

## Supplementary Information Section:

# The Role of Low Levels of Water and Hydrogen-Bonding on the Electrochemical Oxidation of $\alpha$ -Tocopherol (Vitamin E) and Other Phenols in Acetonitrile.

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Zhen Hui Lim, Malcolm E. Tessensohn, Yinlu Zhang and Richard D. Webster\*

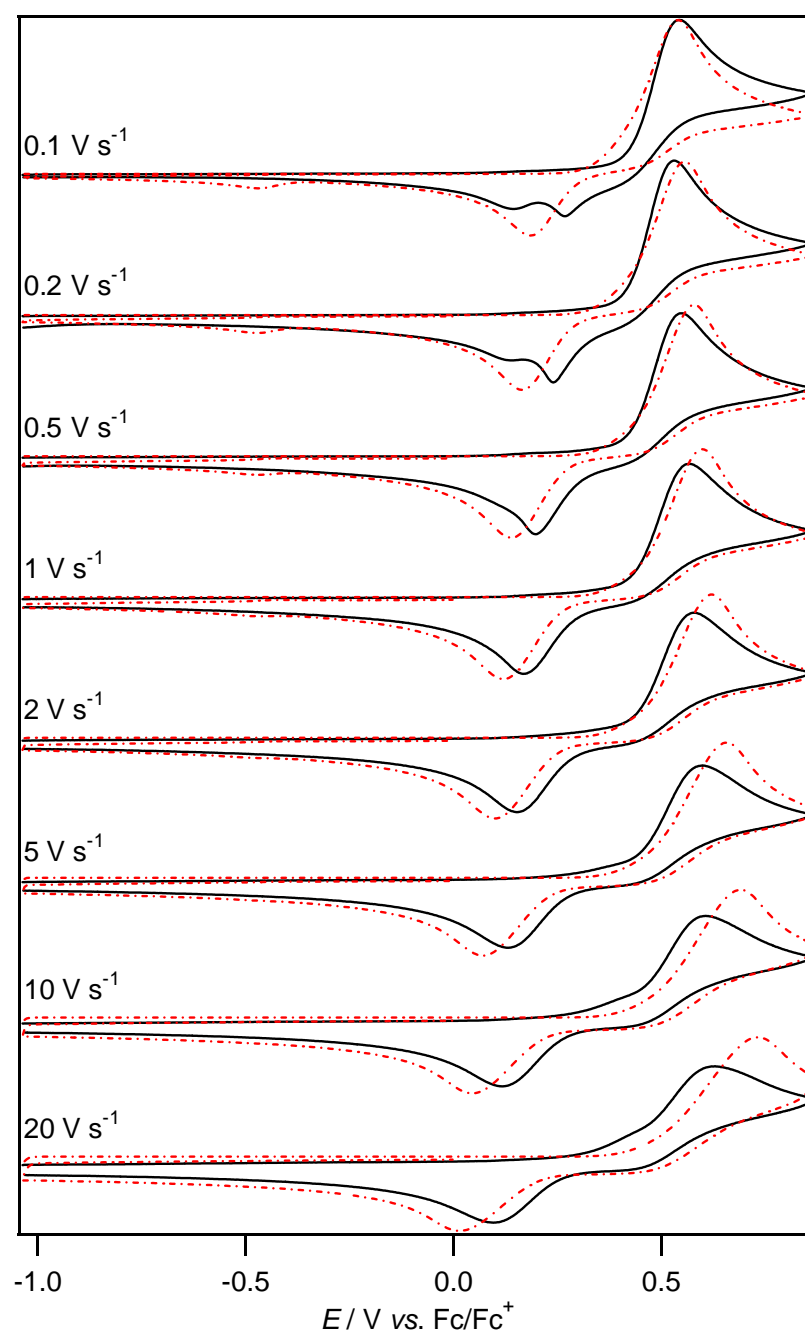
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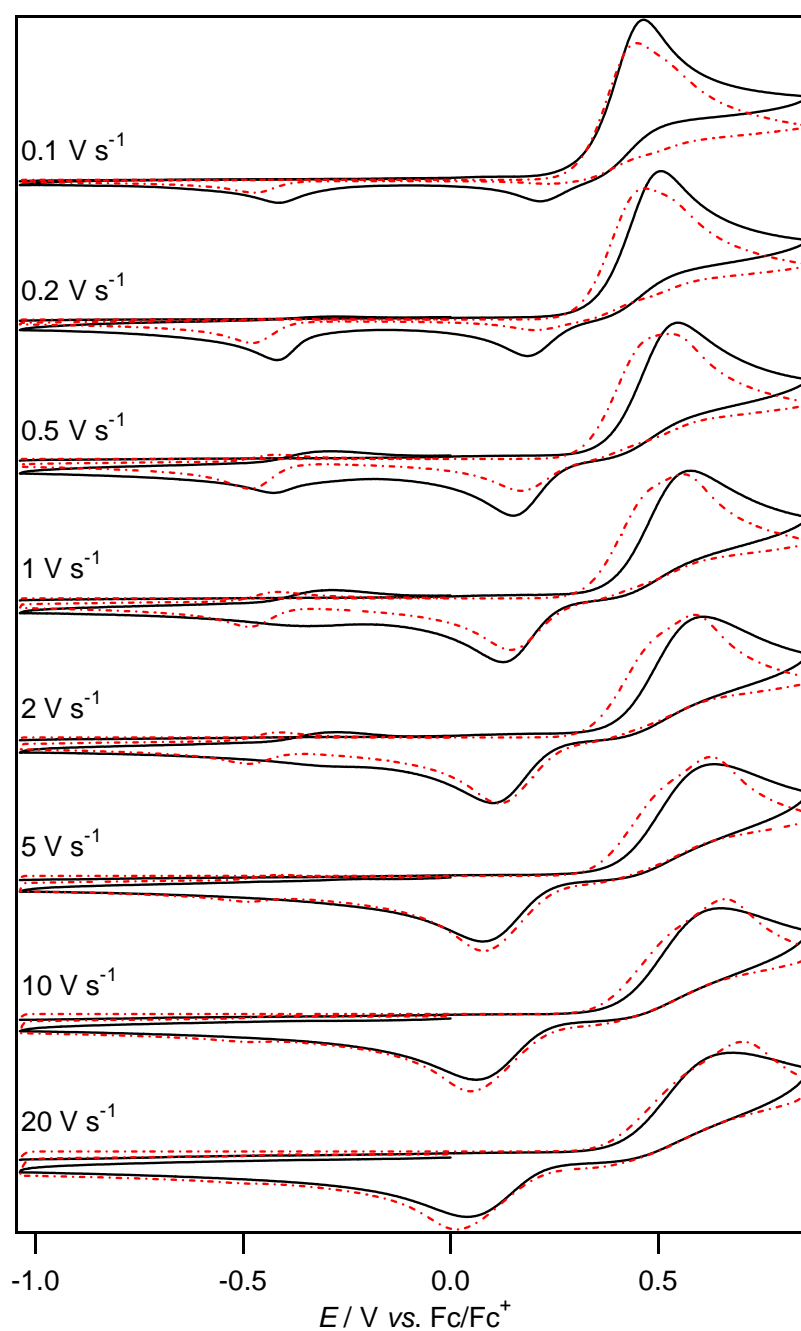
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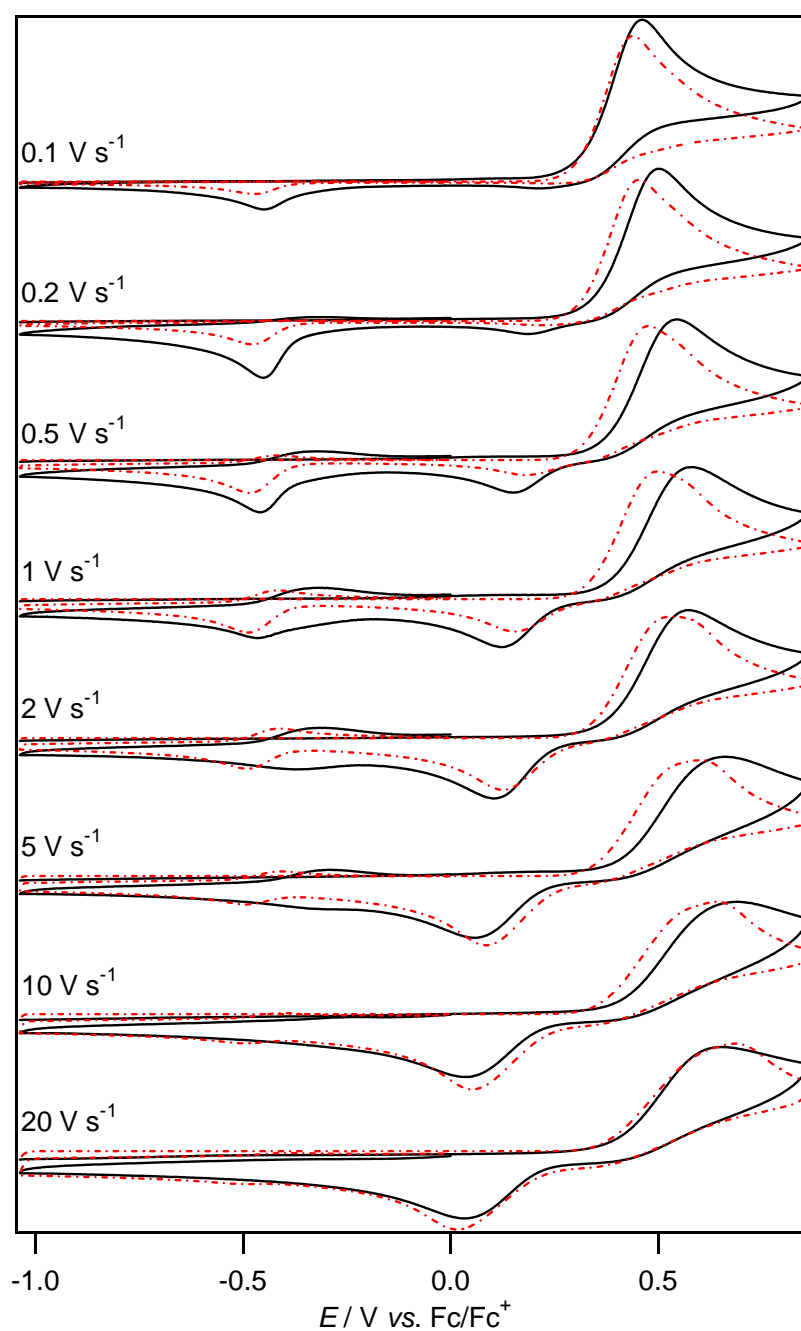
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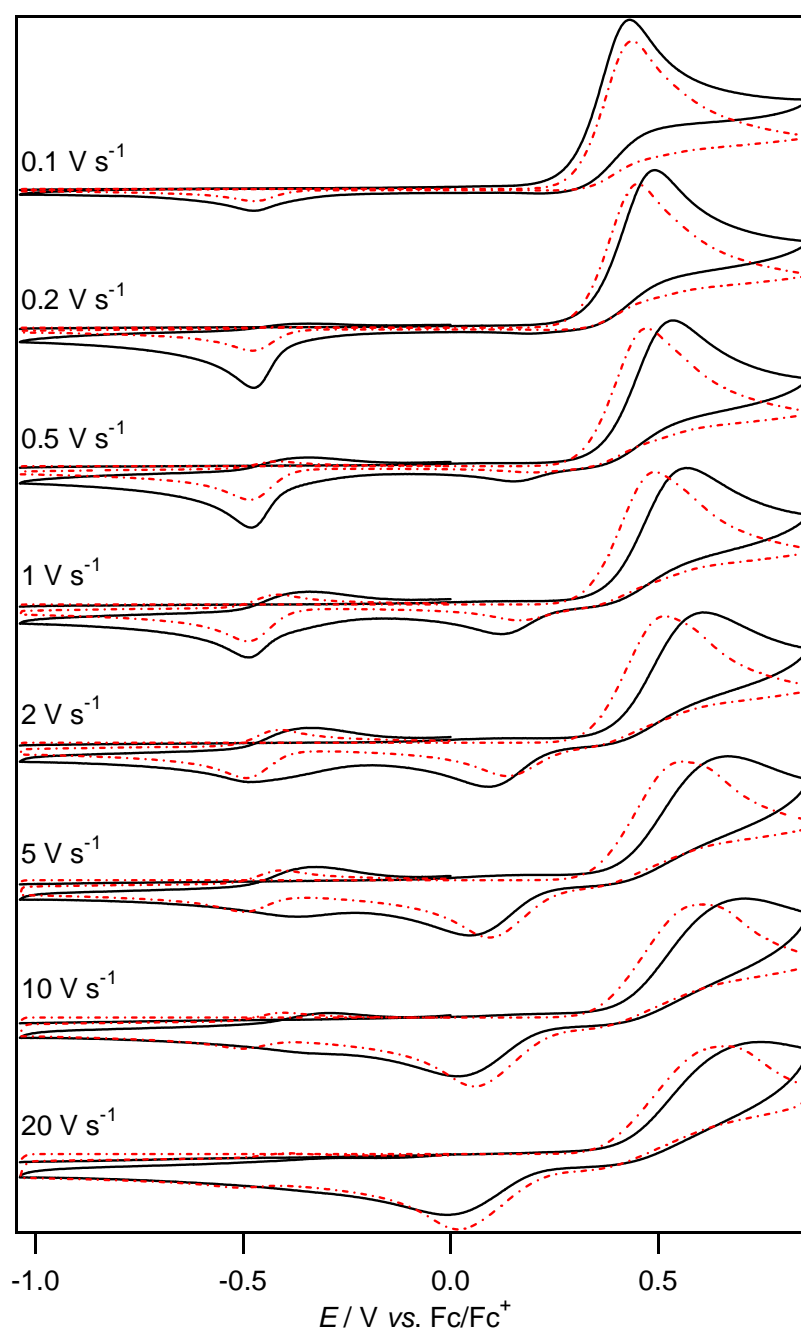
**Figure S1.** (—) Experimental CVs of  $2 \times 10^{-3}$  M  $\alpha$ -TOH in  $\text{CH}_3\text{CN}$  (with 0.013 M  $\text{H}_2\text{O}$ ) containing 0.2 M  $\text{Bu}_4\text{NPF}_6$  at  $22 \pm 2$  °C recorded at a 1 mm diameter Pt electrode at varying scan rates ( $\nu$ ). Positive current is in the upwards direction. Current data were scaled by multiplying by  $\nu^{-0.5}$ . The starting potential is  $-1$  V vs.  $\text{Fc/Fc}^+$  and the finishing potential is 0 V vs.  $\text{Fc/Fc}^+$  on the second scan. (---) Digital simulations of experimental data according to the mechanism in Scheme 2 and parameters in Tables 2 and 3.



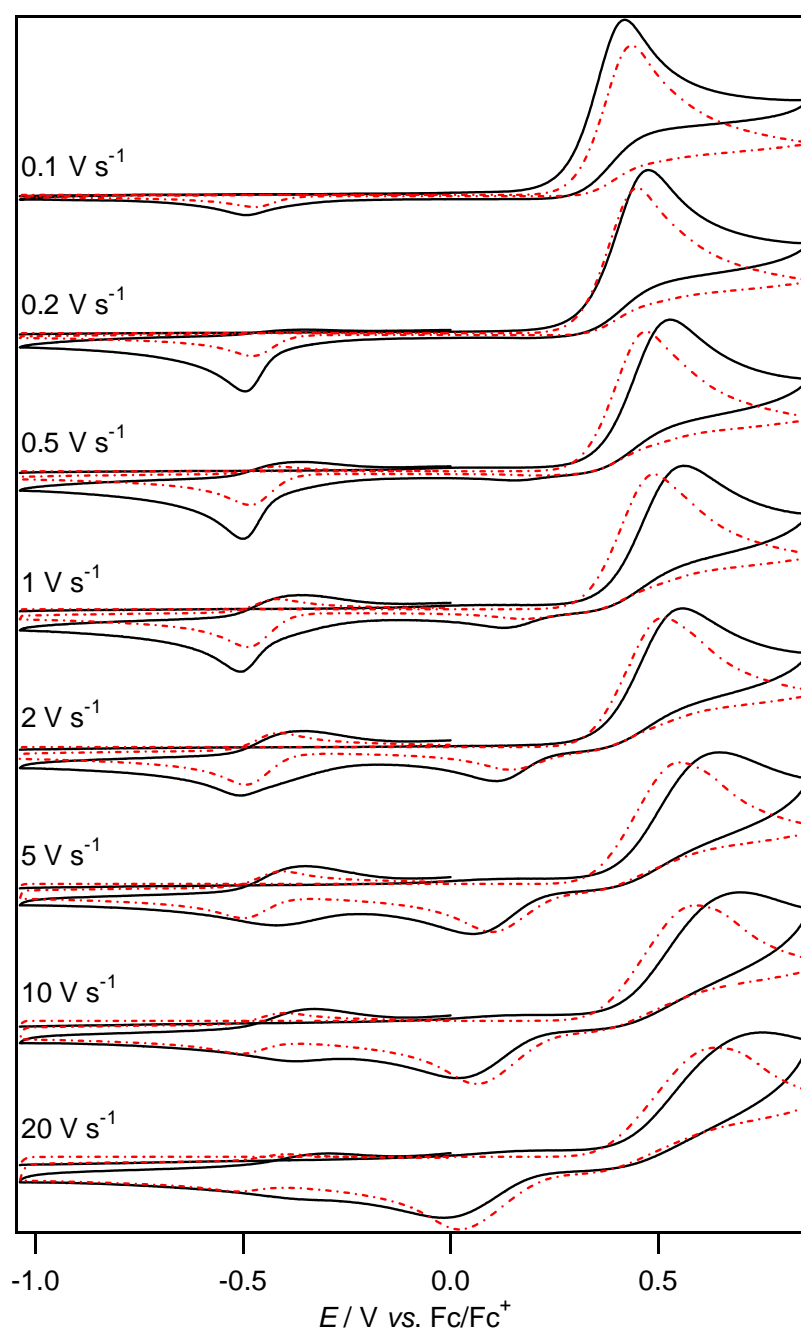
**Figure S2.** (—) Experimental CVs of  $2 \times 10^{-3} \text{ M}$   $\alpha$ -TOH in  $\text{CH}_3\text{CN}$  (with  $0.123 \text{ M H}_2\text{O}$ ) containing  $0.2 \text{ M Bu}_4\text{NPF}_6$  at  $22 \pm 2 \text{ }^\circ\text{C}$  recorded at a  $1 \text{ mm}$  diameter Pt electrode at varying scan rates ( $\nu$ ). Positive current is in the upwards direction. Current data were scaled by multiplying by  $\nu^{-0.5}$ . The starting potential is  $-1 \text{ V vs. Fc/Fc}^+$  and the finishing potential is  $0 \text{ V vs. Fc/Fc}^+$  on the second scan. (---) Digital simulations of experimental data according to the mechanism in Scheme 2 and parameters in Tables 2 and 3.



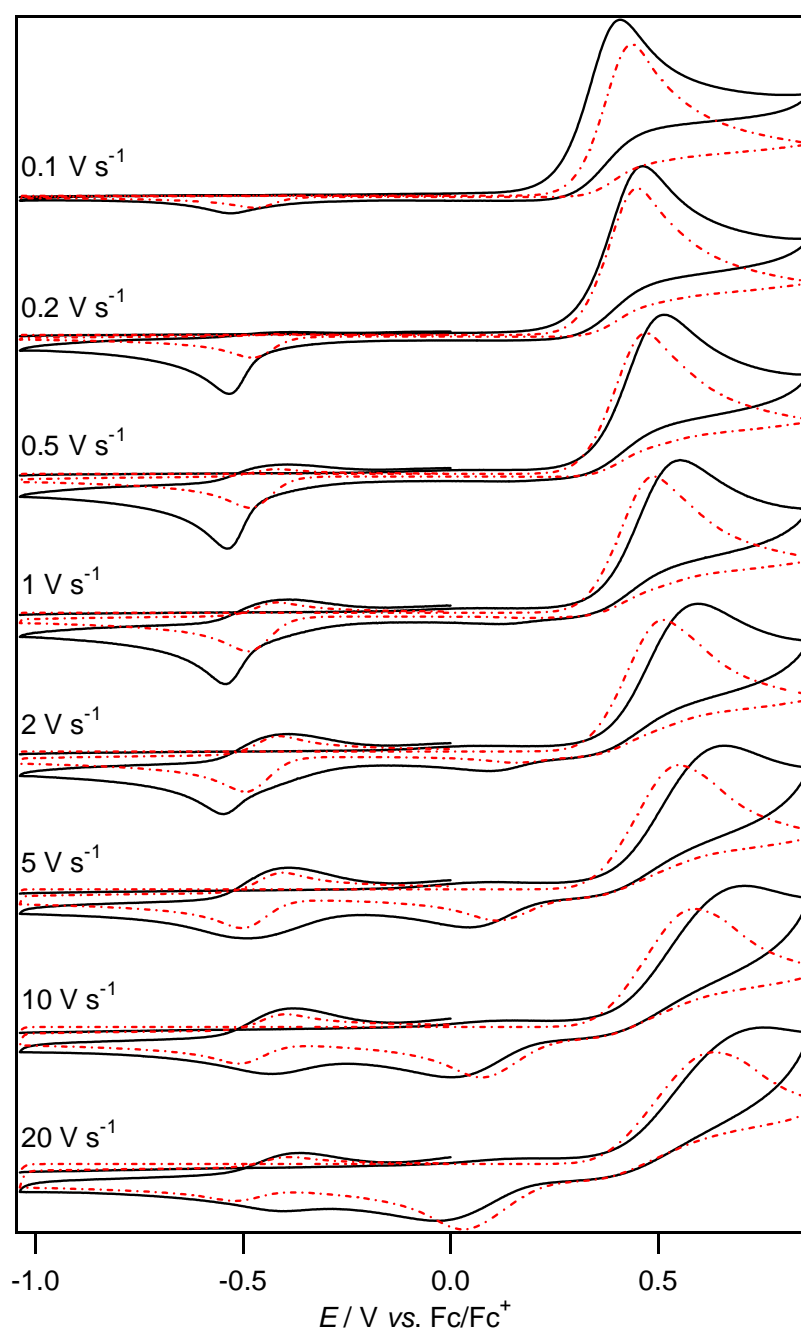
**Figure S3.** (—) Experimental CVs of  $2 \times 10^{-3} \text{ M } \alpha\text{-TOH}$  in  $\text{CH}_3\text{CN}$  (with  $0.233 \text{ M H}_2\text{O}$ ) containing  $0.2 \text{ M Bu}_4\text{NPF}_6$  at  $22 \pm 2 \text{ }^\circ\text{C}$  recorded at a  $1 \text{ mm}$  diameter Pt electrode at varying scan rates ( $\nu$ ). Positive current is in the upwards direction. Current data were scaled by multiplying by  $\nu^{-0.5}$ . The starting potential is  $-1 \text{ V vs. Fc/Fc}^+$  and the finishing potential is  $0 \text{ V vs. Fc/Fc}^+$  on the second scan. (---) Digital simulations of experimental data according to the mechanism in Scheme 2 and parameters in Tables 2 and 3.



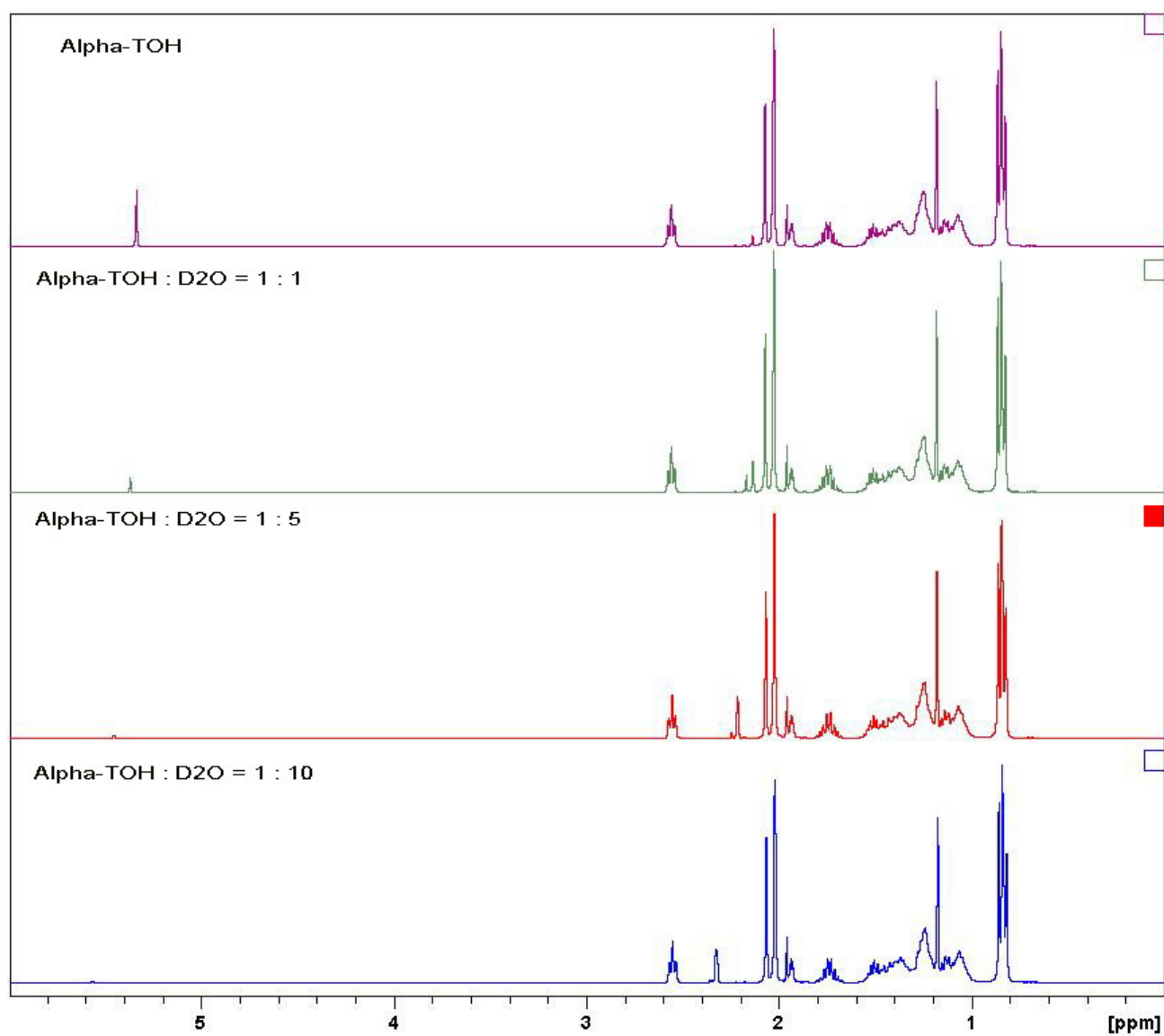
**Figure S4.** (—) Experimental CVs of  $2 \times 10^{-3}$  M  $\alpha$ -TOH in  $CH_3CN$  (with 0.343 M  $H_2O$ ) containing 0.2 M  $Bu_4NPF_6$  at  $22 \pm 2$  °C recorded at a 1 mm diameter Pt electrode at varying scan rates ( $\nu$ ). Positive current is in the upwards direction. Current data were scaled by multiplying by  $\nu^{-0.5}$ . The starting potential is  $-1$  V vs.  $Fc/Fc^+$  and the finishing potential is 0 V vs.  $Fc/Fc^+$  on the second scan. (---) Digital simulations of experimental data according to the mechanism in Scheme 2 and parameters in Tables 2 and 3.



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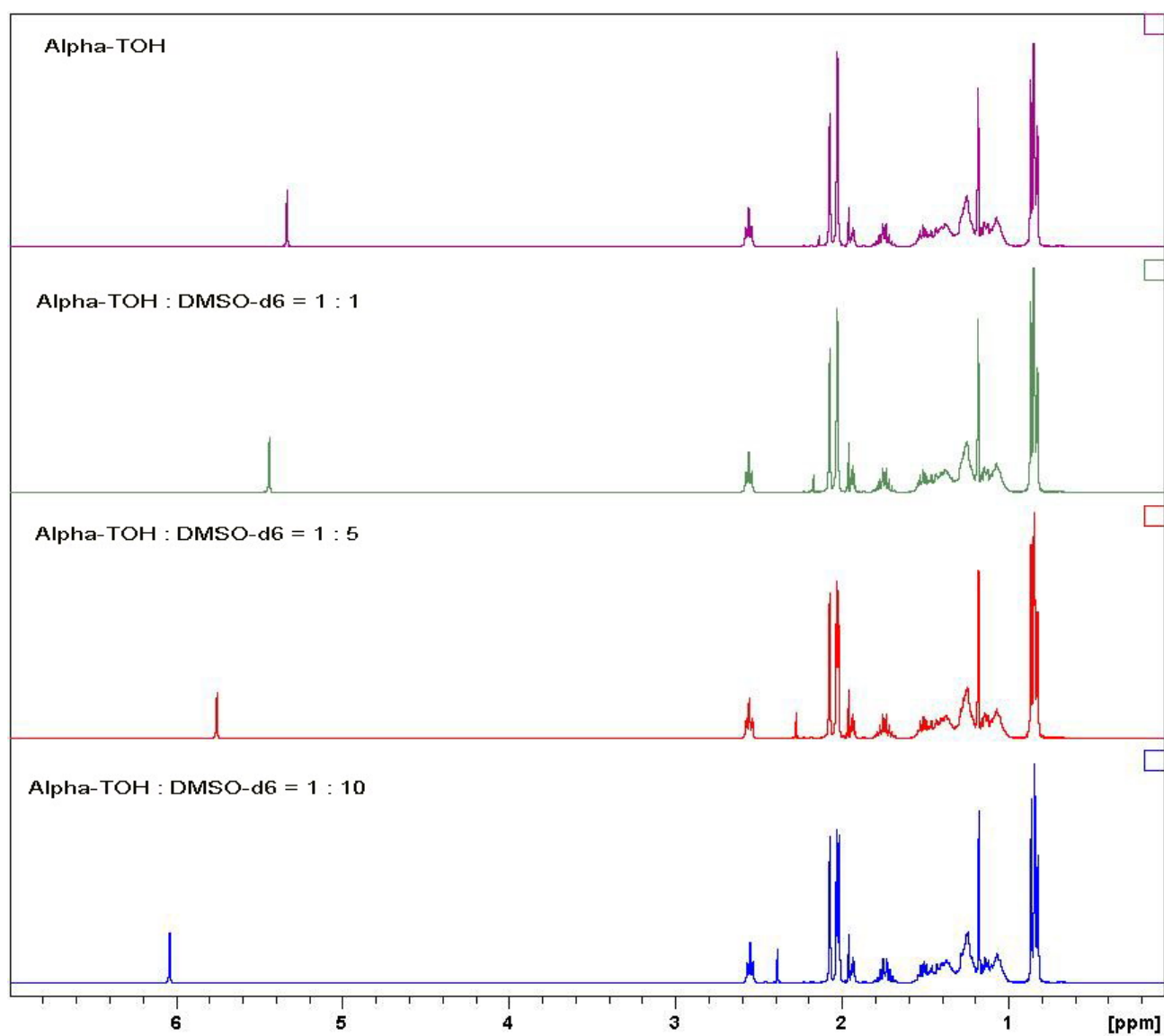


**Figure S6.** (—) Experimental CVs of  $2 \times 10^{-3}$  M  $\alpha$ -TOH in  $CH_3CN$  (with 0.563 M  $H_2O$ ) containing 0.2 M  $Bu_4NPF_6$  at  $22 \pm 2$  °C recorded at a 1 mm diameter Pt electrode at varying scan rates ( $\nu$ ). Positive current is in the upwards direction. Current data were scaled by multiplying by  $\nu^{-0.5}$ . The starting potential is  $-1$  V vs.  $Fc/Fc^+$  and the finishing potential is 0 V vs.  $Fc/Fc^+$  on the second scan. (---) Digital simulations of experimental data according to the mechanism in Scheme 2 and parameters in Tables 2 and 3.

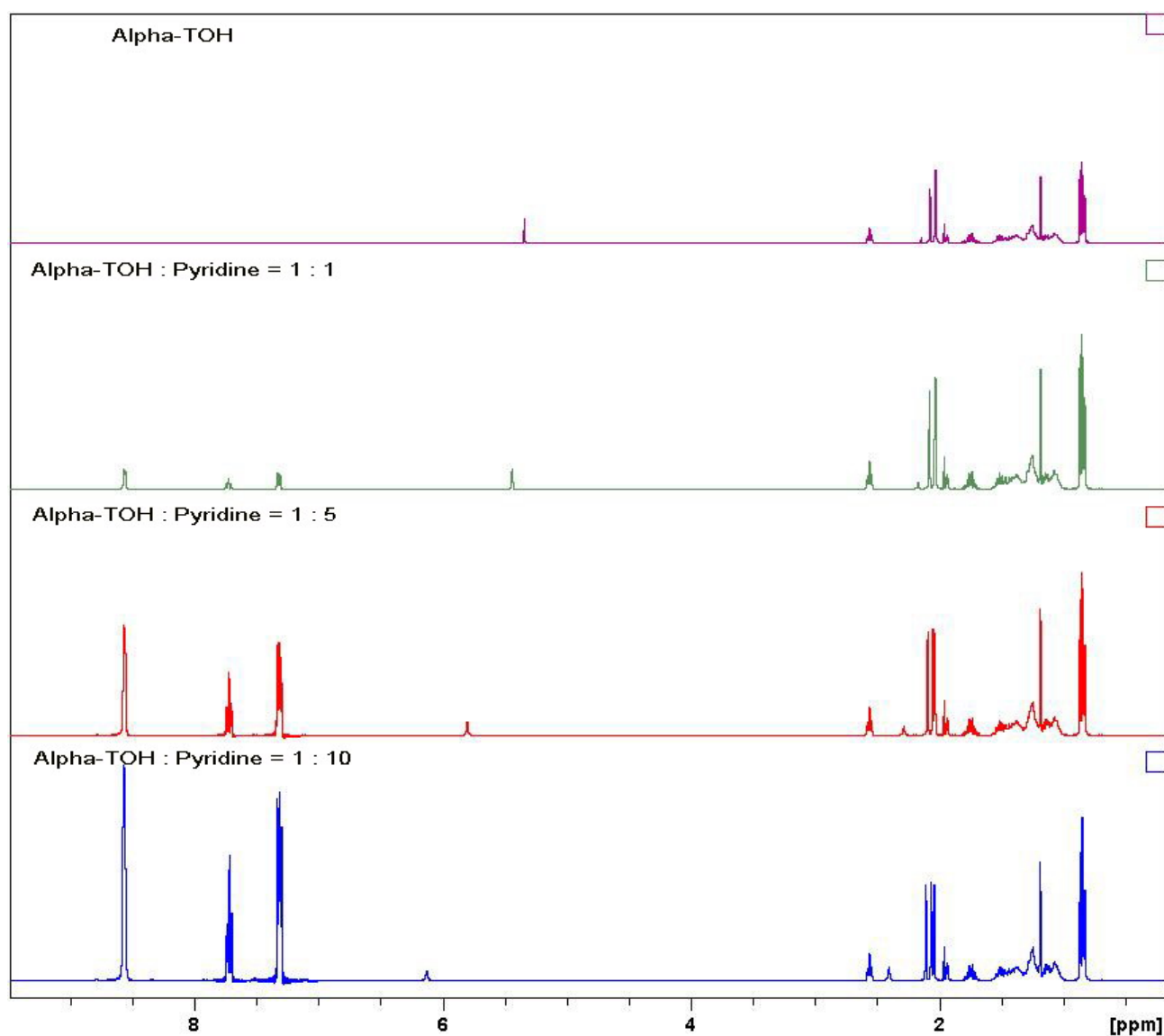


**Figure S7.** 400-MHz <sup>1</sup>H NMR spectra of 80 mM α-TOH in dried CD<sub>3</sub>CN with different ratios of D<sub>2</sub>O.





**Figure S8.** 400-MHz <sup>1</sup>H NMR spectra of 80 mM α-TOH in dried CD<sub>3</sub>CN with different ratios of DMSO.



**Figure S9.** 400-MHz <sup>1</sup>H NMR spectra of 80 mM α-TOH in dried CD<sub>3</sub>CN with different ratios of pyridine.