

Supporting Information

Kinetic Investigations to Enable Development of a Robust Radical Benzylic Bromination for Commercial Manufacturing of AMG 423 Dihydrochloride Hydrate

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1. General Directions

All reactions were performed under anhydrous conditions and an atmosphere of nitrogen in a 100 mL Mettler-Toledo Easymax© reactor or in a 500 mL ChemGlass reactor. Yields refer to chromatographically and spectroscopically (¹H-NMR) homogenous materials, unless otherwise indicated. Solvents and reagents: anhydrous MeCN, CH₂Cl₂, THF, Et₂O and toluene were obtained commercially from Sigma Aldrich®. ¹H NMR spectra: These were recorded at on a Bruker AV-400, AV-500 or AV-600 instrument. Chemical shifts (δ_H) are quoted in parts per million (ppm), referenced to the appropriate residual solvent peak. Coupling constants (J) are reported to the nearest 0.1 Hz. ¹⁹F NMR spectra: These were recorded at 376.64 MHz on Bruker AV-400 instrument. Chemical shifts (δ_F) are quoted in ppm, referenced to the appropriate residual solvent peak. Degenerate peaks are suffixed by the number of carbons. Chiral HPLC assays were conducted on an Agilent 1100 Series Liquid Chromatograph using a ChiralcelX-Bridge column (particle size: 3 μm; dimensions: 4.6 × 250 mm; Lot No. OZ30CE-PL009). All starting materials, additional reagents, solvents, and deuterated solvents for NMR spectra were obtained commercially and used without further purification.

2. CryoFree NMR Spectroscopy

The HTS NMR instrument has several components. The magnet is a high temperature superconducting (HTS) magnet (MR 9T4-54, iron-yoke NMR magnet) supplied by HTS-110 (Lower Hutt, New Zealand) and operating at 9.40 T (400.32 MHz for ¹H observation). The magnet always operates in the driven mode with current regulated by a high-stability power supply (Danfysik System 8500 model 854, Taastrup, Denmark). The cooling of the magnet is achieved by a Cryomech PT807 (Syracuse, NY, USA) pulse-tube cooler with a Cryomech CP2800 helium compressor. An air-cooled chiller (Huber Unichiller 040T, Offenburg, Germany) provides water cooling to the power supply. The shims used in the HTS magnet are passive ferromagnetic shims instead of the typical active superconducting shims found in standard commercial cryogen-bath magnets. The NMR console is an AVANCE III HD NMR (Bruker BioSpin, Billerica, MA, USA). The probe is a 5 mm Bruker multinuclear broadband fluorine observe (BBFO) (¹H on outer coil, inner coil tunable from ¹⁰⁹Ag – ¹⁹F, coil length 24 mm). Additionally, the conventional NMR system was fitted with a BCU-II preconditioner to cool the incoming sample temperature control gas, allowing operation at, below or above room temperature. The shimstack is a Bruker orthogonal shim system-3 (BOSS3) with 38 shims. Additional information on this NMR system can be found in two previous publications with details of electrical requirements and foot-print of the instrument.^{1,2}

The reaction was carried out in a capped 5 mm OD outer reaction sample tube (New Era Enterprises, Inc., part numbers NE-377-ORT and NE-377-SC, Vineland NJ, USA) at 83 °C. Two alternating measurements were acquired over a period of up to 16 hr. These were a 1D ¹H NMR (4 scans with 1 s delay and 30° pulse angle) and a 1D ¹⁹F NMR with inverse gated ¹H decoupling (16 scans with 1 s delay and 90° pulse angle). The system was set to start acquiring NMR data in automation mode, including solvent selection, probe matching/tuning, shimming, and data acquisition using InsightMR software (version 1.1.3, Bruker Biospin, Billerica, MA, USA). The processing of the data was performed with Mnova (version 14) software package (Mestrelab Research, SL, Santiago de Compostela, Spain).

3. Reaction Progress Kinetic Analysis (RPKA) and Variable Time Normalization Analysis (VTNA)

Experimental Design was conducted as described by Blackmond.^{3,4} Variable Time Normalization Analysis (VTNA) was conducted as described by Bures.⁵⁻⁸

Sample Preparation

A sample of nitrotoluene **1** (at appropriate concentration in AcOD-*d*₄) was used to conduct shimming at 83 °C. Reactions were initiated by inserting an NMR tube containing all reaction components into the pre-heated spectrometer. It was demonstrated that no reaction/decomposition occurs at RT.

Calculation of Concentration

The concentration of each species was calculated *via* absolute integration relative to the known concentration of nitrotoluene **1** at *t*₀ using ¹⁹F spectroscopy. The concentration of fluorinated species (nitrotoluene **1**, monobromide **2**, dibromide **3** and SM derived impurities) were determined using ¹⁹F NMR spectroscopy. NBS and succinimide concentration were determined using ¹H spectroscopy using nitrotoluene **1** as internal standard from its known concentration in the corresponding ¹⁹F spectra. The integral ranges analyzed for each species are shown below.

Table S1 – Chemical Shifts Integrated for Reaction Progress

Chemical Shift (ppm, AcOD- <i>d</i> ₄)	¹⁹ F NMR			¹ H NMR	
	Nitrotoluene 1	Monobromide 2	Dibromide 3	NBS	Succinimide
	-124.232,-124.545	-123.929,-124.183	-123.239,-123.572	3.086-2.885	2.854-2.730

Reaction conditions for RPKA are describe below (Table S1 and S2).

Table S2 – Starting Concentrations for RPKA Experiments

Experiment	[NitroTol 1] ₀ (M)	[NBS] ₀ (M)	[BPO] ₀ (M)		
Exp. 1 - Standard	0.90	1.56	0.0255		
Exp. 2 - Diff. XS [1]	0.54	1.56	0.0255	[A]% change	60
Exp. 3 - Diff. XS [NBS]	0.90	0.78	0.0255	[B]% change	50
Exp. 4 - Order in BPO	0.90	1.56	0.0510	x[Cat]	2

Table S3 – Corresponding mass of each component in RPKA experiments from Table S1 in AcOD-*d*₄ (0.7 mL)

Experiment	[NitroTol 1] ₀ (mg)	[NBS] ₀ (mg)	[BPO] ₀ (75 Wt.%) (mg)
Exp. - 1 Standard	97.7	194.4	4.3
Exp. 2 - Diff. XS [1]	68.4	194.4	4.3
Exp. 3- Diff. XS [NBS]	97.7	104.7	4.3
Exp. 4- Order in BPO	97.7	194.4	8.6

3.1 Standard Reaction Profile

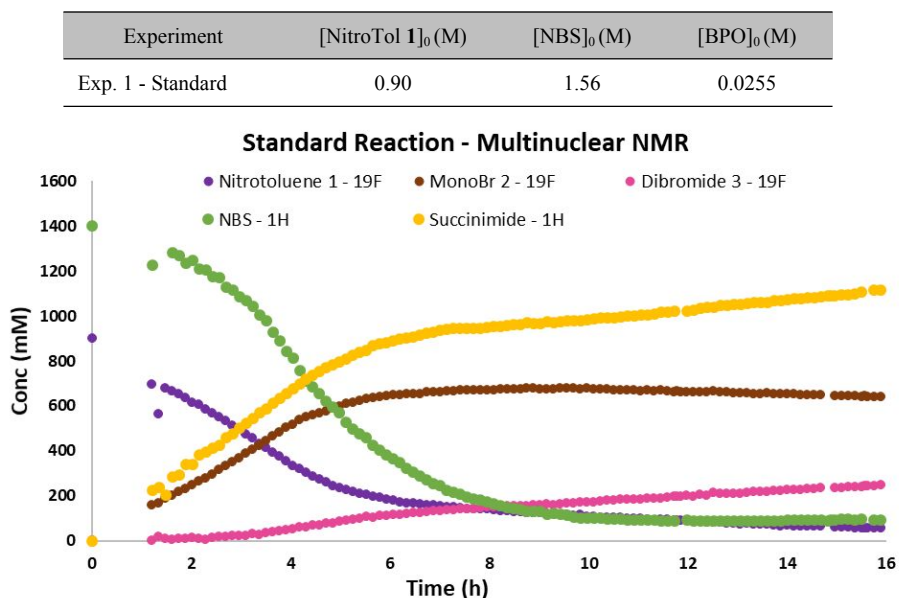


Figure S1 – Reaction Progress – Standard Reaction Conditions

VTNA was used to determine the order in benzoyl peroxide by calculating the decreasing concentration of benzoyl peroxide during reaction progress.⁶ Benzoyl peroxide concentration was calculated using first order decay with a $t_{1/2} = 3$ h at 83 °C.

Table S4 – ¹H / ¹⁹F NMR Reaction Progress data for Standard Reaction

Time (h)	¹⁹ F NMR			¹ H NMR		
	Nitrotoluene 1 (mM)	Monobromide 2 (mM)	Dibromide 3 (mM)	NBS (mM)	Succinimide (mM)	Calculated [BPO] (mM)
0	900	0	0	1400	0	25.5
1.21	697	156.743	1.14	1228	224.609	16.82373
1.345	562.606	166.853	17.862	-	236.203	16.30707
1.479722	680.037	185.889	8.383	-	202.835	15.80729
1.614722	664.04	199.547	4.249	1283.701	285.693	15.32184
1.749444	653.252	215.887	9.969	1269.362	291.42	14.85226
1.884444	636.866	230.611	6.637	1236.76	340.016	14.39614
2.019167	615.906	249.007	13.279	1249.243	339.556	13.95493
2.154167	605.558	263.209	9.831	1210.888	382.016	13.52637
2.288889	585.886	277.864	6.113	1203.881	393.953	13.11182
2.423889	568.045	296.349	14.406	1174.01	412.273	12.70915
2.558611	551.289	315.045	15.845	1169.797	424.666	12.31964
2.693611	533.517	332.19	18.003	1130.313	459.64	11.9413
2.828333	513.58	350.468	19.549	1117.286	475.512	11.57533
2.963333	494.324	368.884	21.876	1086.341	499.736	11.21985
3.098333	473.781	386.21	23.086	1069.637	521.948	10.87528
3.233056	454.882	406.794	28.436	1043.22	543.927	10.54198
3.368056	432.282	424.372	27.291	1002.626	568.608	10.21823
3.502778	412.695	445.557	32.689	980.703	586.223	9.905063
3.637778	392.784	464.094	36.929	927.445	612.43	9.600876
3.7725	373.39	483.751	44.146	887.902	632.358	9.306629
3.9075	353.735	501.506	48.187	843.484	656.259	9.020821
4.042222	333.539	517.027	49.687	811.381	675.893	8.744351

4.177222	319.909	537.587	60.678	757.572	696.666	8.47581
4.311944	301.336	548.402	59.992	709.79	718.159	8.216044
4.446944	287.553	559.017	66.405	684.415	734.773	7.963728
4.581667	272.675	567.194	69.355	656.024	754.619	7.719655
4.716667	258.895	577.047	75.361	619.818	770.901	7.482583
4.851667	245.147	588.634	78.366	595.434	782.576	7.252792
4.986389	234.464	597.032	83.73	567.92	797.416	7.030509
5.121389	226.121	609.052	89.084	528.234	807.449	6.8146
5.256111	215.906	616.145	94.141	496.376	824.744	6.605747
5.391111	208.743	622.427	97.535	475.148	838.799	6.402883
5.526111	205.284	631.271	105.762	458.49	847.578	6.206249
5.660833	194.184	633.466	103.138	423.406	866.938	6.01604
5.795833	191.486	639.729	110.438	402.381	875.308	5.831287
5.930556	183.63	642.473	110.427	380.247	881.999	5.652569
6.065556	180.491	647.043	116.483	363.384	890.564	5.478978
6.200278	171.193	647.596	116.655	346.862	897.33	5.311058
6.335278	168.363	650.533	121.381	320.073	904.106	5.147955
6.47	165.67	651.845	122.385	305.546	907.975	4.990181
6.605	161.613	654.729	124.631	288.583	914.49	4.836931
6.74	159.621	661.257	129.743	271.28	921.342	4.688388
6.874722	157.133	662.974	131.518	252.937	928.552	4.544699
7.009722	151.691	662.416	131.146	247.191	934.651	4.40513
7.144444	151.452	666.098	136.144	224.33	938.915	4.270122
7.279444	148.772	665.497	138.085	213.646	943.378	4.138985
7.414167	146.162	669.243	140.563	206.519	944.377	4.012134
7.549167	142.397	667.826	139.88	195.948	944.648	3.888921
7.684167	140.135	668.892	140.566	186.426	946.272	3.769491
7.818889	142.078	668.743	144.014	182.315	943.078	3.653964
7.953889	139.345	671.628	147.496	172.767	948.77	3.54175
8.088611	136.046	671.128	148.863	164.302	951.279	3.433203
8.223611	133.209	673.474	148.774	157.703	953.48	3.327768
8.358333	132.64	674.591	151.504	148.838	959.595	3.225779
8.493333	129.523	675.803	153.674	144.354	960.974	3.126715
8.628056	129.016	675.51	154.972	138.461	963.57	3.030887
8.763056	124.941	677.432	155.353	128.372	968.995	2.937808
8.897778	125.532	677.501	157.774	128.484	967.975	2.84777
9.032778	122.043	675.645	158.698	128.608	967.245	2.760315
9.1675	119.033	675.77	160.745	115.319	973.129	2.675717
9.3025	117.692	674.079	159.25	120.611	971.205	2.593545
9.4375	114.526	676.333	163.498	116.007	972.725	2.513897
9.572222	116.55	677.267	165.574	111.653	977.48	2.436851
9.707222	110.762	676.943	165.706	106.31	980.548	2.362015
9.842222	113.151	675.921	170.051	100.317	980.821	2.289477
9.976944	108.695	676.421	172.618	101.709	983.421	2.219309
10.11194	106.884	674.376	171.469	101.158	986.977	2.151154
10.24667	104.057	674.009	174.375	99.187	990.034	2.085225
10.38167	103.846	672.144	178.558	97.939	990.106	2.021187
10.51667	101.562	670.032	177.601	94.347	991.257	1.959116
10.65139	102.12	668.524	182.271	94.985	995.556	1.899073
10.78639	96.454	669.94	183.284	90.584	1001.069	1.840753
10.92111	96.295	668.961	183.624	90.76	1001.991	1.784337
11.05611	96.561	666.643	185.279	93.649	1003.292	1.72954
11.19083	95.566	667.612	187.068	91.653	1004.364	1.676533
11.32583	91.029	667.295	186.984	91.661	1010.864	1.625046

11.46083	92.237	668.612	189.442	89.375	1016.434	1.575141
11.59556	92.132	665.25	191.792	89.546	1018.742	1.526866
11.73056	89.666	663.213	194.115	87.725	1020.063	1.479976
11.79167	88.971	663.35	194.382	89.76	1021.548	1.459226
11.85306	90.555	663.013	194.627	86.881	1027.332	1.438674
11.98778	88.202	662.832	198.948	88.161	1033.134	1.394582
12.12278	84.022	662.259	197.25	86.072	1038.382	1.351754
12.2575	83.794	662.372	203.452	89.061	1039.301	1.310326
12.3925	81.331	662.651	200.757	86.929	1045.447	1.270085
12.5275	82.91	664.059	211.362	87.315	1048.145	1.231081
12.66222	81.617	662.866	207.807	85.714	1050.082	1.193351
12.79722	77.564	660.287	206.986	86.986	1053.012	1.156703
12.93194	75.275	657.892	208.88	87.326	1056.272	1.121252
13.06694	74.458	656.562	210.793	86.358	1057.848	1.086818
13.20194	75.206	656.44	212.655	86.936	1058.865	1.053442
13.33667	74.344	654.637	216.807	89.199	1061.759	1.021156
13.47167	72.239	653.103	215.817	86.474	1068.901	0.989796
13.60639	71.995	655.324	219.664	88.727	1069.725	0.959461
13.74139	69.076	653.389	221.006	92.059	1071.035	0.929996
13.87639	64.885	652.528	221.662	90.466	1075.49	0.901435
14.01111	68.023	651.74	225.411	92.62	1077.848	0.873808
14.14611	64.064	651.044	225.193	92.22	1081.811	0.846973
14.28111	65.44	650.104	225.379	92.097	1082.074	0.820963
14.41583	62.543	648.906	228.54	93.63	1085.718	0.795802
14.55083	62.553	647.571	229.451	89.224	1091.706	0.771362
14.68556	63.678	647.049	232.923	91.031	1089.69	0.747722
14.96472	58.6	643.55	234.465	93.644	1090.985	0.701015
15.09944	58.199	643.388	235.946	94.729	1094.662	0.679531
15.23444	58.108	643.768	239.188	95.583	1095.236	0.658662
15.36944	54.325	642.488	239	93.373	1098.036	0.638435
15.50417	55.95	641.582	240.949	93.959	1105.747	0.618868
15.56556	56.829	642.318	242.769	92.043	1113.534	0.610152
15.62667	53.636	641.384	243.817	93.086	1115.835	0.601597
15.76167	55.745	641.819	243.257	94.084	1120.945	0.583122
15.89639	53.435	641.185	245.641	-	-	0.565251
16.03139	53.505	640.308	246.117	-	-	0.547892

Table S5 – Final Mass Balance for Standard Reaction

Time	¹⁹ F NMR				¹ H NMR		
	Nitrotoluene 1 (mM)	Monobromide 2 (mM)	Dibromide 3 (mM)	Total	NBS (mM)	Succinimide (mM)	Total
Start	900	0	0	900	1560	0	1560
End	55.745	641.819	243.257	940.8	94.084	1120.945	1215.0
		Mass Balance		104%			78%
		Total Bromination		1127 mM			1120 mM

3.2 Different Excess – Nitrotoluene

Experiment	[NitroTol 1] ₀ (M)	[NBS] ₀ (M)	[BPO] ₀ (M)
Exp. 2 - Diff. XS [1]	0.54	1.56	0.0255

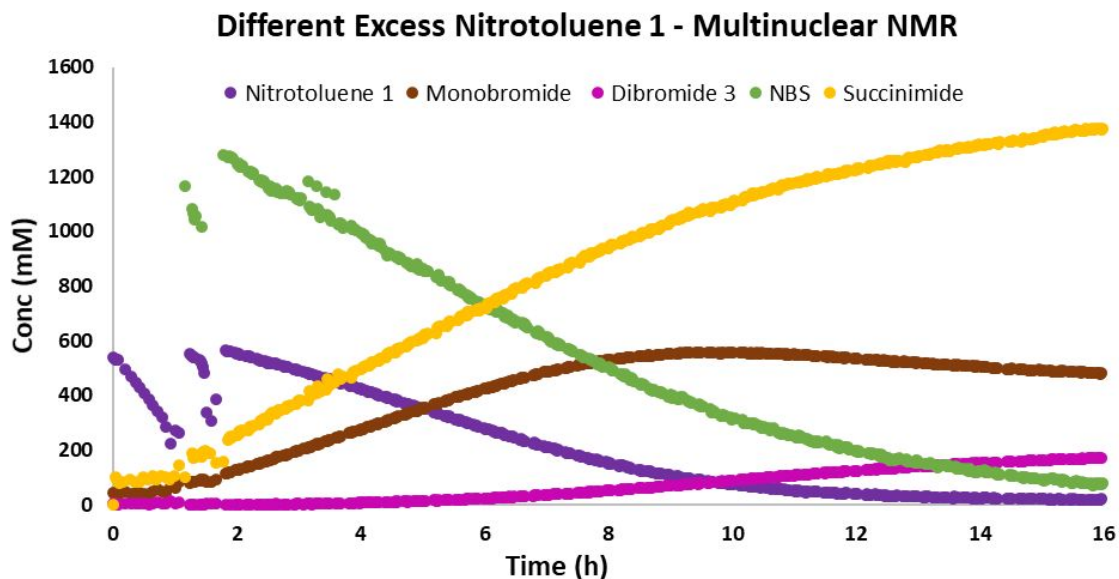


Figure S2 – Reaction Progress data for Different Excess in Nitrotoluene 1

Table S6 – ¹H / ¹⁹F NMR Reaction Progress data for Different Excess in Nitrotoluene 1

¹⁹ F NMR				¹ H NMR		
Time (h)	Monotoluene 1 (mM)	Monobromide 2 (mM)	Dibromide 3 (mM)	Time (h)	NBS (mM)	Succinimide (mM)
0	540	44.154	5.3415	0	-	103.052
0.018611	536.164	39.063	3.277	0.036667	-	94.705
0.037222	530.663	45.029	5.673	0.055278	-	87.245
0.056111	530.514	34.967	2.7645	0.073889	-	82.263
0.074722	531.204	36.058	2.9425	0.0925	-	86.463
0.198056	494.121	47.636	6.3765	0.161667	-	91.705
0.285556	470.528	40.495	4.43	0.272222	-	84.265
0.355833	446.764	43.427	4.6605	0.348611	-	82.584
0.430833	430.945	45.278	5.042	0.418889	-	100.541
0.497222	407.325	40.443	3.77	0.49	-	92.499
0.570278	385.939	38.889	2.4055	0.556389	-	104.9
0.640833	366.235	49.289	5.475	0.633611	-	92.385
0.707222	344.153	59.333	8.3215	0.701944	-	104.511
0.781389	319.294	51.842	6.636	0.775556	-	104.275
0.846111	284.719	45.176	6.156	0.841667	-	94.953
0.916944	224.961	67.628	12.977	0.907222	-	106.956
0.994444	271.751	62.743	5.247	0.986111	-	145.318
1.067778	265.425	84.899	11.8605	1.055278	-	103.038
1.229444	551.854	81.006	0.3305	1.161667	1163.172	190.462

1.248333	548.164	82.787	0.3595
1.266944	543.013	86.144	0.646
1.285556	541.366	83.303	0.1895
1.304167	539.504	85.329	0.916
1.388611	531.032	88.142	0.7585
1.407222	525.896	91.279	1.477
1.426111	517.151	92.65	1.209
1.444722	506.819	89.079	1.5855
1.463611	482.362	91.985	2.4755
1.504722	336.475	84.683	6.4565
1.578889	309.902	86.39	6.323
1.661389	386.811	93.141	6.6065
1.815278	567.844	116.327	0.856
1.834167	563.023	115.714	-0.6625
1.852778	562.182	117.748	-0.197
1.871389	561.068	118.716	-0.2845
1.89	561.736	120.015	0.951
1.979722	555.518	127.749	0.9165
1.998333	554.708	127.723	0.853
2.017222	552.293	130.006	1.2375
2.035833	552.112	130.56	1.1715
2.054444	549.513	132.041	1.012
2.141667	544.727	137.171	1.9155
2.160278	544.873	140.181	1.984
2.178889	543.308	141.455	2.2265
2.1975	542.125	141.426	1.6845
2.216111	539.006	143.163	1.4525
2.314444	534.609	149.463	1.796
2.333056	531.563	150.943	2.0475
2.351944	531.322	150.93	0.527
2.370556	527.911	153.407	1.432
2.389167	527.641	153.956	1.2485
2.461944	524.399	159.334	0.5455
2.480556	523.096	161.169	1.261
2.499444	519.108	162.454	1.627
2.518056	520.607	163.673	1.3455
2.536944	517.465	165.434	2.448
2.596944	516.783	169.32	1.8605
2.615556	516.18	170.417	2.5595
2.634167	515.746	174.968	4.444
2.652778	513.665	175.836	3.3475
2.671667	511.272	175.258	2.114
2.740556	508.793	181.168	3.321

1.266111	1082.02	170.759
1.284722	1063.322	178.589
1.303333	1041.125	184.199
1.322222	1049.874	177.691
1.340833	1054.713	176.868
1.425278	1018.362	192.103
1.443889	-	192.334
1.462778	-	197.927
1.481389	-	193.523
1.5	-	189.014
1.571111	-	153.668
1.6525	-	160.922
1.78	1278.935	237.871
1.851944	1268.501	246.174
1.870833	1274.834	249.024
1.889444	1269.73	248.457
1.908056	1269.455	249.836
1.926667	1266.874	254.659
2.016389	1243.286	266.534
2.035	1248.635	266.034
2.053611	1235.112	270.858
2.0725	1233.688	272.057
2.091111	1238.097	273.353
2.178056	1215.907	284.06
2.196667	1215.93	286.483
2.215278	1215.599	285.142
2.234167	1210.768	288.877
2.252778	1211.669	293.235
2.351111	1185.838	307.587
2.369722	1180.707	305.822
2.388333	1187.017	308.336
2.406944	1176.23	314.948
2.425556	1183.453	314.122
2.498611	1165.874	322.795
2.517222	1157.165	331.649
2.536111	1163.803	332.59
2.554722	1148.837	338.024
2.573333	1148.702	334.448
2.633333	1157.299	341.53
2.651944	1144.42	347.104
2.670833	1146.142	345.271
2.689444	1143.709	348.09
2.708056	1137.978	352.725

2.759167	505.657	181.634	2.057
2.777778	504.434	182.913	2.386
2.796667	504.864	184.657	3.2835
2.815278	503.265	186.966	3.2925
2.916111	497.418	194.293	3.5215
2.934722	496.438	195.723	3.12
2.953611	495.019	197.365	3.9125
2.972222	492.549	198.525	3.8835
2.990833	493.062	199.575	4.171
3.069167	485.085	205.178	3.2365
3.128056	482.664	209.257	3.784
3.146667	481.535	210.308	4.1015
3.165278	479.29	212.117	4.3615
3.183889	478.754	213.577	4.579
3.202778	476.483	214.202	3.686
3.2725	474.657	220.458	5.8435
3.291111	471.001	222.763	5.0885
3.309722	468.873	221.351	4.262
3.328333	468.263	224.12	4.914
3.346944	466.426	224.978	4.799
3.427778	463.411	232.705	6.151
3.446389	460.779	232.521	4.5105
3.465278	459.335	235.329	5.39
3.483889	459.242	235.846	5.301
3.5025	459.563	239.969	7.489
3.604444	452.635	246.083	6.399
3.623056	447.561	247.934	6.2635
3.641944	447.38	248.228	5.9095
3.660556	448.436	249.819	6.787
3.679167	445.425	251.936	6.9815
3.805833	437.362	262.374	7.7025
3.824444	435.763	262.127	6.7575
3.843056	435.459	265.025	7.976
3.861667	434.505	266.248	8.0905
3.880278	433.283	268.055	7.9865
3.959167	427.997	274.491	8.4715
3.977778	426.034	274.287	7.8895
3.996389	424.578	276.708	8.877
4.015278	421.812	277.609	8.2895
4.033889	422.749	278.73	8.708
4.092222	418.708	285.33	9.7765
4.110833	414.814	283.838	8.3485
4.129444	414.22	285.748	8.7895

2.776944	1139.578	358.581
2.795556	1148.519	358.806
2.814444	1140.639	361.705
2.833333	1142.545	364.429
2.851944	1134.098	368.593
2.9525	1120.781	379.901
2.971389	1119.145	381.46
2.99	1122.971	383.316
3.008611	1113.068	384.177
3.027222	1120.868	383.442
3.145833	1182.071	418.664
3.164722	1092.372	404.903
3.183333	1084.505	404.846
3.201944	1078.216	406.024
3.220556	1077.671	406.707
3.290556	1163.529	434.918
3.309167	1081.497	411.811
3.327778	1073.007	417.461
3.346389	1053.098	417.003
3.365	1065.789	421.798
3.445833	1145.07	459.84
3.464444	1058.126	437.794
3.483056	1054.1	438.895
3.501667	1050.196	442.329
3.520278	1039.252	447.724
3.569722	1133.303	478.617
3.641111	1025.272	461.167
3.659722	1029.347	460.234
3.678333	1030.486	463.565
3.696944	1025.885	468.643
3.715556	1011.718	467.282
3.842222	1018.677	483.639
3.860833	1009.443	485.986
3.879444	1006.124	487.228
3.898056	1007.39	492.532
3.916667	1002.382	494.608
3.995833	994.184	502.139
4.014444	990.926	503.044
4.033056	989.801	504.711
4.051667	985.588	510.125
4.070278	977.692	509.396
4.128889	969.566	519.906
4.1475	966.276	516.373

4.148056	413.082	287.745	9.4125
4.166667	412.596	289.817	9.8055
4.225278	407.709	295.157	10.9815
4.243889	405.049	294.379	9.0525
4.2625	405.594	296.772	10.423
4.281111	403.699	297.884	9.944
4.299722	401.142	298.085	10.4775
4.379722	394.874	305.398	11.3305
4.398333	394.402	307.311	10.8955
4.417222	394.69	307.368	11.1605
4.435833	391.978	309.692	11.7635
4.454444	391.911	310.07	11.218
4.531111	384.964	317.166	11.8935
4.549722	381.932	317.302	11.136
4.568333	384.78	319.797	12.557
4.586944	379.931	320.4	11.8
4.605833	380.546	323.384	12.785
4.706389	372.235	330.85	13.088
4.725	371.11	331.062	12.732
4.743611	371.09	333.007	12.992
4.762222	368.105	333.295	12.4095
4.780833	368.455	336.536	13.6325
4.847222	364.641	341.467	14.4595
4.866111	359.955	341.898	13.906
4.884722	358.231	343.381	13.8755
4.903333	357.095	344.785	14.0075
4.921944	357.684	346.779	14.848
4.978333	352.467	350.807	14.5415
4.996944	352.075	353.828	15.8965
5.015556	351.232	353.48	14.797
5.034167	350.293	355.853	15.9775
5.053056	349.539	356.612	15.129
5.181111	339.588	367.115	17.04
5.2	338.391	368.39	16.9305
5.218611	336.424	368.467	16.339
5.2375	335.202	370.696	16.776
5.256111	334.27	372.627	17.6595
5.348611	326.361	378.93	18.059
5.3675	327.116	381.026	19.0555
5.386111	324.465	381.504	18.102
5.404722	322.058	383.449	19.0675
5.423611	323.39	384.346	18.6995
5.531111	313.119	393.156	20.628

4.166111	962.401	521.036
4.184722	955.863	523.345
4.203333	961.525	525.14
4.261944	953.73	528.542
4.280556	953.579	528.384
4.299167	947.362	534.195
4.317778	953.571	533.846
4.336389	941.946	537.657
4.416389	923.427	553.442
4.435	912.838	553.749
4.453611	921.874	555.52
4.4725	920.405	556.063
4.490833	913.699	557.79
4.567778	909.176	568.861
4.586389	905.684	571.757
4.605	905.665	570.577
4.623611	899.772	573.526
4.642222	901.673	579.677
4.742778	887.219	589.897
4.761389	884.338	587.883
4.78	881.573	590.442
4.798889	876.749	594.791
4.8175	874.076	601.858
4.883889	869.418	602.753
4.9025	879.102	604.876
4.921111	864.09	606.146
4.939722	866.307	611.122
4.958333	858.775	611.586
5.015	862.483	621.371
5.033611	855.912	622.306
5.052222	856.226	624.293
5.070833	854.499	628.04
5.089444	853.026	628.331
5.217778	833.598	648.211
5.236389	831.272	647.341
5.255278	840.873	654.008
5.273889	826.894	654.905
5.292778	819.938	655.252
5.385278	813.369	665.176
5.403889	812.017	668.155
5.422778	814.312	670.176
5.441389	807.98	671.338
5.46	801.338	674.305

5.549722	312.241	393.376	19.679
5.568611	311.138	395.255	20.386
5.587222	309.798	395.917	19.8935
5.605833	310.002	398.148	21.1845
5.676389	302.662	402.402	21.0785
5.695278	302.291	404.725	21.9565
5.713889	300.447	404.981	21.759
5.7325	300.212	406.633	22.162
5.751111	298.195	407.6	21.9245
5.817222	293.67	412.384	23.068
5.835833	291.748	413.409	23.219
5.854444	288.778	413.883	22.517
5.873056	289.019	416.069	23.7275
5.891667	285.48	416.076	22.6255
5.991389	280.034	423.76	24.175
6.01	279.042	425.201	25.179
6.028611	277.333	426.082	24.513
6.047222	275.449	426.505	24.165
6.065833	276.351	429.088	25.338
6.128611	271.16	431.867	24.695
6.147222	268.361	433.888	25.916
6.165833	267.652	435.22	25.896
6.184444	265.018	435.863	25.8415
6.203056	265.734	439.003	27.58
6.266667	262.912	442.919	27.6675
6.285278	262.924	444.381	28.4005
6.303889	259.323	444.668	28.2575
6.322778	256.592	445.37	28.021
6.341389	256.435	447.039	27.8875
6.401111	252.302	452.325	30.2975
6.419722	251.951	452.642	29.533
6.438611	250.149	454.195	29.0065
6.457222	249.19	454.499	29.512
6.475833	247.532	456.694	30.69
6.580278	239.554	461.694	30.32
6.598889	240.238	464.638	32.0055
6.6175	236.246	464.441	31.3955
6.636111	235.543	465.306	31.6265
6.654722	233.718	466.764	31.367
6.790278	226.829	474.644	33.8615
6.808889	227.083	474.549	34.417
6.8275	224.032	477.352	35.472
6.846111	221.195	477.594	34.482

5.567778	782.906	680.674
5.586389	787.689	686.479
5.605	784.675	688.593
5.623611	778.448	691.823
5.642222	775.811	694.529
5.713056	766.724	703.845
5.731667	764.036	704.442
5.750278	758.837	704.428
5.768889	752.807	705.783
5.7875	756.746	711.396
5.853889	746.608	713.954
5.8725	742.059	715.216
5.891111	741.224	710.653
5.909722	739.462	719.392
5.928333	737.578	719.41
6.027778	718.843	736.131
6.046667	724.794	736.917
6.065278	717.139	738.492
6.083889	715.279	739.388
6.1025	719.963	739.963
6.165278	712.587	752.971
6.183889	706.035	754.344
6.202222	713.073	752.215
6.220833	708.268	756.569
6.239444	707.925	755.212
6.303333	699.558	768.697
6.321944	689.614	768.946
6.340556	693.949	768.097
6.359167	685.722	772.716
6.377778	692.245	770.932
6.437778	677.173	782.516
6.456389	678.944	789.503
6.475	668.837	787.61
6.493611	667.214	792.977
6.512222	672.285	792.888
6.616667	664.853	803.26
6.635556	656.552	805.68
6.654167	662.217	807.23
6.672778	653.638	809.894
6.691389	649.269	811.601
6.826667	631.681	824.635
6.845278	627.134	828.451
6.864167	636.127	829.296

6.864722	221.718	480.007	35.3375
6.969167	213.88	485.366	36.477
6.987778	212.153	485.387	35.997
7.006389	212.865	485.968	36.68
7.025	210.812	488.339	38.3185
7.043611	212.06	487.872	37.625
7.114167	208.054	493.265	39.5585
7.132778	205.032	493.17	39.1115
7.151389	202.82	493.093	39.643
7.170278	200.603	495.235	40.255
7.188889	201.279	495.868	40.251
7.312778	193.496	501.052	41.3435
7.331389	189.987	501.989	41.9525
7.35	189.719	502.469	42.182
7.368611	188.913	503.848	42.0735
7.387222	189.457	504.244	42.485
7.503333	181.423	510.679	44.548
7.521944	181.463	512.729	45.3665
7.540556	180.653	513.411	46.021
7.559167	178.441	512.35	46.2835
7.577778	178.051	514.888	46.2125
7.653333	173.761	517.514	46.5765
7.671944	173.082	518.487	47.6535
7.690556	167.995	517.838	46.8745
7.709167	169.668	519.463	48.018
7.727778	169.602	520.097	47.553
7.798611	163.34	521.874	48.4375
7.817222	166.509	524.206	50.232
7.836111	162.296	523.839	50.165
7.854722	161.524	525.756	50.348
7.873333	161.108	525.822	50.885
7.967222	158.513	530.257	53.0655
7.985833	155.777	528.125	52.733
8.004444	151.454	529.582	52.6045
8.023056	152.885	530.809	53.194
8.041667	152.19	530.389	52.532
8.1575	146.046	534.885	55.754
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8.213611	145.214	536.924	56.912
8.232222	144.673	537.087	57.261
8.301389	140.279	538.621	57.6715
8.32	137.707	538.355	57.9125

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6.901389	622.474	835.349
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7.043056	608.47	849.715
7.061667	602.129	849.085
7.080278	597.795	852.245
7.150833	589.798	856.802
7.169444	590.878	859.372
7.188056	582.734	859.76
7.206667	587.017	864.951
7.225556	581.567	866.527
7.349167	570.857	879.531
7.367778	569.651	881.612
7.386389	565.94	884.517
7.405	566.874	885.509
7.423889	563.311	887.196
7.539722	547.865	899.372
7.558333	546.409	904.396
7.576944	545.049	904.67
7.595556	538.655	909.841
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7.69	534.699	918.222
7.708611	531.143	917.03
7.727222	530.587	919.638
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7.853889	516.767	930.711
7.8725	515.724	932.647
7.891111	508.679	935.992
7.909722	502.555	939.383
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8.194167	476.923	962.723
8.212778	478.419	963.469
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8.250278	471.66	969.715
8.268889	477.293	968.317
8.338056	463.763	973.427

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8.619444	123.989	545.181	63.5285
8.638056	124.087	546.419	64.6935
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8.773056	116.862	548.116	66.9745
8.791667	114.957	548.024	66.683
8.810278	115.209	549.061	67.7095
8.828889	113.71	548.913	67.183
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8.943611	110.503	552.113	69.7325
8.962222	109.125	551.304	69.5235
8.980833	108.364	551.946	70.2205
8.999444	109.202	553.03	70.895
9.018056	108.268	553.719	71.0285
9.098056	105.885	553.221	72.496
9.116667	103.226	553.353	72.4005
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9.153889	104.353	554.65	73.379
9.1725	101.47	555.308	73.267
9.250278	95.861	555.786	75.649
9.268889	98.369	556.405	76.395
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9.451389	90.594	555.466	77.9145
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9.305556	376.967	1061.699
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9.342778	372.391	1065.98
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9.450556	365.85	1072.752
9.469444	367.735	1073.3
9.488056	359.365	1075.339
9.506667	359.599	1081.445
9.525278	360.028	1074.374
9.645556	353.628	1088.379
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9.682778	340.632	1085.836
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9.860278	79.878	555.986	86.625
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10.12917	71.279	556.626	92.11
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10.185	71.101	556.098	93.1905
10.20361	72.793	556.495	93.5705
10.27417	69.962	554.473	94.742
10.29278	68.201	554.799	94.6525
10.31139	66.555	555.153	95.6225
10.33028	65.215	554.332	96.122
10.34889	67.556	554.883	95.786
10.41083	67.208	555.407	98.3055
10.42917	65.705	554.32	97.676
10.44806	65.141	554.16	98.629
10.46667	64.493	554.669	98.6225
10.48528	66.431	555.532	99.416
10.56528	61.03	552.981	100.607
10.58389	61.318	553.098	100.6555
10.6025	62.243	554.007	101.274
10.62111	61.438	553.466	101.364
10.63972	59.586	552.482	101.934
10.71667	60.238	552.253	103.1195
10.73528	61.3	553.283	103.883
10.75389	59.513	553.499	103.5525
10.7725	60.507	554.051	105.3005
10.79111	56.662	551.729	104.376
10.84889	58.329	552.345	105.914
10.86778	56.034	549.877	105.893
10.88639	55.703	551.352	106.726
10.905	52.269	550.297	106.9485
10.92361	55.72	550.403	106.759
11.00889	54.232	550.832	108.654
11.0275	51.767	547.967	108.873
11.04583	53.169	550.456	109.274

9.72	336.361	1088.065
9.8225	326.802	1094.021
9.841111	328.757	1094.504
9.859722	329.174	1097.269
9.878333	327.328	1100.376
9.896944	325.286	1095.095
9.983611	319.461	1103.872
10.00222	314.208	1106.46
10.02083	314.706	1112.912
10.03944	316.724	1110.019
10.05806	315.388	1113.168
10.16556	310.251	1122.902
10.18417	299.277	1125.409
10.20278	297.933	1126.611
10.22139	299.994	1127.558
10.24	300.272	1129.778
10.31083	299.993	1138.564
10.32944	300.754	1131.502
10.34806	294.725	1137.659
10.36667	299.423	1136.476
10.38528	292.943	1137.793
10.44722	290.344	1139.244
10.46583	287.699	1142.402
10.48444	281.913	1145.435
10.50306	281.081	1144.256
10.52167	284.059	1145.908
10.60194	281.452	1151.895
10.62056	274.523	1152.197
10.63917	277.914	1154.424
10.65778	277.364	1155.582
10.67639	280.953	1153.126
10.75306	263.033	1162.972
10.77167	263.801	1167.045
10.79028	258.785	1170.121
10.80889	257.773	1166.216
10.82778	265.565	1167.76
10.88556	259.969	1172.11
10.90417	253.912	1173.144
10.92278	256.867	1174.377
10.94139	256.281	1173.718
10.96028	256.491	1179.352
11.04528	245.995	1180.104
11.06389	248.828	1179.324

11.06444	50.248	547.77	109.5235
11.08306	52.852	548.404	110.525
11.15333	50.242	549.385	111.8615
11.17194	51.261	547.594	112.1935
11.19056	46.627	546.8	112.396
11.20917	51.473	546.203	112.2525
11.22778	49.014	548.01	111.801
11.30417	47.972	544.763	114.0645
11.32278	48.206	545.988	114.5085
11.34139	49.712	546.046	114.6575
11.36	48.795	544.878	114.274
11.37861	47.862	542.729	115.0905
11.48028	44.974	542.231	117.7765
11.49889	46.721	544.403	117.213
11.5175	46.575	544.314	117.9415
11.53611	45.512	541.639	118.165
11.55472	46.268	542.69	117.579
11.63056	45.989	542.29	119.201
11.64917	44.114	540.824	119.6605
11.66778	46.584	541.665	119.5825
11.68639	44.462	541.813	119.9735
11.705	41.587	538.055	120.9105
11.78472	41.792	538.16	121.662
11.80333	41.198	538.262	122.15
11.82194	41.671	536.772	122.4995
11.84056	45.65	538.874	123.375
11.85917	44.958	539.17	122.845
11.96139	39.639	535.324	125.4875
11.98	41.434	534.654	124.895
11.99861	41.427	533.276	125.5325
12.01722	42.109	536.199	126.0515
12.03583	39.507	535.664	125.797
12.165	38.372	533.064	128.1655
12.18361	39.512	532.187	127.93
12.20222	37.813	531.946	128.1335
12.22083	38.205	532.613	129.0515
12.23944	36.878	532.207	129.3635
12.32472	38.768	530.539	130.6855
12.34333	34.528	529.404	130.2285
12.36194	36.584	529.249	131.039
12.38056	36.465	528.084	131.3415
12.39917	35.863	528.578	131.889
12.45	35.059	529.039	132.4825

11.0825	253.708	1178.328
11.10111	247.727	1182.163
11.11972	250.528	1181.182
11.19	243.954	1190.361
11.20861	242.803	1187.627
11.22722	239.96	1188.051
11.24583	236.237	1192.098
11.26417	232.48	1192.753
11.34056	230.242	1193.391
11.35917	233.849	1202.257
11.37806	230.287	1196.521
11.39667	233.919	1195.372
11.41528	229.013	1199.897
11.51667	231.614	1208.858
11.53556	222.896	1207.543
11.55389	222.634	1203.078
11.57278	221.916	1207.814
11.59111	219.109	1210.229
11.66694	220.315	1208.276
11.68556	214.051	1207.802
11.70417	212.749	1208.347
11.72278	218.821	1215.219
11.74139	208.731	1212.327
11.82139	213.425	1224.079
11.84	209.719	1218.159
11.85861	211.042	1221.871
11.87722	212.096	1222.118
11.89583	203.404	1220.014
11.99806	196.978	1226.437
12.01667	197.988	1231.273
12.03528	195.371	1228.265
12.05389	198.861	1231.076
12.0725	194.712	1228.745
12.20167	188.612	1238.511
12.22028	188.109	1240.174
12.23861	187.501	1239.203
12.25722	186.058	1238.605
12.27583	188.458	1244.226
12.36139	183.377	1245.763
12.38	185.404	1246.381
12.39861	175.676	1245.543
12.41722	184.762	1248.091
12.43583	179.122	1252.356

12.46861	33.489	527.796	133.0855
12.48722	34.987	528.194	133.404
12.50583	33.615	527.445	132.685
12.52444	33.556	527.209	133.7325
12.59361	32.623	524.198	134.677
12.61222	34.191	524.514	134.235
12.63083	33.615	524.047	134.7635
12.64944	32.894	525.272	134.9905
12.66778	34.794	523.464	135.0425
12.75667	34.188	522.286	136.9515
12.77528	33.452	525.076	136.8855
12.79389	32.913	520.396	138.172
12.81278	30.761	521.264	137.5555
12.83139	32.233	521.327	137.861
12.91306	33.224	521.269	139.3785
12.93167	33.02	521.968	139.464
12.95028	32.07	520.465	140.2975
12.96889	33.238	519.563	140.155
12.9875	30.718	520.912	140.222
13.08639	29.217	518.791	142.0715
13.105	30.056	518.441	142.0435
13.12361	28.668	517.012	142.521
13.1425	32.833	518.009	142.095
13.16111	31.043	518.362	142.893
13.24722	29.328	516.767	143.525
13.26611	28.823	514.045	144.636
13.28472	29.222	514.638	144.378
13.30361	28.385	513.836	144.121
13.32222	28.889	514.982	145.2825
13.40583	29.655	514.452	146.0325
13.42472	27.595	512.41	145.8885
13.44333	28.334	512.065	146.1285
13.46194	28.617	514.603	146.513
13.48083	28.171	513.186	147.5305
13.58222	24.961	510.544	148.7805
13.60083	30.995	512.027	148.3765
13.61972	27.196	508.586	148.81
13.63833	26.976	509.664	149.006
13.65722	26.211	511.48	149.4895
13.73444	28.717	509.981	150.075
13.75306	27.811	510.305	150.703
13.77194	26.977	507.166	150.2
13.79056	26.892	509.484	150.7565

12.48667	171.623	1255.151
12.505	171.766	1248.745
12.52361	171.565	1256.176
12.54222	163.314	1255.937
12.56111	166.745	1255.359
12.63	164.805	1253.21
12.64861	167.303	1256.604
12.66722	166.972	1255.022
12.68583	168.442	1256.02
12.70444	173.539	1253.33
12.79333	164.591	1263.312
12.81194	165.625	1264.061
12.83056	160.183	1269.152
12.84917	160.729	1267.902
12.86778	159.378	1272.119
12.94944	156.601	1271.681
12.96833	163.428	1272.33
12.98694	163.663	1273.995
13.00556	156.041	1274.422
13.02417	154.75	1276.982
13.12306	148.936	1278.012
13.14167	150.874	1279.35
13.16028	149.05	1280.468
13.17889	151.482	1282.614
13.1975	152.774	1287.101
13.28389	144.537	1287.431
13.3025	142.264	1288.023
13.32139	139.245	1291.662
13.34	140.748	1295.337
13.35889	144.875	1290.417
13.4425	146.257	1295.639
13.46111	144.963	1295.531
13.48	141.994	1297.27
13.49861	145.622	1292.473
13.51722	142.089	1299.904
13.61861	140.002	1301.765
13.6375	131.67	1300.102
13.65611	135.317	1304.065
13.675	133.68	1303.319
13.69361	134.461	1304.496
13.77083	133.3	1303.106
13.78972	127.771	1305.17
13.80833	127.635	1308.138

13.80917	27.469	509.305	151.3015
13.89306	25.103	507.672	152.5685
13.91167	26.453	508.456	152.132
13.93056	25.065	505.245	152.462
13.94917	26.009	506.262	153.4395
13.96806	24.93	507.542	153.2955
14.04722	24.806	505.373	153.5895
14.06611	25.67	505.788	154.2705
14.08472	26.383	505.596	154.174
14.10361	27.085	503.454	154.253
14.1225	28.267	504.89	154.0845
14.22222	23.971	500.737	155.4175
14.24111	26.486	501.768	155.7065
14.25972	22.347	500.467	156.215
14.27861	24.522	500.016	156.0975
14.2975	25.059	502.074	156.749
14.44111	24.966	497.301	157.7785
14.46	22.858	497.497	158.018
14.47889	23.89	497.478	158.3025
14.49778	22.891	496.041	158.798
14.51639	23.732	498.236	158.9745
14.63611	23.07	495.923	159.8185
14.655	21.353	494.405	160.165
14.67389	23.732	495.929	160.6055
14.69278	23.034	495.651	160.311
14.71139	23.33	495.772	160.4545
14.79	23.327	492.629	161.9155
14.80889	23.869	492.534	161.383
14.82778	23.071	492.587	161.7035
14.84667	23.934	491.249	162.3185
14.86528	22.101	492.06	162.6125
14.96361	21.907	494.093	164.0035
14.9825	21.914	491.224	164.3725
15.00139	24.374	491.041	163.923
15.02028	22.06	491.959	164.3675
15.03917	23.201	492.445	164.405
15.11694	21.022	489.5	165.1935
15.13556	22.525	490.025	165.0545
15.15472	20.434	491.565	166.533
15.17361	20.322	489.067	166.3205
15.1925	19.905	488.347	166.457
15.27806	22.055	487.869	167.5565
15.29694	22.525	487.75	167.498

13.82694	124.898	1305.969
13.84583	131.754	1308.191
13.92972	121.28	1315.088
13.94833	120.658	1312.175
13.96694	119.741	1314.067
13.98583	122.023	1319.626
14.00472	126.233	1313.518
14.08389	126.261	1316.934
14.1025	120.21	1316.462
14.12139	126.156	1320.377
14.14	119.984	1316.697
14.15889	121.015	1321.219
14.25861	118.066	1321.658
14.2775	116.594	1323.727
14.29639	108.993	1319.729
14.315	114.618	1326.297
14.33389	112.876	1326.32
14.47778	111.146	1325.972
14.49667	105.735	1328.168
14.51528	111.532	1329.807
14.53417	106.03	1333.6
14.55306	107.139	1325.997
14.67278	101.689	1332.822
14.69167	102.456	1338.585
14.71028	98.295	1335.47
14.72917	103.11	1336.638
14.74806	102.647	1334.691
14.82667	97.284	1337.13
14.84556	96.95	1338.148
14.86444	99.662	1342.252
14.88306	96.349	1338.552
14.90194	97.1	1346.986
15.00028	92.104	1346.426
15.01917	93.957	1350.651
15.03806	90.425	1354.131
15.05667	95.517	1351.785
15.07583	95.555	1354.929
15.15333	96.534	1355.917
15.17222	98.56	1352.404
15.19111	99.218	1362.039
15.21028	94.422	1354.627
15.22917	93.627	1358.648
15.31472	91.248	1362.898

15.31583	20.06	489.792	167.591
15.33472	17.904	489.051	166.9025
15.35361	20.17	489.836	167.0945
15.45861	20.414	486.748	167.9665
15.47722	21.544	487.826	168.7085
15.49639	20.774	488.603	169.0595
15.51528	20.953	488.985	169.1945
15.53417	21.254	486.782	169.5305
15.60611	21.208	485.13	169.878
15.62528	20.229	485.652	169.6845
15.64417	20.042	483.777	169.819
15.66306	20.167	485.569	170.039
15.68194	21.011	485.55	169.88
15.76889	19.271	481.169	172.188
15.78778	19.668	482.593	171.0845
15.80694	20.632	482.291	171.2845
15.82583	19.111	482.582	171.9485
15.84472	17.971	482.219	171.85
15.90472	19.43	481.418	171.901
15.92361	21.086	483.33	171.824
15.9425	20.024	480.81	172.441
15.96167	21.072	479.857	172.259
15.98056	21.423	481.802	171.7585
16.06583	19.331	480.816	173.762
16.08472	22.337	480.719	172.878
16.10361	20.045	477.185	173.421
16.12278	19.172	477.848	173.3515
16.14167	20.118	477.783	173.436
16.19056	19.312	477.718	174.0145
16.31417	18.661	477.997	175.115
16.33306	20.978	476.314	174.748
16.35194	17.226	475.748	175.236
16.37111	21.416	474.662	174.7645
16.39	19.082	475.152	175.436
16.45222	18.385	475.909	176.3205
16.47111	19.669	474.684	176.4675
16.49028	18.904	475.209	176.4515
16.50917	17.358	475.992	176.8145
16.52833	18.347	476.611	177.4355
16.62944	17.144	474.586	178.108
16.64861	18.704	474.458	178.1815
16.6675	17.17	473.289	177.7015
16.68667	16.931	474.151	178.6325

15.33361	85.563	1361.339
15.3525	91.891	1364.305
15.37139	89.405	1362.223
15.39028	88.195	1363.333
15.495	82.348	1365.881
15.51389	80.527	1364.308
15.53278	86.786	1370.037
15.55167	85.117	1368.894
15.57056	87.755	1366.814
15.64278	81.261	1368.5
15.66167	83.215	1367.633
15.68056	79.862	1367.544
15.69944	79.94	1375.446
15.71861	80.569	1371.576
15.80556	82.043	1375.83
15.82444	74.587	1371.635
15.84333	72.959	1371.49
15.86222	75.963	1374.923
15.88139	80.599	1376.037
15.94111	81.181	1375.596
15.96028	77.607	1372.859
15.97917	78.026	1373.816
15.99806	80.774	1374.216
16.01694	78.505	1372.395
16.10222	70.87	1379.771
16.12139	70.471	1373.805
16.14028	72.633	1377.468
16.15944	71.03	1378.289
16.17833	68.67	1380.407
16.33167	103.731	1475.656
16.35056	63.477	1380.404
16.36944	60.066	1381.628
16.38861	63.731	1382.405
16.4075	63.226	1384.885
16.46972	108.174	1483.712
16.48889	65.445	1384.563
16.50778	64.148	1390.199
16.52667	56.612	1386.75
16.54583	59.798	1394.062
16.64694	105.067	1491.553
16.66611	53.64	1393.97
16.685	61.302	1399.142
16.70417	56.804	1399.333

16.70556	18.105	474.22	178.3
16.78417	15.869	473.694	179.368
16.80306	17.89	473.138	179.3375
16.82222	19.178	473.276	178.89
16.84139	17.208	473.786	179.166
16.86056	16.508	471.133	179.4525
16.95278	16.396	470.251	179.27
16.97194	18.054	471.793	179.3125

16.72306	57.323	1394.825
16.80167	86.594	1498.801
16.82056	49.583	1399.385
16.83972	47.58	1397.129
16.85861	47.49	1395.575
16.87778	44.348	1397.482
16.97028	89.605	1488.165
16.98944	45.576	1395.661

Table S7 – Final Mass Balance for Different Excess Nitrotoluene 1

Time	¹⁹ F NMR			
	Nitrotoluene 1 (mM)	Monobromide 2 (mM)	Dibromide 3 (mM)	Total
Start	540	0	0	540
End	18.054	471.793	179.3125	669.1
		Mass Balance		123%
		Total Bromination		831 mM

¹ H NMR		
NBS (mM)	Succinimide (mM)	Total
1560	0	1560
45.576	1395.661	1441.2
		92%
		1821 mM

3.3 Different Excess – *N*-Bromosuccinimide

Experiment	[NitroTol 1] ₀ (M)	[NBS] ₀ (M)	[BPO] ₀ (M)
Exp. 3 - Diff. XS [NBS]	0.90	0.78	0.0255

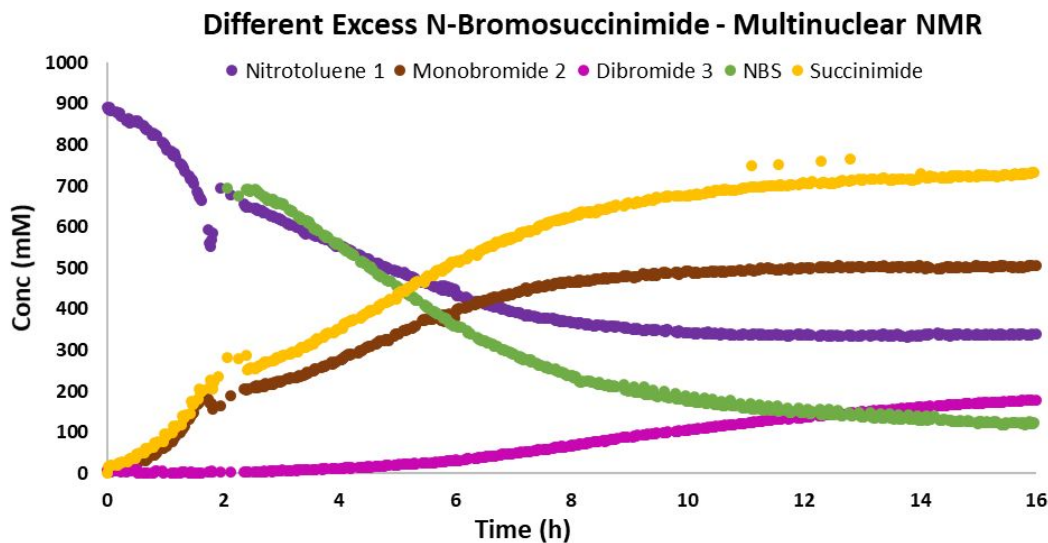


Figure S3 – Reaction Progress data for Different Excess in *N*-Bromosuccinimide

Table S8 – ¹H / ¹⁹F NMR Reaction Progress data for Different Excess in *N*-Bromosuccinimide

¹⁹ F NMR				¹ H NMR		
Time (h)	Nitrotoluene 1 (mM)	Monobromide 2 (mM)	Dibromide 3 (mM)	Time (h)	NBS (mM)	Succinimide (mM)
0	891	8.138	5.3415	0		16.892
0.018611	887.188	8.59	3.277	0.036944		17.497
0.0375	892.56	8.17	5.673	0.055556		18.406
0.056111	887.415	8.681	2.7645	0.074167		18.838
0.074722	884.046	8.654	2.9425	0.093056		20.235
0.156944	881.538	14.635	6.3765	0.175		25.36
0.175556	879.224	10.032	4.43	0.193611		25.366
0.194444	879.142	13.709	4.6605	0.2125		25.532
0.213056	877.941	12.753	5.042	0.231111		26.764
0.231667	870.732	12.96	3.77	0.25		27.801
0.328611	858.133	18.577	2.4055	0.346944		34.232
0.3475	858.474	19.861	5.475	0.365556		33.506
0.366111	865.181	24.941	8.3215	0.384444		35.144
0.385	858.333	23.303	6.636	0.403056		35.663
0.403611	853.842	23.646	6.156	0.421944		36.829
0.475556	856.986	19.658	12.977	0.493889		47.681
0.494444	859.302	26.509	5.247	0.5125		46.095
0.513056	857.094	27.796	11.8605	0.531389		47.768
0.531944	858.342	29.267	0.3305	0.55		49.405

0.550556	853.124	27.286	0.3595
0.625556	848.832	32.782	0.646
0.644167	846.039	35.021	0.1895
0.662778	840.118	31.48	0.916
0.681667	836.203	35.205	0.7585
0.700278	835.911	36.193	1.477
0.778333	824.404	43.276	1.209
0.796944	829.33	45.095	1.5855
0.815833	825.209	44.623	2.4755
0.834444	822.711	49.338	6.4565
0.853056	822.015	49.33	6.323
0.955833	808.015	60.477	6.6065
0.974444	803.079	61.525	0.856
0.993333	802.419	68.022	-0.6625
1.011944	797.003	68.165	-0.197
1.030833	788.481	64.817	-0.2845
1.110556	784.94	79.09	0.951
1.129167	775.939	77.814	0.9165
1.148056	773.993	82.577	0.853
1.166667	778.145	90.851	1.2375
1.185278	771.739	90.153	1.1715
1.260278	754.364	99.929	1.012
1.278889	753.035	106.006	1.9155
1.2975	750.388	108.077	1.984
1.316389	742.728	112.569	2.2265
1.335	735.161	116.21	1.6845
1.415	723.943	130.383	1.4525
1.433611	716.67	136.723	1.796
1.4525	717.61	142.588	2.0475
1.471111	712.563	144.512	0.527
1.49	706.529	149.202	1.432
1.560556	687.809	165.982	1.2485
1.579167	680.476	168.474	0.5455
1.598056	674.219	171.323	1.261
1.616667	669.058	179.122	1.627
1.635278	664.324	183.23	1.3455
1.745278	594.61	182	2.448
1.763889	560.985	172.287	1.8605
1.7825	553.78	170.614	2.5595
1.801389	569.954	170.688	4.444
1.82	585.154	155.481	3.3475
1.951667	695.909	164.638	2.114
2.123056	677.324	187.971	3.321

0.568889		50.568
0.643611		60.905
0.6625		58.099
0.681111		59.757
0.699722		61.081
0.718611		62.57
0.796389		74.665
0.815		72.541
0.833889		74.088
0.8525		76.092
0.871111		77.251
0.973889		95.125
0.992778		91.844
1.011389		93.891
1.030278		95.691
1.048889		97.625
1.128611		116.094
1.1475		111.02
1.166111		113.676
1.184722		116.399
1.203333		119.202
1.278333		140.859
1.296944		135.112
1.315833		137.959
1.334444		141.6
1.353056		145.557
1.433333		173.971
1.451944		165.751
1.470556		168.59
1.489444		174.811
1.508056		179.463
1.578611		206.58
1.5975		197.836
1.616111		200.608
1.634722		203.692
1.653611		207.258
1.763333		227.63
1.782222		208.097
1.800833		206.294
1.819444		221.975
1.838333		235.028
1.9175		280.995
2.067778	694.034	280.478

2.37	657.634	204.996	2.057
2.388889	652.189	204.52	2.386
2.4075	648.525	202.639	3.2835
2.426111	648.612	204.449	3.2925
2.445	649.001	205.683	3.5215
2.528056	646.09	209.516	3.12
2.546667	645.409	209.344	3.9125
2.565278	643.003	209.22	3.8835
2.583889	644.391	212.784	4.171
2.6025	639.465	208.046	3.2365
2.652778	641.386	214.285	3.784
2.671667	639.292	211.334	4.1015
2.690278	634.982	213.017	4.3615
2.708889	635.556	211.717	4.579
2.7275	635.363	217.864	3.686
2.807222	627.9	216.169	5.8435
2.826111	626.981	218.042	5.0885
2.844722	625.518	217.141	4.262
2.863333	625.309	216.929	4.914
2.881944	624.818	220.668	4.799
2.935278	620.24	224.207	6.151
2.953889	620.314	222.118	4.5105
2.9725	617.241	222.803	5.39
2.991111	617.643	224.064	5.301
3.01	615.505	224.045	7.489
3.089444	610.896	229.036	6.399
3.108056	607.123	229.435	6.2635
3.126944	607.783	229.145	5.9095
3.145556	605.42	233.515	6.787
3.164167	603.701	232.398	6.9815
3.245278	602.184	232.516	7.7025
3.264167	599.139	233.989	6.7575
3.282778	600.046	235.779	7.976
3.301389	598.586	238.698	8.0905
3.32	596.297	236.152	7.9865
3.380833	589.4	238.497	8.4715
3.399444	586.08	240.943	7.8895
3.418333	583.121	241.525	8.877
3.436944	584.095	247.055	8.2895
3.455556	584.285	244.454	8.708
3.531111	581.335	248.032	9.7765
3.549722	581.238	248.346	8.3485
3.568611	581.911	253.58	8.7895

2.2725	675.509	286.534
2.406944	692.554	253.05
2.425833	690.052	255.109
2.444444	691.318	255.703
2.463056	687.719	256.448
2.481667	688.974	255.414
2.564722	690.871	258.614
2.583333	688.69	259.328
2.602222	685.865	261.229
2.620833	684.922	263.856
2.639444	682.052	264.399
2.689722	674.732	270.422
2.708333	672.117	271.949
2.726944	673.168	271.369
2.745556	670.149	272.23
2.764444	665.563	274.714
2.844167	666.577	275.033
2.862778	666.957	277.44
2.881389	659.542	277.398
2.900278	661.996	280.928
2.918889	657.6	280.71
2.972222	659.092	284.506
2.990833	656.487	283.763
3.009444	656.264	286.393
3.028056	653.095	286.376
3.046667	655.756	288.846
3.126389	641.902	290.85
3.145	639.039	293.248
3.163611	640.057	291.896
3.1825	638.406	294.239
3.201111	636.44	295.312
3.282222	626.783	302.149
3.300833	622.866	304.59
3.319444	622.82	306.146
3.338056	618.784	306.202
3.356667	618.422	307.41
3.417778	616.246	308.218
3.436389	616.332	311.04
3.455	610.144	313.366
3.473889	611.595	313.251
3.4925	608.182	314.199
3.568056	595.441	324.054
3.586667	595.486	322.759

3.587222	579.014	251.954	9.4125
3.605833	578.484	253.724	9.8055
3.695833	573.603	258.033	10.9815
3.714444	571.985	259.786	9.0525
3.733333	571.963	260.362	10.423
3.751944	571.203	260.509	9.944
3.770556	568.291	263.503	10.4775
3.863333	562.512	270.82	11.3305
3.881944	560.255	266.612	10.8955
3.900556	558.265	269.172	11.1605
3.919167	559.538	270.307	11.7635
3.937778	553.752	272.258	11.218
4.014722	553.888	277.139	11.8935
4.033611	552.934	275.122	11.136
4.052222	553.736	278.261	12.557
4.070833	549.688	281.477	11.8
4.089444	549.917	283.812	12.785
4.145833	543.638	286.448	13.088
4.164444	543.828	290.118	12.732
4.183056	544.971	286.582	12.992
4.201667	542.024	290.621	12.4095
4.220278	540.485	288.741	13.6325
4.327778	532.362	293.541	14.4595
4.346389	531.274	297.076	13.906
4.365278	530.454	299.639	13.8755
4.383889	528.7	298.451	14.0075
4.4025	525.498	301.704	14.848
4.4725	523.272	305.286	14.5415
4.491111	522.149	305.799	15.8965
4.51	522.632	308.55	14.797
4.528611	519.242	308.308	15.9775
4.547222	515.559	309.11	15.129
4.624167	511.644	314.972	17.04
4.642778	511.953	313.942	16.9305
4.661667	510.859	318.29	16.339
4.680278	511.664	319.684	16.776
4.698889	508.018	322.715	17.6595
4.771667	502.4	323.994	18.059
4.790278	502.723	325.482	19.0555
4.808889	501.459	326.404	18.102
4.8275	500.396	324.725	19.0675
4.846111	498.465	324.237	18.6995
4.949167	494.29	333.617	20.628

3.605278	593.598	327.881
3.624167	593.775	325.683
3.642778	589.923	330.842
3.732778	579.037	337.506
3.751389	579.226	338.851
3.77	574.993	339.951
3.788611	576.615	341.305
3.8075	573.784	342.587
3.9	564.082	345.733
3.918611	561.691	347.66
3.937222	559.288	349.362
3.955833	558.943	350.292
3.974444	560.713	352.358
4.051667	549.474	361.661
4.070278	548.368	364.605
4.089167	546.806	364.975
4.107778	548.033	367.552
4.126389	541.619	368.731
4.1825	540.26	371.614
4.201389	535.807	373.458
4.22	534.45	372.922
4.238611	532.79	375.456
4.257222	530.409	378.555
4.364722	513.945	382.214
4.383333	516.405	384.084
4.401944	514.639	386.072
4.420556	511.265	389.088
4.439444	511.691	390.182
4.509444	502.4	396.578
4.528056	499.941	395.19
4.546667	502.677	397.356
4.565278	496.688	397.205
4.583889	495.698	398.551
4.661111	483.429	408.069
4.679722	485.151	407.732
4.698333	482.156	411.546
4.716944	478.361	412.537
4.735833	477.837	415.324
4.808333	471.539	418.881
4.827222	471.18	419.153
4.845833	467.395	423.997
4.864444	467.068	422.152
4.883056	466.789	424.652

4.967778	493.178	339.087	19.679
4.986389	492.334	339.621	20.386
5.005	493.012	340.182	19.8935
5.023611	489.911	339.166	21.1845
5.100556	486.533	346.221	21.0785
5.119167	488.875	347.544	21.9565
5.137778	484.562	348.112	21.759
5.156667	483.922	350.452	22.162
5.175278	482.202	349.357	21.9245
5.243889	478.473	352.967	23.068
5.2625	477.581	353.79	23.219
5.281111	476.551	355.02	22.517
5.299722	475.795	359.359	23.7275
5.318333	472.926	359.209	22.6255
5.425	465.904	371.07	24.175
5.443611	465.772	373.825	25.179
5.462222	464.637	373.178	24.513
5.480833	465.189	376.226	24.165
5.499444	462.801	375.502	25.338
5.592222	458.634	375.744	24.695
5.610833	457.874	375.004	25.916
5.629444	457.823	378.149	25.896
5.648333	454.478	378.744	25.8415
5.666944	455.039	382.833	27.58
5.7375	449.599	386.221	27.6675
5.756111	458.006	372.071	28.4005
5.774722	447.023	386.388	28.2575
5.793333	445.493	386.258	28.021
5.811944	456.201	370.312	27.8875
5.86	445.322	385.716	30.2975
5.878889	454.463	372.206	29.533
5.8975	444.022	388.699	29.0065
5.916111	449.216	375.618	29.512
5.934722	450.248	375.031	30.69
5.993333	448.426	378.2	30.32
6.011944	436.508	394.304	32.0055
6.030556	431.796	398.734	31.3955
6.049167	432.337	399.974	31.6265
6.067778	431.42	401.211	31.367
6.156667	426.899	401.849	33.8615
6.175278	428.59	403.696	34.417
6.193889	426.625	404.837	35.472
6.2125	424.912	405.213	34.482

4.986111	455.915	436.735
5.004444	452.834	437.191
5.023333	452.35	437.878
5.041944	448.79	442.572
5.060556	447.716	441.953
5.1375	439.599	449.212
5.156111	438.402	451.881
5.174722	436.673	452.069
5.193333	436.368	454.642
5.211944	432.86	456.087
5.280833	428.445	462.027
5.299444	426.132	463.773
5.318056	421.041	464.9
5.336667	422.45	467.553
5.355278	420.854	466.081
5.461667	410.925	476.89
5.480278	407.947	476.887
5.498889	406.191	479.033
5.517778	403.672	480.646
5.536389	402.558	481.254
5.629167	393.905	487.847
5.647778	393.716	491.731
5.666389	390.159	491.262
5.685	389.349	494.566
5.703889	388.612	493.06
5.774167	381.073	499.519
5.792778	378.639	498.665
5.811389	378.8	503.812
5.830278	377.813	501.991
5.848889	374.116	505.867
5.896944	366.172	510.726
5.915556	364.743	513.67
5.934167	364.626	514.096
5.953056	362.062	514.488
5.971667	357.731	516.371
6.03	359.714	516.151
6.048611	355.71	515.417
6.067222	355.292	517.716
6.085833	355.761	518.477
6.104722	354.838	522.116
6.193333	346.421	527.005
6.211944	342.894	529.331
6.230556	342.751	530.747

6.231111	424.751	407.182	35.3375
6.334722	418.712	411.163	36.477
6.353333	416.868	414.806	35.997
6.371944	417.568	413.421	36.68
6.390556	418.7	415.955	38.3185
6.409167	414.674	418.975	37.625
6.475278	415.425	415.481	39.5585
6.493889	412.743	420.159	39.1115
6.5125	413.1	421.811	39.643
6.531111	411.565	420.908	40.255
6.55	409.782	420.337	40.251
6.609722	408.706	426.182	41.3435
6.628333	408.541	424.821	41.9525
6.647222	408.352	426.613	42.182
6.665833	405.437	428.939	42.0735
6.684444	404.387	430.458	42.485
6.756944	404.973	428.595	44.548
6.775556	402.033	429.013	45.3665
6.794167	400.207	428.722	46.021
6.812778	401.823	431.295	46.2835
6.831389	400.312	434.029	46.2125
6.896944	397.846	431.254	46.5765
6.915556	397.262	435.345	47.6535
6.934167	394.213	436.585	46.8745
6.952778	393.536	434.132	48.018
6.971389	393.961	434.867	47.553
7.049722	391.429	440.018	48.4375
7.068333	390.486	440.529	50.232
7.086944	390.354	440.845	50.165
7.105556	391.588	441.875	50.348
7.124444	389.261	441.989	50.885
7.2	383.956	450.951	53.0655
7.218889	384.496	451.169	52.733
7.2375	385.067	443.851	52.6045
7.256111	385.672	449.763	53.194
7.274722	382.828	449.639	52.532
7.363333	383.633	452.309	55.754
7.381944	381.43	453.465	55.036
7.400556	379.651	453.932	55.66
7.419167	379.891	452.557	56.912
7.438056	377.18	456.514	57.261
7.521944	377.062	455.472	57.6715
7.540556	378.45	454.483	57.9125

6.249167	341.175	532.632
6.268056	340.193	531.325
6.371389	330.587	539.777
6.39	329.457	540.811
6.408889	325.372	542.907
6.4275	324.494	543.493
6.446111	322.939	546.373
6.512222	322.237	549.289
6.530833	321.215	550.321
6.549444	316.614	552.474
6.568056	316.847	552.836
6.586667	318.139	552.823
6.646667	313.846	557.279
6.665278	310.19	557.702
6.683889	308.498	563.064
6.7025	308.925	560.688
6.721389	309.243	566.34
6.793889	302.178	564.625
6.8125	300.055	568.908
6.831111	300.539	567.319
6.849722	297.847	571.104
6.868333	298.312	569.929
6.933611	295.148	573.233
6.952222	293.864	572.042
6.970833	291.837	573.414
6.989444	289.364	573.908
7.008056	290.638	577.23
7.086667	280.785	584.418
7.105278	283.328	585.206
7.123889	279.843	585.315
7.1425	280.901	588.576
7.161111	277.794	589.347
7.236944	277.47	591.09
7.255556	276.039	589.244
7.274444	277.118	590.25
7.293056	275.257	591.511
7.311667	272.245	593.648
7.400278	267.219	600.179
7.418889	266.508	600.713
7.4375	262.204	601.236
7.456111	263.902	604.047
7.474722	261.795	603.579
7.558611	257.505	610.903

7.559167	377.135	456.379	58.3555
7.577778	378.614	455.911	58.454
7.596389	377.678	458.579	58.7085
7.663889	376.353	457.414	60.895
7.682778	376.928	458.825	60.987
7.701111	375.877	462.702	62.489
7.72	373.304	461.605	61.9815
7.738611	375.568	463.025	62.0745
7.809167	370.468	464.221	63.5285
7.827778	372.387	462.82	64.6935
7.846389	369.12	465.669	64.5855
7.865	371.849	463.001	63.984
7.883611	369.593	465.053	64.507
7.9625	370.469	466.484	66.9745
7.981389	370.121	464.035	66.683
8	366.849	465.578	67.7095
8.018611	366.038	465.401	67.183
8.037222	367.613	464.358	67.636
8.085833	367.401	464.127	69.7325
8.104444	364.677	469.875	69.5235
8.123056	367.877	465.232	70.2205
8.141667	366.398	469.695	70.895
8.160278	367.355	466.731	71.0285
8.229444	363.776	466.591	72.496
8.248056	361.967	467.815	72.4005
8.266667	363.653	466.673	72.973
8.285278	364.909	469.473	73.379
8.303889	361.062	468.5	73.267
8.389167	357.454	471.496	75.649
8.408056	357.244	473.551	76.395
8.426667	359.847	472.494	76.281
8.445278	360.169	472.898	76.769
8.463889	359.949	473.056	76.792
8.539444	362.193	473.082	78.803
8.558056	359.694	476.717	78.601
8.576667	357.585	475.35	77.9145
8.595278	355.628	477.241	79.1615
8.613889	357.189	474.642	79.6955
8.665278	357.442	476.762	82.1495
8.683889	357.994	475.248	81.6715
8.702778	357.726	475.658	83.345
8.721389	357.862	474.835	83.1925
8.739722	355.684	475.437	83.364

7.577222	259.751	608.559
7.595833	256.329	611.011
7.614722	254.993	612.413
7.633333	254.637	614.546
7.700833	252.542	614.255
7.719444	253.503	616.719
7.738056	249.008	616.847
7.756667	249.352	616.18
7.775278	247.332	619.888
7.845833	245.95	619.541
7.864444	243.952	619.964
7.883056	244.122	622.702
7.901667	241.682	621.49
7.920278	239.498	623.528
7.999444	236.954	625.435
8.018056	237.705	627.405
8.036667	233.581	628.617
8.055556	236.283	630.781
8.074167	234.524	629.645
8.1225	225.194	634.235
8.141111	223.336	633.11
8.159722	221.899	636.579
8.178611	223.116	635.304
8.196944	223.231	636.121
8.266389	224.522	634.545
8.285	223.643	636.036
8.303611	224.581	633.886
8.322222	223.502	636.504
8.340833	221.617	635.946
8.426111	220.076	639.973
8.444722	218.432	641.552
8.463333	217.466	641.059
8.482222	220.476	641.938
8.500833	215.226	643.499
8.576111	213.565	642.697
8.594722	213.847	645.11
8.613333	213.619	645.236
8.631944	215.041	647.564
8.650556	211.342	647.857
8.702222	210.155	649.798
8.720833	209.761	649.635
8.739444	213.284	651.555
8.758056	211.245	652.969

8.788333	358.093	475.326	85.999
8.885833	354.403	479.241	86.4955
8.904444	356.224	480.649	86.441
8.923333	354.347	478.316	86.9935
8.941667	354.439	478.434	86.625
8.960556	351.678	482.549	88.9215
9.055556	351.336	479.318	88.5255
9.074167	351.678	476.917	89.6395
9.092778	351.045	480.034	89.793
9.111389	349.824	480.052	89.884
9.13	353.499	479.852	92.11
9.230278	348.746	486.562	92.392
9.249167	348.066	485.448	92.6655
9.267778	347.651	484.74	93.1905
9.286389	351.387	482.501	93.5705
9.305	349.625	484.707	94.742
9.389722	350.557	480.983	94.6525
9.408333	346.35	488.05	95.6225
9.426944	349.339	486	96.122
9.445556	348.039	485.843	95.786
9.464167	351.561	482.675	98.3055
9.581944	347.15	488.877	97.676
9.600556	347.507	486.491	98.629
9.619167	345.677	488.893	98.6225
9.637778	349.251	486.324	99.416
9.656667	349.565	485.821	100.607
9.7825	343.968	489.818	100.6555
9.801111	343.927	489.029	101.274
9.819722	345.993	488.029	101.364
9.838333	342.84	490.833	101.934
9.856944	346.592	485.582	103.1195
9.944444	342.679	491.014	103.883
9.962778	341.163	493.291	103.5525
9.981667	343.007	491.876	105.3005
10.00056	343.087	491.5	104.376
10.01972	342.203	492.879	105.914
10.10194	341.245	487.235	105.893
10.12028	340.651	489.064	106.726
10.13889	342.584	488.964	106.9485
10.1575	340.138	489.606	106.759
10.17639	341.902	487.485	108.654
10.26778	340.94	489.189	108.873
10.28639	339.865	490.18	109.274

8.776667	209.804	652.312
8.904167	215.985	
8.922778	202.029	657.011
8.941389	203.349	657.229
8.96	202.214	659.529
8.978611	200.32	657.434
9.073889	211.739	
9.0925	197.524	658.711
9.111111	197.646	661.235
9.129722	198.923	660.453
9.148333	197.047	661.669
9.248611	209.88	
9.267222	192.639	665.455
9.285833	196.219	665.05
9.304444	194.469	667.808
9.323056	192.16	664.937
9.407778	202.216	
9.426389	192.177	670.154
9.445278	189.802	672.044
9.463611	187.71	671.509
9.4825	187.375	672.323
9.600278	200.023	
9.618889	186.096	676.86
9.6375	185.822	672.528
9.656111	186.056	674.888
9.674722	183.764	674.349
9.800833	194.557	
9.819444	179.446	676.905
9.838056	181.52	676.422
9.856667	182.24	675.224
9.875278	180.087	674.96
9.9625	188.321	
9.981111	175.38	676.437
9.999722	177.637	674.886
10.01833	177.157	677.678
10.03722	176.353	678.02
10.12	187.489	
10.13861	173.594	679.953
10.15722	175.359	679.206
10.17583	173.526	679.712
10.19444	173.677	679.915
10.28583	184.209	
10.30444	170.937	684.174

10.305	341.656	488.599	109.5235
10.32361	339.125	490.178	110.525
10.3425	345.071	490.98	111.8615
10.41833	339.305	492.128	112.1935
10.43694	339.476	491.955	112.396
10.45583	338.838	490.953	112.2525
10.47444	341.304	490.904	111.801
10.49306	340.005	491.525	114.0645
10.56833	337.735	493.637	114.5085
10.58722	342.031	490.005	114.6575
10.60583	339.911	492.878	114.274
10.62444	339.92	493.101	115.0905
10.64306	338.646	489.816	117.7765
10.72167	338.535	492.729	117.213
10.74028	337.921	491.947	117.9415
10.75889	339.521	492.194	118.165
10.7775	337.933	493.68	117.579
10.79611	337.711	491.19	119.201
10.8975	336.702	494.935	119.6605
10.91583	336.619	494.158	119.5825
10.93444	337.218	492.222	119.9735
10.95306	339.031	493.755	120.9105
10.97167	338.054	493.646	121.662
11.07444	335.99	496.595	122.15
11.09278	336.177	495.2	122.4995
11.11167	337.407	495.281	123.375
11.13028	338.037	495.074	122.845
11.14889	338.119	493.342	125.4875
11.215	340.096	495.903	124.895
11.23361	336.793	498.255	125.5325
11.25222	336.006	499.699	126.0515
11.27083	338.499	497.099	125.797
11.28944	336.87	498.459	128.1655
11.375	337.028	501.218	127.93
11.39361	336.877	499.479	128.1335
11.41222	337.071	498.583	129.0515
11.43083	337.227	496.89	129.3635
11.44944	336.719	497.886	130.6855
11.53167	339.673	494.918	130.2285
11.55028	335.688	495.374	131.039
11.56889	337.914	495.163	131.3415
11.5875	336.8	495.279	131.889
11.60611	336.44	498.776	132.4825

10.32333	169.341	684.768
10.34194	172.805	685.955
10.36056	171.175	685.166
10.43639	181.188	
10.45528	169.439	688.222
10.47389	168.115	689.102
10.4925	167.289	689.241
10.51111	166.421	688.998
10.58667	175.039	
10.60528	165.559	691.286
10.62389	164.637	690.479
10.6425	164.702	691.89
10.66111	167.561	689.999
10.73972	178.07	
10.75861	164.642	688.89
10.77694	165.72	690.508
10.79583	165.908	690.349
10.81444	163.884	692.845
10.91556	169.664	
10.93417	160.996	693.753
10.95278	158.53	693.385
10.97139	159.682	695.025
10.99	158.954	697.468
11.0925	168.543	748.992
11.11111	157.475	697.427
11.12972	160.183	696.522
11.14833	157.854	698.08
11.16694	155.979	698.789
11.23306	167.784	
11.25194	155.67	698.272
11.27056	155.808	697.306
11.28917	154.626	699.473
11.30778	155.687	699.312
11.39306	164.942	
11.41167	154.651	700.874
11.43028	156.932	700.619
11.44889	154.512	699.686
11.4675	155.761	701.268
11.54972	165.228	752.207
11.56833	150.79	702.978
11.58722	153.79	702.329
11.60556	153.269	700.858
11.62417	154.636	700.439

11.70611	336.343	499.18	133.0855
11.72472	334.997	498.947	133.404
11.74333	335.08	500.221	132.685
11.76194	337.497	495.536	133.7325
11.78056	335.275	500.7	134.677
11.89472	339.955	497.506	134.235
11.91333	337.016	496.65	134.7635
11.93222	338.149	497.975	134.9905
11.95083	337.015	500.996	135.0425
11.96944	335.252	501.57	136.9515
12.04556	337.876	500.953	136.8855
12.06417	338.701	500.651	138.172
12.08278	336.636	499.576	137.5555
12.10167	337.612	498.942	137.861
12.12028	335.498	500.163	139.3785
12.26	334.6	501.666	139.464
12.27861	333.838	502.188	140.2975
12.29722	336.206	501.972	140.155
12.31583	337.279	501.591	140.222
12.33472	337.657	502.032	142.0715
12.42139	333.307	503.391	142.0435
12.44	335.292	500.589	142.521
12.45889	334.606	500.093	142.095
12.4775	333.38	501.377	142.893
12.49611	335.836	500.891	143.525
12.57361	337.324	503.645	144.636
12.59222	334.365	505.357	144.378
12.61083	334.587	504.774	144.121
12.62944	334.73	503.273	145.2825
12.64833	335.166	501.923	146.0325
12.75611	335.557	503.434	145.8885
12.775	336.978	500.495	146.1285
12.79389	335.014	501.542	146.513
12.8125	337.591	501.865	147.5305
12.83139	333.652	502.96	148.7805
12.94472	334.083	503.768	148.3765
12.96333	335.064	502.65	148.81
12.98222	333.472	503.249	149.006
13.00083	336.106	502.365	149.4895
13.01972	337.654	500.765	150.075
13.13306	335.241	502.775	150.703
13.15194	334.5	502.816	150.2
13.17083	335.472	503.964	150.7565

11.72417	159.717	
11.74278	151.147	703.575
11.76139	148.515	703.132
11.78	148.633	702.133
11.79861	150.175	702.518
11.91306	158.537	
11.93167	149.587	706.465
11.95028	147.242	705.911
11.96889	146.917	708.315
11.9875	147.503	704.69
12.06389	155.966	
12.0825	149.809	704.806
12.10111	144.965	708.689
12.11972	146.48	710.24
12.13833	151.304	706.782
12.27806	156.039	759.65
12.29667	143.199	709.16
12.31528	145.321	707.067
12.33417	143.23	709.229
12.35278	144.33	706.018
12.43944	154.779	
12.45833	143.671	706.9
12.47694	144.401	707.624
12.49556	146.519	706.905
12.51417	143.791	708.754
12.59167	152.27	
12.61028	142.509	711.991
12.62889	141.199	712.496
12.64778	139.646	713.146
12.66639	140.951	712.428
12.77417	149.227	765.008
12.79306	141.972	714.591
12.81194	140.319	714.03
12.83056	143.601	714.828
12.84944	138.624	715.724
12.96278	149.131	
12.98139	138.928	712.789
13.00028	137.155	713.271
13.01889	136.951	716.473
13.03778	137.031	716.547
13.15111	146.612	
13.17	136.613	716.235
13.18889	136.162	717.409

13.18944	335.603	502.286	151.3015
13.20833	335.468	504.503	152.5685
13.29667	335.845	503.313	152.132
13.31556	336.345	502.244	152.462
13.33444	335.205	503.162	153.4395
13.35306	338.395	502.266	153.2955
13.37194	338.972	504.841	153.5895
13.46139	334.461	500.544	154.2705
13.48028	335.242	501.677	154.174
13.49889	335.036	501.447	154.253
13.51778	336.182	501.814	154.0845
13.53667	334.389	503.909	155.4175
13.61806	339.171	502.861	155.7065
13.63694	336.899	502.076	156.215
13.65583	336.5	501.319	156.0975
13.67472	335.152	503.662	156.749
13.69361	334.873	503.502	157.7785
13.79028	331.439	503.813	158.018
13.80917	333.79	501.987	158.3025
13.82806	332.817	501.671	158.798
13.84667	334.426	502.19	158.9745
13.86556	335.42	504.261	159.8185
13.94472	333.943	502.804	160.165
13.96389	337.258	501.081	160.6055
13.98278	335.178	504.783	160.311
14.00167	335.157	505.714	160.4545
14.02056	336.206	503.844	161.9155
14.09806	340.251	499.1	161.383
14.11694	335.304	503.494	161.7035
14.13583	336.062	502.367	162.3185
14.15472	338.439	499.886	162.6125
14.17361	339.364	499.93	164.0035
14.30194	342.57	499.245	164.3725
14.32083	337.298	498.511	163.923
14.33972	337.414	499.015	164.3675
14.35861	340.593	497.598	164.405
14.3775	339.607	500.31	165.1935
14.46694	335.863	503.092	165.0545
14.48583	337.136	503.299	166.533
14.50472	337.192	500.36	166.3205
14.52361	335.173	502.872	166.457
14.5425	337.741	501.727	167.5565
14.60556	338.331	501.615	167.498

13.2075	135.182	
13.22639	135.608	715.417
13.31472	146.382	
13.33361	135.468	718.493
13.35222	135.452	718.507
13.37111	134.272	718.902
13.39	134.943	714.923
13.47944	143.981	
13.49833	134.274	715.975
13.51694	133.744	714.097
13.53583	132.981	717.521
13.55472	132.85	715.821
13.63611	142.533	
13.655	132.882	715.797
13.67389	133.375	717.716
13.6925	131.623	717.208
13.71139	133.384	717.915
13.80833	143.611	
13.82722	130.508	715.056
13.84583	131.072	715.738
13.86472	132.672	715.136
13.88361	131.885	717.982
13.96278	140.777	
13.98167	129.231	721.356
14.00083	130.992	731.503
14.01972	129.442	722.472
14.03861	129.834	719.495
14.11611	139.224	
14.135	130.124	720.693
14.15389	130.864	723.863
14.17278	131.712	722.151
14.19167	131.529	723.085
14.25667	141.038	
14.33889	128.911	720.358
14.35778	129.266	722.314
14.37639	127.744	721.035
14.39528	130.22	719.865
14.41417	130.504	720.132
14.50361	128.348	720.49
14.5225	128.338	723.933
14.54139	129.608	722.171
14.56028	126.621	724.925
14.57917	127.125	725.891

14.62444	338	499.705	167.591
14.64333	336.313	502.185	166.9025
14.66222	339.374	499.417	167.0945
14.68111	338.458	502.916	167.9665
14.76278	337.211	500.061	168.7085
14.78167	335.339	503.006	169.0595
14.80056	338.866	500.773	169.1945
14.81944	340.212	499.7	169.5305
14.83833	336.863	501.678	169.878
14.9375	336.837	503.232	169.6845
14.95639	336.35	505.313	169.819
14.97528	338.494	506.232	170.039
14.99417	336.641	504.306	169.88
15.01306	336.738	502.691	172.188
15.07056	336.778	502.326	171.0845
15.08972	335.556	503.915	171.2845
15.10861	335.393	504.074	171.9485
15.1275	339.004	504.166	171.85
15.14639	336.224	504.225	171.901
15.22444	340.433	500.492	171.824
15.24361	337.199	503.069	172.441
15.2625	337.613	503.302	172.259
15.28139	337.922	502.808	171.7585
15.30056	335.816	503.728	173.762
15.3675	337.991	502.928	172.878
15.38639	335.986	505.73	173.421
15.40528	338.518	505.449	173.3515
15.42444	336.266	503.975	173.436
15.44333	337.596	505.546	174.0145
15.54111	335.878	502.726	175.115
15.56028	338.125	503.703	174.748
15.57917	339.059	504.028	175.236
15.59806	339.038	501.701	174.7645
15.61722	336.888	503.879	175.436
15.70306	339.007	501.05	176.3205
15.72222	337.254	502.948	176.4675
15.74111	338.029	503.854	176.4515
15.76028	339.461	503.729	176.8145
15.77917	340.045	501.622	177.4355
15.84583	336.984	502.795	178.108
15.86472	336.172	506.938	178.1815
15.88389	336.865	505.946	177.7015
15.90278	335.635	506.944	178.6325

14.64222	126.313	723.506
14.66111	127.112	721.738
14.68	126.757	722.987
14.69917	129.236	723.603
14.71806	125.704	724.991
14.79944	125.948	724.53
14.81861	128.619	723.531
14.8375	127.259	723.207
14.85639	127.384	722.861
14.87528	127.094	723.433
14.97444	124.212	728.146
14.99333	121.488	724.428
15.01222	125.507	727.205
15.03111	126.364	724.633
15.05	125.266	725.23
15.1075	122.648	727.625
15.12639	122.619	726.117
15.14528	123.001	724.793
15.16444	125.33	724.691
15.18333	123.182	725.017
15.26139	124.284	724.042
15.28028	125.336	725.078
15.29944	123.13	725.276
15.31833	125.679	723.432
15.33722	123.541	725.016
15.40417	118.539	725.365
15.42333	118.012	727.135
15.44222	119.232	727.055
15.46111	118.811	727.393
15.48	122.061	725.594
15.57806	122.611	726.618
15.59694	123.673	726.219
15.61611	122.448	729.793
15.635	122.962	726.594
15.65389	122.545	728.314
15.74	122.761	730.622
15.75889	121.064	729.172
15.77806	119.691	727.662
15.79694	122.011	730.52
15.81611	118.436	730.943
15.8825	125.478	731.109
15.90167	121.954	731.996
15.92056	122.365	732.27

15.92194	338.305	505.598	178.3
15.99528	340.024	505.098	179.368
16.01417	338.488	503.866	179.3375
16.03333	341.463	502.664	178.89
16.0525	338.033	505.815	179.166
16.07167	343.473	501.628	179.4525
16.14139	339.089	507.279	179.27
16.16056	341.752	504.122	179.3125
17.90083	343.404	495.307	-

15.93972	121.579	731.718
15.95861	123.013	731.579
16.03194	120.78	731.703
16.05111	122.172	734.659
16.07028	120.976	731.632
16.08917	118.343	735.409
16.10833	121.449	733.213
16.17833	120.208	735.756
17.91833	121.196	774.891

Table S9 – Final Mass Balance for Different Excess NBS

Time	¹⁹ F NMR			
	Nitrotoluene 1 (mM)	Monobromide 2 (mM)	Dibromide 3 (mM)	Total
Start	900	0	0	900
End	341.752	504.122	179.3125	1025
		Mass Balance		125%
		Total Bromination		862 mM

¹ H NMR		
NBS (mM)	Succinimide (mM)	Total
780	0	780
121.196	774.891	895
		115%
		775 mM

3.4 Order in Benzoyl Peroxide

Experiment	[NitroTol 1] ₀ (M)	[NBS] ₀ (M)	[BPO] ₀ (M)
Exp. 4 – Order in BPO	0.90	1.56	0.0510

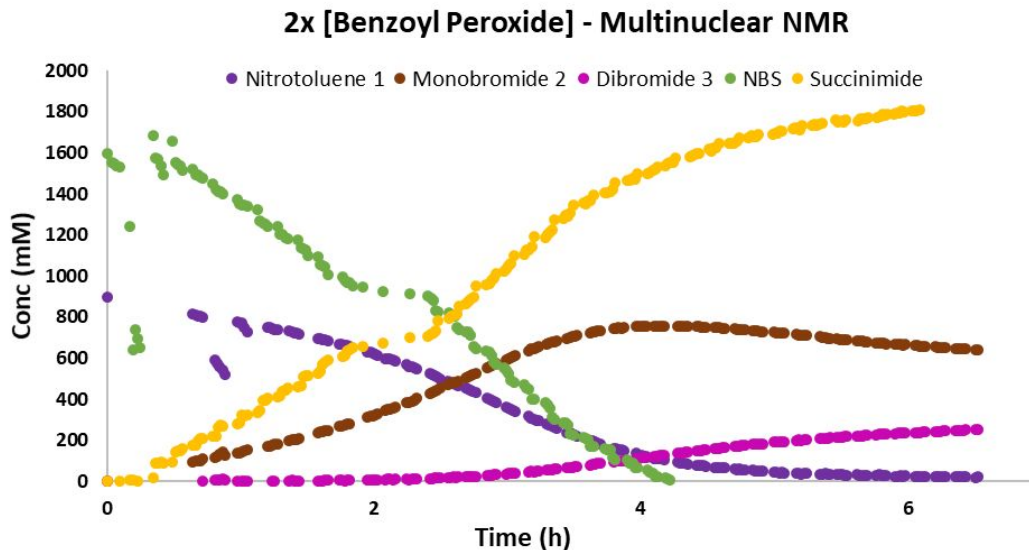


Figure S4 – Reaction Progress data for 2 x [benzoyl peroxide]

VTNA was used to determine the order in benzoyl peroxide by calculating the decreasing concentration of benzoyl peroxide during reaction progress.⁶ Benzoyl peroxide concentration was calculated using first order decay with a $t_{1/2} = 3$ h at 83 °C.

Table S10 – ¹H / ¹⁹F NMR Reaction Progress data for 2 x [benzoyl peroxide]

¹⁹ F NMR			
Time (h)	Nitrotoluene 1 (mM)	Monobromide 2 (mM)	Dibromide 3 (mM)
0	900	0	0
0.644722	815	94.313	-0.468
0.663611	809.003	101.229	-1.009
0.682222	802.357	99.9	-1.5145
0.700833	804.992	100.67	-1.7085
0.719444	796.93	108.021	0.0255
0.809167	590.736	114.79	6.4745
0.827778	576.672	122.861	4.9135
0.846389	555.638	133.523	8.3665
0.865278	539.207	140.288	10.6595
0.883889	518.087	126.229	5.2925
0.973611	779.29	139.752	2.0375
0.992222	770.629	139.176	-0.8735
1.011111	770.208	143.123	0.1455
1.029722	751.128	146.183	0.521

¹ H NMR			
Time (h)	NBS (mM)	Succinimide (mM)	Calculated [BPO] (mM)
0	1600	-	51
0.036944	1554.371	-	43.94167
0.055556	1547.141	-	43.75032
0.074167	1537.467	3.116	43.56259
0.093056	1533.882	5.011	43.37567
0.175	1240.344	8.353	43.18955
0.193611	639.2	-	42.30344
0.2125	737.935	0.373	42.12192
0.231111	695.926	-	41.94118
0.25	648.741	19.135	41.75854
0.346944	1684.784	89.184	41.57936
0.365556	1578.101	85.98	40.72628
0.384444	1568.355	91.162	40.55153
0.403056	1534.648	87.721	40.37494
0.421944	1494.781	94.334	40.2017

1.048611	727.587	152.918	1.7965
1.201111	751.743	169.687	-0.5255
1.22	749.89	171.923	-0.404
1.238889	746.265	177.977	1.5995
1.2575	740.649	180.666	1.084
1.276111	740.585	182.453	-0.0085
1.366389	731.755	198.714	2.261
1.385	729.302	202.882	4.185
1.403889	723.168	204.47	1.8515
1.4225	721.794	205.502	0.916
1.441111	717.167	210.166	2.3765
1.579444	697.528	235.103	2.7265
1.598056	696.458	238.48	2.8515
1.616944	690.664	242.237	2.802
1.635556	689.545	246.024	3.835
1.654167	686.238	249.379	3.7005
1.7425	668.395	265.987	3.4135
1.761111	666.594	270.63	4.4775
1.78	661.958	272.429	2.067
1.798611	660.598	276.911	3.6135
1.8175	659.373	280.57	4.9515
1.953333	628.999	312.421	6.1315
1.972222	627.003	316.664	6.9235
1.990833	622.814	320.225	7.249
2.009722	619.142	324.266	7.483
2.028333	614.101	329.111	8.074
2.085278	599.302	342.45	6.815
2.103889	599.294	348.882	9.4135
2.122778	594.46	352.043	8.7975
2.141389	590.236	355.19	8.169
2.16	586.794	360.53	9.6275
2.246389	567.199	383.018	10.5295
2.265278	560.778	383.858	8.5535
2.283889	557.561	389.217	9.4335
2.3025	554.154	396.084	12.376
2.321389	545.189	402.548	10.5445
2.418889	523.329	427.13	13.6765
2.4375	519.499	430.605	12.952
2.456389	516.324	437.334	15.2255
2.475278	508.792	442.82	16.637
2.493889	499.537	453.819	16.7875
2.556667	484.918	469.829	19.0615
2.575278	480.967	474.181	19.697

0.493889	1656.437	140.223	40.02663
0.5125	1553.553	149.154	38.64085
0.531389	1540.812	150.799	38.47258
0.55	1535.574	158.836	38.30504
0.568889	1513.313	176.488	38.14068
0.643611	1522.364	176.622	37.97702
0.6625	1495.696	196.026	37.19308
0.681111	1490.816	208.411	37.03349
0.699722	1485.183	206.276	36.87222
0.718611	1477.734	218.429	36.71401
0.796389	1451.894	218.742	36.55647
0.815	1423.536	261.289	35.40654
0.833889	1411.412	272.787	35.25461
0.8525	1411.773	270.428	35.10109
0.871111	1399.128	278.78	34.95047
0.973889	1375.582	282.739	34.80051
0.992778	1351.361	321.403	34.09745
1.011389	1346.602	319.821	33.95114
1.030278	1344.779	323.804	33.8033
1.048889	1342.889	331.903	33.65825
1.128611	1323.211	342.581	33.51168
1.1475	1268.106	393.25	32.47627
1.166111	1256.564	392.438	32.33485
1.184722	1255.443	404.72	32.1961
1.203333	1241.723	409.728	32.0559
1.278333	1241.107	415.265	31.91835
1.296944	1201.272	436.461	31.50115
1.315833	1201.055	445.923	31.36599
1.334444	1187.268	452.704	31.2294
1.353056	1180.964	458.93	31.0954
1.433333	1175.251	462.893	30.96197
1.451944	1135.664	506.456	30.35009
1.470556	1130.025	512.915	30.21793
1.489444	1125.989	514.038	30.08827
1.508056	1099.283	525.175	29.95916
1.578611	1094.491	536.88	29.8287
1.5975	1057.212	568.896	29.16425
1.616111	1052.313	579.476	29.03911
1.634722	1042.947	589.119	28.91265
1.653611	1006.566	606.882	28.78674
1.763333	996.842	612.421	28.66323
1.782222	979.162	636.811	28.25047
1.800833	969.926	641.971	28.12925

2.593889	477.298	479.834	19.8585
2.612778	469.841	482.688	19.0545
2.631389	468.007	488.44	20.1895
2.686667	452.52	502.877	20.489
2.705556	447.932	510.363	22.6695
2.724167	442.058	514.066	22.0465
2.743056	435.757	520.594	23.952
2.761667	430.138	524.308	23.948
2.845278	405.059	551.171	28.4845
2.864167	400.387	556.851	27.4255
2.882778	394.711	562.975	29.499
2.901667	391.06	567.552	31.0755
2.920278	385.377	572.204	32.3935
2.988333	362.086	593.581	35.1565
3.006944	357.681	599.277	37.457
3.025556	351.625	602.944	36.3935
3.044167	347.592	608.712	38.4115
3.063056	342.237	614.082	40.606
3.160556	316.42	636.315	46.3525
3.179167	309.077	644.228	47.4495
3.197778	303.989	645.797	46.347
3.216667	296.452	650.238	48.045
3.235556	295.861	655.576	50.7315
3.295556	278.017	666.875	53.249
3.314167	272.094	671.896	56.0005
3.332778	269.206	676.365	57.518
3.351389	262.149	681.137	59.297
3.370278	256.261	683.199	60.286
3.447222	235.665	697.012	64.203
3.466111	233.966	701.33	67.8515
3.484722	228.461	704.791	68.78
3.503333	223.508	707.628	69.261
3.522222	219.91	711.8	72.5505
3.619167	195.53	723.241	78.068
3.637778	198.611	727.841	82.778
3.656667	193.003	729.448	83.08
3.675278	186.945	732.064	86.247
3.694167	181.713	732.756	86.5445
3.796389	159.217	742.242	95.278
3.815278	159.723	745.765	97.675
3.833889	152.848	747.143	98.036
3.8525	152.175	746.866	101.7165
3.871111	146.019	748.753	101.3225

1.819444	966.821	651.846	28.00856
1.838333	954.237	659.31	27.88659
1.9175	947.875	673.713	27.76693
2.067778	922.017	699.795	27.41455
2.2725	915.638	708.186	27.29516
2.406944	903.85	717.37	27.17805
2.425833	891.646	723.423	27.05969
2.444444	883.408	732.842	26.94358
2.463056	833.983	782.026	26.42807
2.481667	825.224	791.691	26.31299
2.564722	821.082	802.153	26.20008
2.583333	808.152	808.668	26.08599
2.602222	802.345	816.554	25.97406
2.620833	748.714	854.708	25.56883
2.639444	739.428	866.382	25.45912
2.689722	729.349	877.577	25.34988
2.708333	725.337	884.201	25.2411
2.726944	709.01	896.559	25.13119
2.745556	654.185	954.479	24.57138
2.764444	643.699	959.792	24.46595
2.844167	632.276	965.265	24.36097
2.862778	628.082	980.395	24.25488
2.881389	610.708	990.762	24.14926
2.900278	577.716	1013.936	23.81679
2.918889	567.895	1024.043	23.71459
2.972222	550.416	1036.028	23.61284
2.990833	540.916	1052.961	23.51152
3.009444	525.715	1060.935	23.40913
3.028056	494.499	1101.211	22.99664
3.046667	484.014	1105.622	22.8965
3.126389	468.813	1124.52	22.79825
3.145	456.233	1128.645	22.70043
3.163611	451.589	1143.714	22.60157
3.1825	399.212	1192.085	22.10095
3.201111	400.736	1188.709	22.00612
3.282222	381.615	1201.094	21.91029
3.300833	372.561	1216.674	21.81627
3.319444	357.817	1226.217	21.72127
3.338056	310.154	1274.41	21.21426
3.356667	299.369	1281.341	21.12188
3.417778	287.619	1297.686	21.03125
3.436389	287.363	1291.891	20.941
3.455	275.308	1305.678	20.85115

3.966111	135.761	755.122	110.122
3.985	129.046	754.451	112.0155
4.003611	126.996	753.513	113.4585
4.022222	121.448	755.236	114.9245
4.040833	120.084	755.544	115.6075
4.101111	111.732	756.81	121.09
4.119722	110.489	757.228	121.9505
4.138611	109.26	756.444	125.1125
4.157222	108.714	757.029	126.9065
4.175833	102.192	757.45	128.0215
4.274722	92.131	754.754	137.738
4.293611	90.746	757.023	137.9595
4.312222	88.74	757.065	138.734
4.330833	85.391	756.45	141.4525
4.349444	82.501	755.878	141.598
4.415278	77.364	752.928	148.103
4.433889	78.962	753.341	147.876
4.452778	76.758	750.92	150.006
4.471389	76.541	751.596	152.366
4.49	70.604	750.661	152.989
4.551944	66.625	749.726	158.2165
4.570556	65.005	748.832	159.836
4.589444	67.239	748.931	160.7885
4.608056	65.989	746.427	162.354
4.626667	64.887	745.787	163.637
4.701944	58.857	743.927	169.7425
4.720556	57.305	739.765	169.997
4.739444	58.566	741.127	172.194
4.758056	55.139	740.493	173.273
4.776667	55.1	738.84	174.3695
4.8375	52.945	732.553	179.221
4.856389	47.76	731.708	179.491
4.875	49.711	733.73	181.863
4.893889	50.204	729.465	182.5085
4.9125	49.404	730.026	183.2295
4.999722	42.421	725.512	190.048
5.018333	43.051	725.051	190.9985
5.037222	40.853	723.963	192.356
5.055833	41.715	722.247	191.9085
5.074444	41.539	720.956	193.839
5.165278	36.626	716.226	198.5595
5.183889	39.482	713.206	200.3615
5.202778	34.694	711.883	200.1025

3.473889	229.967	1347.732	20.39846
3.4925	223.149	1354.032	20.30963
3.568056	214.524	1353.795	20.22248
3.586667	207.972	1368.514	20.13571
3.605278	201.597	1368.344	20.04931
3.624167	171.371	1393.64	19.77202
3.642778	168.556	1403.887	19.68718
3.732778	161.543	1404.233	19.60145
3.751389	154.335	1412.771	19.51734
3.77	155.654	1423.964	19.43359
3.788611	113.126	1456.231	18.99461
3.8075	102.394	1465.995	18.91189
3.9	103.071	1467.526	18.59893
3.918611	88.868	1476.483	18.34758
3.937222	88.218	1473.886	18.09963
3.955833	68.443	1497.79	17.85503
3.974444	64.894	1501.183	17.61374
4.051667	53.678	1506.469	17.3757
4.070278	45.749	1515.949	17.14089
4.089167	41.251	1520.633	16.90924
4.107778	22.507	1532.886	16.68073
4.126389	21.621	1538.67	16.45531
4.1825	14.461	1546.068	16.23293
4.201389	9.392	1556.147	16.01355
4.22	6.149	1554.671	15.79715
4.238611		1577.844	15.58366
4.257222		1579.074	15.37306
4.364722		1586.591	15.16531
4.383333		1590.827	14.96037
4.401944		1594.868	14.75819
4.420556		1599.37	14.55875
4.439444		1617.816	14.362
4.509444		1609.342	14.16791
4.528056		1623.559	13.97644
4.546667		1626.512	13.78756
4.565278		1648.609	13.60124
4.583889		1645.935	13.41743
4.661111		1648.909	13.23611
4.679722		1648.991	13.05723
4.698333		1658.256	12.88078
4.716944		1671.261	12.7067
4.735833		1676.445	12.53498
4.808333		1682.277	12.36559

5.221389	37.322	712.364	201.4695
5.24	36.499	708.836	202.615
5.343333	35.546	704.529	207.776
5.361944	35.021	700.198	208.751
5.380556	37.452	699.479	209.303
5.399444	31.764	697.521	210.2015
5.418056	34.104	693.953	211.5795
5.471111	31.95	695.063	214.5095
5.489722	33.098	690.88	214.689
5.508333	32.925	688.786	216.4135
5.527222	30.541	688.109	216.9175
5.545833	28.286	690.747	218.421
5.619722	33.722	683.863	219.842
5.638333	29.11	683.703	221.5595
5.656944	28.439	682.573	221.423
5.675833	28.042	680.307	223.315
5.694444	27.693	680.685	223.9145
5.765833	25.974	675.175	227.325
5.784444	30.937	671.897	228.1715
5.803056	26.07	670.804	228.4425
5.821667	28.433	672.919	228.425
5.840556	27.754	669.091	230.5145
5.908333	23.481	667.721	231.5085
5.926944	21.718	667.915	233.3245
5.945556	25.821	668.154	233.699
5.964444	24.693	663.172	233.51
5.983056	28.756	665.651	235.5925
6.055556	22.721	661.331	237.2595
6.074444	24.509	659.558	237.675
6.093056	23.913	658.673	238.228
6.111667	22.132	658.748	239.645
6.130556	20.264	657.065	240.5515
6.206389	23.121	654.214	242.999
6.225	23.254	653.605	243.522
6.243889	25.07	652.594	243.392
6.2625	22.227	651.148	244.4345
6.281111	23.005	650.923	245.156
6.3575	22.482	647.479	246.382
6.376389	21.529	646.184	248.1175
6.394722	24.003	646.371	248.1195
6.413611	20.601	644.448	249.2035
6.432222	21.84	644.622	249.401
6.510278	18.642	641.134	252.2855

4.827222		1680.351	12.19848
4.845833		1680.387	12.03363
4.864444		1688.565	11.871
4.883056		1690.37	11.71058
4.986111		1698.06	11.55232
5.004444		1697.405	11.3962
5.023333		1707.682	11.24219
5.041944		1704.151	11.09026
5.060556		1719.807	10.94039
5.1375		1720.501	10.79254
5.156111		1718.248	10.64669
5.174722		1714.307	10.50281
5.193333		1731.821	10.36087
5.211944		1733.5	10.22085
5.280833		1740.688	10.08273
5.299444		1735.084	9.94647
5.318056		1740.042	9.812053
5.336667		1746.312	9.679452
5.355278		1758.944	9.548643
5.461667		1751.524	9.419602
5.480278		1755.286	9.292305
5.498889		1751.225	9.166728
5.517778		1760.214	9.042848
5.536389		1756.822	8.920642
5.629167		1765.367	8.800088
5.647778		1769.438	8.681163
5.666389		1768	8.563845
5.685		1772.328	8.448112
5.703889		1773.614	8.333944
5.774167		1779.716	8.221319
5.792778		1787.889	8.110215
5.811389		1785.151	8.000613
5.830278		1790.039	7.892492
5.848889		1790.682	7.785832
5.896944		1792.997	7.680614
5.915556		1795.987	7.576818
5.934167		1806.385	7.474424
5.953056		1800.447	7.373414
5.971667		1806.527	7.273769
6.03		1805.126	7.175471
6.048611		1807.215	7.078501
6.067222		1810.659	6.982842
6.085833		1821.071	6.888475

Table S11 – Final Mass Balance for Different Excess Benzoyl Peroxide

Time	¹⁹ F NMR				¹ H NMR		
	Nitrotoluene 1 (mM)	Monobromide 2 (mM)	Dibromide 3 (mM)	Total	NBS (mM)	Succinimide (mM)	Total
Start	900	0	0	900	1560	0	1560
End	18.642	641.134	252.2855	912	0	1821	1821
		Mass Balance		101%			116%
		Total Bromination		1145 mM			1821 mM

4. Reaction Progress Kinetic Modelling

DynoChem[®] software from Scale-Up Systems (Build: 1.3.20b340, Data Version: 1.0) was used for reaction modeling.

4.1 Simple Batch Kinetic Model

The ‘All-In’ Batch model was created using DynoChem[®] ‘Simple Batch Reaction’ model template.

Fitting was conducted with the Levenberg-Marquardt fitting algorithm using Weighted SSQ. Initially, the ‘standard reaction’ in Section 3 was included for fitting followed by refining with the other experiments and data described in Section 3. The order in monotonuene 1 set as 1.3 and benzoyl peroxide as 0.6. The radical propagation mechanism described by Goldfinger was utilized for creation of the model and extra terms to account for loss of bromine to the gas phase in a closed system added (Br sink).

HBr + NBS	→	Br ₂ + Succ.	$4.43 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$	± 22.4%
(BzO) ₂	→	2 BzO [•]	$1.31 \times 10^{-5} \text{ s}^{-1} (n = 0.6)$	± 20.3%
BzO [•] + Br ₂	→	Br [•] + BzOH	$29.98 \text{ L mol}^{-1} \text{ s}^{-1}$	± 13.1%
SM 1 + Br [•]	→	SM 1 [•] + HBr	$8.89 \text{ L mol}^{-1} \text{ s}^{-1} (n = 1.3)$	± 12.6%
SM 1 [•] + Br ₂	→	MonoBr 2 + Br [•]	$12.86 \text{ L mol}^{-1} \text{ s}^{-1}$	± 13.1%
MonoBr 2 + Br [•]	→	MonoBr 2 [•] + HBr	$1.47 \text{ L mol}^{-1} \text{ s}^{-1}$	± 12.6%
MonoBr 2 [•] + Br ₂	→	Dibromide 3 + Br [•]	$3.54 \text{ L mol}^{-1} \text{ s}^{-1}$	± 13.1%
2 Br ₂	→	Br sink	$26.39 \text{ L mol}^{-1} \text{ s}^{-1}$	± 16.2%
Br sink	→	2 Br ₂	$2.99 \times 10^{-5} \text{ L mol}^{-1} \text{ s}^{-1}$	± 12.8%
Br [•] + BzOH	→	BzOH + HBr	$4.34 \text{ L mol}^{-1} \text{ s}^{-1}$	± 12.6%

These reaction rates and orders were then used to predict reaction progress under ‘standard reaction’ conditions in an ‘All-In’ experiment. Comparison of the experimental data the modelled data is shown below (Figure S5, Table S12).

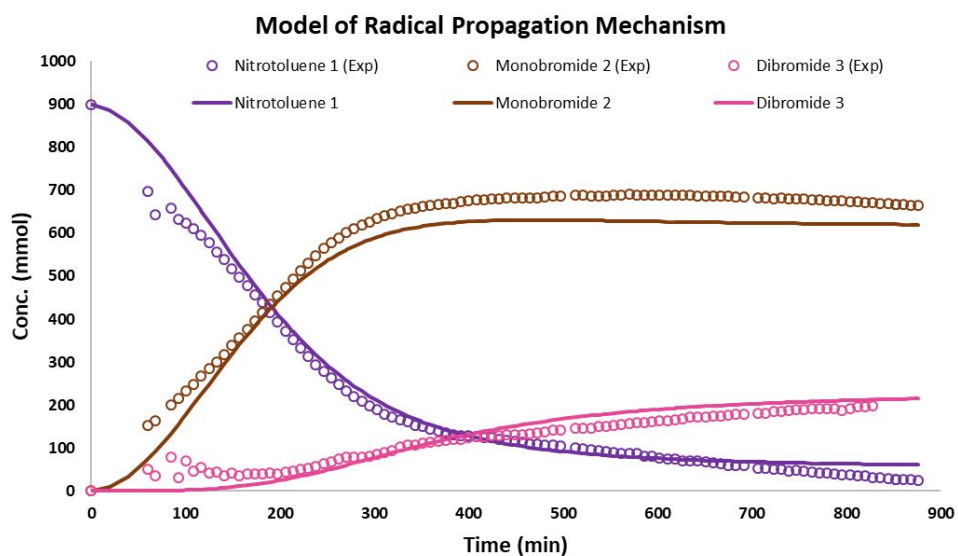


Figure S5 – Modelled Vs. Experimental Reaction Progress for Radical Propagation Mechanism

Table S12 – Modelled Vs. Experimental Reaction Progress Data for Radical Propagation Mechanism

Time (min)	NitroToluene 1 (Exp)	NitroToluene 1 (Model)	Monobromide 2 (Exp)	Monobromide 2 (Model)	Dibromide 3 (Exp)	Dibromide 3 (Model)
min	mmol/L	mmol/L	mmol/L	mmol/L	mmol/L	mmol/L
0	900	900	0	0	0	0
1.667E-12		900		0		0
1.667E-10		900		0		0
1.667E-08		900		0		0
0.000001667		900		0		0
0.0001667		900		0		0
0.0167		900		6.134E-11		0
1.667		899.69		0.0773		7.285E-08
19.373		886.526		9.473		0.0025
38.746		858.706		33.282		0.0419
58.118		818.407		69.896		0.23
60	697	813.941	152.309	74.016	51.826	0.2627
68.083	644.017	793.817	163.348	92.669	35.892	0.4438
76.183		772.29		112.731		0.704
77.491		768.702		116.083		0.7546
84.267	657.647	749.669	200.279	133.882	80.131	1.06
92.367	632.483	726.074	215.267	155.978	30.728	1.53
96.864		712.648		168.553		1.847
100.45	622.404	701.805	232.661	178.705	70.084	2.131
108.55	610.391	676.956	249.074	201.946	46.746	2.883
116.237		653.049		224.252		3.748
116.633	594.958	651.81	266.894	225.407	54.791	3.797
124.733	578.976	626.434	284.077	248.996	42.726	4.894

132.817	556.287	601.089	299.596	272.447	43.92	6.181
135.61		592.354		280.499		6.673
140.917	538.367	575.814	317.867	295.696	35.808	7.678
149.017	517.299	550.794	339.342	318.554	41.461	9.39
154.982		532.597		335.062		10.794
157.1	497.142	526.195	357.349	340.845	35.861	11.322
165.183	478.976	502.07	376.407	362.506	39.264	13.482
173.283	456.632	478.463	395.963	383.483	39.38	15.88
174.355		475.386		386.199		16.215
181.383	438.368	455.503	414.775	403.646	39.213	18.512
189.467	415.65	433.302	435.037	422.89	41.18	21.369
193.728		421.904		432.662		22.967
197.567	393.836	411.824	454.022	441.239	39.326	24.46
205.65	371.585	391.201	473.769	458.578	43.77	27.764
213.101		372.937		473.675		30.997
213.75	352.268	371.38	493.389	474.95	46.054	31.287
221.833	332.494	352.468	513.053	490.274	50.406	35.001
229.933	312.901	334.401	529.79	504.608	53.552	38.91
232.473		328.918		508.893		40.171
238.017	294.538	317.258	547.436	517.899	58.334	42.98
246.117	278.632	300.968	564.217	530.217	63.502	47.212
251.846		289.978		538.338		50.287
254.2	262.878	285.59	577.67	541.535	67.632	51.569
262.3	247.454	271.044	589.739	551.929	74.661	56.049
270.383	233.415	257.372	601.01	561.394	78.043	60.614
271.219		256.006		562.323		61.091
278.483	221.04	244.494	610.408	570.01	78.842	65.262
286.567	209.962	232.434	618.714	577.785	78.283	69.951
290.592		226.714		581.365		72.3
294.667	199.095	221.112	626.38	584.799	80.608	74.682
302.767	189.753	210.522	634.039	591.086	85.752	79.425
309.965		201.696		596.103		83.634
310.867	179.345	200.628	639.809	596.695	90.744	84.16
318.95	171.404	191.414	645.506	601.667	93.846	88.86
327.05	166.407	182.807	651.253	606.071	102.775	93.527
329.337		180.485		607.217		94.835
335.133	160.468	174.806	655.196	609.939	107.032	98.127
343.233	153.348	167.342	658.687	613.332	108.072	102.665
348.71		162.592		615.374		105.687
351.317	149.942	160.412	662.5	616.28	111.979	107.111
359.417	143.94	153.954	664.968	618.839	113.028	111.472
367.5	140.052	147.962	665.923	621.036	116.648	115.721
368.083		147.546		621.182		116.023

375.6	135.946	142.38	668.375	622.919	118.838	119.869
383.7	132.163	137.192	669.991	624.516	119.447	123.901
387.456		134.911		625.168		125.729
391.783	128.942	132.378	672.494	625.856	120.996	127.804
399.883	130.038	127.893	675.393	626.974	124.123	131.591
406.829		124.298		627.773		134.738
407.967	127.123	123.73	677.846	627.891	126.656	135.245
416.067	124.365	119.849	678.04	628.635	127.2	138.779
424.15	124.102	116.244	680.327	629.224	128.731	142.179
426.201		115.369		629.351		143.022
432.25	121.358	112.88	680.419	629.68	129.709	145.459
440.333	119.023	109.751	681.258	630.018	131.893	148.608
445.574		107.837		630.182		150.584
448.433	115.616	106.828	681.343	630.255	131.381	151.641
456.533	113.809	104.101	681.913	630.405	131.884	154.552
464.617	110.518	101.56	682.199	630.479	133.165	157.34
464.947		101.46		630.48		157.452
472.717	109.268	99.181	683.048	630.488	135.953	160.02
480.8	107.111	96.961	684.403	630.441	137.355	162.583
484.32		96.039		630.406		163.665
488.883	108.176	94.883	686.402	630.348	141.405	165.039
496.983	104.504	92.933	687.03	630.215	142.134	167.396
503.693		91.41		630.079		169.273
505.083		91.104		630.048		169.654
513.167	101.851	89.392	688.622	629.854	146.738	171.811
521.267	99.176	87.781	687.865	629.636	146.394	173.881
523.065		87.437		629.585		174.329
529.35	95.873	86.27	686.92	629.401	147.033	175.859
537.45	93.36	84.845	686.639	629.149	150.823	177.756
542.438		84.01		628.989		178.884
545.533	91.22	83.507	687.121	628.887	150.34	179.569
553.633	89.36	82.243	687.748	628.615	152.412	181.309
561.733	86.787	81.05	688.764	628.336	154.291	182.976
561.811		81.039		628.333		182.991
569.817	87.875	79.927	690.023	628.053	157.809	184.569
577.917	87.12	78.863	688.677	627.767	160.131	186.098
581.184		78.451		627.651		186.697
586	81.896	77.86	688.555	627.48	160.4	187.561
594.1	80.504	76.908	689.484	627.192	161.526	188.967
600.556		76.185		626.963		190.045
602.2	77.674	76.006	688.377	626.905	162.637	190.314
610.283	75.455	75.153	688.002	626.62	164.539	191.604
618.383	75.056	74.342	687.768	626.338	165.89	192.844

619.929		74.192		626.284		193.075
626.483	71.28	73.572	688.263	626.058	167.531	194.034
634.567	71.399	72.842	688.777	625.783	171.512	195.174
639.302		72.431		625.624		195.821
642.667	69.776	72.146	687.282	625.512	171.566	196.272
650.75	67.162	71.485	687.025	625.245	172.627	197.324
658.675		70.868		624.989		198.316
658.85	65.553	70.854	685.771	624.983	173.768	198.338
666.933	63.542	70.255	686.003	624.727	175.402	199.31
675.033	59.718	69.682	685.711	624.475	177.525	200.247
678.048		69.475		624.382		200.586
683.133	59.293	69.135	684.688	624.228	178.402	201.148
691.217	58.941	68.614	683.538	623.987	179.861	202.014
697.42		68.23		623.806		202.656
706.667	53.936	67.681	681.025	623.542	180.325	203.58
714.75	53.529	67.224	681.772	623.317	181.856	204.356
716.793		67.112		623.261		204.547
722.85	50.337	66.786	680.872	623.097	184.838	205.105
730.95	50.146	66.366	681.279	622.882	185.989	205.827
736.166		66.105		622.747		206.278
739.033	47.491	65.965	679.75	622.673	187.268	206.522
747.117	47.707	65.58	680.325	622.47	190.316	207.192
755.217	46.739	65.21	679.714	622.271	190.298	207.84
755.539		65.196		622.263		207.865
763.317	44.123	64.855	677.344	622.077	190.983	208.466
771.417	42.839	64.515	677.313	621.888	192.178	209.069
774.912		64.372		621.808		209.324
779.5	41.89	64.188	675.865	621.705	192.151	209.651
787.6	39.151	63.874	674.878	621.526	191.372	210.215
794.284		63.624		621.382		210.665
795.683	38.908	63.572	674.571	621.352	187.748	210.758
803.783	38.141	63.282	673.188	621.182	192.89	211.284
811.883	36.614	63.002	673.759	621.017	195.996	211.793
813.657		62.942		620.981		211.902
819.967	34.706	62.733	672.064	620.857	195.598	212.284
828.067	31.639	62.474	670.303	620.7	198.884	212.76
833.03		62.32		620.606		213.044
836.15	31.189	62.225	669.325	620.548		213.22
844.25	28.991	61.984	668.602	620.4		213.665
852.35	27.866	61.752	667.77	620.256		214.097
852.403	27.866	61.751	667.77	620.255		214.099
860.433	26.788	61.529	666.335	620.116		214.514
868.533	26.426	61.313	665.379	619.979		214.918

871.776		61.229		619.925		215.077
876.633	24.24	61.105	664.596	619.846		215.311
880.95	24.341	60.997	664.299	619.777		215.514
885.267	23.501	60.891	663.883	619.708		215.715
891.148		60.75		619.617		215.983
893.367	22.678	60.697	662.583	619.583		216.082
901.45	21.966	60.51	661.115	619.461		216.438
909.55	19.421	60.33	660.29	619.342		216.783
910.521		60.308		619.328		216.824
917.633	20.547	60.155	660.329	619.226		217.118
929.894		59.902		619.056		217.606
933.083		59.838		619.013		217.729
941.183	19.611	59.679	659.54	618.906		218.036
949.267	19.446	59.526	658.972	618.802		218.334

4.2 – Continuous Addition of N-Bromosuccinimide

4.2.1 - General Procedure for Continuous NBS Addition

Nitrotoluene **1** (30 g or 265 g) was loaded into a ChemGlass[®] reactor (500 mL or 5 L) followed by AcOH (2 V, 60 mL or 530 mL). Benzoyl peroxide (3 mol%) was added via an addition funnel. The reaction mixture was then heated to 83 °C over 1 h. In a separate vessel, NBS (See **Table S8** for equivalents) was stirred vigorously at room temperature as a slurry in AcOH (3.5 V; 105 mL or 930 mL).

As the nitrotoluene solution approached 83 °C, transfer of NBS slurry to the nitrotoluene solution was initiated. Slurry transfer was achieved using a Masterflex[®] peristaltic pump with Viton[®] tubing.

Reaction progress was monitored using ¹⁹F and ¹H NMR analysis.

4.2.2 – Continuous Addition Kinetic Model and Experimental Data

The continuous addition kinetic model was created using DynoChem[®] ‘Fed Batch Reaction’ model template. The reaction rates determined from the All-In RPKA experiments (**Section 3**) and DynoChem[®] modelling of the Goldfinger radical propagation mechanism (**Section 4.1**) were used to predict reaction progress under a variety of continuous addition scenarios (**Table S8**). Experimental data is included below and modelled data obtained from the DynoChem[®] model. For simulations, 1000 points were calculated using the Rosenbrock Intergration with an accuracy of 1×10^{-3} .

It should be noted that as the total volume of the reaction mixture is continually changing during continuous addition, absolute concentration is not an appropriate measurement from which to determine reaction progress. For experimental / modelled data reported using continuous addition mode, *total moles* present in either the Batch or Feed are reported.

Total moles of Nitrotoluene **1**, Monobromide **2** and Dibromide **3** were determined by conversion using ¹⁹F NMR using known starting concentration of nitrotoluene **1** as reference.

Table S13 –Reaction Conditions for Continuous Addition of NBS

Entry	NBS Addition Time (min)	NBS (Eq.)	T ₀ Batch Volume (L)	T ₀ FNT (mol)	T ₀ HBr (mol)	T ₀ BPO (mol)	Feed AcOH Volume (L)	Feed NBS (mol)
1	150	1.68	0.06	0.193	0.03	0.0058	0.1056	0.3248
2	300	1.68	0.06	0.193	0.03	0.0058	0.1056	0.3248
3	480	1.68	0.53	1.711	0.03	0.0506	0.9275	2.869
4	300	1.50	0.06	0.196	0.03	0.0058	0.1056	0.2910
5	300	1.90	0.06	0.196	0.03	0.0058	0.1056	0.3670

2.5 h Addition of NBS

NBS Addition Time (min)	NBS (Eq.)	T ₀ Batch Volume (L)	T ₀ FNT (mol)	T ₀ HBr (mol)	T ₀ BPO (mol)	Feed AcOH Volume (L)	Feed NBS (mol)
150	1.69	0.06	0.193	0.03	0.0058	0.1056	0.3248

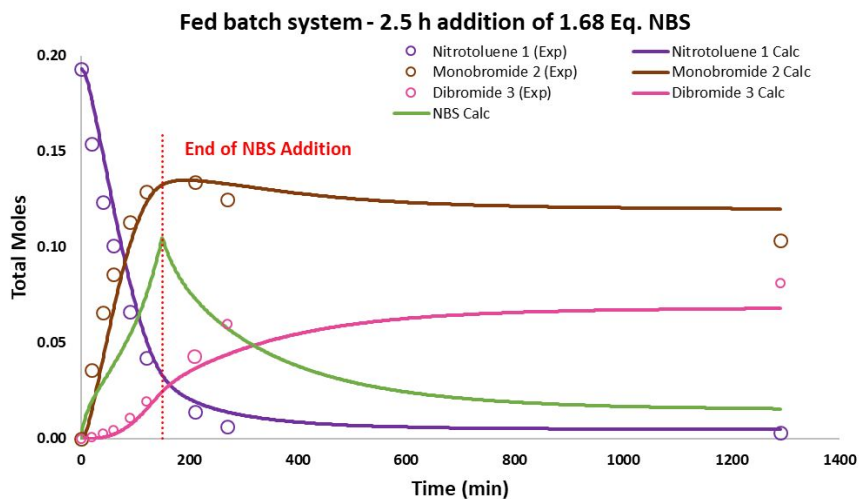


Figure S6 – Modelled Vs. Experimental Reaction Progress for 2.5 h Continuous addition of NBS

Table S14 – Experimental Reaction Progress Data for 2.5 h Continuous addition of NBS

Time (min)	Nitrotoluene 1 (mol)	Monobromide 2 (mol)	Dibromide 3 (mol)
0	0.193	0	0
20	0.15417	0.03592	0.00093
40	0.12337	0.06566	0.00255
60	0.10063	0.086	0.00459
90	0.06633	0.11314	0.011
120	0.04215	0.12921	0.01938
210	0.01393	0.13423	0.04275
270	0.00631	0.12468	0.06008
1290	0.00309	0.10366	0.08108

5 h Addition

NBS Addition Time (min)	NBS (Eq.)	T ₀ Batch Volume (L)	T ₀ FNT (mol)	T ₀ HBr (mol)	T ₀ BPO (mol)	Feed AcOH Volume (L)	Feed NBS (mol)
300	1.68	0.06	0.193	0.03	0.0058	0.1056	0.3248

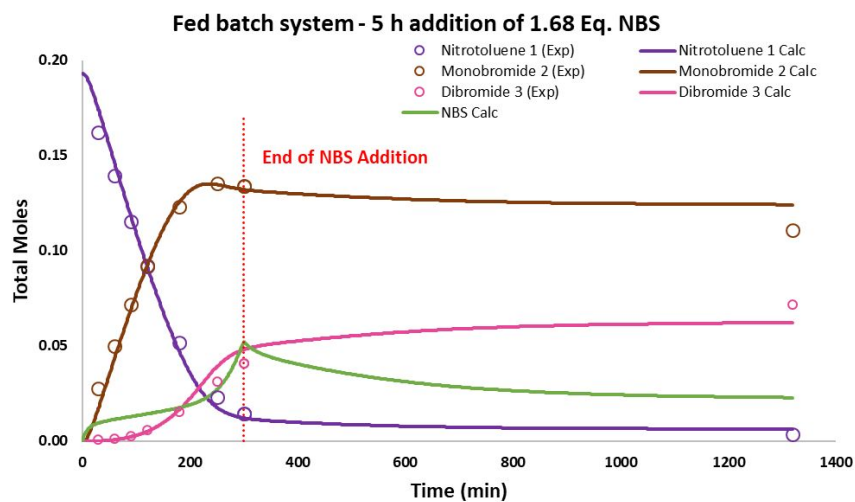


Figure S7 – Modelled Vs. Experimental Reaction Progress for 5 h Continuous addition of NBS

Table S15 – Experimental Reaction Progress Data for 5 h Continuous addition of NBS

Time (min)	Nitrotoluene 1 (mol)	Monobromide 2 (mol)	Dibromide 3 (mol)
0	0.193	0	0
30	0.16231	0.02766	0.001
60	0.13927	0.04985	0.00125
90	0.11553	0.07176	0.00284
120	0.09191	0.09241	0.00569
180	0.05169	0.12335	0.01525
250	0.02328	0.13543	0.03144
300	0.01457	0.13396	0.04068
1320	0.0034	0.11098	0.0718

8 h Addition

NBS Addition Time (min)	NBS (Eq.)	T ₀ Batch Volume (L)	T ₀ FNT (mol)	T ₀ HBr (mol)	T ₀ BPO (mol)	Feed AcOH Volume (L)	Feed NBS (mol)
480	1.68	0.53	1.711	0.03	0.0506	0.9275	2.869

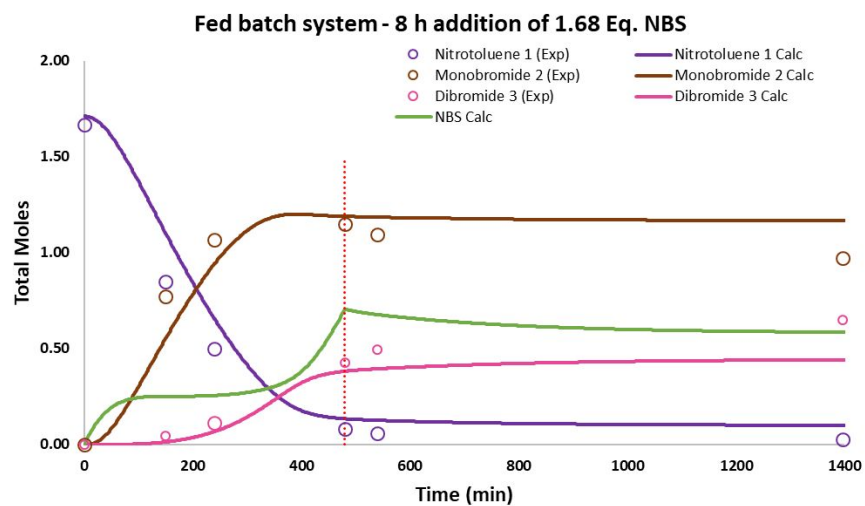


Figure S8 – Modelled Vs. Experimental Reaction Progress for 8 h Continuous addition of NBS

Table S16 – Experimental Reaction Progress Data for 8 h Continuous addition of NBS

Time (min)	Nitrotoluene 1 (mol)	Monobromide 2 (mol)	Dibromide 3 (mol)
0	1.66911	0	0
150	0.8475	0.77175	0.04289
240	0.50114	1.06478	0.11245
480	0.07944	1.1472	0.42519
540	0.05753	1.09637	0.49419
1440	0.02485	0.97189	0.64883

5 h Addition – 1.50 Eq NBS

NBS Addition Time (min)	NBS (Eq.)	T ₀ Batch Volume (L)	T ₀ FNT (mol)	T ₀ HBr (mol)	T ₀ BPO (mol)	Feed AcOH Volume (L)	Feed NBS (mol)
300	1.50	0.06	0.196	0.03	0.0058	0.1056	0.2910

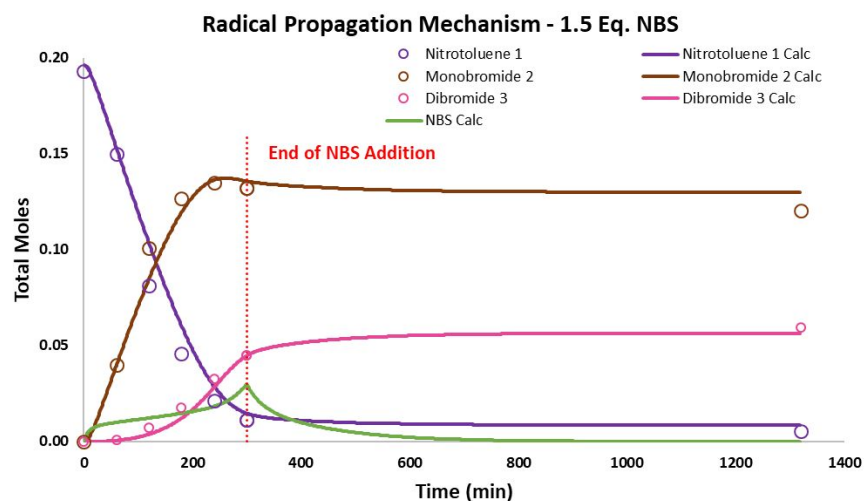


Figure S9 – Modelled Vs. Experimental Reaction Progress for Continuous addition of 1.5 eq. NBS

Table S17 – Experimental Reaction Progress Data for Continuous addition of 1.5 eq. NBS

Time (min)	Nitrotoluene 1 (mol)	Monobromide 2 (mol)	Dibromide 3 (mol)
0	0.193	0	0
60	0.15012	0.04003	0.00068
120	0.08152	0.101	0.00737
180	0.04591	0.12665	0.01752
240	0.02133	0.13506	0.03291
300	0.01152	0.13221	0.04476
1320	0.00562	0.12051	0.05971

5 h Addition – 1.90 Eq NBS

NBS Addition Time (min)	NBS (Eq.)	T ₀ Batch Volume (L)	T ₀ FNT (mol)	T ₀ HBr (mol)	T ₀ BPO (mol)	Feed AcOH Volume (L)	Feed NBS (mol)
300	1.90	0.06	0.196	0.03	0.0058	0.1056	0.3670

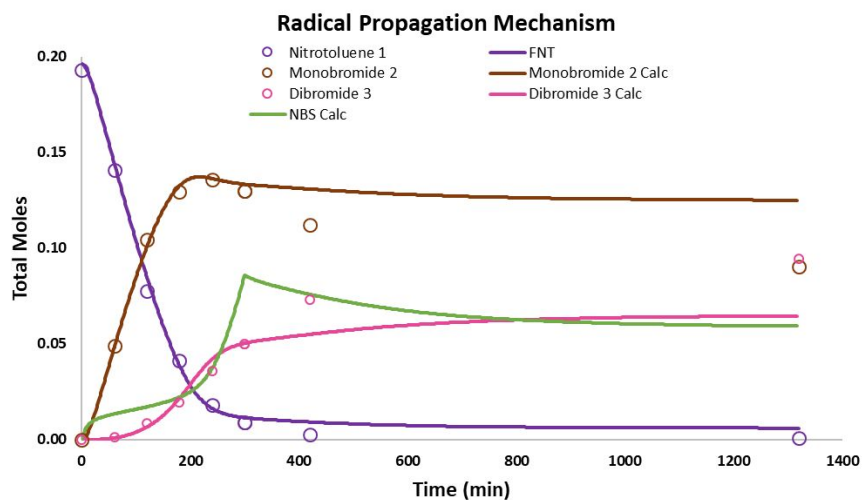


Figure S10 – Modelled Vs. Experimental Reaction Progress for Continuous addition of 1.9 eq. NBS

Table S18 – Experimental Reaction Progress Data for Continuous addition of 1.9 eq. NBS

Time (min)	Nitrotoluene 1 (mol)	Monobromide 2 (mol)	Dibromide 3 (mol)
0	0.193	0	0
60	0.14077	0.04902	0.00118
120	0.07761	0.10451	0.00838
180	0.04113	0.12925	0.01928
240	0.01799	0.13591	0.03603
300	0.00923	0.12966	0.04995
420	0.00268	0.11225	0.07332
1320	0.00097	0.09046	0.09449

5. UV-Vis Analysis of N-Bromosuccinimide

Procedure adapted from Kerr *et al.*⁷ using **Agilent 8453** UV-Vis Spectrometer. A stock solution of Br₂ in MeCN was prepared for calibration of the UV-Vis spectrometer (**Table S14**). This stock solution was further diluted to create a 6-point calibration.

Table S19 – Stock Solution preparation for UV-Vis Br₂ Calibration

Exact Mass Br ₂ (mg)	106.2
MW	159.8
Moles	0.00066458
Volume (mL)	100
Stock Conc. (mmol)	6.64581
Stock Conc. (mg/mL)	1.062

Sample	Stock Volume (uL)	MeCN added (uL)	Final Conc. (mM)	UV Response 395 nm
1	1000	0	6.646	1.3743
2	1000	9000	0.6646	0.14222
3	500	9500	0.3323	0.07011
4	250	9750	0.1661	0.036083
5	125	9825	0.0835	0.01719
6	62.5	9937.5	0.0415	0.0096564

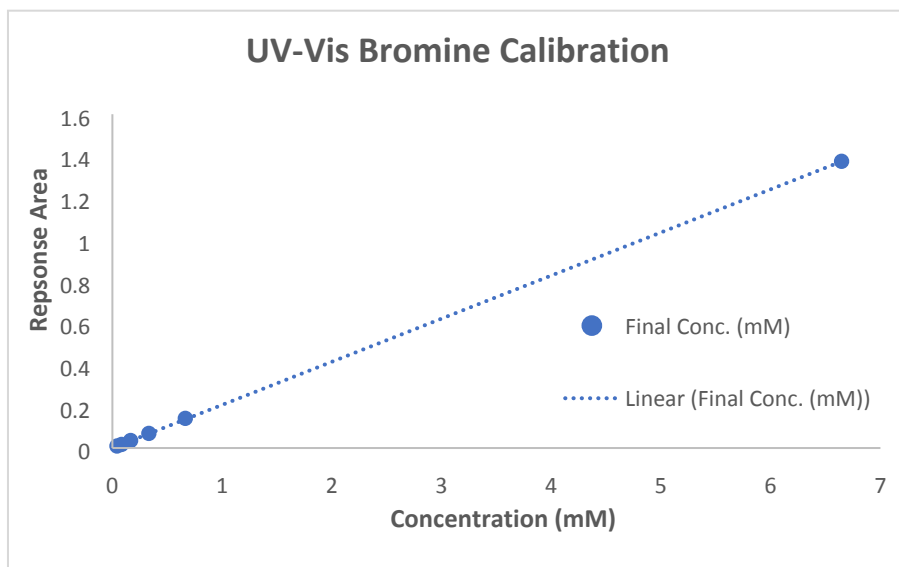


Figure S11 – Calibration of Br₂ Absorption at 395 nm by UV-Vis Spectroscopy

Samples of NBS from Supplier A + B were then dissolved in MeCN and absorbance at 395 nm measured by UV-Vis Spectrometry.

Table S20 – Comparison of Br₂ content in N-Bromosuccinimide from different suppliers.

Entry	NBS Source	Mass Used (g)	Concentration (mM)	UV Absorbance 395 nm	Br ₂ Concentration (mM)	Br ₂ (%) in NBS
1	Supplier A	0.1757	9.87	0.0059352	0.029	0.291
2	Supplier A	1.741	97.82	0.047405	0.229	0.234
3	Supplier B	0.1824	10.25	0.015069	0.073	0.711
4	Supplier B	1.774	99.67	0.1543	0.746	0.748

6. Minimization of NBS Equivalents

DynoChem[®] optimization function was used to minimize the equivalents of NBS used in continuous addition mode whilst ensuring end of reaction specifications were met.

Model variables, specification and end of reaction target are described below (**Table S16**).

Table S21 – Specifications for NBS minimization

Variable	Range	Initial Value
NBS Equivalents	0.1 – 1.0 mol	0.1 mol

Reaction Specifications	Value
Nitrotoluene 1	0.193 moles
NBS Addition Time	300 min
End of Reaction Time	480 min

Target	
Conversion	92 mol%

Optimization was complete within 24 iterations and determined 0.2512 moles of NBS would be required to achieve a yield of > 92% for continuous addition using 0.193 nitrotoluene **1** (Table S17). This corresponds to 1.30 equivalents of NBS relative to nitrotoluene **1**.

Table S22 – Iterations of NBS minimization

Iterations	NBS mol	Yield (%)
0	0.1	44.23435
1	0.1075	47.49251
2	0.11875	52.34783
3	0.12938	56.79435
4	0.15719	67.69733
5	0.19234	79.51556
6	0.26555	93.34394
7	0.26555	93.34394
8	0.26555	93.34394
9	0.26555	93.34394
10	0.26555	93.34394
11	0.26391	93.20718
12	0.25123	91.96275
13	0.25123	91.96275
14	0.25123	91.96275
15	0.25123	91.96275
16	0.25123	91.96275
17	0.25123	91.96275
18	0.25123	91.96275
19	0.25123	91.96275
20	0.25162	92.00596
21	0.25162	92.00596
22	0.25162	92.00596
23	0.25152	91.99483
24	0.25152	91.99483

7. Estimation of Benzoyl Peroxide Half Life

For VTNA analysis of benzoyl peroxide as a initiator of constantly decreasing concentration an approximate value of the half life was required (See Sections 3.1 and 3.4). This value was obtained from *Sanchez and Myers*¹⁰ reported data and calculated for 83 °C as shown in **Figure S12**. A value of $T_{1/2} = 3$ h was utilized for VTNA studies.

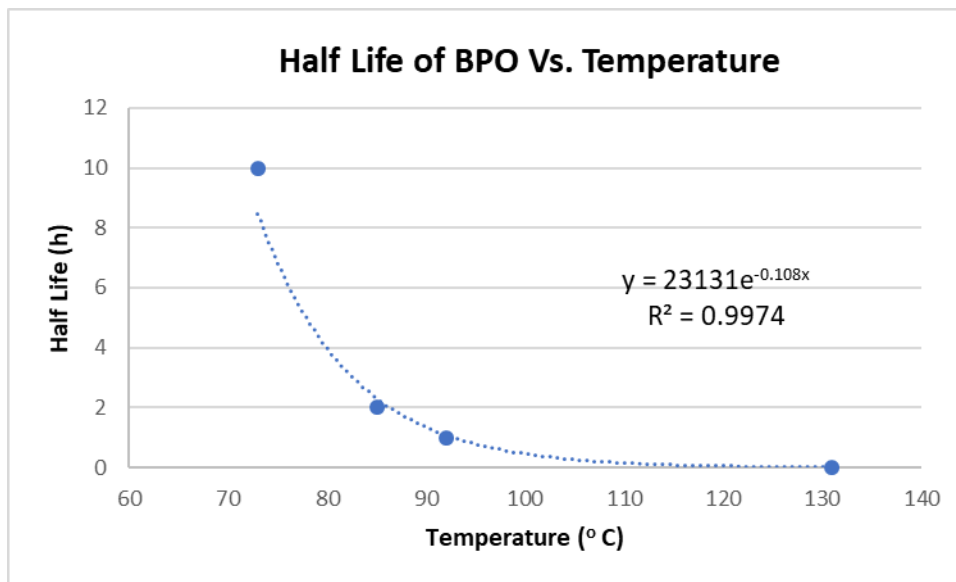


Figure S12 – Half Life of Benzoyl Peroxide as reported by Sanchez and Myers¹⁰

8. Spectral Data for Nitrotoluene 1, Monobromide 2 and Dibromide 3

Nitrotoluene 1

This material was obtained commercially from one of many vendors. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.82 (ddd, J = 8.5, 6.9, 1.8 Hz, 1H), 7.52 – 7.43 (m, 1H), 7.17 (td, J = 8.5, 2.7 Hz, 1H), 2.37 (d, J = 2.7 Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3): δ -122.45. ^{13}C NMR (101 MHz, CDCl_3) δ 155.12, 152.51, 136.82 (d, J = 5.8 Hz), 128.35 (d, J = 16.5 Hz), 123.72 (d, J = 5.0 Hz), 123.41 (d, J = 2.7 Hz), 14.44 (d, J = 4.5 Hz).

Monobromide 2 and Dibromide 3

These materials were obtained from reactions as described in **Section 4.2.1**. Reaction mixtures were diluted with Toluene (8 V) and washed with water (5 V) followed by 1 M NaOH (5 V). The resulting organic phase was conc. *in vacuo* to afford crude material. This was purified by flash chromatography (eluent: 0-20% EtOAc/heptanes) to afford the desired products.

Monobromide 2

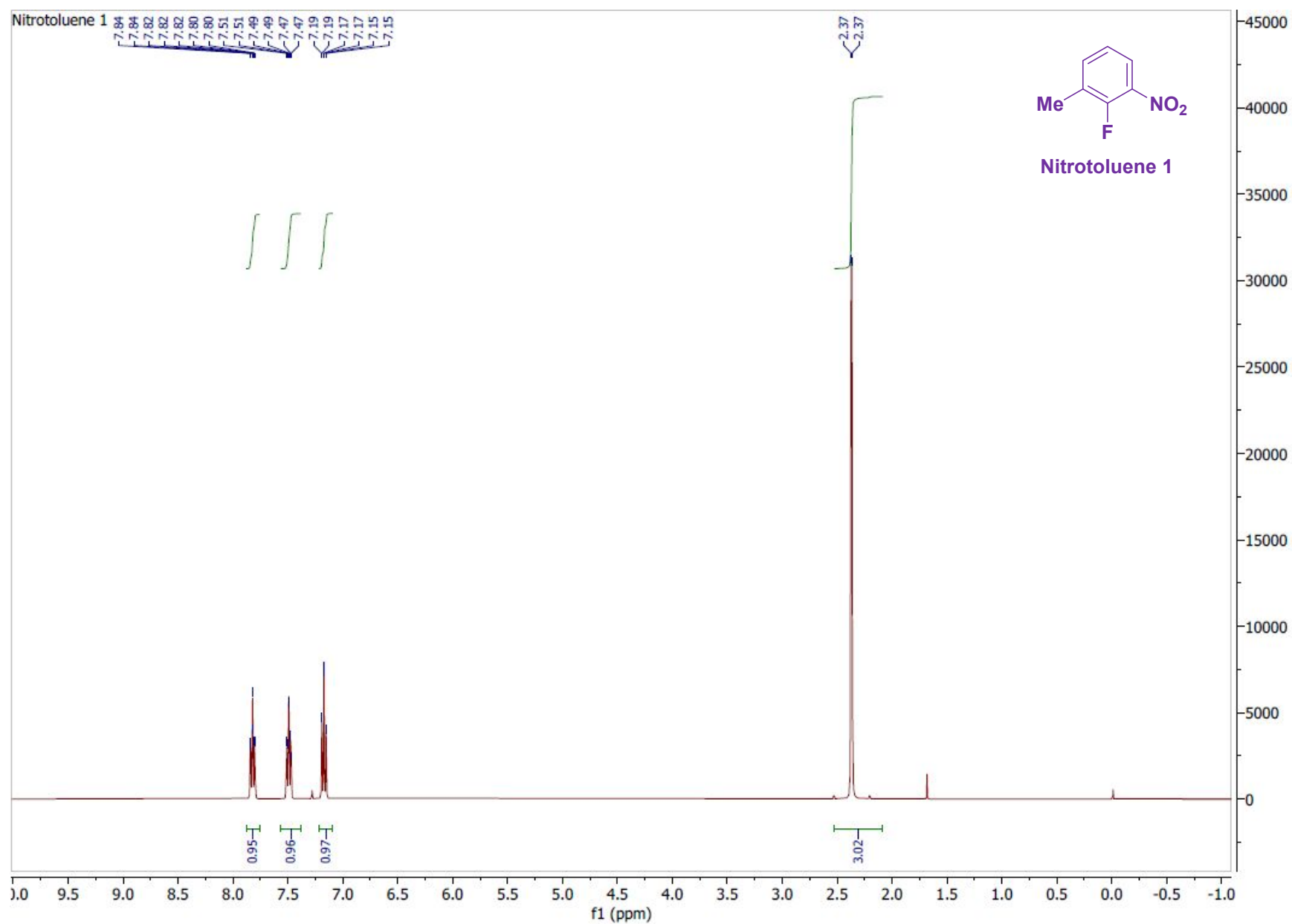
^1H NMR (400 MHz, Chloroform-*d*) δ 8.03 (ddd, J = 8.5, 6.9, 1.8 Hz, 1H), 7.73 (ddd, J = 8.0, 6.9, 1.8 Hz, 1H), 7.32 (td, J = 8.0, 1.3 Hz, 1H), 4.57 (s, 1H). ^{19}F NMR (376 MHz, CDCl_3): δ -122.07. ^{13}C NMR (101 MHz, CDCl_3) δ 154.83, 152.17, 136.47 (d, J = 2.5 Hz), 128.64 (d, J = 13.9 Hz), 126.24 (d, J = 2.5 Hz), 124.49 (d, J = 5.2 Hz), 23.54 (d, J = 5.2 Hz)

Dibromide 3

^1H NMR (400 MHz, CDCl_3): δ 8.19 (ddd, J = 8.0, 6.3, 1.8 Hz, 1H), 8.07 (ddd, J = 8.0, 6.3, 1.8 Hz, 1H), 7.43 (td, J = 8.0, 1.8 Hz, 1H), 6.98 (s, 1H). ^{19}F NMR (376 MHz, CDCl_3): δ -122.72. ^{13}C NMR (101 MHz, CDCl_3) δ 151.22, 148.56, 135.83 (d, J = 2.4 Hz), 132.25 (d, J = 11.7 Hz), 127.20 (d, J = 2.4 Hz), 124.97 (d, J = 5.2 Hz), 29.25 (d, J = 6.8 Hz).

9. References

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Nitrotoluene 1

