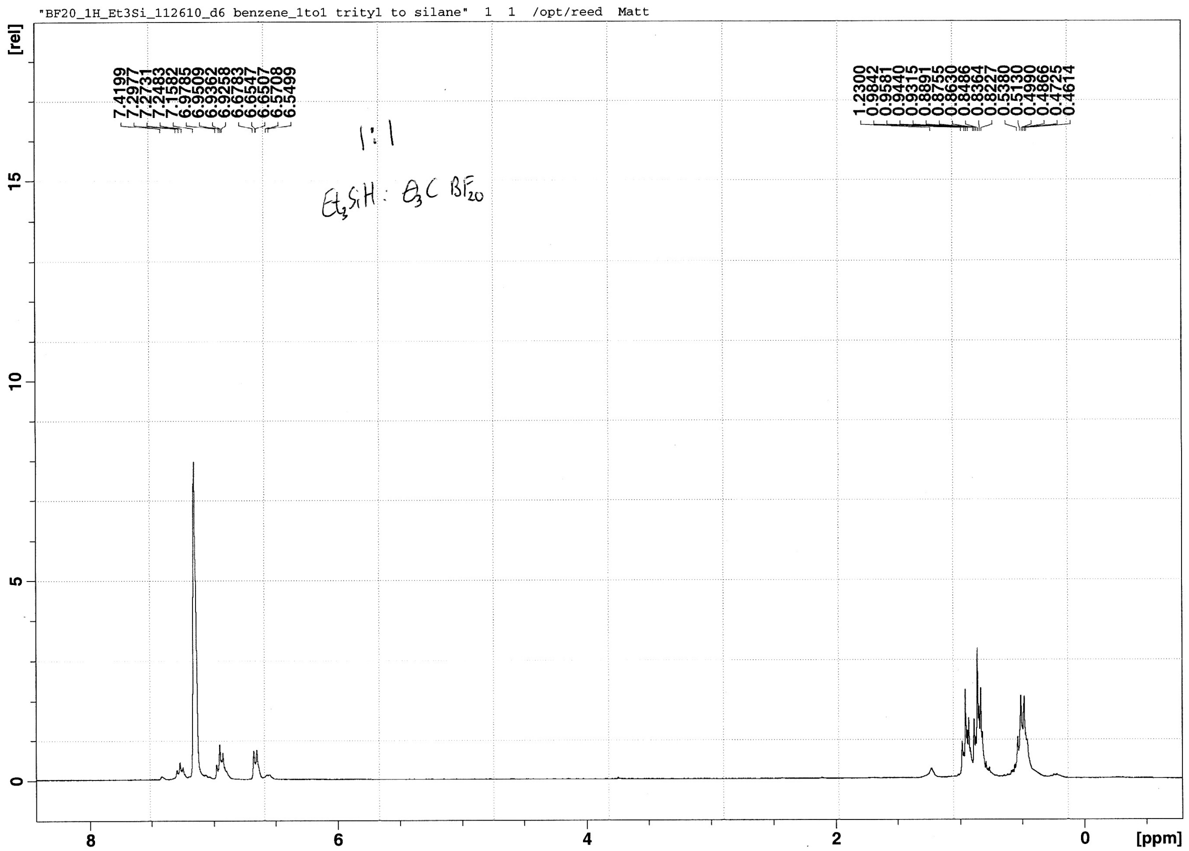
Synthesis of $[Me_3SiHSiMe_3][F_{20}\text{-}BPh_4]$, 4. 1 g of **1** was placed in a thick walled Schlenk tube with a teflon stirbar. The Schlenk tube was removed from the glovebox and placed on a vacuum manifold, evacuated and cooled to -78 °C. After 5 minutes, a large excess (approx 3-5 mL) of trimethylsilane was condensed onto the solid. The Schlenk tube was removed from the vacuum manifold and allowed to stir at room temperature for 24 hours. After 24 hours, it was placed back on the manifold, cooled to -78 °C and *slowly* evacuated to dryness. If the rate of silane removal was too slow, the Schlenk tube was removed from the cold bath and carefully warmed while being evacuated. After the silane was completely removed, a white solid remained. The Schlenk tube was returned to the glove box and the white solid was scrapped out with a spatula. It was placed on a medium filter frit and washed with hexane (2 mL).

Anal calcd for $C_{36}H_{31}F_{20}BSi_2$: C, 43.60; H, 2.32. Found: C, 43.62; H, 2.72. IR(ATR): 3029, 2919, cm^{-1}(weak, methyl), 1941 cm^{-1} (medium, broad, Si-H-Si).

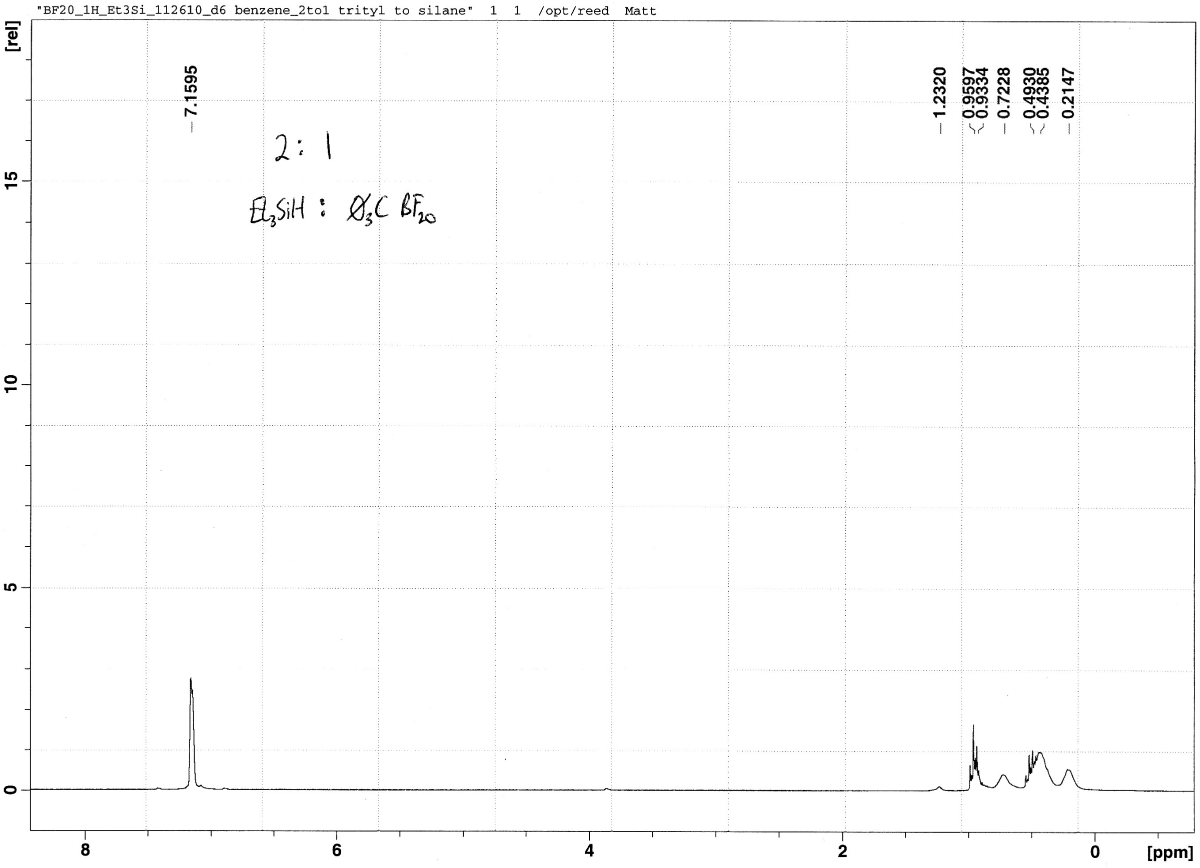
IR $[Me_3SiHSiMe_3][F_{20}\text{-}BPh_4]$, **4**. Black indicates before diffusion pumping, red indicates after pumping for 6 hrs.



Synthesis of [$Et_3SiHSiEt_3$][F_{20}-BPh_4], 2, via controlled addition of triethylsilane. A 1:1 ratio of silane to trityl salt was prepared as follows: 410 mg of **1** was added to a 12 mL vial equipped with a Teflon stirbar and 2 mL of dry hexane was added. 71 µL of triethysilane was added via calibrated pipette. The capped suspension was allowed to stir for 72 hrs. The product was then isolated according to the above procedure for [$Et_3SiHSiEt_3$][F_{20}-BPh_4]. The collected product retained the orange color of the trityl salt and the ^1H NMR indicated the presence of the Ph_3C^+ ion:

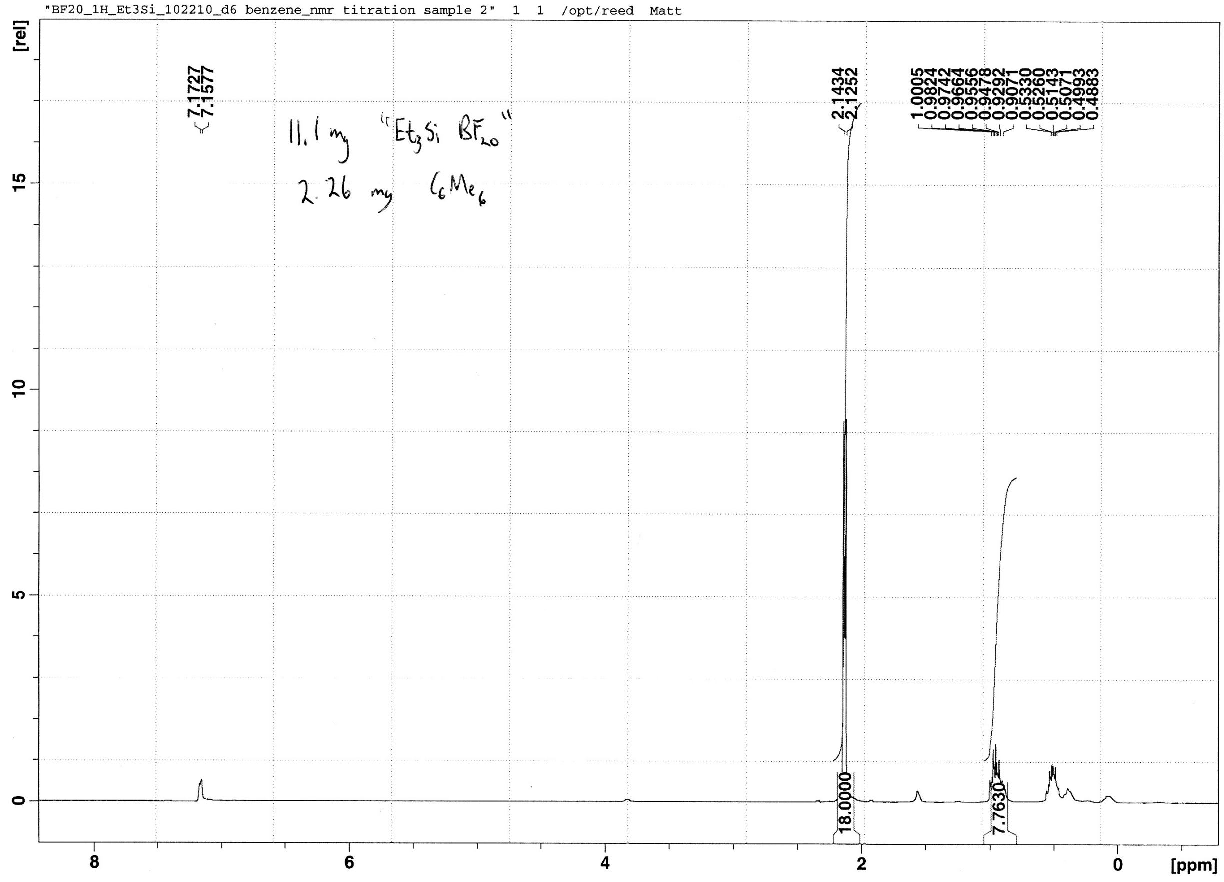


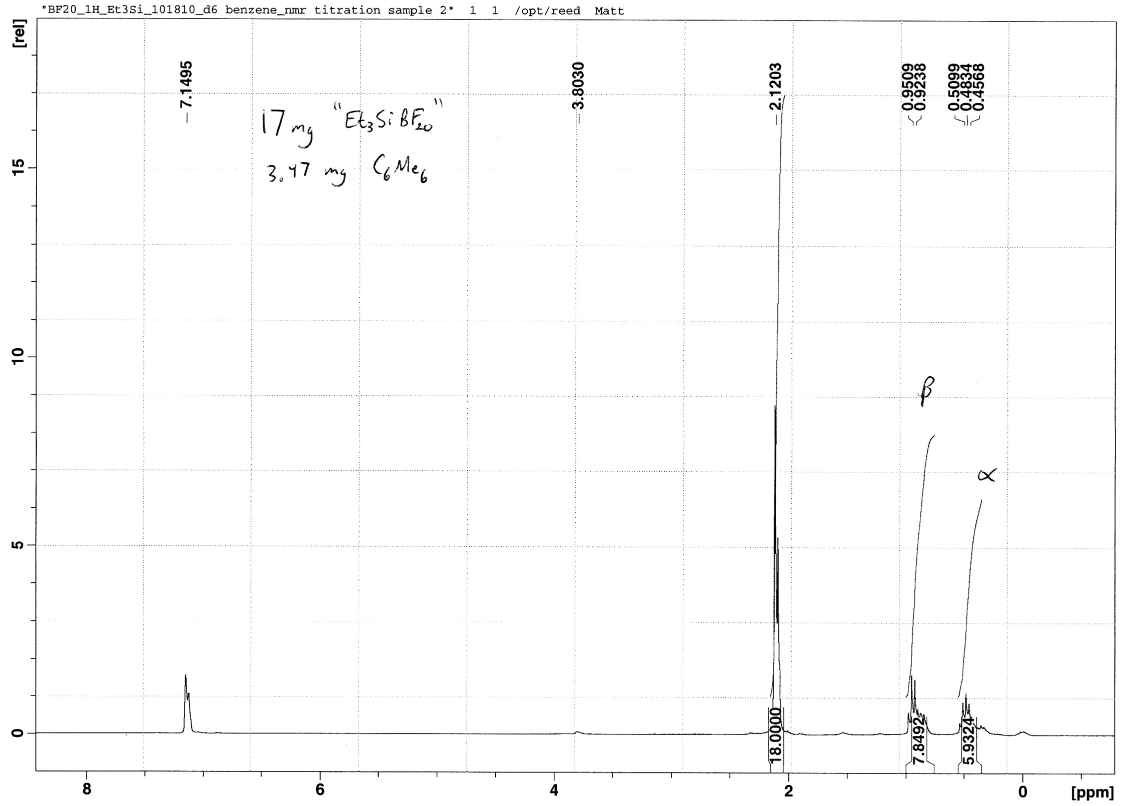
A ca. 2:1 ratio of silane to trityl salt was prepared as follows: 426.7 mg of **1** was added to a 12 mL vial equipped with a Teflon stirbar and 2 mL of dry hexane was added. 170 µL of triethysilane (2.3 equiv) was added via calibrated pipette. The suspension was allowed to stir for 72 hrs. The product was then isolated according to the above procedure for [$Et_3SiHSiEt_3$][F_{20}-BPh_4]. The collected product no longer retained the color of the trityl ion and the ^1H NMR spectrum indicated the absence of the Ph_3C^+:

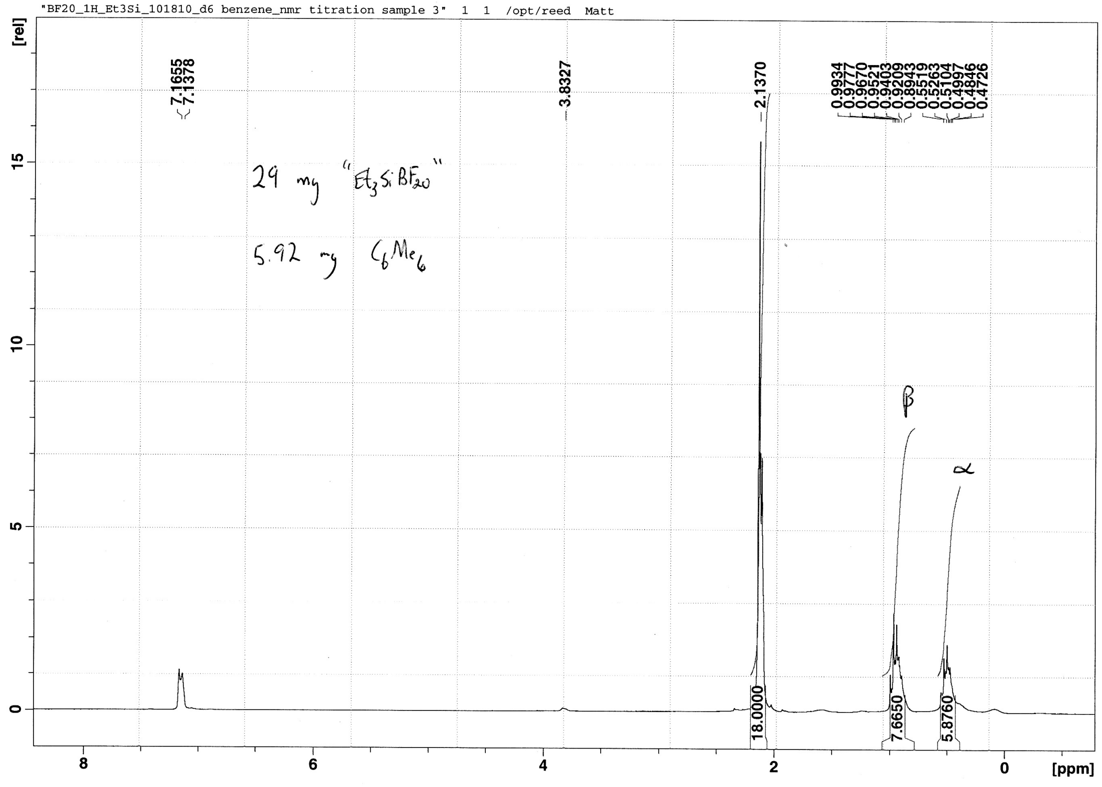

"BF20_1H_Et3Si_112610_d6 benzene_2tol trityl to silane" 1 1 /opt/reed Matt
[rel]
15
10
5
0
7.1595
1.2320
0.9597
0.9334
0.7228
0.4930
0.4385
0.2147
2 : 1
Et_3SiH : $Ø_3C$ BF_{20}
8
6
4
2
0
[ppm]

NMR titration of 2 with C_6Me_6. In a glovebox, six J-Young NMR tubes were loaded with a weighed amounts of **2** (ca. 20-30 mg). Three of the tubes were assumed to contain $Et_3Si(F_{20}\text{-}BPh_4)$ (MW= 794.31) while the other three were assumed to contain $[Et_3SiHSiEt_3][F_{20}\text{-}BPh_4]$ (MW= 910.59). To each tube, 1 molar equivalent of sublimed C_6Me_6 was added, followed by dissolution in C_6D_6. The ^{1}H NMR spectra of each sample was then taken. The 18 protons of C_6Me_6 were integrated against the two β protons of the silylium ion at 0.94 ppm (the alpha protons were not used because free silane, which was always observed, obscures these protons).

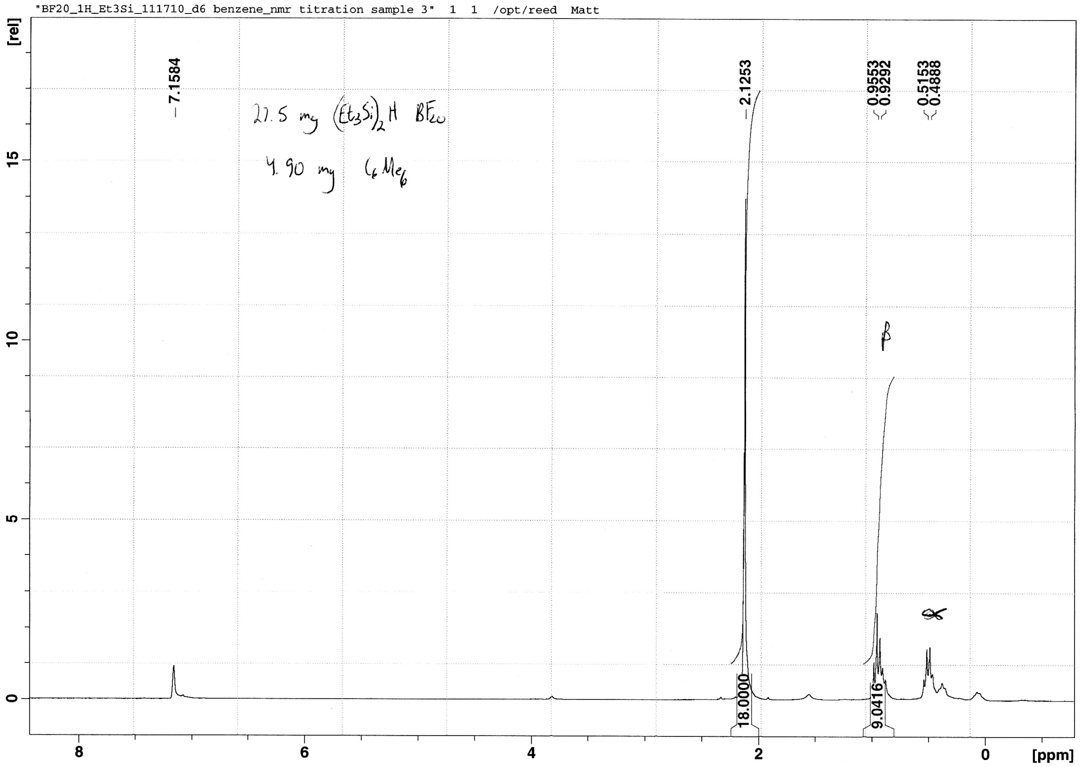
^{1}H NMR assuming the $Et_3Si[F_{20}\text{-}BPh_4]$ formulation:

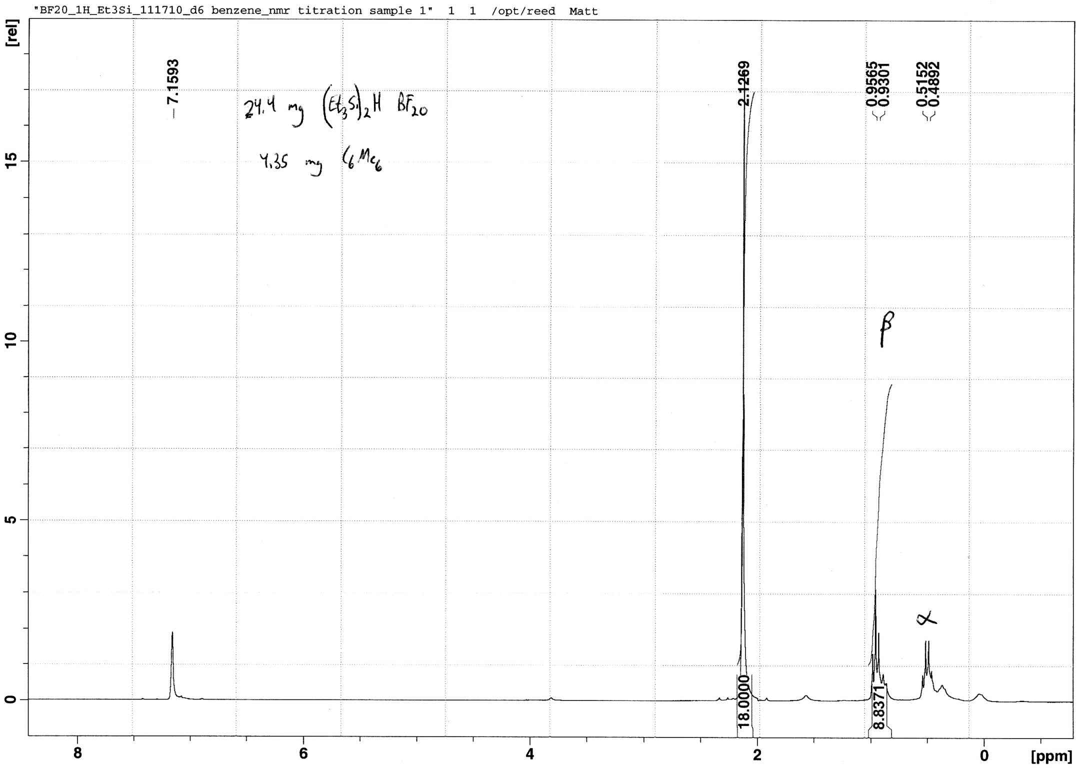


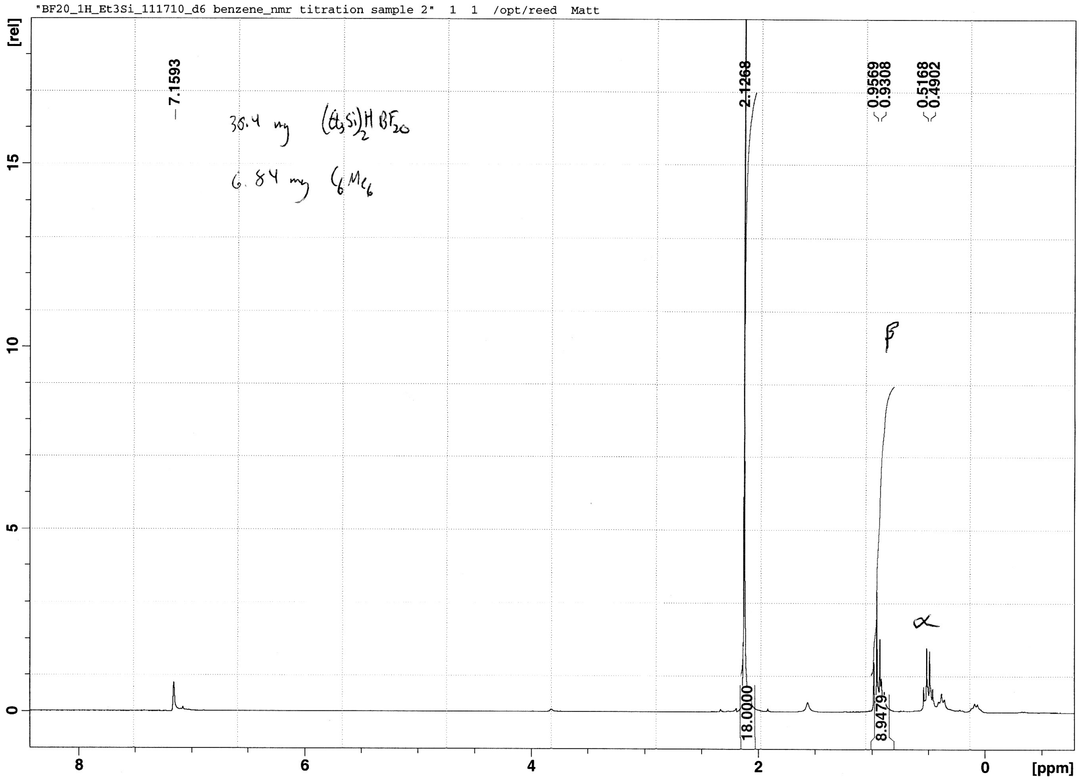

"BF20_1H_Et3Si_101810_d6 benzene_nmr titration sample 2" 1 1 /opt/reed Matt
[rel]
7.1495
3.8030
2.1203
0.9509
0.9238
0.5099
0.4834
0.4568
17 mg "Et3SiBF20"
3.47 mg C6Me6
β
α
18.0000
7.8492
5.9324
15
10
5
0
8
6
4
2
0
[ppm]


"BF20_1H_Et3Si_101810_d6 benzene_nmr titration sample 3" 1 1 /opt/reed Matt
[rel]
7.1655
7.1378
3.8327
2.1370
0.9934
0.9777
0.9670
0.9521
0.9403
0.9209
0.8943
0.5519
0.5263
0.5104
0.4997
0.4846
0.4726
29 mg "Et3SiBF20"
5.92 mg C6Me6
β
α
18.0000
7.6650
5.8760
15
10
5
0
8
6
4
2
0
[ppm]

^{1}H NMR assuming the $Et_3SiHSiEt_3[F_{20}\text{-}BPh_4]$ formulation:







When **2** assumed to have the "Et_3Si^+" formulation, the integrated ratio of protons from the β silyl group to those of C_6Me_6 was always less than 9. This was attributed to the fact that more than a true molar equivalent of C_6Me_6 was placed in the NMR tube because the molecular weight of **2** was underestimated. When **2** was assumed to have the "$Et_3SiHSiEt_3^+$" formulation, the integrated ratio of β silyl protons was correctly integrated against C_6Me_6.

It is noted that the following reaction takes place when **2** is placed in C_6D_6, resulting in formation of free silane:

$$[Et_3SiHSiEt_3]\,[B(C_6F_5)_4] + C_6D_6 \longrightarrow [Et_3Si\cdot C_6D_6]\,[B(C_6F_5)_4] + Et_3SiH$$