What is Your Actual Catalyst? TMS Cleavage Rates of Diarylprolinol Silyl Ethers Studied by Situ NMR

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Electronic Supporting Information

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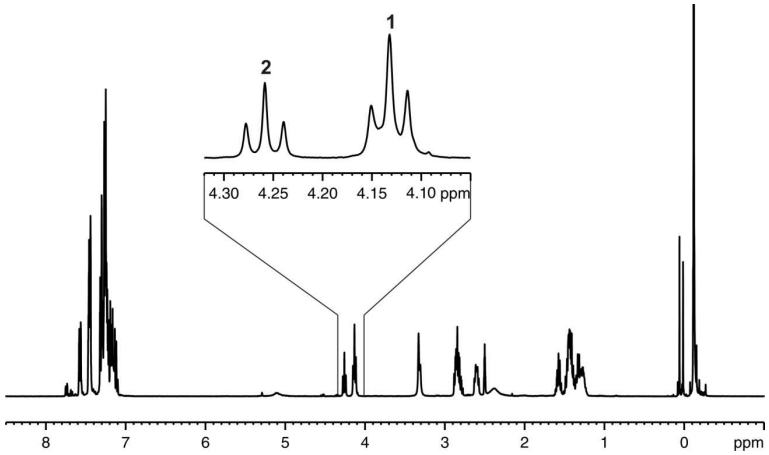
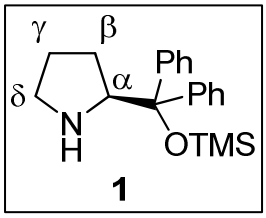
I.Chemical shift assignment of pyrrolidine protons of 1 and 2 in deuterated solvents in ppm

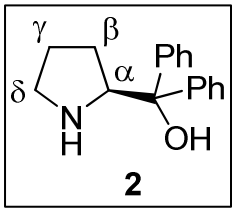


^{1}H Spectrum at 400 MHz of **1** and **2** in DMSO-d_6 at room temperature; enlarged: α proton resonances of **1** and **2.**



1

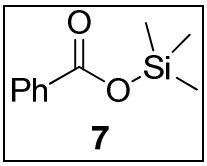
1	THF-d_8	MeOH-d_4	acetone-d_6	DMSO-d_6	DMF-d_7	cyclohexane-d_{12}	$CDCl_3$	MeCN-d_3
α	4.12	4.13	4.19	4.14	4.23	3.97	3.94	4.13
β	1.54	1.75	1.54	1.46	1.53	1.52	1.47	1.51
	1.54	1.75	1.54	1.35	1.53	1.52	1.47	1.51
γ	1.35	1.59	1.38	1.28	1.37	1.35	1.47	1.37
	1.35	1.33	1.38	1.45	1.37	1.35	1.28	1.37
δ	2.81	2.73	2.93	2.61	2.96	2.87	2.74	2.88
	2.92	2.57	2.80	2.86	2.75	2.87	2.69	2.77



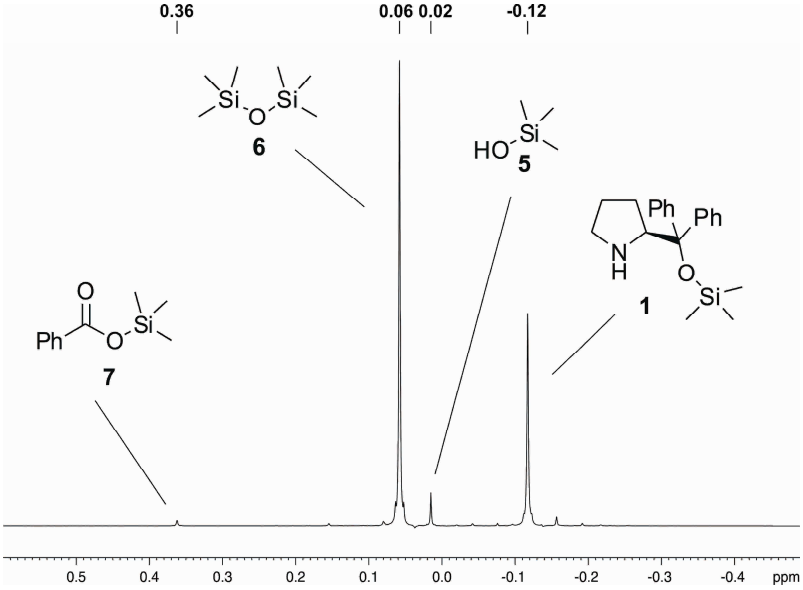
2

2	THF-d_8	MeOH-d_4	acetone-d_6	DMSO-d_6	DMF-d_7	cyclohexane-d_{12}	$CDCl_3$	MeCN-d_3
α	4.29	4.32	4.42	4.26	4.43	4.17	4.25	4.37
β	1.66	1.64	1.38	1.45	1.53	1.65	1.64	1.50
	1.66	1.64	1.38	1.39	1.53	1.65	1.58	1.50
γ	1.57	1.75	1.68	1.58	1.67	1.70	1.73	1.68
	1.44	1.75	1.68	1.58	1.67	1.65	1.73	1.68
δ	2.95	3.00	3.62	2.86	2.96	3.01	3.03	2.92
	2.95	2.87	3.52	2.82	2.75	2.89	2.95	2.92

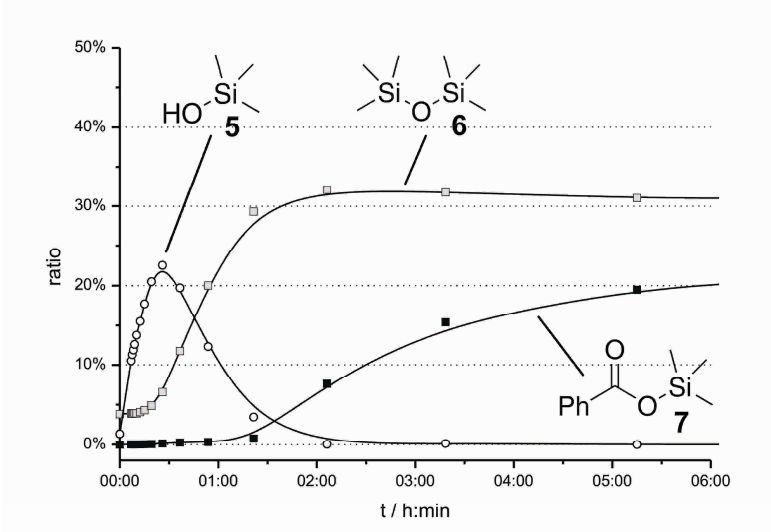
II. Silyl degradation products – $^{1}H/^{29}Si$ chemical shifts, reaction profile



7	*in situ* (DMSO-d_6)	synthesized compound following a literature procedure[1] (DMSO-d_6)	literature assignment (CCl_4)	literature assignment (C_6D_6)
^{1}H: CH_3	0.36-0.37	0.36	0.21[2],0.31[3],0.43[4]	0.57[5]
^{29}Si	24.4	24.4	23.6[4]	-

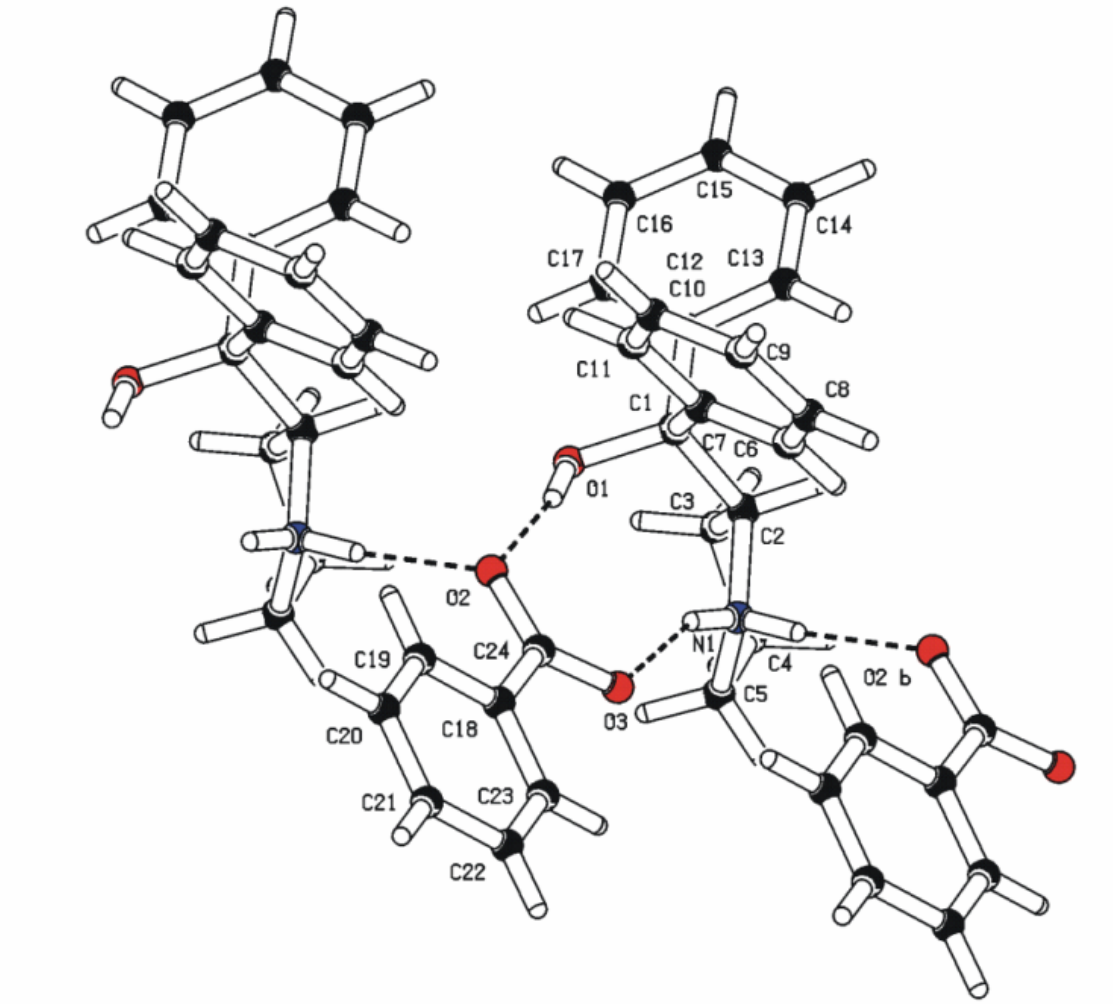


^{1}H spectrum of a mixture of **1** and benzoic acid (100 mol%) in DMSO-d_6 at 600 MHz, room temperature – silyl area



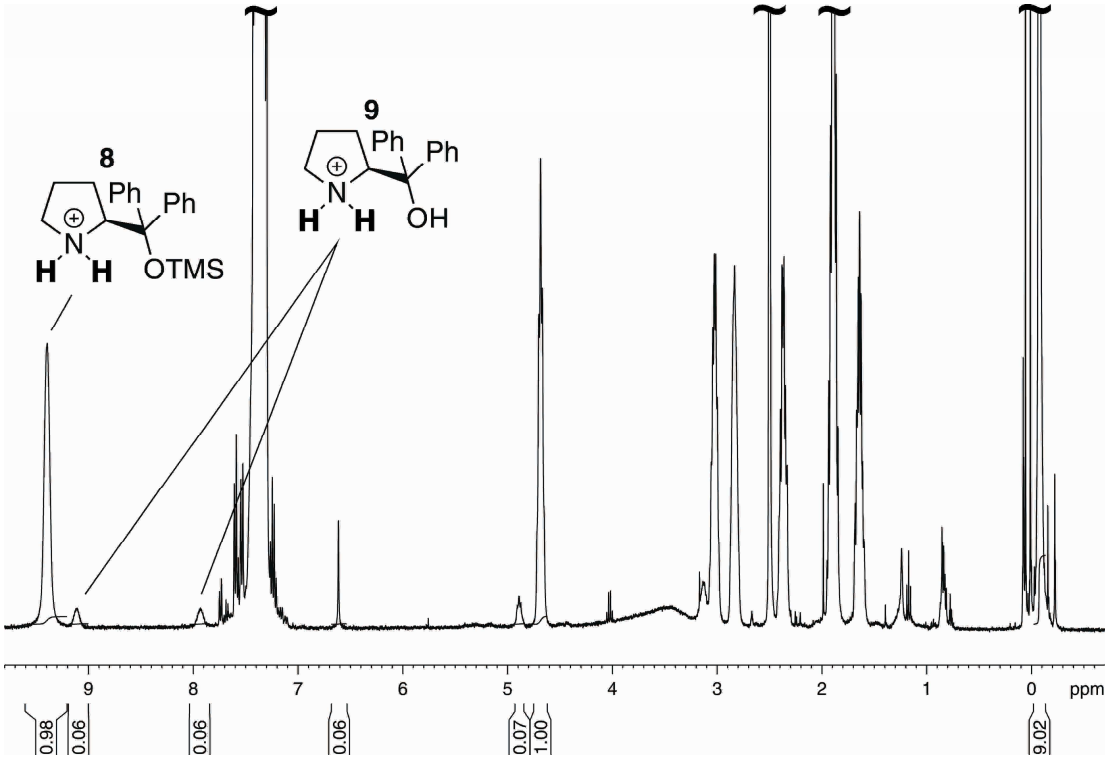
Reaction profile of the detected silyl degradation products during the TMS cleavage of **1** with 100 mol% benzoic acid in DMSO-d_6 at room temperature.

III. Crystal structure of the benzoate salt of 2, crystallized in DMSO-d_6

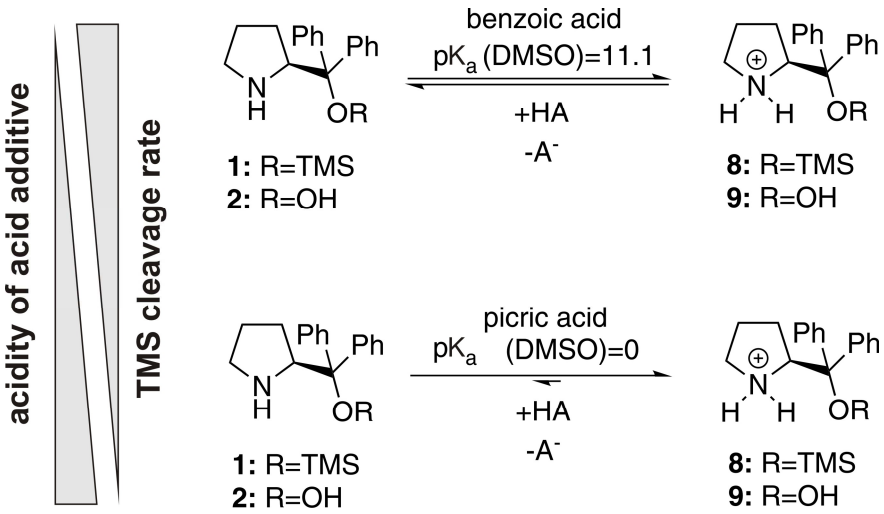


CCDC 869742 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data request/cif.

IV. Influence of strong acids – formation of secondary ammonium ions, equilibria



^{1}H Spectrum of **1** and **2** with 100 mol% TFA at 600 MHz – NH signals of the formed secondary ammonium ions **8** and **9** are highlighted.



Amine, ammonium ion equilibrium positions using weak or strong acids as additives in DMSO. The stronger the acid the greater the amount of catalyst should be in the (protonated) ammonium ion state. Simultaneously the cleavage rate decreases.

Literature

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