Electronic Supporting Information File

Surface Ligand Length Influences Kinetics of H-atom Uptake in Polyoxovanadate-alkoxide Clusters

*Chari Y. M. Peter, Eric Schreiber, Kathryn R. Proe, and Ellen M. Matson**

Department of Chemistry, University of Rochester, Rochester, New York 14627, United States

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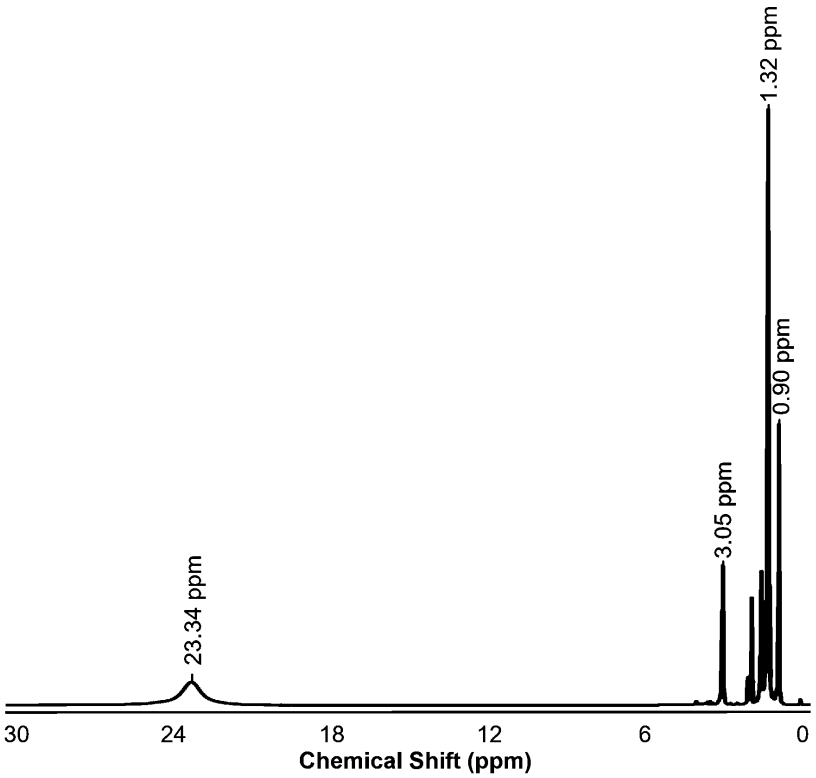

Figure S1. ^{1}H NMR spectrum [^{n}Oct$_4$N][$V_6O_7(OCH_3)_{12}$] in CD_3CN at 21 ^{o}C.

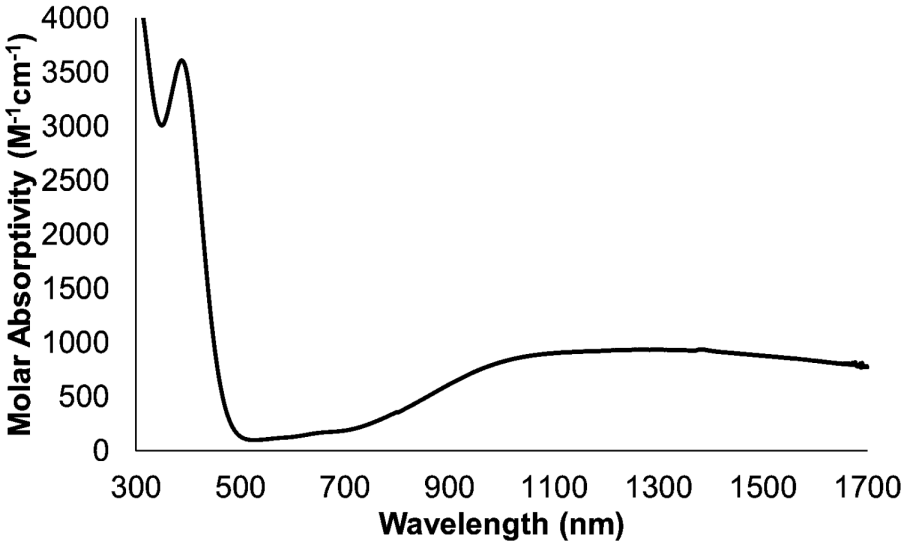

Figure S2. Electronic absorption spectrum of [^{n}Oct$_4$N][$V_6O_7(OCH_3)_{12}$] in THF 21 ^{o}C.

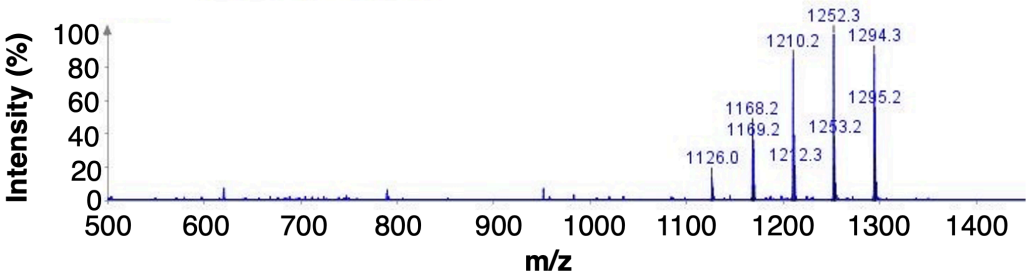

Figure S3. ESI-MS(-ve) of **1-butyl,** $[^{n}Bu_4N][V_6O_7(OC_4H_9)_{12-x}(OCH_3)_x]$ (x = 0, 1, 2, 3, 4).

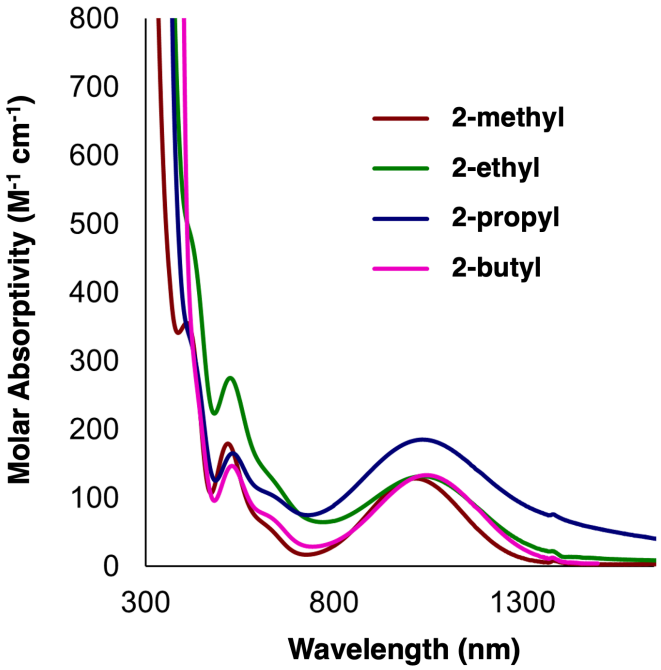

Figure S4. Electronic absorption spectra of **2-methyl**, **2-ethyl**, **2-propyl** and **2-butyl** in acetonitrile at 21 °C

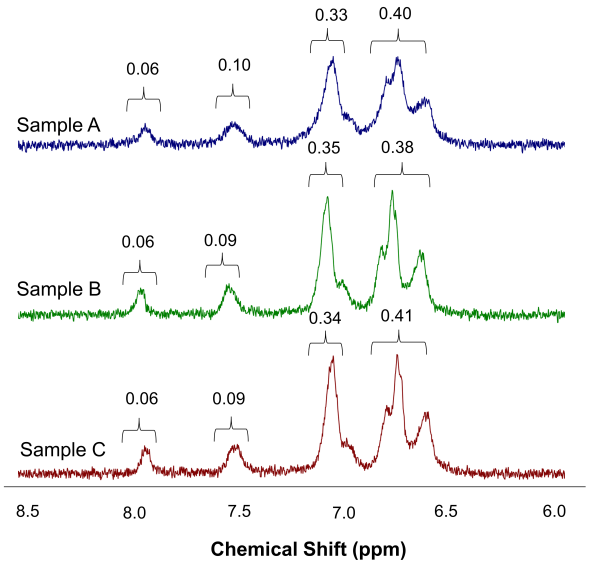

Figure S5. ^{1}H NMR spectra of equilibrium reaction solutions with **1-methyl** and Hydz after 6 hours in THF-d_8 at 21 °C.

Table S1. BDFE(O-H)$_{adj}$ calculated from equilibrium reactions of **1-methyl** with Hydz after 6 hours using the equation outlined in the Experimental section.

	Hydz					**Azobenzene**[b]					
	7.16 ppm (4 H)		**6.77 ppm (6 H)**		**Avg. Conc.**	**7.91 ppm (4 H)**		**7.58 ppm (6 H)**		**Avg. Conc.**	**BDFE$_{adj}$ (kcal/mol)**
Trial	Integral	Relative Conc.[a]	Integral	Relative Conc.[a]		Integral	Relative Conc.[a]	Integral	Relative Conc.[a]		
A	0.33	0.08	0.40	0.07	**0.08**	0.06	0.02	0.10	0.02	**0.02**	**59.9**
B	0.35	0.09	0.38	0.06	**0.08**	0.06	0.02	0.09	0.02	**0.02**	**59.9**
C	0.34	0.09	0.41	0.07	**0.08**	0.06	0.02	0.09	0.02	**0.02**	**59.9**
										Avg.	**59.9**
										Error	**0.1**

[a] Relative concentration of either Hydz or azobenzene was determined by dividing the integral by the number of protons a given signal(s) corresponds with.

[b] Integration of the N-H resonance of Hydz was omitted in this study due to potential broadening of the resonance by H-bonding with **2-V$_6$O$_8^{2-}$**.

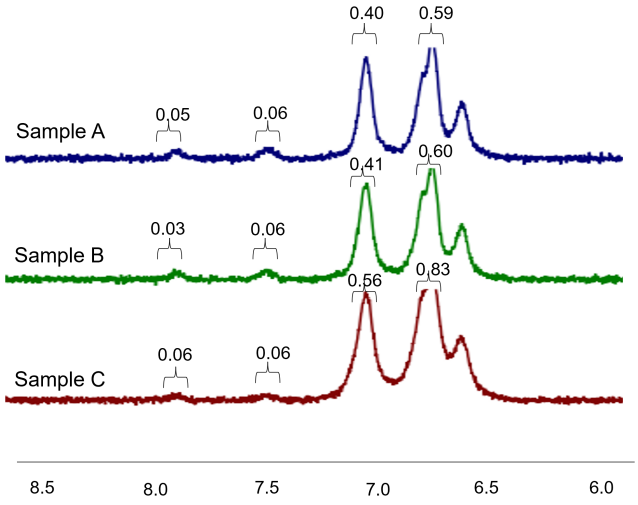

Figure S6. ^{1}H NMR spectra of equilibrium reaction solutions with **1-ethyl** and Hydz after 7 days in THF-d_8 at 21 °C.

Table S2. BDFE(O-H)$_{adj}$ calculated from equilibrium reactions of **1-ethyl** with Hydz after 7 days using the equation outlined in the Experimental section.

	Hydz					**Azobenzene**[b]					
	7.16 ppm (4 H)		**6.77 ppm (6 H)**		**Avg. Conc.**	**7.91 ppm (4 H)**		**7.58 ppm (6 H)**		**Avg. Conc.**	**BDFE$_{adj}$ (kcal/mol)**
Trial	Integral	Relative Conc.[a]	Integral	Relative Conc.[a]		Integral	Relative Conc.[a]	Integral	Relative Conc.[a]		
A	0.40	0.10	0.59	0.01	**0.09**	0.05	0.01	0.06	0.01	**0.01**	**59.8**
B	0.41	0.10	0.60	0.10	**0.10**	0.03	0.01	0.06	0.01	**0.01**	**59.7**
C	0.56	0.14	0.83	0.14	**0.14**	0.06	0.02	0.06	0.02	**0.01**	**59.7**
										Avg.	**59.7**
										Error	**0.1**

[a] Relative concentration of either Hydz or azobenzene was determined by dividing the integral by the number of protons a given signal(s) corresponds with.

[b] Integration of the N-H resonance of Hydz was omitted in this study due to potential broadening of the resonance by H-bonding with **2-V$_6$O$_8^{2-}$**.

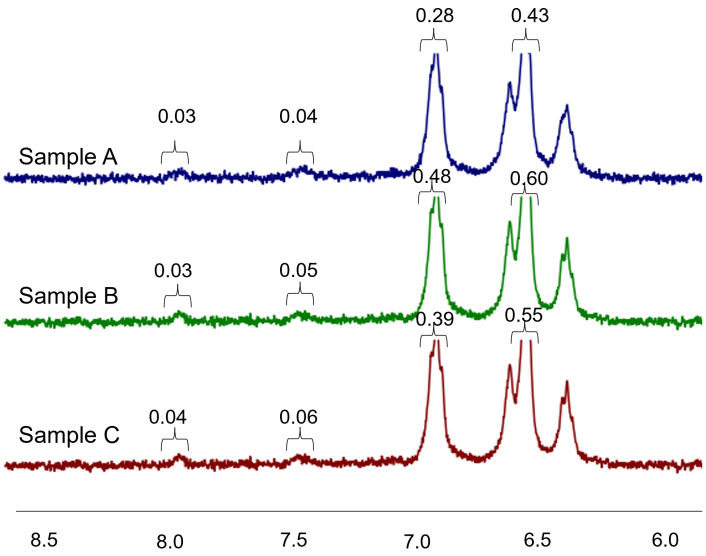

Figure S7. ^{1}H NMR spectra of equilibrium reaction solutions with **1-propyl** and Hydz after 7 days in THF-d_8 at 21 °C.

Table S3. BDFE(O-H)$_{adj}$ calculated from equilibrium reactions of **1-propyl** with Hydz after 7 days using the equation outlined in the Experimental section.

	Hydz					**Azobenzene**[b]					
	7.16 ppm (4 H)		**6.77 ppm (6 H)**		**Avg. Conc.**	**7.91 ppm (4 H)**		**7.58 ppm (6 H)**		**Avg. Conc.**	**BDFE$_{adj}$ (kcal/mol)**
Trial	Integral	Relative Conc.[a]	Integral	Relative Conc.[a]		Integral	Relative Conc.[a]	Integral	Relative Conc.[a]		
A	0.28	0.07	0.43	0.07	**0.07**	0.03	0.01	0.04	0.01	**0.01**	**59.7**
B	0.41	0.10	0.60	0.10	**0.10**	0.03	0.01	0.05	0.01	**0.01**	**59.6**
C	0.39	0.10	0.55	0.09	**0.09**	0.04	0.01	0.06	0.01	**0.01**	**59.7**
										Avg.	**59.7**
										Error	**0.1**

[a] Relative concentration of either Hydz or azobenzene was determined by dividing the integral by the number of protons a given signal(s) corresponds with.
[b] Integration of the N-H resonance of Hydz was omitted in this study due to potential broadening of the resonance by H-bonding with **2-V$_6$O$_8^{2-}$**.

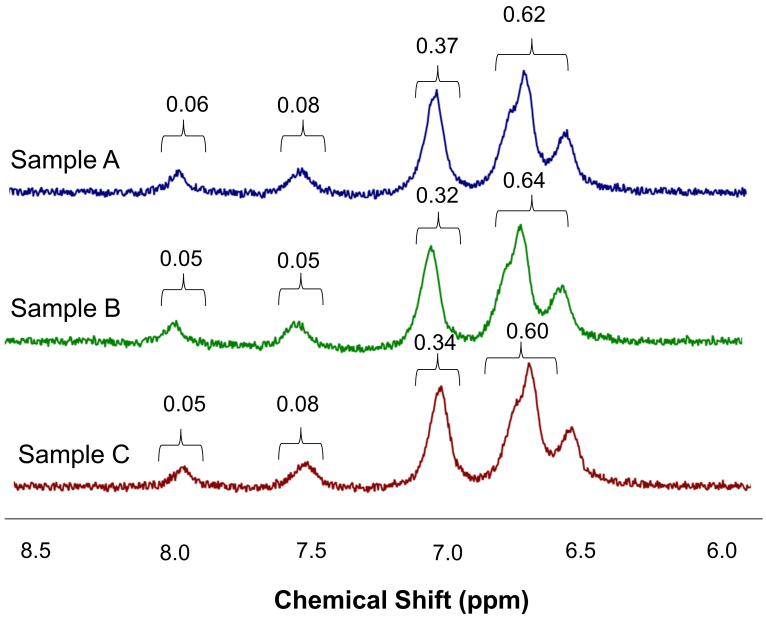

Figure S8. ^{1}H NMR spectra of equilibrium reaction solutions with **1-butyl** and Hydz after 7 days in THF-d_8 at 21 °C.

Table S4. BDFE(O-H)$_{adj}$ calculated from equilibrium reactions of **1-butyl** with Hydz after 7 days using the equation outlined in the Experimental section

	Hydz					Azobenzene[b]					
	7.16 ppm (4 H)		6.77 ppm (6 H)		Avg. Conc.	7.91 ppm (4 H)		7.58 ppm (6 H)		Avg. Conc.	BDFE$_{adj}$ (kcal/mol)
Trial	Integral	Relative Conc.[a]	Integral	Relative Conc.[a]		Integral	Relative Conc.[a]	Integral	Relative Conc.[a]		
A	0.34	0.09	0.60	0.10	**0.09**	0.05	0.01	0.08	0.01	**0.01**	**59.8**
B	0.32	0.08	0.64	0.11	**0.09**	0.04	0.01	0.05	0.01	**0.01**	**59.8**
C	0.37	0.09	0.62	0.10	**0.10**	0.06	0.02	0.08	0.01	**0.01**	**59.8**
										Avg.	**59.8**
										Error	**0.1**

[a] Relative concentration of either Hydz or azobenzene was determined by dividing the integral by the number of protons a given signal(s) corresponds with.
[b] Integration of the N-H resonance of Hydz was omitted in this study due to potential broadening of the resonance by H-bonding with **2-$V_6O_8^{2-}$**.

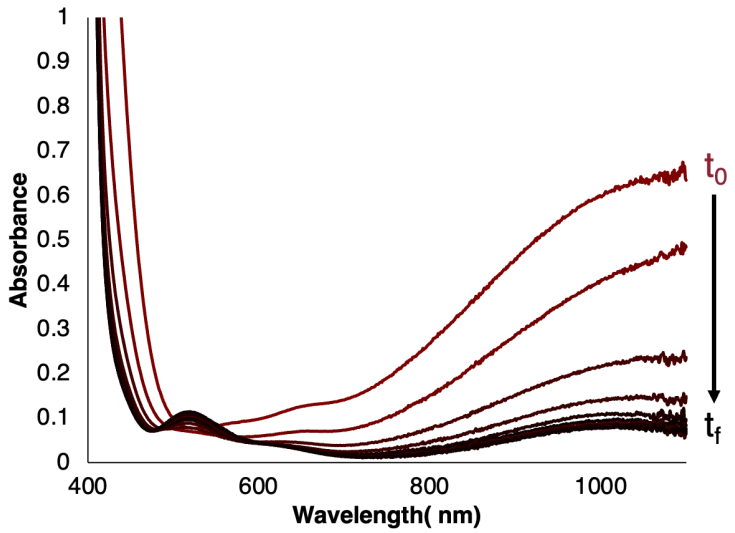

Figure S9. Scanning Kinetics for the reaction between **1-methyl** (0.6 mM) and H_2Phen (8 mM) recorded in acetonitrile at 25 °C. Red is initial spectrum of **1-methyl** (t_0 = 0 min), color of trace darkens as reaction progresses ending in the black trace (t_f = 120 min).

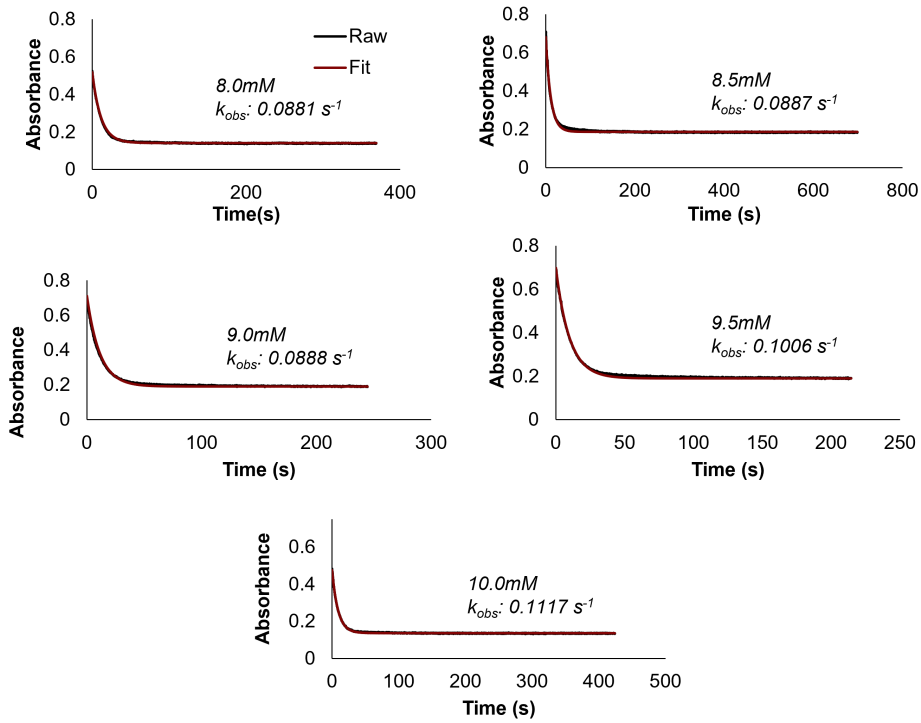

Figure S10. Plots of absorbance at 1025 nm vs. time for the reaction between **1-methyl** (0.6 mM) and excess H_2Phen under pseudo first-order reaction conditions recorded in acetonitrile at 25 °C.

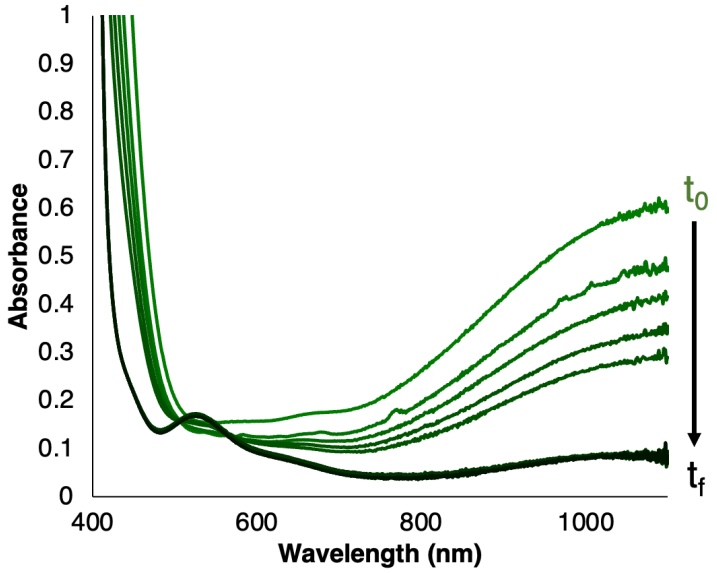

Figure S11. Scanning Kinetics for the reaction between **1-ethyl** (0.6 mM) and H_2Phen (8 mM) recorded in acetonitrile at 25 °C. Green is initial spectrum of **1-ethyl** (t_0 = 0 min), color of trace darkens as reaction progresses ending in the black trace (t_f = 120 min).

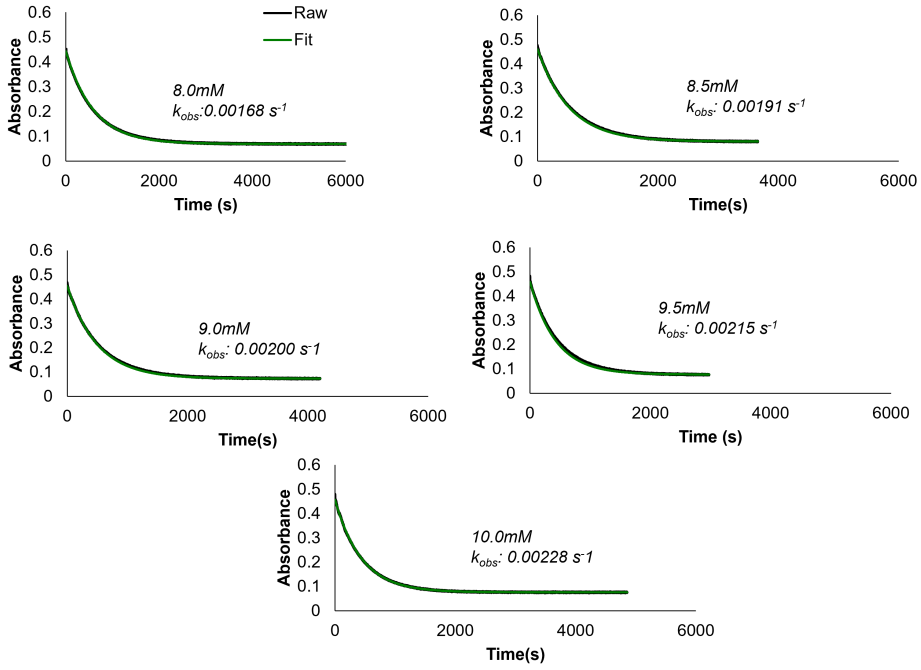

Figure S12. Plots of absorbance at 1025 nm vs. time for the reaction between **1-ethyl** (0.6 mM) and excess H_2Phen under pseudo first-order reaction conditions recorded in acetonitrile at 25 °C.

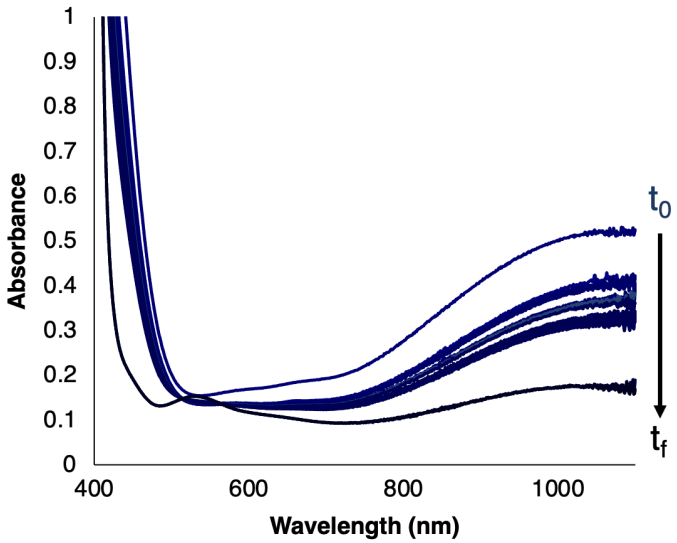

Figure S13. Scanning Kinetics for the reaction between **1-propyl** (0.6 mM) and H_2Phen (8 mM) recorded in acetonitrile at 25 °C. Dark blue is initial spectrum of **1-propyl** (t_0 = 0 min), color of trace darkens as reaction progresses ending in the black trace (t_f = 120 min).

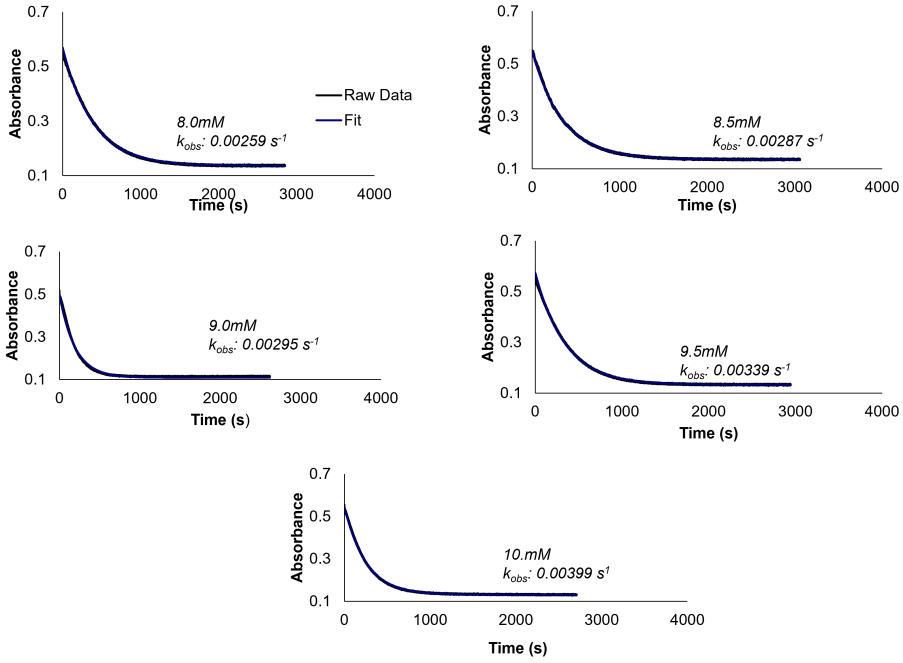

Figure S14. Plots of absorbance at 1025 nm vs. time for the reaction between **1-propyl** (0.6 mM) and excess H_2Phen under pseudo first-order reaction conditions recorded in acetonitrile at 25 °C

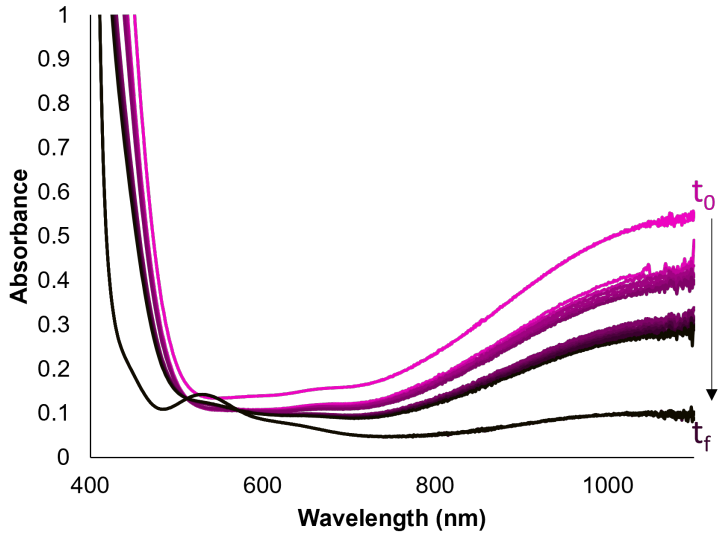

Figure S15. Scanning Kinetics for the reaction between **1-propyl** (0.6 mM) and H_2Phen (8 mM) recorded in acetonitrile at 25 °C. Dark blue is initial spectrum of **1-propyl** (t_0 = 0 min), color of trace darkens as reaction progresses ending in the black trace (t_f = 120 min).

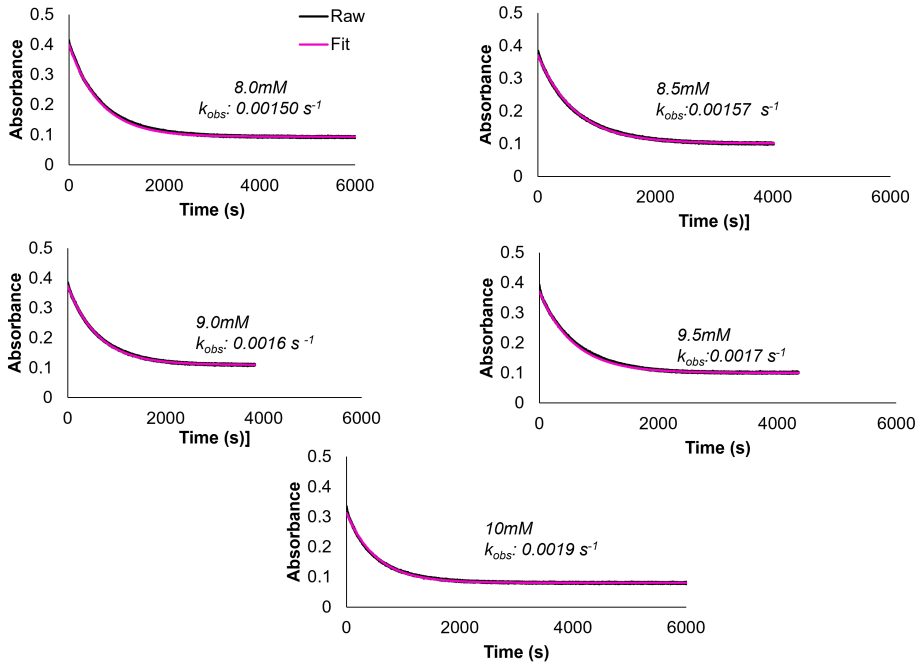

Figure S16. Plots of absorbance at 1025 nm vs. time for the reaction between **1-butyl** (0.6 mM) and excess H_2Phen under pseudo first-order reaction conditions recorded in acetonitrile at 25 °C**.**

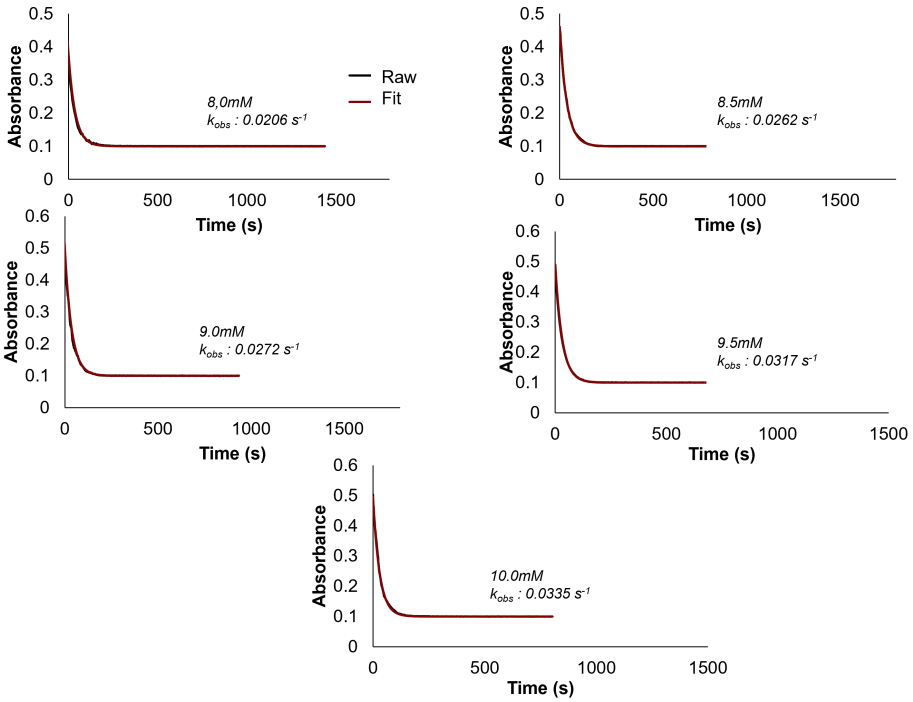

Figure S17. Plots of absorbance at 1025 nm vs. time for the reaction between **1-methyl** (0.6 mM) and excess D_2Phen under pseudo first-order reaction conditions recorded in acetonitrile at 25 °C.

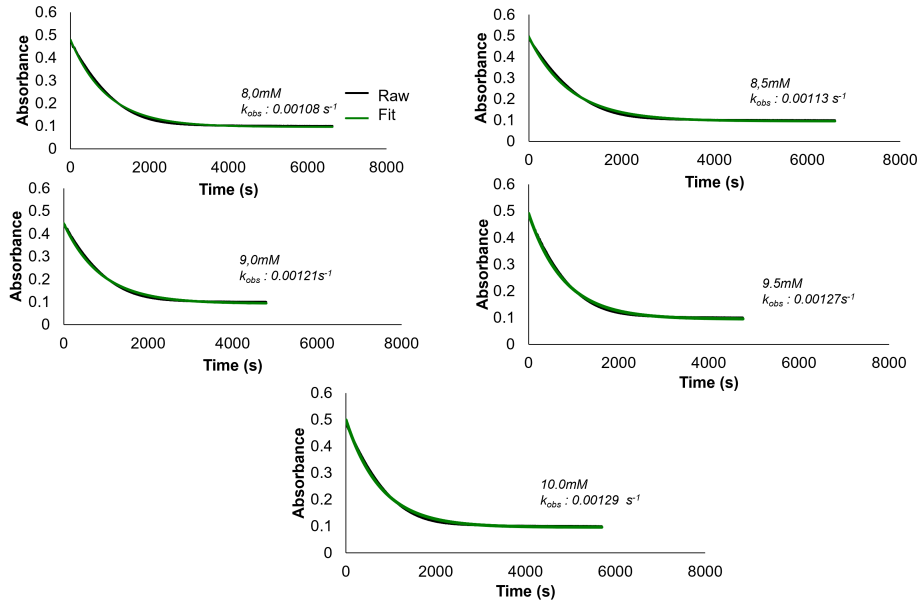

Figure S18. Plots of absorbance at 1025 nm vs. time for the reaction between **1-ethyl** (0.6 mM) and excess D_2Phen under pseudo first-order reaction conditions recorded in acetonitrile at 25 °C

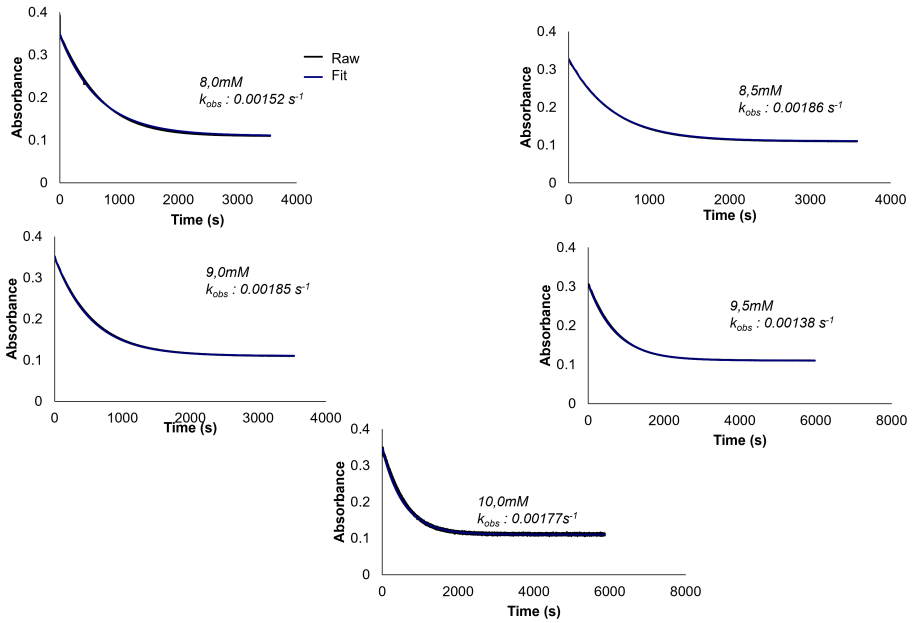

Figure S19. Plots of absorbance at 1025 nm vs. time for the reaction between **1-propyl** (0.6 mM) and excess D_2Phen under pseudo first-order reaction conditions recorded in acetonitrile at 25 °C**.**

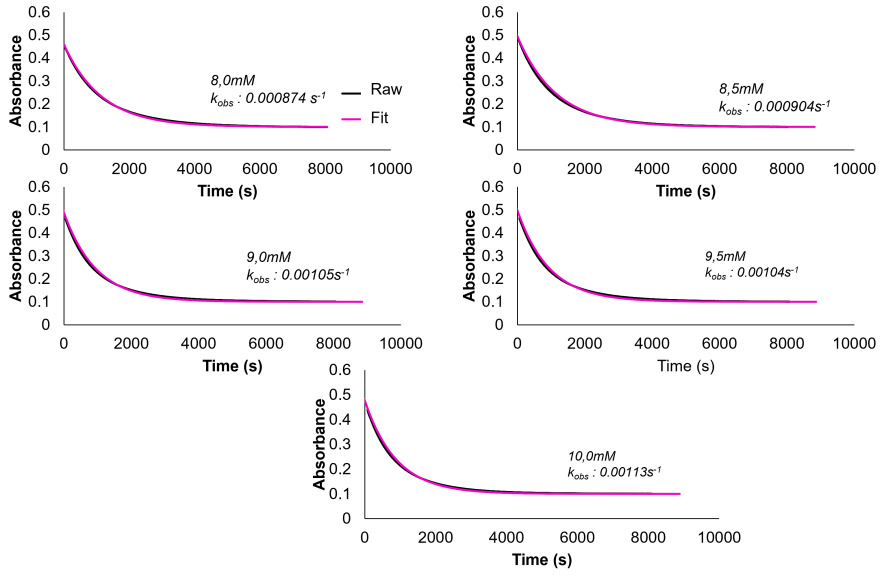

Figure S20. Plots of absorbance at 1025 nm vs. time for the reaction between **1-butyl** (0.6 mM) and excess D_2Phen under pseudo first-order reaction conditions recorded in acetonitrile at 25 °C**.**

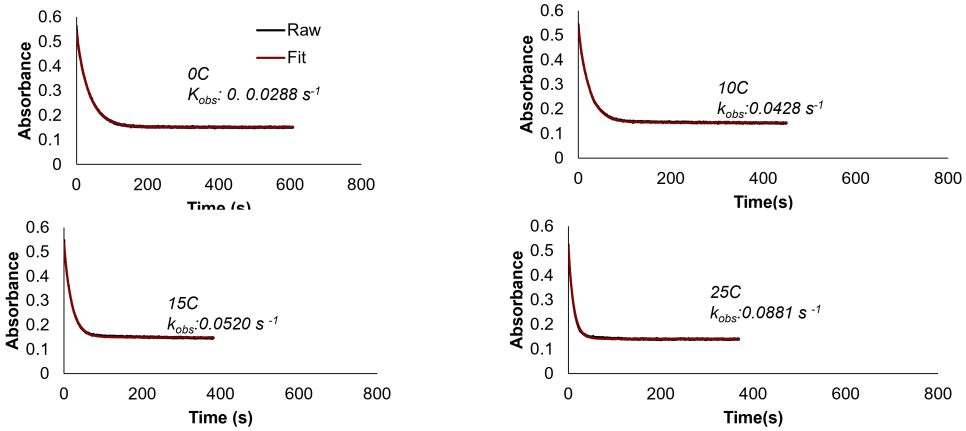

Figure S21. Plots of absorbance at 1025 nm vs. time for the reaction between **1-methyl** (0.6 mM) and H_2Phen (8 mM) recorded in acetonitrile between 0 °C and 35 °C**.**

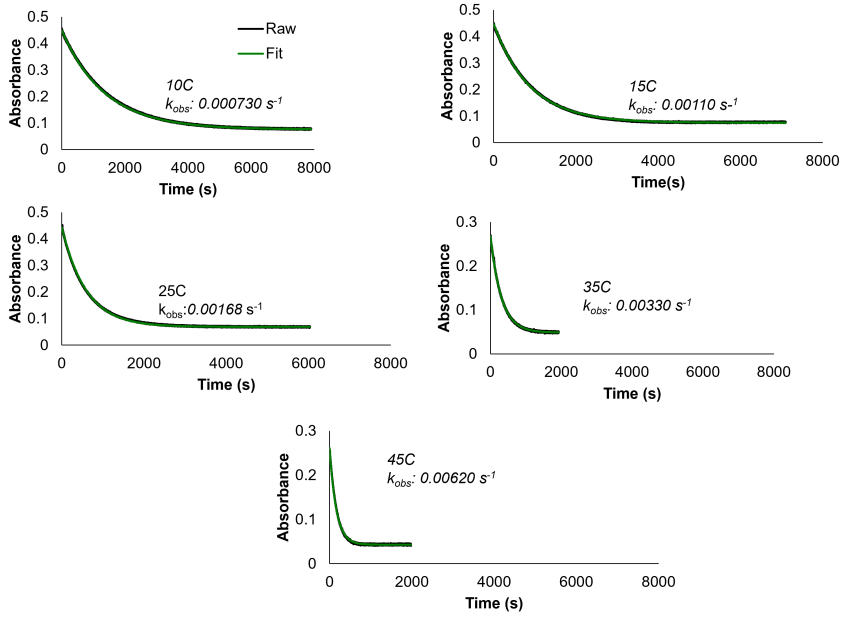

Figure S22. Plots of absorbance at 1025 nm vs. time for the reaction between **1-ethyl** (0.6 mM) and H_2Phen (8 mM) recorded in acetonitrile between 10 °C and 45 °C.

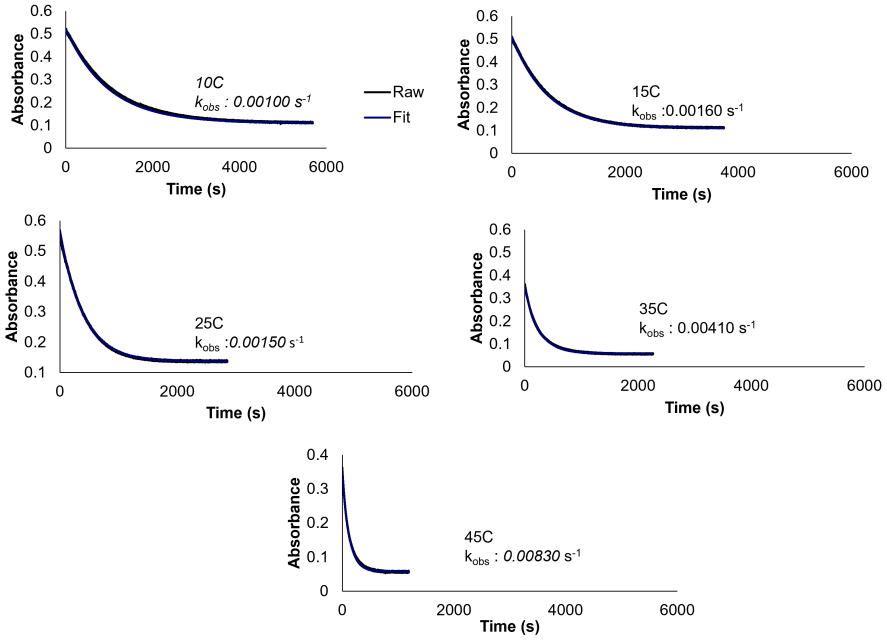

Figure S23. Plots of absorbance at 1025 nm vs. time for the reaction between **1-propyl** (0.6 mM) and H_2Phen (8 mM) recorded in acetonitrile between 10 °C and 45 °C**.**

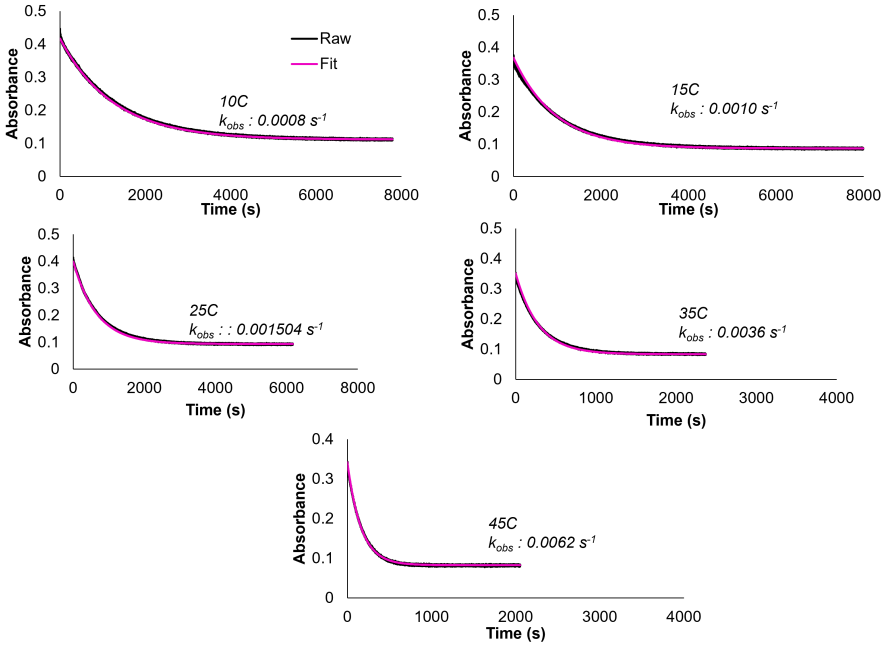

Figure S24. Plots of absorbance at 1025 nm vs. time for the reaction between **1-butyl** (0.6 mM) and H_2Phen (8 mM) recorded in acetonitrile between 10 °C and 45 °C**.**