

## Electronic Supplementary Information

### Reactions of the Simple Nitroalkanes with Hydroxide Ion in Water.

#### Evidence for a Complex Mechanism

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**Table S1. Apparent rate constants and standard deviations for 3 sets of experiments on the reaction of NM (0.10 mM) with NaOH (20.0 mM) in H<sub>2</sub>O at 298 K.**

time/s	Set 1 <sup>a</sup>		Set 2 <sup>b</sup>		Set 3 <sup>c</sup>		Segment
	$k_{app}/s^{-1}$	SD	$k_{app}/s^{-1}$	SD	$k_{app}/s^{-1}$	SD	
0.009	0.550	0.083	0.394	0.119	0.489	0.128	1
0.013	0.545	0.035	0.559	0.070	0.576	0.036	2
0.017	0.548	0.026	0.546	0.032	0.550	0.030	3
0.020	0.542	0.016	0.548	0.012	0.545	0.021	4
0.024	0.542	0.013	0.546	0.009	0.544	0.013	5
0.043	0.537	0.008	0.543	0.007	0.534	0.007	6
0.080	0.532	0.004	0.536	0.003	0.525	0.003	7
0.118	0.528	0.003	0.533	0.002	0.521	0.002	8
0.155	0.525	0.003	0.531	0.002	0.518	0.002	9
0.193	0.523	0.003	0.530	0.001	0.517	0.002	10
0.230	0.522	0.003	0.529	0.001	0.515	0.002	11
0.268	0.520	0.003	0.527	0.001	0.514	0.002	12
0.305	0.519	0.003	0.527	0.001	0.513	0.002	13
0.343	0.518	0.003	0.526	0.001	0.512	0.002	14
0.380	0.517	0.003	0.525	0.001	0.511	0.002	15
0.418	0.516	0.003	0.525	0.001	0.510	0.002	16
0.455	0.515	0.004	0.524	0.001	0.509	0.002	17
0.493	0.514	0.004	0.523	0.001	0.508	0.002	18
0.530	0.513	0.004	0.522	0.001	0.507	0.002	19
0.568	0.512	0.004	0.522	0.001	0.507	0.002	20
0.605	0.511	0.004	0.521	0.001	0.506	0.002	21
0.643	0.511	0.004	0.521	0.001	0.505	0.003	22
0.680	0.510	0.004	0.520	0.001	0.504	0.003	23
0.718	0.509	0.004	0.519	0.001	0.504	0.003	24

<sup>a</sup>Set 1: 20 stopped-flow repetitions.

<sup>b</sup>Set 2: 12 stopped-flow repetitions.

<sup>c</sup>Set 3: 20 stopped-flow repetitions.

**Table S2. Apparent rate constants and standard deviations for 4 sets of experiments on the reaction of NE (0.10 mM) with NaOH (50.0 mM) in H<sub>2</sub>O at 298 K.**

time/s	Set 1 <sup>a</sup>		Set 2 <sup>b</sup>		Set 3 <sup>c</sup>		Set 4 <sup>d</sup>		Segment
	$k_{app}/s^{-1}$	SD	$k_{app}/s^{-1}$	SD	$k_{app}/s^{-1}$	SD	$k_{app}/s^{-1}$	SD	
0.014	0.290	0.097	0.275	0.067	0.289	0.081	0.266	0.110	1
0.021	0.286	0.044	0.274	0.039	0.274	0.046	0.271	0.037	2
0.029	0.280	0.019	0.271	0.028	0.274	0.018	0.267	0.024	3
0.036	0.276	0.014	0.271	0.022	0.269	0.011	0.269	0.017	4
0.044	0.270	0.014	0.269	0.016	0.269	0.008	0.267	0.013	5
0.081	0.265	0.006	0.264	0.005	0.266	0.004	0.264	0.006	6
0.156	0.260	0.002	0.259	0.001	0.262	0.002	0.261	0.002	7
0.231	0.258	0.001	0.257	0.001	0.260	0.001	0.260	0.001	8
0.306	0.256	0.001	0.256	0.001	0.259	0.001	0.259	0.001	9
0.381	0.255	0.001	0.255	0.001	0.259	0.001	0.258	0.001	10
0.456	0.255	0.001	0.255	0.001	0.258	0.001	0.257	0.001	11
0.531	0.254	0.001	0.254	0.001	0.257	0.001	0.257	0.001	12
0.606	0.254	0.001	0.253	0.001	0.257	0.001	0.256	0.001	13
0.681	0.253	0.001	0.253	0.001	0.257	0.001	0.256	0.001	14
0.756	0.253	0.001	0.252	0.001	0.256	0.001	0.255	0.001	15
0.831	0.252	0.001	0.251	0.001	0.256	0.001	0.255	0.001	16
0.906	0.252	0.001	0.251	0.001	0.255	0.001	0.255	0.001	17
0.981	0.251	0.001	0.250	0.001	0.255	0.001	0.254	0.001	18
1.056	0.251	0.001	0.249	0.001	0.255	0.001	0.254	0.001	19
1.131	0.251	0.001	0.248	0.001	0.254	0.001	0.254	0.001	20
1.206	0.250	0.001	0.248	0.001	0.254	0.001	0.254	0.001	21
1.281	0.250	0.001	0.247	0.001	0.254	0.001	0.253	0.001	22
1.356	0.249	0.001	0.246	0.001	0.253	0.001	0.253	0.001	23
1.431	0.249	0.001	0.246	0.001	0.253	0.001	0.253	0.001	24

<sup>a</sup>Set 1: 20 stopped-flow repetitions.

<sup>b</sup>Set 2: 10 stopped-flow repetitions.

<sup>c</sup>Set 3: 20 stopped-flow repetitions.

<sup>d</sup>Set 4: 20 stopped-flow repetitions.

**Table S3. Apparent rate constants and standard deviations for 3 sets of experiments on the reaction of 2-NP (0.10 mM) with NaOH (50.0 mM) in H<sub>2</sub>O at 298 K.**

time/s	Set 1 <sup>a</sup>		Set 2 <sup>b</sup>		Set 3 <sup>c</sup>		Segment
	$k_{app}/s^{-1}$	SD	$k_{app}/s^{-1}$	SD	$k_{app}/s^{-1}$	SD	
0.135	0.0248	0.0045	0.0229	0.0081	0.0267	0.0071	1
0.248	0.0221	0.0013	0.0215	0.0023	0.0233	0.0032	2
0.360	0.0216	0.0012	0.0206	0.0014	0.0219	0.0011	3
0.473	0.0214	0.0008	0.0197	0.0012	0.0218	0.0010	4
0.585	0.0212	0.0006	0.0195	0.0009	0.0212	0.0007	5
1.148	0.0207	0.0002	0.0188	0.0004	0.0204	0.0003	6
2.273	0.0199	0.0002	0.0182	0.0001	0.0197	0.0002	7
3.398	0.0193	0.0002	0.0178	0.0001	0.0192	0.0002	8
4.523	0.0187	0.0002	0.0173	0.0001	0.0188	0.0002	9
5.648	0.0183	0.0002	0.0170	0.0001	0.0184	0.0002	10
6.773	0.0180	0.0002	0.0167	0.0001	0.0181	0.0002	11
7.898	0.0177	0.0002	0.0165	0.0001	0.0179	0.0002	12
9.023	0.0175	0.0002	0.0163	0.0001	0.0177	0.0002	13
10.148	0.0173	0.0002	0.0161	0.0001	0.0175	0.0002	14
11.273	0.0172	0.0002	0.0159	0.0001	0.0174	0.0002	15
12.398	0.0170	0.0002	0.0158	0.0001	0.0172	0.0002	16
13.523	0.0169	0.0002	0.0157	0.0001	0.0171	0.0002	17
14.648	0.0168	0.0002	0.0156	0.0001	0.0171	0.0002	18
15.773	0.0167	0.0002	0.0155	0.0001	0.0170	0.0002	19
16.898	0.0166	0.0002	0.0154	0.0001	0.0169	0.0002	20
18.023	0.0165	0.0002	0.0153	0.0001	0.0169	0.0002	21
19.148	0.0165	0.0002	0.0153	0.0001	0.0168	0.0002	22
20.273	0.0164	0.0002	0.0152	0.0001	0.0167	0.0002	23
21.398	0.0163	0.0002	0.0151	0.0001	0.0167	0.0002	24

<sup>a</sup>Set 1: 15 stopped-flow repetitions.

<sup>b</sup>Set 2: 15 stopped-flow repetitions.

<sup>c</sup>Set 3: 20 stopped-flow repetitions.

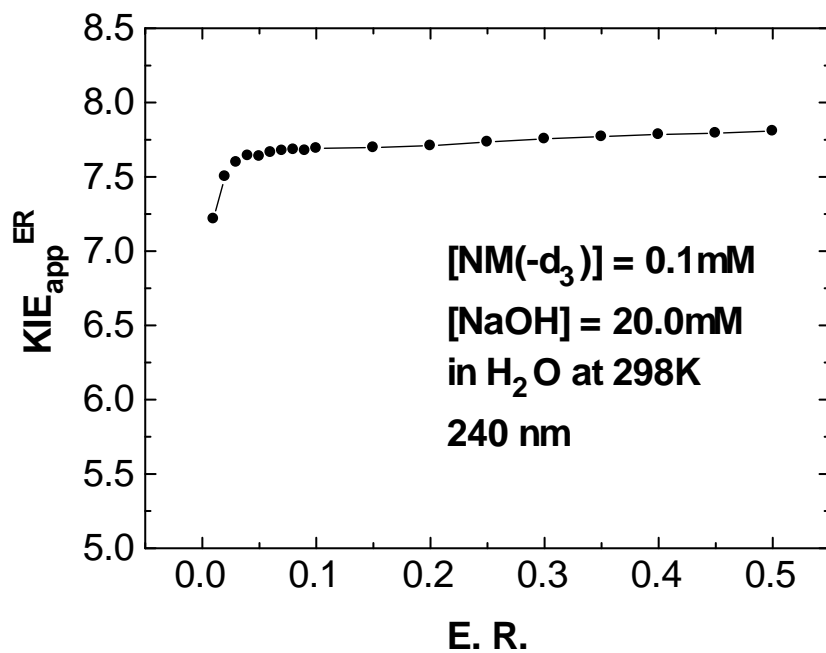


Figure S1. Apparent KIE for the reactions of NM and NM-d<sub>3</sub> in H<sub>2</sub>O at 298K as a function of degree of conversion.

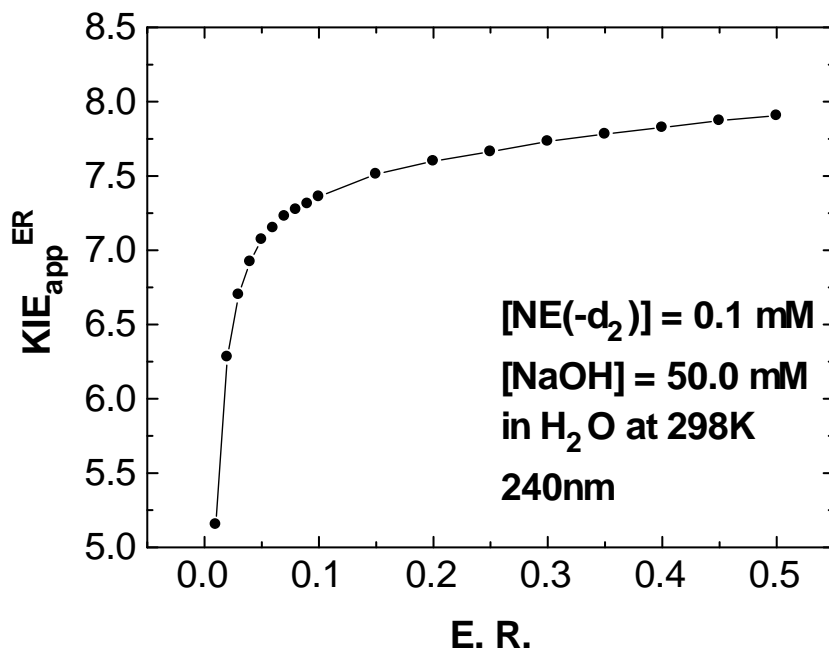
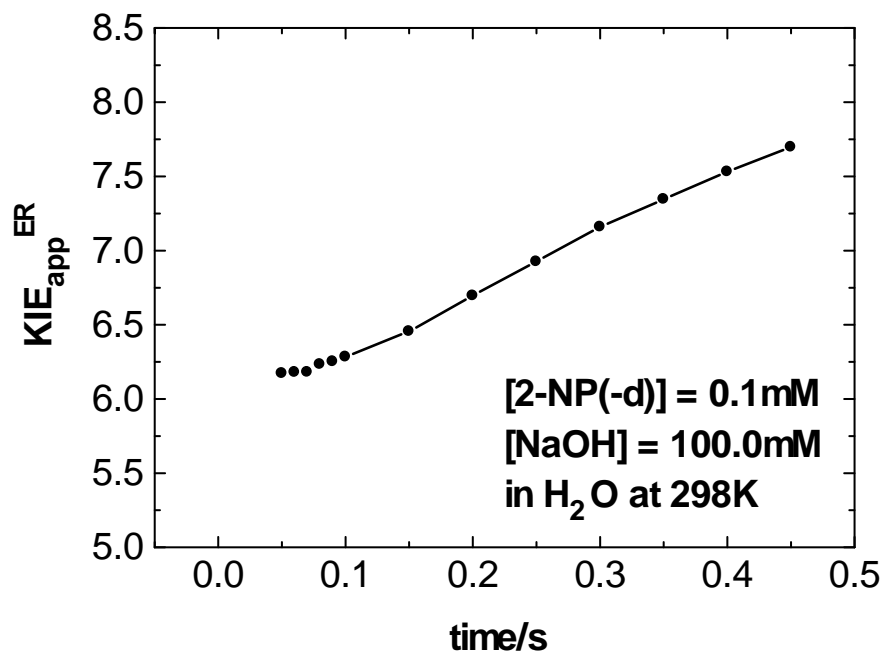
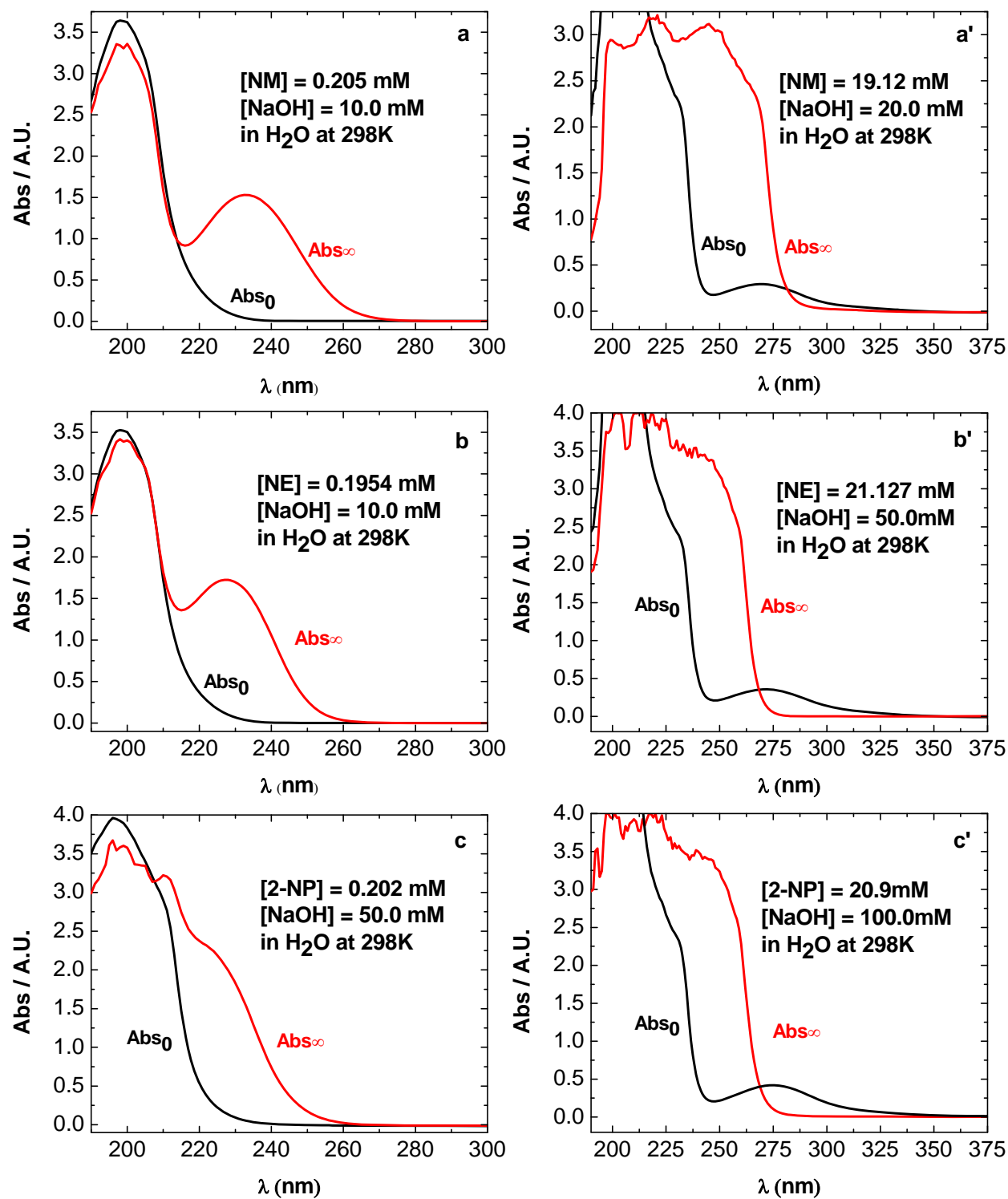


Figure S2. Apparent KIE for the reactions of NE and NE-d<sub>2</sub> in H<sub>2</sub>O at 298K as a function of degree of conversion.



**Figure S3. Apparent KIE for the reactions of 2-NP and 2-NP-d<sub>1</sub> in H<sub>2</sub>O at 298K as a function of degree of conversion.**



	Product Absorption		Reactant Absorption	
	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ (M <sup>-1</sup> cm <sup>-1</sup> )	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ (M <sup>-1</sup> cm <sup>-1</sup> )
NM	234	7310	269	15.9
NE	229	8347	272	17.7
2-NP	224	9779	275	19.5

Figure S4. UV absorption spectra for the reactions of NM (a, a'), NE (b, b'), 2-NP (c, c') with OH<sup>-</sup> in H<sub>2</sub>O under the conditions as shown.



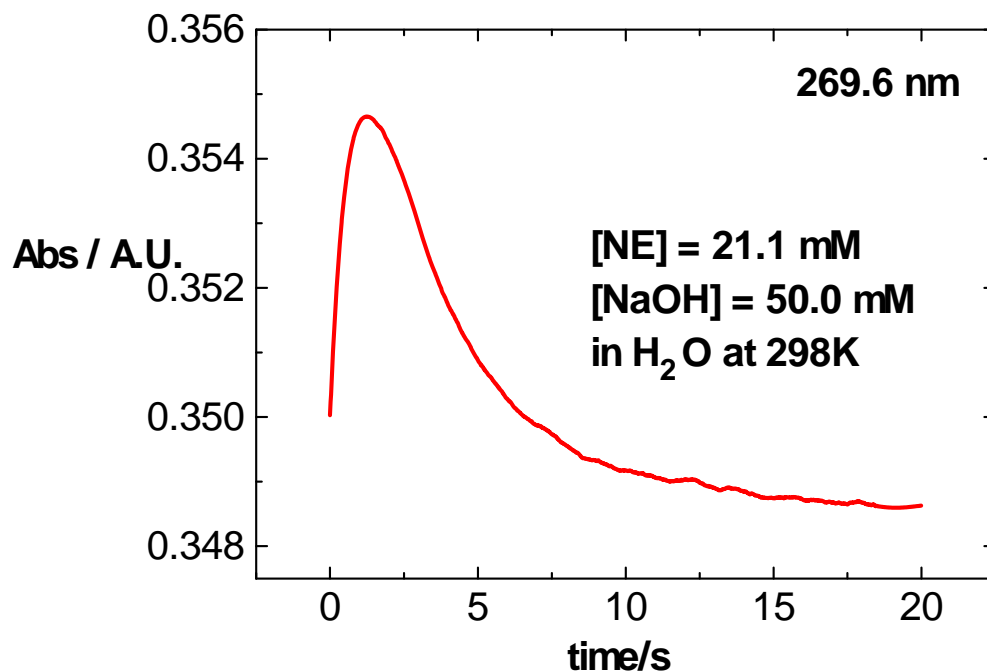


Figure S5. Absorbance – time profile at the isosbestic point near 269.6 nm for the reaction of NE (21.1 mM) with hydroxide ion (50.0 mM) in H<sub>2</sub>O at 298K.

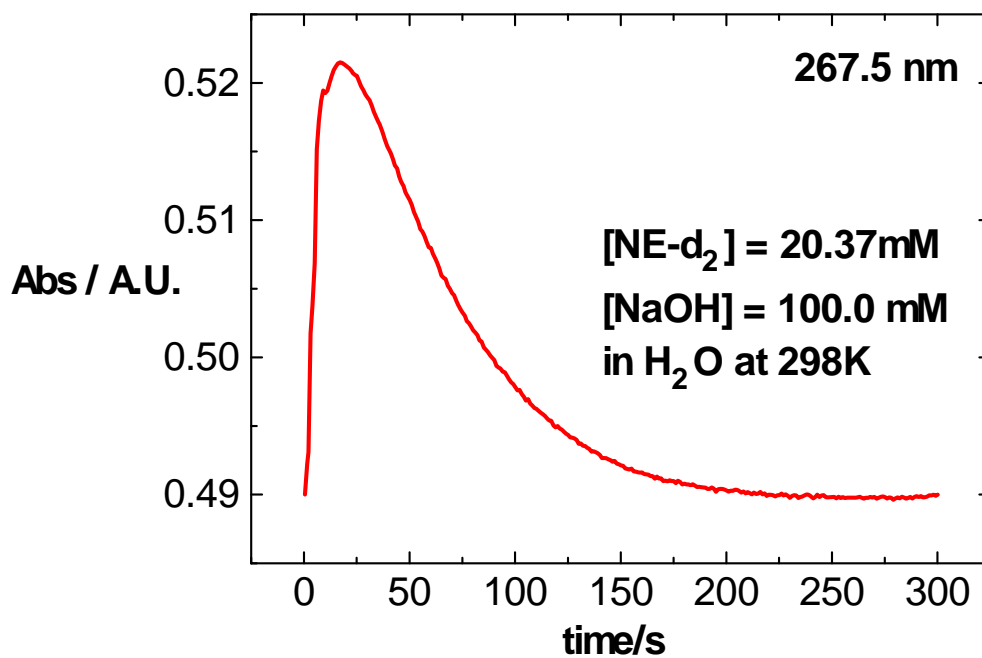


Figure S6. Absorbance – time profile at the isosbestic point near 267.5 nm for the reaction of NE-d<sub>2</sub> (20.37 mM) with hydroxide ion (100.0 mM) in H<sub>2</sub>O at 298K.

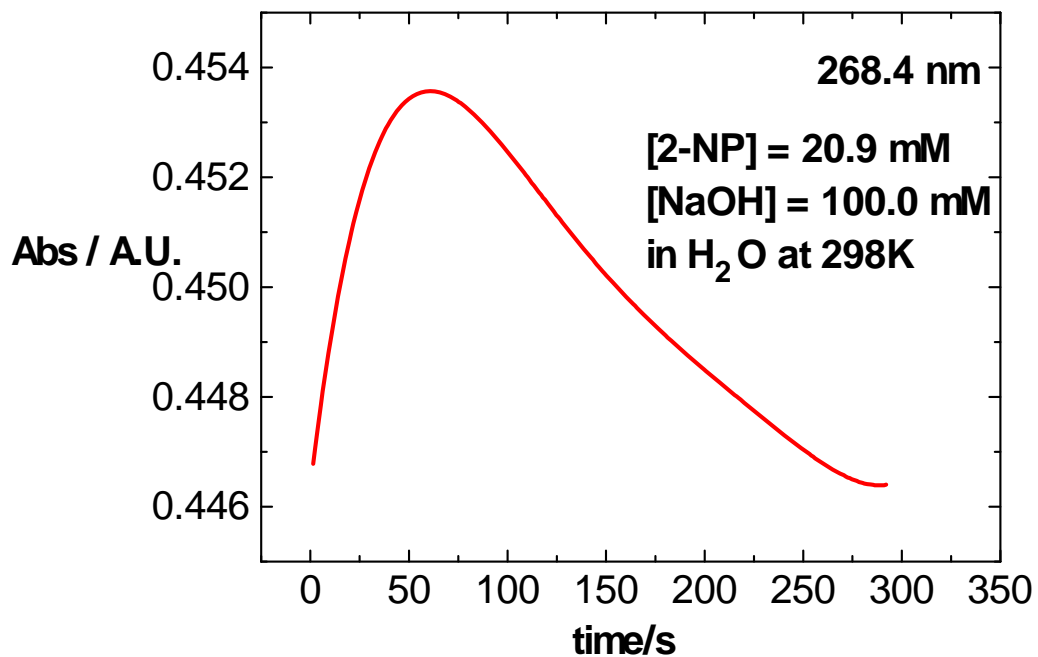


Figure S7. Absorbance – time profile at the isosbestic point near 268.4 nm for the reaction of 2-NP (20.9 mM) with hydroxide ion (100.0 mM) in H<sub>2</sub>O at 298K

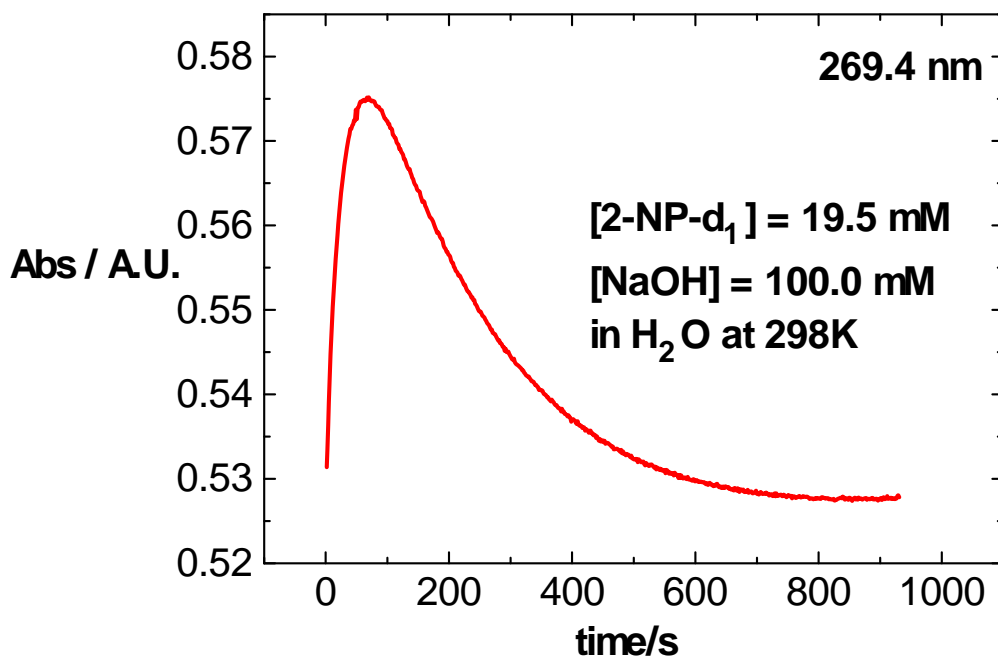


Figure S8. Absorbance – time profile at the isosbestic point near 269.4 nm for the reaction of 2-NP-d<sub>1</sub> (19.5 mM) with hydroxide ion (100.0 mM) in H<sub>2</sub>O at 298K.

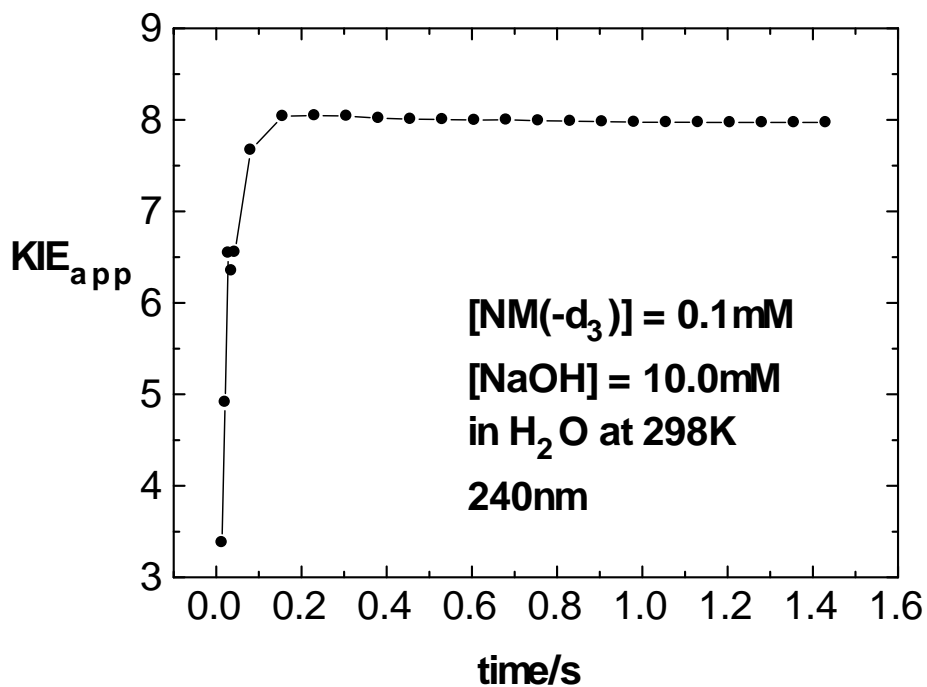


Figure S9. Apparent KIE for the reactions of NM and NM-d<sub>3</sub> in H<sub>2</sub>O at 298K as a function of reaction time.

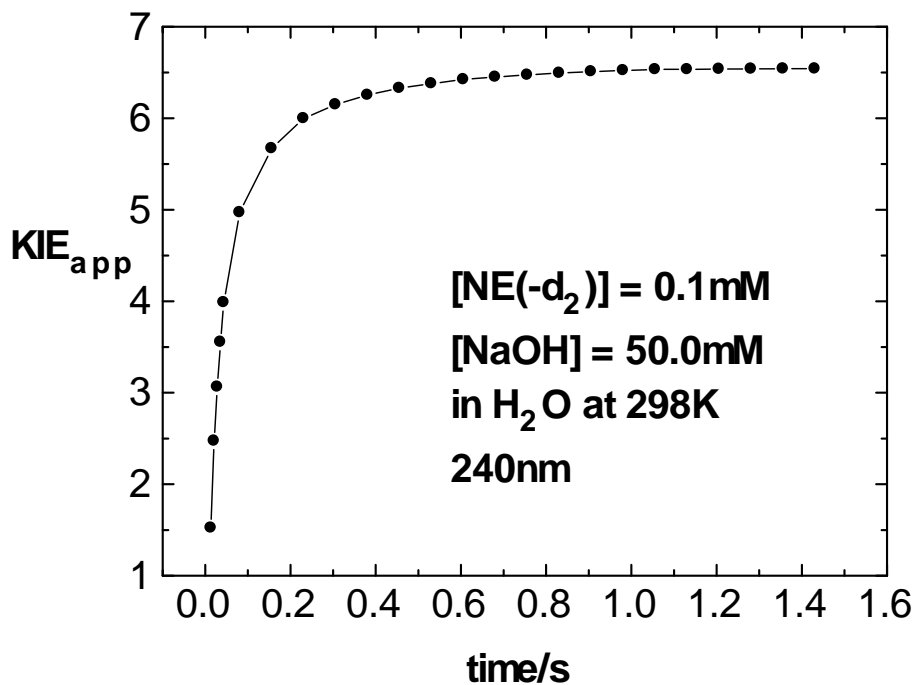
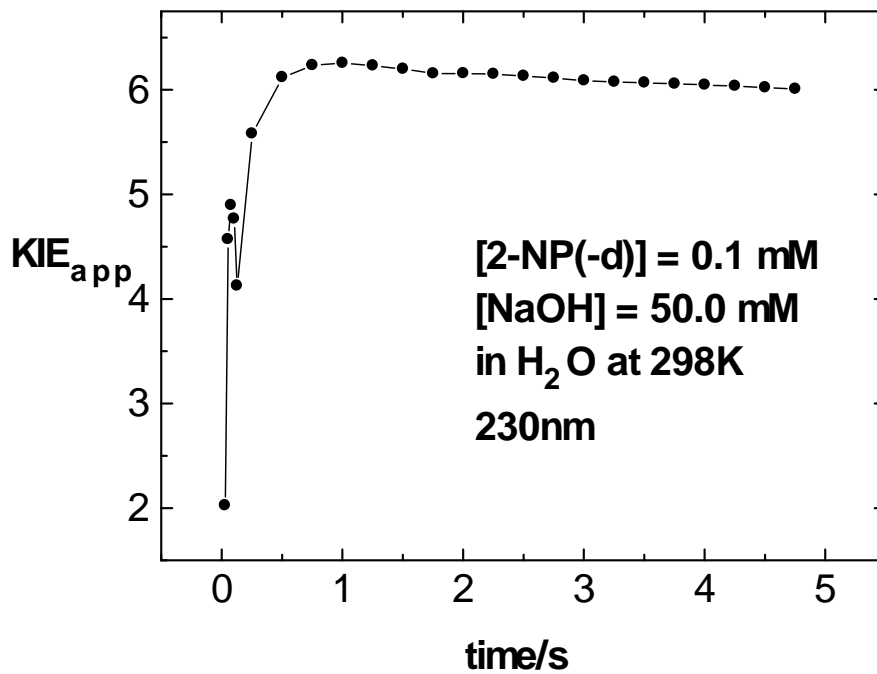


Figure S10. Apparent KIE for the reactions of NE and NE-d<sub>2</sub> in H<sub>2</sub>O at 298K as a function of reaction time.



**Figure S11.** Apparent KIE for the reactions of 2-NP and 2-NP-d<sub>1</sub> in H<sub>2</sub>O at 298K as a function of reaction time.