Supporting Information for

Borane-Induced Dehydration of Silica and the Ensuing Water-Catalyzed Grafting of $B(C_6F_5)_3$ to Give a Supported, Single-Site Lewis Acid, $\equiv SiOB(C_6F_5)_2$

Ying-Jen Wanglee, Jerry Hu, Rosemary E. White, Ming-Yung Lee, S. Michael Stewart, Philippe Perrotin, and Susannah L. Scott

Table of Contents

TABLE S1. Solution-state NMR chemical shifts[a] for borane compounds involved in the reaction of $B(C_6F_5)_3$ with silica

compound	δ (^{1}H) / ppm	δ (^{19}F) / ppm		
		o-F	*p*-F	*m*-F
$(C_6F_5)_3B$	-	-128.0	-141.2	-159.4
$(C_6F_5)_3B•H_2O$	4.75	-134.1	-152.9	-161.6
$(C_6F_5)_2BOH$	6.28	-132.4	-147.5	-160.6
$[(C_6F_5)_2B]_2O$	-	-132.0	-143.4	-161.8
C_6F_5H	5.80	-138.5	-153.5	-161.8

[a] All spectra were acquired at room temperature in toluene-d_8.

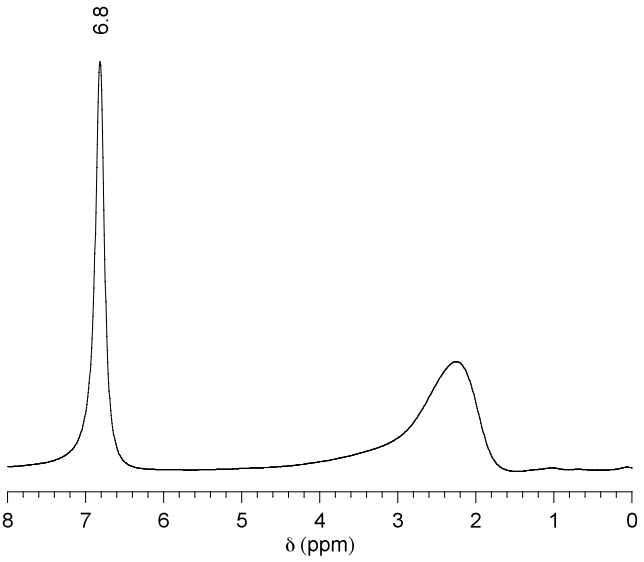

FIGURE S1. Solid-state ^{1}H MAS NMR spectrum of C_6F_5H/A380-200 mixture, recorded with 14 kHz MAS.

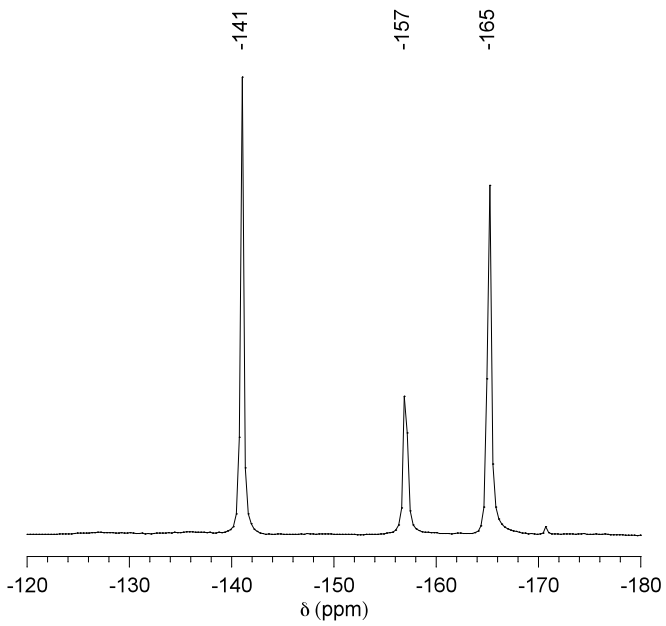

FIGURE S2. Solid-state ^{19}F MAS NMR spectrum of C_6F_5H/A380-200 mixture, recorded with 14 kHz MAS.

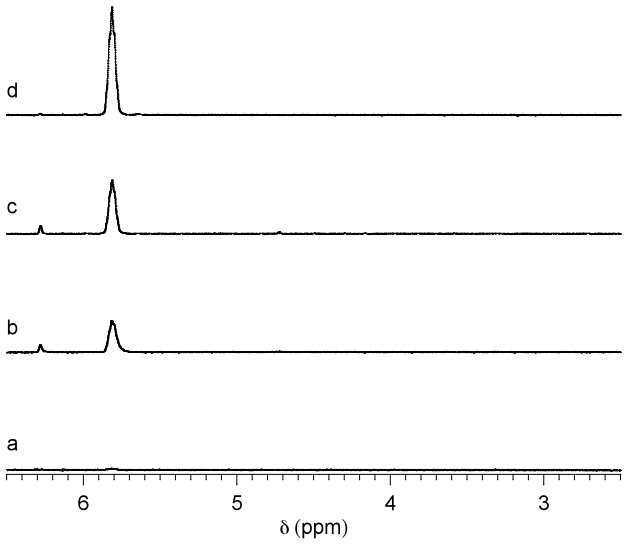

FIGURE S3. Solution-state ^1H NMR spectra of (a) a mixture of $B(C_6F_5)_3$ and A380-200 (B/≡SiOH = 0.41) suspended in toluene-d_8 in an NMR tube at room temperature; (b) after heating at 100 °C for 1 h; (c) after heating for 2.5 h (d) after heating for 3 d.

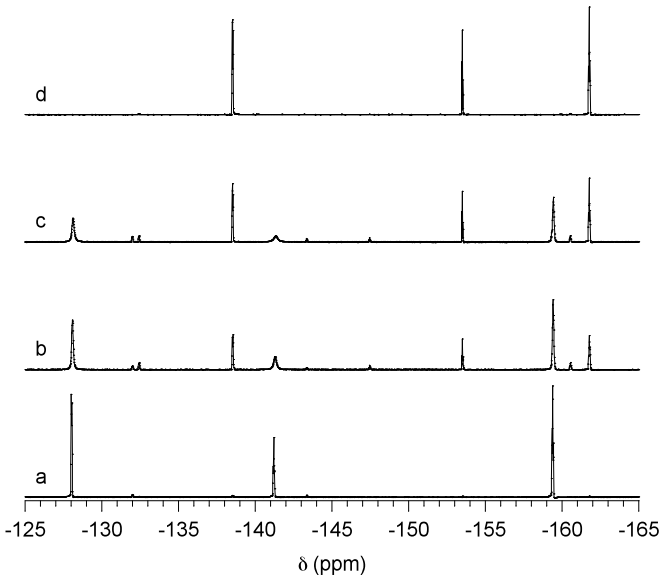

FIGURE S4. Solution-state ^{19}F NMR spectra of (a) a mixture of $B(C_6F_5)_3$ and A380-200 (B/≡SiOH = 0.41) suspended in toluene-d_8 in an NMR tube at room temperature; (b) after heating at 100 °C for 1 h; (c) after heating for 2.5 h; (d) after heating for 3 d. The three signals for $B(C_6F_5)_3$ in (b) and (c) are slightly broader than those in (a), indicating that a trace of H_2O is present.

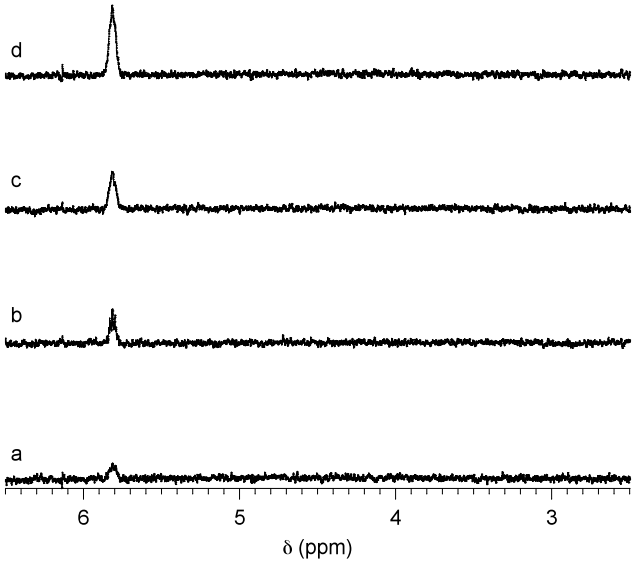

FIGURE S5. Solution-state ^{1}H NMR spectra of (a) a mixture of $B(C_6F_5)_3$ and A380-500 (B/≡SiOH = 0.49) suspended in toluene-d_8 in an NMR tube at room temperature; (b) after heating at 100 °C for 1 h; (c) after heating for 2.5 h; (d) after heating for 1 d.

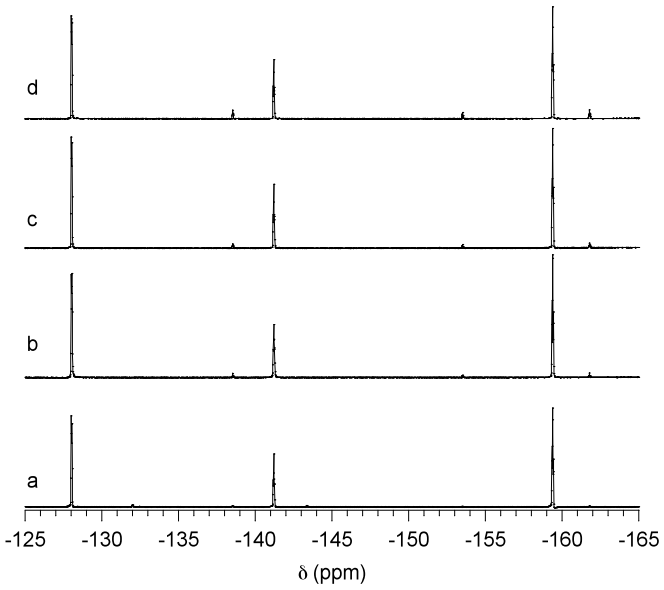

FIGURE S6. Solution-state ^{19}F NMR spectra of (a) a mixture of $B(C_6F_5)_3$ and A380-500 (B/≡SiOH = 0.49) suspended in toluene-d_8 in an NMR tube at room temperature; (b) after heating at 100 °C for 1 h; (c) after heating for 2.5 h; (d) after heating for 1 d.

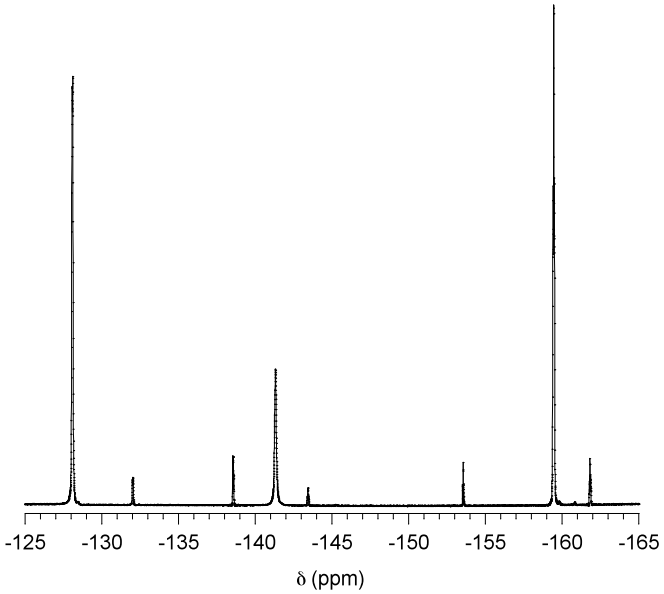

FIGURE S7. Solution-state ^{19}F NMR spectrum of supernatant toluene-d_8 from the reaction of $B(C_6F_5)_3$ with A380-500 (B/≡SiOH = 4.7) catalyzed by 0.1 equiv. H_2O (relative to ≡SiOH).

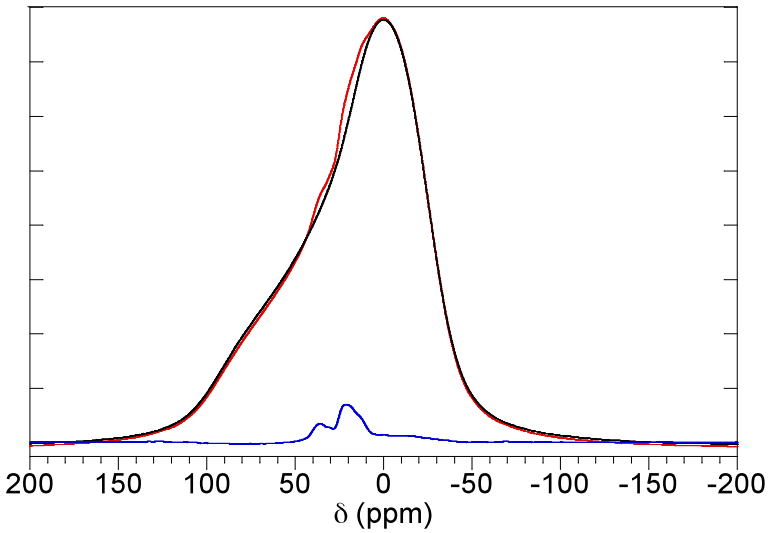

FIGURE S8. Solid-state ^{11}B MAS NMR spectra for $\equiv SiOB(C_6F_5)_2$ (blue), obtained by subtraction of the signal for the probe and rotor (black) from the sample signal (red), recorded at 96.251 MHz, with 14 kHz MAS.

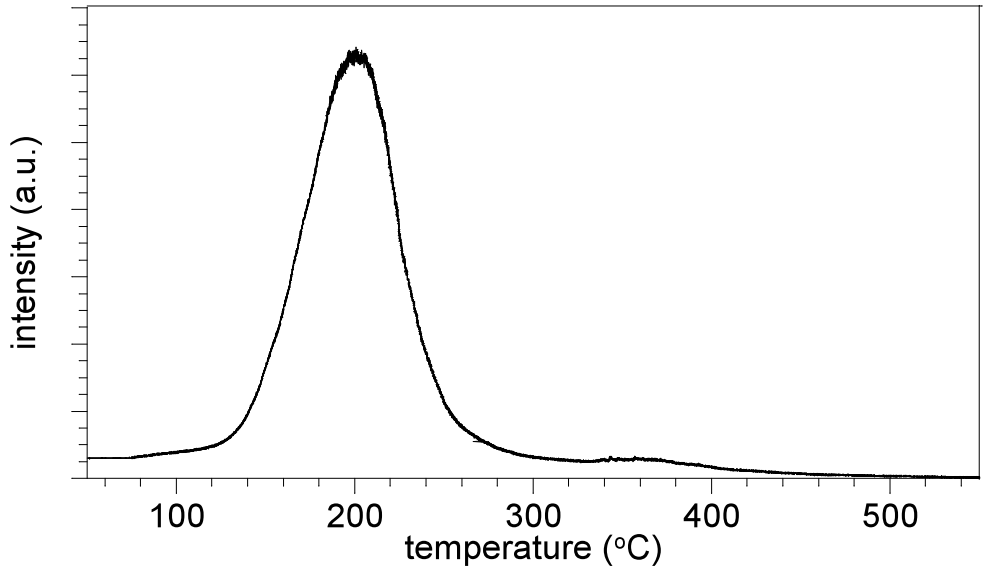

FIGURE S9. Temperature-programmed desorption of C_5H_5N from $B(C_6F_5)_3$-modified A380-500.

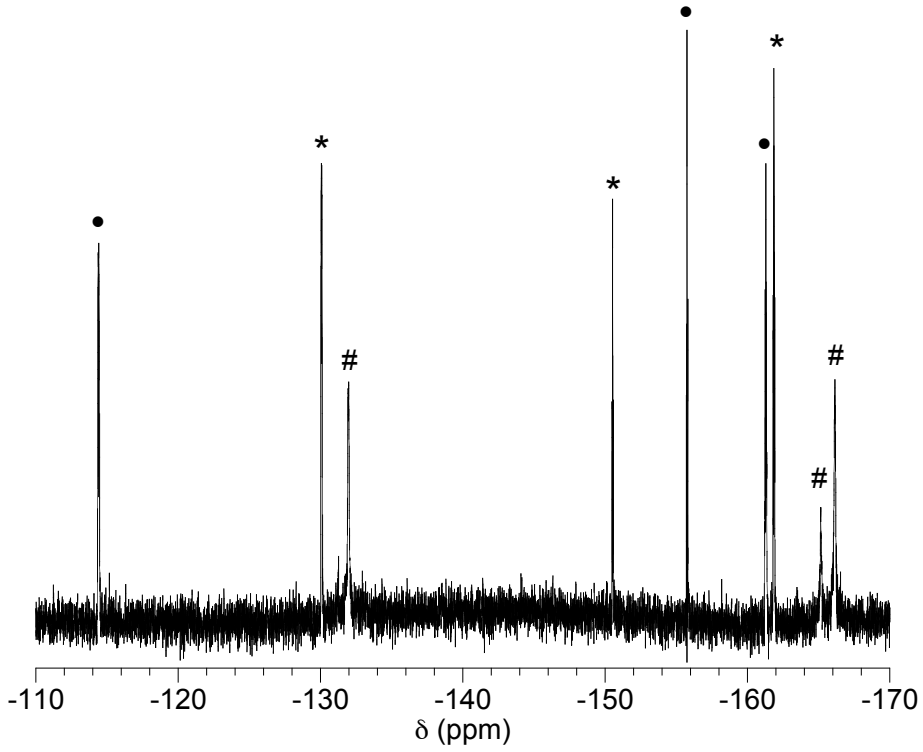

FIGURE S10. Solution-state ^{19}F NMR spectrum for NMR tube experiment involving reaction of $\equiv SiOB(C_6F_5)_2$ with Cp_2ZrMe_2: $Cp_2ZrMe(C_6F_5)$ (•); $Me_2B(C_6F_5)$ (*); $[Me_2B(C_6F_5)_2]^-$ (#).

TABLE S2. Solution-state ^{19}F NMR chemical shifts (δ, ppm, in C_6D_8) for compounds observed in Figure S10

	This work			Literature[a]		
compound	*o*-F	*p*-F	*m*-F	*o*-F	*p*-F	*m*-F
$Me_2B(C_6F_5)$	-130.1	-150.5	-161.9	-130.9	-151.4	-162.6
$Cp_2ZrMe(C_6F_5)$	-114.4	-155.8	-161.3	-115.2	-156.6	-162.2
$[Cp_2ZrMe^+][Me_2B(C_6F_5)_2^-]$	-132.0	-165.1	-166.1	-134.2	-160.9	-164.5

[a] Kohler, K.; Piers, W. E.; Jarvis, A. P.; Xin, S.; Feng, Y.; Bravakis, A. M.; Collins, S.; Clegg, W.; Yap, G. P. A.; Marder, T. B. *Organometallics* **1998**, *17*, 3557-3566; Metcalfe, R. A.; Kreller, D. I.; Tian, J.; Kim, H.; Taylor, N. J.; Corrigan, J. F.; Collins, S. *Organometallics* **2002**, *21*, 1719-1726.

TABLE S3. Cartesian coordinates for DFT-optimized structure of H_3SiOH
Absolute E = -367.22697470 Hartrees (BP86/def2-TZVPP).

Si	0.536135	-0.008750	0.000000
H	1.033836	1.393310	-0.000004
H	1.046521	-0.728180	-1.209580
H	1.046522	-0.728170	1.209578
O	-1.125810	0.112680	0.000000
H	-1.626250	-0.715880	0.000000

TABLE S4. Cartesian coordinates for DFT-optimized structure of $B(C_6F_5)_3$
Absolute E = -2209.20663533 Hartrees (BP86/def2-TZVPP)

B	-0.001520	-0.000480	0.001771
C	-0.876260	-1.303910	0.001016
C	-2.050480	-1.420640	-0.766170
C	-0.538940	-2.434700	0.768424
C	-2.832860	-2.574560	-0.789420
C	-1.309590	-3.596470	0.791026
C	-2.461190	-3.667280	0.000518
C	-0.691290	1.409598	0.000569
C	-0.205340	2.482090	-0.770600
C	-1.836600	1.686792	0.770220
C	-0.811210	3.737684	-0.795050
C	-2.455060	2.936310	0.791702
C	-1.940710	3.966259	-0.002530
C	1.564814	-0.106600	0.000935
C	2.375056	0.739764	0.780587
C	2.253244	-1.054070	-0.779640
C	3.766506	0.652251	0.803474
C	3.643753	-1.155100	-0.802850
C	4.403977	-0.298930	0.000374
F	4.258175	-2.057730	-1.582310
F	1.570428	-1.892520	-1.586450
F	5.737323	-0.389180	0.000050
F	4.497279	1.464215	1.582224
F	1.811796	1.663378	1.586773
F	-2.364250	0.734857	1.567423
F	-3.531110	3.161692	1.560506
F	0.870553	2.312061	-1.566640
F	-0.327210	4.723689	-1.565310
F	-2.527470	5.166936	-0.004080
F	0.552215	-2.415250	1.561662
F	-0.962230	-4.641390	1.557328
F	-3.205440	-4.777220	0.000207
F	-3.931390	-2.649420	-1.555810
F	-2.446380	-0.402840	-1.558270

TABLE S5. Cartesian coordinates for DFT-optimized structure for $B(C_6F_5)_3(H_3SiOH)$ adduct. Absolute E = -2576.43277479 Hartrees (BP86/def2-TZVPP)

B	0.312193	-0.301659	0.139466
C	-1.141533	-0.695052	0.750502
C	-2.317400	-0.802862	-0.007596
C	-1.321145	-0.879323	2.129621
C	-3.568288	-1.087645	0.549043
C	2.815700	2.551049	1.363214
C	-2.546236	-1.171984	2.728756
C	0.575746	3.415169	1.548684
C	-3.684728	-1.277413	1.926783
C	2.267262	1.364003	0.884332
C	0.082669	2.198166	1.066826
C	0.902586	1.113021	0.723847
C	0.502201	-0.495031	-1.467921
C	0.414594	-1.769739	-2.046304
C	0.759469	0.537771	-2.380476
C	0.587370	-2.030409	-3.404288
C	0.851968	-0.965566	-4.269715
C	0.933992	0.327500	-3.753244
C	1.951649	3.594328	1.703027
F	0.122817	-2.846251	-1.262934
F	0.492977	-3.281233	-3.888096
F	1.180145	1.360145	-4.577200
F	1.020828	-1.185654	-5.580868
F	-4.875119	-1.555896	2.475068
F	-2.641311	-1.351708	4.057739
F	-4.659714	-1.175378	-0.229295
F	-0.252952	-0.783804	2.969217
F	-1.257424	2.126249	0.909128
F	-2.304898	-0.601769	-1.343801
F	3.188761	0.383429	0.543731
F	0.834640	1.826432	-1.974061
F	-0.262304	4.416928	1.858174
F	4.143898	2.700983	1.496171
F	2.439310	4.752465	2.166910
H	2.171355	-3.891840	0.629609
H	1.851943	-2.914333	2.844486
H	-0.113383	-3.429688	1.449504
H	2.278498	-1.040026	0.709885
O	1.381174	-1.439396	0.784453
Si	1.305648	-3.022928	1.467431

TABLE S6. Cartesian coordinates for DFT-optimized structure of $H_3SiOB(C_6F_5)_2$
Absolute E = -1847.76618348 Hartrees (BP86/def2-TZVPP)

B	0.048912	1.064854	-0.037836
C	1.450897	0.338155	-0.115817
C	1.630354	-0.878361	-0.793988
C	2.604312	0.883958	0.475355
C	2.865734	-1.519078	-0.895879
C	3.853577	0.264441	0.408298
C	3.983628	-0.942085	-0.286169
C	-1.308218	0.247703	0.079482
C	-2.406219	0.513603	-0.74871
C	-1.481986	-0.779175	1.016951
C	-3.607156	-0.192388	-0.671332
C	-2.671134	-1.499533	1.139945
C	-3.73808	-1.204409	0.285094
F	-0.478609	-1.090748	1.867274
F	-2.804171	-2.464268	2.063812
F	-2.311741	1.475098	-1.698869
F	-4.629411	0.084544	-1.496276
F	-4.884618	-1.888005	0.384112
F	2.534303	2.031798	1.177078
F	4.927433	0.808887	1.002903
F	5.17626	-1.543338	-0.36737
F	2.994267	-2.671971	-1.571975
F	0.586333	-1.470035	-1.415663
O	0.044014	2.419706	-0.076083
Si	-0.989594	3.725736	0.104141
H	-0.327608	4.65872	1.054633
H	-1.151803	4.364424	-1.228237
H	-2.307601	3.289979	0.648853

TABLE S7. Cartesian coordinates for DFT-optimized structure of C_6F_5H
Absolute E = -728.71187224 Hartrees (BP86/def2-TZVPP)

C	-0.000017	-1.680738	0.000013
C	1.197751	-0.971437	0.000038
C	1.214057	0.426370	0.000004
C	-0.000001	1.122209	0.000014
C	-1.214040	0.426406	0.000022
C	-1.197747	-0.971436	-0.000007
H	0.000015	-2.769182	0.000000
F	2.372093	-1.631622	-0.000017
F	2.373230	1.103701	-0.000011
F	0.000048	2.462551	-0.000010
F	-2.373246	1.103683	-0.000001
F	-2.372129	-1.631543	-0.000017

TABLE S8. Cartesian coordinates for DFT-optimized structure of $HO(H_2SiO)_3H$
Absolute E = -1174.71912737 Hartrees (BP86/def2-TZVPP)

Si	0.000000	2.388331	-0.690420
H	1.048161	3.446581	-0.646890
H	-0.071510	1.704947	-2.006520
H	1.185481	-0.332670	2.232106
Si	0.000000	0.000000	1.397098
H	-1.185480	0.332671	2.232106
Si	0.000000	-2.388330	-0.690420
H	-1.048160	-3.446580	-0.646890
H	0.071505	-1.704950	-2.006520
O	0.411790	1.302634	0.481160
O	-0.411790	-1.302630	0.481160
O	1.509809	-3.036100	-0.472990
O	-1.509810	3.036097	-0.472990
H	-1.623190	3.678729	0.242114
H	1.623189	-3.678730	0.242114

TABLE S9. Cartesian coordinates for DFT-optimized structure of $(H_2SiO)_3$
Absolute E = -1098.24773756 Hartrees (BP86/def2-TZVPP)

Si	-1.693820	-0.417940	-0.000360
H	-2.509090	-0.614790	-1.230220
H	-2.507810	-0.623240	1.228966
H	1.782812	-1.856170	1.238886
Si	1.208749	-1.257180	0.002810
H	1.796647	-1.868770	-1.220300
Si	0.484635	1.674787	-0.000910
H	0.721658	2.481980	1.227235
H	0.713581	2.480006	-1.231900
O	-0.431920	-1.492180	-0.005770
O	1.510383	0.372552	-0.004080
O	-1.077440	1.120331	0.005572

TABLE S10. Cartesian coordinates for DFT-optimized structure of $B(C_6F_5)_3 \bullet H_2O$
Absolute E = -2285.68715942 Hartrees (BP86/def2-TZVPP)

B	0.006773	0.032718	0.649131
C	-0.489240	1.535277	0.286893
C	0.204138	2.444723	-0.524310
C	-1.710490	2.010601	0.793801
C	-0.263130	3.731963	-0.808680
C	-2.210570	3.288444	0.540988
C	-1.477450	4.158605	-0.269790
C	1.558911	-0.324970	0.260785
C	1.920899	-1.107500	-0.845260
C	2.646446	0.151208	0.999163
C	3.246889	-1.401740	-1.180510
C	3.984446	-0.113840	0.717258
C	4.287739	-0.905480	-0.393280
C	-1.047450	-1.161420	0.282562
C	-1.135350	-2.343260	1.021966
C	-1.911030	-1.110420	-0.820840
C	-2.001160	-3.398820	0.743935
C	-2.797020	-2.140420	-1.151050
C	-2.846050	-3.292730	-0.362950
F	-3.597530	-2.036280	-2.223060
F	-1.900900	-0.044250	-1.648670
F	-3.691150	-4.286790	-0.665440
F	-2.029790	-4.497690	1.515817
F	-0.317870	-2.520700	2.127774
F	2.421164	0.961179	2.100465
F	4.968733	0.377457	1.487317
F	0.977325	-1.599850	-1.677180
F	3.528728	-2.155110	-2.254680
F	5.561929	-1.182800	-0.697630
F	-2.479810	1.205818	1.565909
F	-3.385640	3.686185	1.058570
F	-1.937530	5.390432	-0.528600
F	0.446462	4.560793	-1.593740
F	1.382326	2.108886	-1.100520
H	0.810506	0.494710	2.619654
O	-0.016420	0.050102	2.320339
H	0.005818	-0.886050	2.630874

TABLE S11. Cartesian coordinates for DFT-optimized structure of $HO(H_2SiO)_2H$
Absolute E = -808.63396758 Hartrees (BP86/def2-TZVPP)

Si	1.507313	-0.314850	-0.385870
H	2.386314	-1.505570	-0.215080
H	1.482259	0.186813	-1.783270
H	-2.439310	-1.428780	-0.211050
Si	-1.570270	-0.345740	0.310656
H	-1.754760	-0.124870	1.775494
O	0.000768	-0.793650	0.078285
O	-2.002400	1.006549	-0.544170
O	2.068933	0.970756	0.502828
H	2.356318	0.789199	1.409478
H	-1.687800	1.862229	-0.218120

TABLE S12. Cartesian coordinates for DFT-optimized structure of $(H_2SiO)_2$
Absolute E = -732.12118382 Hartrees (BP86/def2-TZVPP)

Si	-1.192940	-0.000002	0.000010
H	-2.037680	0.000066	-1.225810
H	-2.037480	-0.000110	1.225973
H	2.037485	-0.000015	1.225969
Si	1.192941	0.000002	0.000010
H	2.037672	0.000058	-1.225820
O	0.000012	-1.202300	-0.000053
O	-0.000014	1.202298	-0.000021

Complete reference 46:

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.