Electronic Supplementary Information

Transannular 1,5-Hydride Shift in 5-Hydroxycyclooctanone: An Experimental and Theoretical Investigation

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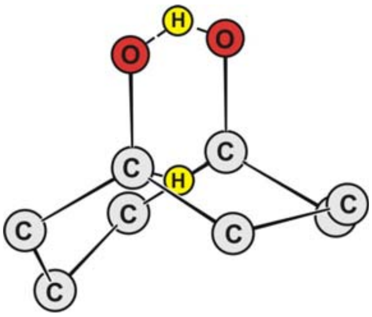

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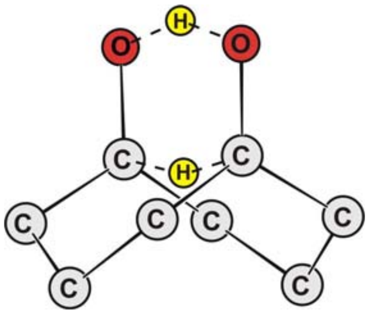

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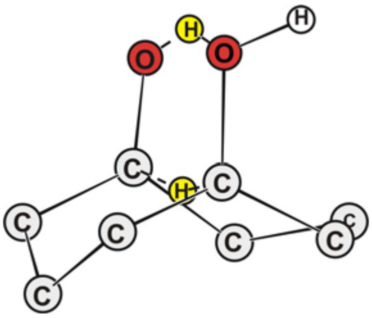

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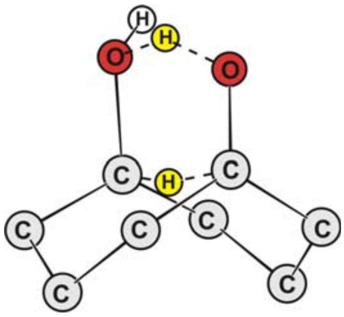

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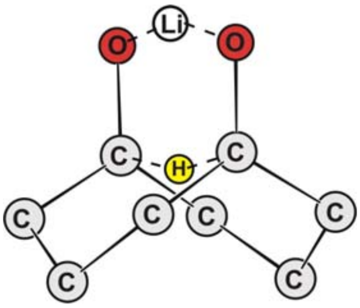

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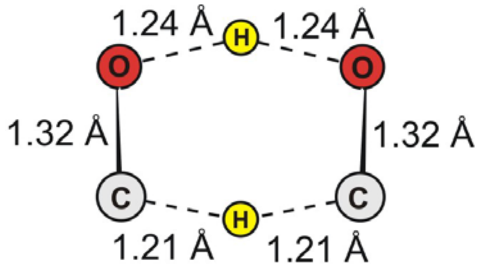
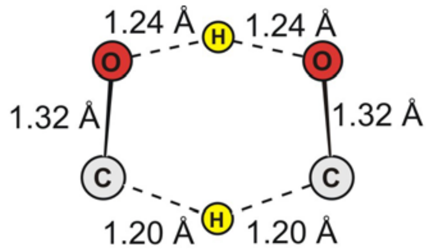
Figure 1 Transition states for 1,5-hydride shift reaction



∠C···H···C = 158°

4bc



∠C···H···C = 161°

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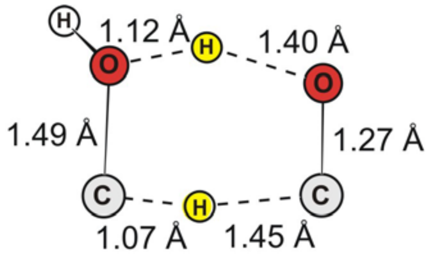

∠C···H···C = 164°

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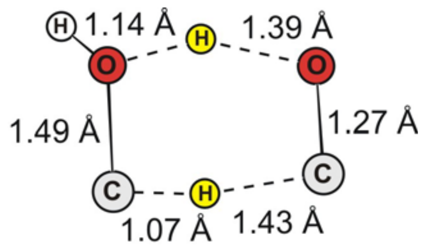

∠C···H···C = 169°

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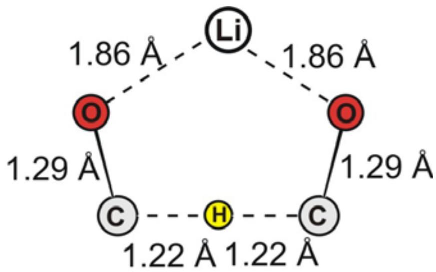
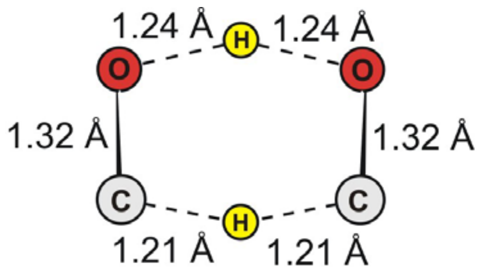


∠C···H···C = 177°

6bb

Figure 2 Six-membered cyclic transition states in hydride shift reaction



∠C···H···C = 158°

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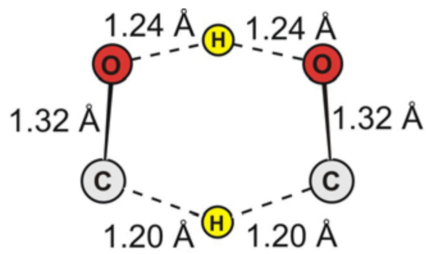

∠C···H···C = 161°

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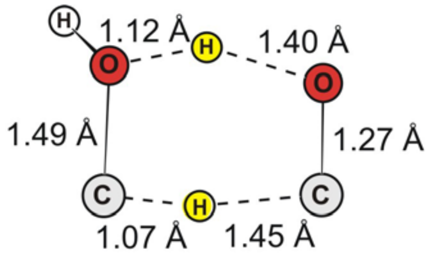

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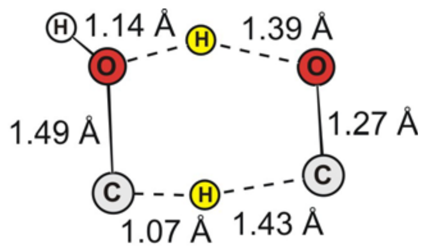

∠C···H···C = 169°

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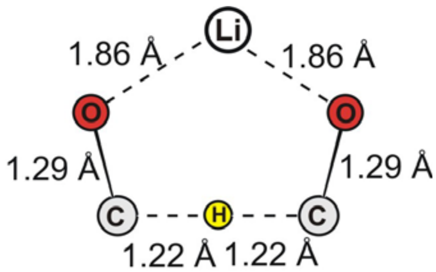

∠C···H···C = 177°

6bb

Figure 3 Natural charges on atoms in the six-membered cyclic transition states in hydride shift reaction

Table ESI-1 H/D-exchange in **1HA** at ambient temperature studied by ^{1}H NMR spectroscopy

Acid or Base M	Time h	Deuteration %	**1HA**[a] M	k[b] sec^{-1}
3.4 DCl	0	0.0	0.64	8.95×10^{-7}
	71	8.3	0.56	
	162	33.3	0.32	
	330	45.8	0.20	
	571	56.3	0.10	
7.9 DCl	0	0.0	0.79	5.12×10^{-6}
	1	6.4	0.71	
	18	32.5	0.41	
	40	49.4	0.21	
	63	55.8	0.13	
	141	61.8	0.06	
7.9 DCl[c]	0	0.0	0.77	3.73×10^{-3}
	0.17	59.9	0.08	
12 DCl	0	9.2	0.57	1.33×10^{-4}
	1	50.2	0.16	
	4	59.8	0.07	
0.65 NaOD	0	12.9	0.54	6.45×10^{-5}
	1	34.2	0.33	
	4	47.0	0.20	
	22	53.6	0.13	
1.30 NaOD	0	14.1	0.51	1.02×10^{-4}
	1	41.3	0.25	
	4	55.8	0.11	
	23	56.6	0.10	

[a] Concentration of undeuterated **1HA**, determined from Degree of Deuteration assuming that at 66.66 % **1HA** = 0.00 M. b Rate constant. c 100 °C.

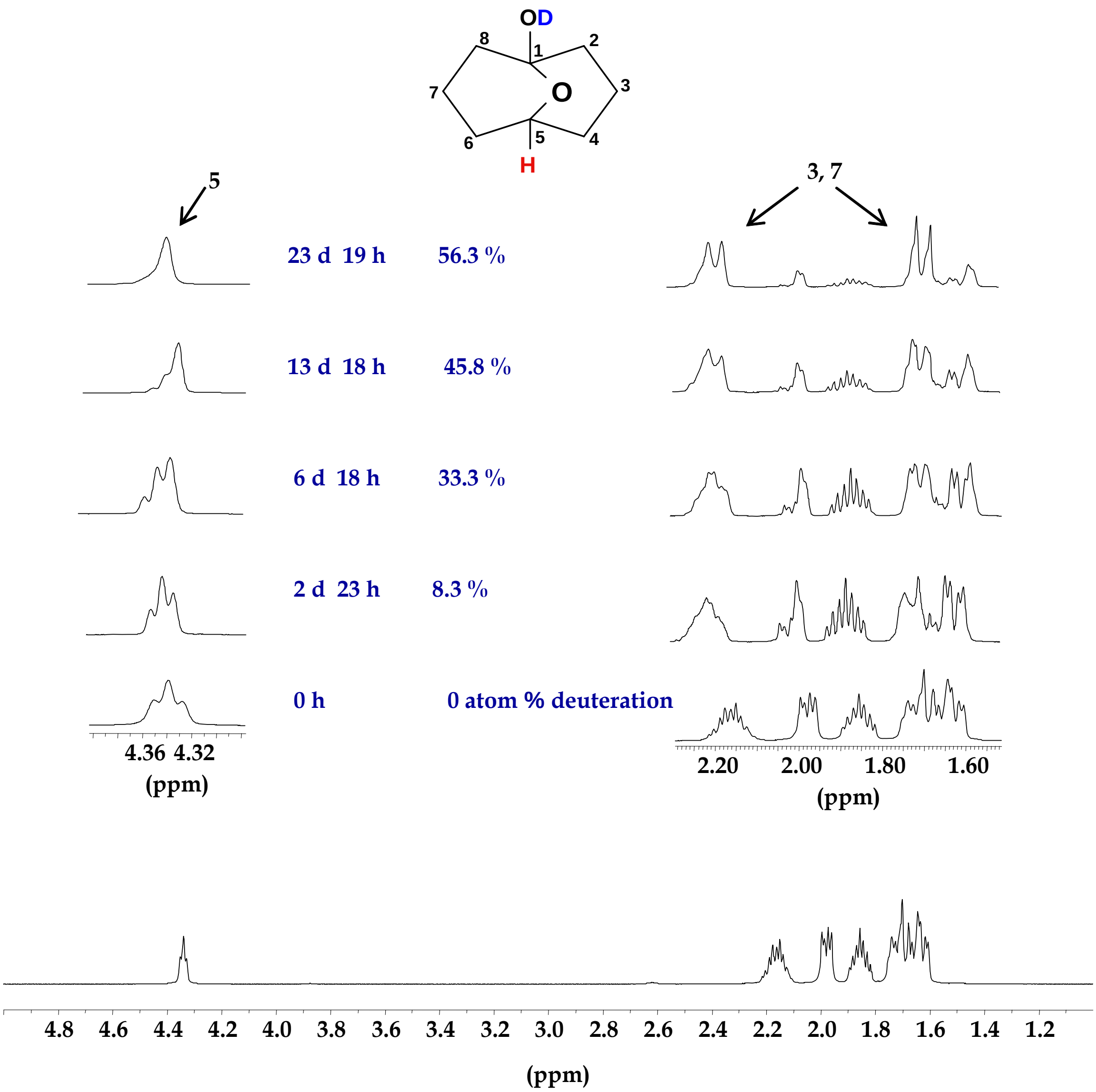

Figure ESI-1 ^{1}H-NMR spectra for **1HA** undergoing H/D exchange in 3.4 M DCl in D_2O at ambient temperature

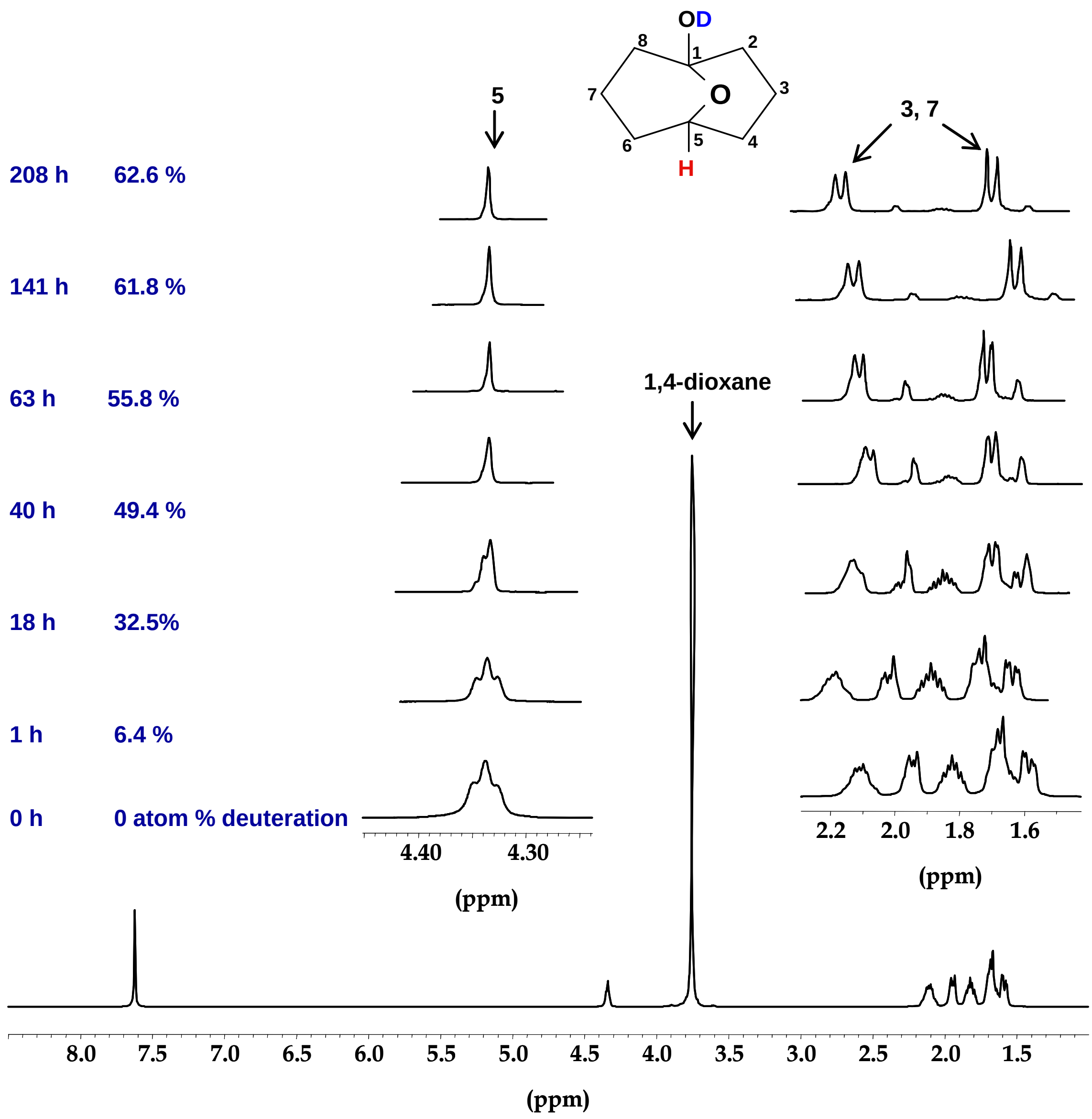

Figure ESI-2 ^{1}H-NMR spectra for **1HA** undergoing H/D exchange in 7.9 M DCl in D_2O at ambient temperature with dioxane as standard

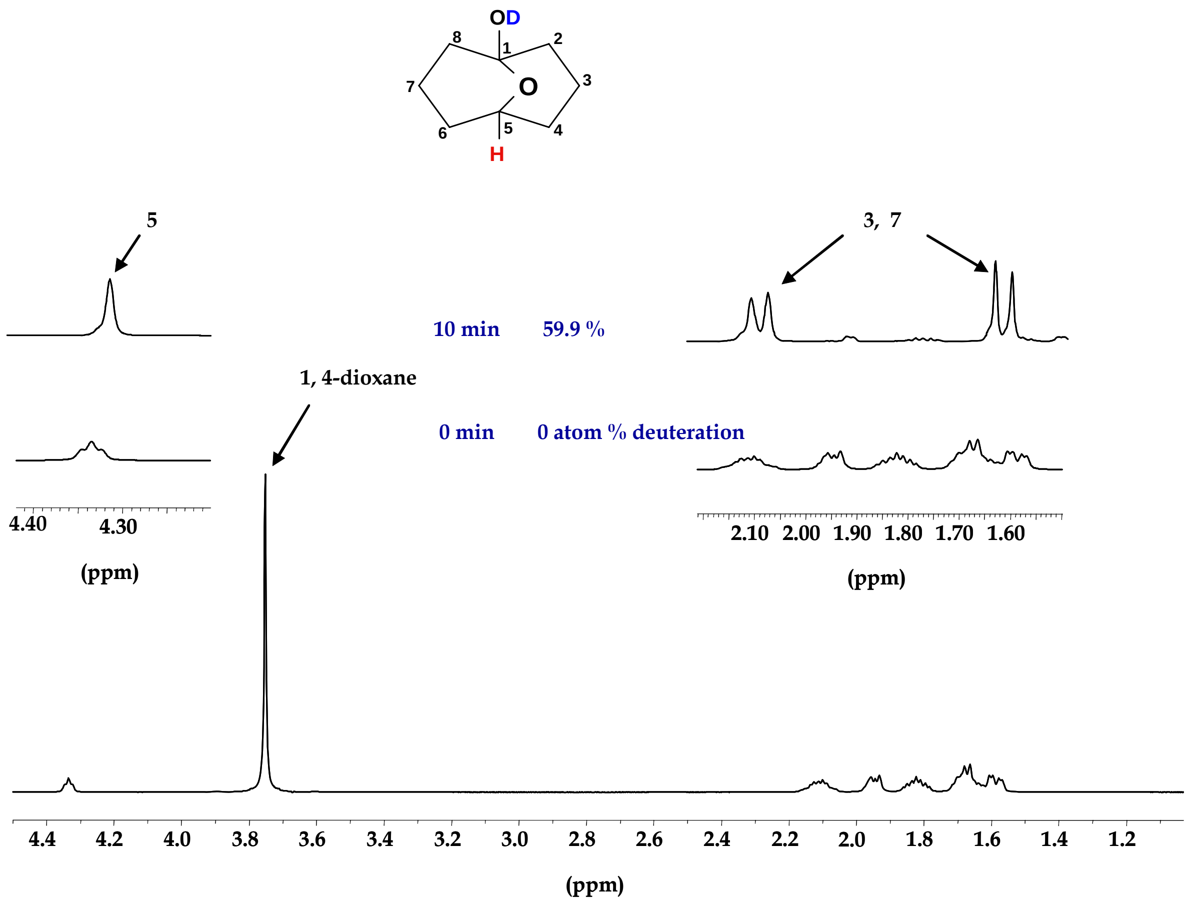

Figure ESI-3 ^{1}H-NMR spectra for **1HA** undergoing H/D exchange in 7.9 M DCl in D_2O at 100 °C with dioxane as standard

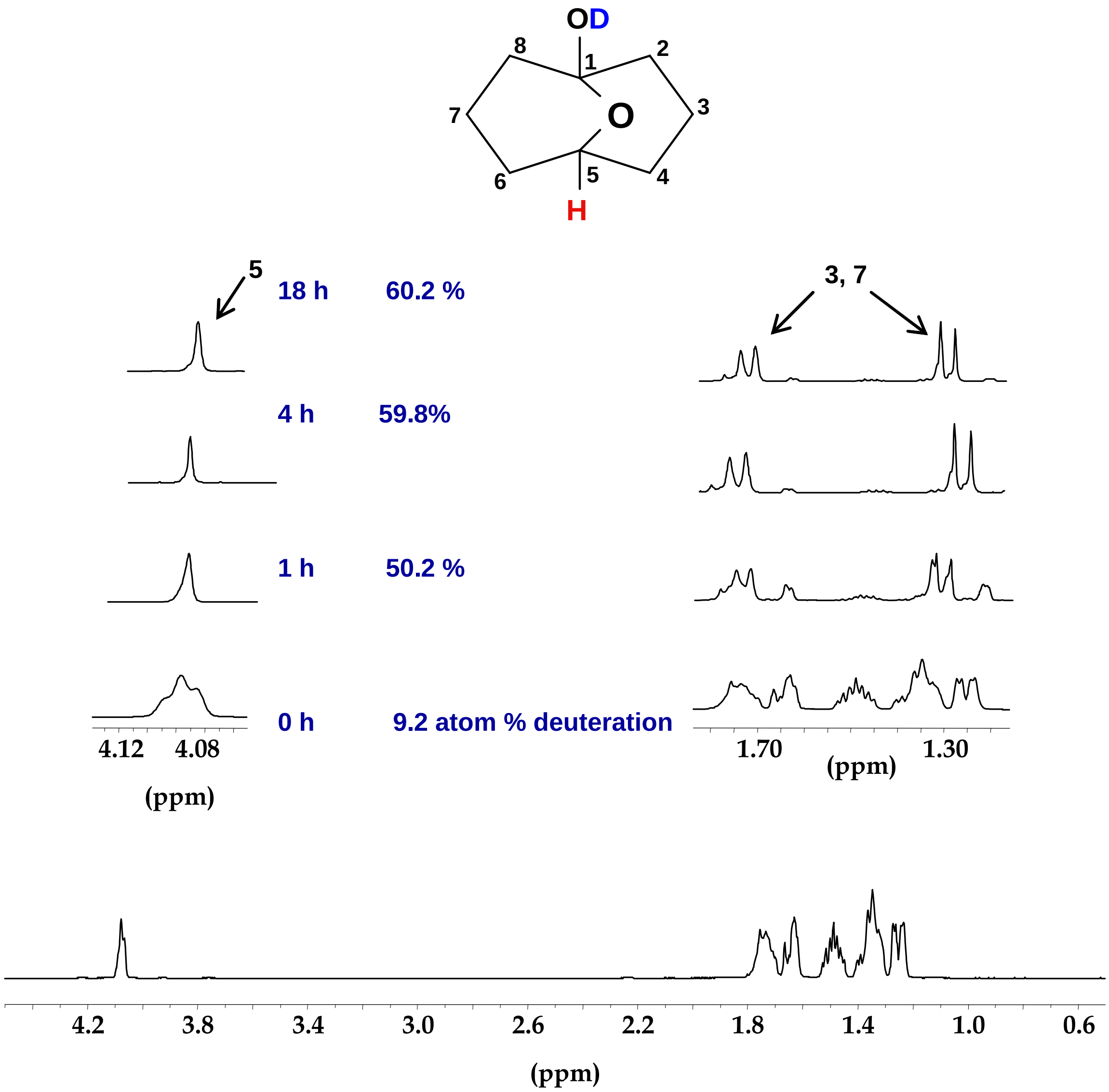

Figure ESI-4 ^{1}H-NMR spectra for **1HA** undergoing H/D exchange in 12.0 M DCl in D_2O at ambient temperature

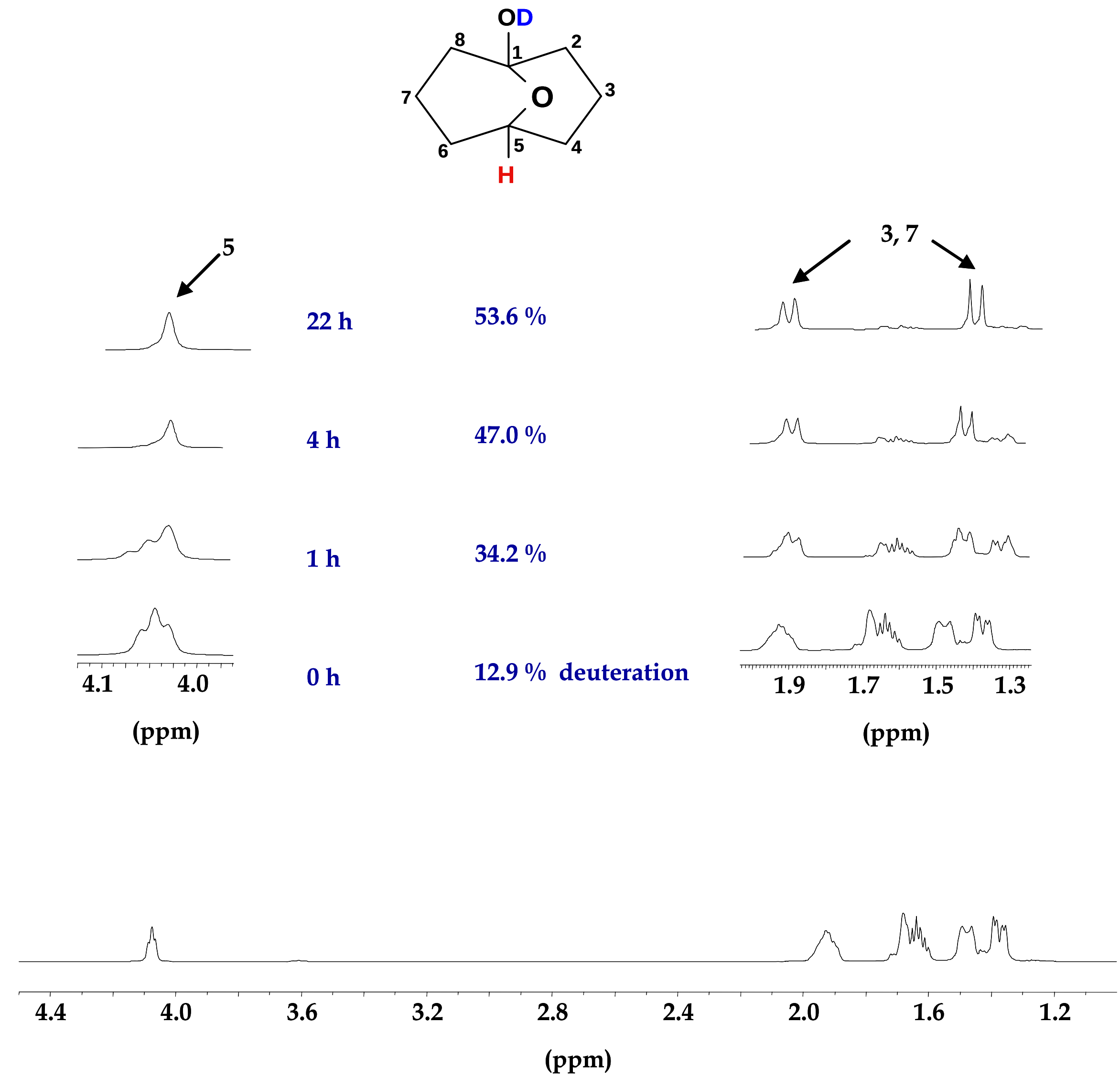

Figure ESI-5 ^{1}H-NMR spectra for **1HA** undergoing H/D exchange in 0.65 M NaOD in D_2O at ambient temperature

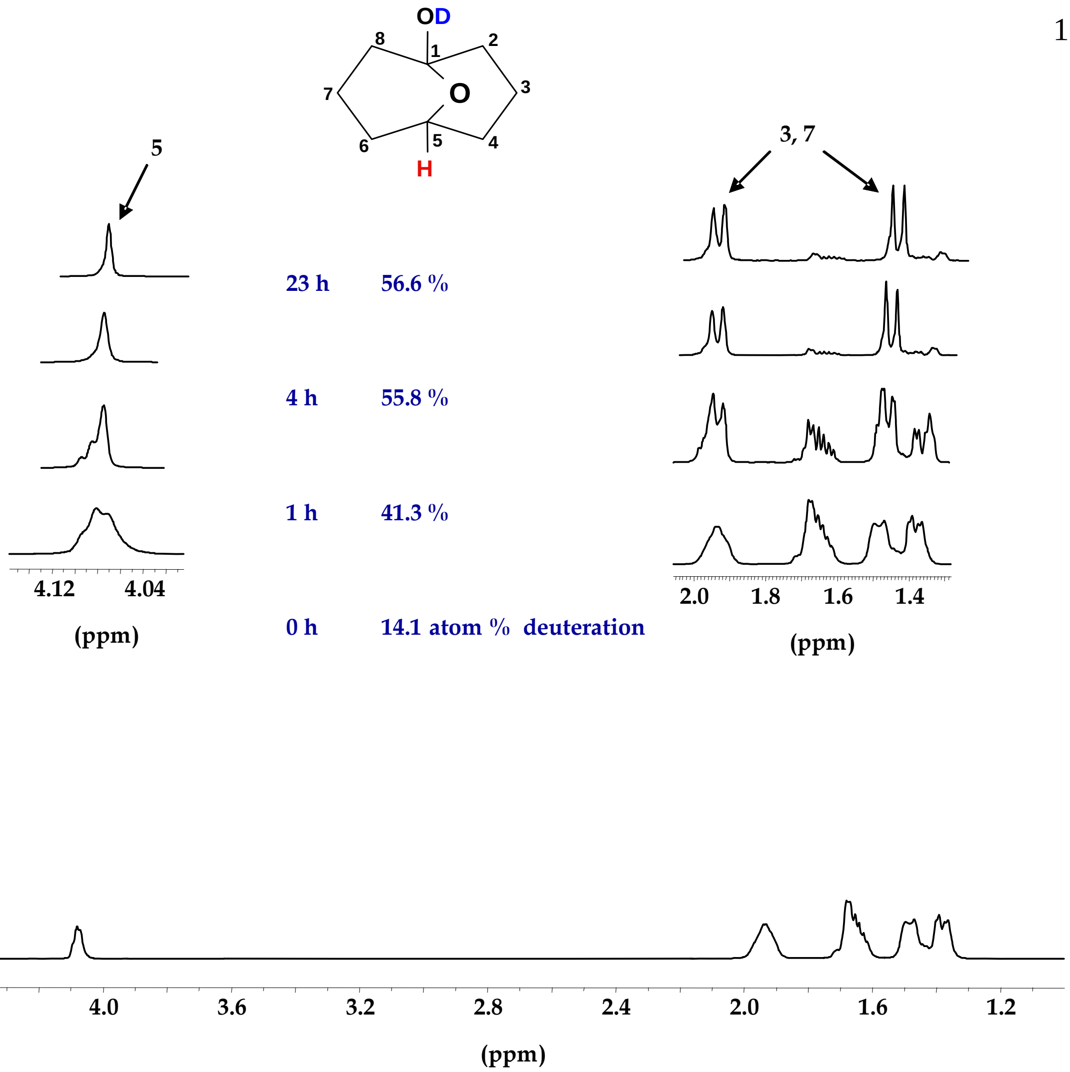

Figure ESI-6 ^{1}H-NMR spectra for **1HA** undergoing H/D exchange in 1.30 M NaOD in D_2O at ambient temperature

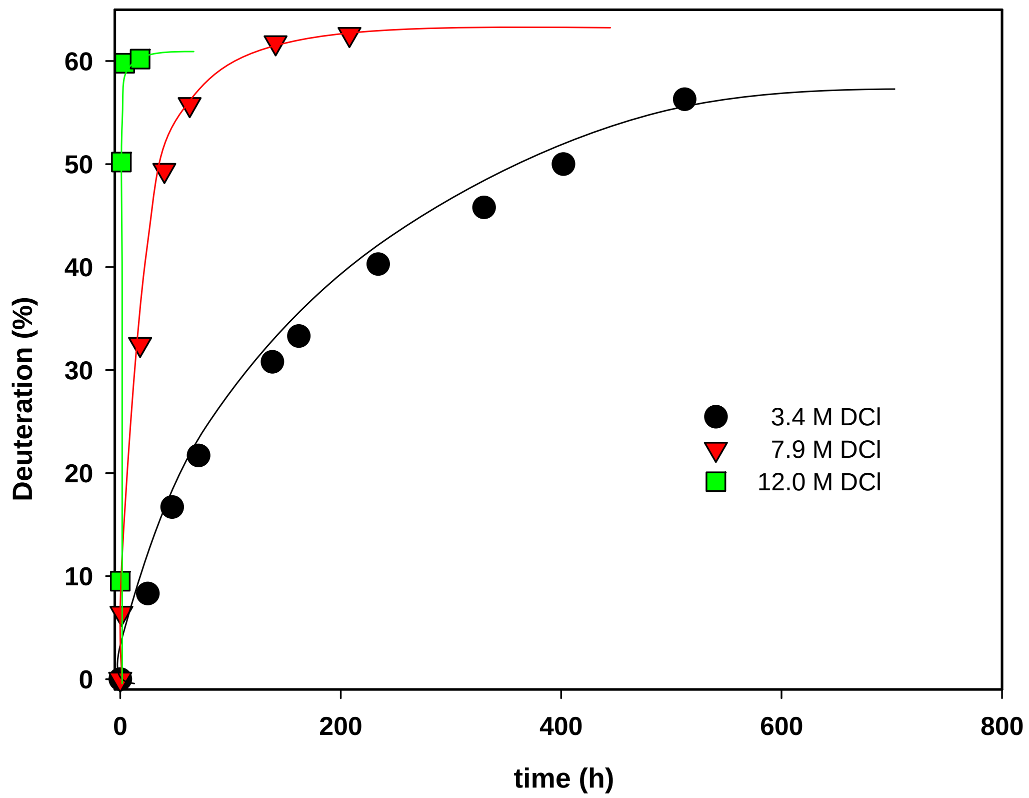

Figure ESI-7 Deuteration of **1HA** as function of time at different concentrations of DCl in D_2O at ambient temperature

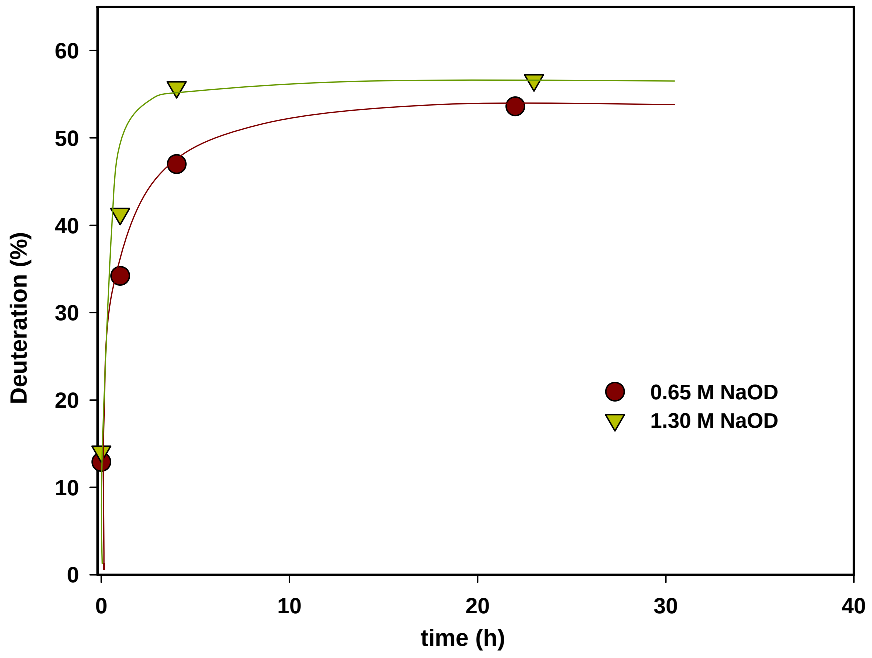

Figure ESI-8 Deuteration of **1HA** as function of time at different concentrations of NaOD in D_2O at ambient temperature