SUPPORTING INFORMATION FOR

"Towards a Simulation Approach for Alkene Ring-Closing Metathesis: Scope and Limitations of a Model"

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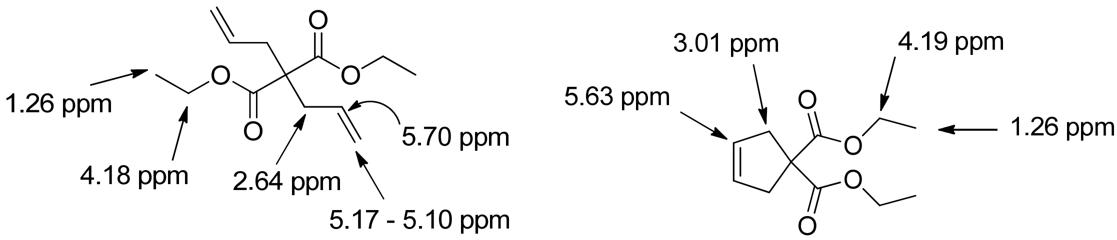
1. TECHNICAL DETAILS

A. T_1 MEASUREMENTS

T1 values were measured at 300 K using the Bruker *t1ir* pulse program with a series of delays from ca. 0.001 to 20 s. Data from the experiment were fitted using the T_1 relaxation module of Bruker Topspin 2.1. The terminal olefinic protons on the diene **7** (δ_H = 5.17 – 5.10 ppm, 4H) and the allylic protons on cyclic product **8** (δ_H = 3.01 ppm, 4H) were used for quantification in each experiment.



Diethyl Diallylmalonate 7		Product 8	
Chemical Shift (ppm)	**Relaxation Time (s)**	**Chemical Shift (ppm)**	**Relaxation Time (s)**
5.70	4.65	5.63	6.81
5.17 – 5.10	2.64	4.19	4.45
4.18	3.51	3.01	2.30
2.64	1.21	1.26	3.70
1.26	3.14		

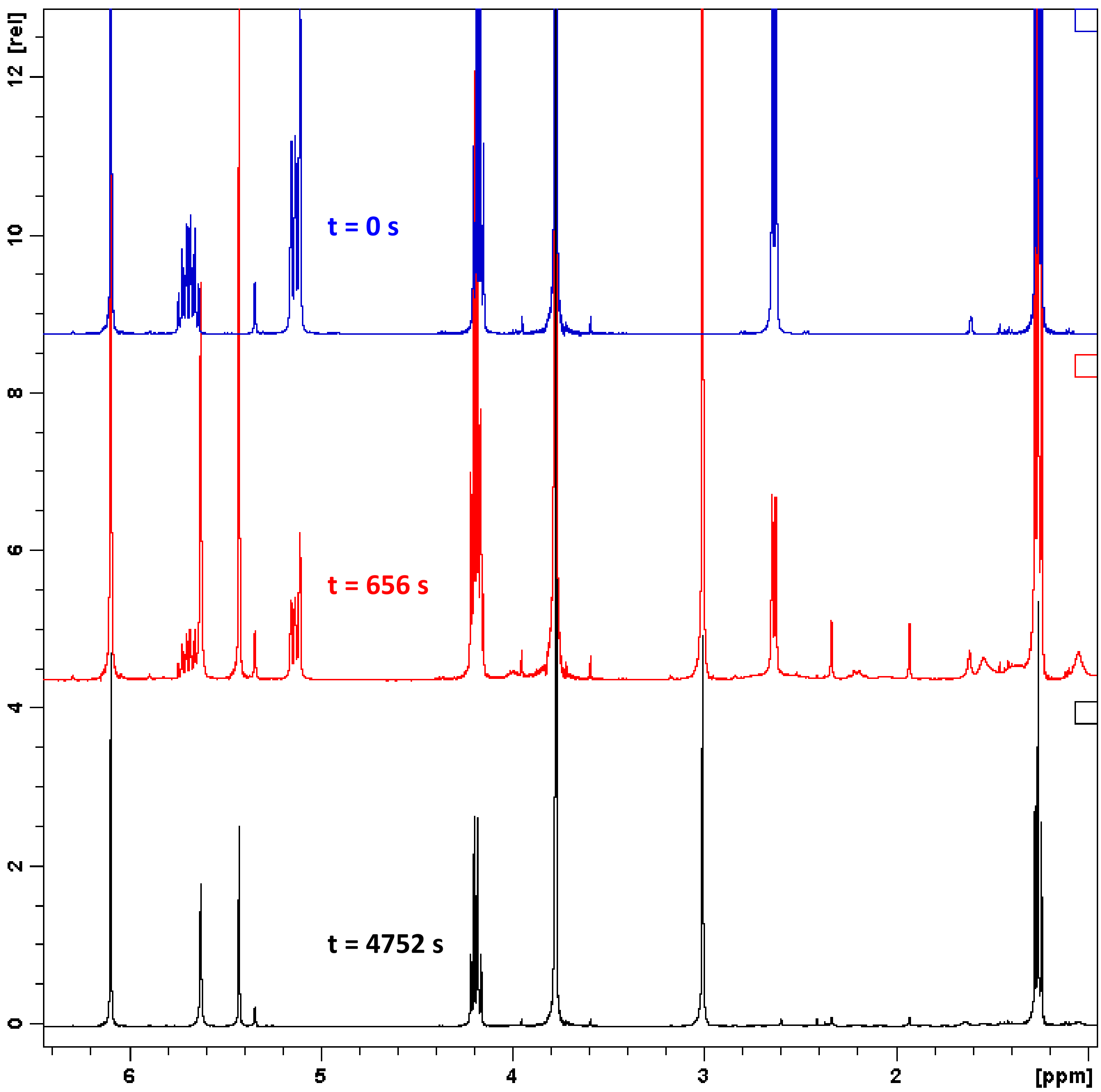
B. INSTRUMENT DETAILS AND SET-UP

Spectra were acquired either on a Bruker Avance 400 spectrometer with a BBFO-*z*-ATMA probe or a Bruker Avance II+ 600 using a BBO-*z*-ATMA probe. Both spectrometers are equipped with temperature control units which were set to 298 K throughout. Data was collected at 400 MHz using 4 scans per data point, or with the AV600 using only 2 scans per data point. Other parameters were the same on both instruments.

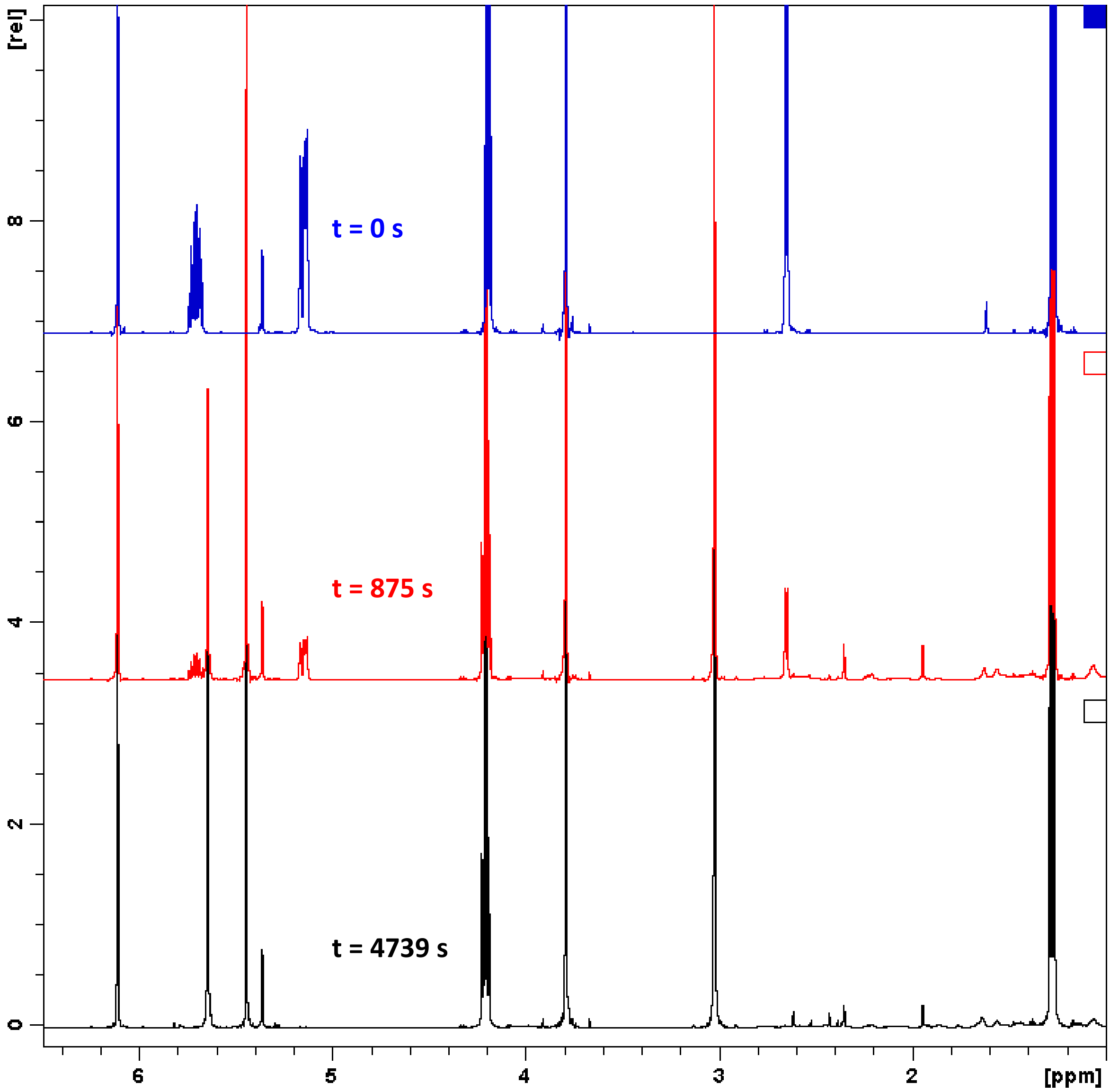
D_1 Delay = 35 s   Spectra Width (ppm) = 24 ppm   Spectra Centre = 10 ppm

2. SAMPLE SPECTRA

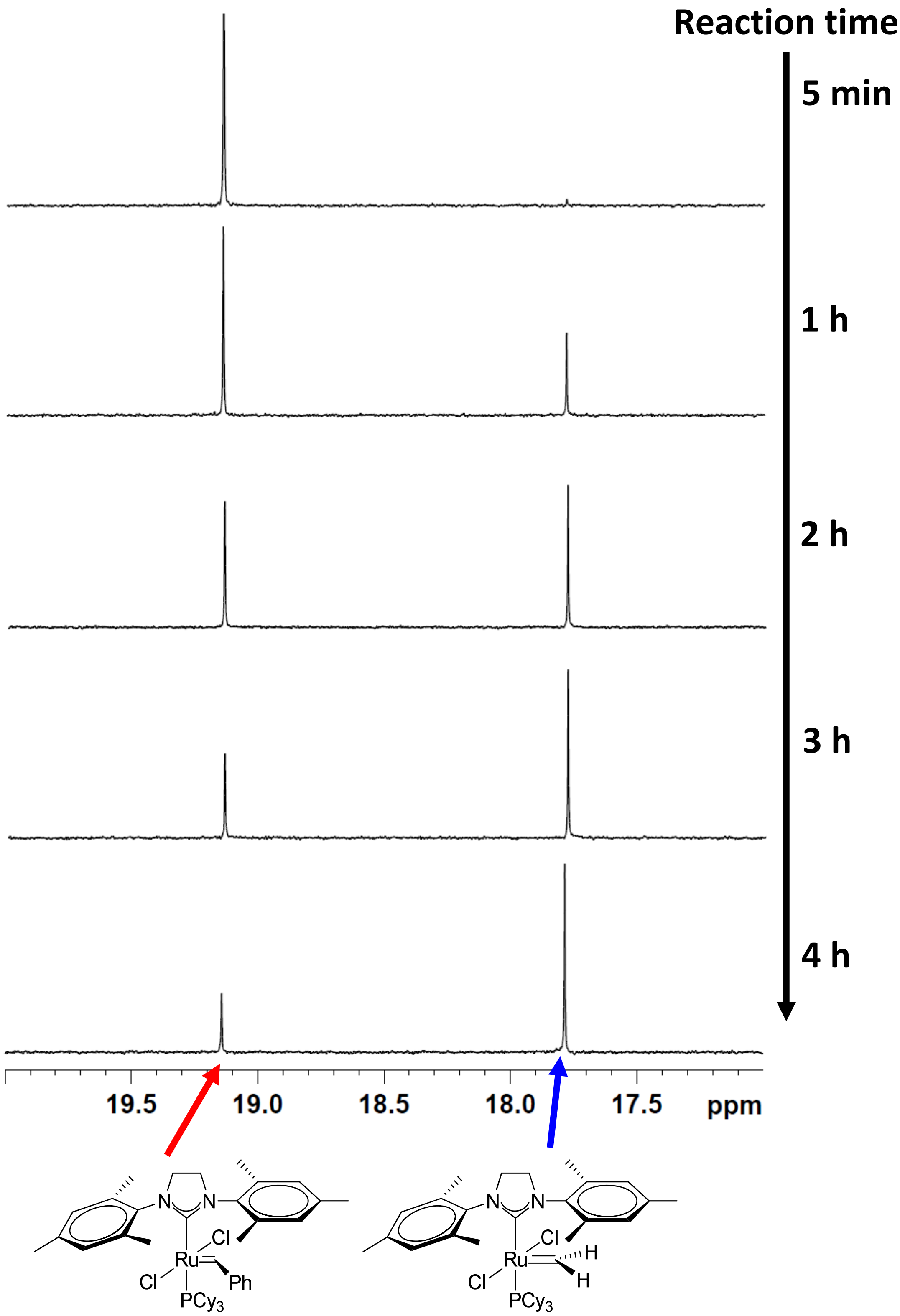
A. RCM OF DIETHYLDIALLYLMALONATE **7** with **1** in DCM-d_2, 400 MHz ^{1}H OBSERVATION



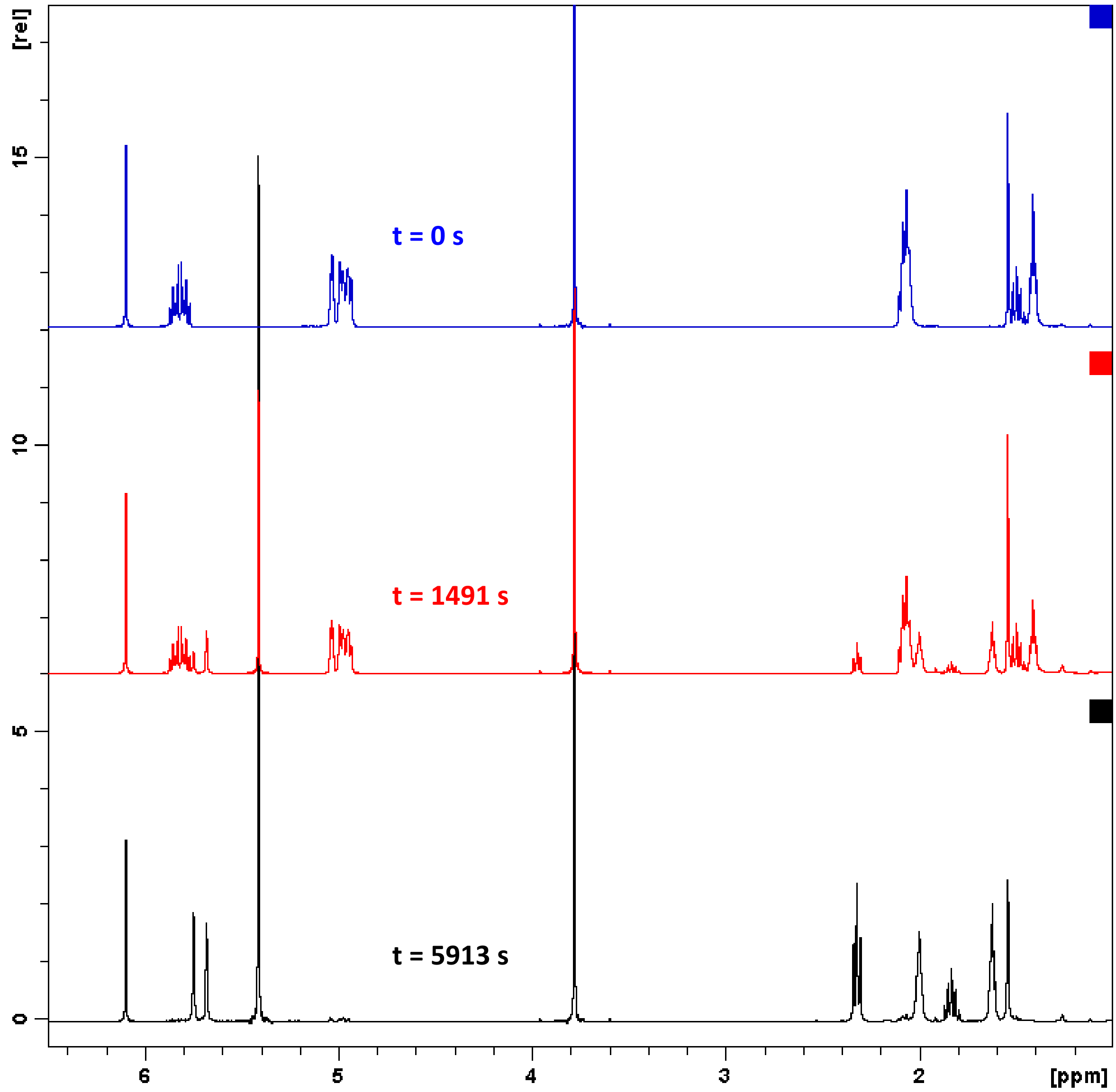
B. RCM OF DIETHYLDIALLYLMALONATE **7** with **1** in DCM-d_2, 600 MHz ^{1}H OBSERVATION



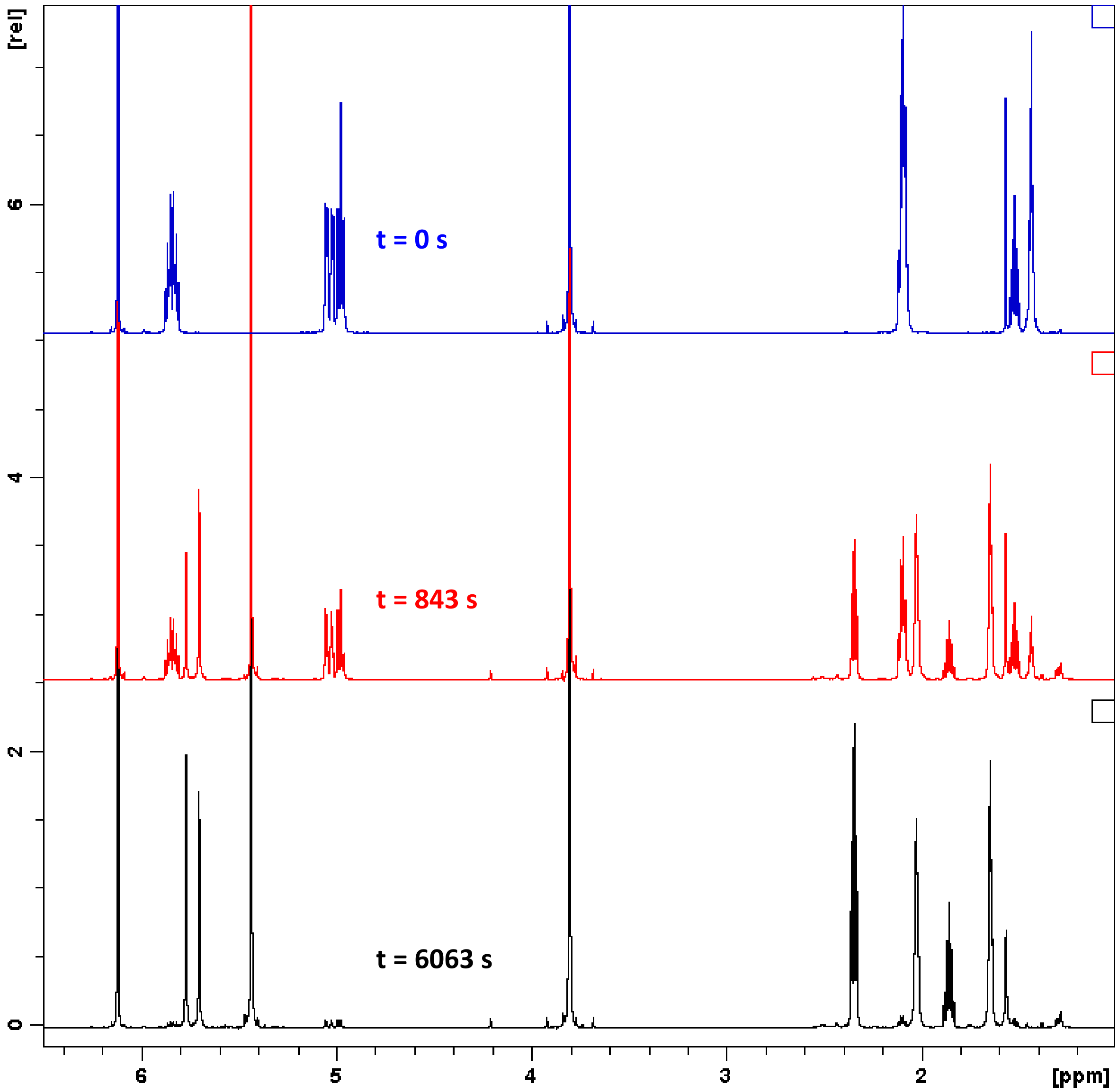
C. LOW-FIELD ^{1}H NMR OF **7** RCM REACTIONS, 600 MHz ^{1}H OBSERVATION



D. RCM OF HEPTADIENE **11**, OCTADIENE **13** with **1** in chloroform-*d*, 400 MHz ^{1}H OBSERVATION



E. RCM OF HEPTADIENE **11**, OCTADIENE **13** with **2** in chloroform-*d*, 600 MHz ^{1}H OBSERVATION



3. KINETIC DATA

Concentration and time data presented here are in mol L^{-1} and seconds. Datasets have been checked for mass balance (within the limits of quantification by ^1H NMR). Diene and product concentration/time profiles were fitted, pre-catalyst concentration/time profiles were not.

A. RCM REACTIONS OF DIETHYL DIALLYLMALONATE **7** IN DCM-d_2

i. 505.9 mM **7** 25.68 mM **1**

t (s)	**[7]**	**[8]**
0	0.50585	0.00000
246	0.35171	0.14942
528	0.19289	0.30903
808	0.10596	0.39429
1088	0.06543	0.43699
1458	0.03517	0.46632
1738	0.02259	0.47809
2017	0.01508	0.48307
2297	0.01154	0.48713
2580	0.00961	0.49050
2860	0.00810	0.49064

ii. 491.7 mM **7** 12.01 mM **1**

t (s)	**[7]**	**[8]**
0	0.49172	0.00000
364	0.31010	0.17586
680	0.18968	0.29818
994	0.11203	0.37725
1309	0.06992	0.42027
1624	0.04595	0.44367
1939	0.03194	0.45855
2254	0.02313	0.46683
2569	0.01692	0.47289
2884	0.01294	0.47685
3199	0.01027	0.47953
3514	0.00682	0.48283
3829	0.00682	0.48270
4144	0.00325	0.48547
4459	0.00562	0.48399
4774	0.00159	0.48836
5089	0.00292	0.48733
5404	0.00226	0.48706
5719	0.00217	0.48789
6034	0.00183	0.48767

iii. 507.0 mM **7** 5.18 mM **1**

t (s)	**[7]**	**[8]**
0	0.50698	0.00000
367	0.38552	0.12075
692	0.27052	0.23595
1018	0.18674	0.31977
1343	0.12316	0.38443
1667	0.08199	0.42511
1992	0.05672	0.45027
2317	0.03795	0.46718
2642	0.02885	0.47705
2968	0.02245	0.48379
3293	0.01649	0.48905
3618	0.01267	0.49264
3943	0.00966	0.49549
4270	0.00778	0.49722
4595	0.00711	0.49788
4920	0.00544	0.49974
5245	0.00464	0.50032
5570	0.00461	0.50066
5895	0.00382	0.50140
6220	0.00308	0.50199
6546	0.00317	0.50201
6871	0.00232	0.50297
7197	0.00270	0.50242
7522	0.00294	0.50241
7847	0.00230	0.50265
8172	0.00152	0.50362
8497	0.00152	0.50349
8822	0.00132	0.50361
9147	0.00180	0.50298
9472	0.00117	0.50378
9798	0.00162	0.50316
10124	0.00108	0.50375
10449	0.00117	0.50349
10775	0.00135	0.50341
11099	0.00080	0.50409
11425	0.00132	0.50334

11750	0.00070	0.50411
12075	0.00095	0.50386
12400	0.00064	0.50420
12725	0.00097	0.50352
13051	0.00096	0.50382

iv. 404.5 mM **7** 5.18 mM **1**

t (s)	**[7]**	**[8]**
0	0.40447	0.00000
337	0.26651	0.13569
653	0.16110	0.24152
968	0.07952	0.32270
1283	0.03637	0.36609
1598	0.01912	0.38306
1913	0.01149	0.39047
2228	0.00831	0.39410
2543	0.00731	0.39502
2858	0.00653	0.39563
3173	0.00361	0.39793
3488	0.00462	0.39766
3803	0.00527	0.39780
4118	0.00412	0.39818
4433	0.00389	0.39874
4748	0.00354	0.39897
5063	0.00133	0.39965
5378	0.00380	0.39820
5692	0.00335	0.39892
6008	0.00182	0.39911
6322	0.00339	0.39859
6637	0.00283	0.39854
6952	0.00112	0.39997
7268	0.00088	0.39956
7583	0.00249	0.39915
7898	0.00066	0.39965
8213	0.00310	0.39871
8528	0.00327	0.39852
8843	0.00251	0.39910
9158	0.00035	0.39961
9473	0.00296	0.39867

v. 250.7 mM **7** 25.91 mM **1**

t (s)	**[7]**	**[8]**
0	0.25069	0.00000
309	0.12602	0.11878
598	0.05272	0.19235
888	0.02466	0.22104
1178	0.01135	0.23238
1468	0.00841	0.23728
1757	0.00433	0.23982
2047	0.00446	0.23988
2336	0.00349	0.24199
2625	0.00369	0.24045
2914	0.00200	0.24159
3203	0.00195	0.24212
3493	0.00164	0.24180
3782	0.00186	0.24150
4071	0.00128	0.24276
4362	0.00177	0.24140
4651	0.00191	0.24192

vi. 250.5 mM **7** 12.72 mM **1**

t (s)	**[7]**	**[8]**
0	0.25045	0.00000
319	0.15116	0.09646
608	0.08681	0.16069
898	0.04634	0.20145
1187	0.02625	0.22145
1477	0.01493	0.23331
1766	0.00992	0.23822
2055	0.00683	0.24012
2344	0.00543	0.24182
2633	0.00461	0.24284
2922	0.00342	0.24330
3211	0.00294	0.24404
3500	0.00305	0.24399
3788	0.00068	0.24685
4077	0.00202	0.24441
4366	0.00056	0.24728
4655	0.00049	0.24697
4944	0.00167	0.24506
5233	0.00041	0.24728
5522	0.00038	0.24735
6100	0.00181	0.24485

vii. 121.7 mM **7** 6.74 mM **1**

t (s)	**[7]**	**[8]**
0	0.12169	0.00000
341	0.07072	0.04958
656	0.03380	0.08678
971	0.01503	0.10529

1287	0.00789	0.11290
1602	0.00348	0.11620
1917	0.00204	0.11785
2232	0.00112	0.11763
2546	0.00068	0.11794
2861	0.00171	0.11939
3176	0.00037	0.11905
3491	0.00022	0.11746
3806	0.00016	0.11862
4122	0.00008	0.11899
4436	0.00136	0.11927
4752	0.00010	0.11826
5067	0.00094	0.11924
5382	0.00026	0.11640

viii. 121.8 mM **7** 6.74 mM **1**

t (s)	**[7]**	**[8]**
0	0.12176	0.00000
340	0.07529	0.04516
655	0.03725	0.08344
970	0.01585	0.10436
1285	0.00838	0.11287
1600	0.00434	0.11653
1914	0.00187	0.11836
2229	0.00128	0.11876
2544	0.00062	0.11920
2859	0.00048	0.11922
3174	0.00087	0.11978
3489	0.00015	0.11917
3804	0.00014	0.11987
4119	0.00008	0.11941
4435	0.00012	0.11999
4750	0.00088	0.11956
5065	0.00003	0.11982
5380	0.00005	0.11945
5694	0.00002	0.11937
6009	0.00077	0.11960
6324	0.00102	0.11925
6639	0.00008	0.11950

ix. 119.6 mM **7** 6.69 mM **1**
(600 MHz ^{1}H obs.)

t (s)	**[7]**	**[8]**
0	0.119551448	0
231	0.086442004	0.030511659
392	0.066450219	0.050645318
553	0.050147015	0.068893233
714	0.036781501	0.08170604
875	0.026621769	0.091695708
1036	0.019263829	0.099395001
1197	0.013508703	0.103168761
1358	0.009060636	0.10693616
1518	0.005892057	0.110758609
1679	0.003797376	0.114129857
1840	0.00263705	0.115465835
2002	0.00172544	0.115619247
2166	0.001376116	0.115729495
2327	0.001009899	0.116069587
2487	0.000779905	0.116308869
2648	0.000767772	0.117542107
2809	0.000681758	0.116089946
2970	0.000569199	0.117499621
3131	0.000595203	0.115845936
3292	0.000568664	0.116844492
3452	0.000543977	0.11673024
3613	0.00052096	0.116344297
3774	0.000389243	0.116730908
3935	0.000411199	0.117313793
4095	0.000560202	0.118073207
4256	0.000426981	0.116457306
4418	0.000436969	0.117851131
4578	0.000501634	0.116273037
4739	0.000466487	0.116338907
4900	0.000357629	0.117084206
5061	0.000431639	0.117527124
5222	0.000436687	0.115785627
5382	0.000354125	0.116844886
5543	0.000407591	0.117816737
5704	0.000359864	0.115860866
5865	0.000445114	0.115192625
6026	0.000399917	0.117946943
6187	0.000416885	0.11578441
6351	0.000442291	0.116536676
6512	0.000407019	0.117132588
6672	0.000322026	0.118361202
6833	0.000278553	0.116652247
6994	0.000264169	0.118182619
7154	0.000346317	0.117474381
7315	0.00026391	0.116620855
7478	0.000963005	0.116629724
7638	0.000168847	0.116866709
7799	0.000179104	0.117935636
7960	0.000328467	0.115379494

8120	0.000182899	0.116458868
8281	0.000332585	0.117470838
8441	0.000209249	0.116441616
8602	0.000924872	0.117944345
8762	0.000281602	0.118100002
8923	0.0001514	0.116300397
9084	0.000957124	0.115725251
9248	0.000953385	0.117066054
9408	0.000148653	0.117299953
9569	0.000318691	0.1164099
9730	0.000911317	0.116298963
9890	0.000907347	0.116033053
10051	0.00093973	0.117109422
10212	0.000942406	0.117666744
10373	0.000166808	0.118893855
10534	0.000872562	0.117977262
10695	0.000947354	0.116801925
10855	0.000268433	0.118009714
11016	0.000219404	0.118883504
11177	0.000257067	0.116304437
11338	0.00024415	0.11768523
11499	0.000902123	0.11764078
11660	0.000190007	0.117964151
11821	0.000212012	0.117790506
11981	0.000912209	0.116557192
12142	0.00086695	0.118144073
12303	0.000906369	0.116749046
12463	0.00078124	0.116785919
12624	0.000188838	0.117596509
12785	0.000286493	0.117397489
12946	0.000926758	0.116923443
13106	0.000925042	0.115836384
13267	0.000197677	0.117732685
13428	0.000211635	0.115920253
13591	0.000132069	0.117680312
13751	0.000135709	0.115653065

x. 123.4 mM **7** (wet DCM-d_2) 6.60 mM **1**

t (s)	**[7]**	**[8]**
0	0.123416	0.000000
324	0.114580	0.005201
640	0.090957	0.029358
956	0.060879	0.059466
1271	0.036949	0.082701
1586	0.021091	0.098367
1901	0.011057	0.108396
2216	0.005583	0.113841
2531	0.001697	0.117701
2847	0.000792	0.118331
3162	0.000438	0.118712
3477	0.000000	0.119856
3792	0.000000	0.119325
4107	0.000357	0.118823
4422	0.000354	0.118696
4738	0.000162	0.118788
5053	0.000000	0.119044
5368	0.000008	0.119040
5683	0.000147	0.118857
5998	0.000151	0.118927
6313	0.000094	0.119164
6628	0.000263	0.118776
6943	0.000116	0.118909
7258	0.000000	0.119585
7574	0.000252	0.118565
7889	0.000224	0.119075
8204	0.000246	0.118542
8519	0.000274	0.118544
8834	0.000147	0.118794
9149	0.000410	0.118506
9464	0.000248	0.118519
9779	0.000235	0.119161
10095	0.000237	0.118323
10410	0.000233	0.118413
10726	0.000181	0.118524
11041	0.000234	0.118259
11356	0.000188	0.118593
11671	0.000199	0.118485
11986	0.000159	0.118351
12301	0.000213	0.118364
12616	0.000222	0.117741
12931	0.000371	0.118682
13247	0.000192	0.119007
13562	0.000207	0.117948
13877	0.000250	0.118806

xi. 76.1 mM **7** 1.21 mM **1**

t (s)	**[7]**	**[8]**
0	0.076102	0.000000
342	0.063398	0.012771
658	0.047348	0.028613
973	0.035444	0.040547

1288	0.026272	0.049731
1604	0.019393	0.056607
1919	0.014312	0.061671
2234	0.010573	0.065351
2549	0.007799	0.068116
2864	0.005700	0.070216
3179	0.004111	0.071816
3494	0.002987	0.072908
3810	0.002159	0.073689
4125	0.001542	0.074433
4440	0.001157	0.074742
4755	0.000824	0.074941
5070	0.000684	0.075218
5385	0.000544	0.075309
5701	0.000338	0.075562
6016	0.000375	0.075568
6331	0.000176	0.075584
6646	0.000257	0.075658
6960	0.000238	0.075644
7275	0.000079	0.075533
7590	0.000103	0.075640
7905	0.000193	0.075717
8220	0.000218	0.075749
8535	0.000070	0.075645
8850	0.000278	0.075692
9165	0.000210	0.075703
9480	0.000165	0.075680

xii. 50.2 mM **7** 5.07 mM **1**

t (s)	[7]	[8]
0	0.050224	0.000000
327	0.027469	0.022247
642	0.012752	0.036947
957	0.005106	0.044433
1273	0.001758	0.047796
1588	0.000837	0.048720
1903	0.000602	0.049036
2218	0.000487	0.049028
2533	0.000470	0.049077
2849	0.000500	0.049028
3164	0.000529	0.049003
3478	0.000465	0.049032
3793	0.000460	0.049015
4108	0.000426	0.049045
4423	0.000437	0.048966
4738	0.000412	0.048969
5053	0.000404	0.049031
5369	0.000458	0.048981
5684	0.000453	0.048991
5998	0.000389	0.048980
6313	0.000487	0.048992
6628	0.000425	0.049016
6943	0.000401	0.049059
7258	0.000595	0.049073
7573	0.000388	0.049060
7888	0.000521	0.049050
8203	0.000467	0.049068
8518	0.000462	0.049033
8833	0.000503	0.049050
9149	0.000518	0.049081

xiii. 48.1 mM **7** 1.21 mM **1**

t(s)	[7]	[8]
0	0.048146	0.000000
344	0.036641	0.010602
661	0.026510	0.021348
976	0.018625	0.029138
1291	0.012926	0.034833
1606	0.008865	0.038853
1921	0.006054	0.041616
2236	0.004125	0.043518
2552	0.002814	0.044777
2867	0.001954	0.045653
3182	0.001314	0.046183
3497	0.000837	0.046793
3812	0.000604	0.047037
4127	0.000337	0.047300
4442	0.000262	0.047328
4757	0.000000	0.047537
5072	0.000161	0.047458
5387	0.000104	0.047551
5702	0.000123	0.047513
6017	0.000000	0.047562
6332	0.000078	0.047547
6647	0.000181	0.047450
6962	0.000018	0.047596
7277	0.000000	0.047712
7592	0.000034	0.047521
7906	0.000174	0.047481
8221	0.000000	0.047632
8536	0.000005	0.047568
8851	0.000068	0.047557

9166	0.000048	0.047547
9481	0.000000	0.047538
9795	0.000058	0.047486
10110	0.000000	0.047714
10425	0.000151	0.047391
10740	0.000000	0.047552
11055	0.000108	0.047453
11370	0.000055	0.047496
11685	0.000000	0.047515
12000	0.000000	0.047541
12316	0.000174	0.047352
12631	0.000068	0.047497
12946	0.000000	0.047605
13261	0.000169	0.047396
13576	0.000183	0.047023

xiv. 9.9 mM **7** 0.10 mM **1**

t(s)	**[7]**	**[8]**
0	0.009909	0.000024
266	0.009595	0.000271
582	0.008615	0.001256
898	0.007585	0.002289
1213	0.006679	0.003188
1528	0.005931	0.003949
1843	0.005251	0.004605
2158	0.004673	0.005154
2473	0.004185	0.005643
2788	0.003783	0.006070
3103	0.003373	0.006431
3418	0.003086	0.006740
3733	0.002814	0.006994
4048	0.002537	0.007237
4363	0.002334	0.007443
4678	0.002171	0.007614
4994	0.001976	0.007820
5309	0.001800	0.007929
5624	0.001673	0.008072
5939	0.001553	0.008189
6254	0.001505	0.008299
6569	0.001389	0.008406
6885	0.001323	0.008452

B. RCM REACTIONS OF HEPTADIENE **11** AND OCTADIENE **13** WITH **1** IN CHLOROFORM-*d*

i. 9.23 mM **13**, 0.1 mM **1**

t(s)	**[13]**	**[14]**
0	0.00923	0.00010
332	0.00810	0.00139
617	0.00676	0.00275
901	0.00560	0.00394
1186	0.00460	0.00498
1471	0.00375	0.00584
1755	0.00303	0.00658
2040	0.00246	0.00716
2324	0.00201	0.00766
2609	0.00162	0.00805
2893	0.00127	0.00839
3178	0.00090	0.00860
3463	0.00079	0.00883
3747	0.00064	0.00895
4031	0.00051	0.00909
4316	0.00035	0.00916
4601	0.00029	0.00923
4885	0.00036	0.00929
5170	0.00029	0.00932
5455	0.00018	0.00935
5739	0.00019	0.00936
6024	0.00024	0.00938
6308	0.00023	0.00939
6593	0.00024	0.00941
6878	0.00019	0.00939
7162	0.00024	0.00944
7447	0.00024	0.00941
7732	0.00021	0.00941
8016	0.00020	0.00944
8301	0.00023	0.00947
8585	0.00024	0.00947
8870	0.00021	0.00943
9155	0.00020	0.00944
9439	0.00013	0.00944
9724	0.00022	0.00943
10009	0.00021	0.00943
10293	0.00025	0.00946
10578	0.00022	0.00945
10862	0.00022	0.00945
11147	0.00012	0.00941
11431	0.00013	0.00942
11716	0.00023	0.00944
12000	0.00021	0.00947
12285	0.00018	0.00946
12569	0.00025	0.00946
12854	0.00014	0.00943
13138	0.00023	0.00945
13423	0.00023	0.00945
13707	0.00019	0.00946
13992	0.00024	0.00944
14278	0.00020	0.00944

ii. 9.23 mM **13**, 0.1 mM **1**

t (s)	**[13]**	**[14]**
0	0.00923	0.00018
285	0.00822	0.00128
630	0.00659	0.00294
915	0.00541	0.00416
1200	0.00440	0.00517
1484	0.00356	0.00601
1769	0.00286	0.00673
2053	0.00230	0.00728
2338	0.00183	0.00775
2622	0.00146	0.00812
2907	0.00121	0.00842
3191	0.00096	0.00862
3476	0.00082	0.00879
3760	0.00072	0.00890
4045	0.00061	0.00901
4329	0.00054	0.00907
4614	0.00054	0.00912
4898	0.00043	0.00913
5183	0.00043	0.00917
5468	0.00042	0.00919
5753	0.00039	0.00921
6037	0.00036	0.00921
6322	0.00037	0.00921
6607	0.00035	0.00921
6891	0.00038	0.00921
7176	0.00034	0.00921
7460	0.00035	0.00923

iii. 9.22 mM **11**, 0.1 mM **1**

t(s)	[11]	[12]
0	0.00922	0.00003
303	0.00871	0.00049
598	0.00808	0.00108
893	0.00728	0.00195
1188	0.00644	0.00272
1482	0.00564	0.00353
1777	0.00480	0.00435
2072	0.00411	0.00508
2367	0.00344	0.00572
2661	0.00287	0.00633
2956	0.00235	0.00682
3250	0.00193	0.00722
3545	0.00159	0.00757
3839	0.00128	0.00791
4134	0.00105	0.00813
4429	0.00085	0.00835
4724	0.00068	0.00854
5019	0.00055	0.00862
5313	0.00045	0.00880
5608	0.00036	0.00885
5903	0.00037	0.00878
6197	0.00025	0.00898
6492	0.00020	0.00901
6787	0.00016	0.00905
7081	0.00014	0.00910

iv. 9.23 mM **11**, 0.1 mM **1**

t (s)	[11]	[12]
0	0.00925	0.00003
319	0.00864	0.00045
613	0.00798	0.00108
908	0.00730	0.00181
1203	0.00647	0.00266
1497	0.00567	0.00342
1792	0.00492	0.00415
2087	0.00421	0.00486
2381	0.00357	0.00554
2676	0.00302	0.00608
2970	0.00252	0.00656
3265	0.00210	0.00698
3560	0.00176	0.00732
3854	0.00146	0.00764
4149	0.00121	0.00787
4443	0.00102	0.00810

v. 0.93 mM **11**, 8.59 mM **13**, 0.1 mM **1**

t (s)	[11]	[13]	[12]	[14]
0	0.00093	0.00859	0.00008	0.00005
299	0.00079	0.00738	0.00027	0.00122
594	0.00075	0.00619	0.00035	0.00242
889	0.00062	0.00522	0.00040	0.00346
1184	0.00053	0.00434	0.00050	0.00438
1479	0.00047	0.00354	0.00053	0.00518
1774	0.00038	0.00289	0.00062	0.00582
2069	0.00033	0.00234	0.00066	0.00640
2363	0.00023	0.00194	0.00075	0.00683
2658	0.00018	0.00155	0.00080	0.00722
2953	0.00015	0.00125	0.00088	0.00750
3248	0.00009	0.00102	0.00091	0.00776
3542	0.00004	0.00084	0.00098	0.00793
3837	0.00003	0.00065	0.00098	0.00808
4132	0.00000	0.00063	0.00102	0.00817
4426	0.00000	0.00051	0.00108	0.00826
4721	0.00000	0.00047	0.00111	0.00833
5016	0.00000	0.00035	0.00117	0.00837

5311	0.00000	0.00039	0.00118	0.00841
5605	0.00000	0.00034	0.00119	0.00846
5900	0.00000	0.00030	0.00118	0.00845
6194	0.00000	0.00026	0.00120	0.00850
6489	0.00000	0.00032	0.00126	0.00850
6783	0.00000	0.00027	0.00123	0.00851
7078	0.00000	0.00027	0.00123	0.00851

vi. 1.12 mM **11**, 8.65 mM **13**, 0.1 mM **1**

t (s)	[11]	[13]	[12]	[14]
0	0.00112	0.00865	0.00013	0.00005
319	0.00087	0.00740	0.00028	0.00140
614	0.00075	0.00617	0.00034	0.00264
909	0.00064	0.00514	0.00047	0.00372
1204	0.00057	0.00420	0.00047	0.00467
1498	0.00047	0.00344	0.00059	0.00548
1793	0.00040	0.00278	0.00066	0.00614
2088	0.00035	0.00220	0.00071	0.00671
2383	0.00023	0.00178	0.00079	0.00716
2677	0.00020	0.00140	0.00084	0.00752
2972	0.00011	0.00111	0.00090	0.00782
3266	0.00006	0.00090	0.00097	0.00806
3561	0.00004	0.00070	0.00100	0.00822
3855	0.00000	0.00058	0.00108	0.00834
4150	0.00000	0.00052	0.00110	0.00847
4445	0.00000	0.00042	0.00113	0.00853
4740	0.00000	0.00037	0.00116	0.00857
5034	0.00000	0.00034	0.00119	0.00863
5329	0.00000	0.00030	0.00121	0.00864

vii. 2.45 mM **11**, 7.17 mM **13**, 0.1 mM **1**

t (s)	[11]	[13]	[12]	[14]
0	0.00245	0.00717	0.00010	0.00008
335	0.00246	0.00610	0.00039	0.00115
630	0.00198	0.00521	0.00052	0.00215
925	0.00179	0.00430	0.00073	0.00314
1219	0.00156	0.00348	0.00088	0.00394
1514	0.00137	0.00283	0.00106	0.00464
1809	0.00118	0.00227	0.00120	0.00521
2104	0.00101	0.00181	0.00141	0.00567
2399	0.00084	0.00147	0.00155	0.00603
2694	0.00067	0.00121	0.00172	0.00631
2988	0.00053	0.00100	0.00182	0.00653
3283	0.00039	0.00083	0.00197	0.00670
3578	0.00030	0.00067	0.00207	0.00684

3873	0.00021	0.00060	0.00218	0.00695
4168	0.00015	0.00051	0.00224	0.00701
4462	0.00006	0.00048	0.00235	0.00707
4757	0.00000	0.00043	0.00237	0.00711
5051	0.00000	0.00040	0.00245	0.00714
5346	0.00000	0.00038	0.00245	0.00716
5641	0.00000	0.00040	0.00250	0.00717
5935	0.00000	0.00036	0.00250	0.00720
6230	0.00000	0.00037	0.00256	0.00722

viii. 2.29 mM **11**, 7.28 mM **13**, 0.1 mM **1**

t (s)	**[11]**	**[13]**	**[12]**	**[14]**
0	0.00229	0.00728	0.00015	0.00006
311	0.00210	0.00636	0.00029	0.00092
606	0.00189	0.00541	0.00043	0.00189
901	0.00175	0.00453	0.00061	0.00279
1196	0.00156	0.00379	0.00077	0.00356
1490	0.00141	0.00310	0.00091	0.00424
1785	0.00124	0.00254	0.00108	0.00481
2080	0.00108	0.00209	0.00124	0.00529
2375	0.00093	0.00170	0.00139	0.00567
2669	0.00077	0.00143	0.00153	0.00599
2964	0.00063	0.00118	0.00167	0.00623
3258	0.00053	0.00097	0.00181	0.00643
3553	0.00043	0.00081	0.00189	0.00660
3848	0.00033	0.00069	0.00199	0.00672
4142	0.00024	0.00062	0.00204	0.00682
4437	0.00019	0.00054	0.00214	0.00687
4732	0.00011	0.00051	0.00220	0.00694
5026	0.00006	0.00043	0.00228	0.00701
5321	0.00003	0.00041	0.00233	0.00701

ix. 4.46 mM **11**, 4.67 mM **13**, 0.1 mM **1**

t (s)	**[11]**	**[13]**	**[12]**	**[14]**
0	0.00446	0.00467	0.00006	0.00007
129	0.00424	0.00425	0.00037	0.00051
424	0.00390	0.00351	0.00069	0.00128
719	0.00356	0.00281	0.00103	0.00199
1014	0.00318	0.00226	0.00138	0.00257
1309	0.00288	0.00177	0.00171	0.00306
1604	0.00248	0.00140	0.00208	0.00343
1898	0.00216	0.00111	0.00242	0.00373
2193	0.00186	0.00090	0.00269	0.00395
2488	0.00156	0.00071	0.00299	0.00412
2783	0.00134	0.00057	0.00323	0.00427

3077	0.00107	0.00050	0.00350	0.00436
3372	0.00091	0.00040	0.00367	0.00442
3667	0.00076	0.00034	0.00385	0.00449
3962	0.00060	0.00031	0.00399	0.00452
4257	0.00047	0.00029	0.00411	0.00455
4551	0.00036	0.00027	0.00422	0.00454
4846	0.00029	0.00024	0.00431	0.00459
5141	0.00022	0.00026	0.00436	0.00457
5436	0.00019	0.00023	0.00445	0.00459
5731	0.00011	0.00025	0.00448	0.00459
6025	0.00010	0.00021	0.00450	0.00459

x. 4.60 mM **11**, 4.67 mM **13**, 0.1 mM **1**

t (s)	[11]	[13]	[12]	[14]
0	0.00460	0.00467	0.00006	0.00007
314	0.00428	0.00423	0.00034	0.00053
609	0.00392	0.00356	0.00069	0.00125
903	0.00359	0.00286	0.00102	0.00195
1198	0.00323	0.00230	0.00132	0.00249
1493	0.00289	0.00186	0.00170	0.00297
1788	0.00255	0.00149	0.00204	0.00334
2083	0.00224	0.00119	0.00231	0.00364
2377	0.00193	0.00098	0.00264	0.00387
2672	0.00171	0.00077	0.00289	0.00406
2966	0.00145	0.00063	0.00314	0.00422
3260	0.00126	0.00050	0.00336	0.00432
3555	0.00106	0.00041	0.00353	0.00440
3850	0.00084	0.00041	0.00373	0.00445
4144	0.00074	0.00032	0.00388	0.00450
4439	0.00061	0.00031	0.00398	0.00452
4734	0.00048	0.00030	0.00410	0.00454
5028	0.00039	0.00029	0.00422	0.00455
5323	0.00034	0.00025	0.00428	0.00459
5617	0.00025	0.00025	0.00432	0.00458
5912	0.00020	0.00023	0.00438	0.00459
6207	0.00019	0.00023	0.00445	0.00461

xi. 8.14 mM **11**, 1.07 mM **13**, 0.1 mM **1**

t (s)	[11]	[13]	[12]	[14]
0	0.00814	0.00107	0.00006	0.00005
314	0.00750	0.00115	0.00062	0.00010
608	0.00699	0.00097	0.00112	0.00027
903	0.00636	0.00077	0.00176	0.00047
1198	0.00563	0.00068	0.00247	0.00058
1492	0.00500	0.00050	0.00314	0.00070

1787	0.00436	0.00039	0.00374	0.00081
2082	0.00374	0.00035	0.00439	0.00086
2377	0.00316	0.00032	0.00496	0.00091
2672	0.00266	0.00026	0.00545	0.00096
2967	0.00221	0.00025	0.00586	0.00096
3262	0.00183	0.00021	0.00625	0.00097
3556	0.00149	0.00023	0.00658	0.00098
3851	0.00122	0.00022	0.00686	0.00099
4146	0.00099	0.00023	0.00712	0.00101
4440	0.00081	0.00020	0.00725	0.00100
4735	0.00068	0.00019	0.00740	0.00101
5031	0.00055	0.00020	0.00752	0.00102
5325	0.00043	0.00021	0.00766	0.00100
5620	0.00038	0.00019	0.00774	0.00102

xii. 8.31 mM **11**, 1.01 mM **13**, 0.1 mM **1**

t (s)	**[11]**	**[13]**	**[12]**	**[14]**
0	0.00831	0.00101	0.00003	0.00011
328	0.00796	0.00105	0.00045	0.00025
623	0.00724	0.00114	0.00105	0.00022
917	0.00674	0.00098	0.00154	0.00038
1212	0.00622	0.00081	0.00206	0.00051
1507	0.00575	0.00062	0.00258	0.00066
1802	0.00517	0.00055	0.00316	0.00074
2097	0.00467	0.00044	0.00364	0.00083
2392	0.00406	0.00047	0.00421	0.00083
2687	0.00365	0.00034	0.00464	0.00093
2981	0.00319	0.00032	0.00509	0.00097
3276	0.00277	0.00030	0.00553	0.00098
3571	0.00240	0.00027	0.00587	0.00100
3866	0.00205	0.00028	0.00618	0.00101
4161	0.00178	0.00026	0.00650	0.00102
4455	0.00151	0.00025	0.00676	0.00102
4750	0.00130	0.00025	0.00700	0.00104
5044	0.00115	0.00023	0.00715	0.00103
5339	0.00094	0.00023	0.00729	0.00103
5634	0.00082	0.00024	0.00745	0.00105
5929	0.00070	0.00024	0.00756	0.00105

xiii. 6.72 mM **11**, 2.57 mM **13**, 0.1 mM **1**

t (s)	**[11]**	**[13]**	**[12]**	**[14]**
0	0.00672	0.00257	0.00006	0.00008
287	0.00603	0.00251	0.00052	0.00023
582	0.00560	0.00209	0.00097	0.00066
876	0.00506	0.00176	0.00147	0.00099

1171	0.00464	0.00140	0.00194	0.00134
1466	0.00410	0.00118	0.00242	0.00158
1761	0.00370	0.00089	0.00284	0.00182
2056	0.00323	0.00076	0.00332	0.00198
2350	0.00279	0.00062	0.00375	0.00212
2645	0.00238	0.00055	0.00416	0.00222
2940	0.00207	0.00044	0.00452	0.00232
3235	0.00173	0.00039	0.00479	0.00236
3529	0.00142	0.00035	0.00508	0.00241
3824	0.00119	0.00031	0.00532	0.00244
4119	0.00098	0.00029	0.00554	0.00246
4413	0.00083	0.00026	0.00572	0.00250
4708	0.00070	0.00025	0.00587	0.00249
5003	0.00055	0.00024	0.00600	0.00251
5297	0.00042	0.00026	0.00610	0.00250
5592	0.00038	0.00024	0.00618	0.00254
5887	0.00026	0.00024	0.00627	0.00253
6181	0.00021	0.00025	0.00635	0.00253

xiv. 6.86 mM **11**, 2.57 mM **13**, 0.1 mM **1**

t (s)	**[11]**	**[13]**	**[12]**	**[14]**
0	0.00686	0.00257	0.00005	0.00010
296	0.00618	0.00246	0.00032	0.00026
591	0.00569	0.00208	0.00083	0.00066
886	0.00514	0.00170	0.00132	0.00103
1181	0.00464	0.00132	0.00188	0.00141
1475	0.00408	0.00110	0.00238	0.00164
1770	0.00365	0.00082	0.00288	0.00189
2065	0.00313	0.00068	0.00333	0.00205
2359	0.00269	0.00057	0.00378	0.00217
2654	0.00228	0.00048	0.00421	0.00225
2949	0.00197	0.00039	0.00454	0.00233
3244	0.00161	0.00038	0.00486	0.00238
3538	0.00138	0.00030	0.00513	0.00243
3833	0.00112	0.00030	0.00534	0.00245
4127	0.00095	0.00026	0.00554	0.00247
4422	0.00077	0.00026	0.00568	0.00247
4717	0.00065	0.00025	0.00588	0.00247
5011	0.00054	0.00023	0.00599	0.00249
5306	0.00043	0.00023	0.00607	0.00247
5600	0.00037	0.00022	0.00616	0.00250
5895	0.00026	0.00022	0.00621	0.00252
6190	0.00024	0.00020	0.00626	0.00252
6485	0.00018	0.00023	0.00632	0.00252

C. RCM REACTIONS OF HEPTADIENE **11** AND OCTADIENE **13** WITH **2** IN CHLOROFORM-*d*

i. 5.14 mM **11**, 5.17 mM **13**, 0.1 mM **2**

t (s)	[11]	[13]	[12]	[14]
0	0.00514	0.00517	0.00000	0.00000
173	0.00496	0.00468	0.00020	0.00055
348	0.00452	0.00355	0.00064	0.00171
525	0.00394	0.00235	0.00124	0.00291
698	0.00343	0.00153	0.00181	0.00373
871	0.00301	0.00099	0.00230	0.00423
1047	0.00246	0.00073	0.00275	0.00455
1221	0.00208	0.00054	0.00313	0.00474
1397	0.00187	0.00038	0.00340	0.00488
1573	0.00163	0.00030	0.00362	0.00495
1746	0.00138	0.00026	0.00383	0.00501
1919	0.00127	0.00020	0.00400	0.00504
2093	0.00121	0.00014	0.00411	0.00507
2266	0.00100	0.00016	0.00424	0.00509
2439	0.00097	0.00013	0.00430	0.00511
2616	0.00087	0.00012	0.00442	0.00513
2789	0.00080	0.00012	0.00448	0.00514
2962	0.00072	0.00011	0.00452	0.00514
3138	0.00070	0.00011	0.00456	0.00514
3312	0.00070	0.00008	0.00461	0.00514
3486	0.00063	0.00009	0.00465	0.00515
3662	0.00058	0.00010	0.00468	0.00516
3838	0.00057	0.00008	0.00471	0.00516
4012	0.00053	0.00008	0.00473	0.00516
4185	0.00051	0.00009	0.00475	0.00516
4358	0.00051	0.00008	0.00477	0.00516
4535	0.00043	0.00010	0.00481	0.00516
4711	0.00045	0.00009	0.00482	0.00517
4884	0.00047	0.00007	0.00483	0.00516
5061	0.00043	0.00008	0.00485	0.00517
5234	0.00042	0.00008	0.00486	0.00517
5408	0.00042	0.00007	0.00486	0.00516
5581	0.00044	0.00006	0.00486	0.00516
5754	0.00037	0.00008	0.00490	0.00517
5930	0.00040	0.00006	0.00489	0.00516
6104	0.00042	0.00006	0.00489	0.00516
6279	0.00036	0.00008	0.00492	0.00518
6453	0.00035	0.00007	0.00491	0.00517
6626	0.00038	0.00006	0.00491	0.00517
6799	0.00039	0.00005	0.00491	0.00516
6972	0.00035	0.00006	0.00492	0.00518
7146	0.00037	0.00006	0.00493	0.00517

7319	0.00033	0.00006	0.00493	0.00516
7495	0.00035	0.00007	0.00494	0.00517
7672	0.00034	0.00006	0.00494	0.00517
7845	0.00031	0.00006	0.00495	0.00518
8018	0.00034	0.00005	0.00496	0.00517
8195	0.00036	0.00005	0.00494	0.00518
8368	0.00032	0.00006	0.00496	0.00517
8541	0.00029	0.00008	0.00498	0.00517
8718	0.00029	0.00007	0.00497	0.00517
8891	0.00035	0.00005	0.00497	0.00517
9065	0.00031	0.00006	0.00498	0.00517
9238	0.00030	0.00007	0.00497	0.00519
9412	0.00032	0.00006	0.00497	0.00517
9585	0.00030	0.00006	0.00497	0.00517
9762	0.00029	0.00006	0.00497	0.00517
9938	0.00028	0.00007	0.00499	0.00518
10111	0.00032	0.00005	0.00498	0.00517
10285	0.00028	0.00007	0.00498	0.00517
10458	0.00028	0.00007	0.00499	0.00518
10634	0.00033	0.00004	0.00497	0.00517
10808	0.00025	0.00007	0.00500	0.00518
10981	0.00025	0.00008	0.00498	0.00516
11158	0.00029	0.00006	0.00497	0.00516
11331	0.00027	0.00006	0.00499	0.00517
11507	0.00025	0.00007	0.00499	0.00517
11680	0.00028	0.00006	0.00498	0.00517
11854	0.00029	0.00005	0.00499	0.00518
12027	0.00026	0.00007	0.00501	0.00517

ii. 4.89 mM **11**, 4.94 mM **13**, 0.1 mM **2**

t (s)	**[11]**	**[13]**	**[12]**	**[14]**
0	0.00489	0.00494	0.00004	0.00007
123	0.00465	0.00447	0.00023	0.00056
303	0.00436	0.00347	0.00059	0.00158
483	0.00381	0.00242	0.00112	0.00263
663	0.00328	0.00167	0.00167	0.00340
843	0.00287	0.00113	0.00213	0.00393
1023	0.00242	0.00083	0.00256	0.00425
1203	0.00215	0.00059	0.00288	0.00446
1383	0.00187	0.00045	0.00315	0.00460
1563	0.00162	0.00035	0.00339	0.00469
1743	0.00141	0.00030	0.00357	0.00476
1863	0.00130	0.00023	0.00372	0.00482
2043	0.00119	0.00020	0.00387	0.00485
2223	0.00108	0.00016	0.00397	0.00487
2403	0.00098	0.00014	0.00406	0.00489

2583	0.00088	0.00014	0.00415	0.00491
2763	0.00084	0.00012	0.00420	0.00492
2943	0.00077	0.00012	0.00426	0.00493
3123	0.00068	0.00012	0.00432	0.00493
3303	0.00072	0.00008	0.00435	0.00493
3483	0.00061	0.00010	0.00439	0.00494
3603	0.00058	0.00010	0.00442	0.00493
3783	0.00057	0.00009	0.00447	0.00495
3963	0.00056	0.00007	0.00450	0.00495
4143	0.00053	0.00008	0.00452	0.00496
4323	0.00053	0.00008	0.00453	0.00496
4503	0.00050	0.00007	0.00456	0.00496
4683	0.00047	0.00007	0.00458	0.00495
4863	0.00047	0.00007	0.00460	0.00496
5043	0.00045	0.00007	0.00460	0.00497
5223	0.00041	0.00007	0.00460	0.00496
5343	0.00039	0.00008	0.00463	0.00496
5523	0.00035	0.00009	0.00468	0.00496
5703	0.00039	0.00008	0.00465	0.00496
5883	0.00033	0.00008	0.00466	0.00496
6063	0.00035	0.00008	0.00466	0.00497
6243	0.00032	0.00008	0.00470	0.00497

D. COMPETITION RCM BETWEEN **7** AND **11** WITH **1** IN DCM-d_2

i. 4.86 mM **7**, 4.64 mM **11**, 0.1 mM **1**

t (s)	**[7]**	**[11]**	**[8]**	**[12]**
0	0.00486	0.00464	0.00000	0.00000
269	0.00462	0.00410	0.00028	0.00065
585	0.00404	0.00318	0.00084	0.00152
900	0.00356	0.00248	0.00130	0.00217
1215	0.00315	0.00195	0.00170	0.00265
1530	0.00281	0.00156	0.00205	0.00301
1846	0.00251	0.00127	0.00233	0.00328
2160	0.00224	0.00105	0.00259	0.00349
2475	0.00204	0.00090	0.00282	0.00367
2791	0.00183	0.00074	0.00300	0.00377
3105	0.00168	0.00066	0.00316	0.00386
3420	0.00155	0.00061	0.00331	0.00393
3736	0.00142	0.00052	0.00345	0.00402
4051	0.00131	0.00046	0.00355	0.00404
4366	0.00121	0.00045	0.00367	0.00409
4681	0.00112	0.00039	0.00373	0.00412
4996	0.00103	0.00037	0.00382	0.00414
5311	0.00097	0.00035	0.00389	0.00417
5626	0.00092	0.00034	0.00396	0.00417
5941	0.00084	0.00029	0.00401	0.00418
6256	0.00078	0.00028	0.00405	0.00420
6571	0.00077	0.00029	0.00410	0.00421
6886	0.00068	0.00024	0.00412	0.00419
7201	0.00068	0.00026	0.00418	0.00421
7516	0.00064	0.00025	0.00422	0.00423
7831	0.00062	0.00026	0.00425	0.00423
8146	0.00059	0.00026	0.00426	0.00423
8461	0.00059	0.00027	0.00432	0.00423
8776	0.00052	0.00024	0.00432	0.00423
9091	0.00051	0.00023	0.00434	0.00423
9406	0.00049	0.00021	0.00436	0.00422
9721	0.00048	0.00024	0.00439	0.00423
10036	0.00043	0.00020	0.00438	0.00420
10351	0.00045	0.00023	0.00441	0.00424
10666	0.00044	0.00023	0.00443	0.00424
10981	0.00042	0.00023	0.00444	0.00423
11297	0.00039	0.00020	0.00443	0.00423
11612	0.00040	0.00020	0.00445	0.00423
11927	0.00036	0.00019	0.00446	0.00424
12242	0.00037	0.00021	0.00447	0.00424

E. INITIATION RATE MEASUREMENTS FOR **1** AND **2**

For 1: [1] *versus* time is first order in the presence of an excess of ethyl vinyl ether.

For 2: [2] *versus* time is first order in 2 and first order in ethyl vinyl ether.

i. 1 (21.2 mM) in DCM-d_2

416.3 mM ethyl vinyl ether

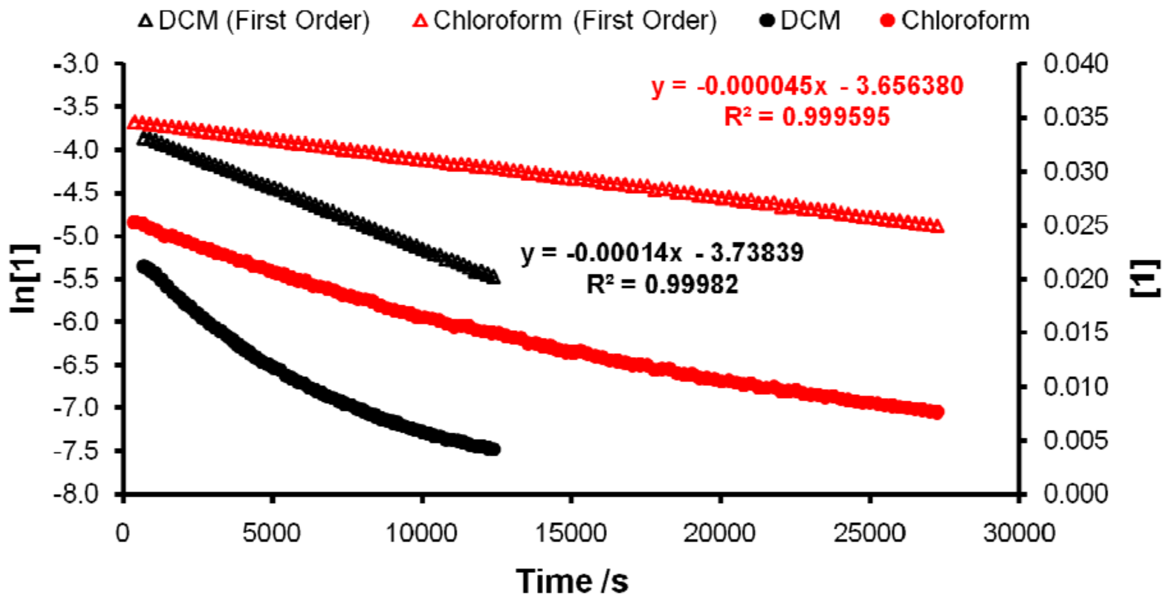
t(s)	**[1]**	**ln[1]**
672	0.02115	-3.8561
871	0.02088	-3.8691
1070	0.02050	-3.8876
1268	0.01993	-3.9155
1466	0.01937	-3.9443
1665	0.01880	-3.9738
1864	0.01834	-3.9986
2062	0.01778	-4.0297
2261	0.01741	-4.0507
2460	0.01682	-4.0852
2659	0.01638	-4.1118
2857	0.01588	-4.1427
3056	0.01547	-4.1690
3255	0.01513	-4.1908
3454	0.01473	-4.2180
3652	0.01429	-4.2484
3851	0.01385	-4.2796
4049	0.01349	-4.3060
4248	0.01312	-4.3333
4447	0.01274	-4.3626
4645	0.01237	-4.3928
4843	0.01210	-4.4146
5042	0.01180	-4.4400
5240	0.01156	-4.4602
5439	0.01104	-4.5062
5637	0.01078	-4.5302
5836	0.01047	-4.5596
6034	0.01029	-4.5770
6233	0.00991	-4.6146
6432	0.00962	-4.6439
6630	0.00942	-4.6646
6829	0.00908	-4.7021
7027	0.00893	-4.7180
7226	0.00867	-4.7479
7425	0.00835	-4.7859
7623	0.00824	-4.7988
7822	0.00792	-4.8385
8021	0.00774	-4.8615
8220	0.00748	-4.8953
8419	0.00730	-4.9197
8617	0.00705	-4.9546
8816	0.00690	-4.9758
9015	0.00671	-5.0042
9213	0.00655	-5.0284
9411	0.00635	-5.0586
9610	0.00614	-5.0924
9808	0.00599	-5.1170
10007	0.00578	-5.1533
10205	0.00563	-5.1795
10404	0.00543	-5.2162
10603	0.00538	-5.2256
10801	0.00513	-5.2733
10999	0.00509	-5.2799
11198	0.00497	-5.3048
11396	0.00482	-5.3349
11595	0.00464	-5.3732
11793	0.00449	-5.4050
11992	0.00444	-5.4163
12190	0.00431	-5.4462
12389	0.00419	-5.4747

ii. 1 (25.3 mM) in chloroform-*d*

336.7 mM ethyl vinyl ether

t (s)	**[1]**	**ln[1]**
382	0.02528	-3.6778
631	0.02514	-3.6835
880	0.02479	-3.6973
1129	0.02449	-3.7094
1378	0.02404	-3.7282
1626	0.02403	-3.7285
1875	0.02377	-3.7394
2123	0.02348	-3.7516
2372	0.02324	-3.7617
2621	0.02291	-3.7760
2869	0.02273	-3.7842
3118	0.02245	-3.7964
3366	0.02224	-3.8057
3615	0.02203	-3.8154
3863	0.02169	-3.8308
4111	0.02162	-3.8341
4360	0.02119	-3.8543

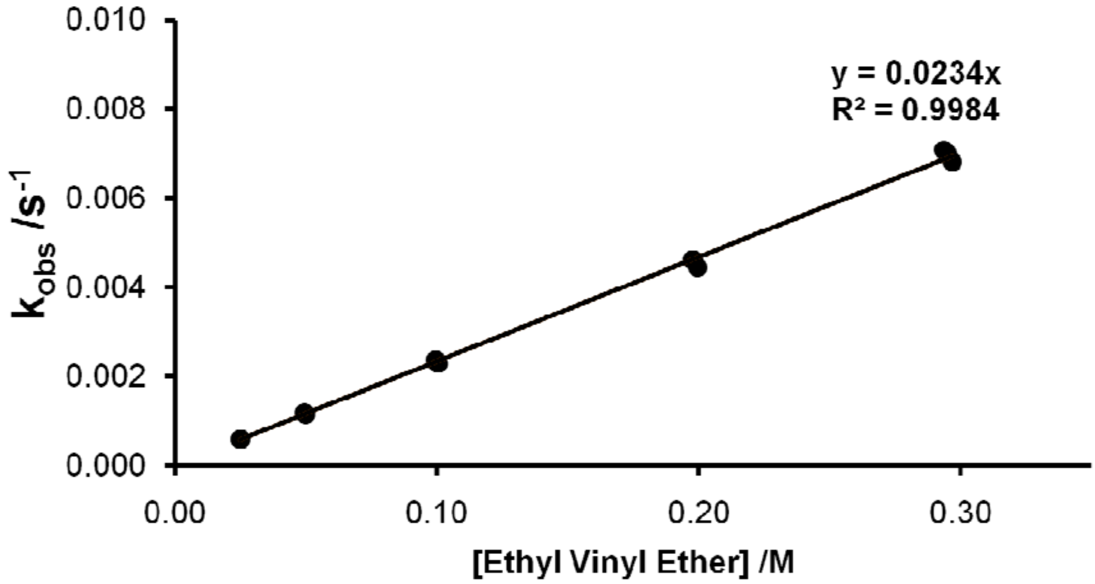
4609	0.02111	-3.8581	16043	0.01271	-4.3655
4857	0.02083	-3.8713	16292	0.01245	-4.3862
5105	0.02060	-3.8824	16541	0.01243	-4.3873
5354	0.02039	-3.8928	16790	0.01228	-4.3999
5603	0.02011	-3.9068	17038	0.01204	-4.4198
5852	0.01990	-3.9171	17287	0.01206	-4.4176
6100	0.01978	-3.9230	17537	0.01202	-4.4209
6349	0.01941	-3.9419	17785	0.01155	-4.4614
6597	0.01932	-3.9465	18034	0.01169	-4.4489
6846	0.01914	-3.9561	18283	0.01166	-4.4514
7094	0.01895	-3.9662	18532	0.01126	-4.4866
7343	0.01856	-3.9870	18781	0.01115	-4.4963
7591	0.01846	-3.9922	19029	0.01113	-4.4980
7840	0.01821	-4.0059	19278	0.01081	-4.5276
8089	0.01810	-4.0117	19527	0.01079	-4.5293
8337	0.01792	-4.0220	19776	0.01068	-4.5393
8586	0.01756	-4.0422	20025	0.01050	-4.5565
8834	0.01730	-4.0572	20273	0.01059	-4.5478
9083	0.01708	-4.0698	20522	0.01036	-4.5699
9331	0.01692	-4.0790	20771	0.01018	-4.5874
9580	0.01678	-4.0875	21020	0.01027	-4.5785
9829	0.01651	-4.1036	21268	0.00995	-4.6102
10077	0.01644	-4.1081	21517	0.00990	-4.6147
10326	0.01631	-4.1160	21766	0.00997	-4.6077
10574	0.01610	-4.1292	22015	0.00955	-4.6508
10823	0.01585	-4.1446	22263	0.00957	-4.6489
11072	0.01557	-4.1624	22512	0.00965	-4.6412
11320	0.01564	-4.1581	22761	0.00935	-4.6721
11569	0.01558	-4.1617	23010	0.00925	-4.6833
11818	0.01524	-4.1840	23259	0.00924	-4.6840
12066	0.01510	-4.1931	23508	0.00906	-4.7043
12314	0.01501	-4.1993	23756	0.00909	-4.7006
12563	0.01494	-4.2040	24006	0.00884	-4.7288
12812	0.01469	-4.2208	24254	0.00875	-4.7384
13060	0.01453	-4.2313	24503	0.00863	-4.7524
13309	0.01446	-4.2363	24752	0.00849	-4.7694
13557	0.01403	-4.2664	25001	0.00846	-4.7719
13806	0.01404	-4.2660	25249	0.00840	-4.7795
14054	0.01377	-4.2853	25498	0.00825	-4.7978
14303	0.01372	-4.2887	25747	0.00821	-4.8029
14551	0.01340	-4.3121	25996	0.00811	-4.8143
14800	0.01325	-4.3241	26245	0.00803	-4.8245
15049	0.01317	-4.3300	26494	0.00788	-4.8431
15297	0.01328	-4.3212	26742	0.00784	-4.8484
15546	0.01307	-4.3375	26991	0.00773	-4.8625
15795	0.01289	-4.3513	27240	0.00765	-4.8731



iv. **2** in chloroform-*d*

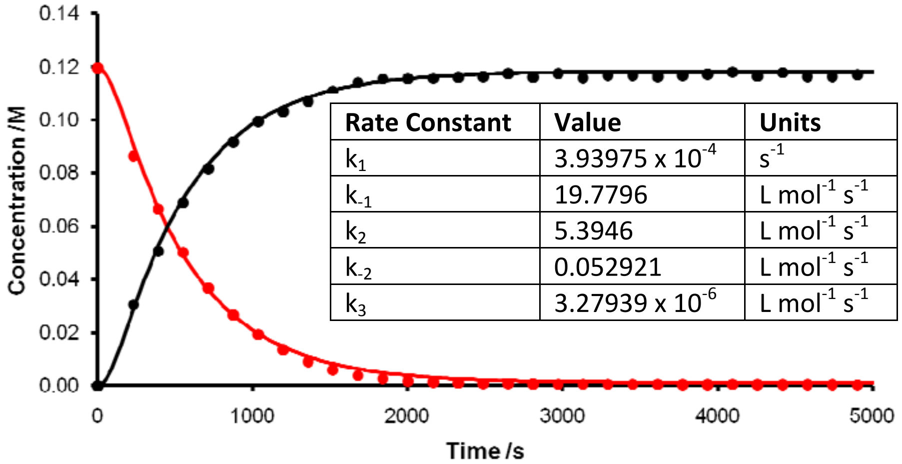
0.1 mM pre-catalyst

24.9 to 296.8 mM ethyl vinyl ether (in triplicate)



4. RATE CONSTANTS AND SIMULATIONS FROM SIMULATION SOFTWARE

A. FITTING OF DATA FOR THE RCM REACTION OF **7** IN DCM-d_2 (120 mM, 5.6 % **1**)
(Best fit, no constraints, all constants fitted)



Rate Constant	Value	Units
k_1	3.93975×10^{-4}	s^{-1}
k_{-1}	19.7796	$L\ mol^{-1}\ s^{-1}$
k_2	5.3946	$L\ mol^{-1}\ s^{-1}$
k_{-2}	0.052921	$L\ mol^{-1}\ s^{-1}$
k_3	3.27939×10^{-6}	$L\ mol^{-1}\ s^{-1}$

B. FITTING WITH VARIED k_1 (k_3 FITTED)

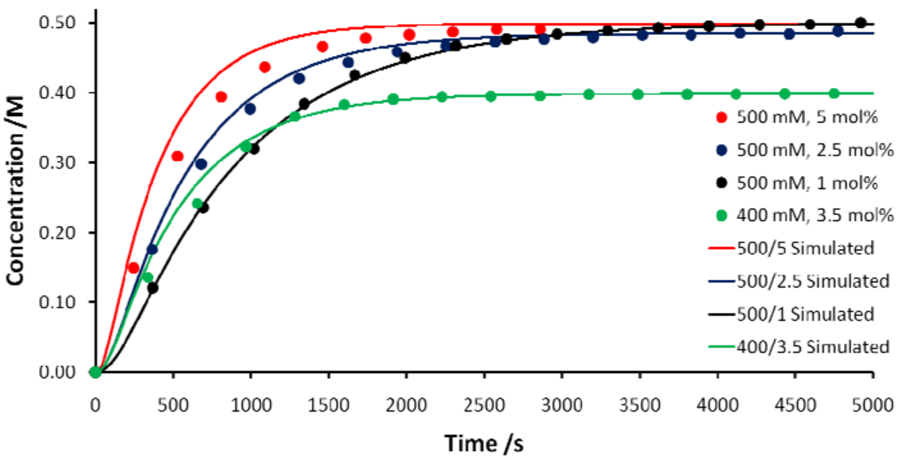
k_1 (fixed)	k_{-1} /L mol^{-1} s^{-1}	k_2/L mol^{-1} s^{-1}	k_{-2}/L mol^{-1} s^{-1}	k_3/L mol^{-1} s^{-1}
10^{-10} s^{-1}	2.80638×10^{-2}	9.90936×10^{6}	4.89704×10^{5}	2.75671×10^{6}
10^{-9} s^{-1}	1.72119×10^{6}	1.77858×10^{6}	1.01610×10^{4}	1.39485×10^{6}
10^{-8} s^{-1}	7.63628×10^{5}	2.05788×10^{5}	2.20155×10^{3}	1.60242×10^{-2}
10^{-7} s^{-1}	2.19783×10^{4}	1.77247×10^{4}	9.71998×10^{1}	1.12147×10^{4}
10^{-6} s^{-1}	1.13090×10^{4}	2.41404×10^{3}	1.81659×10^{1}	1.31303×10^{-4}
10^{-5} s^{-1}	1.00405×10^{-4}	2.29359×10^{2}	1.99667×10^{0}	4.95539×10^{2}
10^{-4} s^{-1}	5.64178×10^{1}	1.84433×10^{1}	2.03633×10^{-1}	2.44289×10^{-1}
10^{-3} s^{-1}	7.56591×10^{1}	5.85899×10^{0}	2.47255×10^{-2}	1.99528×10^{-7}
10^{-2} s^{-1}	5.86009×10^{1}	1.66765×10^{1}	4.53130×10^{-3}	4.37630×10^{-8}

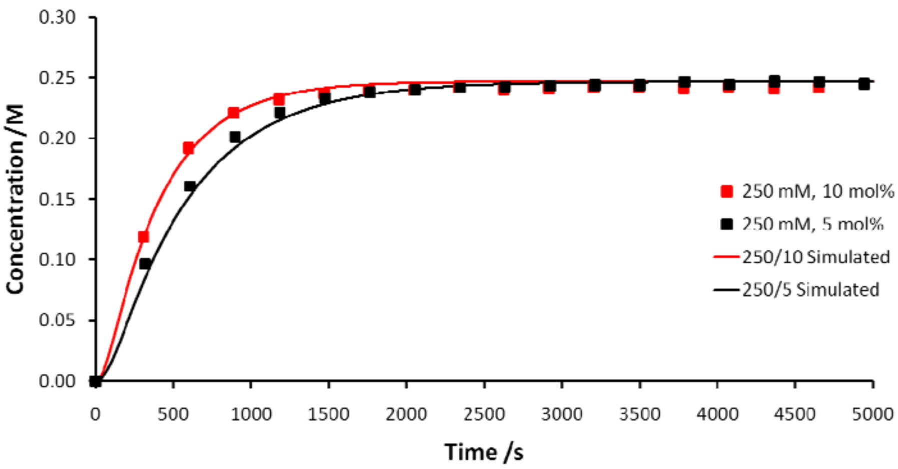
C. FITTING WITH VARIED k_1 (k_3 FIXED TO ZERO)

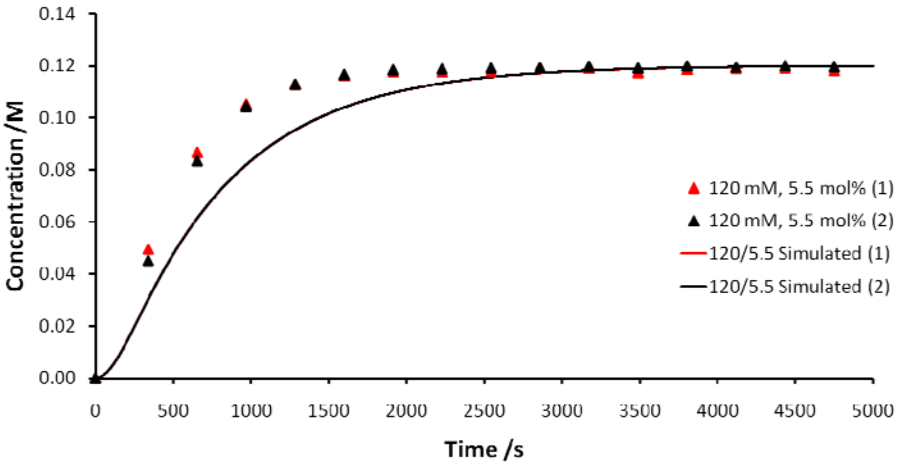
k_1 (fixed)	k_{-1} /L mol^{-1} s^{-1}	k_2/L mol^{-1} s^{-1}	k_{-2}/L mol^{-1} s^{-1}
10^{-8} s^{-1}	1.04×10^{6}	2.38×10^{5}	2.08×10^{3}
10^{-7} s^{-1}	1.04×10^{5}	2.38×10^{4}	2.08×10^{2}
10^{-6} s^{-1}	1.04×10^{4}	2.38×10^{3}	2.08×10^{1}
10^{-5} s^{-1}	1.04×10^{3}	2.38×10^{2}	2.08×10^{0}
10^{-4} s^{-1}	1.03×10^{2}	2.39×10^{1}	2.09×10^{-1}

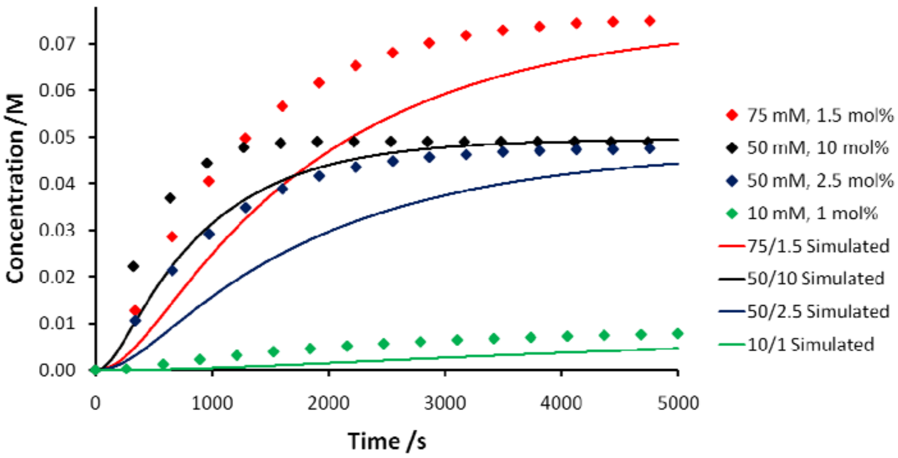
D. BATCH FITTING OF 13 RCM EXPERIMENTS (ALL RATE CONSTANTS FITTED)

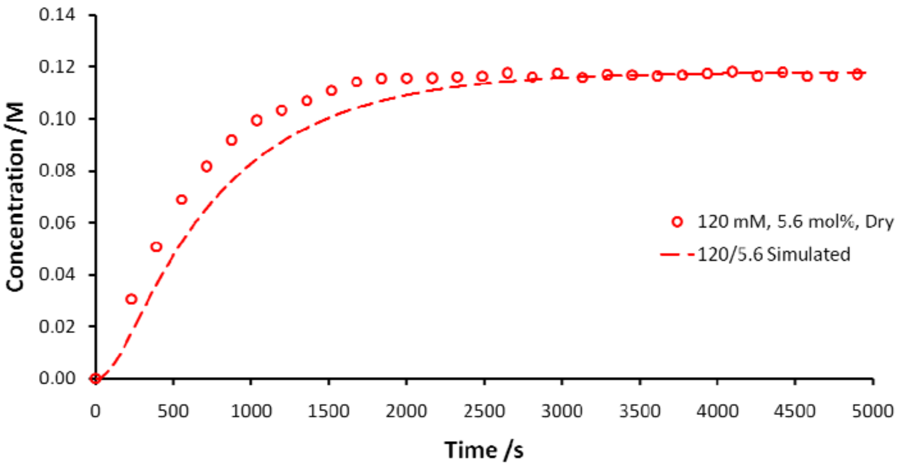
Rate Constant	Value	Units
k_1	1.63684 x 10^{-5}	s^{-1}
k_{-1}	243.646	L mol^{-1} s^{-1}
k_2	65.0545	L mol^{-1} s^{-1}
k_{-2}	0.889673	L mol^{-1} s^{-1}
k_3	0.566982	L mol^{-1} s^{-1}





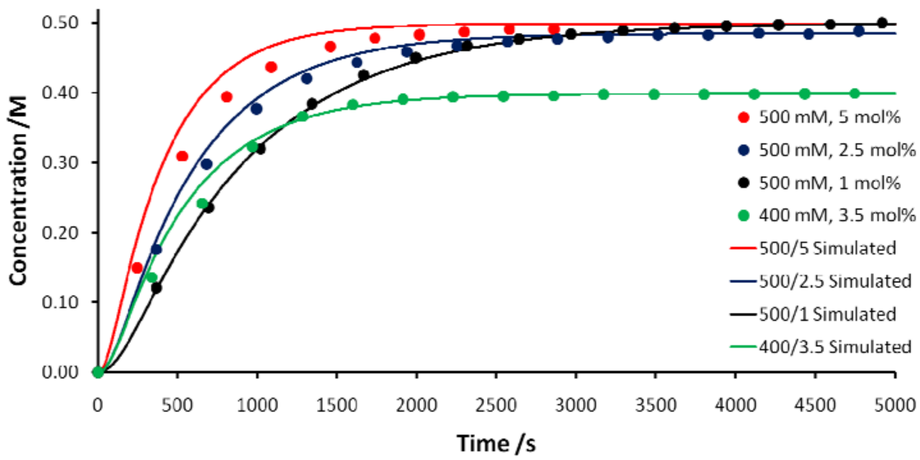

0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
Concentration /M
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
Time /s
120 mM, 5.5 mol% (1)
120 mM, 5.5 mol% (2)
120/5.5 Simulated (1)
120/5.5 Simulated (2)

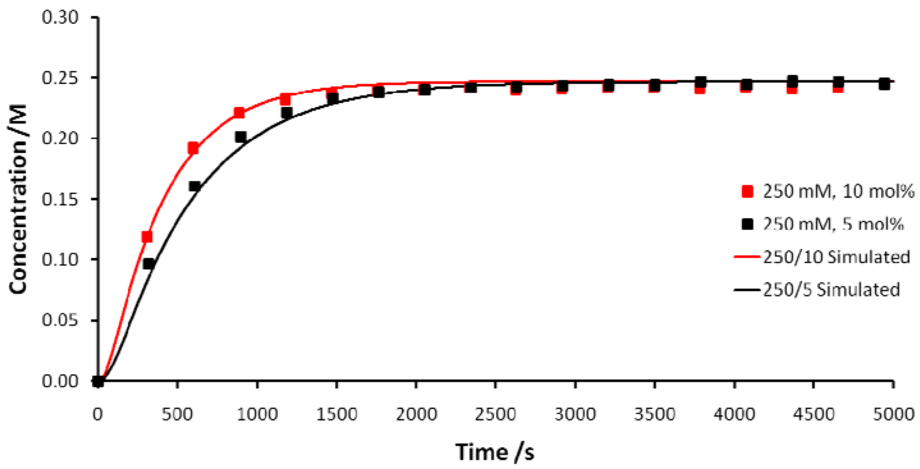

0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
Concentration /M
0
1000
2000
3000
4000
5000
Time /s
75 mM, 1.5 mol%
50 mM, 10 mol%
50 mM, 2.5 mol%
10 mM, 1 mol%
75/1.5 Simulated
50/10 Simulated
50/2.5 Simulated
10/1 Simulated

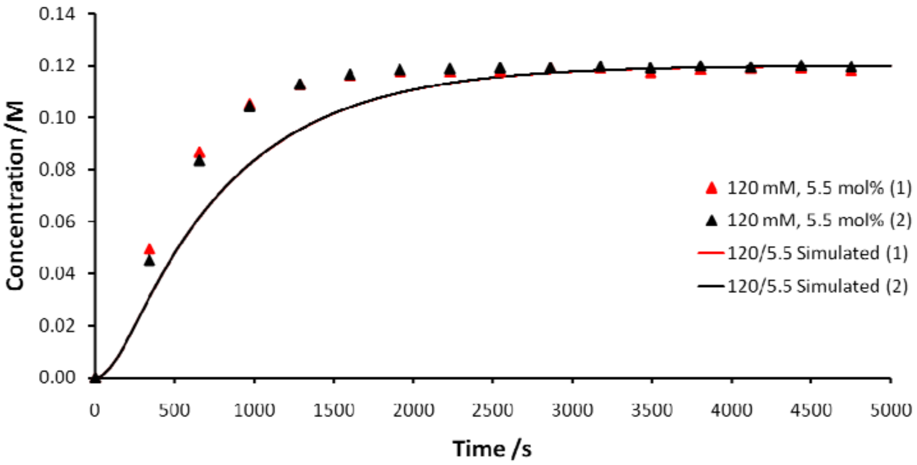

0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
Concentration /M
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
Time /s
120 mM, 5.6 mol%, Dry
120/5.6 Simulated

E. BATCH FITTING OF 13 RCM EXPERIMENTS ($k_1 = 1.4 \times 10^{-4}$ s^{-1}, $k_3 = 0$)

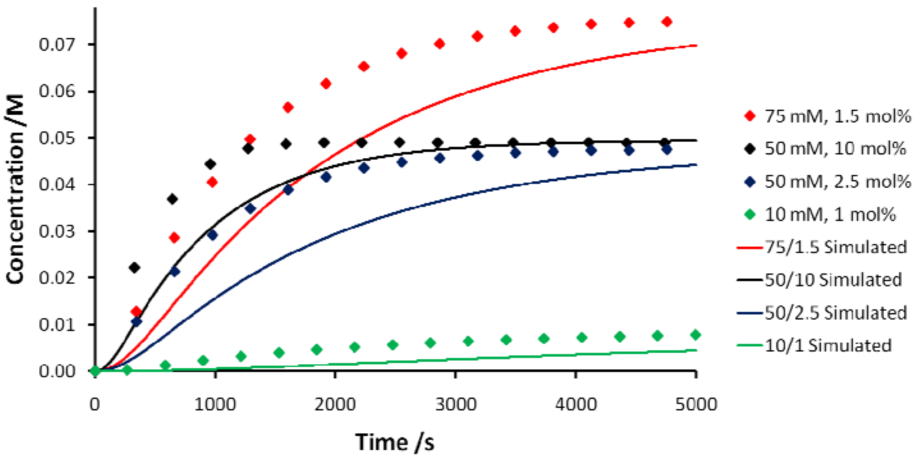
Rate Constant	Value	Units
k_1 (fixed)	1.4×10^{-4}	s^{-1}
k_{-1}	29.8027	L mol^{-1} s^{-1}
k_2	7.68974	L mol^{-1} s^{-1}
k_{-2}	0.109507	L mol^{-1} s^{-1}
k_3 (fixed)	0	L mol^{-1} s^{-1}



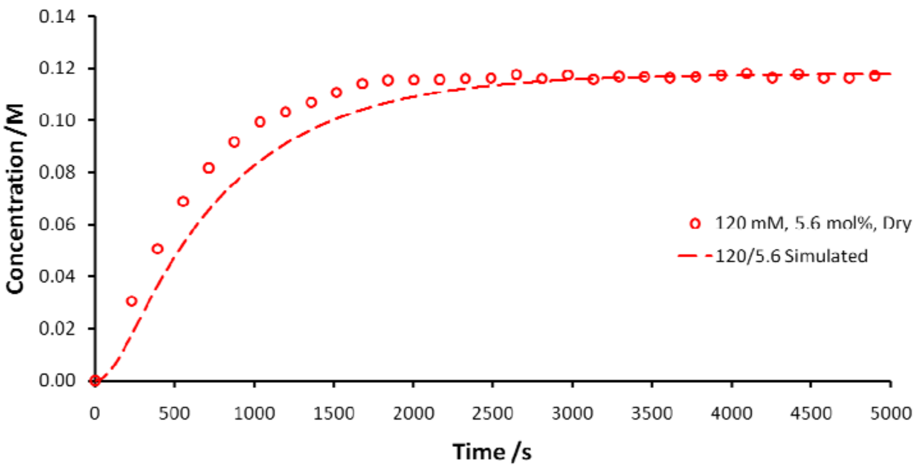




Concentration /M
Time /s
120 mM, 5.5 mol% (1)
120 mM, 5.5 mol% (2)
120/5.5 Simulated (1)
120/5.5 Simulated (2)



Concentration /M
Time /s
75 mM, 1.5 mol%
50 mM, 10 mol%
50 mM, 2.5 mol%
10 mM, 1 mol%
75/1.5 Simulated
50/10 Simulated
50/2.5 Simulated
10/1 Simulated

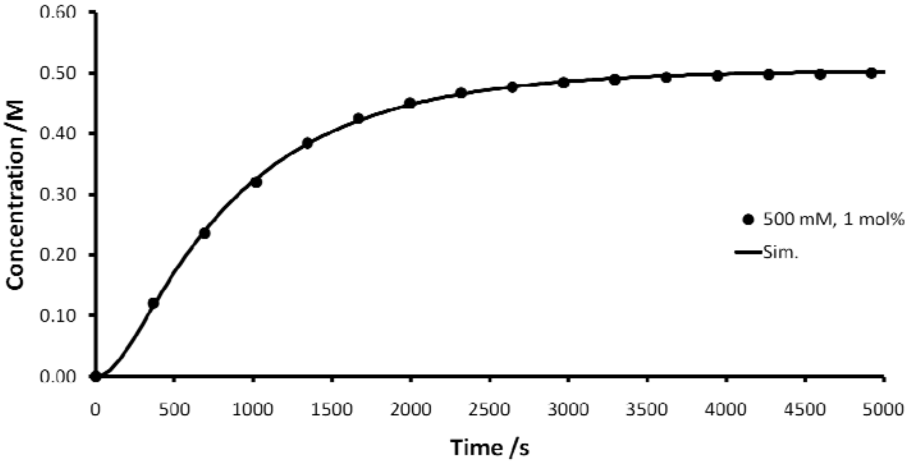


Concentration /M
Time /s
120 mM, 5.6 mol%, Dry
120/5.6 Simulated

F. FITTING USING MICROMATH SCIENTIST

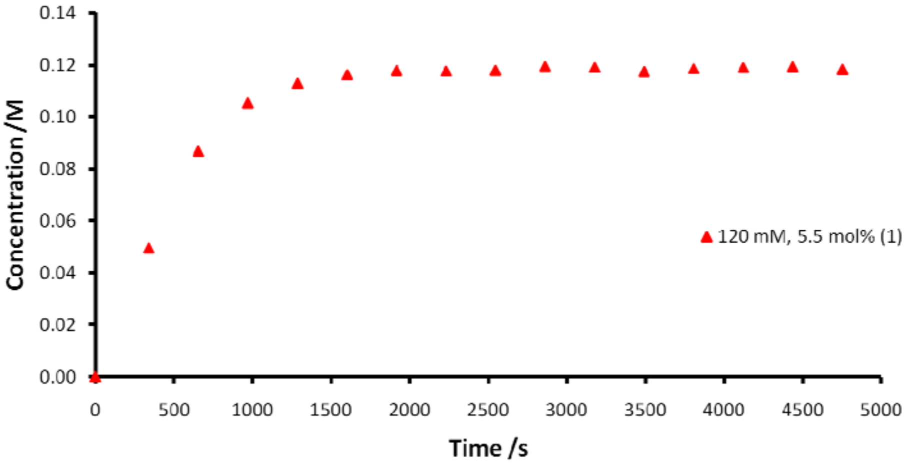
i. *Entry 1 in TABLE 5; DATASET 3 in TABLE 2*

Rate Constant	Value	Units	Confidence Interval (95%)	
k_1 (fixed)	1.4×10^{-4}	s^{-1}	N/A	N/A
k_{-1}	23.394	$L\ mol^{-1}\ s^{-1}$	17.454	29.334
k_2	7.1909	$L\ mol^{-1}\ s^{-1}$	6.6659	7.716
k_{-2}	0.039433	$L\ mol^{-1}\ s^{-1}$	0.027986	0.050879
k_3	0.46066	$L\ mol^{-1}\ s^{-1}$	-0.040161	0.96147



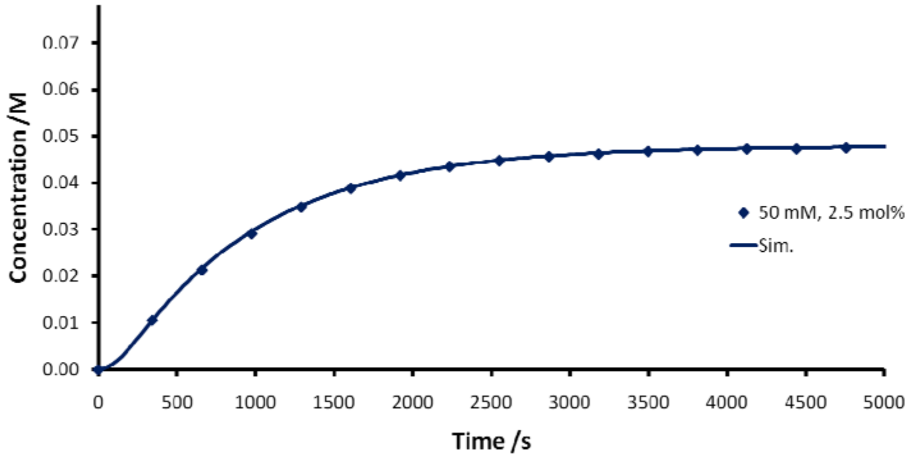
ii. *Entry 2 in TABLE 5; DATASET 7 in TABLE 2*

Rate Constant	Value	Units	Confidence Interval (95%)	
k_1 (fixed)	1.4×10^{-4}	s^{-1}	N/A	N/A
k_{-1}	28.757	$L\ mol^{-1}\ s^{-1}$	17.238	40.276
k_2	13.923	$L\ mol^{-1}\ s^{-1}$	11.977	15.868
k_{-2}	0.2126	$L\ mol^{-1}\ s^{-1}$	0.13288	0.29232
k_3	1.4211×10^{-14}	$L\ mol^{-1}\ s^{-1}$	-9.5521×10^{-13}	9.8364×10^{-13}



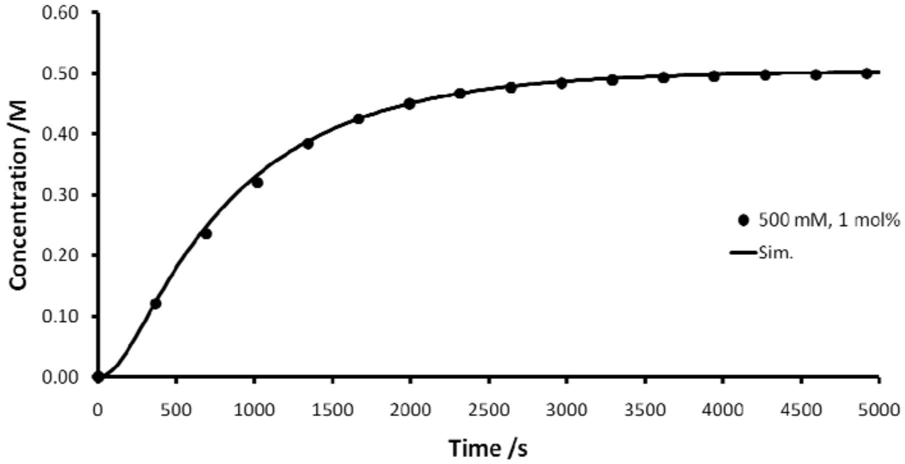
iii. *ENTRY 3 in TABLE 5; DATASET 12 in TABLE 2*

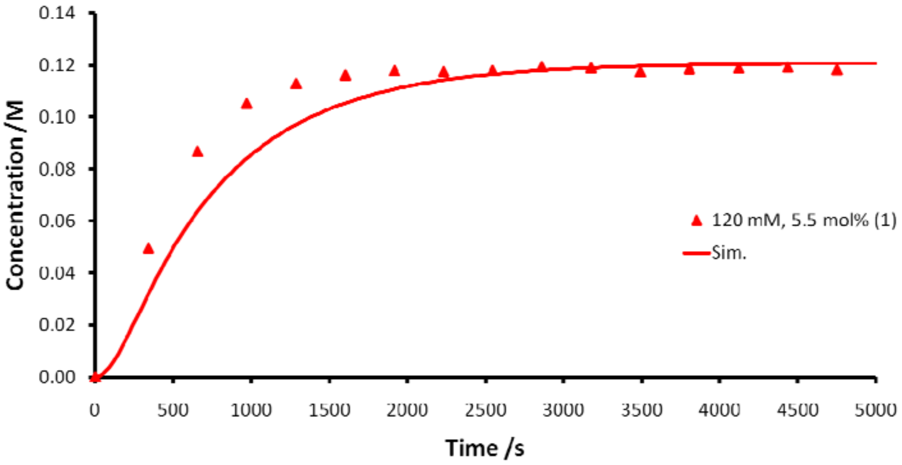
Rate Constant	Value	Units	Confidence Interval (95%)	
k_1 (fixed)	1.4×10^{-4}	s^{-1}	N/A	N/A
k_{-1}	165.99	$L\ mol^{-1}\ s^{-1}$	105.36	226.63
k_2	35.943	$L\ mol^{-1}\ s^{-1}$	30.835	41.051
k_{-2}	0.19547	$L\ mol^{-1}\ s^{-1}$	0.07773	0.31322
k_3	0.030765	$L\ mol^{-1}\ s^{-1}$	-2.3455	2.4071



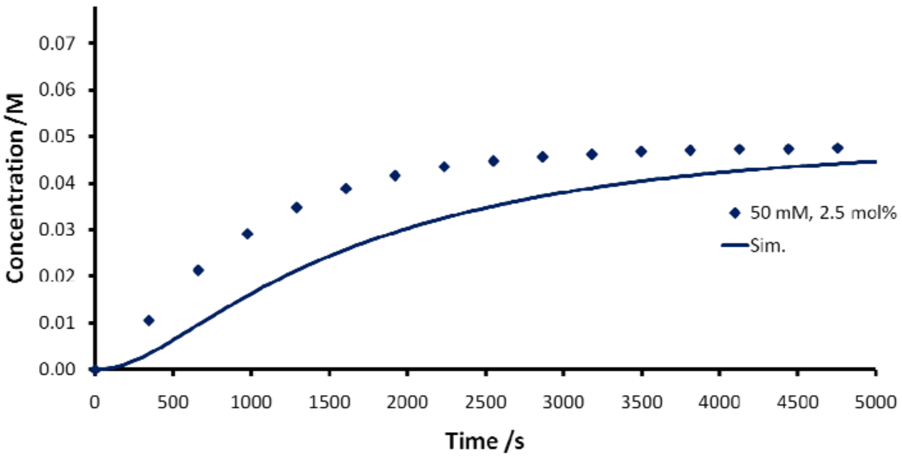
iv. *ENTRY 4 in TABLE 5; DATASETS 3, 7, 12 in TABLE 2*

Rate Constant	Value	Units	Confidence Interval (95%)	
k_1 (fixed)	1.4×10^{-4}	s^{-1}	N/A	N/A
k_{-1}	27.356	$L\ mol^{-1}\ s^{-1}$	12.877	41.835
k_2	7.9923	$L\ mol^{-1}\ s^{-1}$	6.6966	9.288
k_{-2}	0.045229	$L\ mol^{-1}\ s^{-1}$	0.018126	0.072332
k_3	0.62067	$L\ mol^{-1}\ s^{-1}$	-0.42827	1.6696





0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
Concentration /M
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
Time /s
120 mM, 5.5 mol% (1)
Sim.



0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
Concentration /M
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
Time /s
50 mM, 2.5 mol%
Sim.

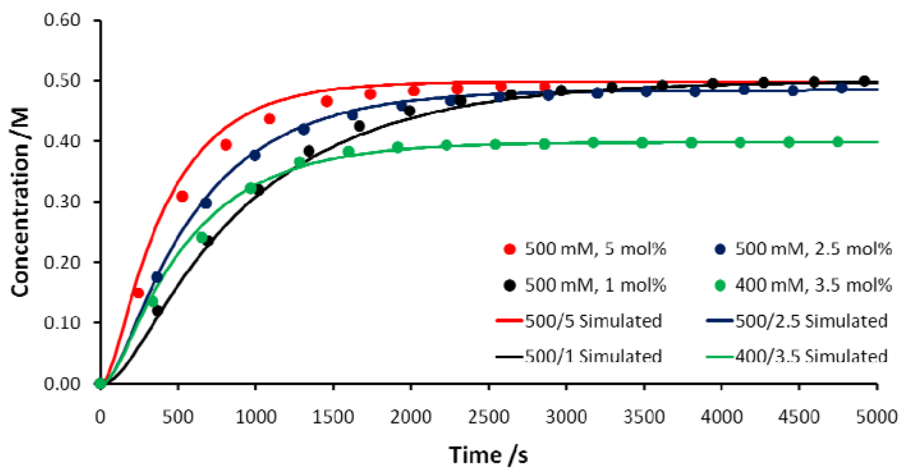
G. PRE-CATALYST CONCENTRATION SIMULATIONS

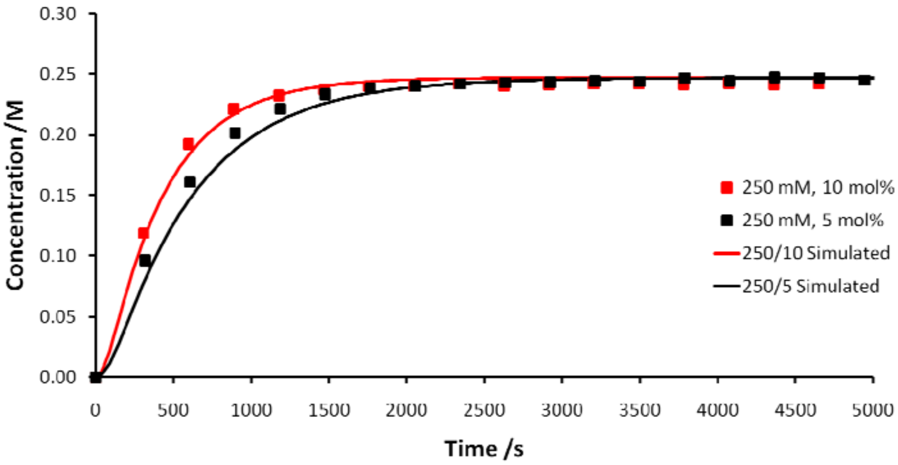
Initial	**Time**	**Measured**		**Constants from TABLE 4**		**Constants from Adjiman and Taylor**	
[1] /M		**[1] /M**	**%left**	**[1] /M**	**%left**	**[1] /M**	**%left**
0.02568	2017	0.0178	69.4%	0.02533	98.6%	0.00309	12.0%
0.02591	2047	0.0180	69.4%	0.02557	98.7%	0.00314	12.1%
0.01272	2055	0.0081	63.8%	0.01248	98.1%	0.00085	6.7%
0.00518	1992	0.0045	86.6%	0.00503	97.0%	0.00015	3.0%
0.01201	1939	0.0090	75.0%	0.01178	98.0%	0.00076	6.4%
0.00674	1917	0.0040	60.0%	0.00656	97.4%	0.00025	3.8%
0.00674	1914	0.0047	69.8%	0.00656	97.4%	0.00025	3.8%
0.00507	1903	0.0037	72.5%	0.00491	97.0%	0.00015	2.9%
0.00121	1921	0.0009	70.2%	0.00114	94.0%	0.00001	0.7%
0.01437	1913	0.0108	75.1%	0.01411	98.2%	0.00107	7.4%
0.00121	1919	0.0009	71.3%	0.00114	94.0%	0.00001	0.7%
0.00660	2002	0.0050	75.7%	0.00672	101.9%	0.00027	4.0%
0.02568	2017	0.0178	69.4%	0.02533	98.6%	0.00309	12.0%

H. FITTING BATCHES OF DATA ACROSS NARROWER [**7**] RANGES

i. 250 to 500 mM **7**

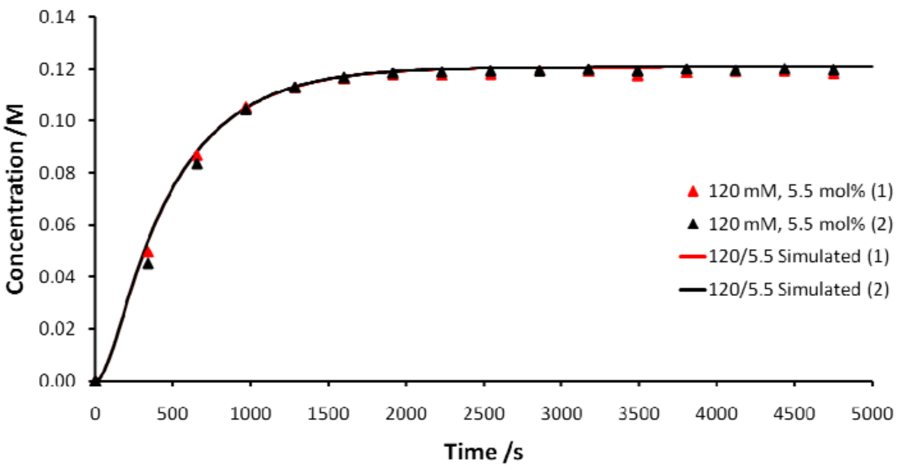
Rate Constant	**Value**	**Units**
k_1 (fixed)	1.4×10^{-4}	s^{-1}
k_{-1}	26.5567	L mol^{-1} s^{-1}
k_2	6.90318	L mol^{-1} s^{-1}
k_{-2}	0.103154	L mol^{-1} s^{-1}
k_3 (fixed)	0	L mol^{-1} s^{-1}

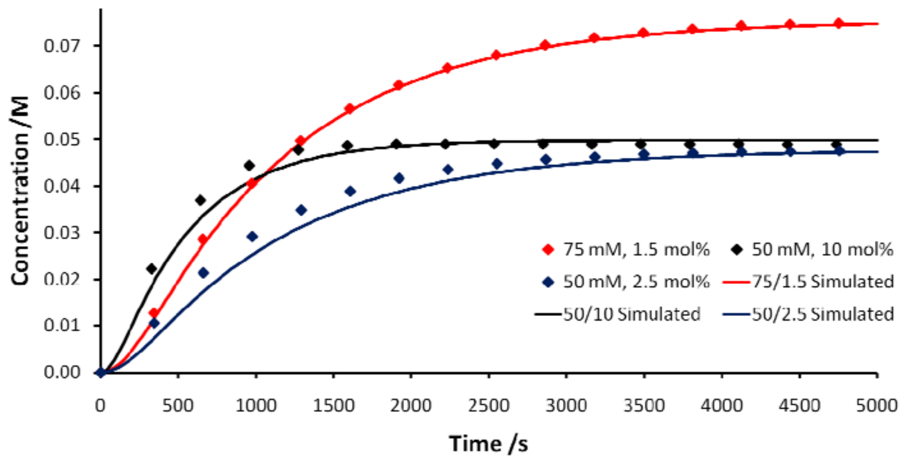




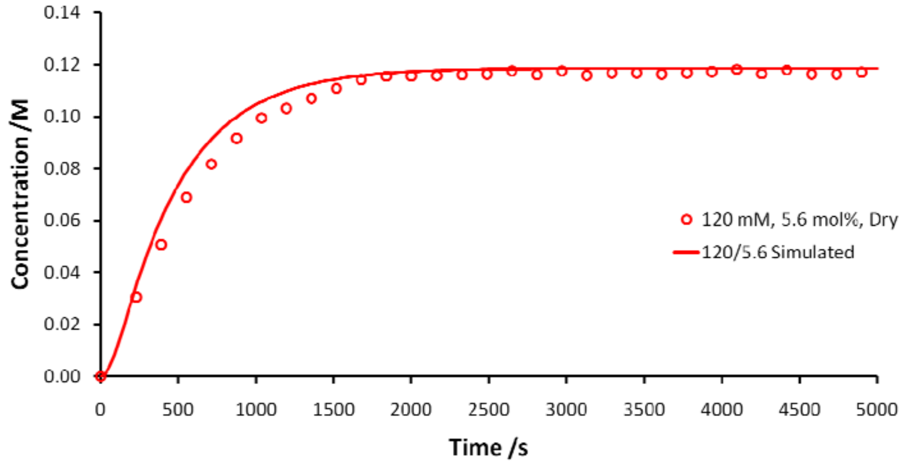
ii. 50 to 120 mM **7**

Rate Constant	**Value**	**Units**
k_1 (fixed)	1.4×10^{-4}	s^{-1}
k_{-1}	71.1433	$L\ mol^{-1}\ s^{-1}$
k_2	20.0102	$L\ mol^{-1}\ s^{-1}$
k_{-2}	0.164878	$L\ mol^{-1}\ s^{-1}$
k_3 (fixed)	0	$L\ mol^{-1}\ s^{-1}$





Concentration /M
Time /s
75 mM, 1.5 mol%
50 mM, 10 mol%
50 mM, 2.5 mol%
75/1.5 Simulated
50/10 Simulated
50/2.5 Simulated



Concentration /M
Time /s
120 mM, 5.6 mol%, Dry
120/5.6 Simulated

I. FITTING KINETIC DATA FOR **7**/**11**/**13** SIMULTANEOUSLY

	Rate Constant	**Value**	**Units**	**k_{rel}**
	k_1 (fixed)	1.4×10^{-4}	s^{-1}	
	k_{-1}	2733.45	L mol^{-1} s^{-1}	
	k_3 (fixed)	0	L mol^{-1} s^{-1}	
Heptadiene	k_2	358.886	L mol^{-1} s^{-1}	0.589
	k_{-2}	11.559	L mol^{-1} s^{-1}	
Octadiene	k_2	610.208	L mol^{-1} s^{-1}	1
	k_{-2}	3.32059	L mol^{-1} s^{-1}	
Diethyl Diallylmalonate	k_2	165.578	L mol^{-1} s^{-1}	0.272
	k_{-2}	13.1433	L mol^{-1} s^{-1}	

J. FITTING **11**/**13** RCM DATA IN CHLOROFORM-*d*

i. FITTING DATA FOR **11**, **13** AND MIXTURES OF **11** AND **13** WITH **1** (*TABLE 8, ENTRY 1*)

	Rate Constant	Value	Units
	k_1 (fixed)	4.5 x 10^{-5}	s^{-1}
	k_{-1}	983.638	L mol^{-1} s^{-1}
	k_3 (fixed)	0	L mol^{-1} s^{-1}
Heptadiene	k_2	223.501	L mol^{-1} s^{-1}
	k_{-2}	1.44169 x 10^{-6}	L mol^{-1} s^{-1}
Octadiene	k_2	405.238	L mol^{-1} s^{-1}
	k_{-2}	8.27762	L mol^{-1} s^{-1}

ii. FITTING DATA FOR 5 mM/5 mM MIXTURES OF **11** AND **13** WITH **1** OR **2** (*TABLE 8, ENTRY 2*) TREATING THE INITIATION MECHANISM OF **2** AS DISSOCIATIVE

	Rate Constant	Value	Units
Grubbs II **1**	k_1 (fixed)	4.5 x 10^{-5}	s^{-1}
	k_{-1}	789.142	L mol^{-1} s^{-1}
Grubbs-Hoveyda II **2**	k_1	8.88943 x 10^{-5}	s^{-1} (See text)
	k_3 (fixed)	0	L mol^{-1} s^{-1}
Heptadiene	k_2	199.777	L mol^{-1} s^{-1}
	k_{-2}	0.0510947	L mol^{-1} s^{-1}
Octadiene	k_2	426.357	L mol^{-1} s^{-1}
	k_{-2}	0.0136101	L mol^{-1} s^{-1}

iii. FITTING DATA FOR 5 mM/ 5 mM MIXTURES OF **11** AND **13** WITH **1** OR **2** (*TABLE 8, ENTRY 3*) TREATING THE INITIATION MECHANISM OF **2** AS INTERCHANGE

	Rate Constant	Value	Units
Grubbs II **1**	k_1 (fixed)	4.5 x 10^{-5}	s^{-1}
	k_{-1}	22.6705	L mol^{-1} s^{-1}
Grubbs-Hoveyda II **2**	k_1 (fixed)	0.0234	L mol^{-1} s^{-1}
	k_3 (fixed)	0	L mol^{-1} s^{-1}
Heptadiene	k_2	83.6314	L mol^{-1} s^{-1}
	k_{-2}	6.68835	L mol^{-1} s^{-1}
Octadiene	k_2	252.384	L mol^{-1} s^{-1}
	k_{-2}	6.00645	L mol^{-1} s^{-1}

K. COMPARISON OF MICROMATH SCIENTIST AND BERKELEY MADONNA

In order to assess potential differences in fitting approach between the two software packages, the same dataset was treated in each package in the same way, and the resulting fits were compared. Concentration/time data for the RCM of **7** with pre-catalyst **1** (120 mM **7**, 5.6 mol% **1**, dataset 7 in **Table 2** of the manuscript) was imported and fitted to the model in **Scheme 2**. The two packages generated almost identical simulated profiles and rate constants.

Software	**k_{-1}**	**k_2**	**k_{-2}**
Micromath Scientist	29.6651	14.0673	0.193955
Berkeley Madonna	28.738	13.919	0.20937