Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information

Accelerated thermal reaction kinetics by indirect microwave heating of a microwave-transparent substrate

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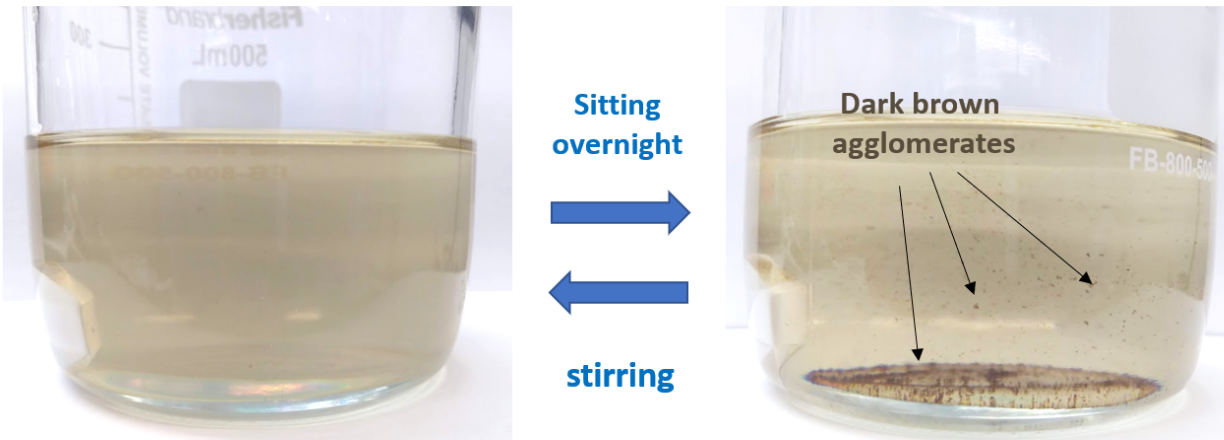
Aggregation of pNA in mesitylene:

We observed formation of brown particles in the solution A after sitting overnight; pure pNA has a soft beige color. These particulates redissolved within a few seconds of stirring at room temperature (Figure S1), with solution A remaining macroscopically homogeneous throughout the high-temperature aryl Claisen rearrangement experiments.

Figure S1. Agglomerate formation in solution A



Procedures for Microwave and Conventional Heating Experiments

Microwave experiments were carried out in a CEM Discover SP system equipped with a fiber optic temperature control assembly. The temperatures were monitored using the fiber optic probe, with the probe inserted into the reaction mixture in a sapphire thermowell. This option allows for measuring the internal temperature up to 250°C. The reactor has a self-tuning, single-mode cavity, which allows for focused and consistent wattages to be supplied while eliminating any positional sensitivity or reflected power issues. The reactor is capable of supplying constant power in 1 W increments from 0 to 300 W. It has an automated power control so that a constant reaction temperature can be automatically maintained throughout the reaction. The microwave is equipped with an active air-cooling system that can be used to remove heat from the sample by constant flow of air in a controlled manner. The reactor is also capable of doing dynamic power cycling, whereby cycling between a specified high and low temperature can be performed at a fixed power. In this configuration, the power is on during the heating phase of the cycle and off during the cooling phase of the cycle. The reaction vessel used for our experiment was a 10 mL quartz tube. A quartz vessel was used because it absorbs very little microwave radiation.

Conventional experiments were performed in a pre-heated insulated silicon oil bath at desired temperatures set by an external fiber optic probe which was verified to be consistent with the microwave fiber optic probe (see Table S1). All reactions were performed in oven-dried 10 mL reaction vessels. Aliquots (0.2 mL) were taken immediately following the reaction period followed by dissolving in $CDCl_3$ (0.40 mL) for ^1H NMR analysis. Baselines in all NMRs were corrected using full auto (Whittaker Smoother) prior to integration to ensure consistent results. The methylene peak of diphenylmethane (internal standard) and allylic protons of ANE were used for monitoring reaction progress.

To make sure that the temperature readings are consistent in MW and CH condition, both fiber optic probes were inserted into a preheated oil bath at 160 °C (Figure S2). The oil bath was allowed to cool down while recoding the temperatures of both instruments (Table S1).

Figure S2. Experiment setup for measuring temperature of an oil bath cooling from 160 °C using fiber optic probes of CEM MW instrument and yellow fiber optic used for conventional heating experiments.

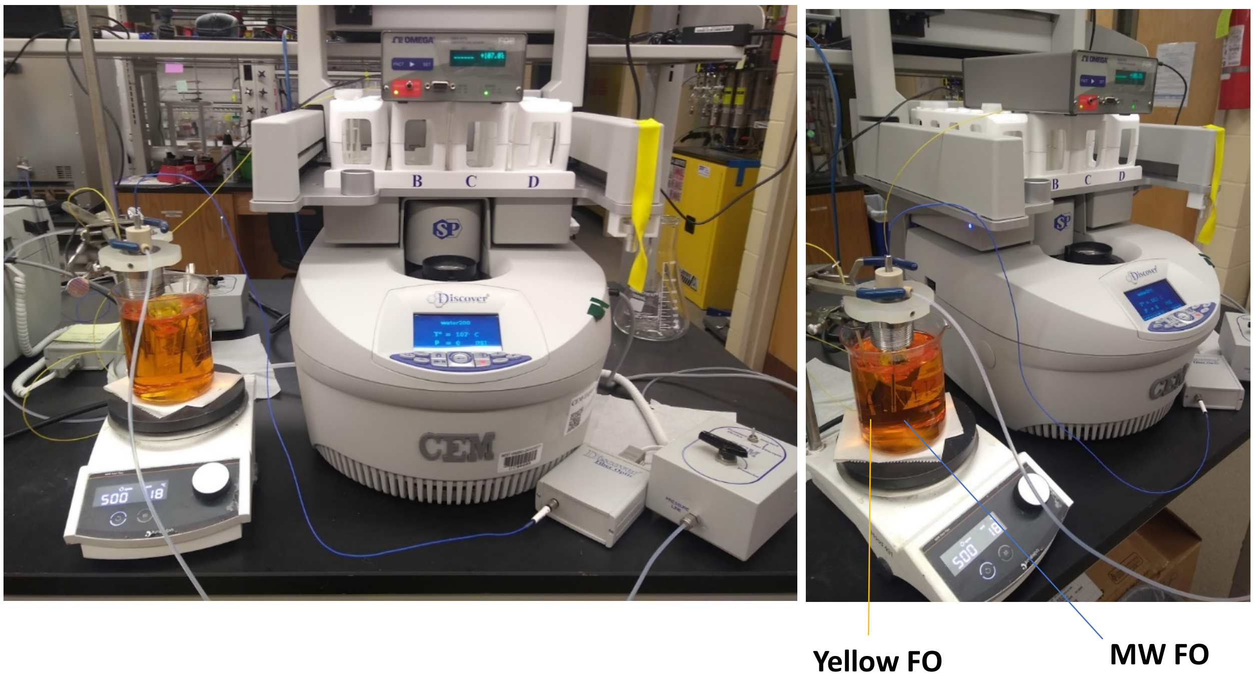
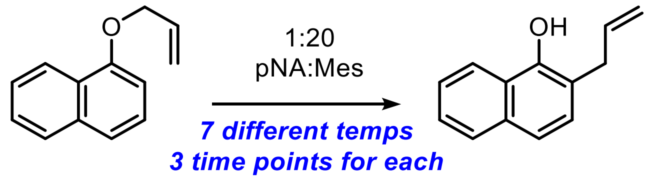


Table S1. Temperature readings of MW and CH fiber optic instruments

MW FO temp (°C)	CH FO temp range (°C)			MW FO temp (°C)	CH FO temp range (°C)		
160	160.3	-	159.3	139	139.3	-	138.5
159	159.3	-	158.3	138	138.5	-	137.2
158	158.3	-	157.3	137	137.2	-	136.4
157	157.3	-	156.2	136	136.4	-	135.5
156	156.2	-	155.3	135	135.5	-	134.4
155	155.3	-	154.1	134	134.4	-	133.5
154	154.1	-	153.1	133	133.5	-	132.2
153	153.1	-	152.2	132	132.2	-	131.4
152	152.2	-	151.2	131	131.4	-	130.4
151	151.2	-	150.2	130	130.4	-	129.4
150	150.2	-	149.3	129	129.4	-	128.4
149	149.3	-	148.2	128	128.4	-	127.4
148	148.2	-	147.2	127	127.4	-	127.4
147	147.2	-	146.4	126	127.4	-	126.4
146	146.4	-	145.2	125	126.4	-	125.5
145	145.2	-	144.3	124	125.5	-	124.5
144	144.3	-	143.1	123	124.5	-	123.5
143	143.1	-	142.3	122	123.5	-	122.5
142	142.3	-	141.4	121	122.5	-	121.5
141	141.4	-	140.2	120	121.5	-	120.5
140	140.2	-	139.3				

General Procedure for Conventional Heating Kinetic Experiments



To obtain the kinetic data, the thermal reaction of ANE in 1:20 pNA:Mes was carried out in silicon oil bath, heated on a temperature controlled Heidolph hotplate with the temperature controlled to within ±1 °C by an integrated controller. The precise reaction temperatures (within ±0.1 °C) were measured by an external fiber optic probe. Kinetic data was collected for seven different temperatures between 130 and 160°C in 5°C increments over a period of 3 hours for four higher temperatures, and 5 hours for the lower ones. At each temperature, three identical samples containing 3.0 mL of solution A were first preheated at 100 °C for 10 minutes before they were inserted into the oil bath, which had been preheated to the desired temperature. It was confirmed that during this time, there was not any observable conversion. In all cases, ramping times to reach the desired temperatures were decreased to less than 5 minutes. Once each experiment was finished, the hot tubes were immediately submerged into a cold water bath to terminate the thermal reaction. This process was performed for three reaction times for each temperature and kinetic data were obtained as follows.

Conversion yields were obtained by quantitative NMR analysis and the average values were used to determine the starting material concentration (Table S2). ^{1}H NMR spectra of the stock solution A and 3 samples at 150 °C after 1, 2, 3h of heating are illustrated in Figure S5. Kinetic plots of the time dependent concentration data collected at different temperatures are shown in Figures S3 (combined) and S4 (separate). The average rate constants obtained from linear squares fit of the linearized data (Ln(ANE) vs time) are given in Table S3.

Figure S3.

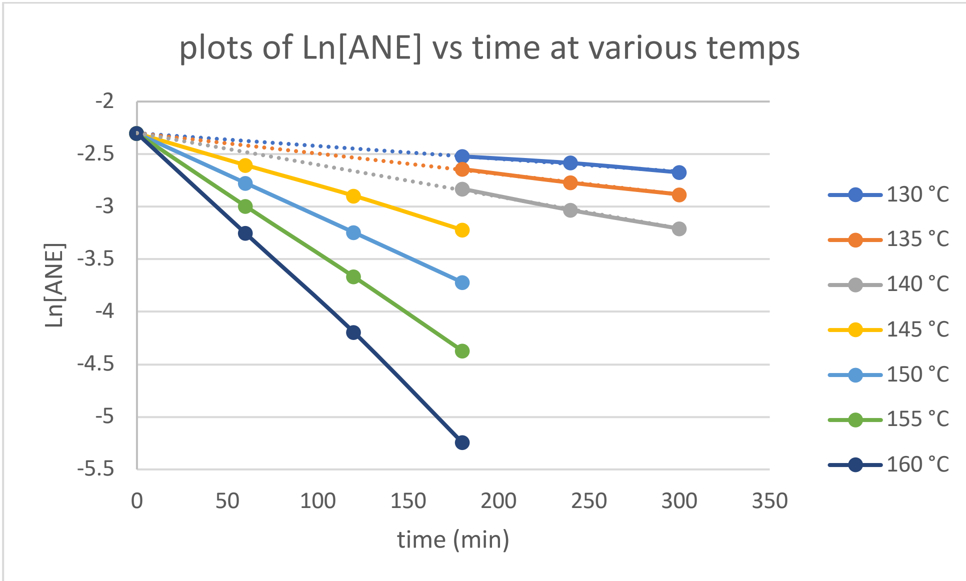
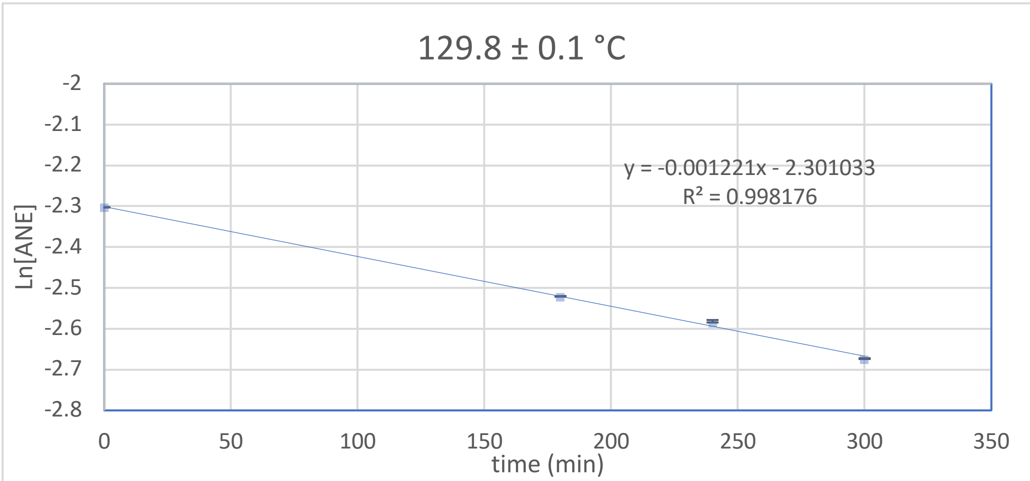
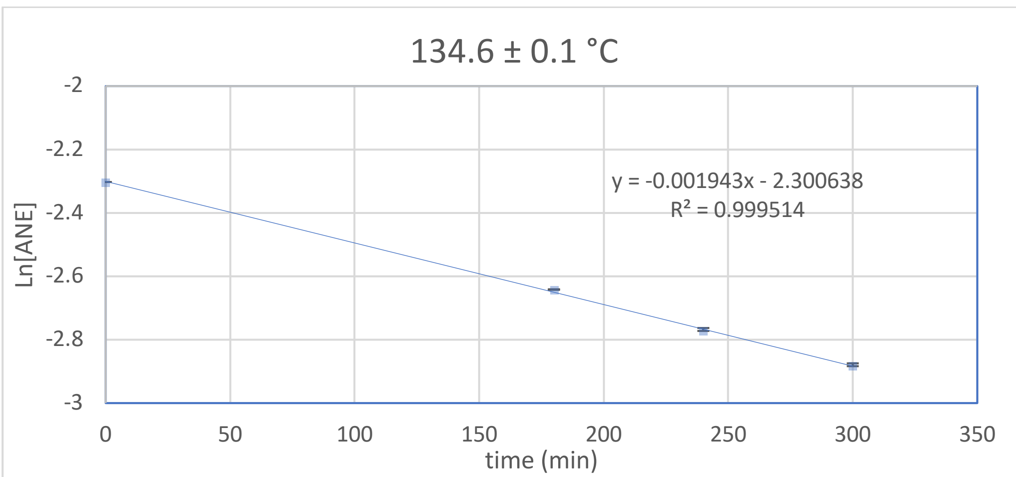

plots of Ln[ANE] vs time at various temps
-2
-2.5
-3
-3.5
-4
-4.5
-5
-5.5
Ln[ANE]
0
50
100
150
200
250
300
350
time (min)
130 °C
135 °C
140 °C
145 °C
150 °C
155 °C
160 °C

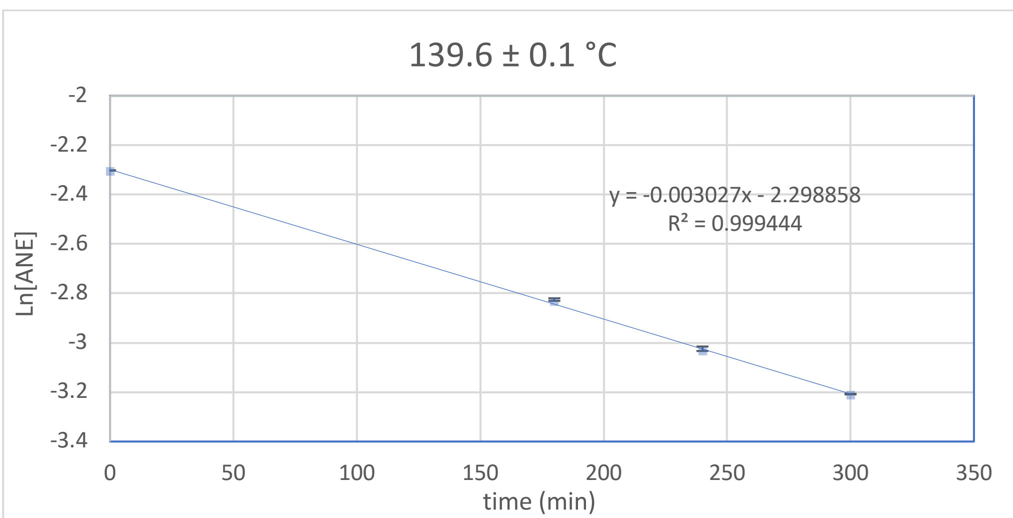
Table S2. change of concentration over time at various temps

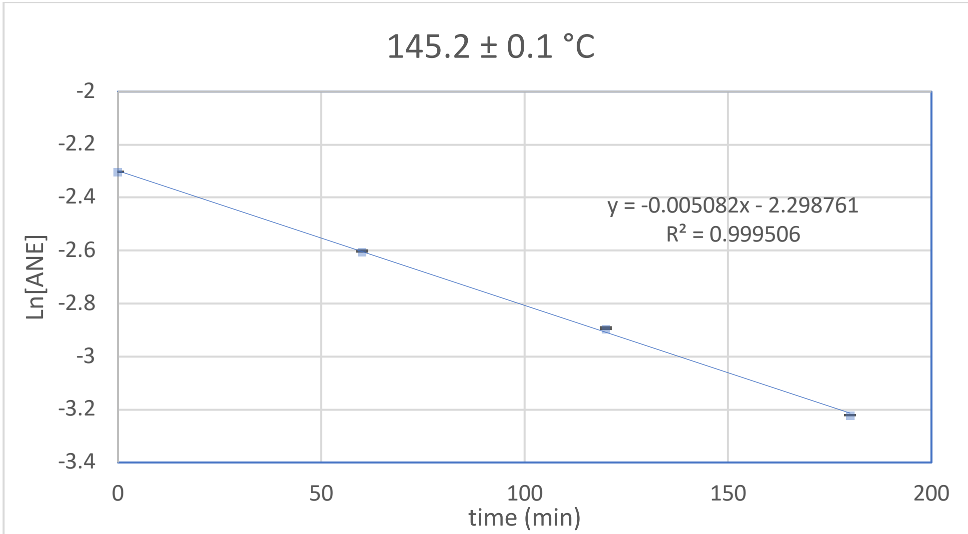
	Duration (min)		Heating Temp (°C) 129.8 ± 0.1	134.6 ± 0.1	139.6 ± 0.1	145.2 ± 0.1	149.9 ± 0.1	155.1 ± 0.1	160.0 ± 0.1
[ANE] (×10^{-3} M)	0		100.0	100.0	100.0	100.0	100.0	100.0	100.0
	60	1	-	-	-	73.61	62.27	49.57	37.65
		2	-	-	-	74.48	61.97	50.36	38.53
		3	-	-	-	73.82	62.86	50.28	39.75
		Ave (± σ)	-	-	-	73.97 (± 0.37)	62.37 (± 0.37)	50.07 (± 0.36)	38.64 (± 0.86)
	120	1	-	-	-	54.69	38.44	25.54	12.01
		2	-	-	-	55.34	39.85	25.56	12.37
		3	-	-	-	55.64	38.60	25.53	15.31
		Ave (± σ)	-	-	-	55.22 (± 0.39)	38.96 (± 0.63)	25.54 (± 0.01)	13.23 (± 0.20)
	180	1	80.23	71.01	59.25	39.92	24.30	12.5	5.330
		2	80.51	71.31	59.58	39.89	24.26	12.70	5.055
		3	80.27	71.12	58.12	39.86	24.12	12.67	5.430
		Ave (± σ)	80.34 (± 0.12)	71.17 (± 0.12)	58.98 (± 0.62)	39.89 (± 0.02)	24.23 (± 0.08)	12.62 (± 0.09)	5.272 (± 0.16)
	240	1	75.92	62.01	49.24	-	-	-	-
		2	75.53	63.33	48.11	-	-	-	-
		3	74.80	62.20	47.11	-	-	-	-
		Ave (± σ)	75.42 (± 0.46)	62.51 (± 0.58)	48.15 (± 0.87)	-	-	-	-
	300	1	68.79	55.49	40.48	-	-	-	-
		2	68.97	55.67	40.35	-	-	-	-
		3	69.13	56.64	40.40	-	-	-	-
		Ave (± σ)	68.96 (± 0.14)	55.93 (± 0.50)	40.41 (± 0.05)	-	-	-	-

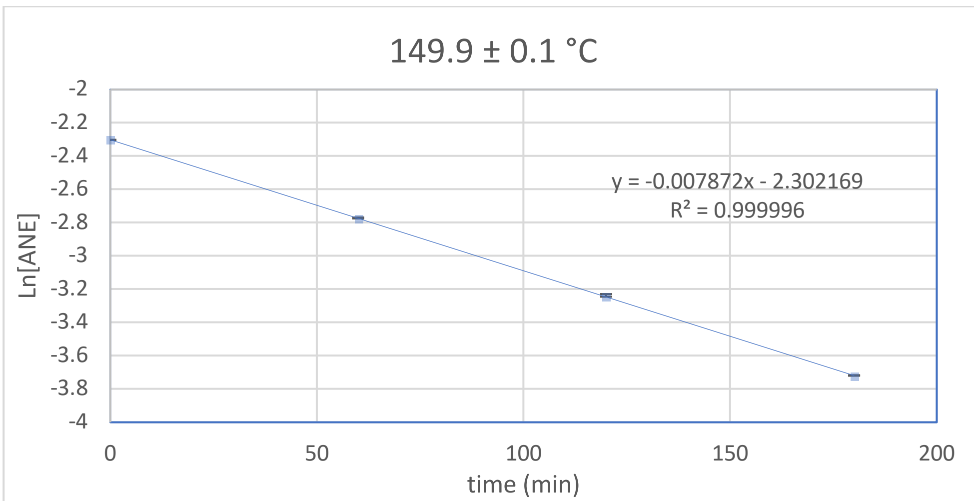
Figure S4. Plots of Ln[ANE] against time to obtain rate constants at various temps

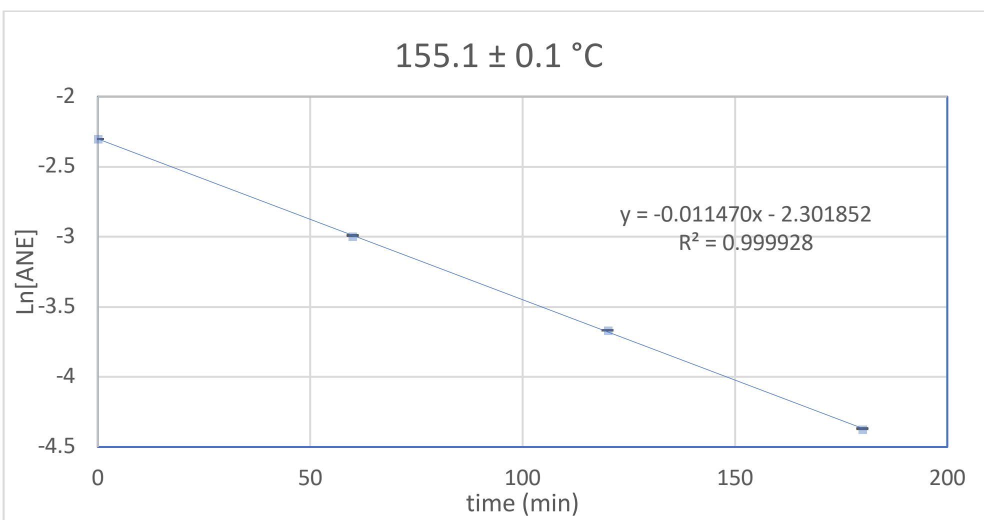







145.2 ± 0.1 °C
y = -0.005082x - 2.298761
R² = 0.999506
Ln[ANE]
time (min)
-2
-2.2
-2.4
-2.6
-2.8
-3
-3.2
-3.4
0
50
100
150
200


149.9 ± 0.1 °C
y = -0.007872x - 2.302169
R² = 0.999996
Ln[ANE]
time (min)
-2
-2.2
-2.4
-2.6
-2.8
-3
-3.2
-3.4
-3.6
-3.8
-4
0
50
100
150
200


155.1 ± 0.1 °C
y = -0.011470x - 2.301852
R² = 0.999928
Ln[ANE]
time (min)
-2
-2.5
-3
-3.5
-4
-4.5
0
50
100
150
200

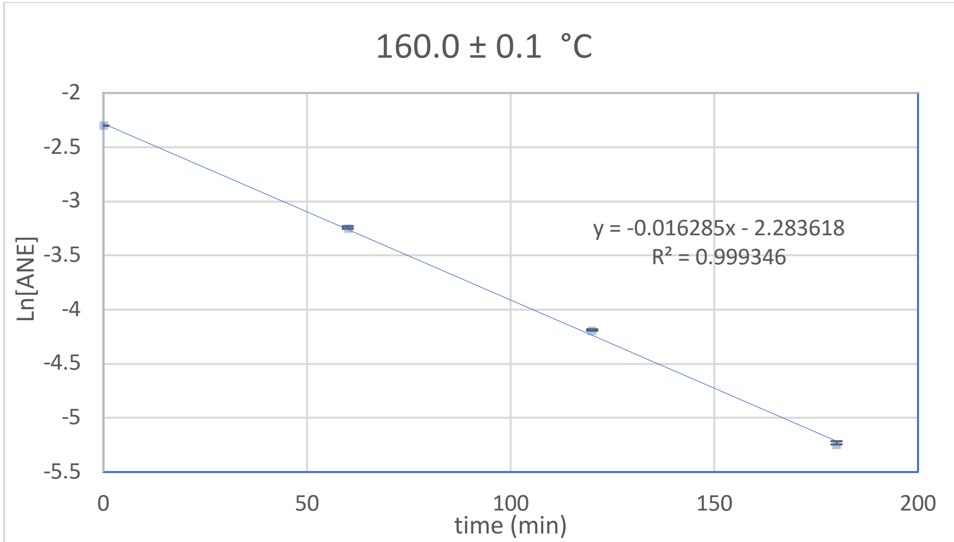
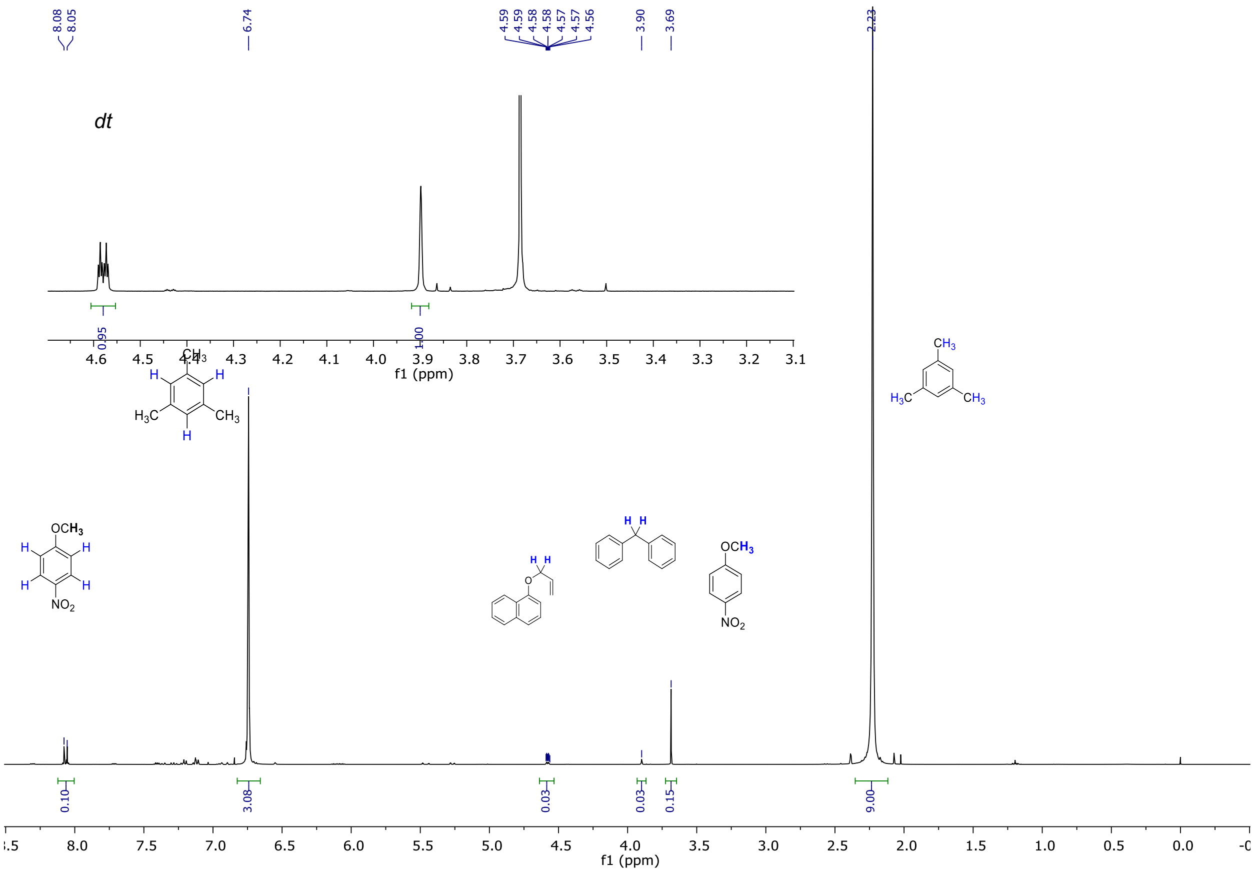


Table S3. Average rate constants at various temps

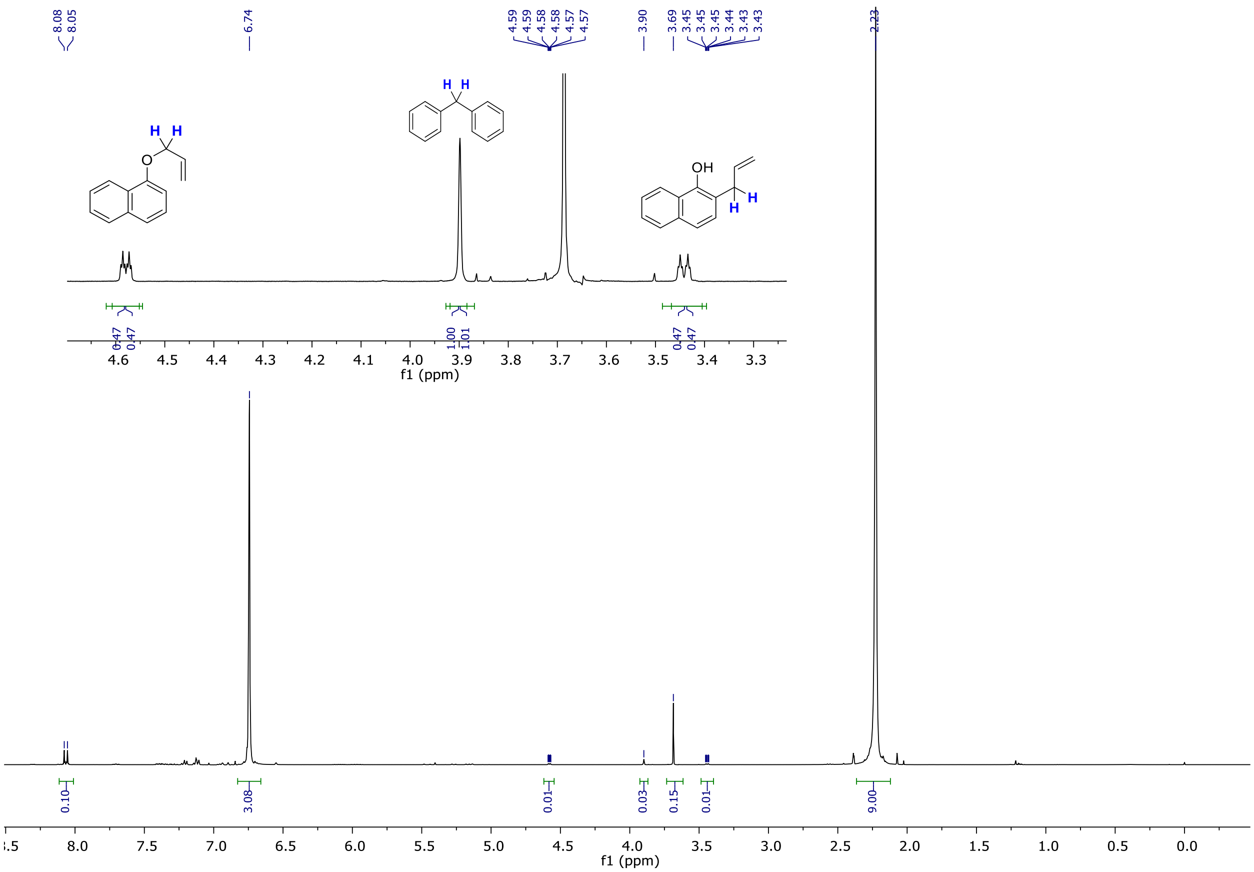
Temp (°C)	k (×10^{-3}) (min^{-1})	R^2	Stnd. Dev (×10^{-3})	95% Confidence Interval (×10^{-3})
130	1.220	0.99817636	0.037	0.036
135	1.942	0.99951432	0.030	0.029
140	3.027	0.99944405	0.050	0.049
145	5.082	0.99950576	0.080	0.078
150	7.872	0.99999619	0.011	0.010
155	11.47	0.99992821	0.07	0.07
160	16.28	0.99934588	0.29	0.29

Figure S5. Samples of ^{1}H NMR spectra for: a) stock solution A; solutions after b) 1h; c) 2h; and d) 3h at 150 °C in oil bath

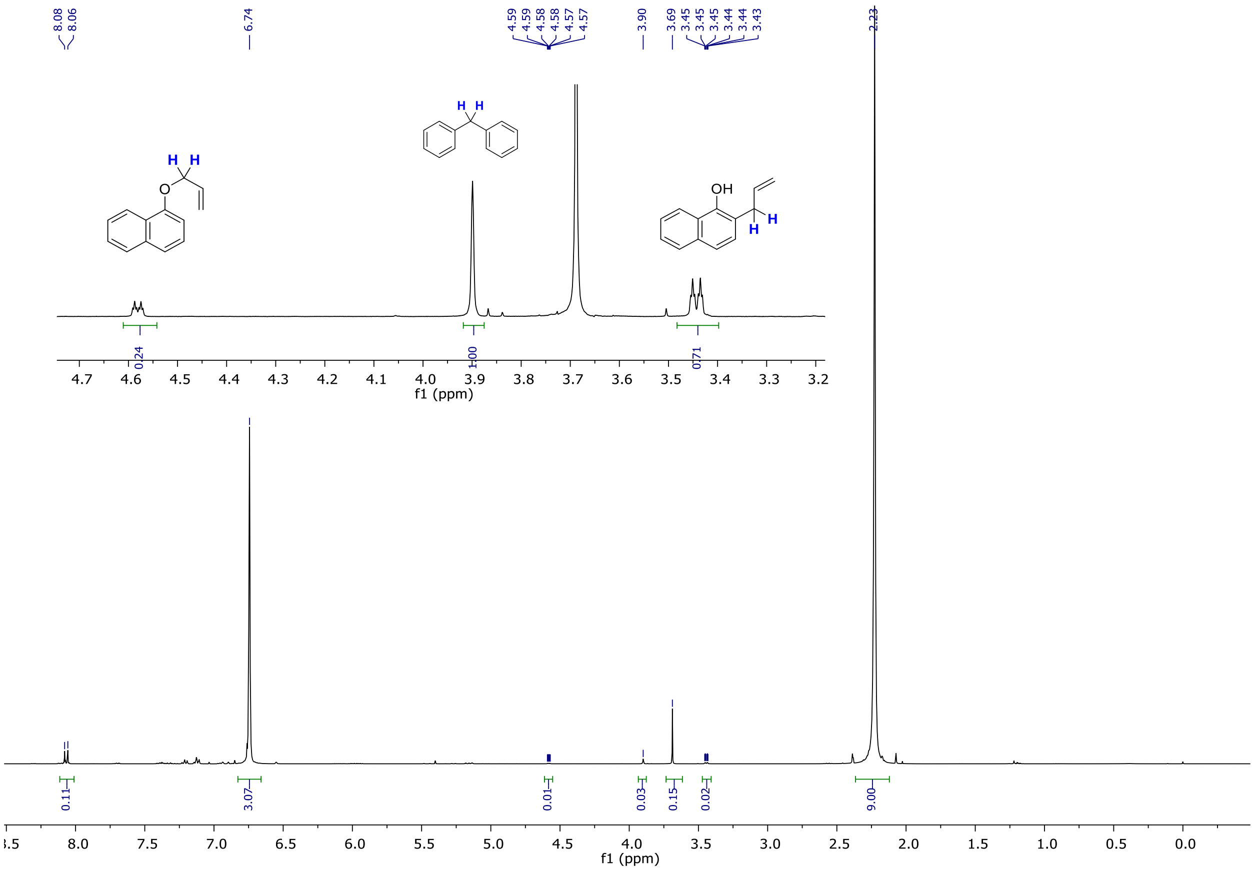
a)



b)

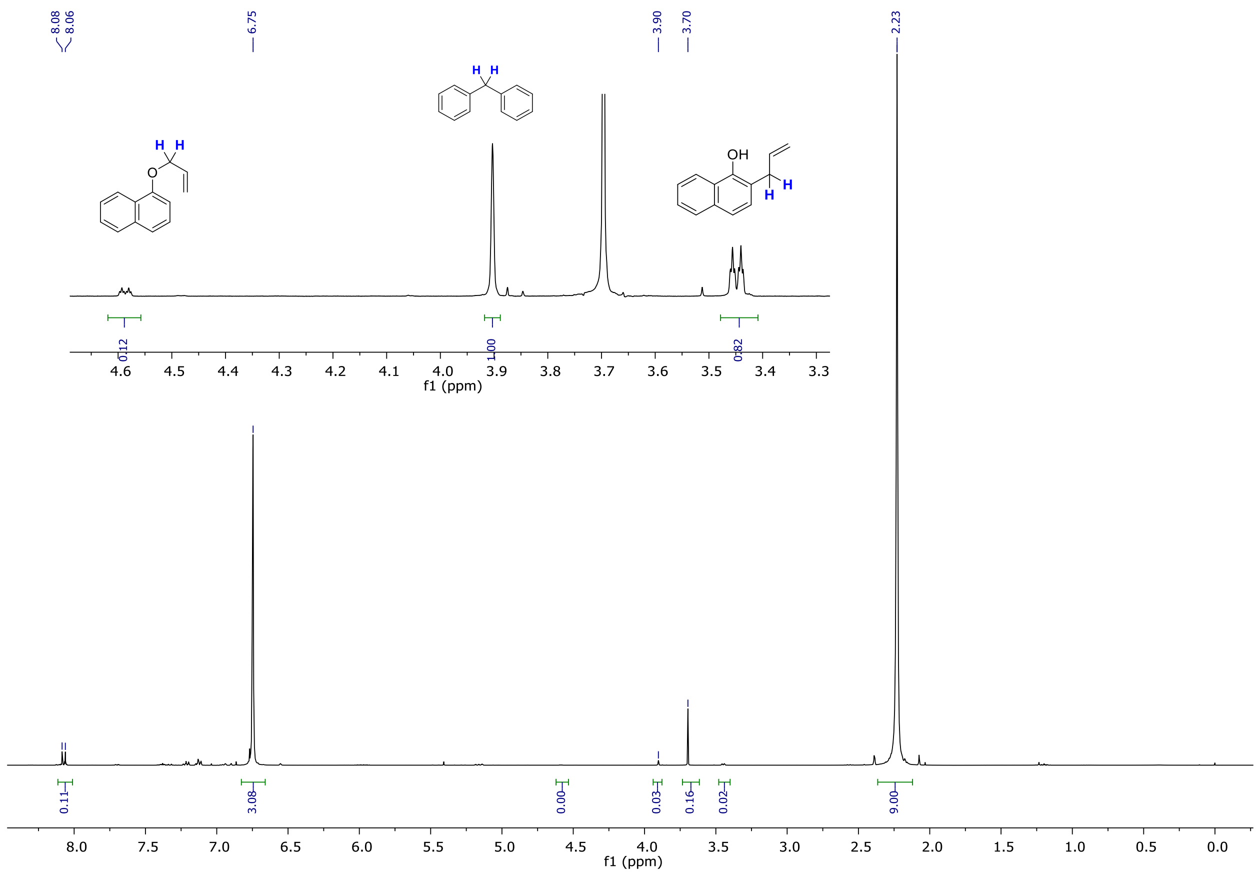

8.08
8.05
6.74
4.59
4.59
4.58
4.58
4.57
4.57
3.90
3.69
3.45
3.45
3.45
3.44
3.43
3.43
2.23
OH
0.47
0.47
1.00
1.01
0.47
0.47
f1 (ppm)
0.10
3.08
0.01
0.03
0.15
0.01
9.00
f1 (ppm)

c)



8.08
8.06
6.74
4.59
4.59
4.58
4.58
4.57
4.57
3.90
3.69
3.45
3.45
3.45
3.44
3.44
3.43
2.23
OH
0.24
1.00
0.71
f1 (ppm)
0.11
3.07
0.01
0.03
0.15
0.02
9.00
f1 (ppm)

d)



8.08
8.06
6.75
3.90
3.70
2.23
OH
H
H
0.12
1.00
0.82
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
f1 (ppm)
0.11
3.08
0.00
0.03
0.16
0.02
9.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

Finally, the natural logs of the average rate constants at each temperature were plotted against inverse absolute temperatures to obtain activation energy and exponential factor of the Arrhenius equation. (Figure S6 and Table S4)

Figure S6. Plot of logarithmic rate constants versus T^{-1}

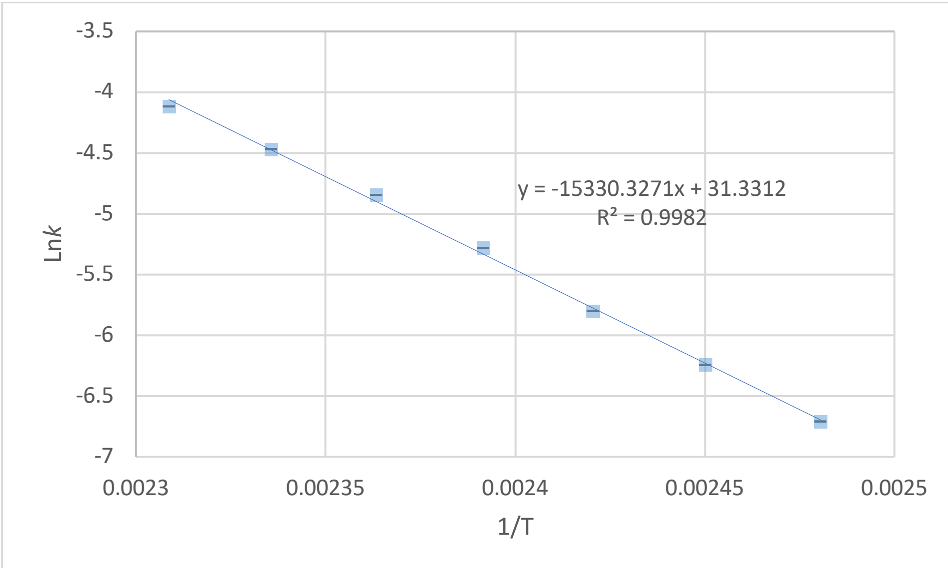


Table S4. Least square results for Arrhenius analysis of ANE rearrangement

	quantity	Std. dev.	95% Conf. Interval	R^2
Slope	-15330.33	287.45	212.94	0.998245
Intercept	31.33	0.69	0.51	
E_a	**127.46 kJ.mol^{-1}**	**2.39 kJ.mol^{-1}**		
A	**4.05 × 10^{13} min^{-1}**	**3.01 × 10^{13} min^{-1}**		

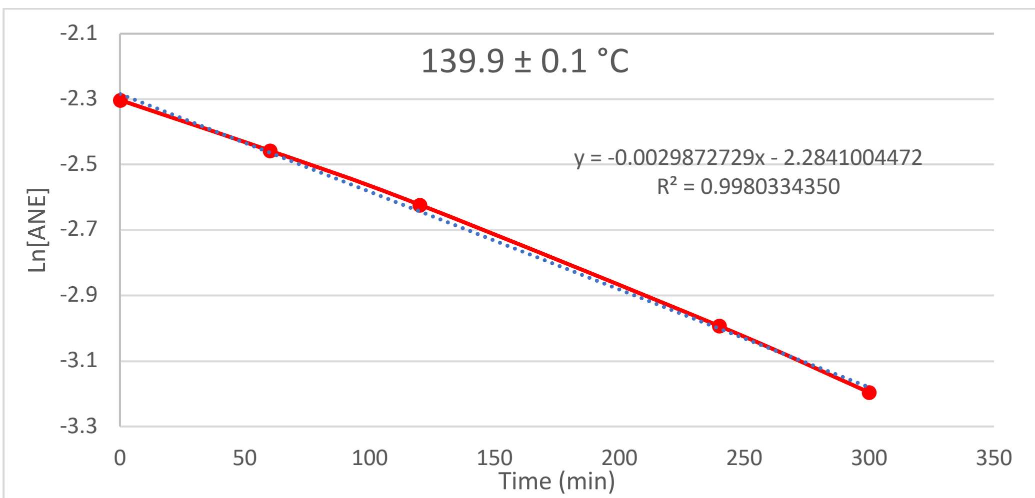
Conventional heating in absence of pNA:

Table S5. conversion yields and rate constants for two sets of experiments at 140 and 150 °C in absence of pNA in oil bath.

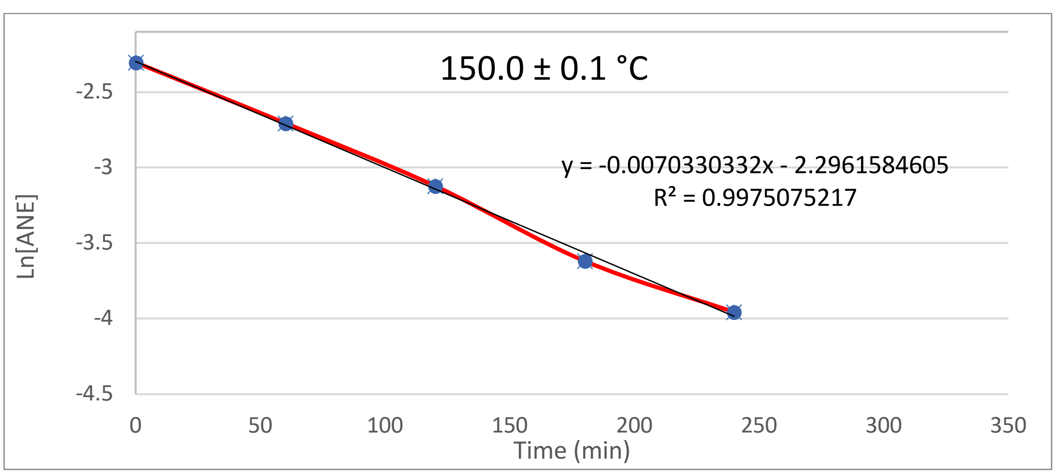
Temp (°C)	Conversion yields (%)				*k* (×10^{-3}) (min^{-1})
150	60 min	120 min	180 min	240 min	7.033
	33.09	55.86	73.14	80.86	
140	60 min	120 min	240 min	300 min	2.987
	14.34	27.37	49.87	59.07	

Figure S7. Plots of Ln[ANE] against time in absence of pNA at a) 140 °C; b) 150 °C

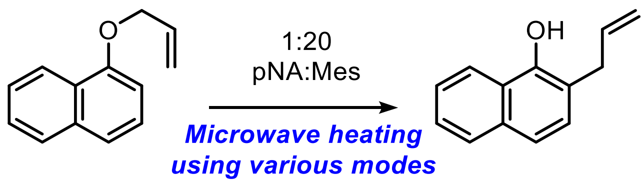
a)



b)



General Procedure for Microwave Heating Experiments



Microwave experiments were conducted using pulsed heating and fixed temperature modes. For closed vessel experiments, Identical samples containing 3.0 mL of solution A, and for open vessel experiments, 30 mL samples were prepared. In each experiment, predicted conversion yield was calculated by determining the extent of the reaction that would be expected if the same temperature profile were produced using thermal pulses, following the kinetic data. This was done by calculating the expected extent of thermal conversion for every second of the experiment and then summing over the total number of seconds to produce an expected thermal conversion and an integrated average temperature or so-called “effective temperatures”.

$$k_n = \mathrm{A}e^{-\mathrm{E_a}/\mathrm{RT_n}}$$
$$[\mathrm{ANE}]_\mathrm{n} = \text{concentration of ANE at t} = \mathrm{n};$$
$$\ln[\mathrm{ANE}]_\mathrm{n} = \ln[\mathrm{ANE}]_{\mathrm{n}-1} - k_n(\mathrm{t_n} - \mathrm{t_{n-1}})$$
$$\text{since } \mathrm{t_n} - \mathrm{t_{n-1}} = 1$$
$$\ln[\mathrm{ANE}]_\mathrm{n} - \ln[\mathrm{ANE}]_{\mathrm{n}-1} = -k_n = -\mathrm{A}e^{-\mathrm{E_a}/\mathrm{RT_n}}$$
$$\ln(1 - 0.01\mathrm{x}) = -\sum_{\mathrm{n}=1}^{\mathrm{f}} \mathrm{A}e^{-\mathrm{E_a}/\mathrm{RT_n}}$$
$$\mathrm{x} = \text{conversion yield (\%)}$$

Pulsed heating microwave experiments:

Pulsed heating experiments were performed in various temperature ranges, amounts of applied power, and number of cycles. The maximum number of cycles and applied power available in the CEM instrument are 300 cycles and 300W respectively. The lower value in the temperature ranges for all experiments were set to 50 °C while the higher value varied from 130 to 150 °C. To investigate the effect of power, three different amounts of fixed power were applied: 50, 100, and 300W. For 900 cycles, the experiment was repeated twice after the first run. Results are summarized in Table S6.

Table S6. Results of microwave pulsed heating experiments under closed vessel condition

Entry		Temp. Range (°C)	Power (W)	Duration (mins)	Number of Cycles	Min-Max Temp (°C)	Ave Temp (°C)	Actual yield (%)	Predicted yield (%)	Actual – Predicted (%)	k_{eff}/k_{CH}	k_{MW}/k_{CH}
1	a	50-130	300	639.2	300	49 – 137	86.44	21.01	15.80	5.21	1.371	3.054
	b	50-130	300	654.8	300	49 – 137	86.66	22.84	16.24	6.60	1.463	3.514
	c	50-130	300	650.3	300	49 – 137	86.37	21.78	15.85	5.93	1.423	3.268
2	a	50-130	100	883.2	300	48 – 131	90.57	24.31	18.43	5.88	1.367	1.649
	b	50-130	100	911.2	300	48 – 131	90.31	21.61	18.93	2.68	1.160	1.295
3	a	50-130	50	1529.7	300	48 – 130	96.34	40.79	34.68	6.11	1.231	1.274
	b	50-130	50	1502.4	300	48 – 130	95.87	41.12	33.50	7.62	1.298	1.362
4	a	50-130	300	1957.3	900	49 – 137	86.79	57.34	41.76	15.58	1.576	3.539
	b	50-130	300	1954.3	900	49 – 137	87.02	59.67	42.48	17.19	1.642	3.856
	c	50-130	300	1932.5	900	49 – 137	86.59	53.89	40.64	13.25	1.484	3.178
5	a	50-140	300	714.2	300	49 – 146	90.37	44.67	33.40	11.27	1.456	2.695
	b	50-140	300	698.1	300	49 – 146	90.38	40.52	32.64	7.88	1.315	2.181
	c	50-140	300	723.0	300	49 – 146	90.41	43.84	33.67	10.17	1.405	2.490
6	a	50-150	300	775.8	300	49 – 155	94.37	69.87	60.19	9.68	1.302	1.683
	b	50-150	300	783.0	300	49 – 155	94.63	69.44	60.86	8.58	1.264	1.598
	c	50-150	300	783.9	300	49 – 155	94.67	71.14	61.14	10.00	1.315	1.689

A sample of Excel work to obtain predicted yields using temperature profile:

Here we show the method used for determining each predicted conversion yield for microwave experiments. To simplify the process, only 130 data points over 130 seconds of the experiment are shown in Table S7. During this time, one cycle of heating and cooling is completed.

Table S7. Excel work for the first 130 seconds of a pulsed heating microwave experiment

Column D formula = 4.05*10^13/60*EXP(-15330.33/(B1+273.15))

Column E formula = E3-D4

Column F formula = EXP(E3)

Column F formula = F3-F4

1	A	B	C	D	E	F	G
2	Time (s)	Temp (C)	Power (W)	k_n =Aexp(Ea/RT$_n$) (s^{-1})	Ln[A]$_n$ = Ln[A]$_{n-1}$ – k_n	[A]$_n$ (M^{-1})	[A]$_n$ – [A]$_{n-1}$ (M^{-1})
3	0				-2.302585093	0.1	
4	1	22	300	1.86938E-11	-2.302585093	0.1	1.86939E-12
5	2	22	300	1.86938E-11	-2.302585093	0.1	1.86939E-12
6	3	23	300	2.22775E-11	-2.302585093	0.1	2.22773E-12
7	4	26	300	3.74386E-11	-2.302585093	0.1	3.74384E-12
8	5	28	300	5.2617E-11	-2.302585093	0.1	5.26171E-12
9	6	33	300	1.20835E-10	-2.302585093	0.1	1.20835E-11
10	7	43	300	5.88934E-10	-2.302585094	0.1	5.88934E-11
11	8	49	300	1.45309E-09	-2.302585095	0.1	1.45309E-10
12	9	55	300	3.46876E-09	-2.302585099	0.099999999	3.46876E-10
13	10	58	300	5.2964E-09	-2.302585104	0.099999999	5.2964E-10
14	11	64	300	1.2072E-08	-2.302585116	0.099999998	1.2072E-09
15	12	71	300	3.04399E-08	-2.302585147	0.099999995	3.04399E-09
16	13	76	300	5.76084E-08	-2.302585204	0.099999989	5.76084E-09
17	14	78	300	7.39765E-08	-2.302585278	0.099999981	7.39765E-09
18	15	82	300	1.20959E-07	-2.302585399	0.099999969	1.20959E-08
19	16	88	300	2.47793E-07	-2.302585647	0.099999945	2.47793E-08
20	17	92	300	3.9449E-07	-2.302586041	0.099999905	3.9449E-08
21	18	95	300	5.55413E-07	-2.302586597	0.09999985	5.55413E-08
22	19	98	300	7.77668E-07	-2.302587374	0.099999772	7.77667E-08
23	20	101	300	1.083E-06	-2.302588457	0.099999664	1.083E-07
24	21	104	300	1.50029E-06	-2.302589958	0.099999514	1.50028E-07
25	22	106	300	1.85906E-06	-2.302591817	0.099999328	1.85905E-07
26	23	109	300	2.55356E-06	-2.30259437	0.099999072	2.55354E-07
27	24	111	300	3.14667E-06	-2.302597517	0.099998758	3.14663E-07
28	25	113	300	3.86915E-06	-2.302601386	0.099998371	3.8691E-07
29	26	116	300	5.25453E-06	-2.302606641	0.099997845	5.25443E-07

30	27	118	300	6.42708E-06	-2.302613068	0.099997203	6.42692E-07
31	28	120	300	7.84518E-06	-2.302620913	0.099996418	7.84493E-07
32	29	122	300	9.55687E-06	-2.30263047	0.099995462	9.55648E-07
33	30	124	300	1.16189E-05	-2.302642089	0.099994301	1.16183E-06
34	31	126	300	1.40982E-05	-2.302656187	0.099992891	1.40973E-06
35	32	128	300	1.70736E-05	-2.302673261	0.099991184	1.70723E-06
36	33	130	300	2.06377E-05	-2.302693898	0.09998912	2.06357E-06
37	34	131	0	2.26738E-05	-2.302716572	0.099986853	2.26711E-06
38	35	133	0	2.73304E-05	-2.302743903	0.09998412	2.73265E-06
39	36	135	0	3.28831E-05	-2.302776786	0.099980833	3.28774E-06
40	37	135	0	3.28831E-05	-2.302809669	0.099977545	3.28763E-06
41	38	136	0	3.60448E-05	-2.302845714	0.099973941	3.6036E-06
42	39	136	0	3.60448E-05	-2.302881758	0.099970338	3.60347E-06
43	40	135	0	3.28831E-05	-2.302914642	0.099967051	3.28728E-06
44	41	134	0	2.99853E-05	-2.302944627	0.099964053	2.9975E-06
45	42	133	0	2.73304E-05	-2.302971957	0.099961321	2.73202E-06
46	43	132	0	2.48992E-05	-2.302996856	0.099958832	2.48893E-06
47	44	131	0	2.26738E-05	-2.30301953	0.099956566	2.26642E-06
48	45	129	0	1.87757E-05	-2.303038306	0.099954689	1.87674E-06
49	46	127	0	1.55185E-05	-2.303053825	0.099953138	1.55113E-06
50	47	125	0	1.28018E-05	-2.303066626	0.099951858	1.27957E-06
51	48	124	0	1.16189E-05	-2.303078245	0.099950697	1.16132E-06
52	49	122	0	9.55687E-06	-2.303087802	0.099949742	9.55211E-07
53	50	120	0	7.84518E-06	-2.303095647	0.099948958	7.8412E-07
54	51	119	0	7.10262E-06	-2.30310275	0.099948248	7.09897E-07
55	52	117	0	5.81281E-06	-2.303108563	0.099947667	5.80978E-07
56	53	115	0	4.74741E-06	-2.30311331	0.099947192	4.74491E-07
57	54	114	0	4.28697E-06	-2.303117597	0.099946764	4.2847E-07
58	55	112	0	3.4902E-06	-2.303121087	0.099946415	3.48833E-07
59	56	111	0	3.14667E-06	-2.303124234	0.0999461	3.14497E-07
60	57	110	0	2.83541E-06	-2.303127069	0.099945817	2.83388E-07
61	58	108	0	2.29846E-06	-2.303129368	0.099945587	2.29721E-07
62	59	107	0	2.06769E-06	-2.303131435	0.099945381	2.06657E-07
63	60	105	0	1.67054E-06	-2.303133106	0.099945214	1.66963E-07
64	61	104	0	1.50029E-06	-2.303134606	0.099945064	1.49946E-07
65	62	102	0	1.20799E-06	-2.303135814	0.099944943	1.20732E-07
66	63	101	0	1.083E-06	-2.303136897	0.099944835	1.0824E-07
67	64	100	0	9.70378E-07	-2.303137868	0.099944738	9.69842E-08
68	65	98	0	7.77668E-07	-2.303138645	0.09994466	7.77238E-08
69	66	97	0	6.95555E-07	-2.303139341	0.099944591	6.9517E-08
70	67	96	0	6.21736E-07	-2.303139963	0.099944528	6.21392E-08
71	68	95	0	5.55413E-07	-2.303140518	0.099944473	5.55105E-08
72	69	94	0	4.9586E-07	-2.303141014	0.099944423	4.95585E-08
73	70	92	0	3.9449E-07	-2.303141408	0.099944384	3.94271E-08
74	71	91	0	3.51532E-07	-2.30314176	0.099944349	3.51337E-08

75	72	90	0	3.13054E-07	-2.303142073	0.099944318	3.12879E-08
76	73	89	0	2.78608E-07	-2.303142352	0.09994429	2.78453E-08
77	74	88	0	2.47793E-07	-2.303142599	0.099944265	2.47655E-08
78	75	87	0	2.20243E-07	-2.30314282	0.099944243	2.2012E-08
79	76	86	0	1.95627E-07	-2.303143015	0.099944223	1.95518E-08
80	77	85	0	1.73648E-07	-2.303143189	0.099944206	1.73551E-08
81	78	84	0	1.54035E-07	-2.303143343	0.099944191	1.53949E-08
82	79	83	0	1.36545E-07	-2.303143479	0.099944177	1.36469E-08
83	80	82	0	1.20959E-07	-2.3031436	0.099944165	1.20892E-08
84	81	81	0	1.07079E-07	-2.303143707	0.099944154	1.0702E-08
85	82	80	0	9.47265E-08	-2.303143802	0.099944145	9.46736E-09
86	83	79	0	8.37404E-08	-2.303143886	0.099944136	8.36936E-09
87	84	78	0	7.39765E-08	-2.30314396	0.099944129	7.39352E-09
88	85	77	0	6.53048E-08	-2.303144025	0.099944122	6.52683E-09
89	86	76	0	5.76084E-08	-2.303144083	0.099944117	5.75762E-09
90	87	75	0	5.07825E-08	-2.303144134	0.099944112	5.07541E-09
91	88	75	0	5.07825E-08	-2.303144184	0.099944106	5.07541E-09
92	89	74	0	4.47329E-08	-2.303144229	0.099944102	4.47079E-09
93	90	73	0	3.9375E-08	-2.303144269	0.099944098	3.9353E-09
94	91	72	0	3.46333E-08	-2.303144303	0.099944095	3.4614E-09
95	92	71	0	3.04399E-08	-2.303144334	0.099944092	3.04229E-09
96	93	71	0	3.04399E-08	-2.303144364	0.099944089	3.04229E-09
97	94	70	0	2.67342E-08	-2.303144391	0.099944086	2.67192E-09
98	95	69	0	2.34617E-08	-2.303144414	0.099944084	2.34486E-09
99	96	68	0	2.05741E-08	-2.303144435	0.099944081	2.05626E-09
100	97	68	0	2.05741E-08	-2.303144455	0.099944079	2.05626E-09
101	98	67	0	1.80279E-08	-2.303144473	0.099944078	1.80178E-09
102	99	66	0	1.57846E-08	-2.303144489	0.099944076	1.57757E-09
103	100	66	0	1.57846E-08	-2.303144505	0.099944074	1.57757E-09
104	101	65	0	1.38095E-08	-2.303144519	0.099944073	1.38018E-09
105	102	64	0	1.2072E-08	-2.303144531	0.099944072	1.20653E-09
106	103	64	0	1.2072E-08	-2.303144543	0.099944071	1.20653E-09
107	104	63	0	1.05447E-08	-2.303144553	0.09994407	1.05388E-09
108	105	62	0	9.20316E-09	-2.303144563	0.099944069	9.19801E-10
109	106	62	0	9.20316E-09	-2.303144572	0.099944068	9.19801E-10
110	107	61	0	8.02576E-09	-2.30314458	0.099944067	8.02128E-10
111	108	60	0	6.99325E-09	-2.303144587	0.099944066	6.98934E-10
112	109	60	0	6.99325E-09	-2.303144594	0.099944066	6.98934E-10
113	110	59	0	6.08852E-09	-2.3031446	0.099944065	6.08511E-10
114	111	59	0	6.08852E-09	-2.303144606	0.099944064	6.08511E-10
115	112	58	0	5.2964E-09	-2.303144611	0.099944064	5.29344E-10
116	113	58	0	5.2964E-09	-2.303144617	0.099944063	5.29344E-10
117	114	57	0	4.60345E-09	-2.303144621	0.099944063	4.60087E-10
118	115	56	0	3.99775E-09	-2.303144625	0.099944062	3.99551E-10
119	116	56	0	3.99775E-09	-2.303144629	0.099944062	3.99551E-10

120	117	55	0	3.46876E-09	-2.303144633	0.099944062	3.46682E-10
121	118	55	0	3.46876E-09	-2.303144636	0.099944061	3.46682E-10
122	119	54	0	3.00716E-09	-2.303144639	0.099944061	3.00548E-10
123	120	54	0	3.00716E-09	-2.303144642	0.099944061	3.00548E-10
124	121	53	0	2.60471E-09	-2.303144645	0.09994406	2.60325E-10
125	122	53	0	2.60471E-09	-2.303144647	0.09994406	2.60325E-10
126	123	52	0	2.25412E-09	-2.30314465	0.09994406	2.25286E-10
127	124	52	0	2.25412E-09	-2.303144652	0.09994406	2.25286E-10
128	125	52	0	2.25412E-09	-2.303144654	0.09994406	2.25286E-10
129	126	51	0	1.94898E-09	-2.303144656	0.099944059	1.94789E-10
130	127	51	0	1.94898E-09	-2.303144658	0.099944059	1.94789E-10
131	128	50	0	1.68363E-09	-2.30314466	0.099944059	1.68269E-10
132	129	50	0	1.68363E-09	-2.303144661	0.099944059	1.68269E-10
133	130	50	0	1.68363E-09	-2.303144663	0.099944059	1.68269E-10

Determining k_{eff}/k_{CH} and k_{MW}/k_{CH}

$$\ln(1-0.01\mathrm{x}) = -k\mathrm{t} = -\mathrm{A}e^{-\mathrm{E_a}/\mathrm{RT}}\mathrm{t}$$

$$\mathrm{T_{eff}} = \frac{-\mathrm{E_a}}{\mathrm{A.t.R.}\ln[-\ln(1-0.01\mathrm{x})]}$$

$$\frac{k_{eff}}{k_{CH}} = \frac{\ln(1-0.01x_{actual})}{\ln\left(1-0.01x_{predicted}\right)}$$

All the small conversions for each second of the experiments were sorted based on whether or not the power is on. For example, the calculated conversions over the first 33 seconds in Table S5 are obtained when the power is on (i.e. heating) and the ones from 34 seconds until 130 seconds are related to the cooling time.

$$\text{total conversion} = \text{sum of conversions with power on} + \text{sum of conversions with power off} = x_{on} + x_{off}$$

$$\ln\left(1-0.01x_{off}\right) = -\sum\nolimits_{off} \mathrm{A}e^{-\mathrm{E_a}/\mathrm{RT}_c}\ ; T_c = cooling\ temperatures$$

$$x_{on} = x_{overall} - x_{off}$$

$$\frac{k_{MW}}{k_{CH}} = \frac{\ln(1-0.01x_{on})}{\ln\left(1-0.01x_{predicted}\right)}$$

$$\ln\left(1-0.01x_{predicted}\right) = -\sum_{on} \mathrm{A}e^{-\mathrm{E_a}/\mathrm{RT}_h}\ ; T_h = heating\ temperatures$$

Table S8. Results of microwave pulsed heating experiments under open vessel condition

Entry		Temp. Range (°C)	Power (W)	Duration (mins)	Number of Cycles	Min-Max Temp (°C)	Ave Temp (°C)	Actual yield (%)	Predicted yield (%)	rate enhancement (%)	k_{eff}/k_{CH}	k_{MW}/k_{CH}
1	a	50-130	300	1256	300	49 - 134	84.76	22.21	20.59	1.62	1.089	1.341
	b	50-130	300	1267	300	49 - 134	84.66	22.03	20.69	1.34	1.074	1.283
	c	50-130	300	1213	300	49 - 134	84.81	21.52	20.15	1.37	1.077	1.294

Figure S8. Long-neck round-bottom flask used for open vessel experiments: a) The fiber optic setup inside the flask, b) the flask inside the microwave cavity

a) b)

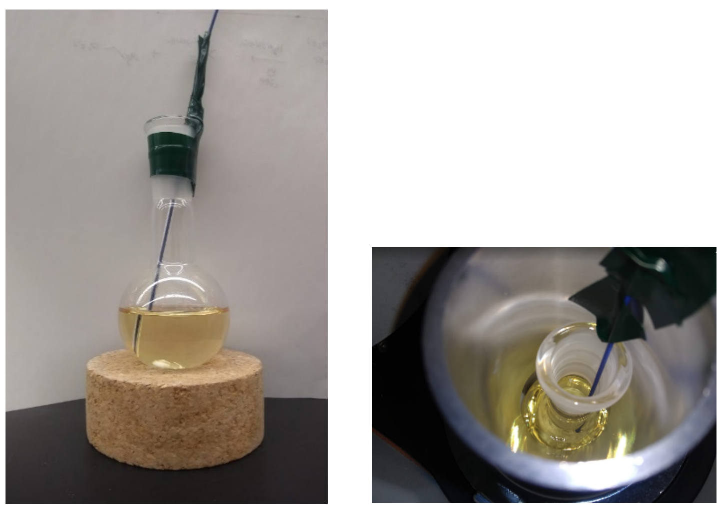


Table S9. Fixed power microwave experiments:

Entry		Power (W)	Power Max	Duration (mins)	Max Temp (°C)	Steady State Temp (°C)	Ave Temp (°C)	Actual yield (%)	Predicted yield (%)	Actual – Predicted (%)	k_{eff}/k_{CH}
1	a	145	on	300	130	127	126.30	28.71	24.67	4.04	1.194
	b	145	on	300	128	126	125.10	28.48	22.45	6.03	1.318
2	a	170	on	300	135	133	132.88	47.14	40.93	6.21	1.211
3	a	200	on	300	146	145	143.52	79.38	74.81	4.57	1.145
4	a	250	on	120	160	160	154.49	86.40	82.10	4.30	1.160
5	a	62	off	120	161	160	156.15	87.92	84.51	3.41	1.133
6	a	69	off	60	167	167	158.63	78.14	77.05	1.09	1.033