Supporting Information

for

Intramolecular ortho-Assisted Activation of Silicon-Hydrogen Bond in Arylsilanes: An Experimental and Theoretical Study

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1. Labile nature of compound 9.

VT ^{1}H NMR studies of compound **9** were undertaken and a spectrum recorded at 223 K showed sharp singlets of two non-equivalent methyl groups at 0.57 and -0.15 ppm (**Figure S2a**). They become gradually broader upon heating and their coalescence occurs at ca. 283 K. The averaged signal of $SiMe_2$ protons appears at 0.25 ppm. It becomes sharp at 323 K indicating a rapid inversion at the Si centre. The rate constants k of the process were calculated on the basis of peak half-widths. Assuming, the first order of the observed exchange, the Eyring plot, k/T vs T^{-1}, afforded activation enthalpy and entropy of 72 kJ mol^{-1} and 59 Jmol^{-1}K^{-1}, respectively. Taking into account results of X-ray diffraction analysis, it seems that the H-bonded dimeric structure of **9** is conformationally stable (on the NMR time scale) at low temperatures in $CDCl_3$. Apparently, increased proton mobility at higher temperature is responsible for a rapid inversion (**Figure S2b**). A mechanism of the process is presumably based on the breakage of one of B-O bonds due to the protonation of the oxygen atoms. This enables the rotation of $SiMe_2OH$ around aryl-Si bond which makes the methyl groups equivalent. This is supported by the positive value of activation entropy which can be interpreted in terms of an increased rotational freedom in a transition state. The theoretical calculations (M06-2X/6-31+G(d) level of theory) show that both forms may coexist in solution as the free Gibbs energy difference does not exceed 3 kJmol^{-1}. Furthermore, we have found that the process is strongly affected by solvent effects as in acetone-d_6 single sharp resonance of $SiMe_2$ group is observed at room temperature indicating a rapid inversion. The ^{11}B NMR chemical shift is 17.8 ppm, i.e., the boron nucleus is deshielded by ca. 5 ppm with respect to the value obtained for $CDCl_3$ solution. This difference may be interpreted in terms of a weaker donation of electron density from oxygen to boron. It is to remind here that the synthesis of a non-fluorinated carbon analogue of **9** was reported.[a) K. Oshima and Y. Aoyama, *J. Am. Chem. Soc.,* 1999, **121***,* 2315–2316; b) K. Oshima, T. Yamauchi, M. Shimomura, S. Miyauchi and Y. Aoyama, *Bull. Chem. Soc. Jpn.,* 2002*,* **75***,* 1319–1324] The ^{1}H NMR spectrum of this compound shows a single resonance of two methyl groups consistent with a rapid inversion.

Finally, we have found that compound **9** is not stable in diluted acetone solution and undergoes slow (within several hours) isomerization to an eight-membered cyclic siloxane **10** with a postulated structure presented in **Figure S1**. The ^{11}B chemical shift of this compound is 48 ppm indicating the appearance of a three-coordinated borinic species, whereas in the respective ^{1}H and ^{29}Si spectra single resonances of $SiMe_2$ group point to the formation of a stable symmetrical structure. This also points to conformational flexibility of siloxane bridge leading to fast inversion of $SiMe_2$ groups. Furthermore, the ^{29}Si chemical shift is 1.92 ppm, which is in accordance with the formation of a Si-O-Si bridge. The MS spectrum of this compound (acetone solution) does not change over the period of several days. According to

our theoretical calculations (M062X/6-31G**, PCM – acetone as a solvent) compound **10** is more stable than **9** by 13.5 kJ/mol (ΔG). On the other hand, the process is reversible as after solvent evaporation the re-formation of single crystals of **9** was confirmed by X-ray diffraction. This can be explained by significant stabilization of solid **9** in the form of a centrosymmetric dimer featuring strong OH…O bonds (dimerization free Gibbs energy is -81 kJmol^{-1}). In contrast, in a polar donor solvent (such as acetone) cleavage of H-bonded dimers of **9** may promote isomerization to **10**. It is also notable that a related (albeit bearing boronic groups attached at subsidiary positions) cyclic siloxane was obtained by us recently [K. Durka, A. Górska, T. Kliś, M. Kublicki, J. Serwatowski, K. Woźniak, *Tetrahedron Letters*, **2015**, *56*, 1855–1859]. In addition, we have also found that compound **10** undergoes slow degradation in acetone solution after prolonged exposure to air (> 7 d) which is typical for diarylborinic acids.

Comparison of multinuclear NMR data for **9** and **10** (acetone-d_6). Compound **9**: ^{1}H NMR δ 7.32 (ddd, J = 8.1, 7.2, 5.7 Hz, 2H), 6.96-6.87 (m, 4H), 0.48 (s, 12H) ppm. ^{11}B NMR δ 17.6 ppm. ^{19}F NMR δ –105.96 (ddd, J = 8.1, 5.7, 2.6 Hz) ppm. Compound **10**: ^{1}H NMR δ 7.42-7.35 (m, 4H), 6.93-6.90 (m, 2H), 0.41 (d, J = 1.3 Hz, 12H) ppm. ^{11}B NMR δ 48.0 ppm. ^{19}F NMR δ –103.80 ppm. ^{29}Si NMR δ 1.92 ppm.

Notably, the acidity of **9** (pK_a = 3.5 in MeOH/H_2O, 1:1) is strongly enhanced with respect to the related benzosiloxaborole (pK_a = 7.2 ppm). It is also worth noting that generation of an borinate anion by dissolving **9** in 0.5 M K_2CO_3 (in D_2O/DMSO-$d6$, 5:1) resulted in significant spectral changes. The ^{11}B NMR resonance was shifted upfield to ca. 8 ppm whereas in the ^{1}H and ^{13}C NMR spectra the sharp well-resolved resonances of two non-equivalent methyl groups at 0.28 and 0.31 ppm were observed which indicates that deprotonation results in the increased conformational stabilization of the spiro boron-centred molecular framework.

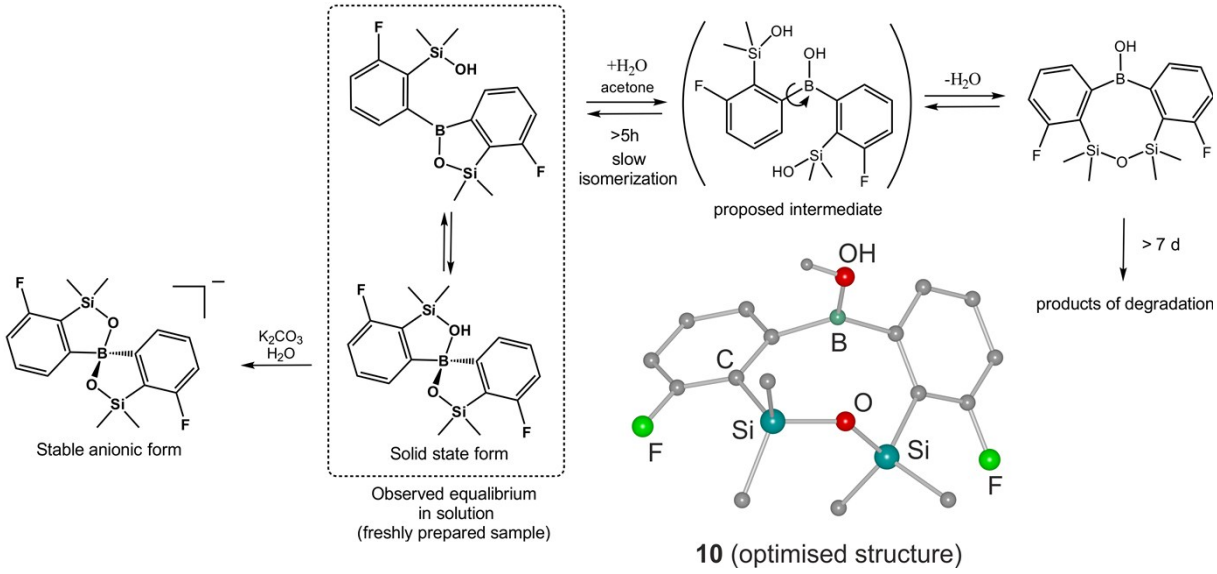


Figure S1. Labile nature of compound **9**.

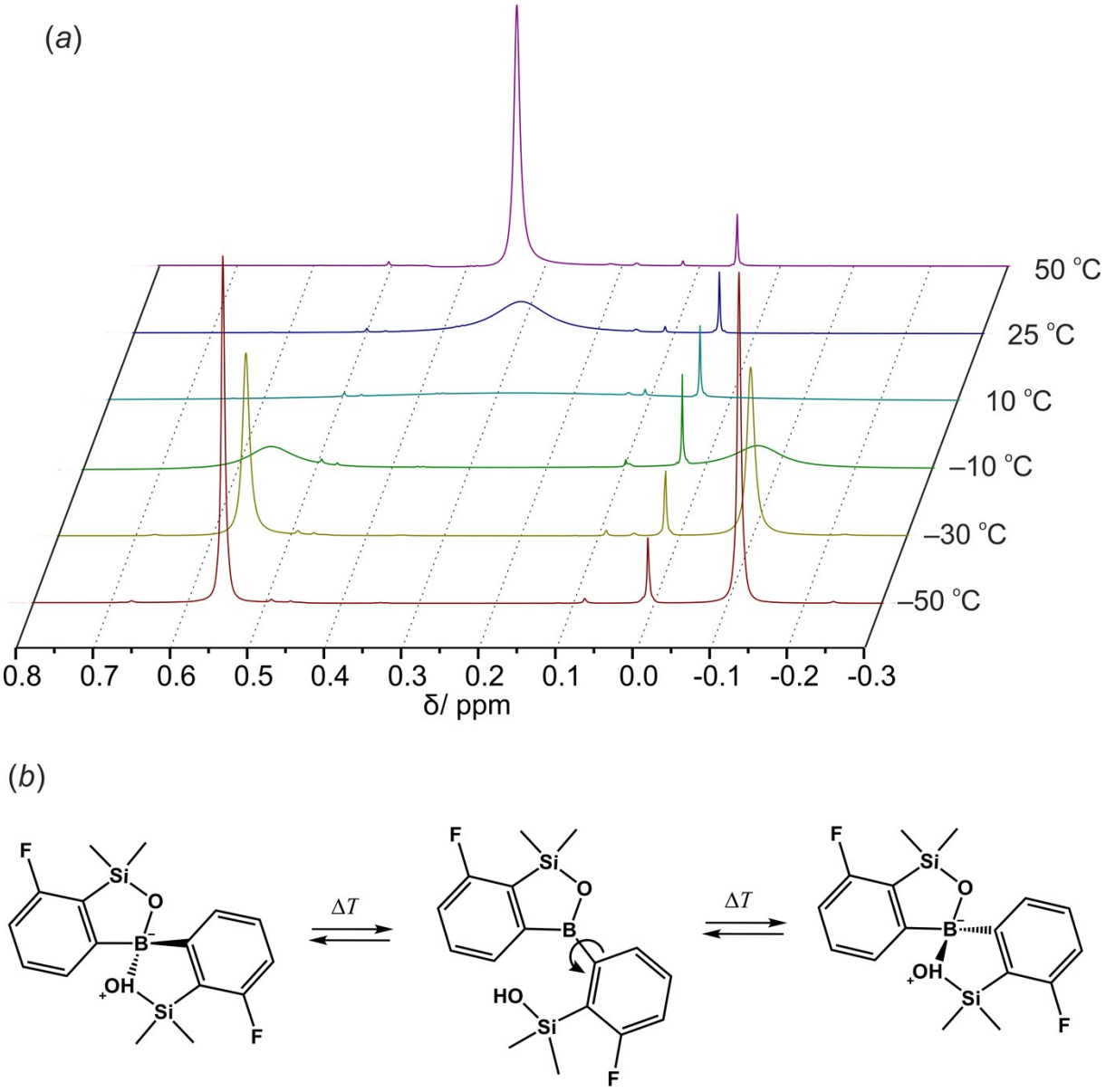
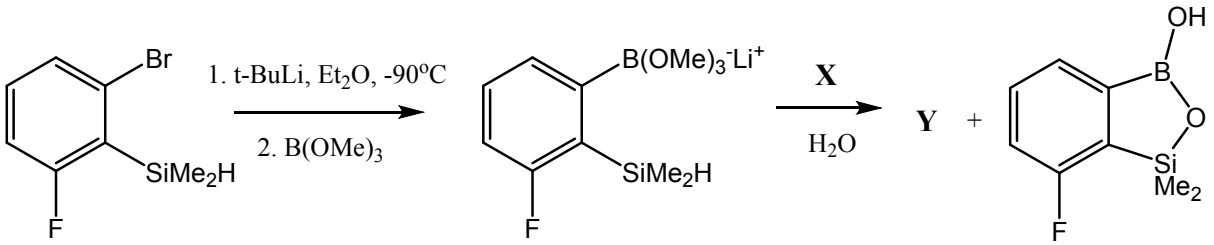


Figure S2. (a) VT ^{1}H NMR studies on **9**, (b) dynamic behavior in solution.

2. Studies on the boronic group-assisted hydrosilylation

A solution of 1-bromo-3-fluoro-2-dimethylsilylbenzene **1**[13] (0.60 g, 2.5 mmol) in Et_2O (5 mL) was added dropwise to a solution of *t*-BuLi (1.7 M in pentane, 3 mL, 5 mmol) in Et_2O (10 mL) at –90 °C. A mixture was stirred for 20 min at –90 °C and the obtained white suspension of **1-Li** was treated with $B(OMe)_3$ (0.55 mL, 5 mmol). The reaction mixture was warmed to –60 °C, and a solution of a functionalized benzaldehyde or a different tested reagent (2.5 mmol or 1.25 mmol in the case of terephtalaldehyde) in THF (5 mL) was added (for details, see Scheme 2 and Table 1). After warming to room temperature a mixture was quenched with 2 M aq. H_2SO_4 to reach the pH = 2-3 and stirred for 1 hour. The aqueous phase was separated followed by the extraction with Et_2O (2 × 20 mL). The extracts were added to the organic phase, which was concentrated under reduced pressure. A crude residue was subjected to ^1H NMR analysis. In all cases the spectra showed the presence of 4-fluoro-1,3-dihydro-3-hydroxy-1,1-dimethyl-1,2,3-benzosiloxaborole - the organoboron by-product of the reaction. In the case of functionalized benzaldehydes the formation of corresponding benzyl alcohol derivatives was confirmed by the disappearance of a signal of the formyl group at ca. 10 ppm. In contrast, 3-bromobenzonitrile, ethyl 4-iodobenzoate and 2-fluoroacetophenone were completely unreactive.

Table S1. Hydrosilylation of selected compounds.



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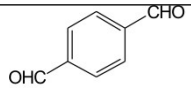
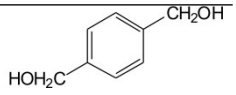
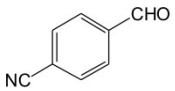
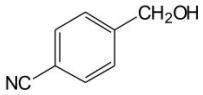
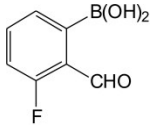
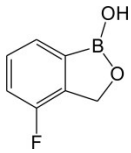
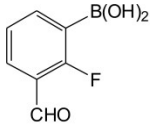
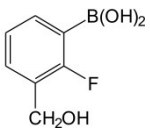
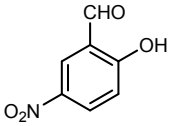
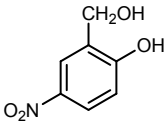
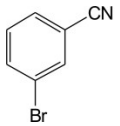
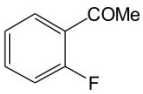
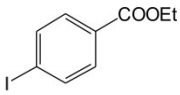
1		
2		
3		
4		
5		
6		No reaction
7		No reaction
8		No reaction

3. Results of quantum chemical calculations.

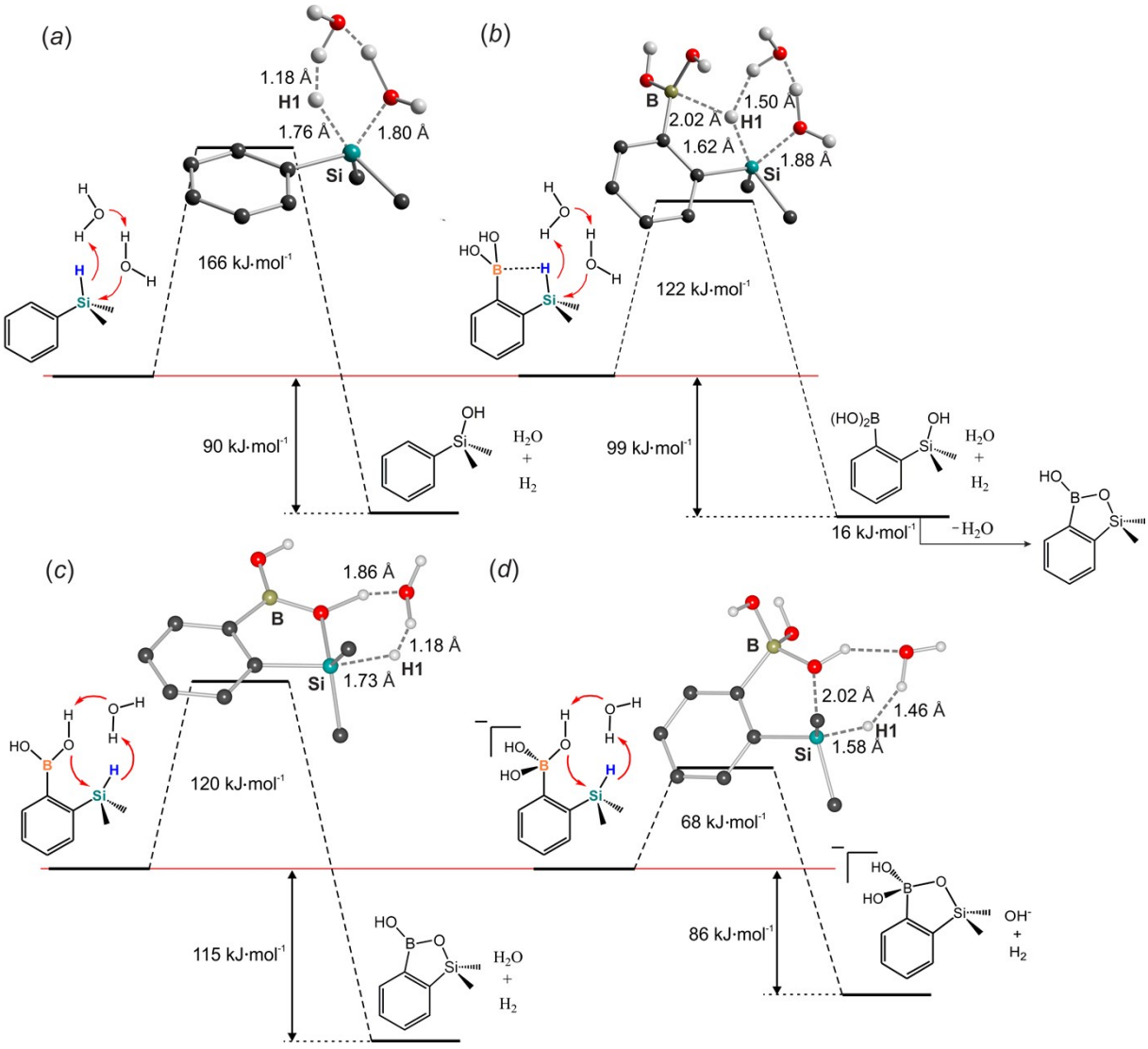


Figure S3. Reaction pathways for the activation of Si–H bond in (*a*) unsubstituted arylsilane, and by (*b*) boronic acid-assisted group Si-H…B coordination, (*c*) boronic acid-assisted group O…B coordination, (*d*) boronate group. Transition state structures are depicted.

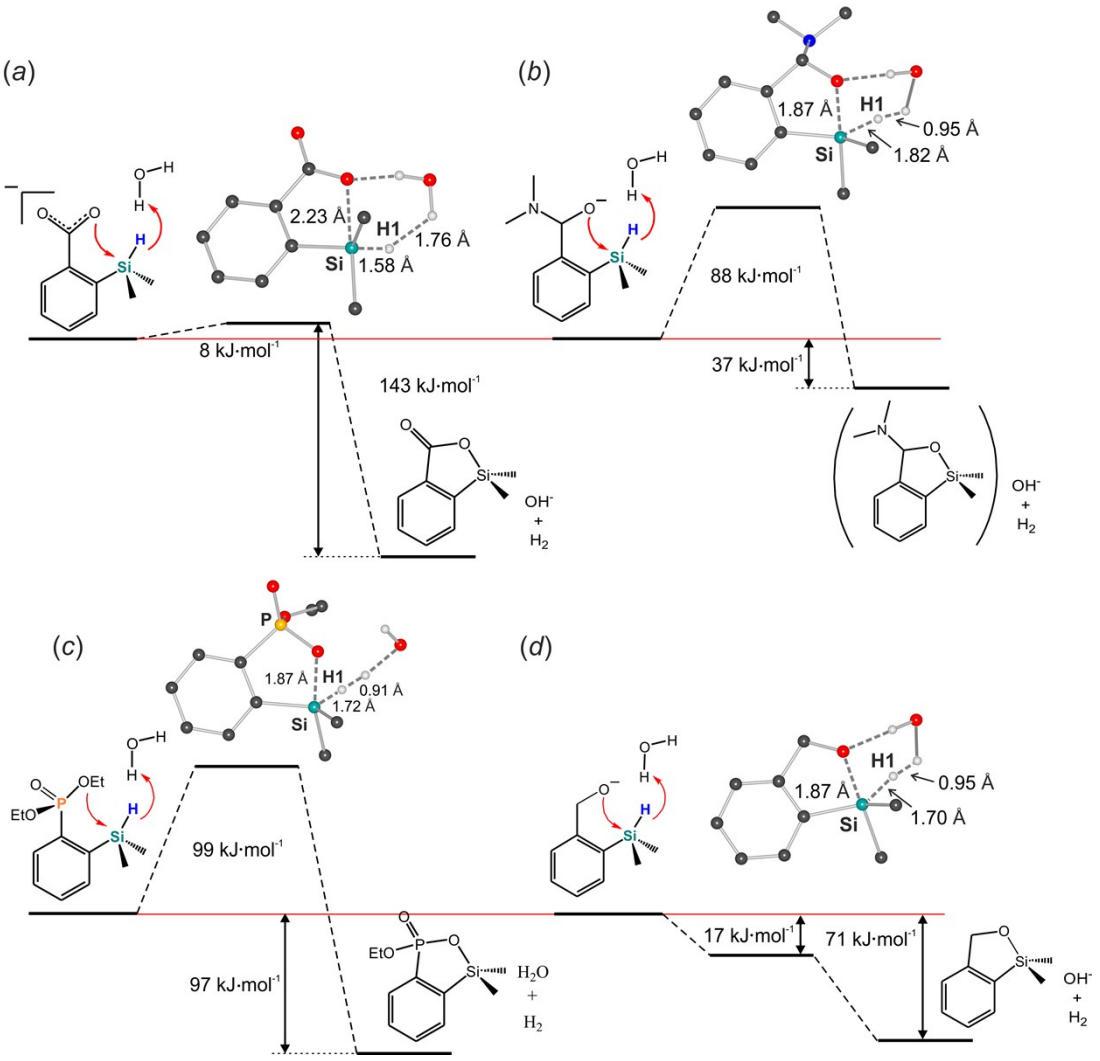


Figure S4. Reaction pathways for the activation of Si–H bond with *ortho*-assisted functional groups: (*a*) COO-, (*b*) $CH(NMe_2)O^-$, (*c*) $P(O)(OEt)_2$, (*d*) CH_2O^-. Transition state structures (*a*-*c*) and the structure of penta-coordinated complex *d* are depicted.

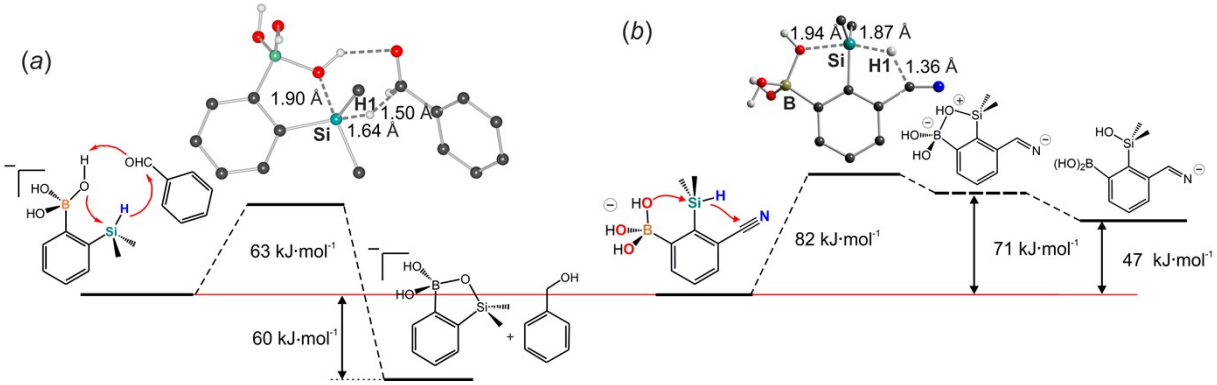
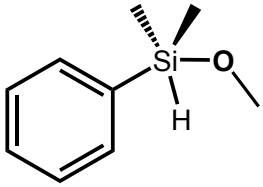


Figure S5. Reaction pathways for the reduction of (*a*) benzaldehyde and (*b*) benzonitrile (itramolecular). Transition state structures are depicted.

Transition states cartesian coordinates



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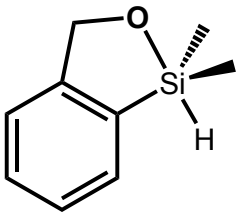
C2	3.4198	0.0944	-0.0044
C3	2.8532	-1.0687	-0.5225
C4	1.4714	-1.2528	-0.4705
C5	0.6066	-0.2847	0.0592
C6	1.2077	0.8822	0.5607
H7	3.0211	1.9782	0.9594
H8	4.4963	0.2383	-0.028
H9	3.4902	-1.8357	-0.9559
H10	1.045	-2.182	-0.8449
Si11	-1.3125	-0.5674	0.1642
C12	-2.0988	-0.7327	1.9043
H13	-1.3985	-1.2327	2.5833
H14	-2.4012	0.2183	2.3502
H15	-2.9809	-1.3823	1.8401
O16	-1.6312	1.2264	0.1903
H17	0.5604	1.6566	0.964
C18	-1.3302	1.9775	-0.9404
H19	-0.7775	2.8944	-0.6756
H20	-0.6983	1.4368	-1.6674
H21	-2.2368	2.2937	-1.4848
C22	-2.3691	-0.8441	-1.4284
H23	-3.1616	-1.5573	-1.1681
H24	-2.8361	0.0496	-1.8571
H25	-1.768	-1.3289	-2.2076
H26	-1.0301	-2.1569	0.1411



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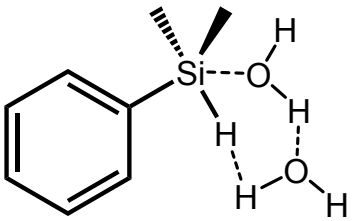
C3	2.7466	-1.3038	0.0443
C4	1.3683	-1.5238	0.0552
C5	0.4701	-0.4571	-0.0172
C6	0.9856	0.8389	-0.0804
H7	2.7425	2.0984	-0.1223
H8	4.3128	0.1757	-0.0256
H9	3.4384	-2.1409	0.0876
H10	0.9798	-2.5397	0.1222
O11	-1.3154	1.2934	-0.4134
Si12	-1.4568	-0.5034	0.0604
C13	-2.6991	-0.7596	-1.3751
H14	-2.1752	-1.1802	-2.2431
H15	-3.4688	-1.4859	-1.0922
H16	-3.1783	0.1694	-1.696
C17	-0.1011	1.8981	-0.1398
H18	0.1558	2.6552	-0.9029
H19	-0.1055	2.4442	0.8274
C20	-2.2356	-0.0487	1.7533
H21	-2.4826	-0.9069	2.3845
H22	-1.5498	0.5995	2.3129
H23	-3.1486	0.5368	1.5959
H24	-1.4029	-2.079	0.3337



	x	*y*	*z*
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C3	2.8960	-0.7589	-0.8003
C4	1.5180	-0.9511	-0.7060
C5	0.7103	-0.1223	0.0894
C6	1.3534	0.9058	0.7963
H7	3.2002	1.8939	1.2927

H8	4.5807	0.4140	-0.1473
H9	3.4924	-1.4096	-1.4330
H10	1.0675	-1.7640	-1.2673
Si11	-1.1702	-0.4223	0.2504
H12	-1.2742	1.2254	0.8465
C13	-1.3579	-2.1430	-0.6095
H14	-0.7277	-2.8904	-0.1146
H15	-2.3945	-2.4887	-0.5103
H16	-1.1077	-2.1655	-1.6776
C17	-1.8376	-0.8879	1.9615
H18	-1.7344	-1.9573	2.1694
H19	-1.3435	-0.3145	2.7503
H20	-2.9046	-0.6390	1.9999
H21	0.7560	1.5740	1.4121
O22	-2.2698	0.3108	-0.9793
H23	-2.2640	1.5699	-1.0631
H24	-2.4627	-0.2545	-1.7376
O25	-2.0629	2.6279	-0.6802
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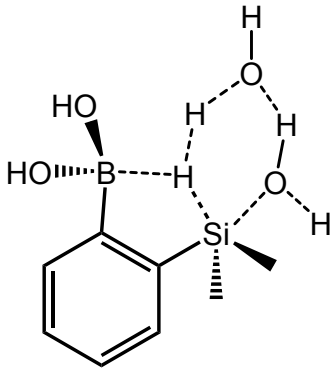
H27	-1.3661	3.0541	-1.2010



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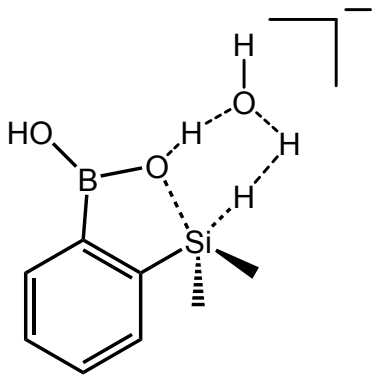
C4	1.5408	-1.8103	-0.2174
C5	0.7106	-0.6846	-0.0288
C6	1.3263	0.5921	0.0393
H7	3.2087	1.6683	-0.0292
H8	4.6128	-0.3378	-0.3608

H9	3.5386	-2.5954	-0.4749
H10	1.0998	-2.8037	-0.2746
B11	0.5591	1.9602	0.2327
O12	0.5981	2.5807	1.4661
H13	0.1827	3.4539	1.4488
O14	0.1308	2.7282	-0.8416
Si15	-1.1821	-0.9578	0.2028
C16	-1.4092	-2.8222	-0.2978
H17	-0.8816	-3.4982	0.3908
H18	-2.4781	-3.0804	-0.2352
H19	-1.0710	-3.0679	-1.3177
C20	-1.8455	-1.0797	1.9887
H21	-1.4343	-1.9727	2.4825
H22	-1.6184	-0.1963	2.5980
H23	-2.9402	-1.2006	1.9588
H24	0.2384	2.2711	-1.6841
H25	-1.2136	0.8295	0.4759
O26	-2.3434	-0.4417	-1.0876
H27	-2.7078	0.8386	-1.1263
H28	-2.4309	-1.0609	-1.8218
O29	-2.7723	1.8654	-0.7163
H30	-2.4124	2.4895	-1.3642
H31	-1.9198	1.5645	-0.0353



	x	*y*	*z*
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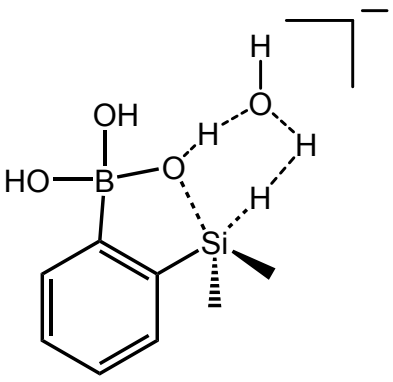
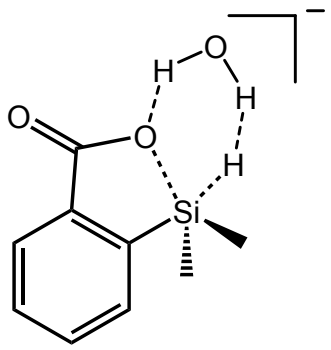
C2	3.4943	-0.5302	0.0244
C3	3.2733	0.8506	0.0308
C4	1.9757	1.3602	0.0194
C5	0.8724	0.4985	0.0022

C6	1.1100	-0.8868	-0.0040
H7	2.5748	-2.4771	0.0011
H8	4.5093	-0.9156	0.0332
H9	4.1228	1.5281	0.0446
H10	1.8317	2.4404	0.0241
B11	-0.2339	-1.6609	-0.0231
O12	-1.3376	-0.8112	-0.0242
H13	-2.5791	-1.1178	-0.0106
O14	-0.3520	-3.0130	-0.0368
Si15	-1.0035	1.0137	-0.0159
C16	-1.0970	1.9610	1.6178
H17	-0.1538	2.4675	1.8431
H18	-1.9128	2.6883	1.6101
H19	-1.2928	1.2539	2.4322
C20	-1.0489	2.0021	-1.6279
H21	-0.0955	2.5031	-1.8201
H22	-1.2357	1.3174	-2.4631
H23	-1.8574	2.7376	-1.6192
H24	-2.7326	1.0526	-0.0489
O25	-3.6947	-0.9392	-0.0411
H26	-3.4647	0.1226	-0.0377
H27	-4.1037	-1.1672	0.8071
H28	-1.2603	-3.3353	-0.0570



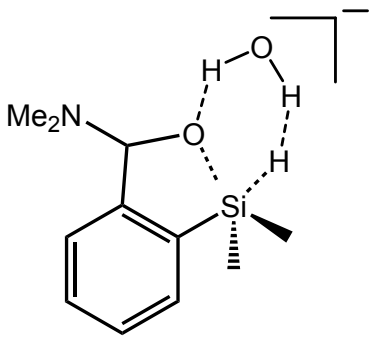
	x	*y*	*z*
C1	2.4908	-1.1030	-0.0349
C2	3.5261	-0.1707	-0.0862
C3	3.2329	1.1927	-0.1383
C4	1.9019	1.6073	-0.1470
C5	0.8570	0.6725	-0.0946

C6	1.1463	-0.7102	-0.0316
H7	2.7338	-2.1647	0.0072
H8	4.5622	-0.5010	-0.0850
H9	4.0368	1.9230	-0.1786
H10	1.6764	2.6728	-0.2105
B11	-0.1123	-1.7567	0.0447
O12	-0.2771	-2.5512	-1.1743
H13	-0.1137	-3.4660	-0.9275
O14	-0.0423	-2.6900	1.1731
Si15	-0.9593	1.2129	-0.0389
C16	-1.6207	1.5470	1.7090
H17	-0.9822	2.2680	2.2328
H18	-2.6235	1.9851	1.6536
H19	-1.6733	0.6330	2.3033
C20	-0.9750	3.0123	-0.7442
H21	-0.3613	3.7269	-0.1781
H22	-0.6373	3.0514	-1.7865
H23	-2.0088	3.3733	-0.7153
H24	0.2917	-2.2200	1.9428
H25	-2.1592	0.8535	-0.9985
O26	-1.2444	-0.7769	0.1563
H27	-2.1516	-1.1050	0.0392
O28	-3.6833	-0.8277	-0.6220
H29	-4.5982	-0.8468	-0.9140
H30	-3.3789	0.0969	-0.7229



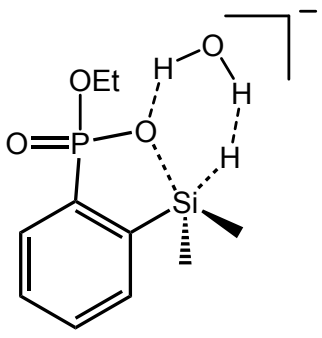
	x	*y*	*z*
C1	2.3452	-1.3044	0.0445
C2	3.3971	-0.4155	-0.1568

C3	3.1274	0.9412	-0.3389
C4	1.8121	1.4062	-0.3184
C5	0.7385	0.5298	-0.1140
C6	1.0372	-0.8267	0.0631
H7	2.5163	-2.3673	0.1850
H8	4.4220	-0.7743	-0.1749
H9	3.9451	1.6385	-0.4975
H10	1.6284	2.4673	-0.4623
O11	0.0372	-2.9700	0.4086
O12	-1.2607	-1.1380	0.2673
Si13	-1.0897	1.0761	-0.0143
C14	-1.8491	1.1181	1.7237
H15	-1.2967	0.4429	2.3813
H16	-1.7900	2.1358	2.1214
H17	-2.8935	0.7950	1.7233
C18	-0.8970	2.9579	-0.3912
H19	-0.2973	3.4792	0.3650
H20	-0.4341	3.1426	-1.3680
H21	-1.8835	3.4380	-0.4054
H22	-1.9801	0.7062	-1.1556
C23	-0.1366	-1.7570	0.2573
H24	-3.4849	-0.4907	-1.5716
O25	-3.5201	-1.4046	-1.2760
H26	-2.6970	-1.4758	-0.7559

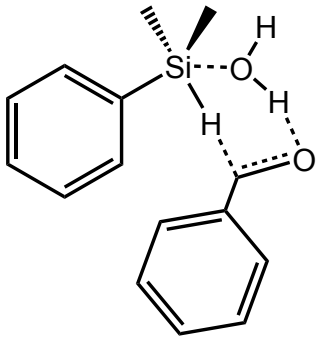


	x	*y*	*z*
C1	2.4185	1.0661	-0.6190
C2	3.5633	0.3006	-0.4024
C3	3.4465	-1.0076	0.0668
C4	2.1840	-1.5542	0.2988
C5	1.0239	-0.8097	0.0583

C6	1.1661	0.5117	-0.3632
H7	2.5048	2.0838	-0.9942
H8	4.5443	0.7223	-0.6015
H9	4.3391	-1.6023	0.2396
H10	2.1078	-2.5795	0.6531
O11	-1.1168	0.2218	-0.7156
Si12	-0.8118	-1.3869	0.1787
C13	-1.7516	-2.3402	-1.1955
H14	-1.0143	-2.7143	-1.9183
H15	-2.2379	-3.2249	-0.7667
H16	-2.4932	-1.7399	-1.7338
C17	-0.4961	-2.9211	1.3484
H18	0.0577	-3.7090	0.8211
H19	0.0663	-2.6738	2.2580
H20	-1.4518	-3.3565	1.6674
H21	-2.1188	-0.7688	1.2834
C22	-0.1733	1.2065	-0.5704
H23	-0.1217	1.8352	-1.4910
N24	-0.5296	2.0983	0.5633
C25	0.4253	3.1835	0.7123
H26	0.0690	3.8713	1.4842
H27	1.4036	2.8075	1.0187
H28	0.5546	3.7661	-0.2216
C29	-1.8641	2.6732	0.3632
H30	-2.0992	3.3018	1.2286
H31	-1.888	3.3234	-0.5345
H32	-2.6537	1.9197	0.2568
H33	-2.8466	0.0345	-0.7627
O34	-3.6659	0.0732	-0.2301
H35	-3.0424	-0.781	1.0494

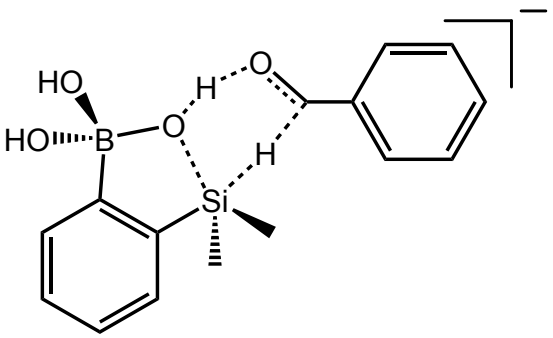


	x	*y*	*z*
C1	-2.2473	-1.8399	-0.2570
C2	-3.5064	-1.5083	0.2409
C3	-3.7473	-0.2236	0.7258
C4	-2.7334	0.7349	0.7147
C5	-1.4648	0.4244	0.2171
C6	-1.2392	-0.8810	-0.2571
H7	-2.0503	-2.8345	-0.6478
H8	-4.3008	-2.2482	0.2455
H9	-4.7301	0.0338	1.1090
H10	-2.9414	1.7338	1.0926
O11	0.8387	0.4018	-1.1379
Si12	-0.0298	1.6605	0.0266
C13	-0.2355	2.8778	-1.3934
H14	-1.1621	3.4435	-1.2513
H15	0.5924	3.5941	-1.4117
H16	-0.2698	2.3610	-2.3534
C17	-0.1774	2.8286	1.5452
H18	-1.0792	3.4556	1.5250
H19	-0.1821	2.2625	2.4828
H20	0.6902	3.4960	1.5565
P21	0.4390	-1.0793	-0.8929
O22	0.5928	-2.0497	-2.0148
O23	1.1774	-1.5953	0.4582
C24	2.5461	-1.3301	0.8031
H25	3.2253	-1.8974	0.1547
H26	2.7755	-0.2661	0.6766
C27	2.6817	-1.7635	2.2492
H28	3.6779	-1.565	2.6492
H29	1.9701	-1.2083	2.8671
H30	2.4611	-2.8295	2.3468
H31	1.3972	1.4053	0.8769
H32	3.1639	0.891	-1.2047
O33	3.5261	1.4595	-0.5026
H34	2.2544	1.4684	0.3539



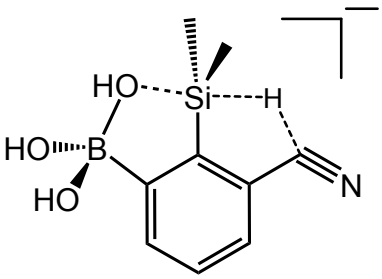
	x	*y*	*z*
C1	-0.6137	2.5981	0.5668
C2	0.0515	3.5936	-0.1472
C3	1.2958	3.3230	-0.7117
C4	1.8737	2.0633	-0.5543
C5	1.2216	1.0424	0.1530
C6	-0.0369	1.3376	0.7001
H7	-1.5875	2.7968	1.0054
H8	-0.3993	4.5743	-0.2665
H9	1.8177	4.0937	-1.2713
H10	2.8507	1.8774	-0.9924
Si11	1.9694	-0.6948	0.4179
H12	0.4756	-1.3049	0.3233
C13	3.8131	-0.3743	-0.0140
H14	4.1897	0.4500	0.6014
H15	4.4170	-1.2582	0.2228
H16	4.0059	-0.1114	-1.0609
C17	2.1147	-1.2373	2.2269
H18	2.9448	-0.7369	2.7344
H19	1.1874	-1.0424	2.7727
H20	2.3004	-2.3166	2.2658
H21	-0.5807	0.5619	1.2368
O22	2.1058	-2.1445	-0.9144
H23	2.8595	-2.0877	-1.5171
H24	1.2243	-2.2734	-1.4421
C25	-2.2929	-0.2851	-1.1959
C26	-3.3620	0.5311	-0.8425
C27	-3.9995	0.3526	0.3852
C28	-3.5758	-0.6489	1.2604
C29	-2.5115	-1.4695	0.9059
C30	-1.8672	-1.2846	-0.3196
H31	-1.772	-0.1585	-2.1395

H32	-3.6955	1.312	-1.5181
H33	-4.8304	0.9939	0.6613
H34	-4.0752	-0.7863	2.2137
H35	-2.1635	-2.2458	1.5832
C36	-0.7065	-2.1334	-0.6664
H37	-0.5223	-2.979	0.0156
O38	-0.1865	-2.1159	-1.8054



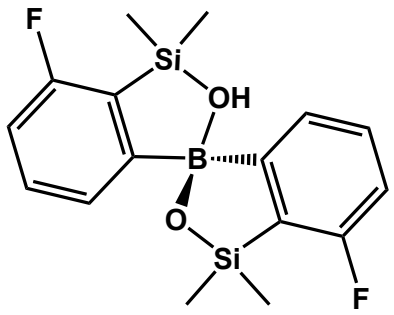
	x	*y*	*z*
C1	-4.3583	-0.2699	-0.2778
C2	-4.7759	-1.5999	-0.2423
C3	-3.8383	-2.6175	-0.0645
C4	-2.4893	-2.2953	0.0804
C5	-2.0622	-0.9608	0.0531
C6	-3.0092	0.0698	-0.1350
H7	-5.0949	0.5171	-0.4323
H8	-5.8280	-1.8474	-0.3605
H9	-4.1585	-3.6558	-0.0449
H10	-1.7672	-3.0987	0.2074
B11	-2.4346	1.5844	-0.1481
O12	-2.9295	2.3932	-1.2342
H13	-2.9548	3.3052	-0.9265
O14	-2.5788	2.3124	1.1063
Si15	-0.2563	-0.3974	0.2856
C16	0.1953	0.2844	1.9877
H17	0.2480	-0.5058	2.7423
H18	1.1821	0.7574	1.9152
H19	-0.5084	1.0541	2.3136
C20	0.6746	-2.0973	0.2730
H21	0.2919	-2.7735	1.0481
H22	0.5927	-2.6139	-0.6908

H23	1.7406	-1.9333	0.4682
H24	-2.5921	1.6924	1.8407
H25	0.9569	0.1120	-0.6953
O26	-0.9190	1.2593	-0.3854
H27	-0.2693	1.9801	-0.2729
C28	3.8528	0.7604	0.6273
C29	4.9814	0.0190	0.9727
C30	5.4080	-1.0247	0.1543
C31	4.7074	-1.3245	-1.0155
C32	3.5809	-0.5847	-1.3572
C33	3.1460	0.4559	-0.5345
H34	3.5058	1.5871	1.2396
H35	5.5304	0.2569	1.8786
H36	6.2865	-1.6028	0.4235
H37	5.0399	-2.1359	-1.6554
C39	1.9199	1.2526	-0.8924
H40	1.6790	1.2123	-1.9739
O41	1.5851	2.2540	-0.2118
H38	3.0192	-0.8220	-2.2586



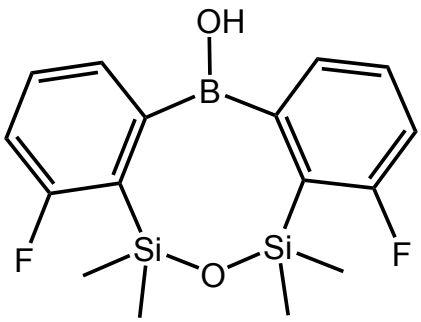
	x	*y*	*z*
C1	0.2789	2.5568	-0.0507
C2	-1.0555	2.9768	-0.0127
C3	-2.0982	2.0512	0.0346
C4	-1.7936	0.6901	0.0391
C5	-0.4652	0.2866	-0.0046
C6	0.6031	1.1946	-0.0410
H7	1.0688	3.3051	-0.0914
H8	-1.2838	4.0399	-0.0183
H9	-3.1380	2.3659	0.0683
B10	2.0829	0.5470	-0.0232
O11	2.7542	0.4652	1.2631

O12	1.7354	-1.0273	-0.2479
Si13	-0.0227	-1.5200	-0.0491
C14	0.1512	-2.5312	1.5284
H15	-0.7797	-3.0376	1.7894
H16	0.9316	-3.2923	1.4165
H17	0.4333	-1.8791	2.3608
C18	-0.2263	-2.5611	-1.5997
H19	-1.0140	-3.3073	-1.4745
H20	-0.4947	-1.9260	-2.4490
H21	0.7097	-3.0740	-1.8422
C22	-2.8263	-0.4007	0.0915
H23	-2.0566	-1.4383	0.1059
N24	-4.0390	-0.4398	0.1187
H25	2.3713	-1.5458	0.2638
H26	3.1066	1.3315	1.4898
O27	2.8989	1.0326	-1.0914
H28	3.8054	0.7384	-0.9471



	x	*y*	*z*
H1	-0.2285	1.9863	-1.1983
Si2	2.3759	1.1093	1.0424
Si3	-2.4443	1.1158	-1.0100
O4	-0.6966	1.1580	-1.0207
O5	0.7029	1.1648	1.0287
C6	3.4524	-1.9015	-1.7605
H7	4.3298	-2.3813	-2.1801
C8	2.5181	-0.2484	-0.2400
C9	1.2174	-0.6196	-0.6342
C10	-2.4720	-0.2361	0.2554
C11	-1.1884	-0.5799	0.7195

C12	3.5962	-0.8995	-0.8134
C13	-3.4769	-1.9152	1.7021
H14	-4.3703	-2.4117	2.0634
C15	-3.5746	-0.9110	0.7554
C16	3.1264	2.7365	0.5084
H17	2.9117	3.5269	1.2337
H18	2.7370	3.0477	-0.4650
H19	4.2140	2.6434	0.4254
C20	-1.0722	-1.6003	1.6710
H21	-0.0880	-1.8886	2.0337
C22	-3.0330	0.6319	-2.7044
H23	-2.5313	-0.2805	-3.0370
H24	-2.8460	1.4235	-3.4348
H25	-4.1100	0.4401	-2.6781
B26	0.0743	0.2289	0.1302
C27	-2.2010	-2.2550	2.1586
H28	-2.0972	-3.0412	2.9000
C29	3.0197	0.6155	2.7265
H30	2.5616	-0.3212	3.0564
H31	2.8051	1.3854	3.4736
H32	4.1043	0.4718	2.6936
C33	2.1587	-2.2639	-2.1439
H34	2.0272	-3.0475	-2.8840
C35	1.0489	-1.6323	-1.5841
H36	0.0480	-1.9323	-1.8880
C37	-3.0741	2.7738	-0.4515
H38	-2.6275	3.0569	0.5051
H39	-4.1598	2.7284	-0.3226
H40	-2.8556	3.5521	-1.1878
F41	-4.7993	-0.5659	0.2930
F42	4.8477	-0.5459	-0.4336



	x	*y*	*z*
C1	1.6884	1.1103	0.6375
C2	0.4324	-1.6457	-2.0528
H3	-0.0930	-2.5881	-2.2325
H4	-0.2556	-0.8186	-2.2578
H5	1.2626	-1.5788	-2.7630
C6	2.0221	-3.1028	0.1612
H7	2.8544	-3.2775	-0.5249
H8	2.4245	-3.0231	1.1749
H9	1.3537	-3.9685	0.1251
O10	-0.1532	-1.3414	0.7938
Si11	1.0906	-1.5537	-0.3032
C12	2.1531	-0.0178	-0.0718
C13	3.4579	0.0232	-0.5435
C14	2.5498	2.1958	0.8480
C15	4.3236	1.0900	-0.3596
C16	3.8531	2.1889	0.3525
H17	2.1998	3.0607	1.4056
H18	5.3300	1.0454	-0.7601
H19	4.5068	3.0386	0.5218
C20	-2.0438	0.5117	-0.0109
C21	-3.1222	0.8653	-0.8103
C22	-1.0201	1.4708	0.1590
C23	-3.2452	2.0868	-1.4540
C24	-1.1179	2.7076	-0.4927
C25	-2.2200	3.0139	-1.2897
H26	-4.1159	2.2912	-2.0668
H27	-0.3266	3.4444	-0.3769
H28	-2.2842	3.9765	-1.7868
B29	0.2005	1.2409	1.1458
O30	0.0129	1.3686	2.4886

H31	-0.9035	1.5696	2.7182
Si32	-1.8176	-1.2156	0.7045
C33	-2.4819	-1.3708	2.4418
H34	-1.9626	-0.6937	3.1252
H35	-3.5499	-1.1359	2.4687
H36	-2.3485	-2.3923	2.8101
C37	-2.5459	-2.5275	-0.4111
H38	-2.0745	-3.4957	-0.2140
H39	-3.6186	-2.6261	-0.2232
H40	-2.4115	-2.2850	-1.4681
F41	-4.1157	-0.0393	-0.9765
F42	3.9169	-1.0488	-1.2351

4. NMR spectra of new compounds.

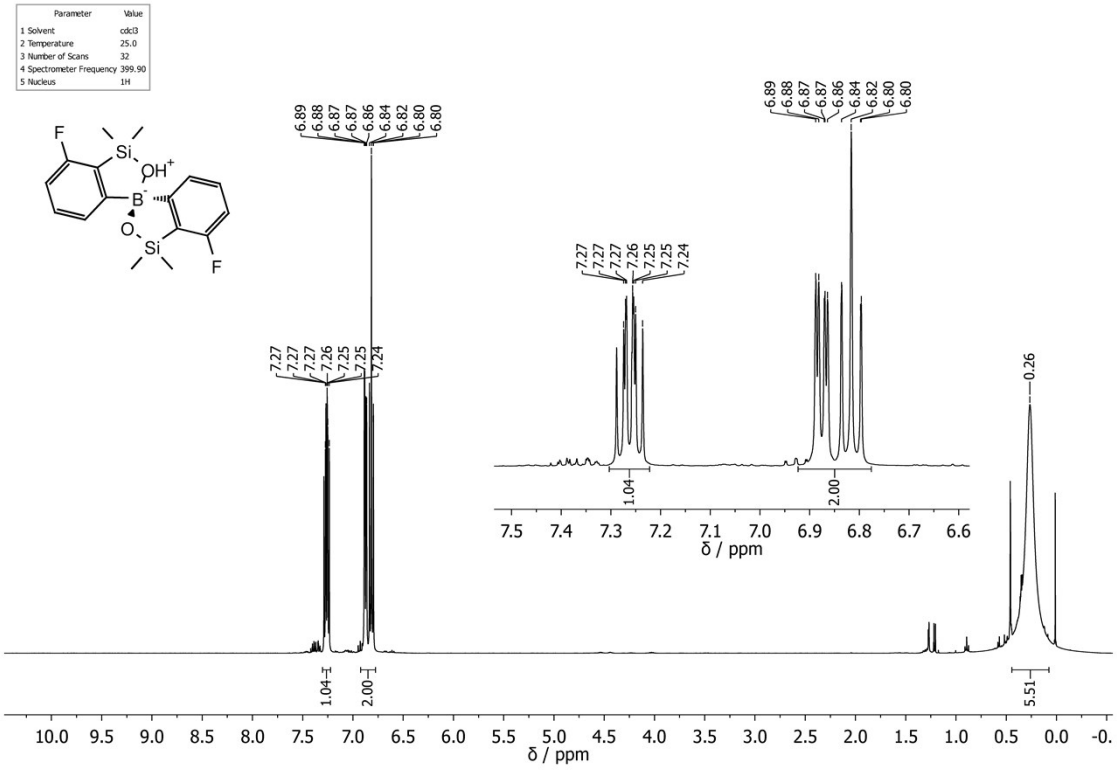


Figure S6. ^{1}H NMR spectrum of compound **9** (400 MHz, $CDCl_3$ solution).

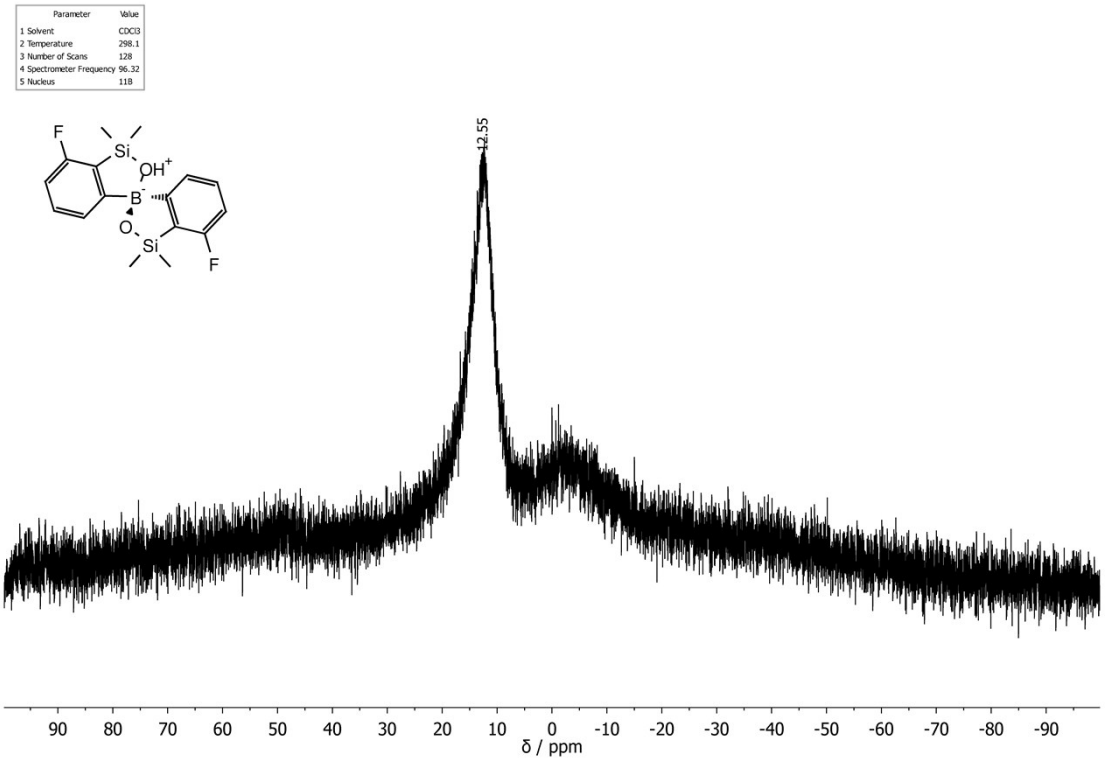


Figure S7. ^{11}B NMR spectrum of compound **9** (96 MHz, $CDCl_3$ solution).

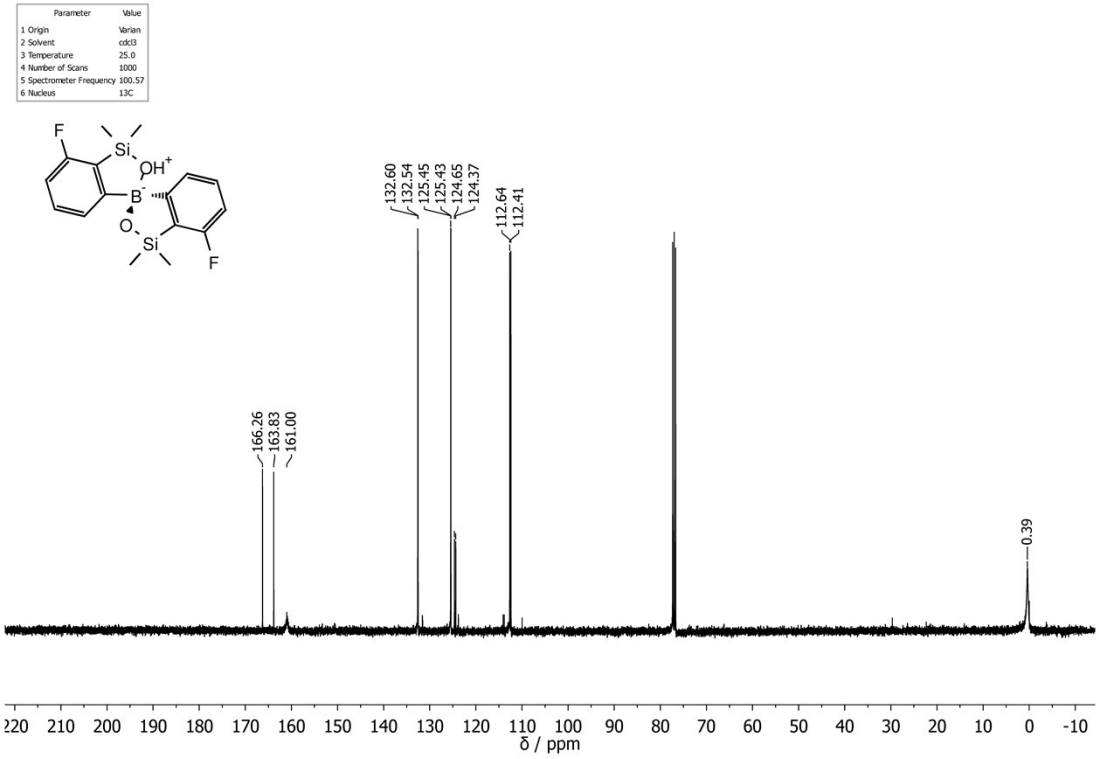


Figure S8. ^{13}C NMR spectrum of compound **9** (101 MHz, $CDCl_3$ solution).

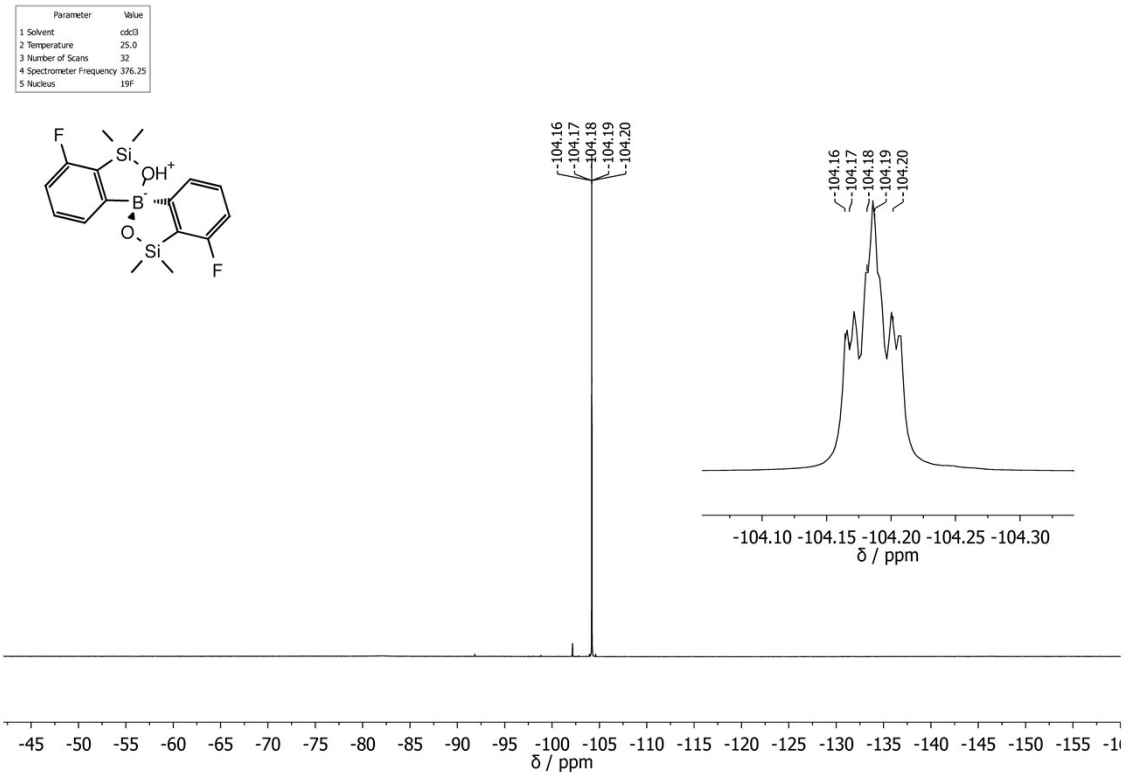


Figure S9. ^{19}F NMR spectrum of compound **9** (376 MHz, $CDCl_3$ solution).

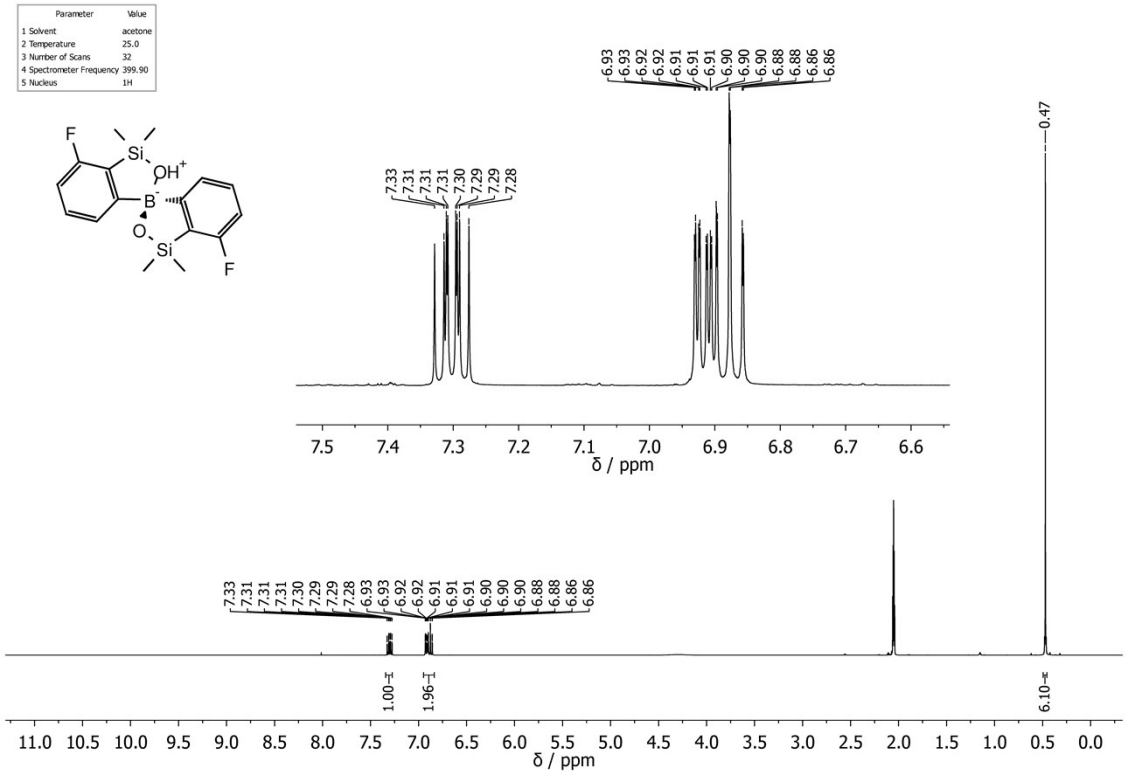


Figure S10. ^{1}H NMR spectrum of compound **9** (300 MHz, Acetone-d_6 solution).

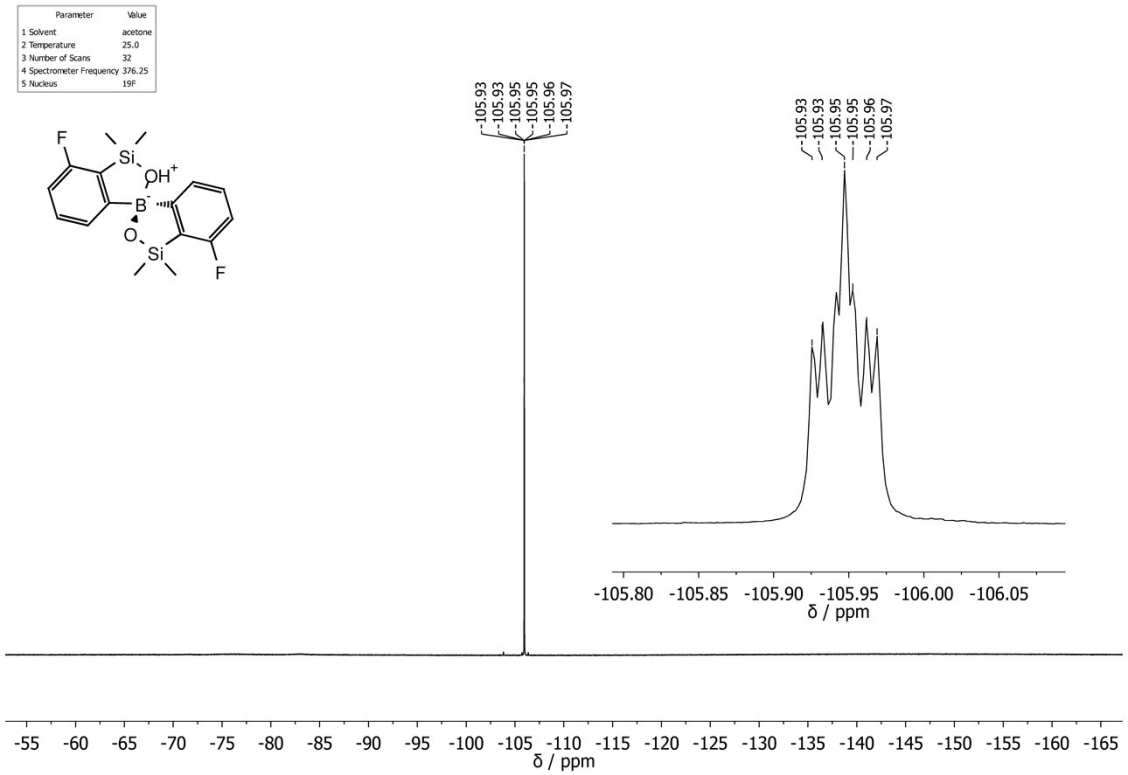


Figure S11. ^{19}F NMR spectrum of compound **9** (282 MHz, Acetone-d_6 solution).

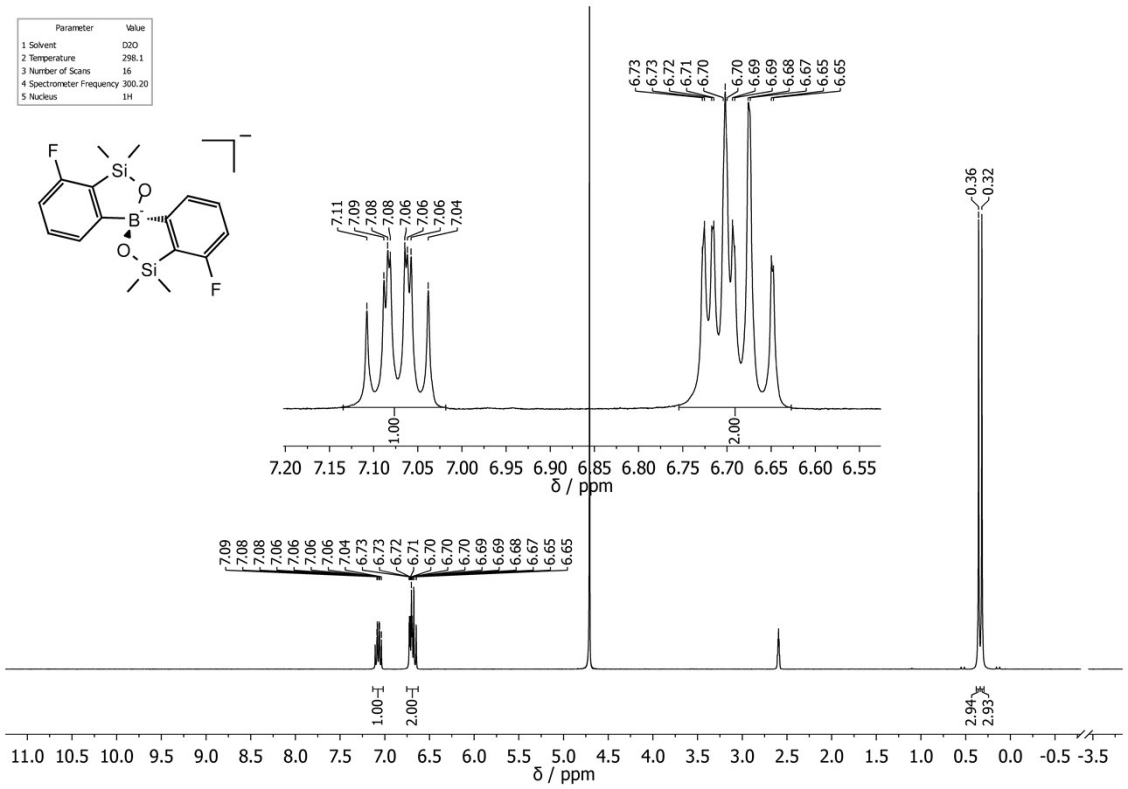


Figure S12. ^{1}H NMR spectrum of compound **9** (300 MHz, D_2O + K_2CO_3 solution).

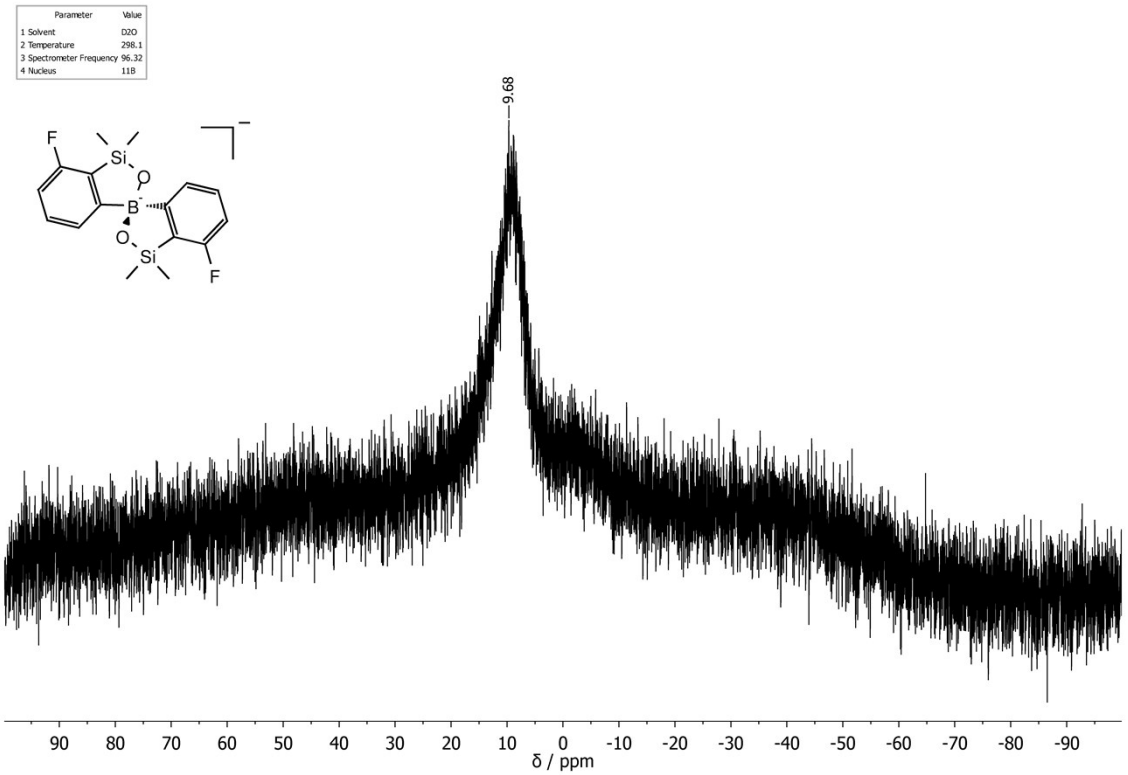


Figure S13. ^{11}B NMR spectrum of compound **9** (96 MHz, D_2O + K_2CO_3 solution).

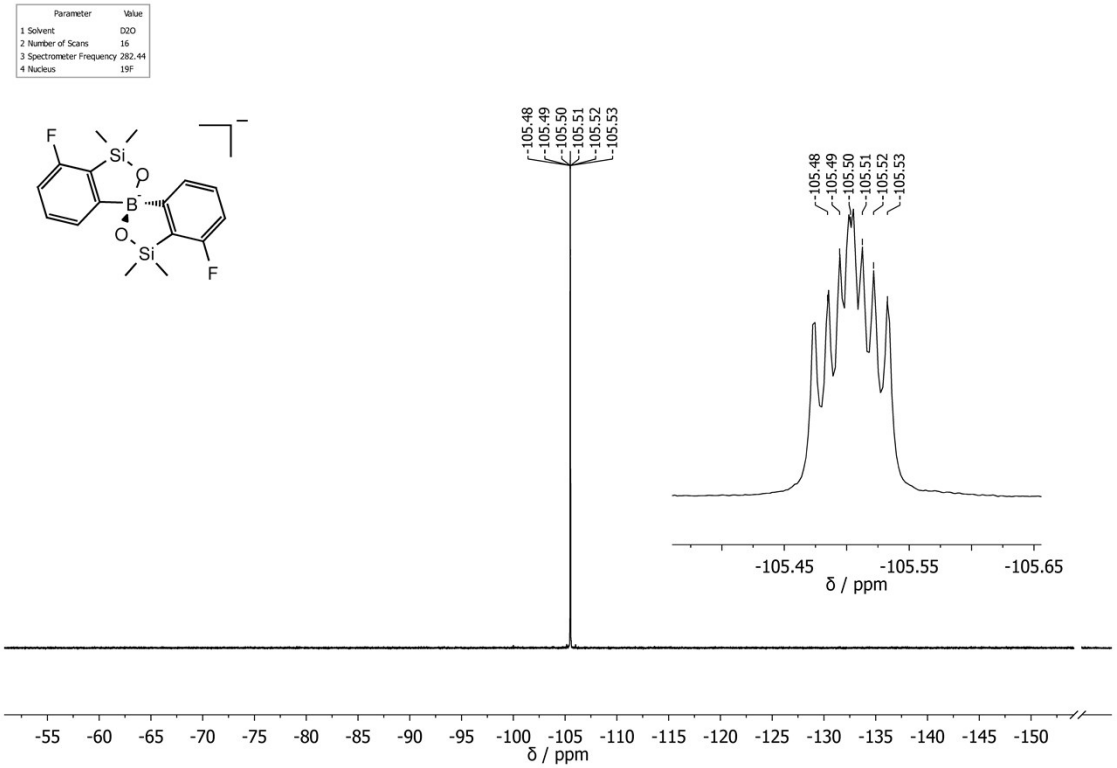


Figure S14. ^{19}F NMR spectrum of compound **9** (96 MHz, D_2O + K_2CO_3 solution).

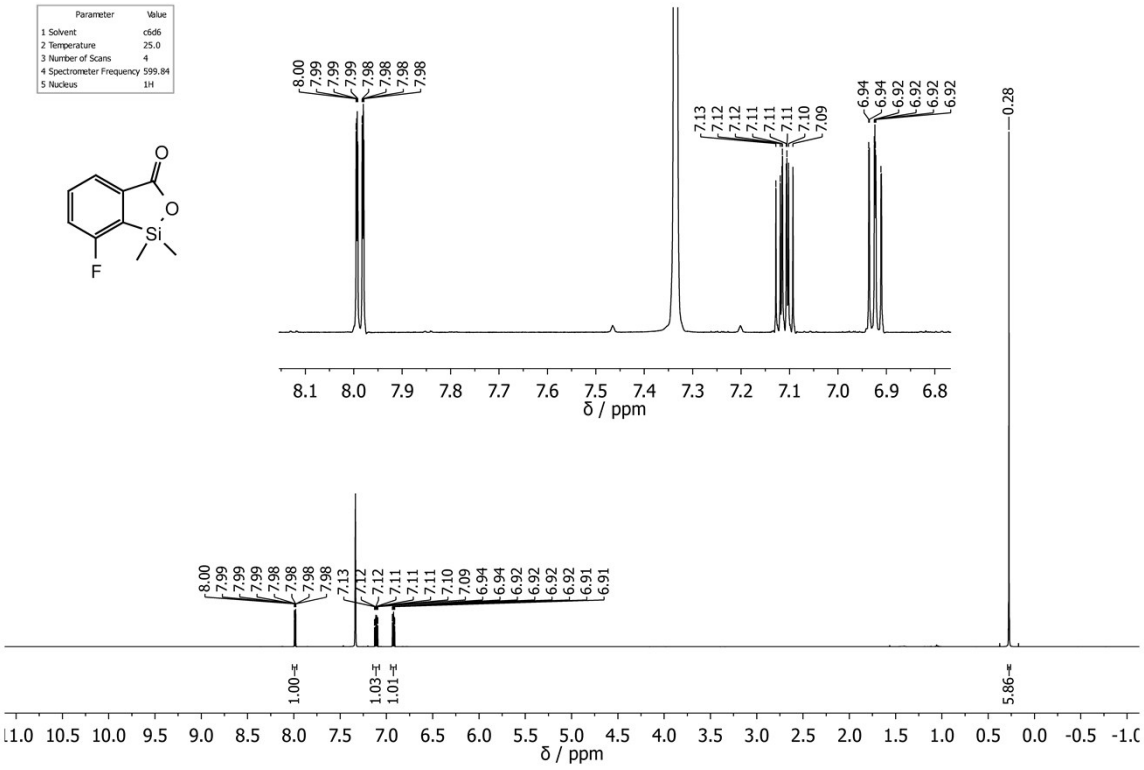


Figure S15. ^{1}H NMR spectrum of compound **12** (600 MHz, $CDCl_3$ solution).

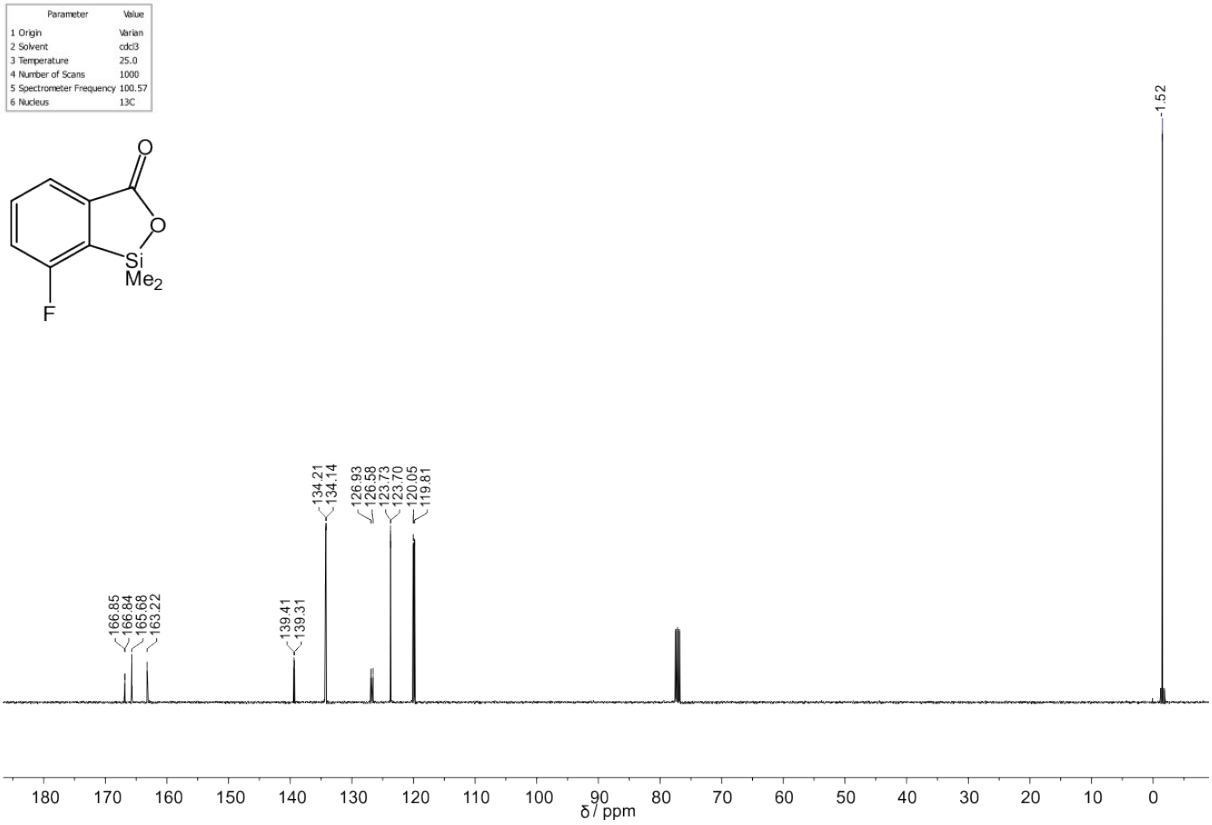


Figure S16. ^{13}C NMR spectrum of compound **12** (100 MHz, $CDCl_3$ solution).

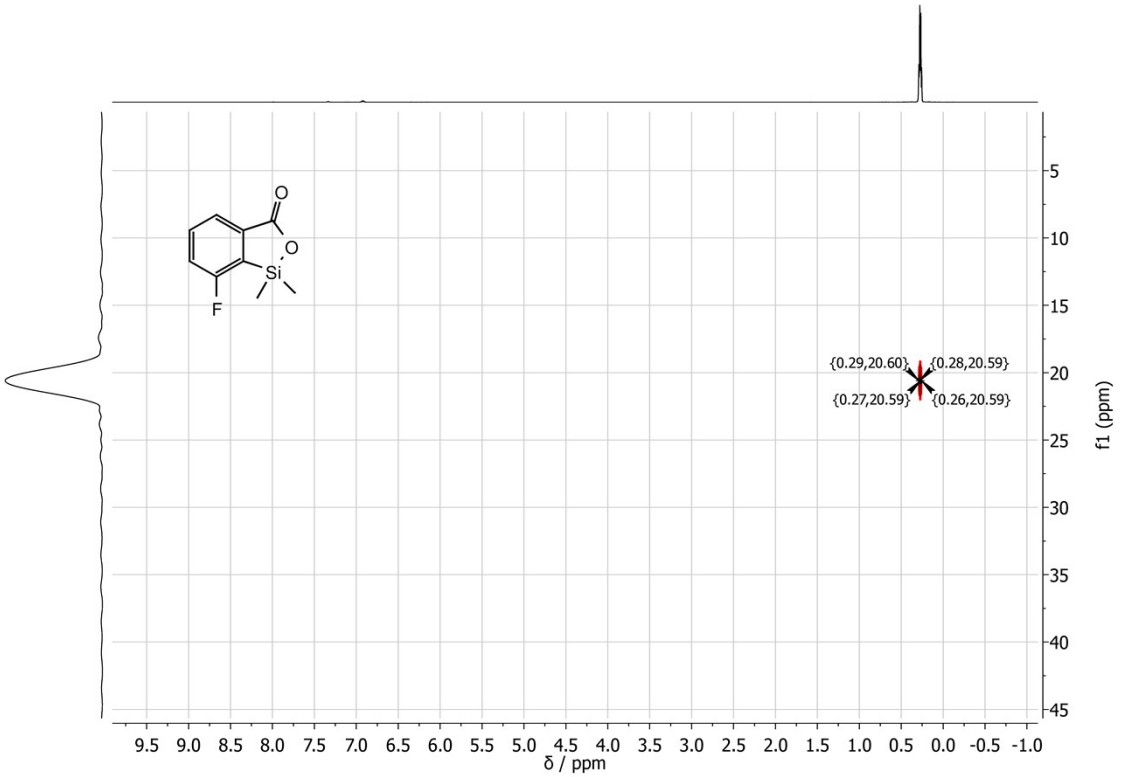


Figure S17. $^{1}H/^{29}Si$ HMBC NMR spectrum of compound **12** (600/119 MHz, $CDCl_3$ solution).

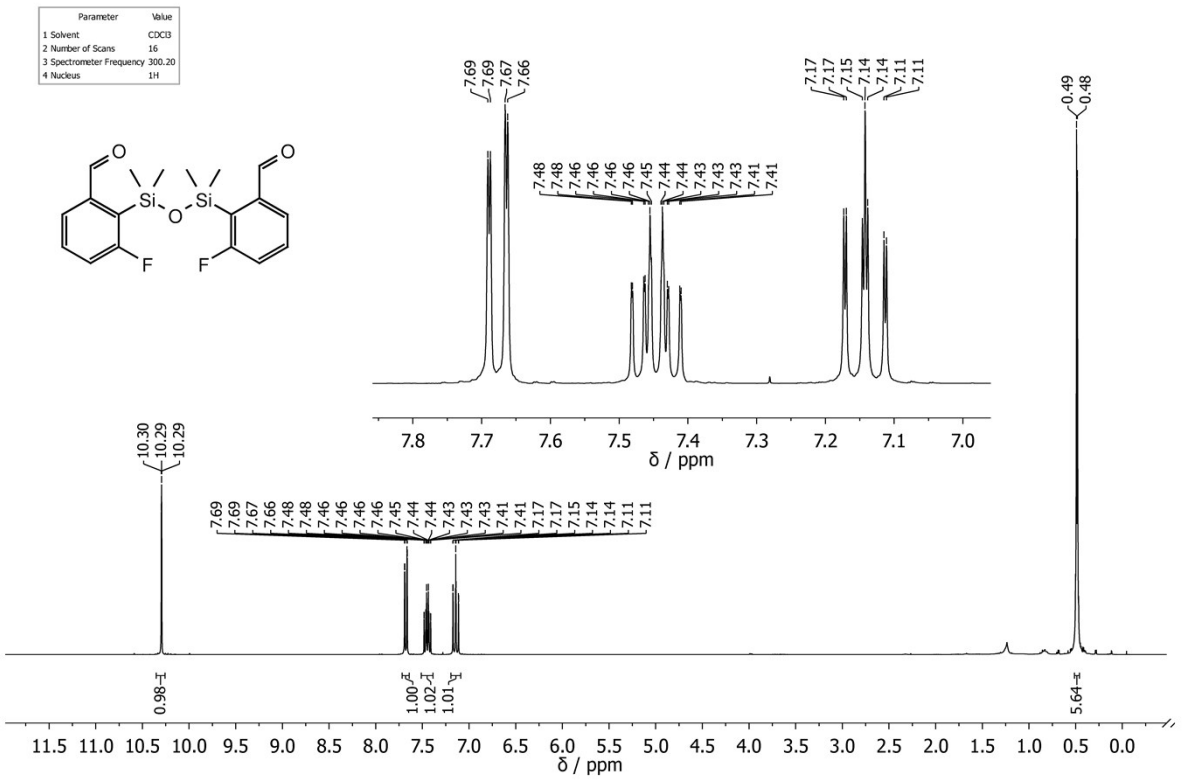


Figure S18. ^{1}H NMR spectrum of compound **14** (300 MHz, $CDCl_3$ solution).

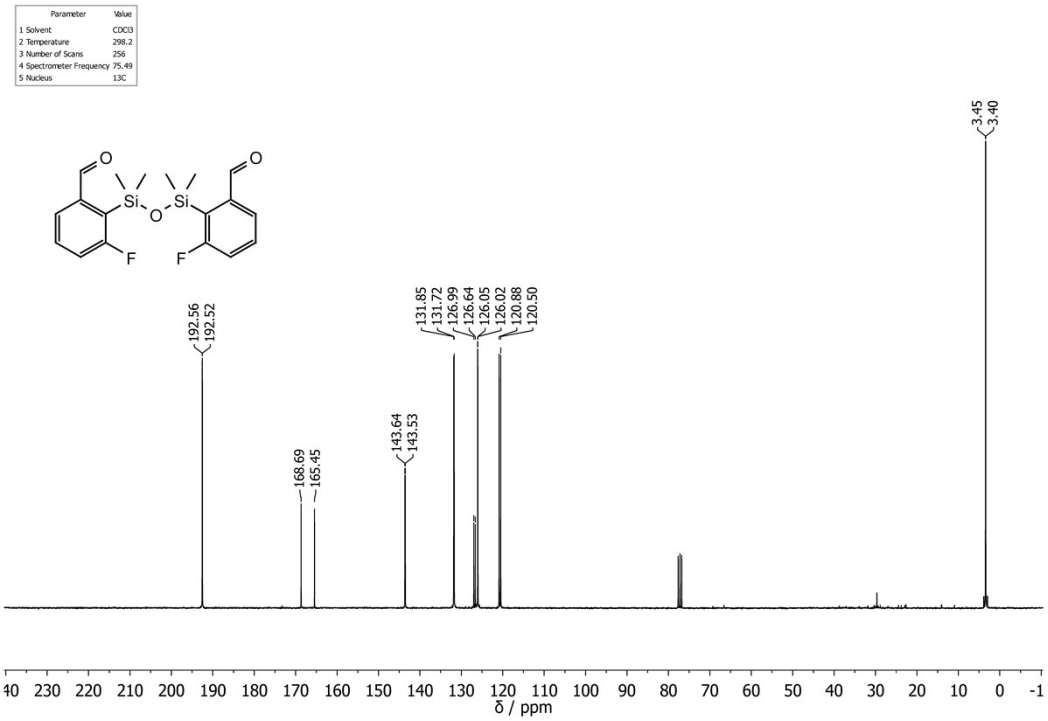


Figure S19. ^{13}C NMR spectrum of compound **14** (75 MHz, $CDCl_3$ solution).

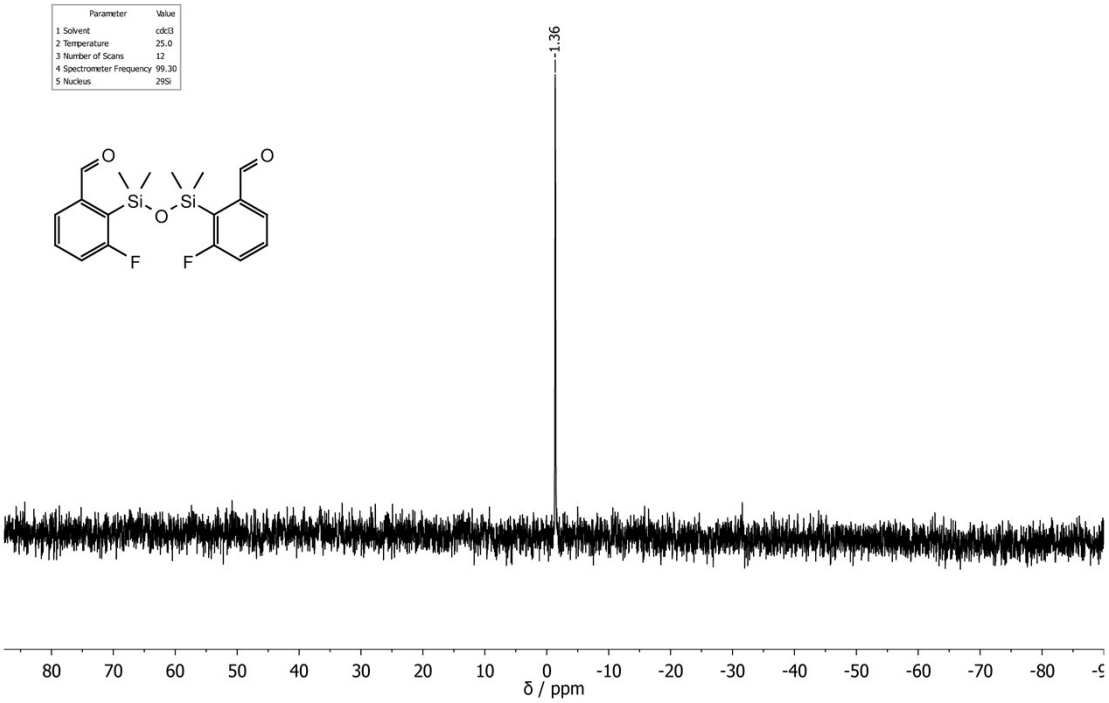


Figure S20. ^{29}Si NMR spectrum of compound **14** (99 MHz, $CDCl_3$ solution).

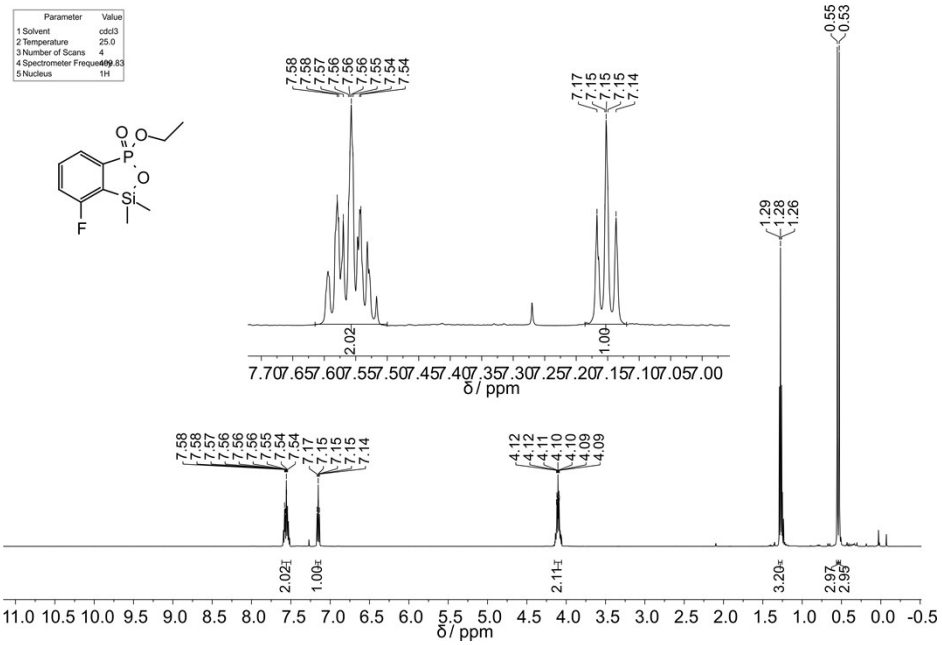


Figure S21. ^{1}H NMR spectrum of compound **16** (400 MHz, $CDCl_3$ solution).

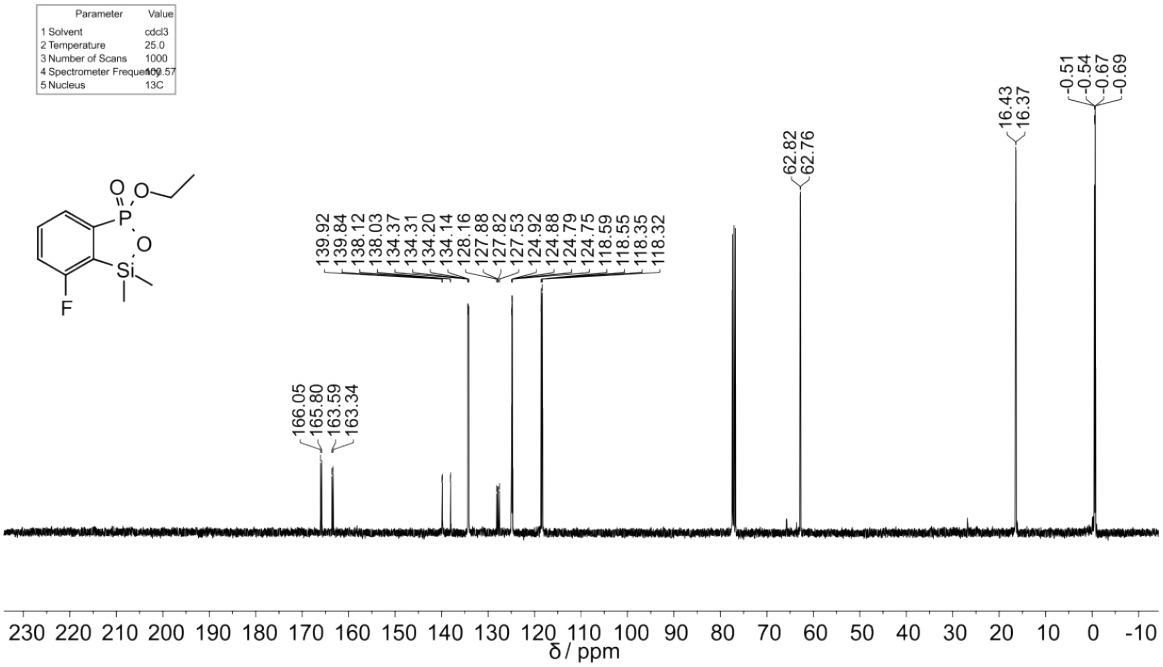


Figure S22. ^{13}C NMR spectrum of compound **16** (100 MHz, $CDCl_3$ solution).

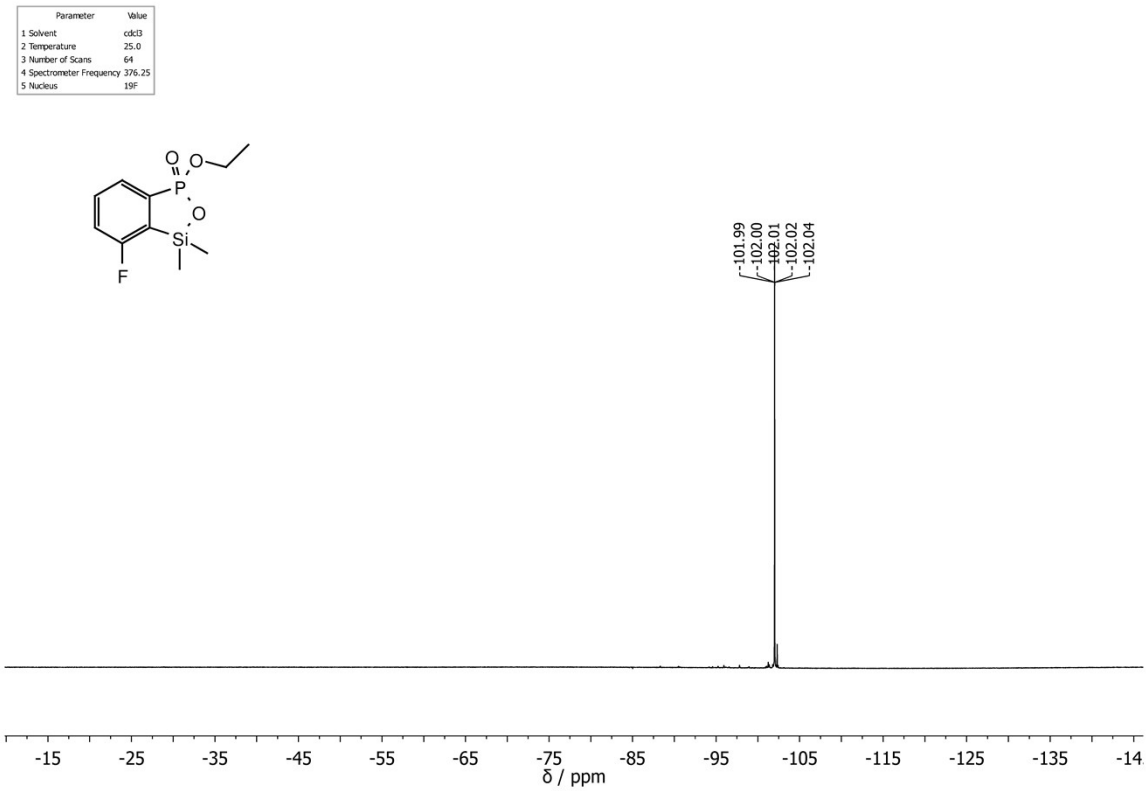


Figure S23. ^{19}F NMR spectrum of compound **16** (375 MHz, $CDCl_3$ solution).

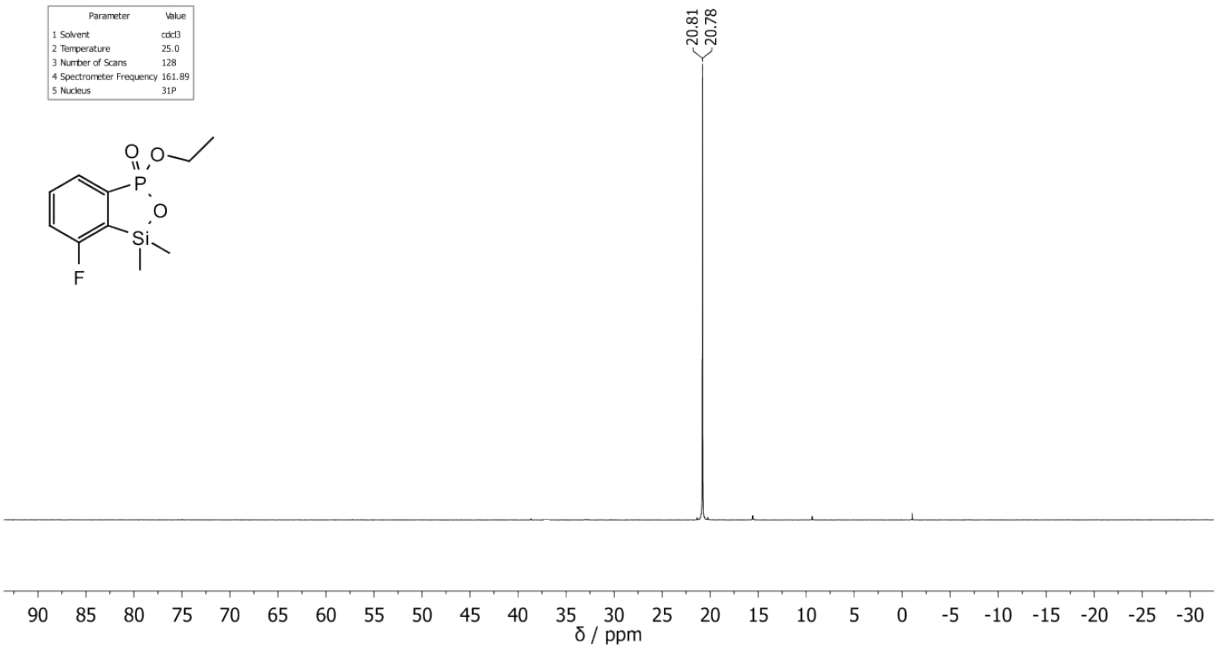


Figure S24. ^{31}P NMR spectrum of compound **16** (162 MHz, $CDCl_3$ solution).

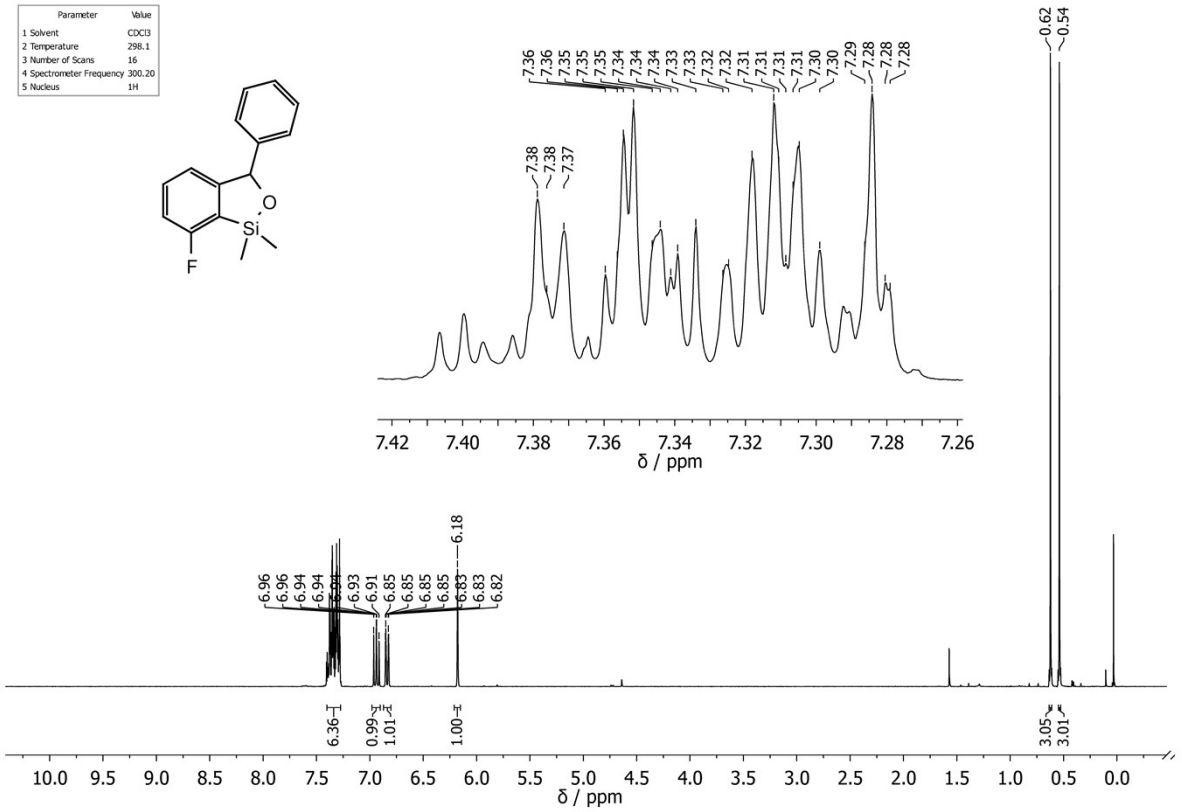


Figure S25. ^{1}H NMR spectrum of compound **17** (300 MHz, $CDCl_3$ solution).

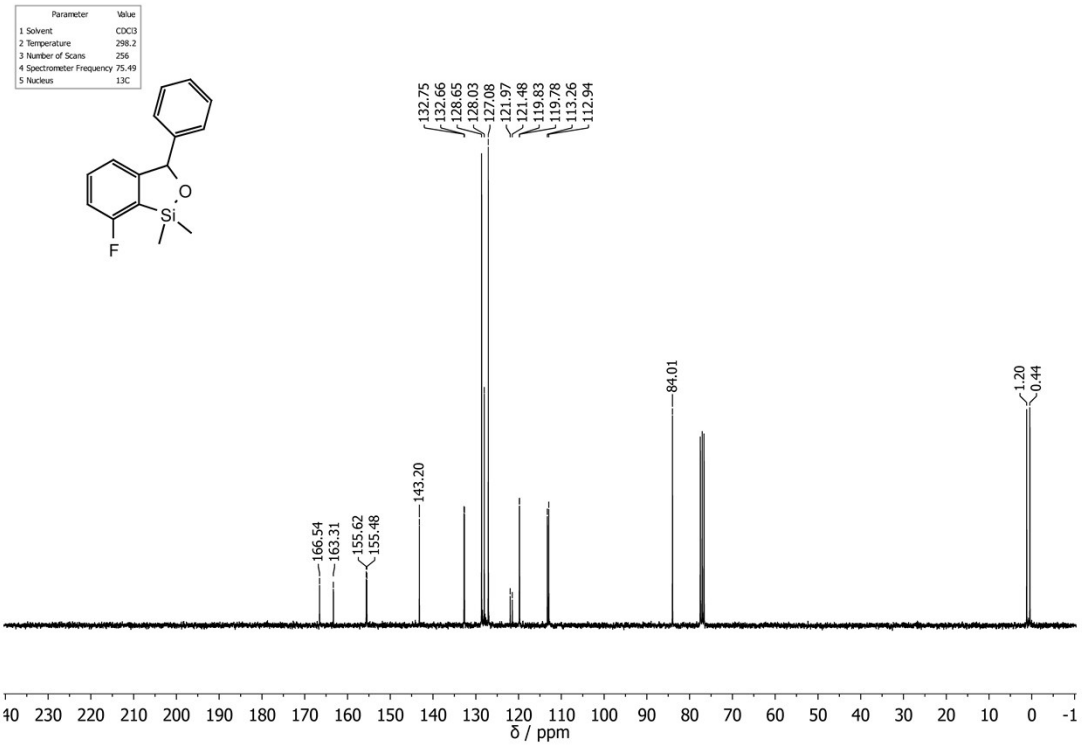


Figure S26. ^{13}C NMR spectrum of compound **17** (75 MHz, $CDCl_3$ solution).

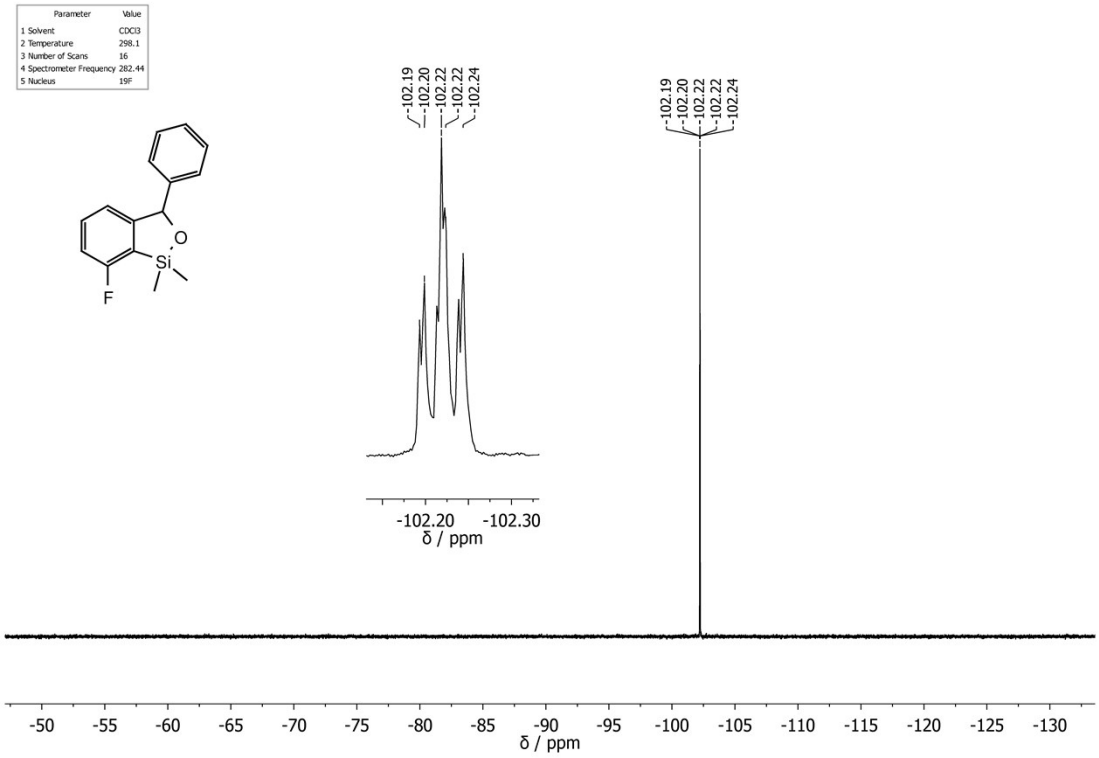


Figure S27. ^{19}F NMR spectrum of compound **17** (282 MHz, $CDCl_3$ solution).

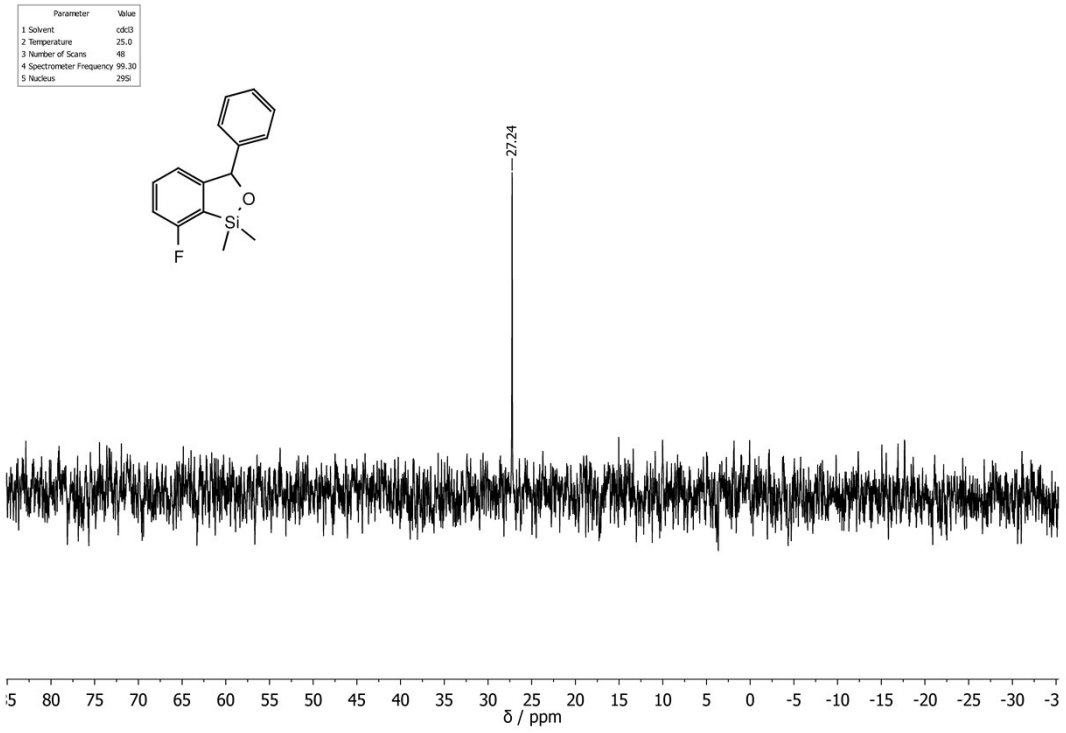


Figure S28. ^{29}Si NMR spectrum of compound **17** (99 MHz, $CDCl_3$ solution).

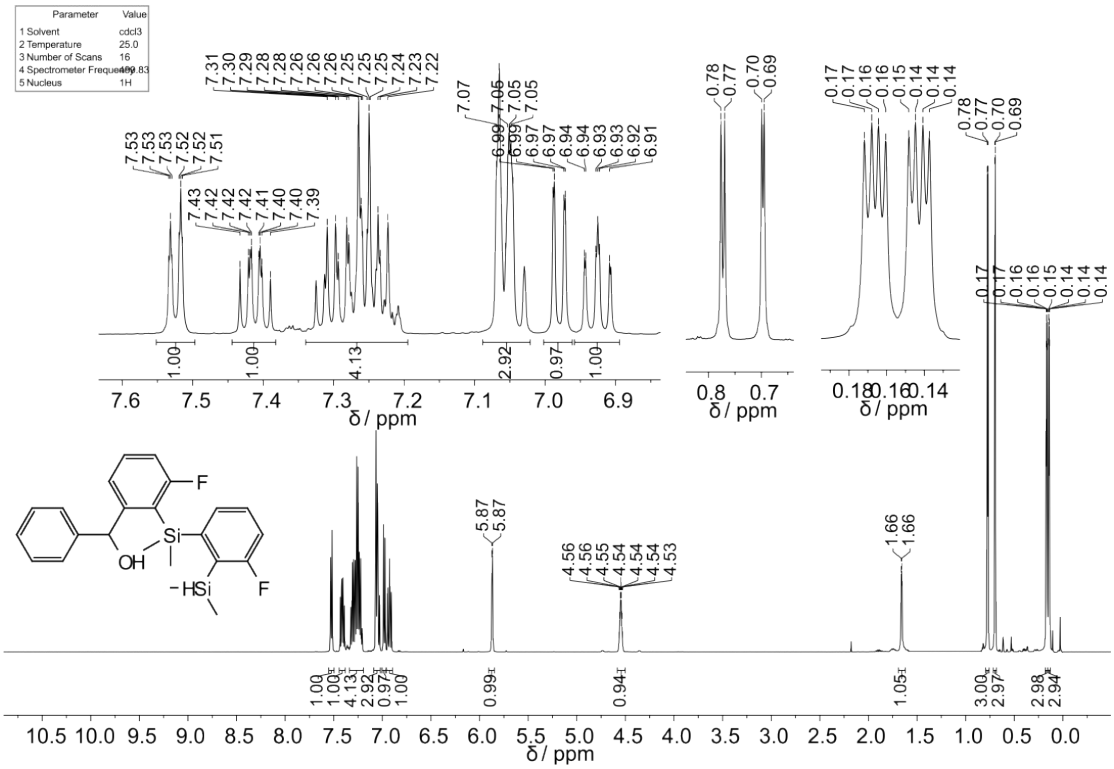


Figure S29. ^{1}H NMR spectrum of compound **18** (400 MHz, $CDCl_3$ solution).

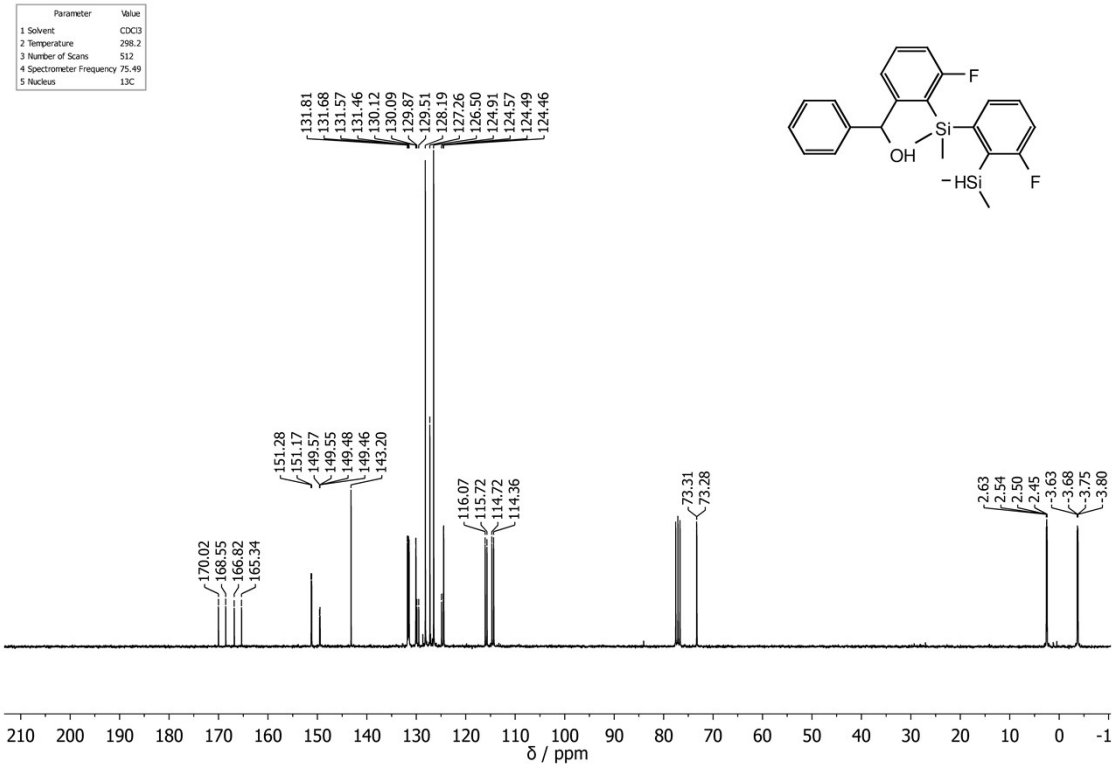


Figure S30. ^{13}C NMR spectrum of compound **18** (75 MHz, $CDCl_3$ solution).

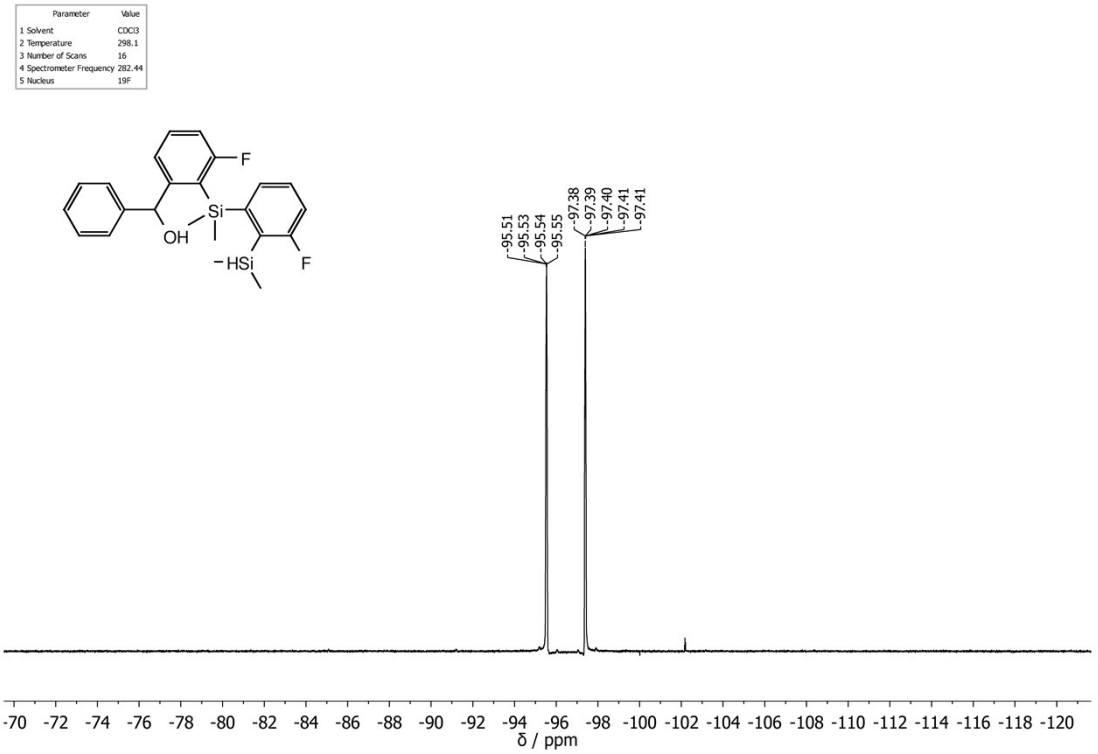


Figure S31. ^{19}F NMR spectrum of compound **18** (282 MHz, $CDCl_3$ solution).

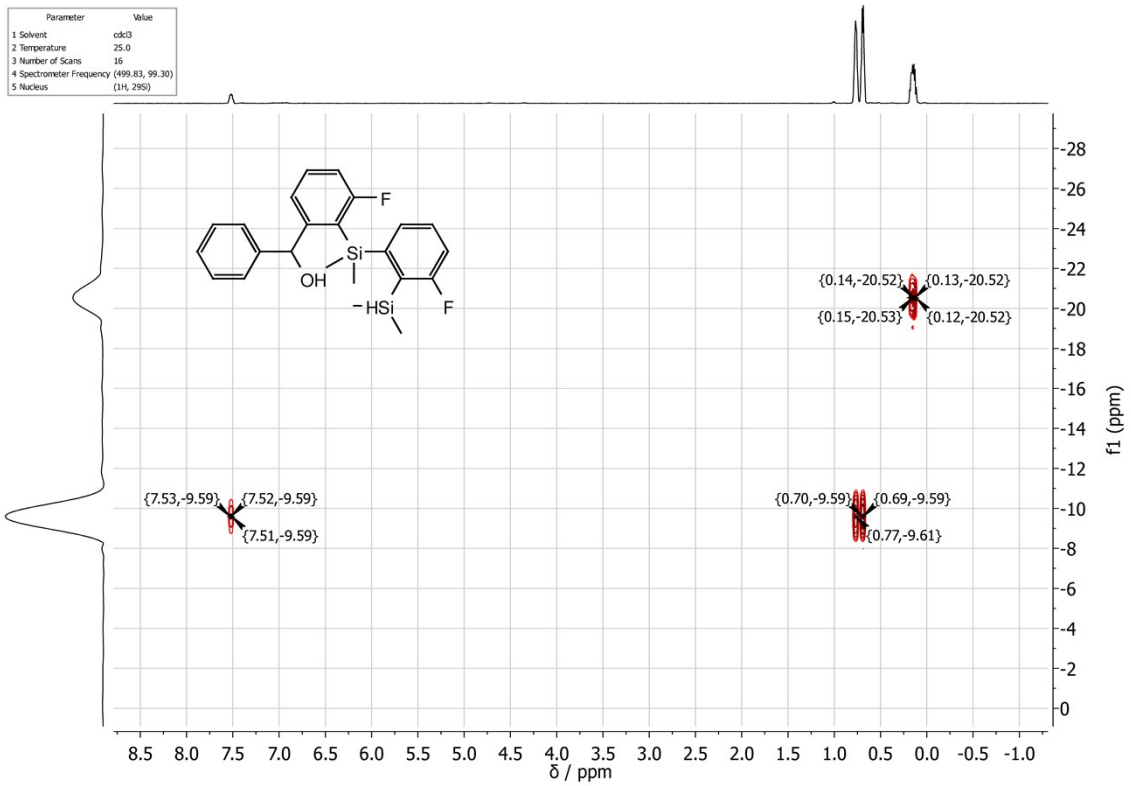


Figure S32. $^{1}H/^{29}Si$ HMBC NMR spectrum of compound **18** (500/99 MHz, $CDCl_3$ solution).

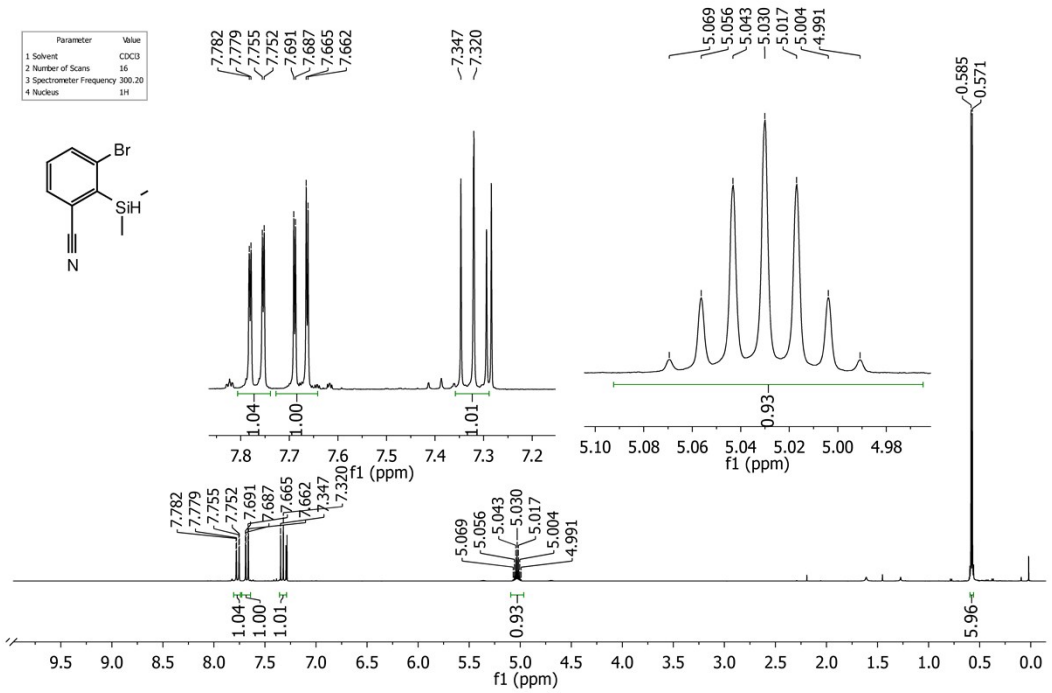


Figure S33. ^{1}H NMR spectrum of compound **19** (300 MHz, $CDCl_3$ solution).

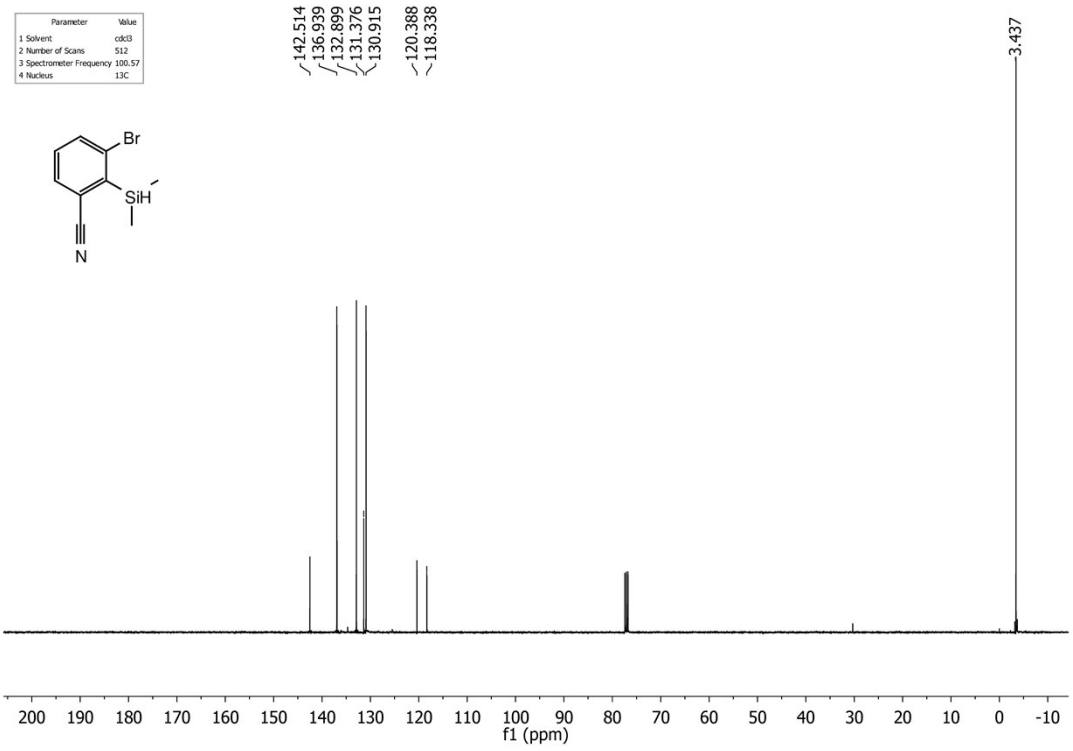


Figure S34. ^{13}C NMR spectrum of compound **19** (100.6 MHz, $CDCl_3$ solution).

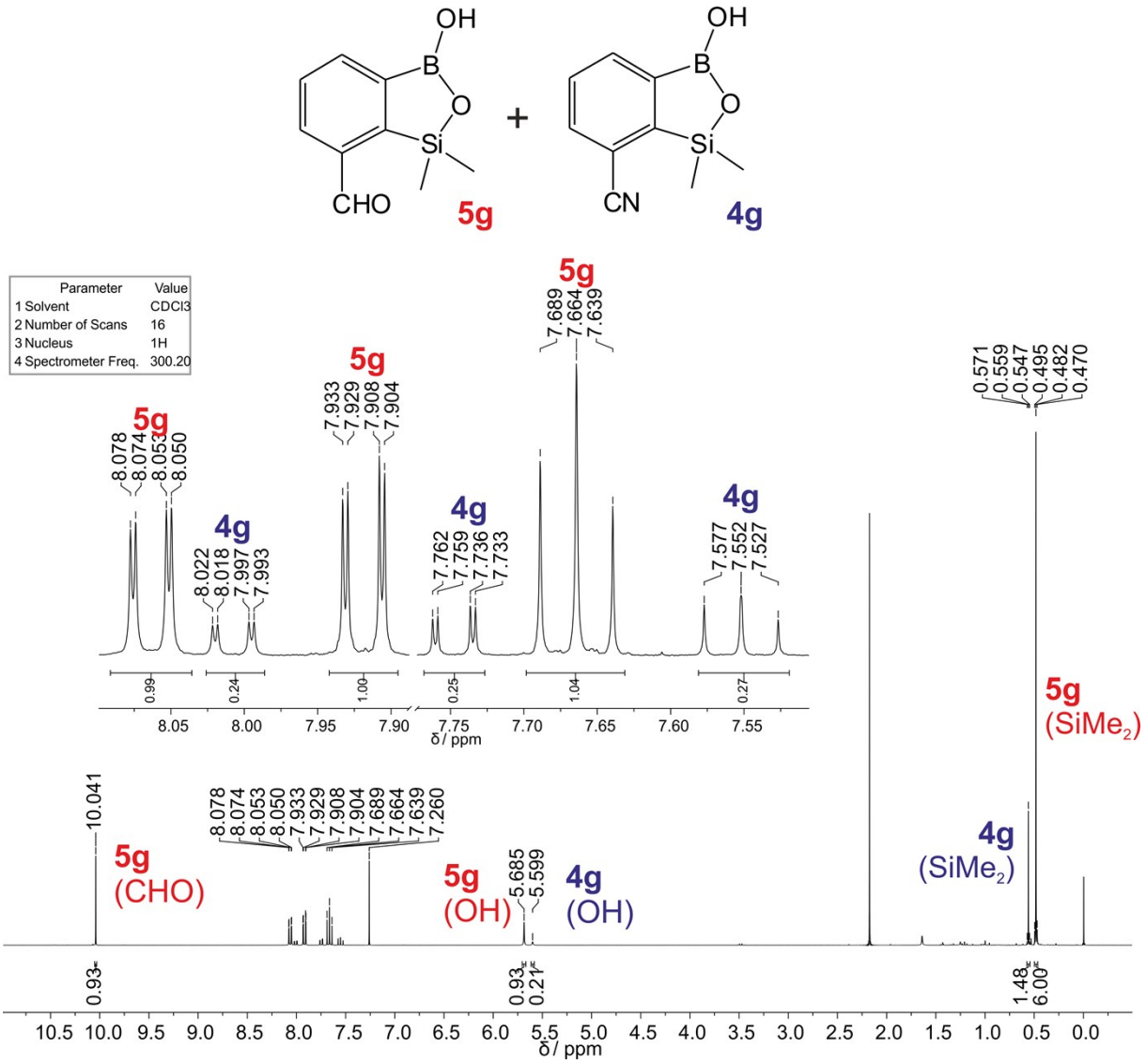


Figure S35. ^{1}H NMR spectrum of compound **4g**+**5g** (300 MHz, $CDCl_3$ solution).

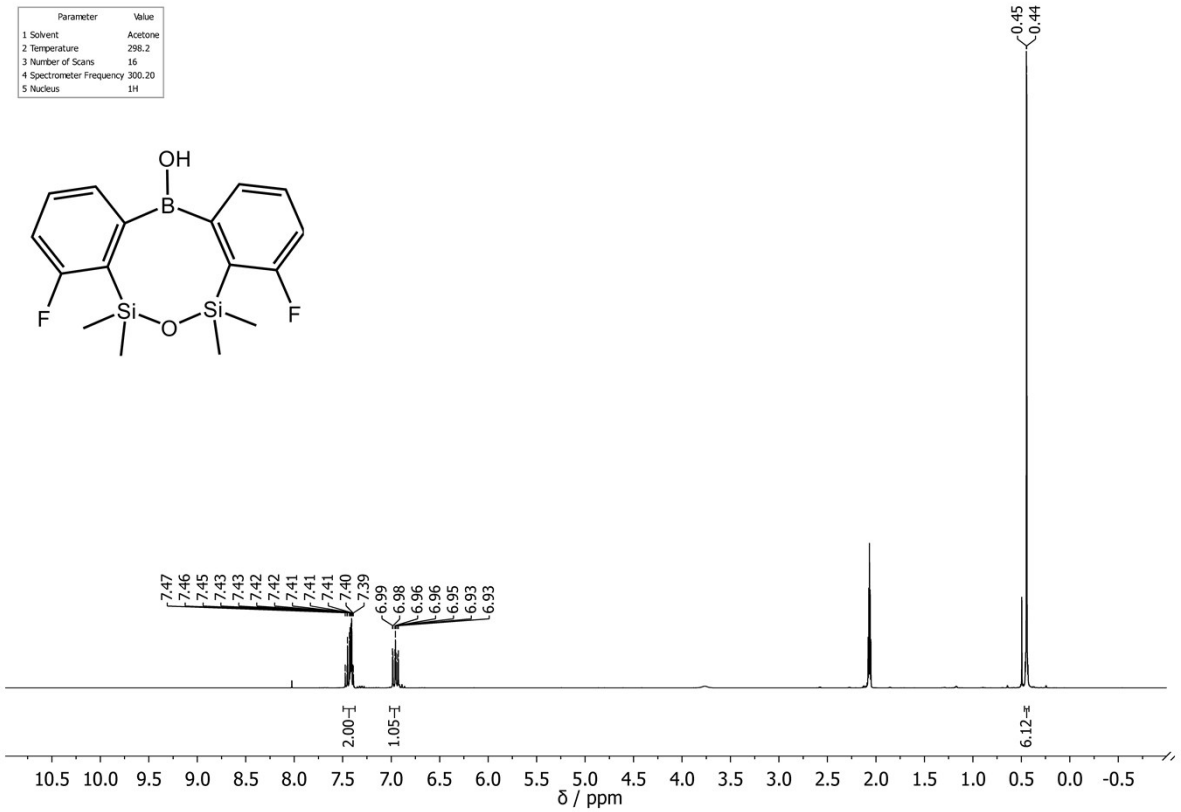


Figure S36. ^{1}H NMR spectrum of compound **9** measured 2 days after acetone solution preparation (300 MHz, Acetone-d_6 solution).

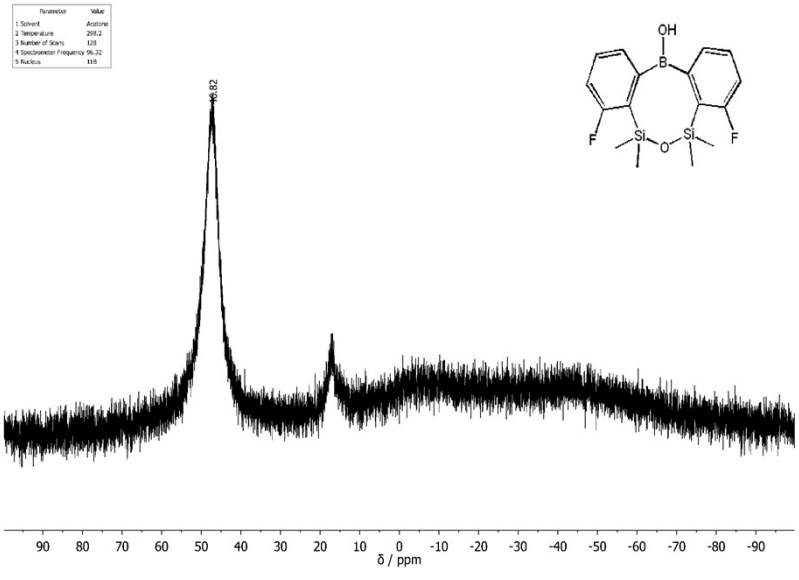


Figure S37. ^{11}B NMR spectrum of compound **9** measured 2 days after acetone solution preparation (96 MHz, Acetone-d_6 solution).

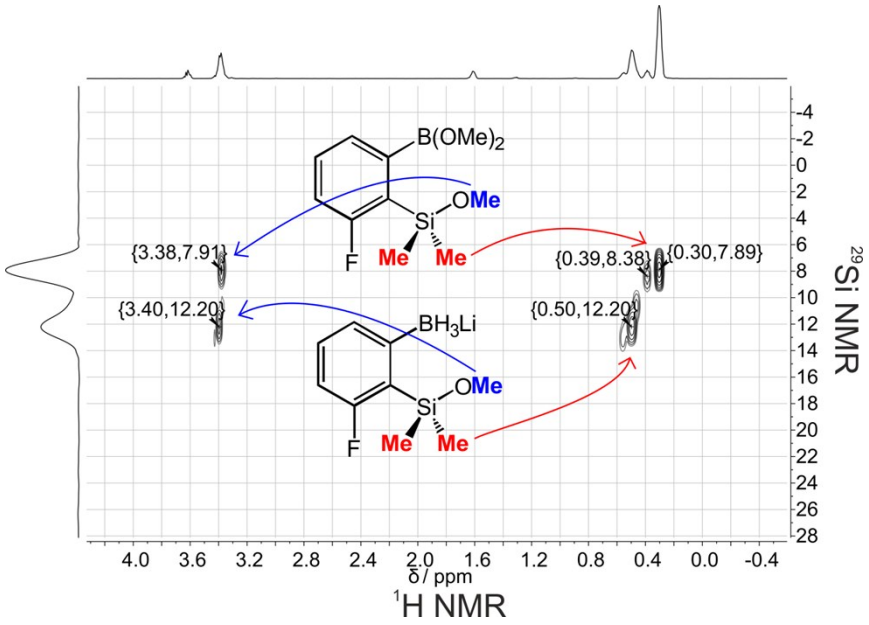


Figure S38. $^{1}H/^{29}Si$ HMBC spectra of a reaction mixture obtained upon treatment of **2** with $B(OMe)_3$.