Supporting Information for "On the relationship between structure and reaction rate in olefin ring-closing metathesis"

Ashworth, Carboni, Hillier, Nelson, Percy, Rinaudo and Vincent

Contents

T_1 Values for Dienes and Cycloalkenes

Compound	δ_H ($CDCl_3$)	T_1	δ_H ($CDCl_3$)	T_1	δ_H ($CDCl_3$)	T_1	δ_H ($CDCl_3$)	T_1
Octadiene	5.82 ppm	5.94 s	4.97 ppm	5.08 s	2.06 ppm	3.73 s	1.41 ppm	3.49 s
Cyclopentene	5.76 ppm	6.93 s	2.33 ppm	5.42 s	1.84 ppm	5.46 s	-	-
Cyclohexene	5.75 ppm	6.84 s	2.00 ppm	4.89 s	1.62 ppm	5.00 s	-	-
Cycloheptene	5.81 ppm	6.54 s	2.14 ppm	4.82 s	1.74 ppm	4.50 s	1.52 ppm	4.66 s
Cyclooctene	5.64 ppm	6.05 s	2.16 ppm	4.16 s	1.51 ppm	4.08 s	-	-

Octadiene is representative of all diene substrates; olefinic protons exhibited the highest T_1 values in each molecule. D_1 = 35 s was selected, being the longest T_1 x 5.

Procedure for Kinetic Experiments

Grubbs' second generation pre-catalyst **9** and 1,3,5-trimethoxybenzene were purchased from Sigma Aldrich and used as supplied. The pre-catalyst was handled under a flow of dry oxygen-free nitrogen at all times. Deuterated chloroform and dichloromethane were purchased from Sigma Aldrich and Goss Scientific respectively; solvents were dried over activated 4 Å molecular sieves for at least 12 h before use. Karl-Fischer analysis confirmed that water content in both solvents was < 10 ppm.

The use of disposable plastic syringes was avoided to prevent contamination of the chlorinated solvents with plasticisers that might interfere with the metathesis catalyst.

A clean and dry volumetric flask was flushed with nitrogen and charged with an appropriate mass of 1,3,5-trimethoxybenzene and an appropriate mass of diene. The flask was made up to volume with dry solvent under a gentle nitrogen flow. This concentrated stock solution(s) (typically approx. 100 mM total diene concentration) was then diluted to an appropriate concentration in a second volumetric flask, using a clean and dry gastight syringe. The flask was made up to volume using dry solvent. This solution (typically 10 mM total diene concentration) was used as a stock solution.

A clean, oven-dried NMR tube was flushed with nitrogen using a balloon. The 10 mM stock solution (600 μL) was added and the tube capped. The tube was inserted into the magnet and the instrument internal temperature was set to 298K and allowed to equilibrate. NMR analysis was carried out before pre-catalyst addition to confirm that the solution did not contain acetone (δ_H = 2.2 ppm) or water (broad peak at δ_H = 1.5 ppm) and that it contained the correct concentration of diene with respect to the internal standard.

A dry volumetric flask was flushed with nitrogen and charged with an appropriate mass of Grubbs' second generation pre-catalyst **9** and stored in a bag filled with nitrogen. The flask was made up to volume using dry solvent approximately 5 minutes before charging the solution to the NMR tube.

This catalyst solution was charged to the NMR tube *via* a dry glass syringe and the time noted. The tube was shaken vigorously for approx. 15 seconds before the cap was exchanged for a pierced cap.

The sample was then analysed at appropriate intervals using a Brüker Topspin automated script, *multi_zgvd2b*. Samples were automatically shimmed using *topshim 1dfast* between acquisitions.

NMR spectra were acquired on a Brüker AV400 instrument fitted with BBFO-z-ATMA probe or a Brüker AV600 instrument fitted with a TBI-z or BBO-z-ATMA probe; both instruments are fitted with temperature control units. Settings for spectra acquisition were as follows: NS = 4 scans; D1 = 35 s; SW = 24 ppm and O1P = 10 ppm. The sample was held at 298 K for the duration of the experiment.

Kinetic Data

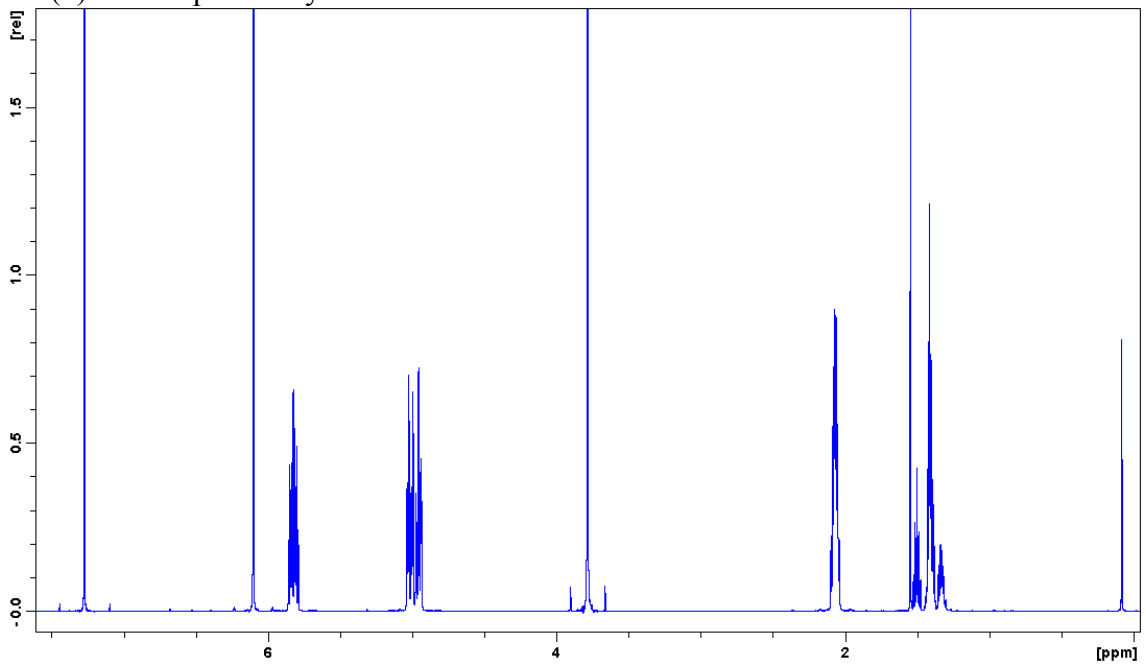
Ternary Competition RCM in Chloroform

3.3 mM heptadiene **7b**, 3.4 mM octadiene **7c**, 3.5 mM nonadiene **7d**, 0.1 mM pre-catalyst **9**

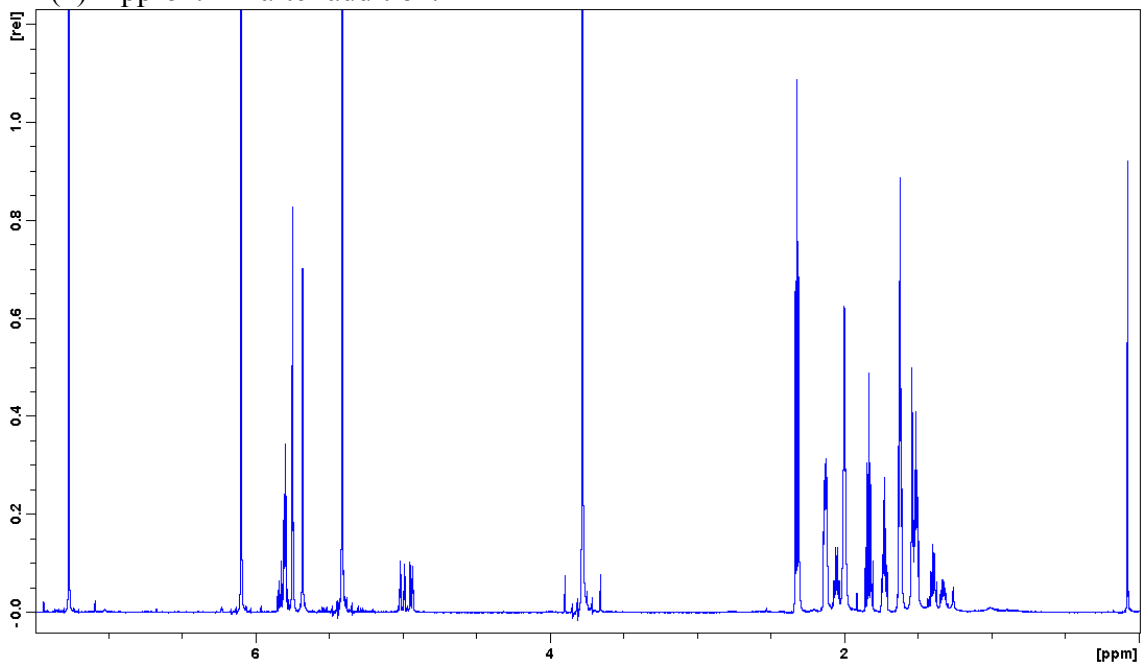
Analysis was by ^{1}H NMR at 600 MHz using a Bruker AV600 equipped with TBI-z probe; the temperature was maintained at 298 K throughout.

Sample spectra:

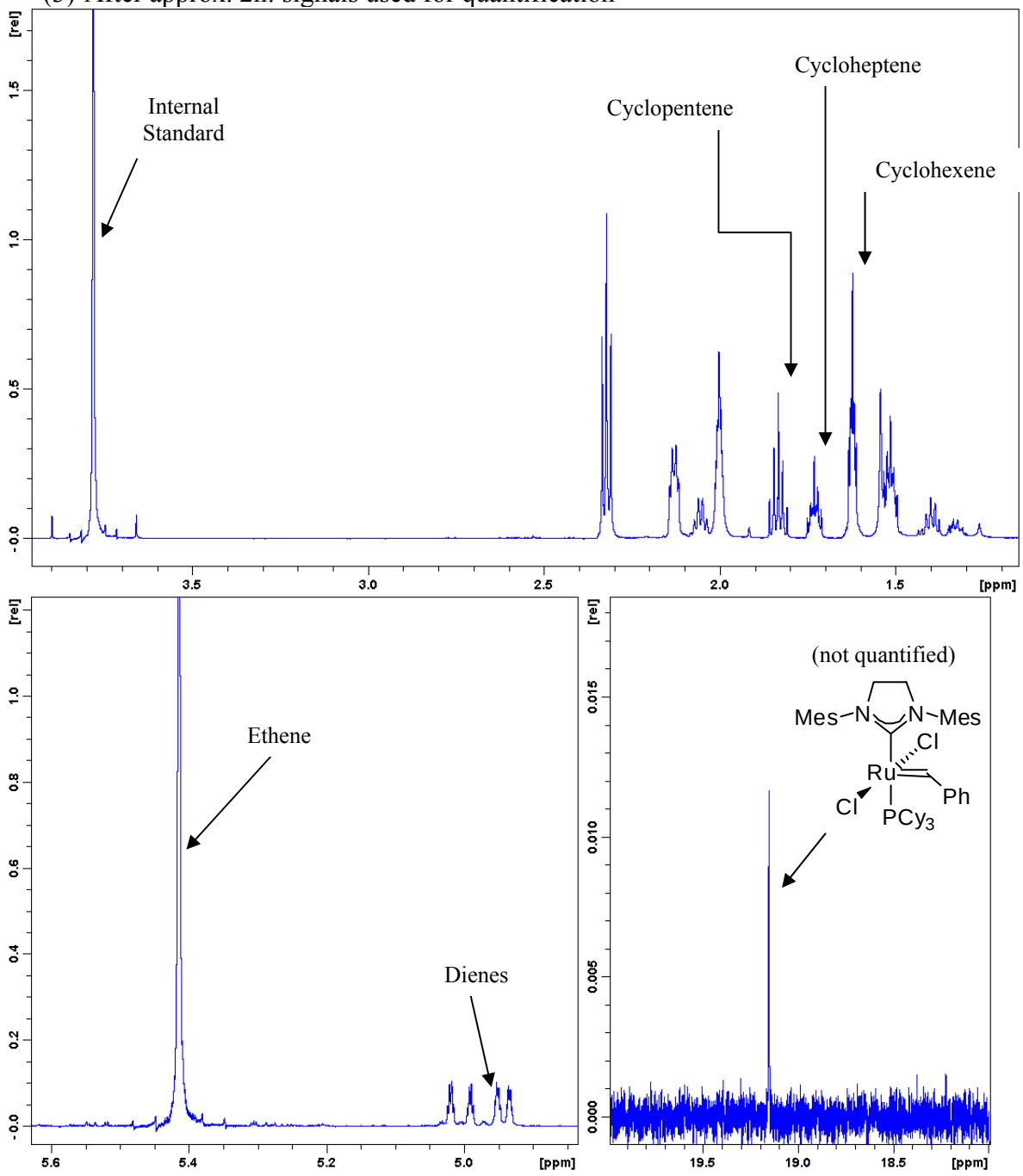
(1) Before pre-catalyst addition.



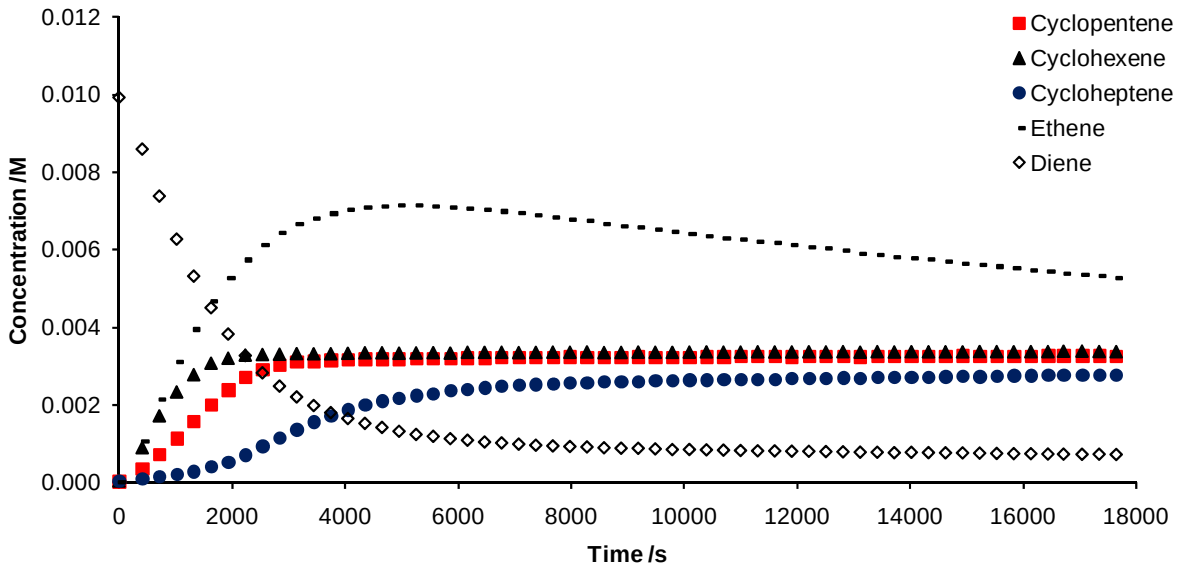
(2) Approx. 2 h after addition.

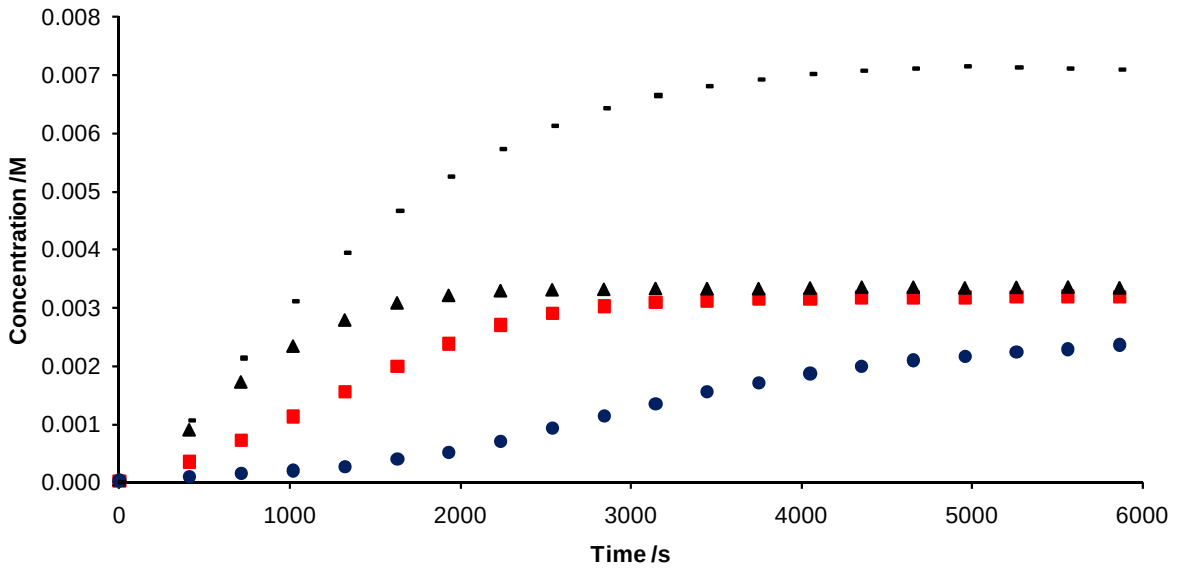


(3) After approx. 2h: signals used for quantification



*Concentration/time data for the RCM of heptadiene **7b**, octadiene **7c**, nonadiene **7d** with pre-catalyst **9** in $CDCl_3$ at 298 K (AV600, TBI-z probe); 4 scans with D_1 = 35 s; TE = 298 K; concentrations obtained by integration of the appropriate signal and the internal standard (see above).*





t (s)	Diene (M)	Ethene (M)	Cyclopentene (M)	Cyclohexene (M)	Cycloheptene (M)
0	0.009938	0.000007	0.000024	0.000043	0.000031
411	0.008604	0.001065	0.000359	0.000900	0.000095
714	0.007390	0.002138	0.000723	0.001720	0.000155
1020	0.006279	0.003106	0.001135	0.002336	0.000202
1323	0.005323	0.003947	0.001566	0.002784	0.000277
1630	0.004506	0.004668	0.001995	0.003078	0.000400
1932	0.003827	0.005258	0.002386	0.003207	0.000523
2236	0.003271	0.005739	0.002704	0.003288	0.000705
2539	0.002826	0.006132	0.002909	0.003303	0.000928
2842	0.002483	0.006425	0.003030	0.003311	0.001145
3145	0.002204	0.006651	0.003098	0.003326	0.001357
3447	0.001981	0.006816	0.003126	0.003322	0.001554
3749	0.001798	0.006934	0.003150	0.003323	0.001716
4051	0.001646	0.007024	0.003157	0.003334	0.001870
4354	0.001520	0.007084	0.003182	0.003347	0.001990
4656	0.001417	0.007120	0.003179	0.003348	0.002098
4958	0.001316	0.007145	0.003180	0.003337	0.002170
5260	0.001234	0.007134	0.003189	0.003344	0.002237
5563	0.001186	0.007115	0.003199	0.003351	0.002292
5865	0.001125	0.007093	0.003196	0.003338	0.002366
6170	0.001085	0.007062	0.003207	0.003361	0.002398
6472	0.001039	0.007021	0.003209	0.003358	0.002444
6774	0.001016	0.006990	0.003215	0.003361	0.002480
7077	0.000984	0.006939	0.003214	0.003352	0.002504
7379	0.000957	0.006891	0.003214	0.003359	0.002527
7681	0.000939	0.006837	0.003226	0.003365	0.002535
7983	0.000922	0.006781	0.003232	0.003362	0.002563
8285	0.000911	0.006736	0.003224	0.003369	0.002574
8587	0.000890	0.006674	0.003219	0.003353	0.002591
8890	0.000879	0.006613	0.003227	0.003358	0.002598
9192	0.000877	0.006570	0.003237	0.003366	0.002598
9494	0.000862	0.006511	0.003231	0.003360	0.002617
9796	0.000844	0.006460	0.003226	0.003359	0.002631
10098	0.000846	0.006412	0.003226	0.003365	0.002635
10400	0.000837	0.006363	0.003238	0.003371	0.002637
10702	0.000829	0.006306	0.003238	0.003365	0.002656
11004	0.000819	0.006263	0.003244	0.003366	0.002659
11307	0.000812	0.006201	0.003240	0.003374	0.002658
11609	0.000809	0.006168	0.003242	0.003368	0.002660
11911	0.000802	0.006117	0.003238	0.003368	0.002673
12213	0.000799	0.006077	0.003246	0.003373	0.002675
12515	0.000792	0.006025	0.003243	0.003370	0.002686
12818	0.000786	0.005972	0.003252	0.003376	0.002693
13122	0.000776	0.005908	0.003239	0.003363	0.002688

13424	0.000774	0.005864	0.003244	0.003376	0.002705
13726	0.000763	0.005817	0.003247	0.003369	0.002718
14028	0.000773	0.005787	0.003256	0.003375	0.002715
14331	0.000765	0.005747	0.003251	0.003375	0.002715
14633	0.000760	0.005699	0.003260	0.003374	0.002728
14935	0.000758	0.005652	0.003263	0.003371	0.002730
15237	0.000752	0.005603	0.003257	0.003380	0.002723
15539	0.000744	0.005567	0.003259	0.003378	0.002741
15841	0.000739	0.005519	0.003255	0.003372	0.002750
16144	0.000737	0.005479	0.003258	0.003376	0.002757
16446	0.000729	0.005430	0.003262	0.003378	0.002759
16722	0.000726	0.005391	0.003264	0.003388	0.002759
17050	0.000722	0.005343	0.003261	0.003391	0.002762
17353	0.000724	0.005314	0.003261	0.003380	0.002763
17655	0.000716	0.005273	0.003251	0.003377	0.002774

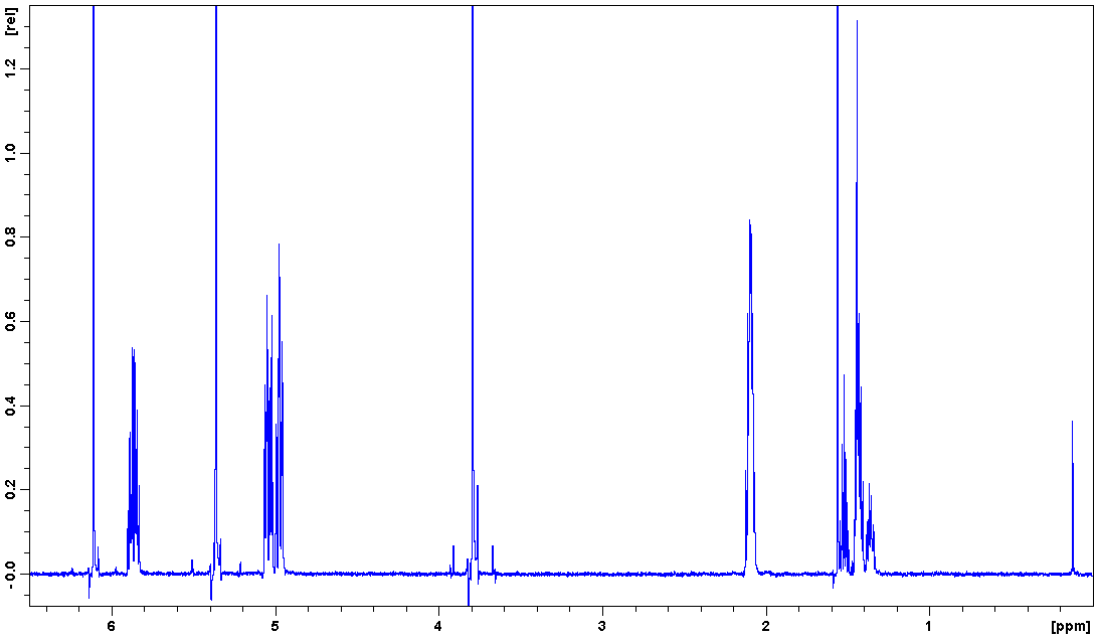
Ternary Competition RCM in Dichloromethane

3.4 mM heptadiene **7b**, 3.4 mM octadiene **7c**, 3.5 mM nonadiene **7d**, 0.1 mM pre-catalyst **9**

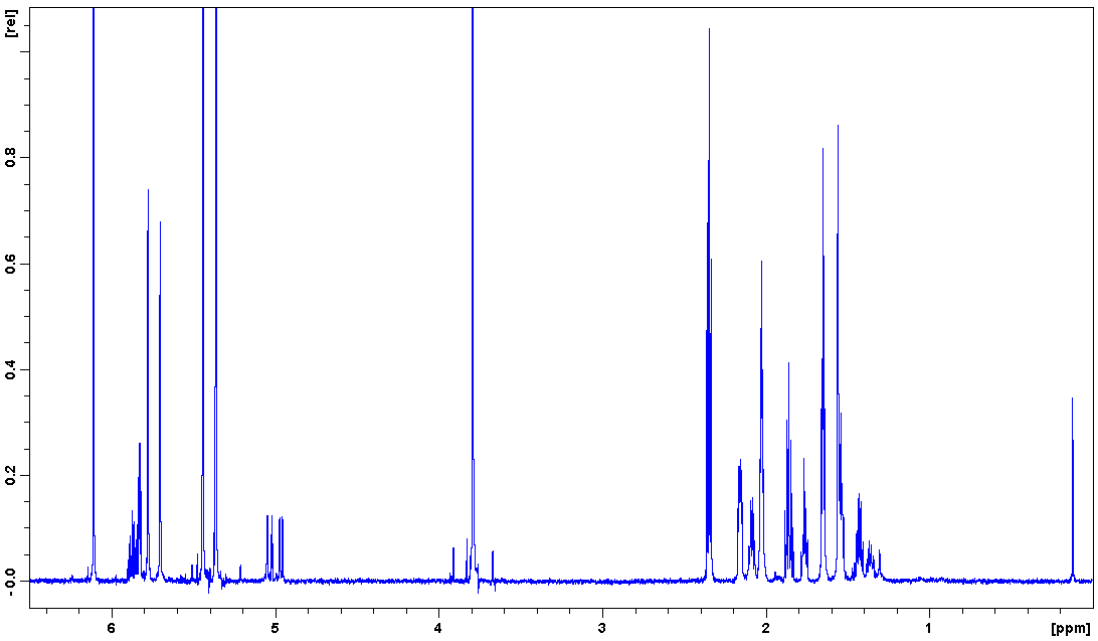
Analysis was by ^{1}H NMR at 600 MHz using a Bruker AV600 equipped with BBO-z-ATMA probe; the temperature was maintained at 298 K throughout.

Sample spectra:

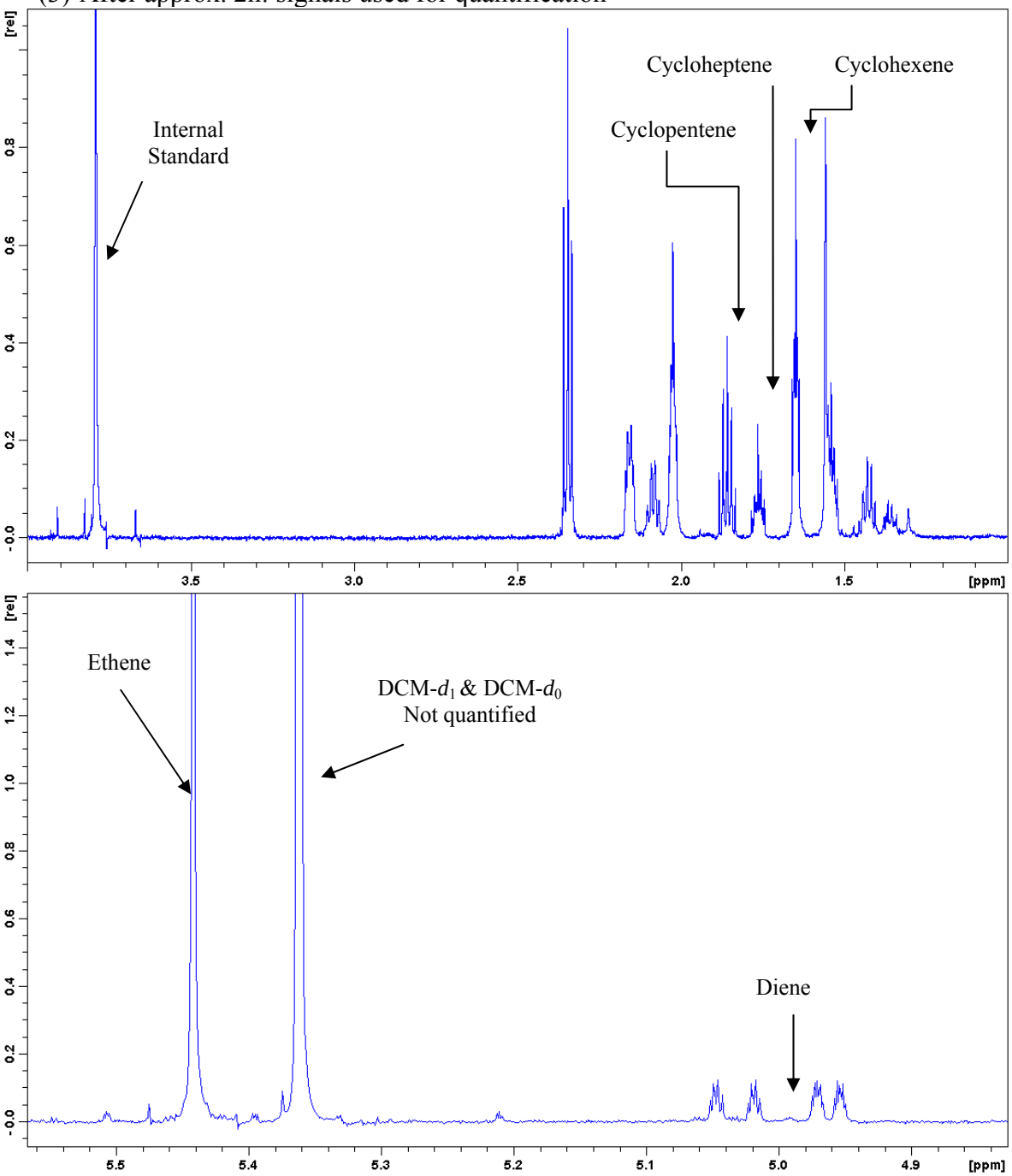
(1) Before pre-catalyst addition.



(2) Approx 2 h after addition.

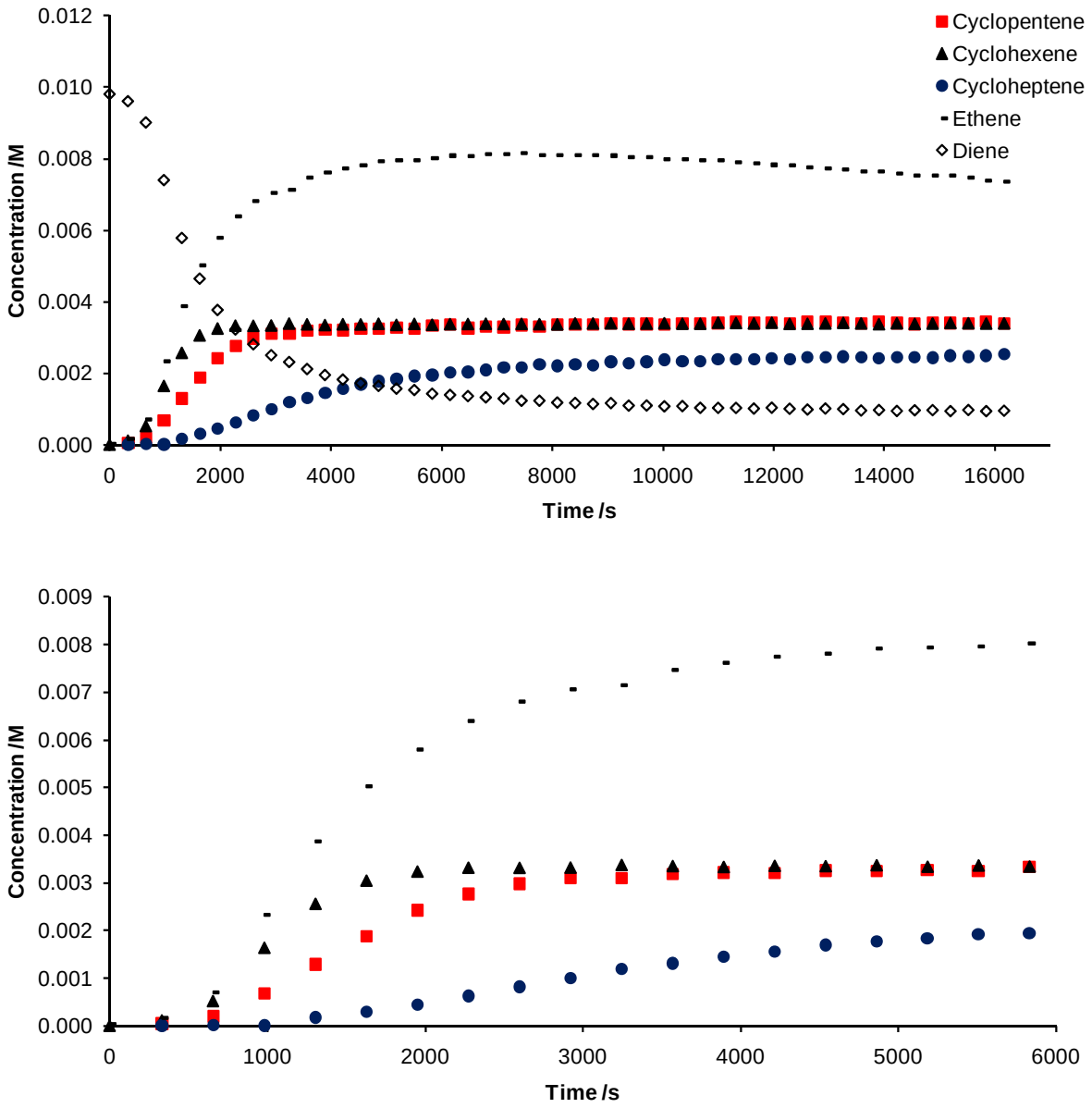


(3) After approx. 2h: signals used for quantification



*Pre-catalyst **9** cannot be detected due to the lower sensitivity of the BBO-z-ATMA probe.*

*Concentration/time data for the RCM of heptadiene **7b**, octadiene **7c**, nonadiene **7d** with pre-catalyst **9** in CD_2Cl_2 at 298 K (AV600, BBO-z-ATMA probe); 4 scans with D_1 = 35 s; TE = 298 K; concentrations obtained by integration of the appropriate signal and the internal standard (see above).*



t (s)	Diene (M)	Ethene (M)	Cyclopentene (M)	Cyclohexene (M)	Cycloheptene (M)
0	0.009822	0.000030	-0.000030	0.000004	-0.000001
331	0.009621	0.000178	0.000052	0.000117	0.000010
655	0.009025	0.000707	0.000199	0.000524	0.000017
981	0.007410	0.002327	0.000680	0.001642	0.000009
1305	0.005787	0.003878	0.001294	0.002563	0.000177
1628	0.004646	0.005017	0.001880	0.003049	0.000305
1951	0.003768	0.005793	0.002427	0.003240	0.000445
2274	0.003222	0.006396	0.002769	0.003320	0.000629
2598	0.002806	0.006806	0.002982	0.003316	0.000824
2921	0.002499	0.007052	0.003100	0.003323	0.000998
3245	0.002309	0.007137	0.003106	0.003378	0.001196
3569	0.002112	0.007471	0.003189	0.003355	0.001312
3892	0.001945	0.007609	0.003217	0.003335	0.001454
4215	0.001817	0.007734	0.003204	0.003359	0.001563
4538	0.001717	0.007807	0.003259	0.003353	0.001697
4861	0.001639	0.007923	0.003248	0.003372	0.001779
5184	0.001562	0.007944	0.003274	0.003341	0.001837
5507	0.001524	0.007955	0.003256	0.003368	0.001928
5830	0.001420	0.008012	0.003331	0.003344	0.001951
6153	0.001385	0.008085	0.003357	0.003363	0.002026
6476	0.001353	0.008079	0.003261	0.003365	0.002037
6799	0.001317	0.008132	0.003310	0.003374	0.002096
7122	0.001284	0.008130	0.003291	0.003364	0.002159
7445	0.001223	0.008156	0.003346	0.003370	0.002159
7768	0.001223	0.008107	0.003301	0.003360	0.002251
8091	0.001172	0.008105	0.003357	0.003355	0.002212
8414	0.001160	0.008090	0.003369	0.003381	0.002260
8737	0.001131	0.008088	0.003373	0.003382	0.002217
9060	0.001156	0.008086	0.003402	0.003386	0.002319
9382	0.001087	0.008035	0.003375	0.003373	0.002273
9706	0.001089	0.008052	0.003381	0.003377	0.002324
10026	0.001066	0.007990	0.003371	0.003388	0.002378
10352	0.001072	0.007984	0.003402	0.003373	0.002346
10675	0.001025	0.007969	0.003387	0.003375	0.002331
10998	0.001022	0.007970	0.003408	0.003404	0.002403
11321	0.001021	0.007913	0.003458	0.003394	0.002391
11644	0.001004	0.007865	0.003409	0.003382	0.002399
11967	0.001027	0.007829	0.003412	0.003401	0.002413
12290	0.000998	0.007813	0.003394	0.003369	0.002397
12613	0.000976	0.007766	0.003440	0.003373	0.002445
12936	0.001004	0.007736	0.003446	0.003383	0.002443
13259	0.000987	0.007707	0.003423	0.003397	0.002462
13582	0.000949	0.007650	0.003386	0.003382	0.002446
13905	0.000961	0.007632	0.003457	0.003362	0.002425

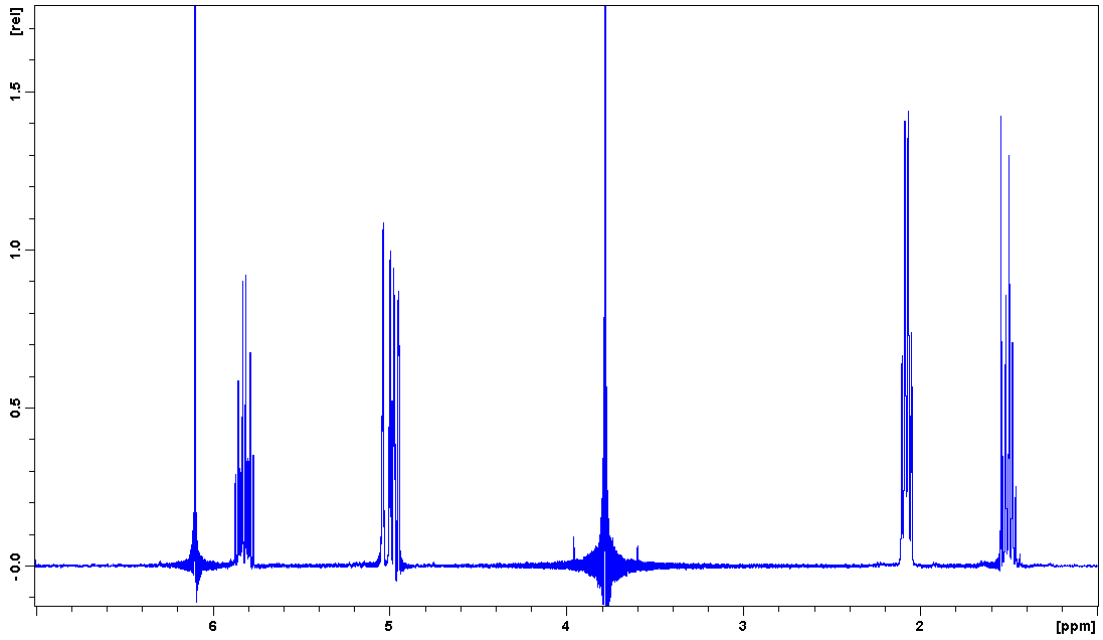
14228	0.000936	0.007581	0.003410	0.003385	0.002441
14551	0.000956	0.007518	0.003381	0.003371	0.002442
14874	0.000959	0.007525	0.003417	0.003379	0.002440
15197	0.000932	0.007540	0.003407	0.003396	0.002490
15520	0.000963	0.007467	0.003393	0.003388	0.002465
15843	0.000931	0.007394	0.003444	0.003379	0.002498
16166	0.000943	0.007355	0.003398	0.003383	0.002544

Heptadiene RCM in Chloroform

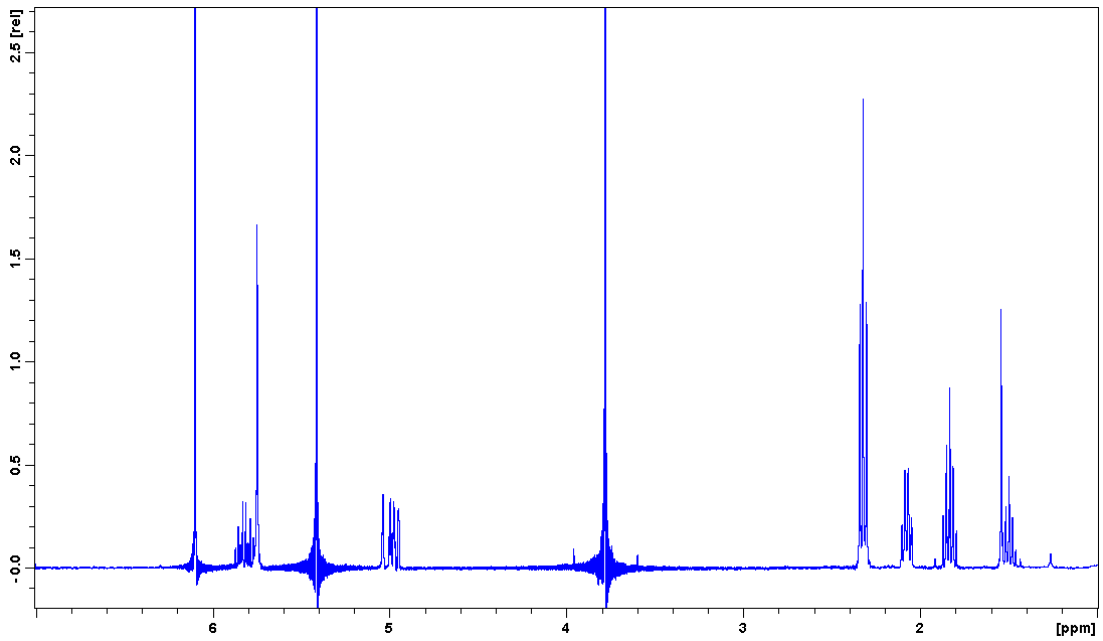
9.1 mM heptadiene **7b** (dataset 1) or 9.2 mM heptadiene **7b** (dataset 2); both with 0.1 mM pre-catalyst **9**. *Analysis was by ^{1}H NMR at 400 MHz using a Bruker AV400 equipped with BBFO-z-ATMA probe; the temperature was maintained at 298 K throughout.*

Sample Spectra

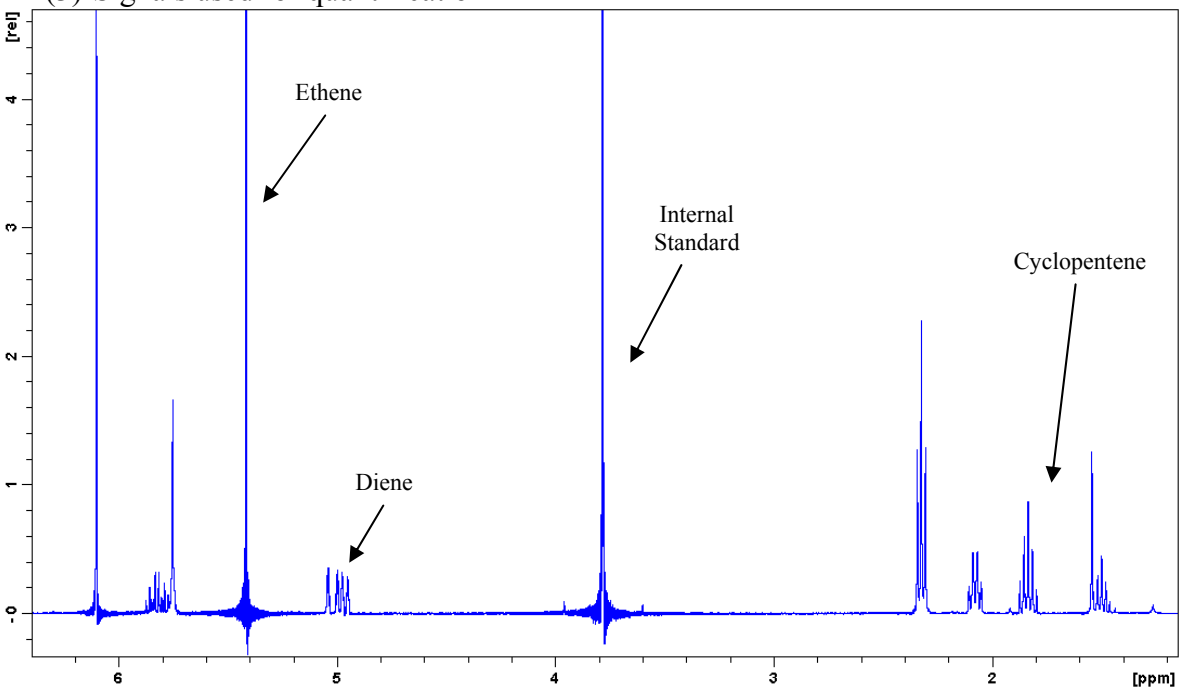
(1) Before pre-catalyst addition

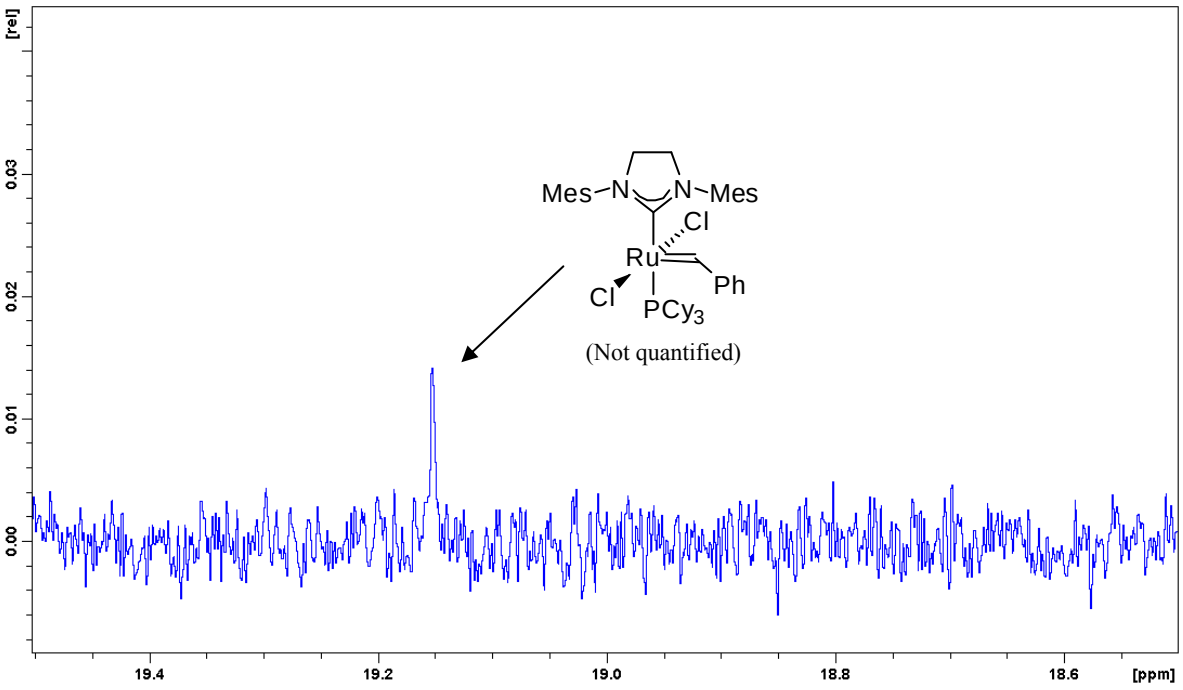


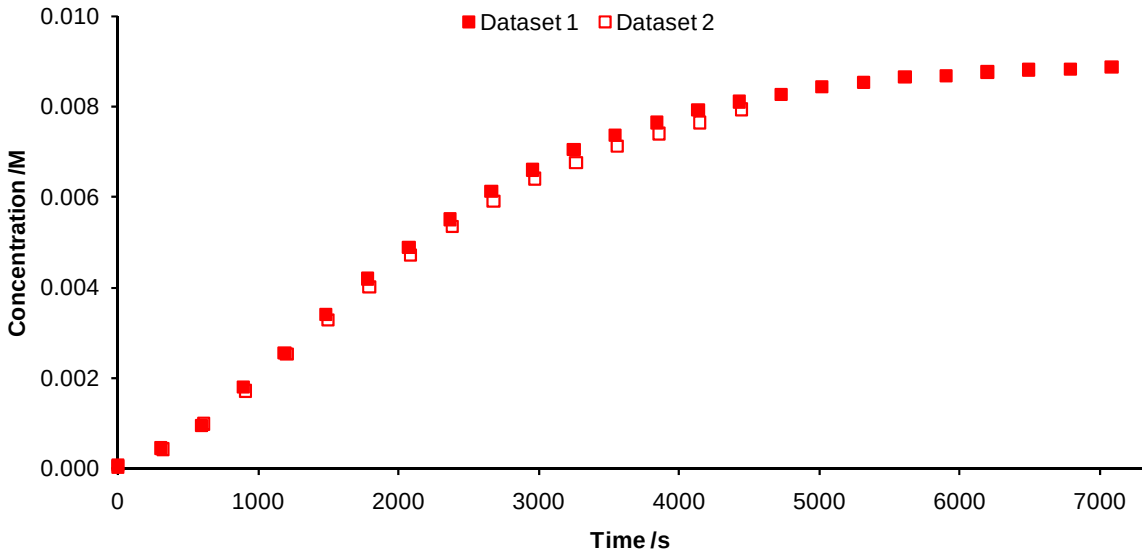
(2) Approx. 1 h after addition

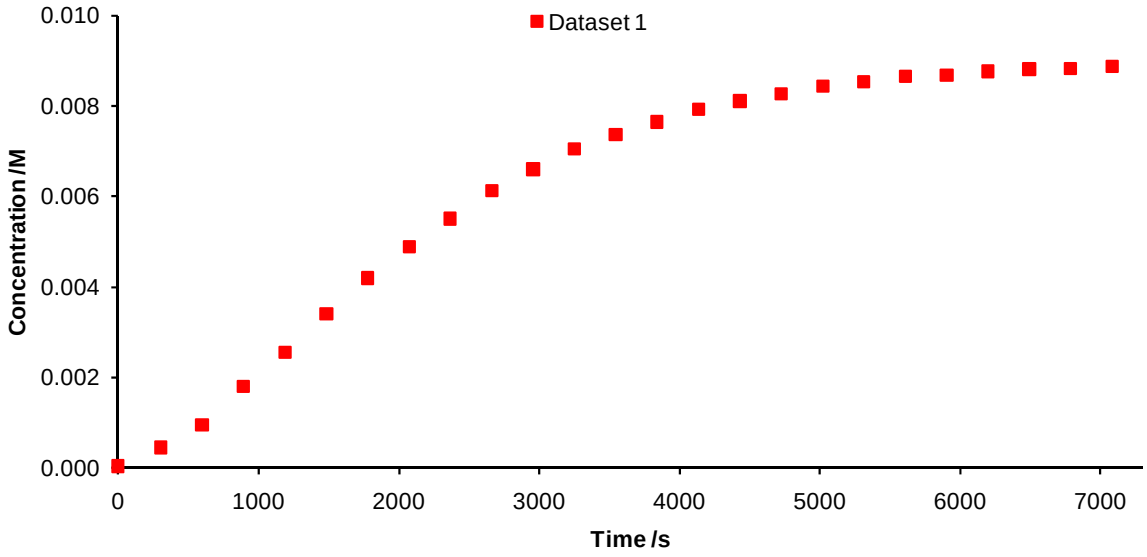


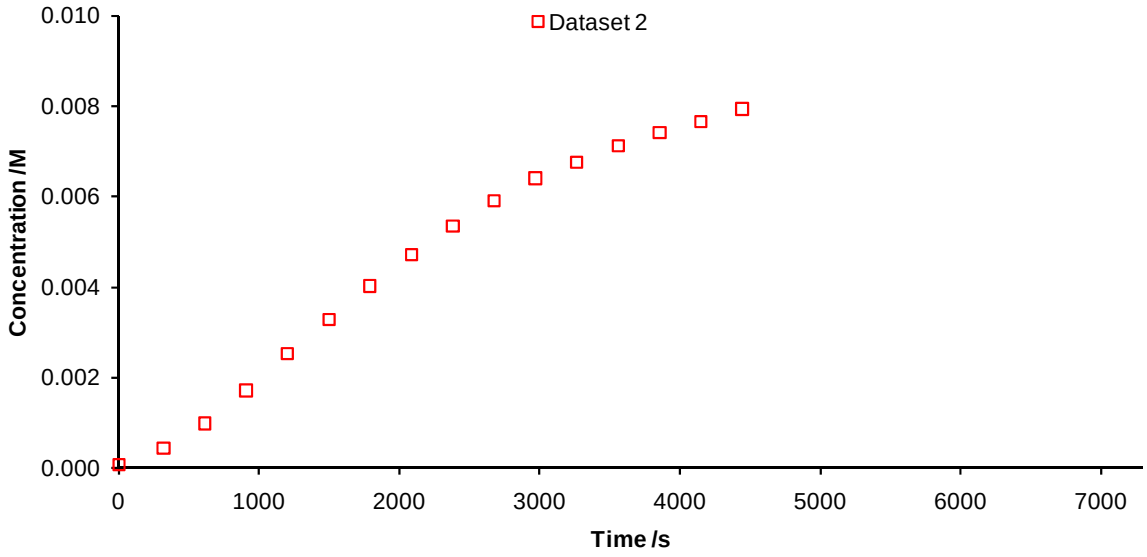
(3) Signals used for quantification






Dataset 1
Dataset 2
Concentration /M
0.010
0.008
0.006
0.004
0.002
0.000
0
1000
2000
3000
4000
5000
6000
7000
Time /s


Dataset 1
Concentration /M
0.010
0.008
0.006
0.004
0.002
0.000
0
1000
2000
3000
4000
5000
6000
7000
Time /s


Dataset 2
Concentration /M
0.010
0.008
0.006
0.004
0.002
0.000
0
1000
2000
3000
4000
5000
6000
7000
Time /s

*Concentration/time data for the RCM of heptadiene **7b** with pre-catalyst **9** in $CDCl_3$ at 298 K (AV400, BBFO-z-ATMA probe); 4 scans with D_1 = 35 s; TE = 298 K; concentrations obtained by integration of the appropriate signal and the internal standard (see above).*

Dataset 1

t (s)	Diene (M)	Cyclopentene (M)	Ethene (M)
0	0.009111	0.000044	0.000097
303	0.008802	0.000456	0.000347
598	0.008188	0.000954	0.000993
893	0.007422	0.001796	0.001724
1188	0.006596	0.002562	0.002525
1482	0.005776	0.003404	0.003314
1777	0.004943	0.004200	0.004011
2072	0.004247	0.004894	0.004727
2367	0.003573	0.005512	0.005337
2661	0.002989	0.006133	0.005857
2956	0.002442	0.006604	0.006273
3250	0.001987	0.007051	0.006676
3545	0.001680	0.007379	0.007035
3839	0.001382	0.007651	0.007310
4134	0.001181	0.007925	0.007547
4429	0.000946	0.008115	0.007703
4724	0.000757	0.008278	0.007845
5019	0.000624	0.008436	0.007928
5313	0.000545	0.008546	0.007992
5608	0.000375	0.008653	0.007993
5903	0.000344	0.008677	0.008031
6197	0.000216	0.008769	0.008000
6492	0.000201	0.008818	0.007996
6787	0.000295	0.008826	0.008074
7081	0.000179	0.008885	0.008030

*Concentration/time data for the RCM of heptadiene **7b** with pre-catalyst **9** in $CDCl_3$ at 298 K (AV400, BBFO-z-ATMA probe); 4 scans with D_1 = 35 s; TE = 298 K; concentrations obtained by integration of the appropriate signal and the internal standard (see above).*

Dataset 2

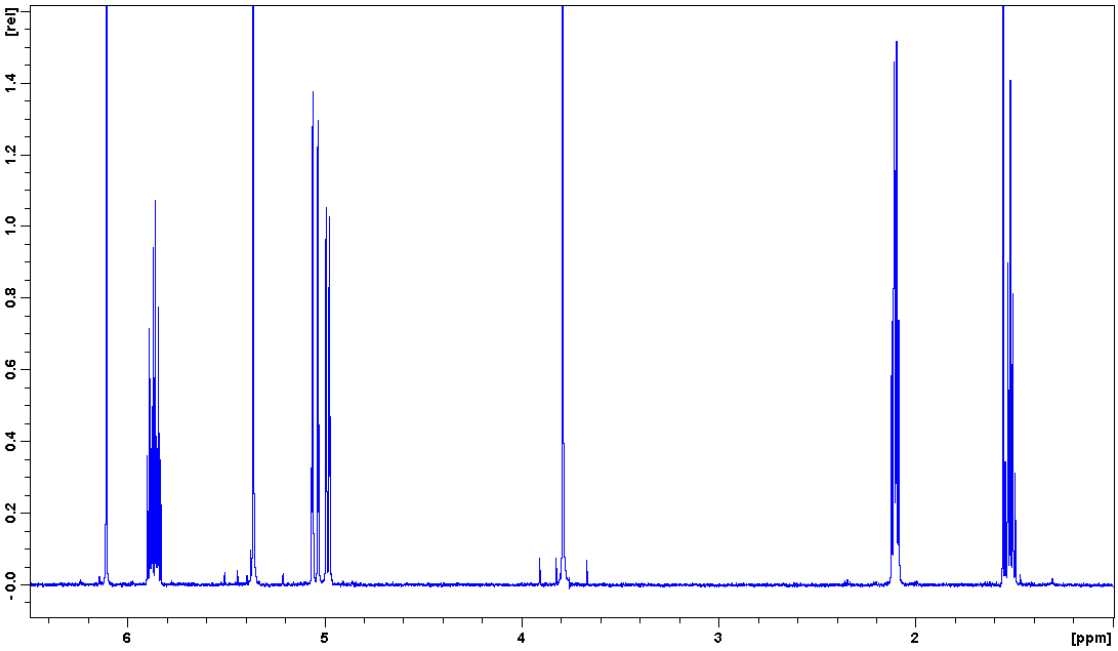
t (s)	Diene (M)	Cyclopentene (M)	Ethene (M)
0	0.009155	0.000071	0.000052
319	0.008723	0.000433	0.000377
613	0.008165	0.000988	0.000937
908	0.007425	0.001720	0.001669
1203	0.006601	0.002536	0.002402
1497	0.005805	0.003291	0.003159
1792	0.005028	0.004024	0.003831
2087	0.004333	0.004721	0.004521
2381	0.003701	0.005359	0.005074
2676	0.003162	0.005908	0.005604
2970	0.002631	0.006410	0.006011
3265	0.002230	0.006763	0.006402
3560	0.001904	0.007121	0.006724
3854	0.001594	0.007411	0.006978
4149	0.001357	0.007653	0.007203
4443	0.001092	0.007943	0.007333

Heptadiene RCM in Dichloromethane

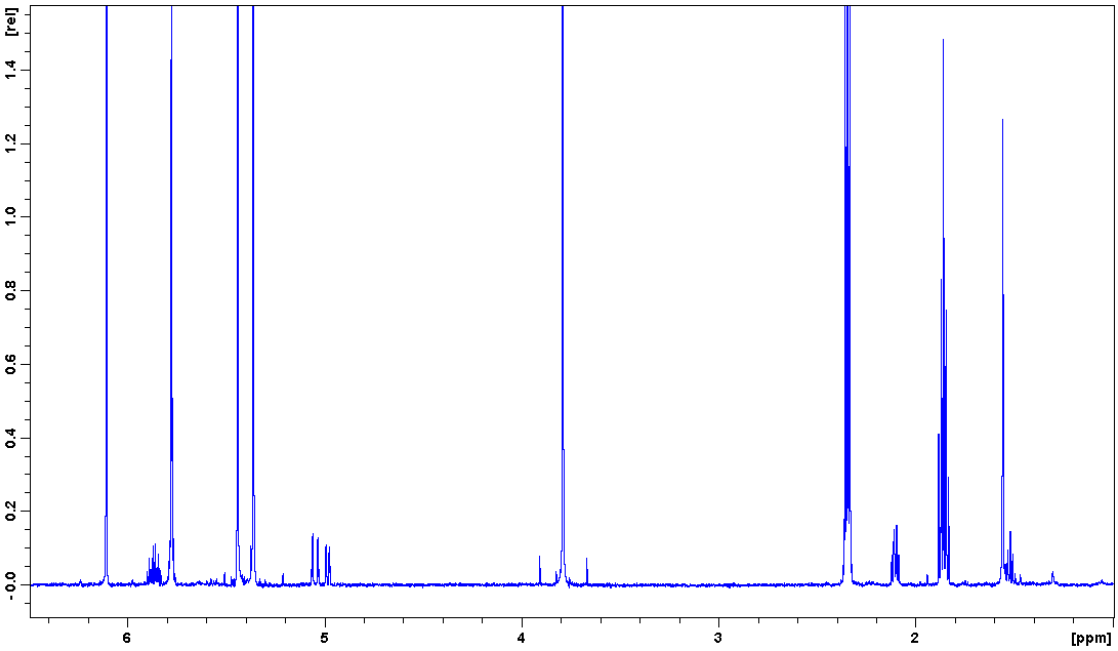
9.6 mM heptadiene **7b** (dataset 1) or 9.2 mM heptadiene **7b** (dataset 2); both with 0.1 mM pre-catalyst **9**. *Analysis was by ^{1}H NMR at 600 MHz using a Bruker AV600 equipped with BBO-z-ATMA probe; the temperature was maintained at 298 K throughout.*

Sample Spectra

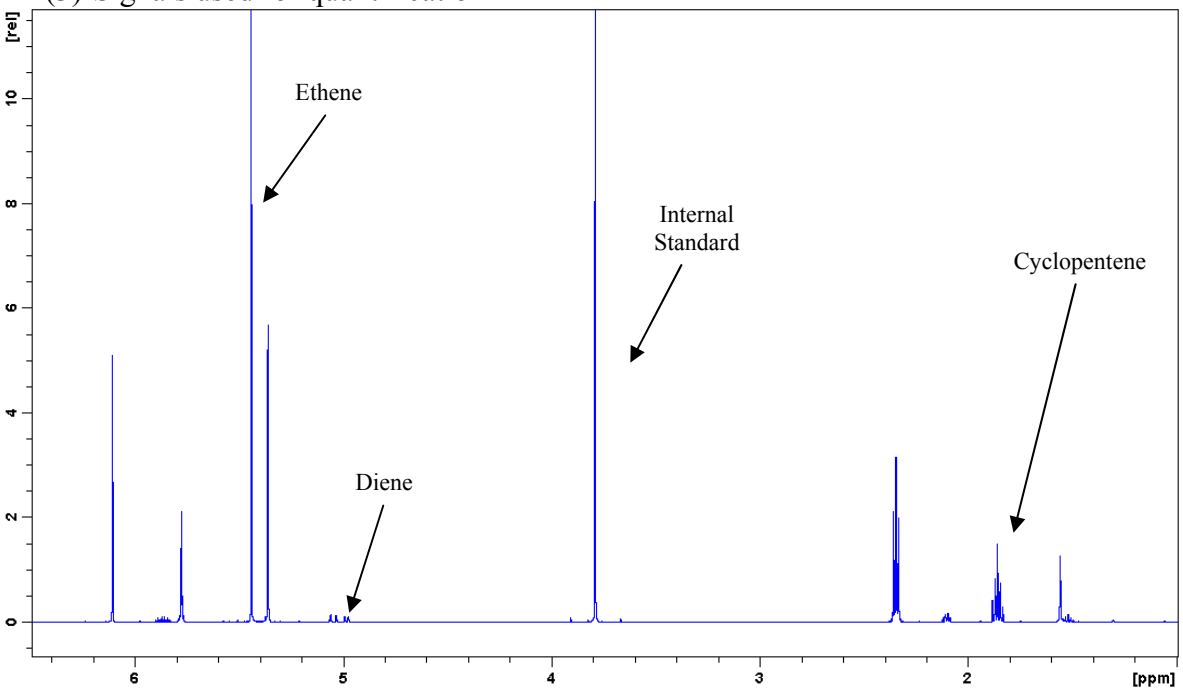
(1) Before pre-catalyst addition

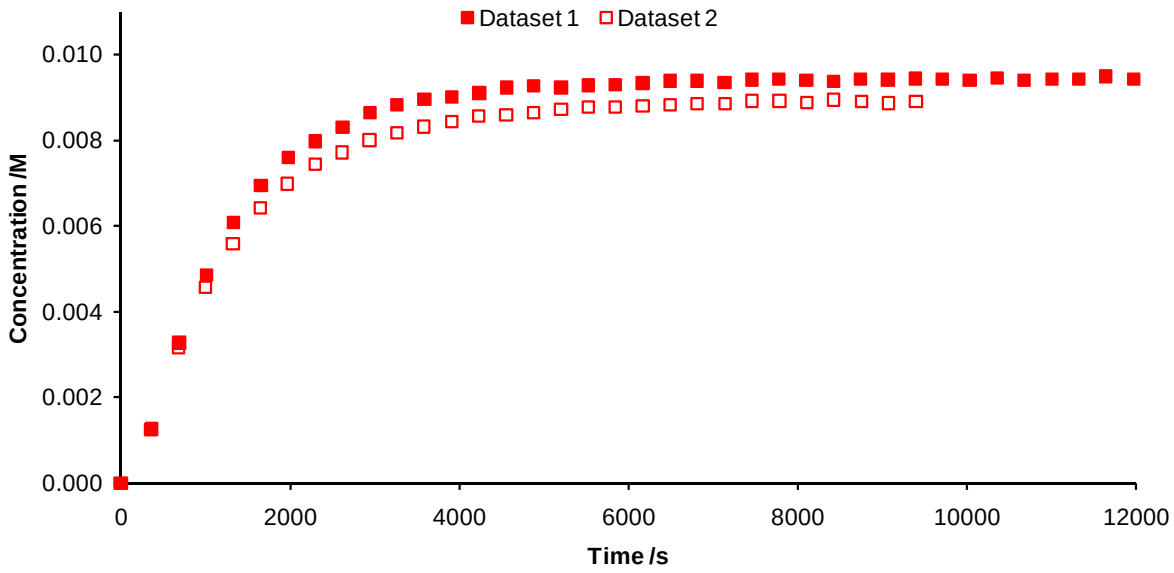


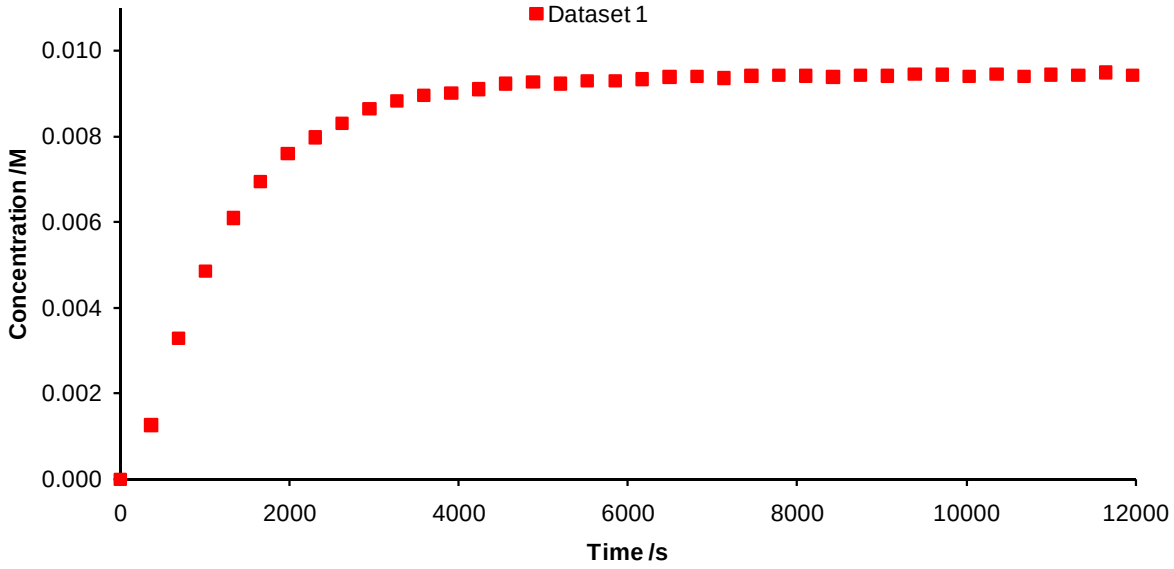
(2) Approx. 1 h after addition

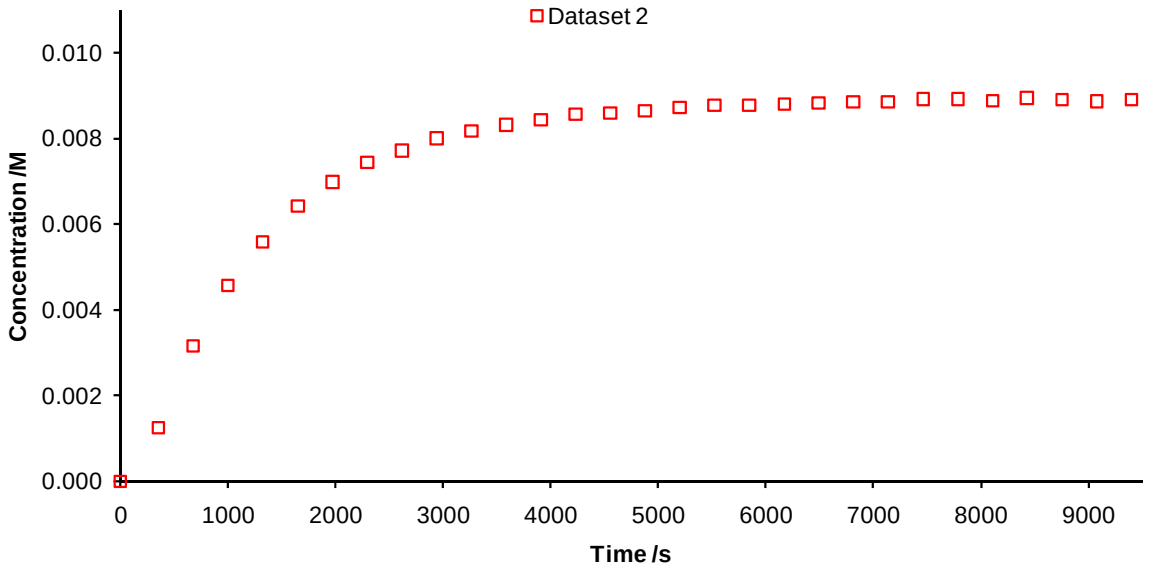


(3) Signals used for quantification




Dataset 1
Dataset 2
Concentration /M
0.010
0.008
0.006
0.004
0.002
0.000
0
2000
4000
6000
8000
10000
12000
Time /s


Dataset 1
Concentration /M
0.010
0.008
0.006
0.004
0.002
0.000
0
2000
4000
6000
8000
10000
12000
Time /s


Dataset 2
Concentration /M
0.010
0.008
0.006
0.004
0.002
0.000
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
Time /s

*Concentration/time data for the RCM of heptadiene **7b** with pre-catalyst **9** in CD_2Cl_2 at 298 K (AV600, BBO-z-ATMA probe); 4 scans with D_1 = 35 s; TE = 298 K; concentrations obtained by integration of the appropriate signal and the internal standard (see above).*

Dataset 1

t (s)	Diene (M)	Cyclopentene (M)	Ethene (M)
0	0.009641	0.000000	0.000084
364	0.008293	0.001266	0.001322
687	0.006322	0.003282	0.003284
1010	0.004710	0.004861	0.004847
1333	0.003529	0.006091	0.005999
1656	0.002691	0.006952	0.006814
1978	0.002053	0.007598	0.007427
2300	0.001635	0.007977	0.007826
2623	0.001304	0.008300	0.008136
2945	0.001028	0.008642	0.008389
3267	0.000902	0.008819	0.008467
3589	0.000768	0.008955	0.008600
3911	0.000660	0.009008	0.008731
4234	0.000609	0.009101	0.008792
4556	0.000517	0.009229	0.008857
4878	0.000505	0.009270	0.008899
5200	0.000447	0.009230	0.008824
5523	0.000411	0.009287	0.008843
5845	0.000404	0.009290	0.008834
6167	0.000422	0.009334	0.008780
6490	0.000393	0.009386	0.008717
6812	0.000369	0.009391	0.008715
7134	0.000349	0.009357	0.008728
7456	0.000341	0.009411	0.008676
7779	0.000338	0.009428	0.008625
8101	0.000342	0.009409	0.008590
8423	0.000340	0.009382	0.008502
8746	0.000314	0.009427	0.008515
9068	0.000296	0.009414	0.008424
9390	0.000300	0.009444	0.008421
9712	0.000290	0.009434	0.008363
10034	0.000322	0.009400	0.008251
10357	0.000298	0.009449	0.008225
10679	0.000297	0.009398	0.008167
11001	0.000318	0.009435	0.008160
11323	0.000276	0.009432	0.008091
11645	0.000303	0.009490	0.008060
11968	0.000299	0.009426	0.007941

*Concentration/time data for the RCM of heptadiene **7b** with pre-catalyst **9** in CD_2Cl_3 at 298 K (AV600, BBO-z-ATMA probe); 4 scans with D_1 = 35 s; TE = 298 K; concentrations obtained by integration of the appropriate signal and the internal standard (see above).*

Dataset 2

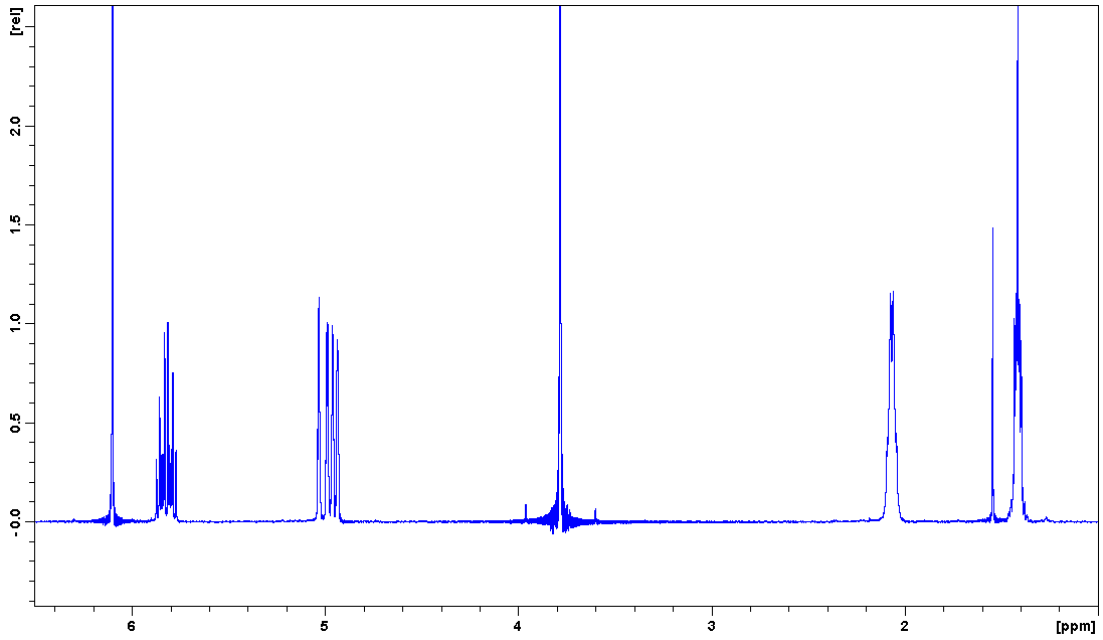
t (s)	Diene (M)	Cyclopentene (M)	Ethene (M)
0	0.009168	0.000000	0.000040
354	0.007844	0.001253	0.001277
678	0.005991	0.003157	0.003094
1001	0.004573	0.004567	0.004498
1324	0.003487	0.005590	0.005488
1647	0.002717	0.006424	0.006261
1970	0.002141	0.006985	0.006840
2293	0.001671	0.007442	0.007318
2616	0.001383	0.007717	0.007584
2939	0.001146	0.008001	0.007839
3262	0.000948	0.008174	0.007976
3585	0.000839	0.008319	0.008121
3908	0.000703	0.008434	0.008234
4231	0.000651	0.008564	0.008258
4554	0.000575	0.008591	0.008342
4877	0.000546	0.008653	0.008365
5200	0.000486	0.008723	0.008318
5523	0.000482	0.008767	0.008283
5846	0.000450	0.008776	0.008288
6169	0.000413	0.008806	0.008291
6491	0.000410	0.008836	0.008276
6814	0.000390	0.008856	0.008285
7137	0.000363	0.008856	0.008219
7460	0.000338	0.008922	0.008304
7783	0.000346	0.008922	0.008133
8106	0.000334	0.008879	0.008120
8428	0.000335	0.008948	0.008107
8751	0.000302	0.008897	0.008104
9074	0.000323	0.008867	0.008025
9397	0.000299	0.008899	0.007928

Octadiene RCM in Chloroform

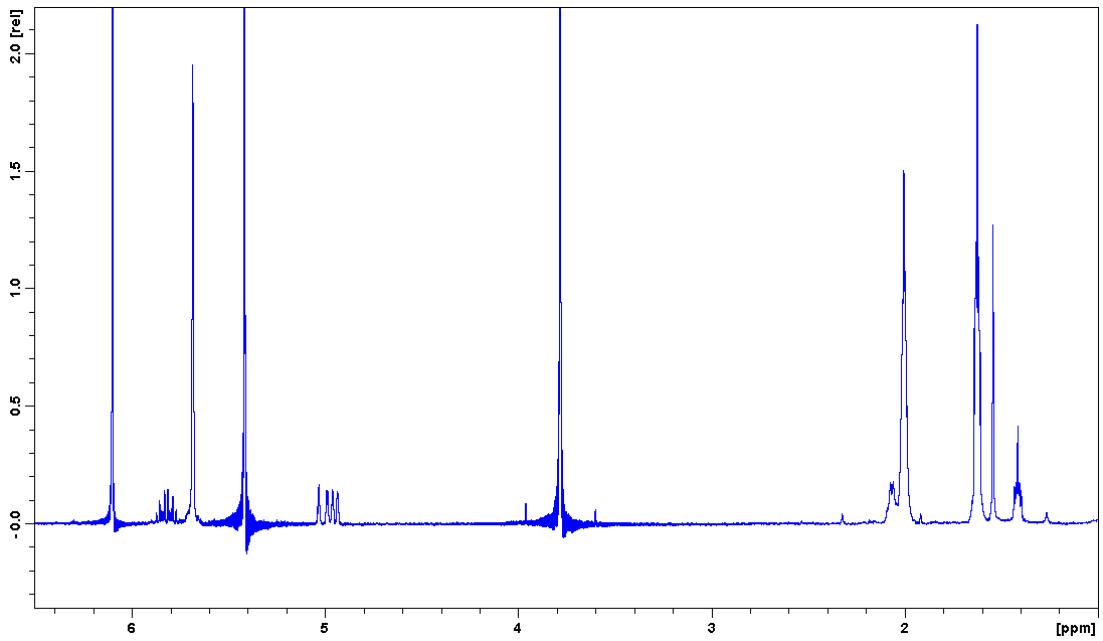
9.3 mM octadiene **7c** (dataset 1) or 8.8 mM octadiene **7c** (dataset 2); both using 0.1 mM pre-catalyst **9**. *Analysis was by ^{1}H NMR at 400 MHz using a Bruker AV400 equipped with BBFO-z-ATMA probe; the temperature was maintained at 298 K throughout.*

Sample Spectra

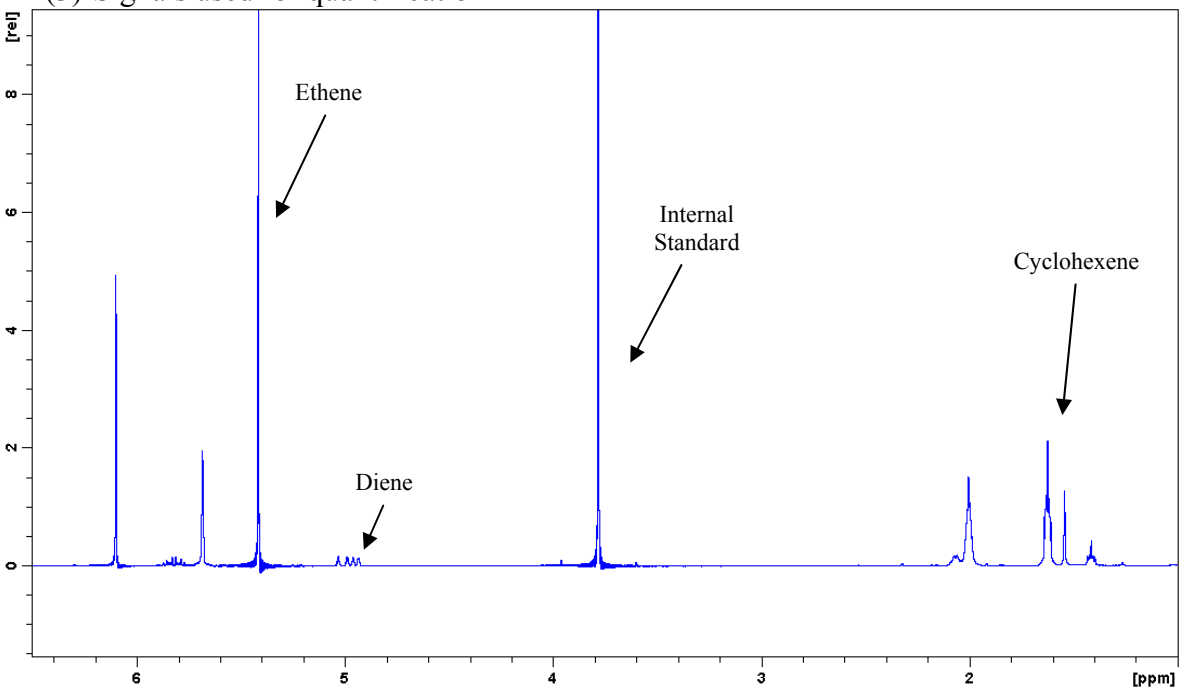
(1) Before pre-catalyst addition

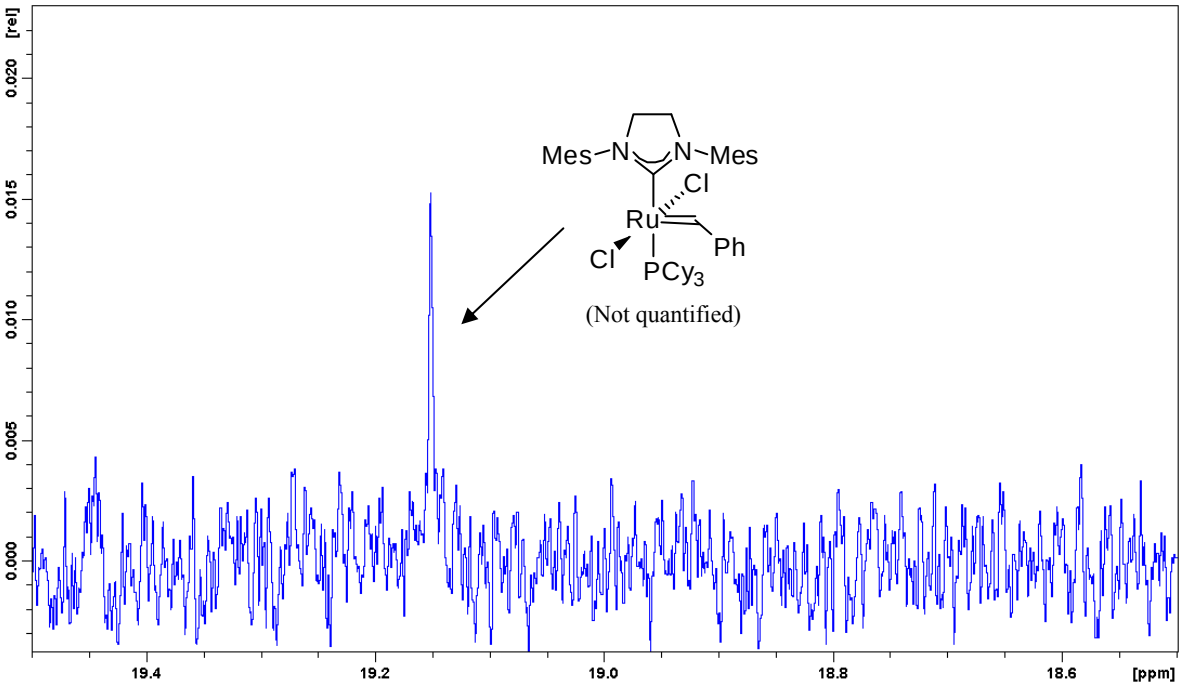


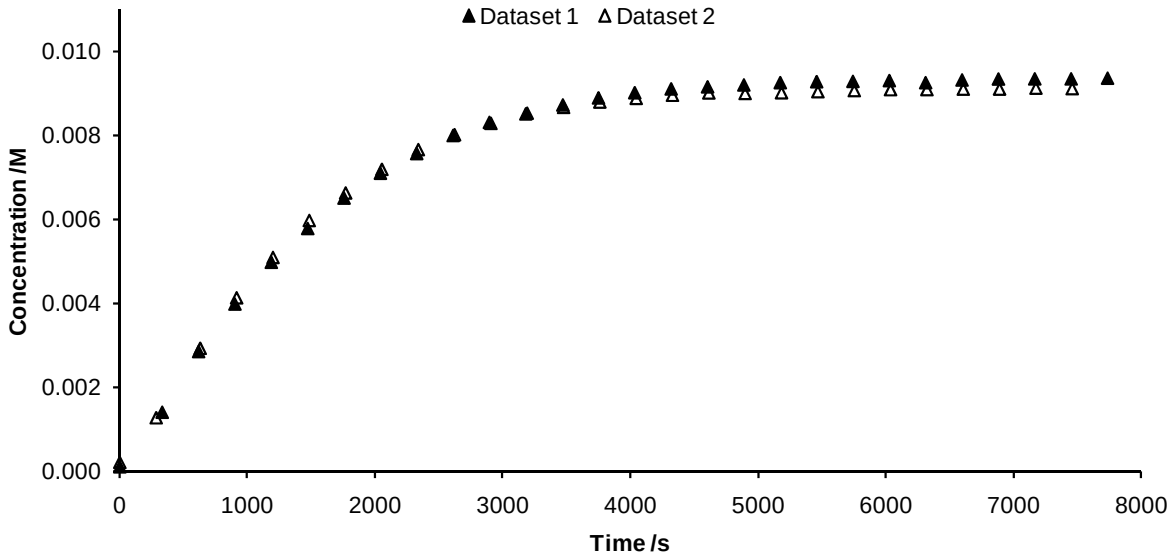
(2) Approx. 1 h after addition

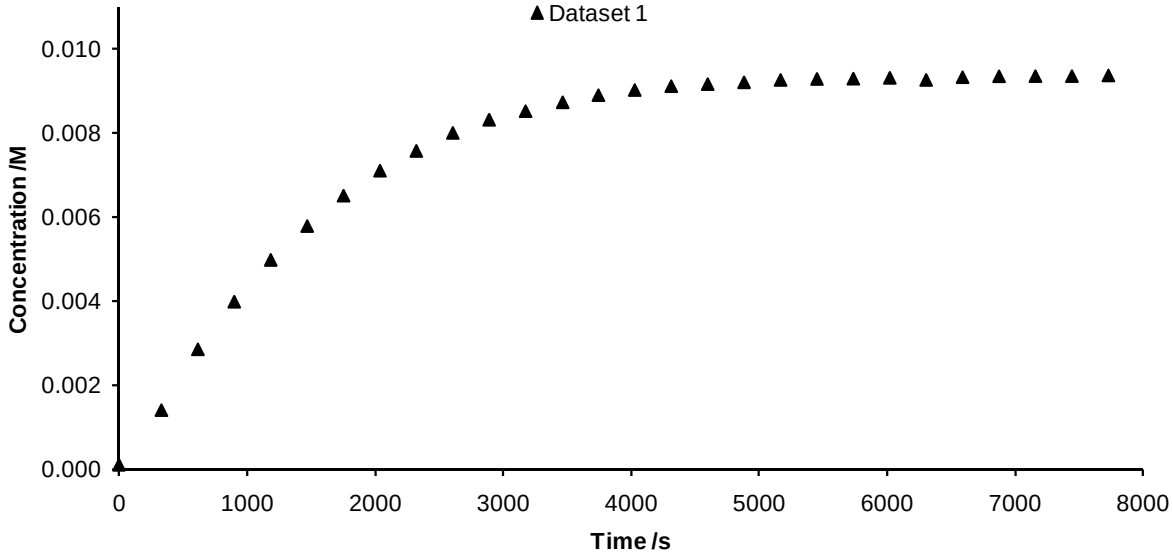


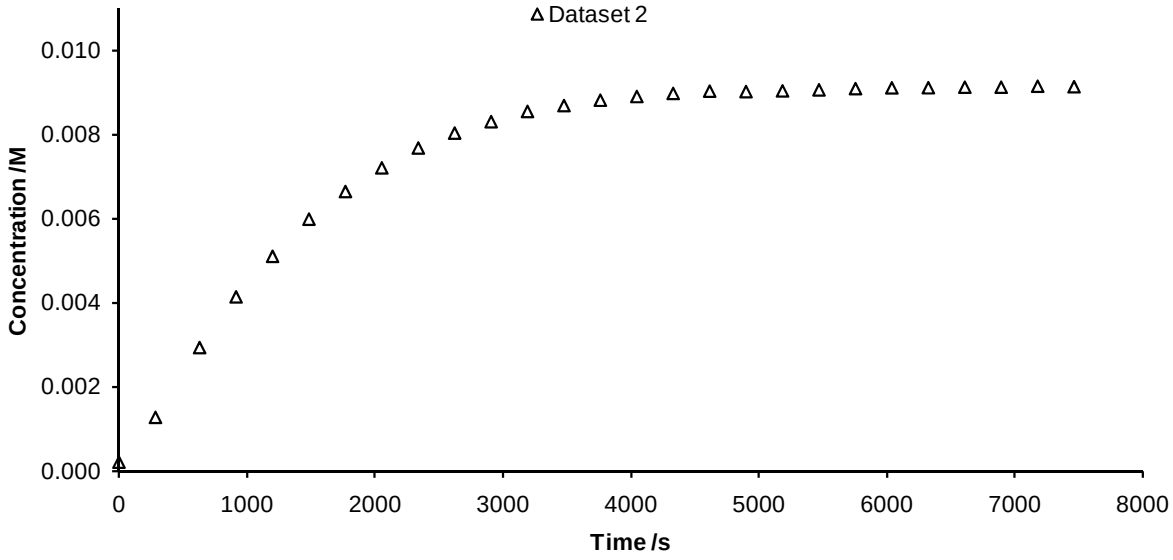
(3) Signals used for quantification






Dataset 1
Dataset 2
Concentration /M
0.010
0.008
0.006
0.004
0.002
0.000
0
1000
2000
3000
4000
5000
6000
7000
8000
Time /s


Dataset 1
Concentration /M
0.010
0.008
0.006
0.004
0.002
0.000
0
1000
2000
3000
4000
5000
6000
7000
8000
Time /s


Dataset 2
Concentration /M
0.010
0.008
0.006
0.004
0.002
0.000
0
1000
2000
3000
4000
5000
6000
7000
8000
Time /s

*Concentration/time data for the RCM of octadiene **7c** with pre-catalyst **9** in $CDCl_3$ at 298 K (AV400, BBFO-z-ATMA probe); 4 scans with D_1 = 35 s; TE = 298 K; concentrations obtained by integration of the appropriate signal and the internal standard (see above).*

Dataset 1

t (s)	Diene (M)	Cyclohexene (M)	Ethene (M)
0	0.009325	0.000109	0.000040
332	0.007914	0.001409	0.001225
617	0.006562	0.002857	0.002595
901	0.005399	0.003989	0.003749
1186	0.004385	0.004983	0.004722
1471	0.003529	0.005788	0.005558
1755	0.002814	0.006512	0.006297
2040	0.002231	0.007106	0.006881
2324	0.001752	0.007576	0.007363
2609	0.001321	0.008005	0.007705
2893	0.001007	0.008318	0.007995
3178	0.000780	0.008521	0.008254
3468	0.000603	0.008733	0.008467
3747	0.000414	0.008901	0.008587
4031	0.000302	0.009025	0.008735
4316	0.000193	0.009116	0.008740
4601	0.000131	0.009164	0.008822
4885	0.000126	0.009209	0.008933
5170	0.000064	0.009265	0.008912
5455	0.000062	0.009288	0.008945
5739	0.000029	0.009296	0.008960
6024	0.000019	0.009315	0.008994
6308	0.000045	0.009265	0.008956
6593	-0.000008	0.009329	0.008942
6878	0.000030	0.009351	0.008946
7162	0.000020	0.009355	0.008945
7447	-0.000013	0.009355	0.008877
7732	-0.000021	0.009372	0.008900
8016	0.000048	0.009318	0.008886
8301	0.000036	0.009335	0.008900
8585	-0.000007	0.009399	0.008826
8870	0.000021	0.009329	0.008843
9155	0.000004	0.009370	0.008810
9439	-0.000004	0.009365	0.008816
9724	-0.000014	0.009339	0.008778
10009	0.000013	0.009330	0.008783
10293	0.000000	0.009372	0.008719

10578	-0.000022	0.009384	0.008735
10862	-0.000031	0.009402	0.008669
11147	-0.000002	0.009373	0.008669
11431	0.000005	0.009384	0.008635
11716	-0.000012	0.009389	0.008611
12000	-0.000001	0.009410	0.008580
12285	0.000007	0.009397	0.008582
12569	0.000004	0.009388	0.008551
12854	-0.000002	0.009377	0.008533
13138	0.000017	0.009370	0.008503
13423	0.000007	0.009376	0.008464
13707	0.000009	0.009436	0.008463
13992	-0.000003	0.009383	0.008438
14278	-0.000004	0.009389	0.008405
34416	0.000023	0.009465	0.002364
73906	0.000005	0.009511	0.000384

*Concentration/time data for the RCM of octadiene **7c** with pre-catalyst **9** in $CDCl_3$ at 298 K (AV400, BBFO-z-ATMA probe); 4 scans with D_1 = 35 s; TE = 298 K; concentrations obtained by integration of the appropriate signal and the internal standard (see above).*

Dataset 2

t (s)	Diene (M)	Cyclohexene (M)	Ethene (M)
0	0.008844	0.000206	0.000061
285	0.007728	0.001271	0.000948
630	0.006140	0.002930	0.002262
915	0.004961	0.004134	0.003226
1200	0.003977	0.005099	0.003984
1484	0.003138	0.005982	0.004677
1769	0.002464	0.006638	0.005223
2053	0.001896	0.007202	0.005681
2338	0.001480	0.007673	0.006045
2622	0.001098	0.008028	0.006298
2907	0.000825	0.008299	0.006544
3191	0.000614	0.008543	0.006729
3476	0.000482	0.008682	0.006866
3760	0.000339	0.008809	0.006932
4045	0.000240	0.008897	0.007007
4329	0.000192	0.008971	0.007047
4614	0.000140	0.009025	0.007087
4898	0.000110	0.009014	0.007057
5183	0.000062	0.009031	0.007054

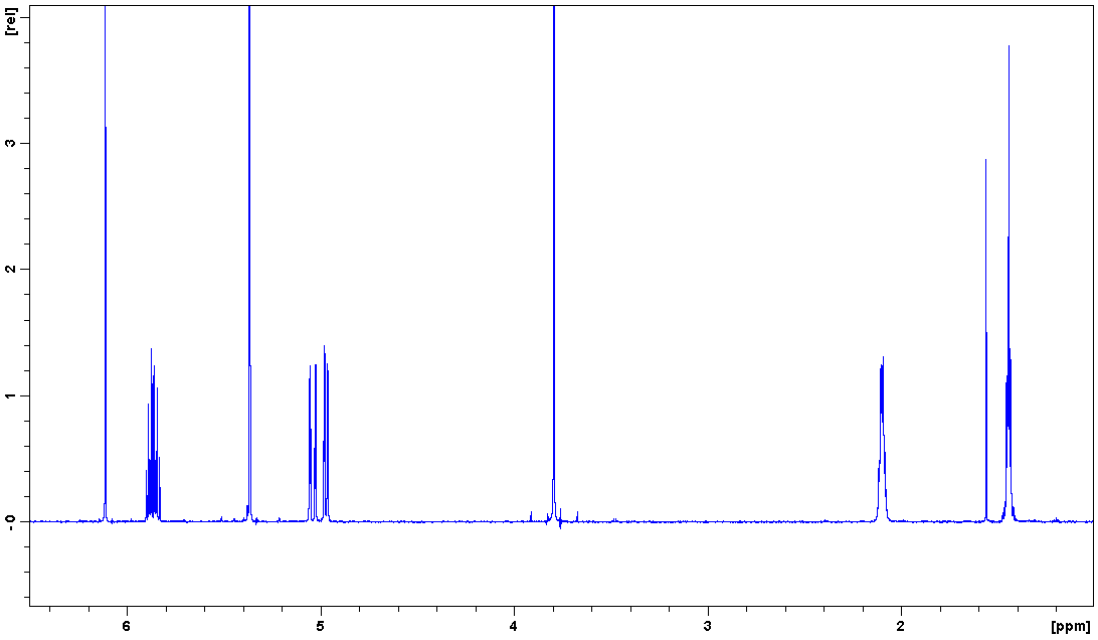
5468	0.000111	0.009056	0.007064
5753	0.000029	0.009084	0.007035
6037	0.000017	0.009104	0.007024
6322	0.000068	0.009106	0.007039
6607	0.000024	0.009118	0.006985
6891	0.000056	0.009119	0.006996
7176	0.000052	0.009142	0.006992
7460	0.000024	0.009129	0.006955
9811	-0.000011	0.009414	0.006997
10154	0.000008	0.009387	0.006897
11390	0.000023	0.009366	0.006135
86144	0.000015	0.009656	0.001627

Octadiene RCM in Dichloromethane

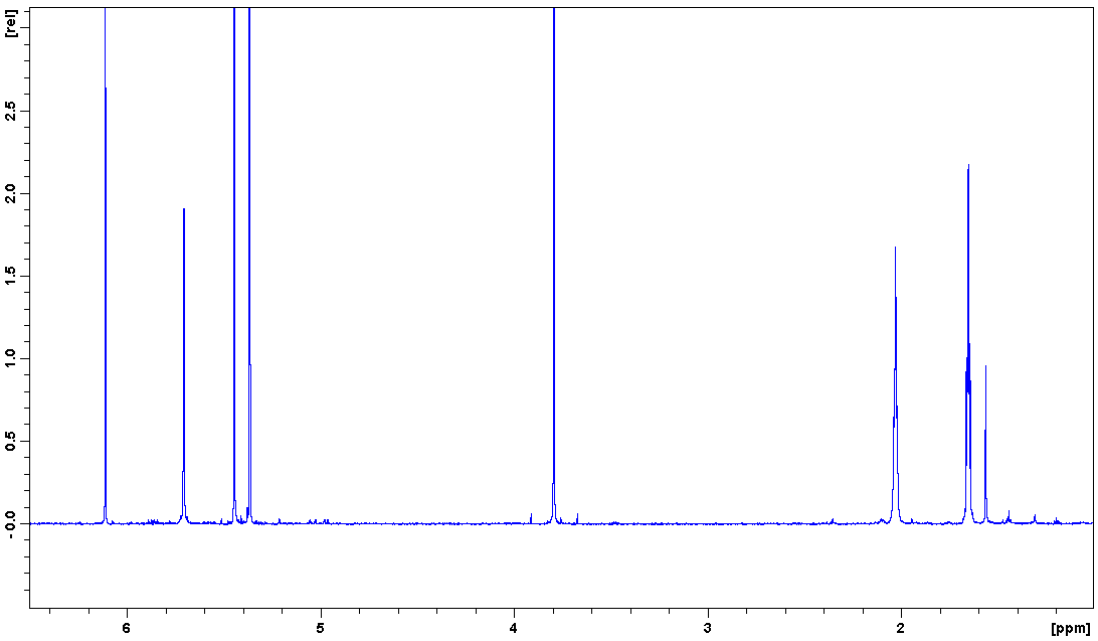
10.1 mM octadiene **7c** (dataset 1) or 10.3 mM octadiene **7c** (dataset 2); both using 0.1 mM pre-catalyst **9**. *Analysis was by ^{1}H NMR at 600 MHz using a Bruker AV600 equipped with BBO-z-ATMA probe; the temperature was maintained at 298 K throughout.*

Sample Spectra

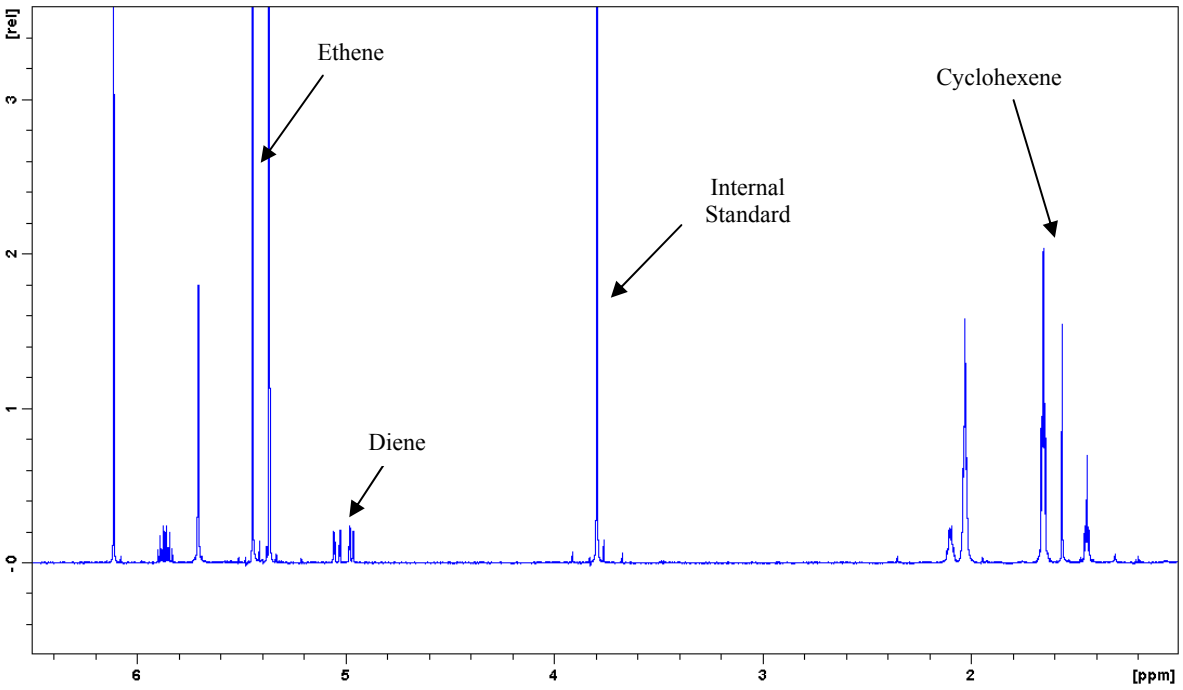
(1) Before pre-catalyst addition

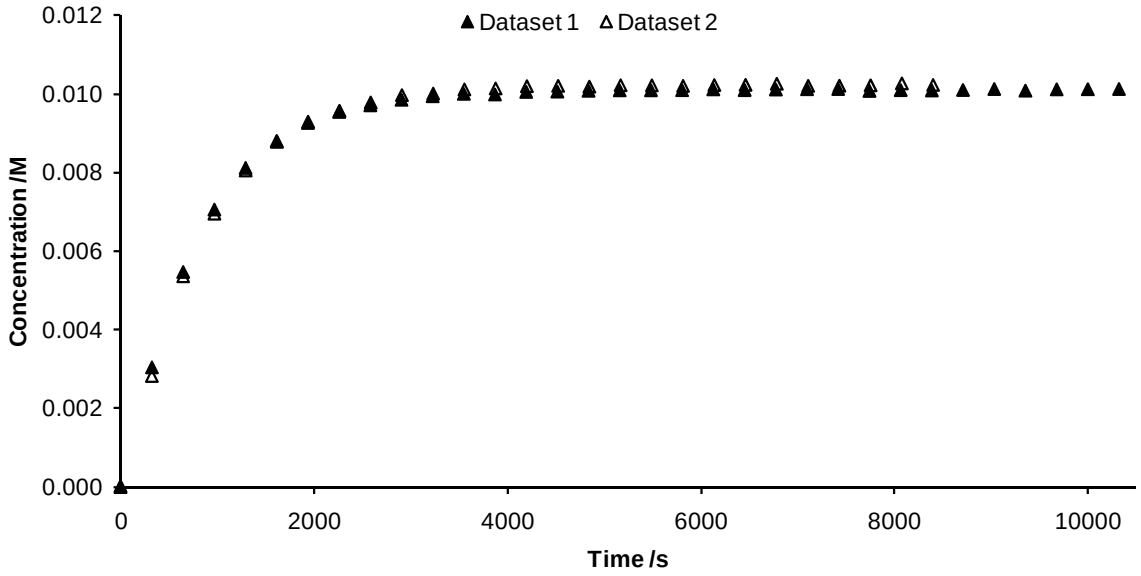


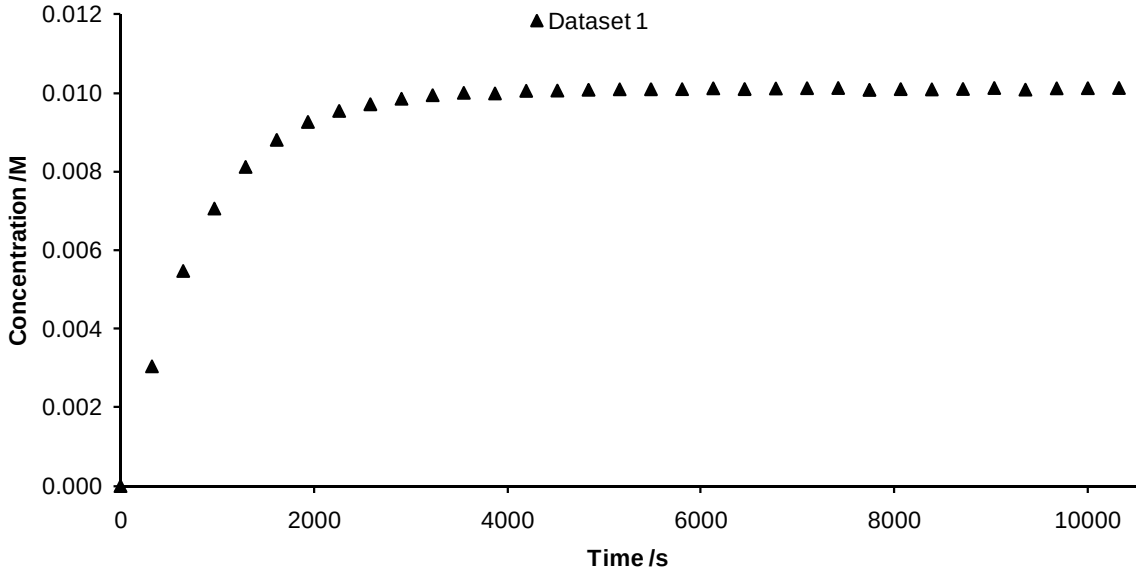
(2) Approx. 1 h after addition

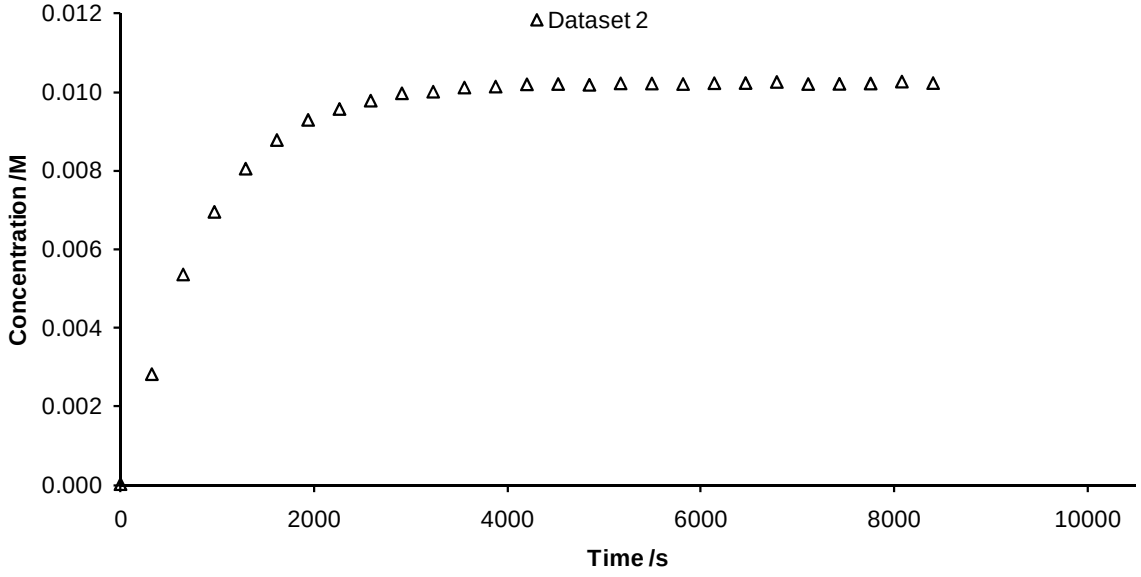


(3) Signals used for quantification




Dataset 1
Dataset 2
Concentration /M
0.012
0.010
0.008
0.006
0.004
0.002
0.000
0
2000
4000
6000
8000
10000
Time /s


Dataset 1
Concentration /M
0.012
0.010
0.008
0.006
0.004
0.002
0.000
0
2000
4000
6000
8000
10000
Time /s


Dataset 2
Concentration /M
0.012
0.010
0.008
0.006
0.004
0.002
0.000
0
2000
4000
6000
8000
10000
Time /s

*Concentration/time data for the RCM of octadiene **7c** with pre-catalyst **9** in CD_2Cl_2 at 298 K (AV600, BBO-z-ATMA probe); 4 scans with D_1 = 35 s; TE = 298 K; concentrations obtained by integration of the appropriate signal and the internal standard (see above).*

Dataset 1

t (s)	Diene (M)	Cyclohexene (M)	Ethene (M)
0	0.010148	0.000004	0.000044
325	0.007012	0.003050	0.002870
648	0.004665	0.005476	0.005151
970	0.003078	0.007063	0.006668
1293	0.002033	0.008122	0.007633
1615	0.001356	0.008808	0.008311
1937	0.000894	0.009264	0.008754
2260	0.000607	0.009544	0.009077
2582	0.000440	0.009714	0.009172
2904	0.000284	0.009855	0.009419
3226	0.000212	0.009945	0.009475
3548	0.000173	0.010004	0.009476
3870	0.000119	0.009990	0.009461
4193	0.000109	0.010056	0.009403
4515	0.000109	0.010063	0.009468
4837	0.000049	0.010082	0.009481
5159	0.000064	0.010096	0.009434
5482	0.000072	0.010096	0.009333
5804	0.000049	0.010098	0.009347
6126	0.000063	0.010119	0.009355
6450	0.000044	0.010101	0.009219
6773	0.000039	0.010116	0.009270
7095	0.000035	0.010123	0.009196
7417	0.000052	0.010129	0.009148
7740	0.000029	0.010080	0.009164
8063	0.000049	0.010100	0.009098
8385	0.000038	0.010093	0.009090
8707	0.000051	0.010104	0.009022
9030	0.000059	0.010129	0.008927
9352	0.000062	0.010086	0.008908
9675	0.000049	0.010121	0.008881
9997	0.000046	0.010123	0.008737
10319	0.000031	0.010129	0.008674

*Concentration/time data for the RCM of octadiene **7c** with pre-catalyst **9** in CD_2Cl_2 at 298 K (AV600, BBO-z-ATMA probe); 4 scans with D_1 = 35 s; TE = 298 K; concentrations obtained by integration of the appropriate signal and the internal standard (see above).*

Dataset 2

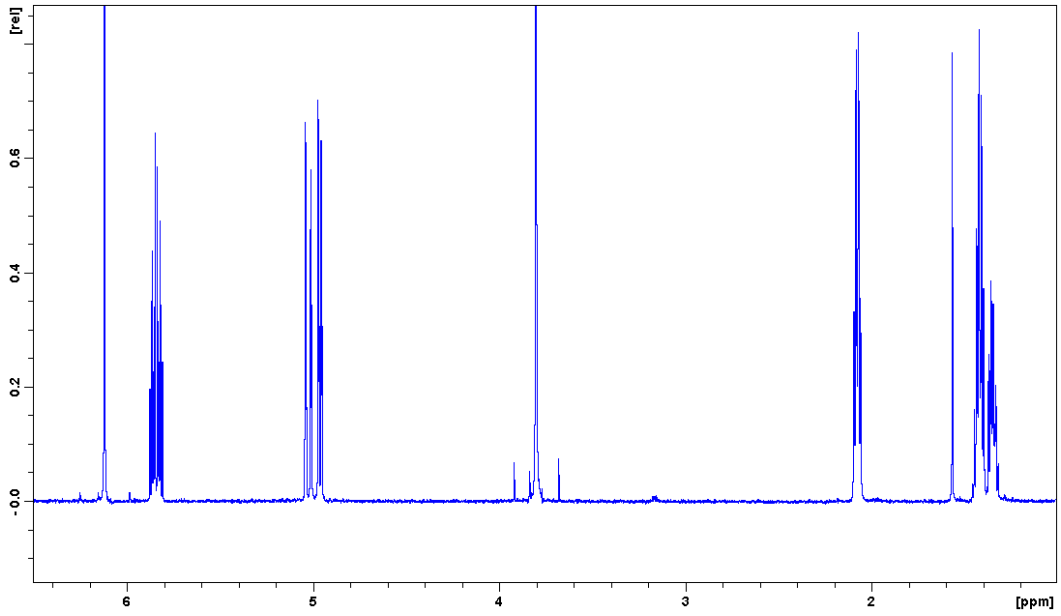
t (s)	Diene (M)	Cyclohexene (M)	Ethene (M)
0	0.010318	0.000023	0.000028
324	0.007448	0.002827	0.002681
648	0.004978	0.005366	0.005126
971	0.003325	0.006960	0.006695
1294	0.002241	0.008061	0.007791
1617	0.001480	0.008789	0.008549
1940	0.000979	0.009301	0.008979
2264	0.000674	0.009580	0.009250
2587	0.000455	0.009792	0.009486
2910	0.000316	0.009979	0.009623
3233	0.000217	0.010021	0.009668
3556	0.000164	0.010125	0.009742
3879	0.000074	0.010151	0.009811
4202	0.000082	0.010208	0.009752
4525	0.000088	0.010215	0.009717
4848	0.000075	0.010196	0.009759
5171	0.000036	0.010233	0.009734
5494	0.000042	0.010229	0.009737
5817	0.000039	0.010216	0.009730
6140	0.000025	0.010237	0.009647
6463	0.000004	0.010241	0.009677
6786	0.000036	0.010268	0.009674
7110	0.000055	0.010215	0.009548
7433	0.000024	0.010220	0.009550
7756	0.000049	0.010230	0.009511
8079	0.000016	0.010279	0.009475
8402	0.000028	0.010238	0.009411

Nonadiene RCM in Chloroform

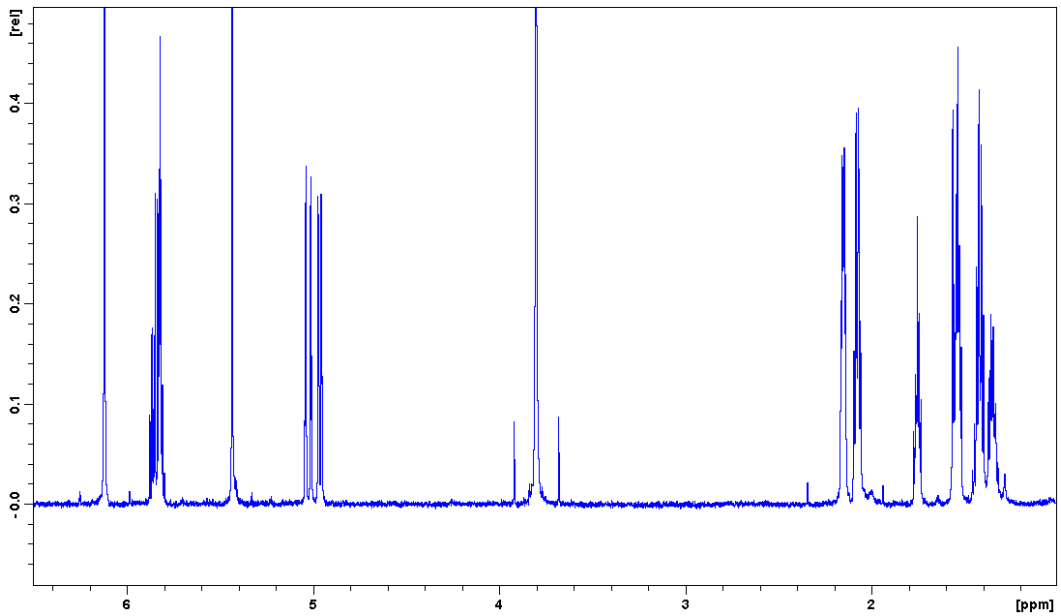
10.2 mM nonadiene **7d** (dataset 1) or 9.7 mM nonadiene **7d** (dataset 2); both using 0.1 mM pre-catalyst **9**. *Analysis was by ^{1}H NMR at 600 MHz using a Brüker AV600 equipped with BBO-z-ATMA probe or 400 MHz using a Brüker AV400 equipped with BBFO-z-ATMA probe; the temperature was maintained at 298 K throughout.*

Sample Spectra

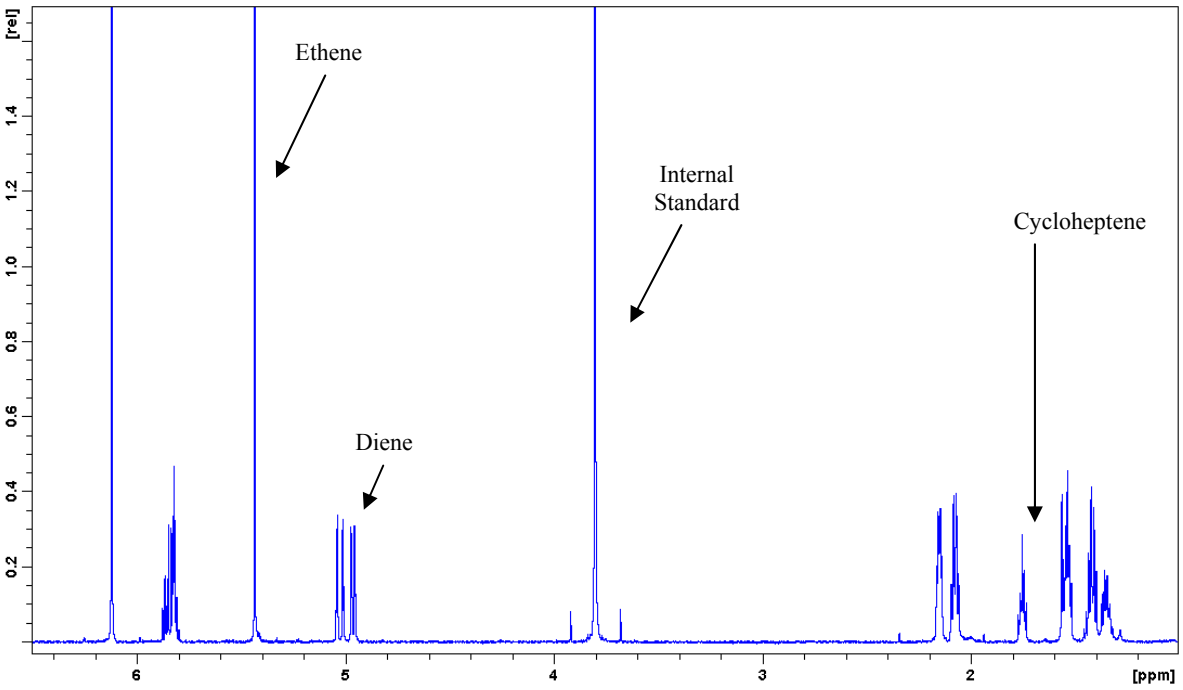
(1) Before pre-catalyst addition

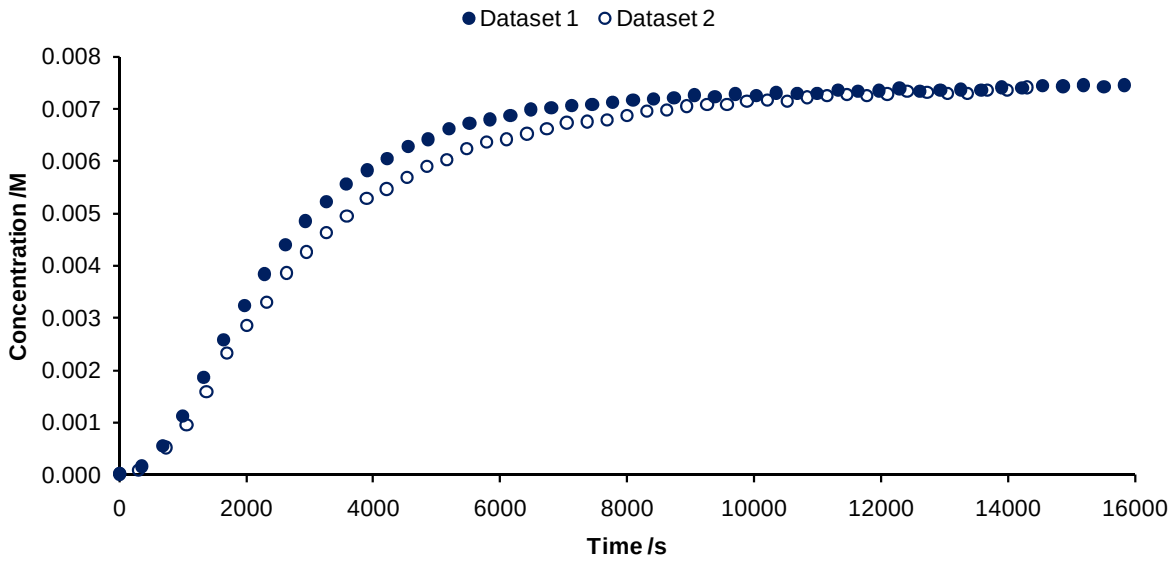


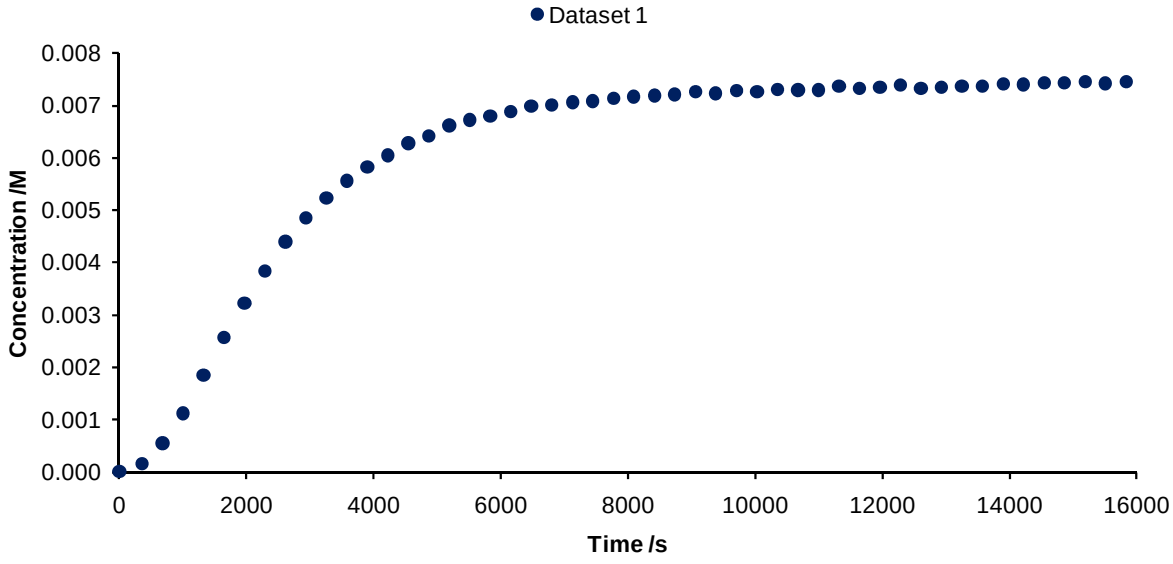
(2) Approx. 1 h after addition

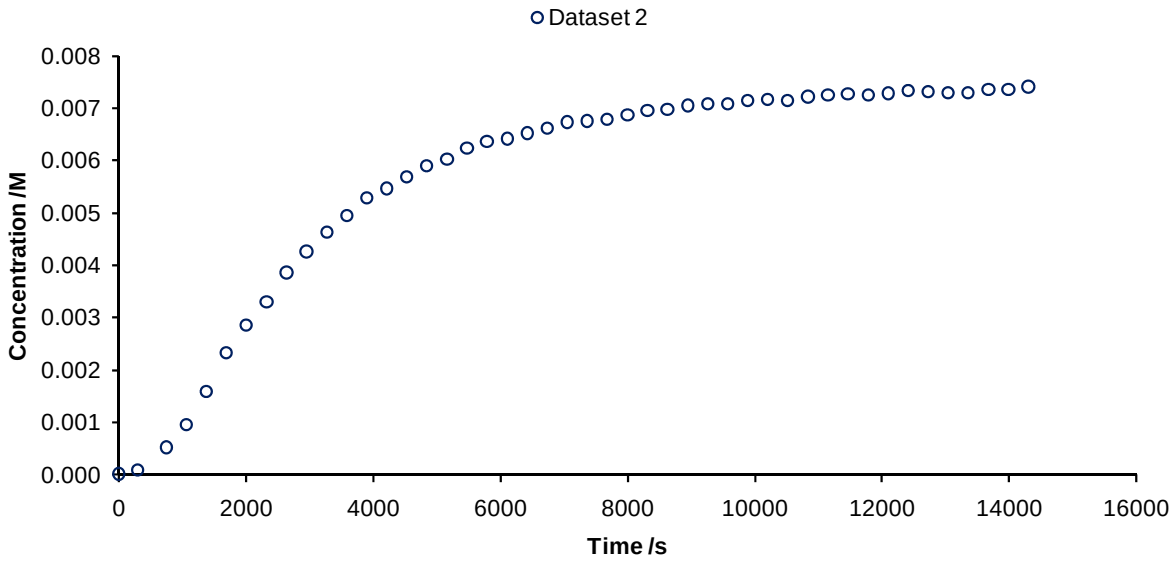


(3) Signals used for quantification




Dataset 1
Dataset 2
Concentration /M
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0.000
0
2000
4000
6000
8000
10000
12000
14000
16000
Time /s


Dataset 1
Concentration /M
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0.000
0
2000
4000
6000
8000
10000
12000
14000
16000
Time /s


Dataset 2
Concentration /M
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0.000
0
2000
4000
6000
8000
10000
12000
14000
16000
Time /s

*Concentration/time data for the RCM of nonadiene **7d** with pre-catalyst **9** in $CDCl_3$ at 298 K (AV600, BBO-z-ATMA probe); 4 scans with D_1 = 35 s; TE = 298 K; concentrations obtained by integration of the appropriate signal and the internal standard (see above).*

Dataset 1

t (s)	Diene (M)	Cycloheptene (M)	Ethene (M)
0	0.010177	0.000022	0.000000
354	0.009900	0.000168	0.000198
678	0.009479	0.000553	0.000610
1000	0.008867	0.001123	0.001225
1323	0.008130	0.001860	0.001975
1646	0.007318	0.002579	0.002766
1968	0.006618	0.003234	0.003476
2290	0.005958	0.003844	0.004110
2612	0.005419	0.004399	0.004650
2934	0.004927	0.004857	0.005117
3257	0.004525	0.005232	0.005520
3579	0.004181	0.005563	0.005855
3901	0.003862	0.005829	0.006165
4224	0.003591	0.006053	0.006430
4546	0.003371	0.006286	0.006617
4868	0.003212	0.006423	0.006801
5191	0.003027	0.006618	0.006969
5513	0.002907	0.006726	0.007105
5836	0.002784	0.006800	0.007186
6158	0.002708	0.006879	0.007280
6480	0.002652	0.006989	0.007358
6803	0.002539	0.007017	0.007414
7126	0.002480	0.007063	0.007471
7448	0.002439	0.007083	0.007491
7770	0.002413	0.007137	0.007528
8093	0.002386	0.007171	0.007547
8415	0.002335	0.007188	0.007576
8738	0.002316	0.007215	0.007580
9060	0.002294	0.007266	0.007597
9382	0.002251	0.007231	0.007599
9707	0.002273	0.007285	0.007611
10029	0.002231	0.007260	0.007580
10351	0.002226	0.007306	0.007584
10674	0.002230	0.007297	0.007595
10996	0.002184	0.007295	0.007569
11318	0.002182	0.007368	0.007556
11641	0.002150	0.007336	0.007527

11963	0.002172	0.007354	0.007528
12286	0.002180	0.007391	0.007550
12608	0.002136	0.007336	0.007506
12930	0.002127	0.007356	0.007469
13253	0.002137	0.007371	0.007429
13576	0.002104	0.007367	0.007392
13898	0.002119	0.007417	0.007388
14221	0.002118	0.007406	0.007378
14543	0.002108	0.007442	0.007364
14866	0.002084	0.007438	0.007311
15188	0.002088	0.007459	0.007281
15510	0.002086	0.007427	0.007267
15833	0.002066	0.007458	0.007247
16155	0.002059	0.007464	0.007219
16477	0.002059	0.007435	0.007154
16799	0.002051	0.007463	0.007163
17122	0.002029	0.007517	0.007116
17444	0.002036	0.007469	0.007070
17766	0.002017	0.007513	0.007085
18089	0.002030	0.007507	0.007017
18412	0.002012	0.007562	0.007021
18734	0.001990	0.007537	0.006953
19056	0.001993	0.007539	0.006968
19379	0.001982	0.007542	0.006922
19701	0.001961	0.007515	0.006881
20023	0.001986	0.007520	0.006860

*Concentration/time data for the RCM of nonadiene **7d** with pre-catalyst **9** in $CDCl_3$ at 298 K (AV400, BBFO-z-ATMA probe); 4 scans with D_1 = 35 s; TE = 298 K; concentrations obtained by integration of the appropriate signal and the internal standard (see above).*

Dataset 2

t (s)	Diene (M)	Cycloheptene (M)	Ethene (M)
0	0.009717	0.000016	0.000018
298	0.009585	0.000086	0.000124
741	0.009196	0.000525	0.000514
1058	0.008715	0.000954	0.000962
1373	0.008127	0.001596	0.001535
1688	0.007456	0.002326	0.002186
2004	0.006811	0.002859	0.002768
2320	0.006186	0.003298	0.003285
2635	0.005682	0.003863	0.003770
2950	0.005270	0.004265	0.004193
3266	0.004881	0.004632	0.004578
3581	0.004492	0.004956	0.004860
3897	0.004208	0.005292	0.005121
4212	0.003921	0.005472	0.005347
4527	0.003675	0.005698	0.005554
4842	0.003489	0.005904	0.005714
5158	0.003335	0.006027	0.005886
5473	0.003159	0.006244	0.006002
5788	0.003037	0.006361	0.006107
6104	0.002939	0.006422	0.006213
6419	0.002810	0.006527	0.006281
6735	0.002724	0.006620	0.006349
7050	0.002672	0.006742	0.006415
7365	0.002550	0.006758	0.006417
7681	0.002508	0.006796	0.006465
7996	0.002488	0.006872	0.006492
8311	0.002407	0.006967	0.006489
8627	0.002355	0.006985	0.006495
8942	0.002298	0.007055	0.006493
9258	0.002278	0.007094	0.006487
9573	0.002221	0.007090	0.006479
9888	0.002199	0.007148	0.006455
10204	0.002207	0.007167	0.006479
10519	0.002138	0.007156	0.006442
10834	0.002110	0.007226	0.006445
11149	0.002128	0.007253	0.006425

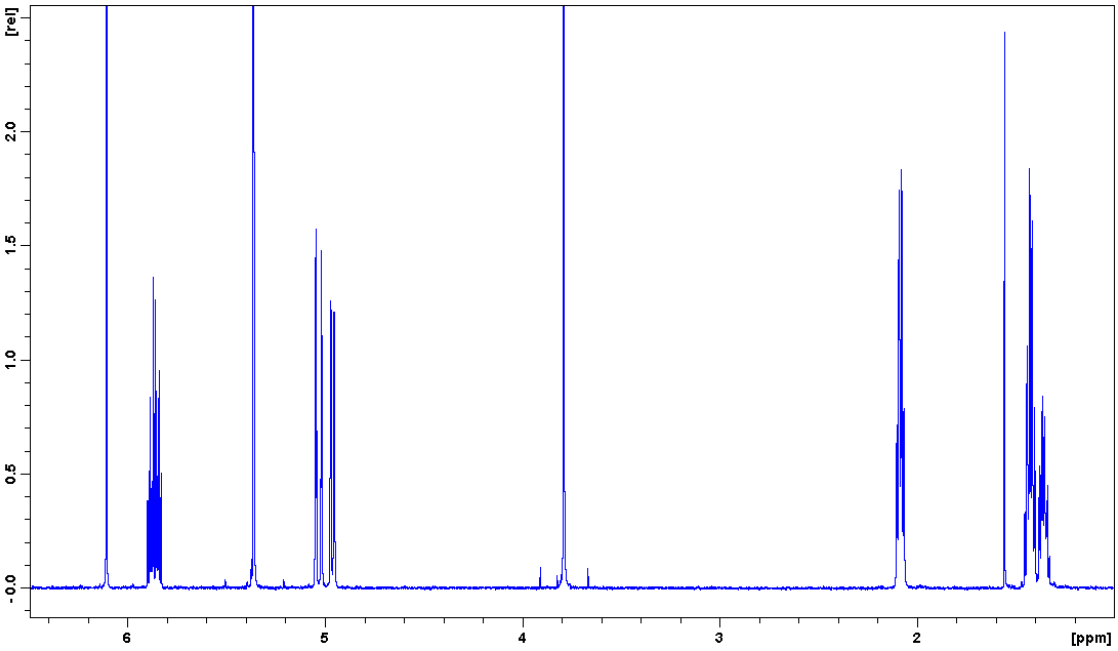
11465	0.002094	0.007274	0.006411
11780	0.002077	0.007250	0.006372
12096	0.002026	0.007286	0.006343
12411	0.002011	0.007340	0.006308
12726	0.002013	0.007320	0.006281
13042	0.001944	0.007296	0.006254
13357	0.001973	0.007299	0.006208
13673	0.001954	0.007356	0.006208
13988	0.001957	0.007358	0.006178
14303	0.001966	0.007412	0.006142

Nonadiene RCM in Dichloromethane

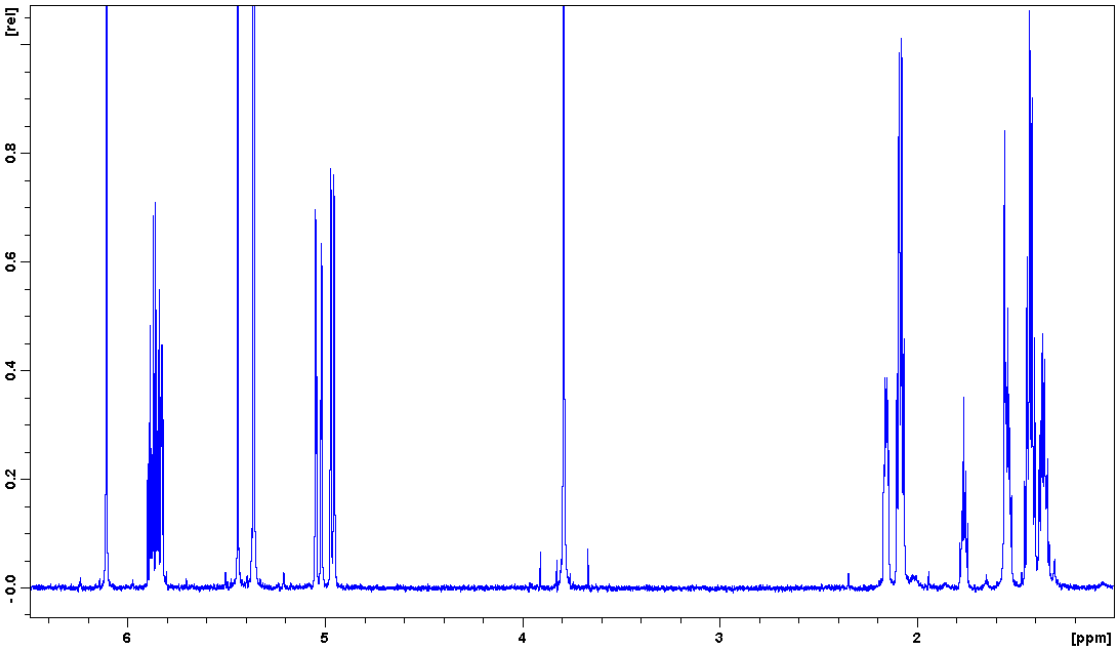
*9.8 mM nonadiene **7d** (dataset 1) or 9.9 mM nonadiene **7d** (dataset 2); both using 0.1 mM pre-catalyst **9**. Analysis was by ^{1}H NMR at 600 MHz using a Bruker AV600 equipped with BBO-z-ATMA probe; the temperature was maintained at 298 K throughout.*

Sample Spectra (600 MHz)

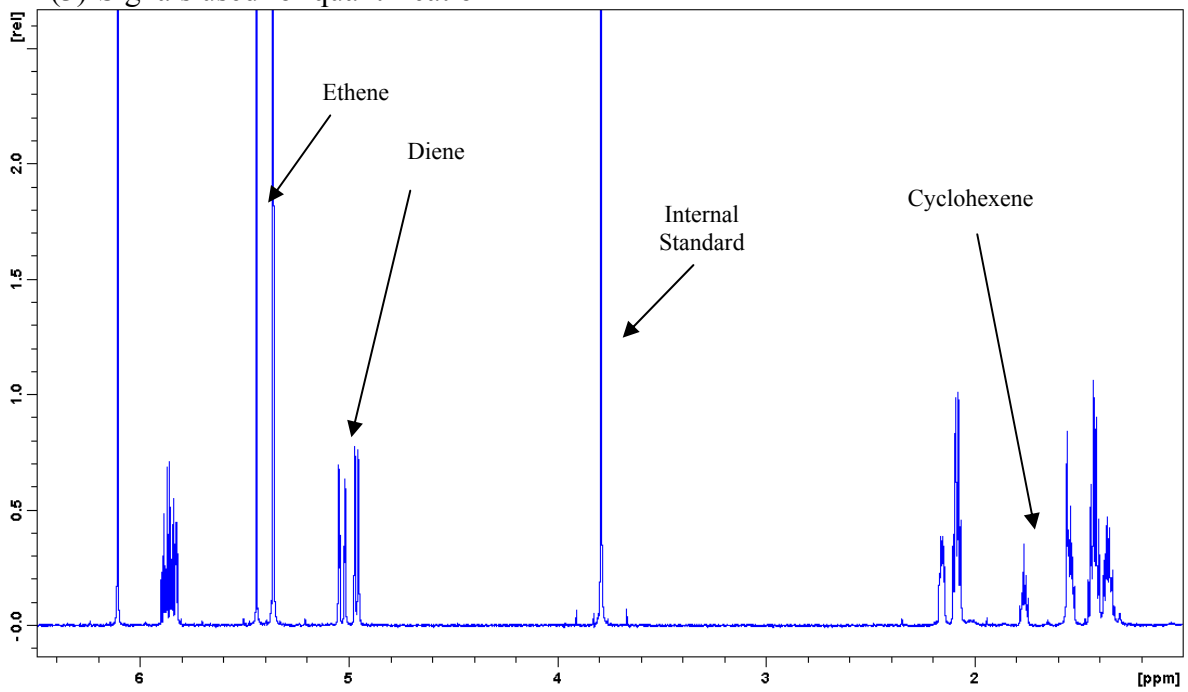
(1) Before pre-catalyst addition

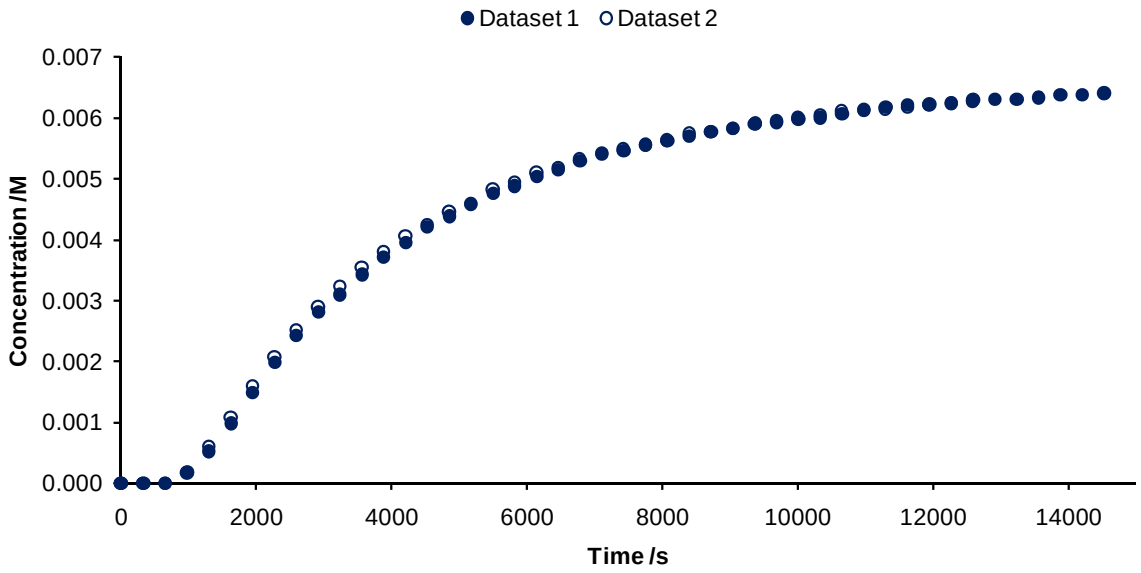


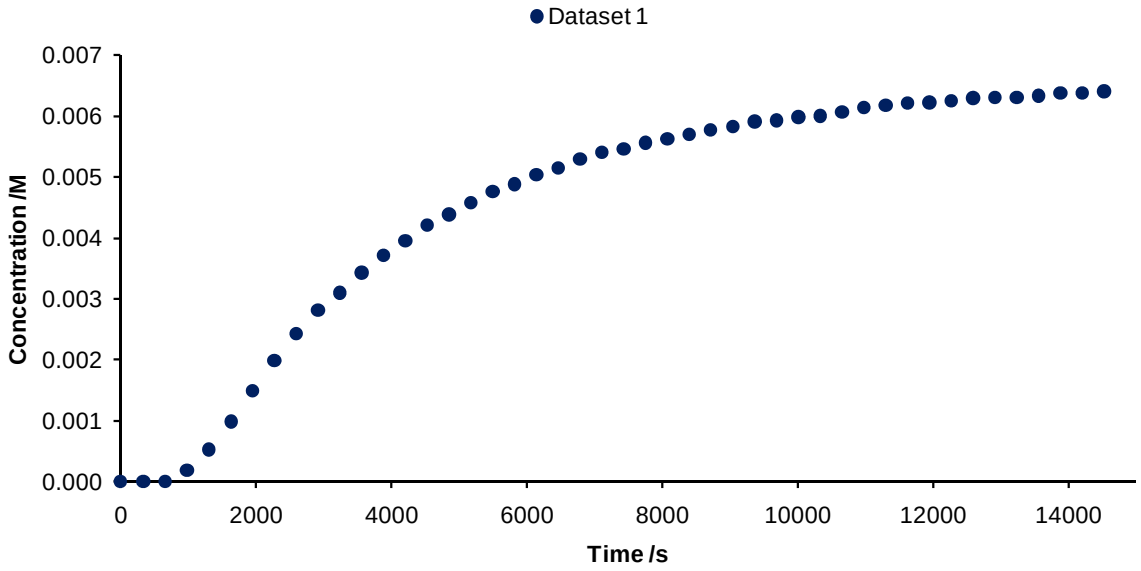
(2) Approx. 1 h after addition

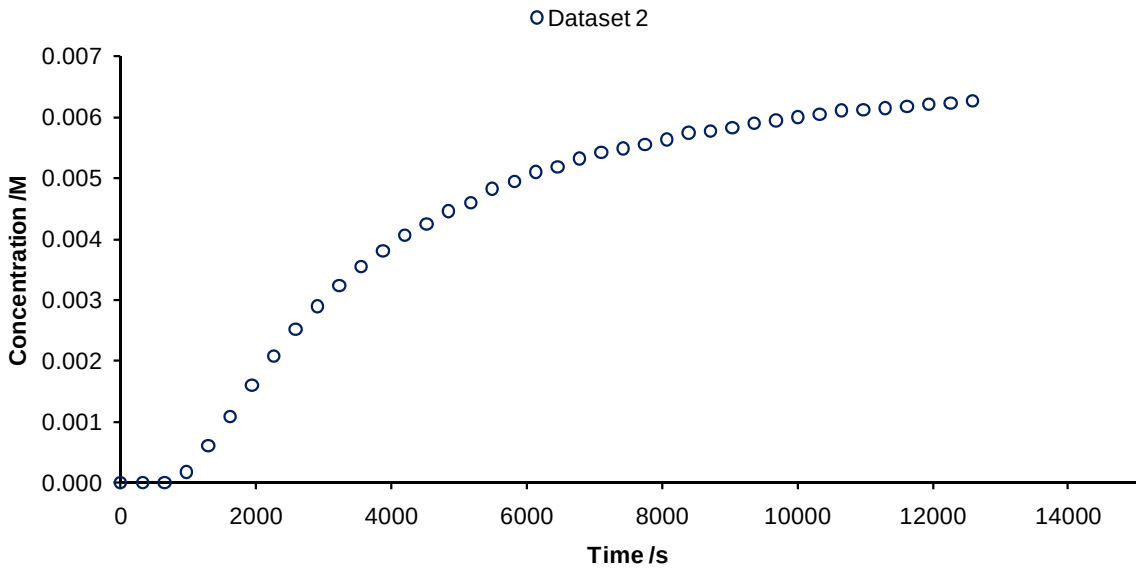


(3) Signals used for quantification




Dataset 1
Dataset 2
Concentration /M
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0.000
0
2000
4000
6000
8000
10000
12000
14000
Time /s


Dataset 1
Concentration /M
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0.000
0
2000
4000
6000
8000
10000
12000
14000
Time /s


Dataset 2
Concentration /M
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0.000
0
2000
4000
6000
8000
10000
12000
14000
Time /s

*Concentration/time data for the RCM of nonadiene **7d** with pre-catalyst **9** in CD_2Cl_2 at 298 K (AV600, BBO-z-ATMA probe); 4 scans with D_1 = 35 s; TE = 298 K; concentrations obtained by integration of the appropriate signal and the internal standard (see above).*

Dataset 1

t (s)	Diene (M)	Cycloheptene (M)	Ethene (M)
0	0.009774	0.000000	0.000012
334	0.009753	0.000000	0.000021
657	0.009704	0.000000	0.000036
981	0.009571	0.000181	0.000215
1305	0.009194	0.000525	0.000569
1627	0.008687	0.000989	0.001066
1950	0.008143	0.001496	0.001634
2272	0.007629	0.001995	0.002112
2595	0.007156	0.002436	0.002579
2917	0.006780	0.002819	0.002966
3239	0.006398	0.003103	0.003392
3562	0.006078	0.003433	0.003657
3884	0.005764	0.003714	0.003962
4207	0.005489	0.003957	0.004213
4529	0.005255	0.004210	0.004456
4851	0.005054	0.004386	0.004660
5173	0.004841	0.004580	0.004829
5496	0.004647	0.004766	0.005044
5818	0.004508	0.004885	0.005170
6141	0.004388	0.005044	0.005326
6463	0.004259	0.005151	0.005419
6785	0.004120	0.005300	0.005566
7108	0.004011	0.005402	0.005674
7430	0.003884	0.005461	0.005751
7752	0.003810	0.005563	0.005817
8074	0.003727	0.005632	0.005903
8397	0.003659	0.005697	0.005971
8719	0.003573	0.005777	0.006027
9044	0.003487	0.005824	0.006096
9367	0.003452	0.005914	0.006112
9689	0.003376	0.005930	0.006159
10012	0.003366	0.005988	0.006223
10334	0.003287	0.006007	0.006255
10656	0.003243	0.006068	0.006305
10979	0.003191	0.006143	0.006327
11302	0.003174	0.006183	0.006360
11625	0.003140	0.006218	0.006352

11947	0.003072	0.006228	0.006375
12269	0.003081	0.006259	0.006361
12592	0.003031	0.006300	0.006398
12914	0.002981	0.006307	0.006425
13237	0.002991	0.006312	0.006433
13559	0.002953	0.006339	0.006412
13882	0.002919	0.006386	0.006442
14204	0.002880	0.006381	0.006470
14526	0.002875	0.006410	0.006458

*Concentration/time data for the RCM of nonadiene **7d** with pre-catalyst **9** in CD_2Cl_2 at 298 K (AV600, BBO-z-ATMA probe); 4 scans with D_1 = 35 s; TE = 298 K; concentrations obtained by integration of the appropriate signal and the internal standard (see above).*

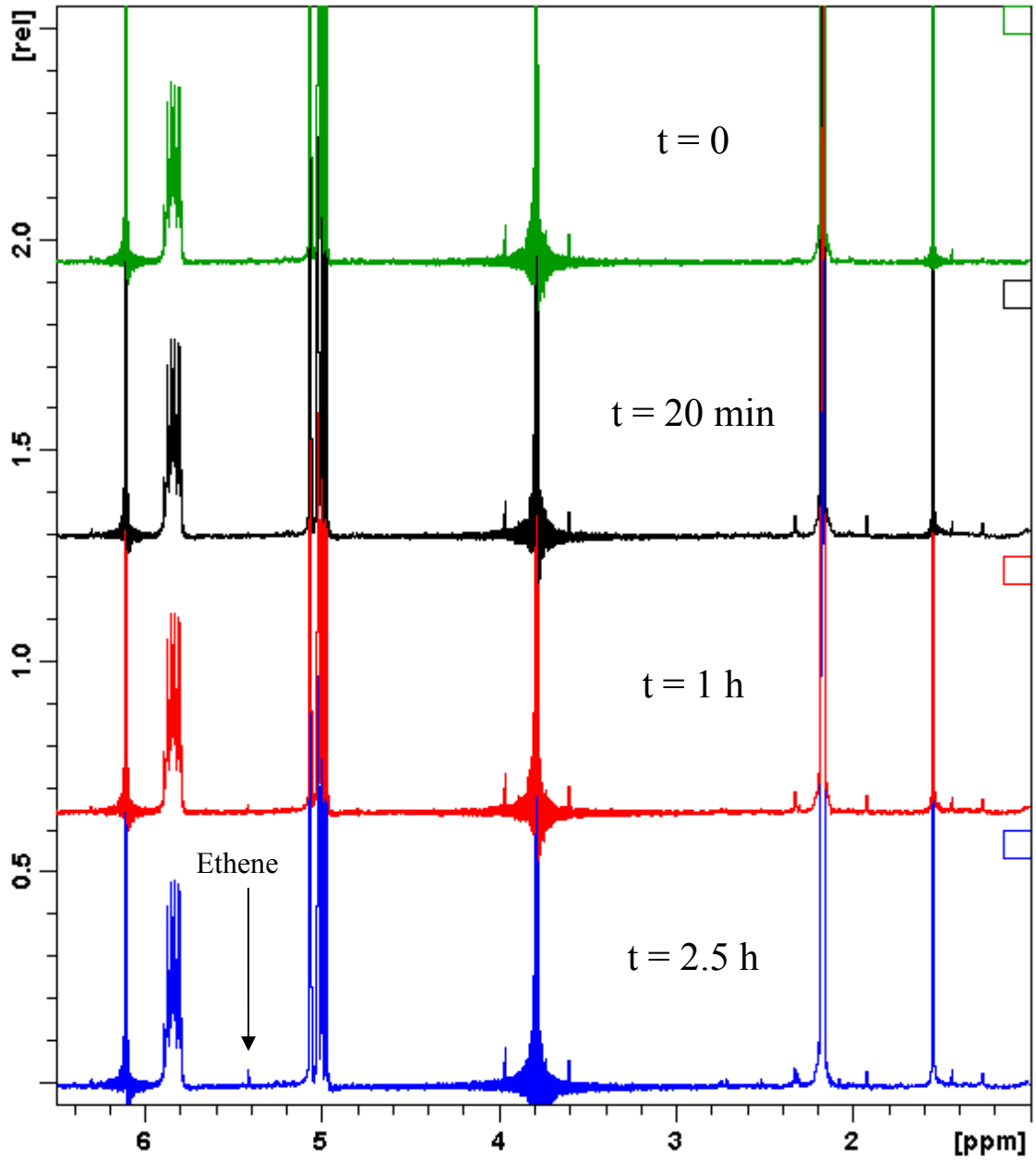
Dataset 2

t (s)	Diene (M)	Cycloheptene (M)	Ethene (M)
0	0.009887	0.000000	0.000037
330	0.009804	0.000000	0.000072
653	0.009806	0.000006	0.000086
976	0.009594	0.000178	0.000287
1298	0.009139	0.000613	0.000716
1620	0.008634	0.001088	0.001205
1943	0.008090	0.001605	0.001791
2265	0.007557	0.002078	0.002267
2588	0.007039	0.002526	0.002751
2911	0.006683	0.002899	0.003141
3234	0.006334	0.003245	0.003499
3557	0.006000	0.003555	0.003792
3879	0.005710	0.003814	0.004070
4201	0.005424	0.004064	0.004318
4524	0.005223	0.004255	0.004552
4847	0.005014	0.004461	0.004774
5170	0.004820	0.004599	0.004926
5492	0.004643	0.004827	0.005133
5815	0.004484	0.004948	0.005273
6137	0.004314	0.005104	0.005421
6459	0.004208	0.005184	0.005516
6781	0.004074	0.005324	0.005617
7104	0.004010	0.005424	0.005709
7426	0.003880	0.005491	0.005788
7748	0.003824	0.005558	0.005852
8070	0.003686	0.005640	0.005952
8392	0.003637	0.005750	0.006020
8715	0.003623	0.005777	0.005987
9037	0.003541	0.005832	0.006060
9362	0.003471	0.005901	0.006209
9685	0.003412	0.005948	0.006222
10007	0.003340	0.006006	0.006251
10329	0.003299	0.006053	0.006282
10652	0.003254	0.006113	0.006308
10974	0.003201	0.006121	0.006358
11296	0.003196	0.006152	0.006322
11619	0.003154	0.006175	0.006377

11941	0.003105	0.006215	0.006361
12263	0.003103	0.006235	0.006374
12585	0.003013	0.006277	0.006413

Attempted Hexadiene Metathesis in Chloroform

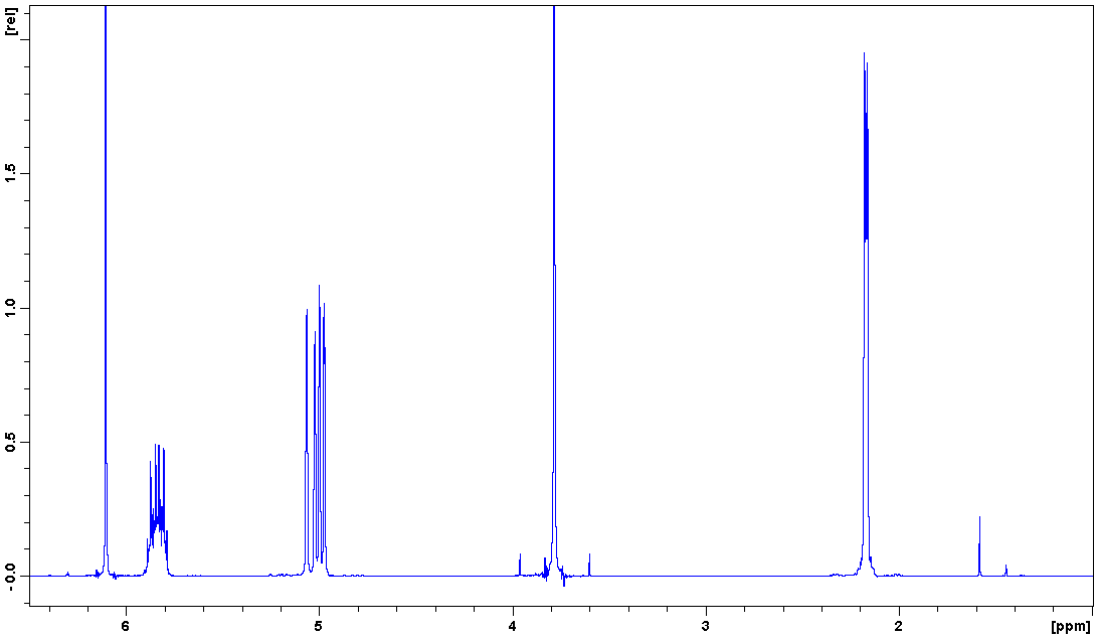
8.7 mM hexadiene **7a**, 0.1 mM pre-catalyst **9**. *Analysis was by ^{1}H NMR at 400 MHz using a Brüker AV400 equipped with BBFO-z-ATMA probe; the temperature was maintained at 298 K throughout.*



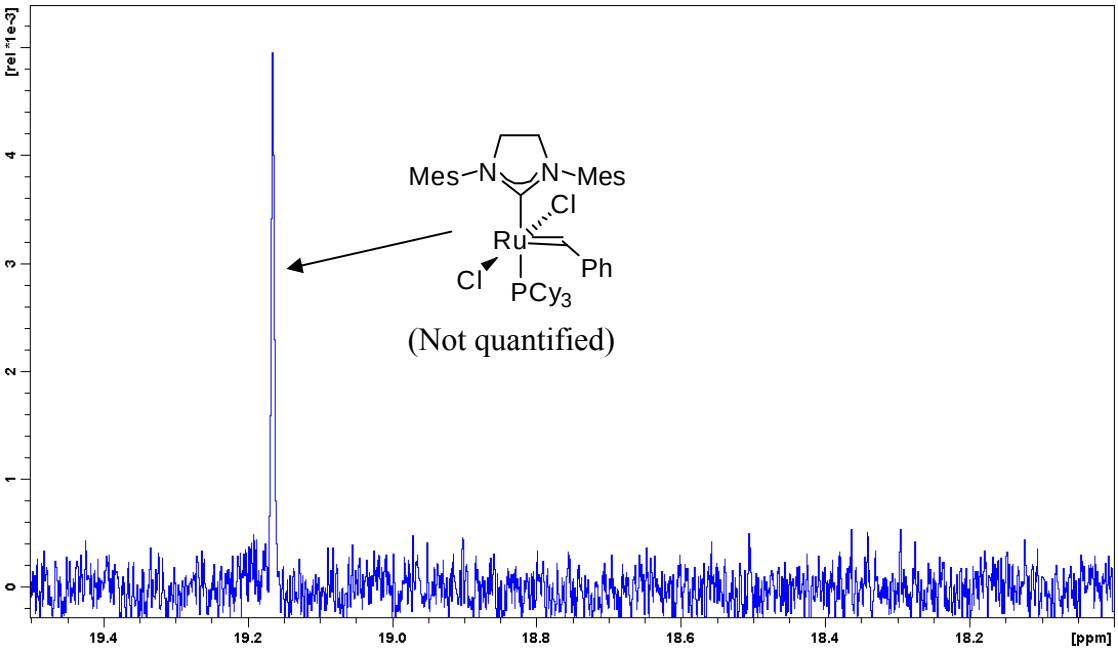
Hexadiene Metathesis, Concentrated Solution in Chloroform

252.6 mM hexadiene **7a**, 4.7 mM pre-catalyst **9**. *Analysis by ^{1}H NMR at 400 MHz using a Brüker AV400 equipped with BBFO-z-ATMA probe; the sample was analysed periodically at 298K and stored on an auto-sampler carousel in a temperature controlled room 294 K when analysis was not being performed.*

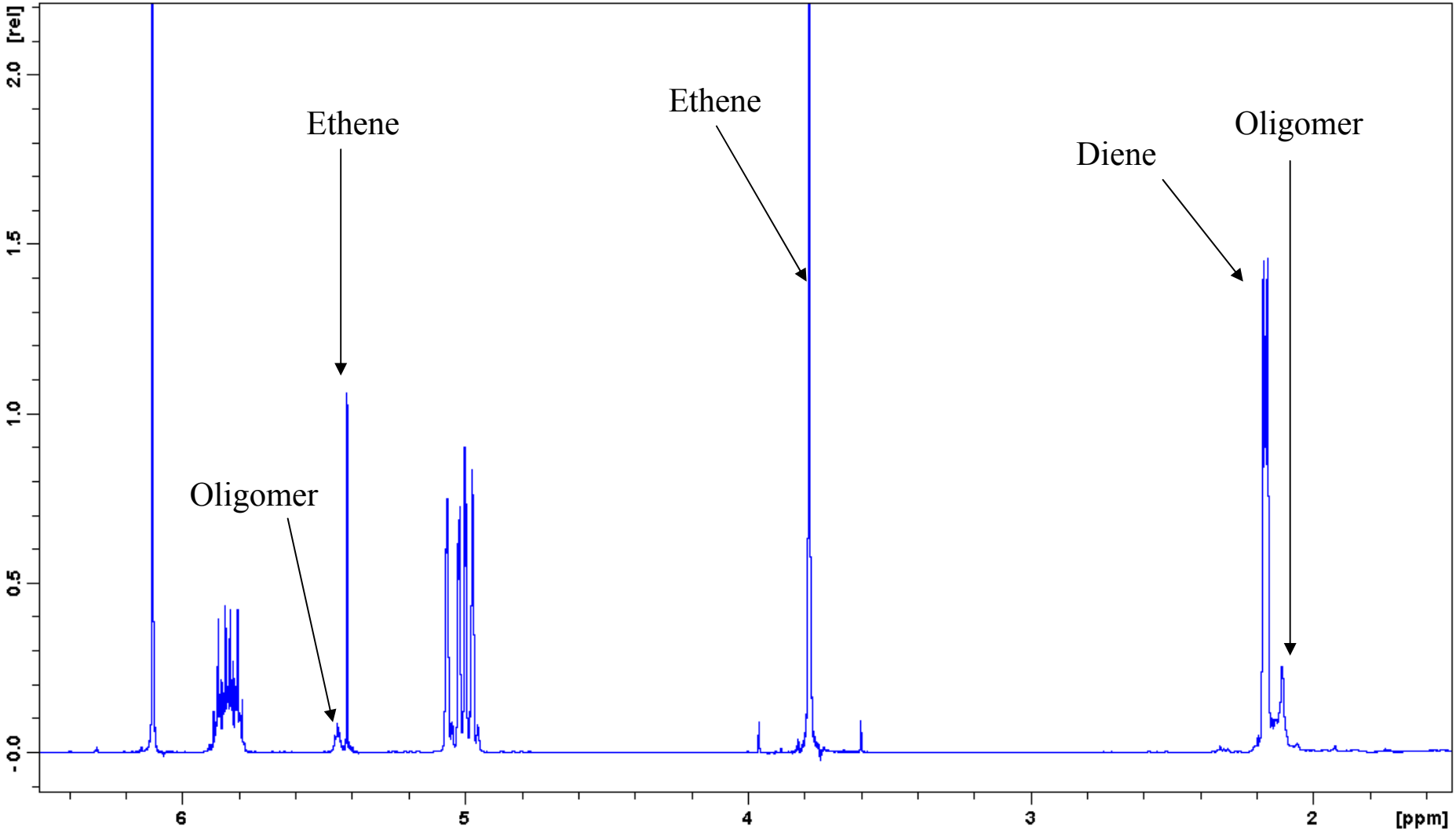
(1) Before pre-catalyst addition



(2) Approx 8 h after addition



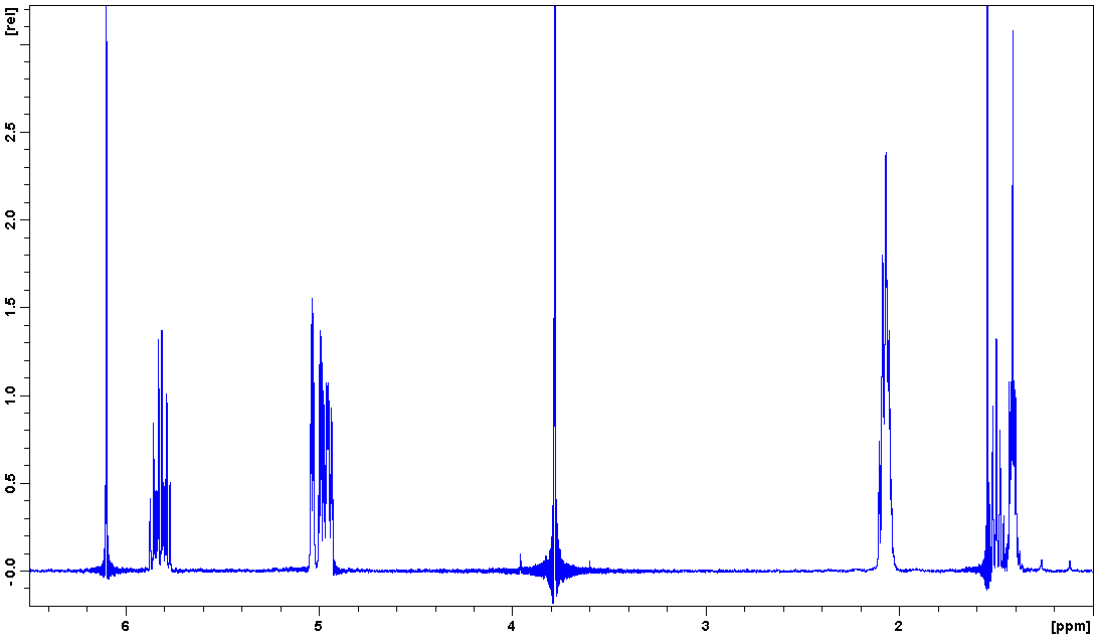
(3) Approx. 8 h after addition (continued)



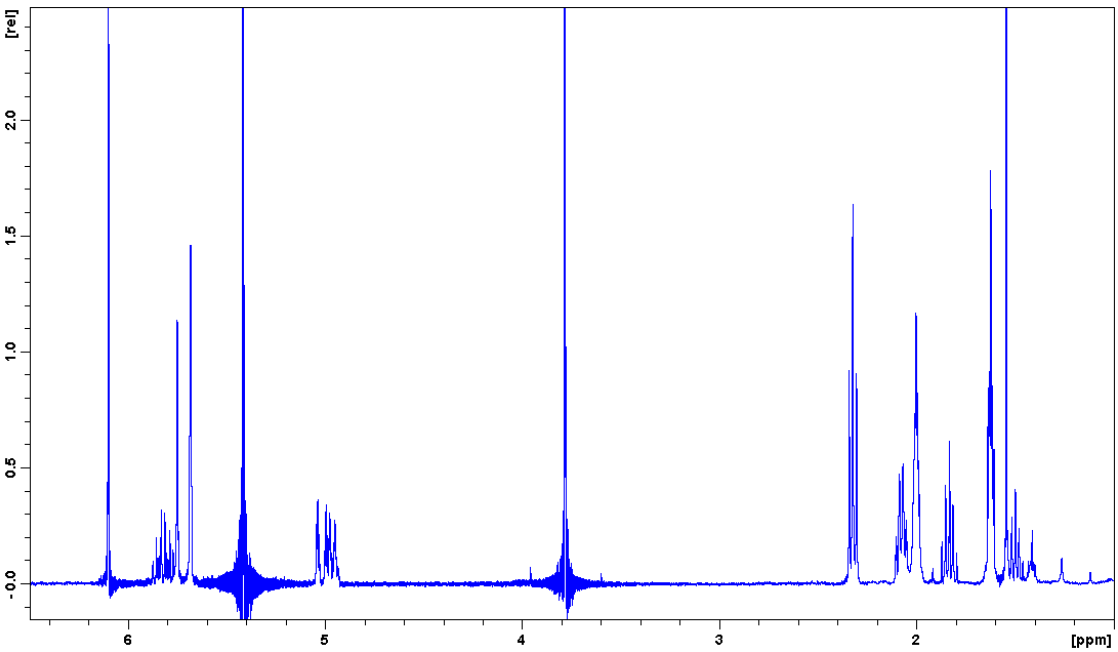
Heptadiene/Octadiene Competition RCM in Chloroform

4.4 mM heptadiene **7b** and 4.5 mM octadiene **7c** (dataset 1) and 4.5 mM heptadiene **7b** and 4.6 mM octadiene **7c**; both with 0.1 mM pre-catalyst **9**. *Analysis by ^{1}H NMR at 400 MHz using a Brüker AV400 equipped with BBFO-z-ATMA probe; the sample temperature was maintained at 298K throughout.*

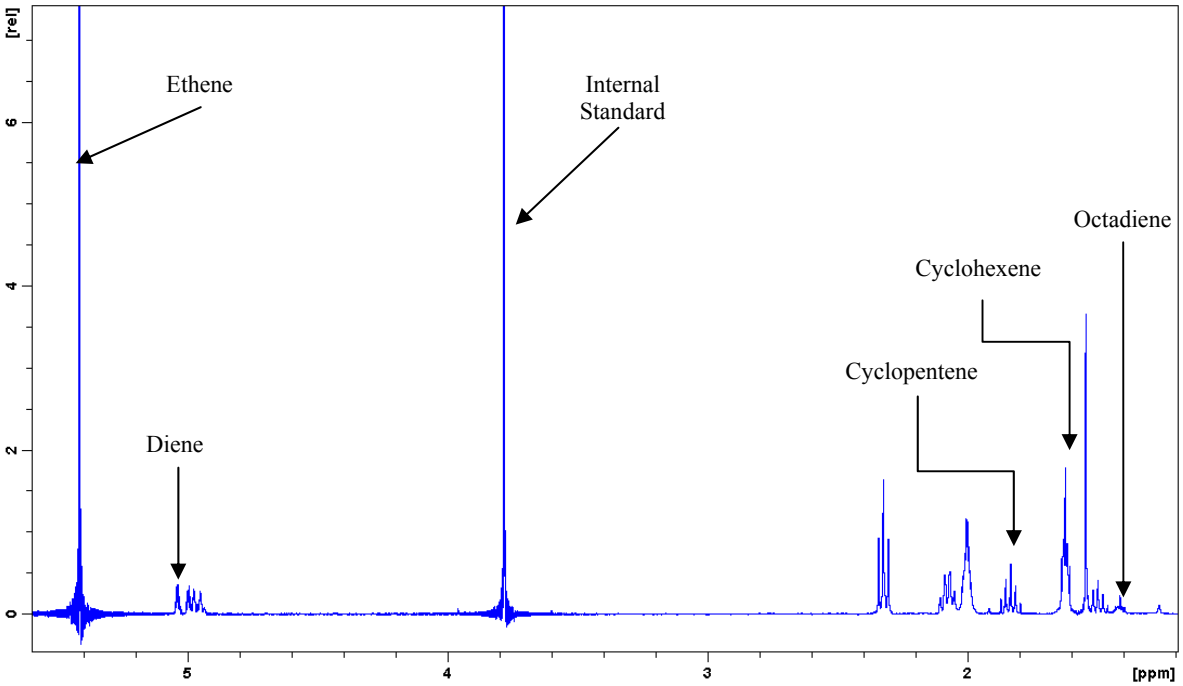
(1) Before pre-catalyst addition

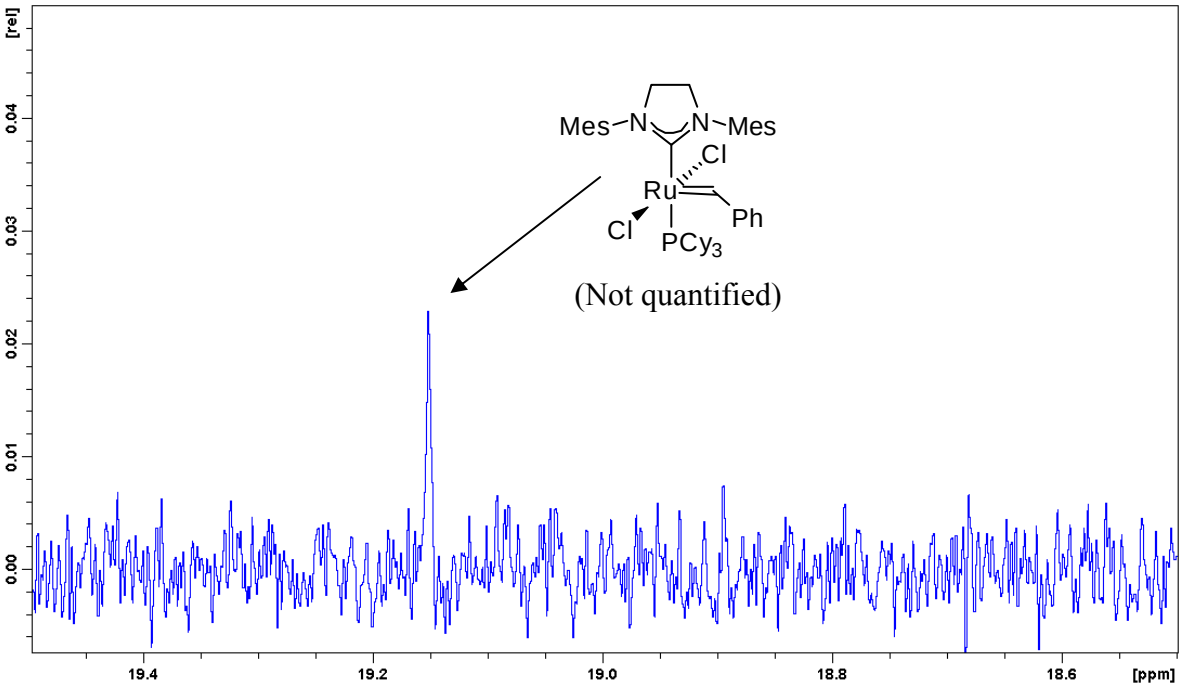


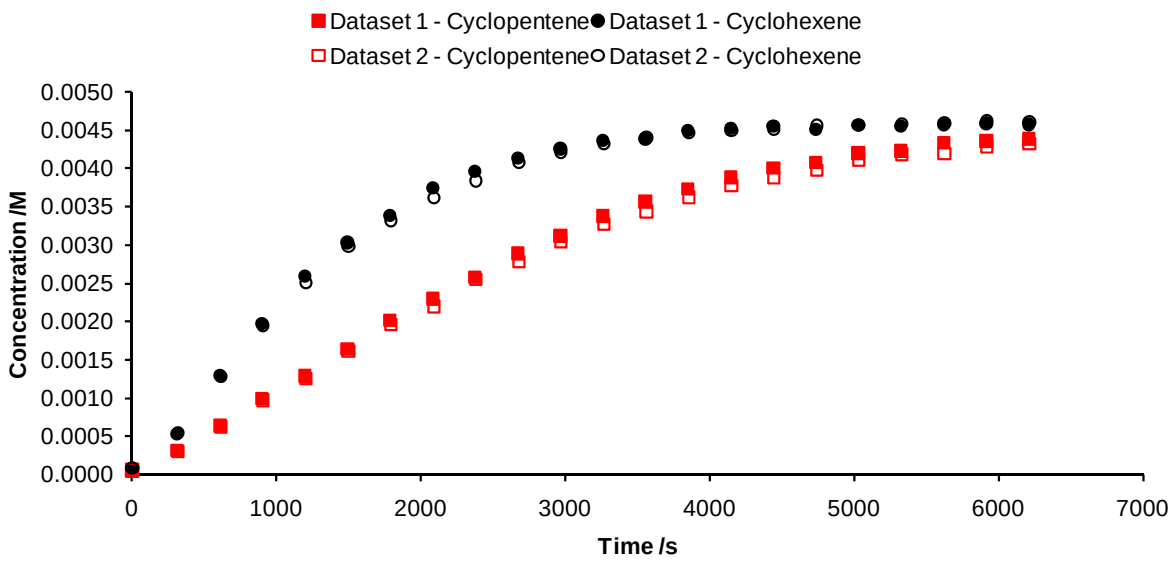
(2) Approx. 1 h after addition

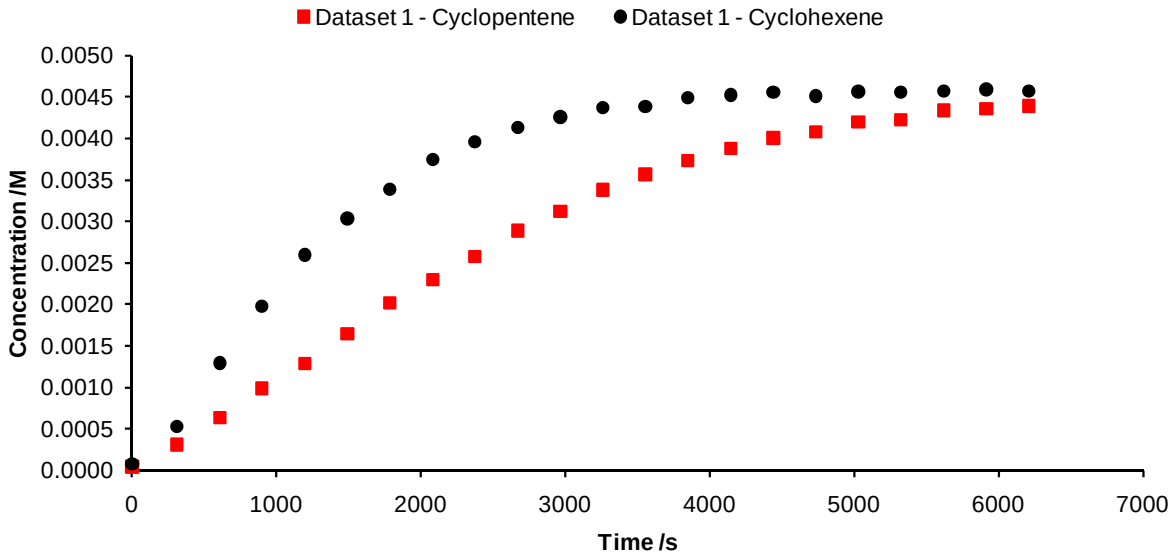


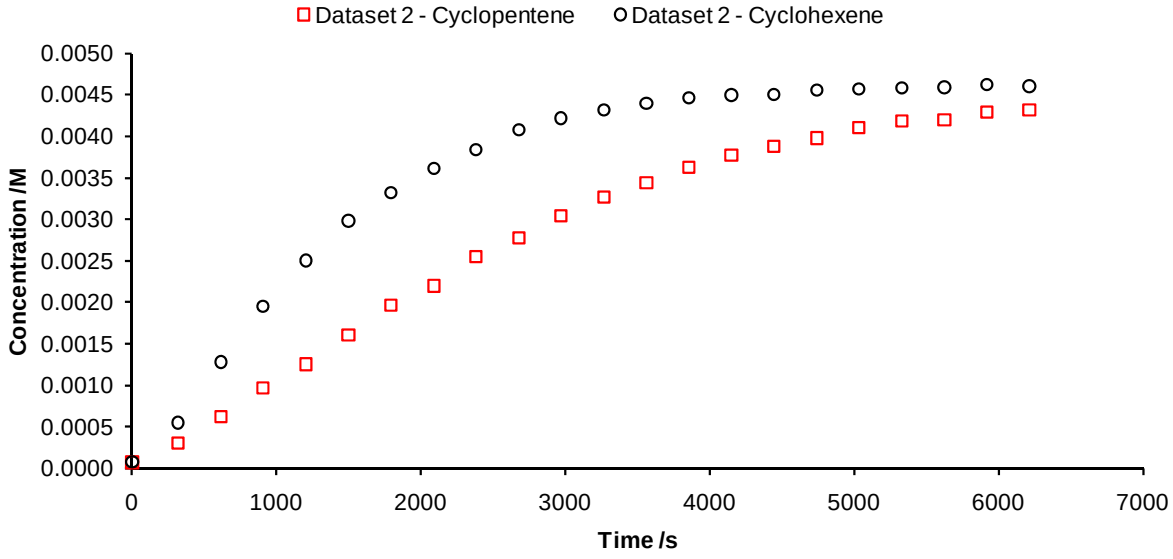
(3) Signals used for quantification






Dataset 1 - Cyclopentene
Dataset 1 - Cyclohexene
Dataset 2 - Cyclopentene
Dataset 2 - Cyclohexene
Concentration /M
0.0050
0.0045
0.0040
0.0035
0.0030
0.0025
0.0020
0.0015
0.0010
0.0005
0.0000
0
1000
2000
3000
4000
5000
6000
7000
Time /s


Dataset 1 - Cyclopentene
Dataset 1 - Cyclohexene
Concentration /M
0.0050
0.0045
0.0040
0.0035
0.0030
0.0025
0.0020
0.0015
0.0010
0.0005
0.0000
0
1000
2000
3000
4000
5000
6000
7000
Time /s


Dataset 2 - Cyclopentene
Dataset 2 - Cyclohexene
Concentration /M
0.0050
0.0045
0.0040
0.0035
0.0030
0.0025
0.0020
0.0015
0.0010
0.0005
0.0000
0
1000
2000
3000
4000
5000
6000
7000
Time /s

*Concentration/time data for the RCM of heptadiene **7b** and octadiene **7c** with pre-catalyst **9** in $CDCl_3$ at 298 K (AV400, BBFO-z-ATMA probe); 4 scans with D_1 = 35 s; TE = 298 K; concentrations obtained by integration of the appropriate signal and the internal standard (see above), with the exception of heptadiene which was calculated from [diene]-[octadiene].*

Dataset 1

t (s)	Cyclohexene (M)	Octadiene (M)	Cyclopentene (M)	Heptadiene (M)
0	0.000085	0.004503	0.000047	0.004389
311	0.000537	0.004061	0.000313	0.004244
606	0.001297	0.003327	0.000641	0.003899
901	0.001978	0.002671	0.000992	0.003547
1196	0.002599	0.002085	0.001293	0.003241
1491	0.003034	0.001654	0.001648	0.002864
1786	0.003387	0.001299	0.002022	0.002492
2080	0.003749	0.000951	0.002299	0.002221
2375	0.003959	0.000740	0.002576	0.001923
2670	0.004133	0.000575	0.002889	0.001626
2965	0.004257	0.000459	0.003118	0.001379
3259	0.004368	0.000375	0.003380	0.001117
3554	0.004386	0.000322	0.003568	0.000943
3849	0.004491	0.000238	0.003730	0.000808
4144	0.004524	0.000208	0.003884	0.000644
4439	0.004555	0.000192	0.004005	0.000505
4733	0.004510	0.000156	0.004081	0.000450
5028	0.004564	0.000184	0.004202	0.000311
5323	0.004553	0.000165	0.004228	0.000233
5618	0.004574	0.000152	0.004336	0.000205
5913	0.004588	0.000135	0.004361	0.000167
6207	0.004574	0.000141	0.004390	0.000139

*Concentration/time data for the RCM of heptadiene **7b** and octadiene **7c** with pre-catalyst **9** in $CDCl_3$ at 298 K (AV400, BBFO-z-ATMA probe); 4 scans with D_1 = 35 s; TE = 298 K; concentrations obtained by integration of the appropriate signal and the internal standard (see above), with the exception of heptadiene which was calculated from [diene]-[octadiene].*

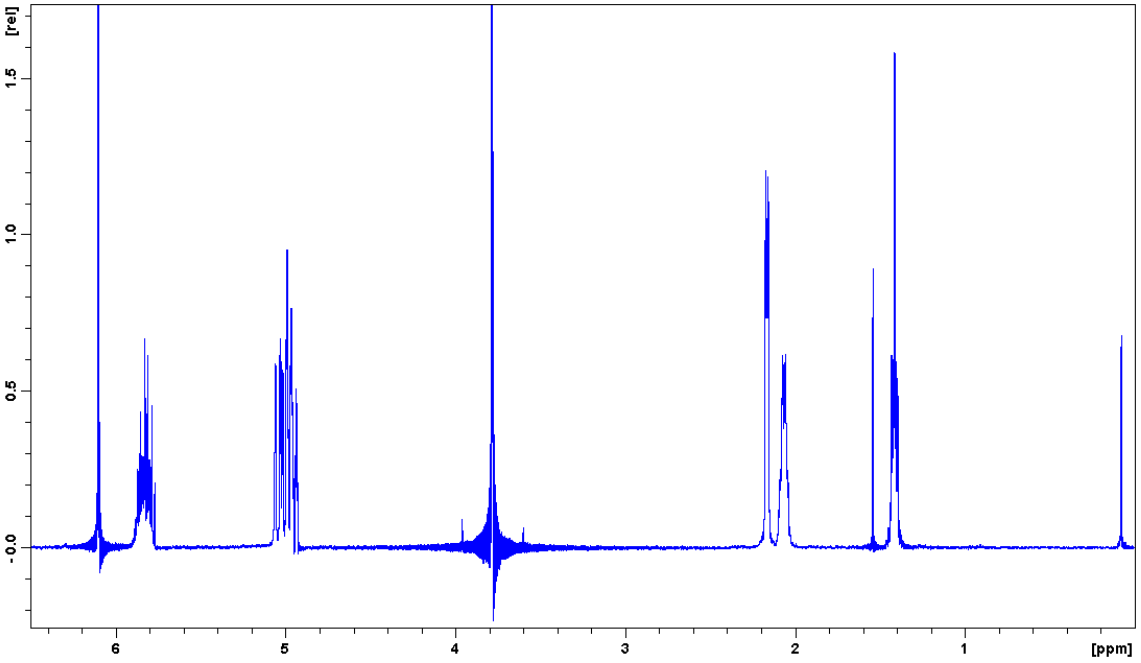
Dataset 2

t (s)	Cyclohexene (M)	Octadiene (M)	Cyclopentene (M)	Heptadiene (M)
0	0.000084	0.004642	0.000073	0.004456
319	0.000554	0.004158	0.000305	0.004154
614	0.001284	0.003438	0.000629	0.003855
908	0.001953	0.002774	0.000973	0.003515
1203	0.002505	0.002210	0.001257	0.003188
1498	0.002984	0.001734	0.001612	0.002871
1793	0.003322	0.001416	0.001965	0.002524
2088	0.003617	0.001094	0.002200	0.002225
2382	0.003840	0.000903	0.002550	0.001913
2677	0.004078	0.000668	0.002777	0.001723
2971	0.004216	0.000564	0.003042	0.001419
3265	0.004318	0.000430	0.003271	0.001232
3560	0.004401	0.000341	0.003437	0.001087
3855	0.004466	0.000322	0.003627	0.000858
4149	0.004499	0.000275	0.003777	0.000719
4444	0.004508	0.000256	0.003876	0.000583
4739	0.004560	0.000205	0.003980	0.000486
5033	0.004568	0.000197	0.004104	0.000391
5328	0.004582	0.000201	0.004188	0.000340
5622	0.004589	0.000164	0.004196	0.000253
5917	0.004623	0.000151	0.004287	0.000208
6212	0.004605	0.000143	0.004319	0.000199

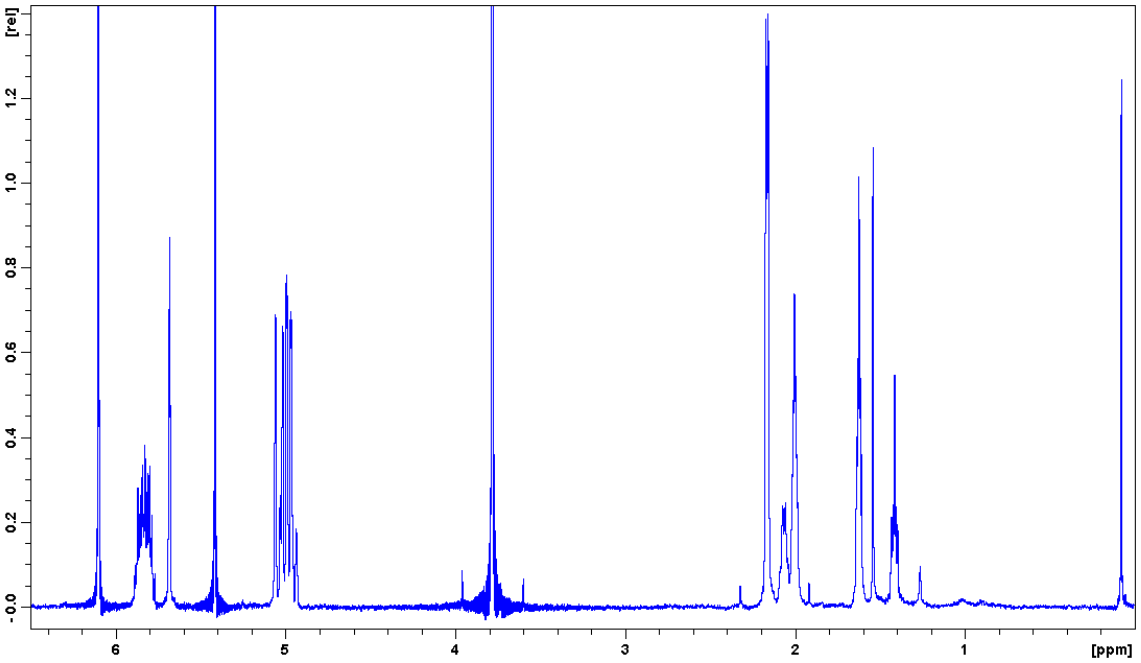
Inhibited Octadiene RCM in Chloroform

5.7 mM hexadiene **7a** and 5.0 mM octadiene **7c** with 0.1 mM pre-catalyst **9**. *Analysis by ^{1}H NMR at 400 MHz using a Brüker AV400 equipped with BBFO-z-ATMA probe; the sample temperature was maintained at 298K throughout.*

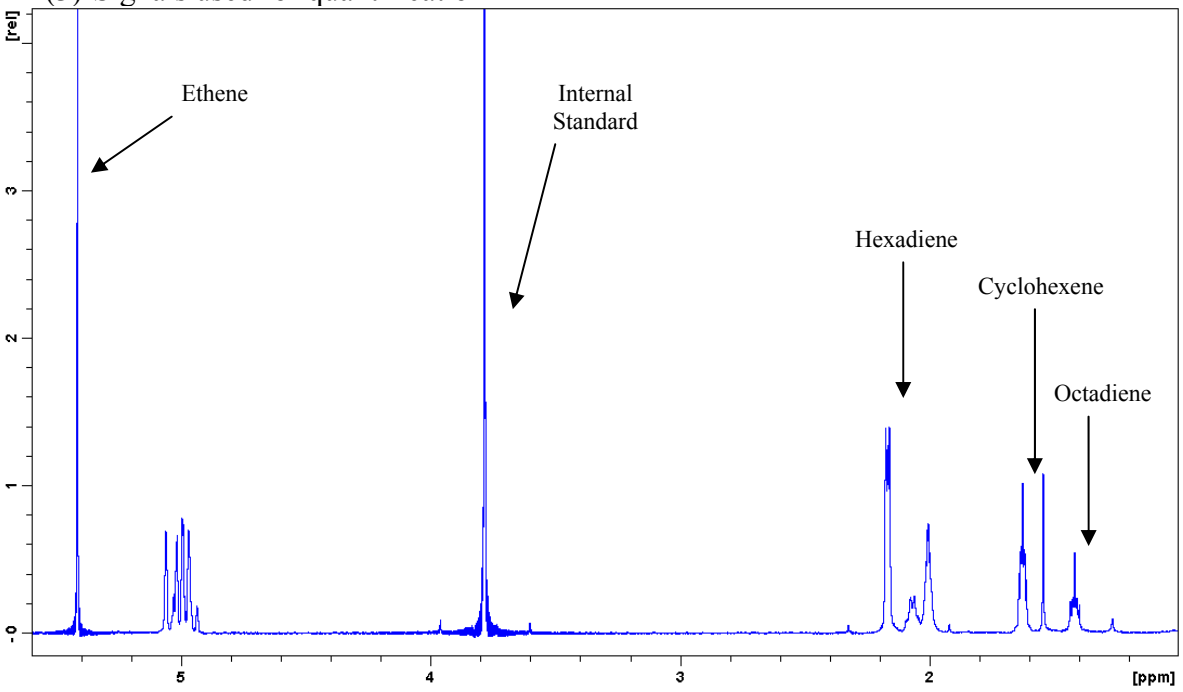
(1) Before pre-catalyst addition

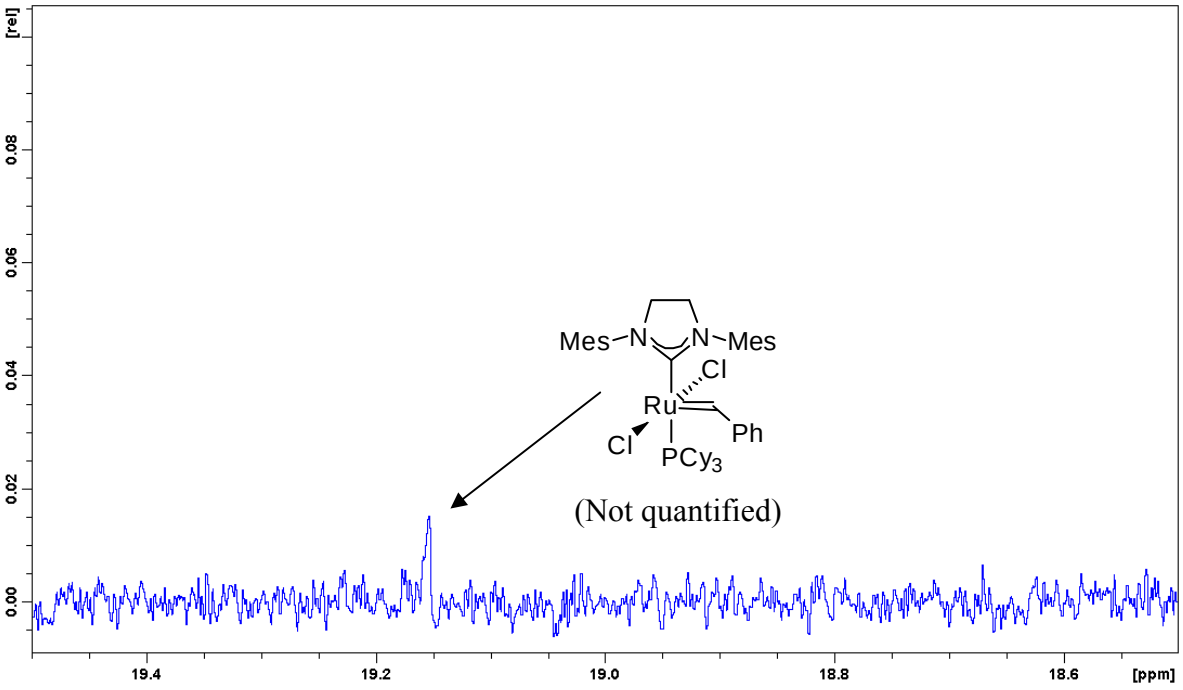


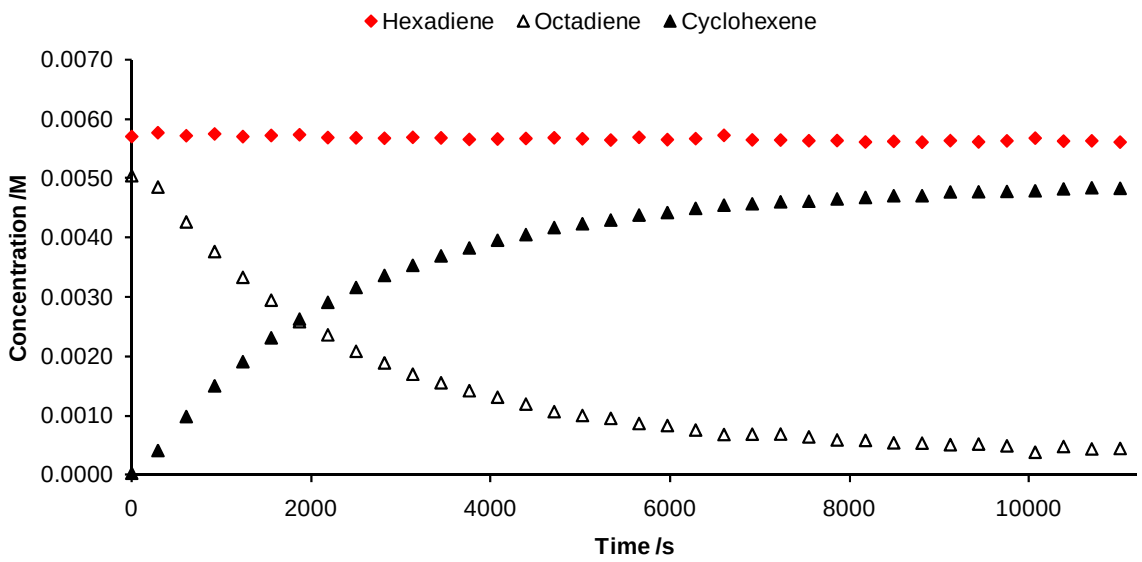
(2) Approx. 1 h after addition

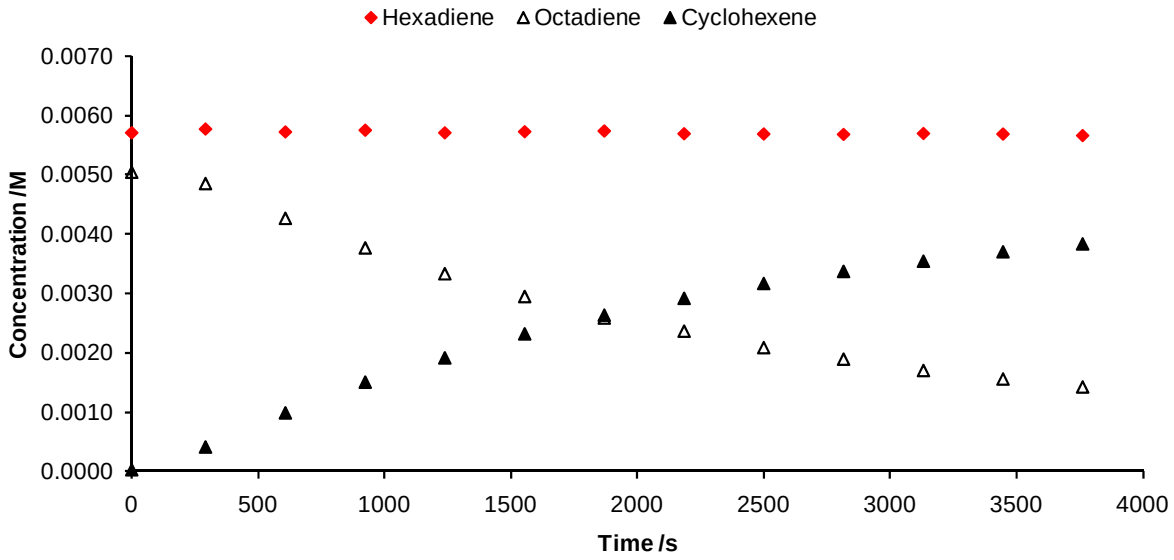


(3) Signals used for quantification






Hexadiene
Octadiene
Cyclohexene
Concentration /M
0.0070
0.0060
0.0050
0.0040
0.0030
0.0020
0.0010
0.0000
0
2000
4000
6000
8000
10000
Time /s


Hexadiene
Octadiene
Cyclohexene
Concentration /M
0.0070
0.0060
0.0050
0.0040
0.0030
0.0020
0.0010
0.0000
0
500
1000
1500
2000
2500
3000
3500
4000
Time /s

*Concentration/time data for the RCM of octadiene **7c** with pre-catalyst **9** in the presence of hexadiene **7a**, in $CDCl_3$ at 298 K (AV400, BBFO-z-ATMA probe); 4 scans with D_1 = 35 s; TE = 298 K; concentrations obtained by integration of the appropriate signal and the internal standard (see above).*

t (s)	Cyclohexene (M)	Octadiene (M)	Hexadiene (M)
0	0.000023	0.005038	0.005702
292	0.000405	0.004847	0.005766
608	0.000980	0.004260	0.005716
924	0.001497	0.003763	0.005746
1239	0.001905	0.003328	0.005701
1555	0.002309	0.002945	0.005720
1870	0.002625	0.002584	0.005733
2186	0.002907	0.002362	0.005685
2501	0.003158	0.002086	0.005680
2817	0.003362	0.001891	0.005674
3133	0.003532	0.001701	0.005689
3448	0.003691	0.001557	0.005680
3763	0.003824	0.001423	0.005654
4078	0.003955	0.001314	0.005661
4394	0.004051	0.001199	0.005670
4709	0.004170	0.001071	0.005682
5024	0.004234	0.001007	0.005665
5340	0.004296	0.000958	0.005644
5655	0.004380	0.000872	0.005690
5971	0.004422	0.000838	0.005650
6286	0.004493	0.000762	0.005667
6602	0.004547	0.000687	0.005722
6917	0.004570	0.000693	0.005646
7233	0.004604	0.000694	0.005643
7548	0.004613	0.000648	0.005632
7863	0.004653	0.000597	0.005635
8179	0.004678	0.000589	0.005611
8494	0.004707	0.000548	0.005622
8810	0.004706	0.000543	0.005607
9125	0.004770	0.000517	0.005634
9440	0.004773	0.000527	0.005613
9756	0.004778	0.000497	0.005630
10071	0.004789	0.000390	0.005676
10387	0.004821	0.000486	0.005626
10702	0.004840	0.000445	0.005631
11018	0.004832	0.000453	0.005609

Coordinates (Å) and Energies (au)

Hexadiene-derived 14e Propagating Carbene 10a

Energy: -2135.863489

1	6	0	-3.545370	-0.853234	0.949496
2	6	0	-2.762773	-0.820096	-0.215486
3	6	0	-3.169154	-0.102841	-1.353495
4	6	0	-4.319791	0.675244	-1.259204
5	6	0	-5.078271	0.730527	-0.091225
6	6	0	-4.688851	-0.057990	0.989323
7	7	0	-1.548730	-1.575551	-0.262100
8	6	0	-0.311979	-1.025756	-0.083429
9	7	0	0.598490	-1.970012	-0.435257
10	6	0	-0.022071	-3.254545	-0.773027
11	6	0	-1.496000	-2.891229	-0.896510
12	6	0	2.011858	-1.871220	-0.295516
13	6	0	2.607544	-2.227189	0.920117
14	6	0	3.992801	-2.108750	1.027218
15	6	0	4.775229	-1.641812	-0.029407
16	6	0	4.139940	-1.277563	-1.217169
17	6	0	2.758986	-1.383060	-1.373651
18	6	0	1.765788	-2.616937	2.095761
19	6	0	2.078342	-0.915112	-2.621414
20	6	0	6.264686	-1.545362	0.101205
21	44	0	-0.104742	0.777264	0.558672
22	6	0	2.794002	5.358062	-0.679551
23	6	0	3.267184	4.392721	0.102010
24	6	0	-2.454656	-0.215927	-2.666244
25	6	0	-6.276733	1.623544	0.004155
26	6	0	-3.221335	-1.753736	2.101408
27	17	0	-0.368329	1.951248	-1.448337
28	17	0	-0.820896	0.387487	2.740124
29	1	0	3.908516	4.652769	0.945397
30	1	0	3.036555	6.402072	-0.513497
31	1	0	-2.158773	-3.593623	-0.381967

32	1	0	-1.824485	-2.823562	-1.942449
33	1	0	0.162709	-3.988312	0.022303
34	1	0	0.405293	-3.654651	-1.697337
35	1	0	4.470460	-2.369502	1.969143
36	1	0	4.733483	-0.890076	-2.042436
37	1	0	-4.629979	1.254698	-2.125558
38	1	0	-5.291438	-0.056454	1.894748
39	1	0	-3.911260	-2.605937	2.118017
40	1	0	-3.324898	-1.229729	3.053298
41	1	0	-2.202838	-2.138763	2.052361
42	1	0	-1.402620	-0.482626	-2.557169
43	1	0	-2.488595	0.727201	-3.213295
44	1	0	-2.935968	-0.977399	-3.292658
45	1	0	1.135197	-3.487194	1.888560
46	1	0	1.089806	-1.800887	2.379437
47	1	0	2.384549	-2.857498	2.961315
48	1	0	1.486221	-0.012003	-2.428456
49	1	0	1.381929	-1.661885	-3.015254
50	1	0	2.802695	-0.682402	-3.403609
51	1	0	-7.049237	1.197696	0.648594
52	1	0	-6.717694	1.815987	-0.976080
53	1	0	-6.005029	2.594920	0.430945
54	1	0	6.573631	-1.444228	1.143616
55	1	0	6.664725	-0.695333	-0.456354
56	1	0	6.753660	-2.442673	-0.293395
57	1	0	2.138367	5.132878	-1.516991
58	6	0	2.942837	2.945574	-0.062272
59	1	0	3.860706	2.344303	-0.103455
60	1	0	2.411409	2.785711	-1.006723
61	6	0	2.066651	2.411825	1.090498
62	1	0	2.610879	2.466342	2.044831
63	1	0	1.188216	3.065000	1.200720
64	6	0	1.666360	1.003860	0.808402
65	1	0	2.470271	0.263538	0.749637

Hexadiene-derived η^2-complex 11a

Energy: -2135.880350

1	6	0	-3.024457	-1.352089	0.923278
2	6	0	-2.266880	-1.370406	-0.260861
3	6	0	-2.833211	-1.013137	-1.497770
4	6	0	-4.116312	-0.471386	-1.494999
5	6	0	-4.851507	-0.323607	-0.319570
6	6	0	-4.303974	-0.802597	0.869309
7	7	0	-0.902234	-1.798520	-0.211291
8	6	0	0.137849	-0.937310	-0.084261
9	7	0	1.266375	-1.671256	-0.132892
10	6	0	1.013775	-3.117058	-0.239372
11	6	0	-0.494228	-3.183888	-0.450583
12	6	0	2.607440	-1.196148	-0.045560
13	6	0	3.216609	-1.096935	1.210153
14	6	0	4.531147	-0.634562	1.260408
15	6	0	5.228517	-0.274975	0.107223
16	6	0	4.579122	-0.376557	-1.123989
17	6	0	3.267690	-0.836175	-1.226399
18	6	0	2.442705	-1.395065	2.455824
19	6	0	2.549384	-0.883742	-2.538130
20	6	0	6.650253	0.192097	0.183713
21	44	0	-0.368036	1.033793	0.158085
22	6	0	-1.901597	2.741760	0.188570
23	6	0	-0.766304	3.302444	0.706437
24	6	0	-2.140211	-1.287497	-2.796535
25	6	0	-6.196056	0.335193	-0.334322
26	6	0	-2.528784	-1.978561	2.189775
27	17	0	-0.499234	1.381460	-2.233728
28	17	0	-0.793723	0.674481	2.481119
29	1	0	-0.642264	3.298860	1.789158
30	1	0	-2.673710	2.361813	0.854848
31	1	0	-0.997695	-3.858989	0.248587
32	1	0	-0.768009	-3.489968	-1.468467
33	1	0	1.337835	-3.621879	0.678933

34	1	0	1.587510	-3.542167	-1.068526
35	1	0	5.017527	-0.541264	2.228768
36	1	0	5.104535	-0.081961	-2.029789
37	1	0	-4.552234	-0.159819	-2.441527
38	1	0	-4.888296	-0.751430	1.785216
39	1	0	-2.958953	-2.982373	2.296045
40	1	0	-2.825069	-1.397024	3.063688
41	1	0	-1.442554	-2.064525	2.214503
42	1	0	-1.055559	-1.324146	-2.697335
43	1	0	-2.366075	-0.517662	-3.535291
44	1	0	-2.483450	-2.248492	-3.200264
45	1	0	1.998632	-2.395668	2.437157
46	1	0	1.609737	-0.692293	2.581236
47	1	0	3.077629	-1.329662	3.340652
48	1	0	1.698650	-0.190949	-2.547258
49	1	0	2.141201	-1.879051	-2.745260
50	1	0	3.213386	-0.618416	-3.362216
51	1	0	-6.829426	-0.017524	0.482463
52	1	0	-6.722919	0.162108	-1.275443
53	1	0	-6.098447	1.420232	-0.218947
54	1	0	6.885735	0.613237	1.163253
55	1	0	6.868225	0.949212	-0.572980
56	1	0	7.346499	-0.636292	0.013850
57	1	0	-2.163241	2.859054	-0.858691
58	6	0	0.308747	3.972365	-0.082389
59	1	0	0.431270	5.019527	0.216412
60	1	0	0.061815	3.948974	-1.147189
61	6	0	1.598388	3.187458	0.171603
62	1	0	2.374983	3.380796	-0.583562
63	1	0	2.053248	3.479085	1.133461
64	6	0	1.313244	1.734567	0.251987
65	1	0	2.186507	1.087335	0.385431

Heptadiene-derived 14e Propagating Carbene 10b

Energy: -2175.155185

1	44	0	-0.508283	-0.337861	-0.934876
2	17	0	0.137242	-0.561593	-3.160840
3	17	0	-0.997090	-1.378879	1.103750
4	6	0	-3.260865	-0.035170	-1.337601
5	1	0	-3.700474	0.276651	-2.297403
6	6	0	-5.562271	-0.467498	-0.334774
7	1	0	-6.048709	-0.179464	-1.274949
8	6	0	-4.230060	0.266034	-0.188921
9	1	0	-4.405176	1.348569	-0.137078
10	1	0	-3.751311	-0.013282	0.758067
11	1	0	-3.104024	-1.121749	-1.411229
12	6	0	0.869997	0.854128	-0.312187
13	7	0	0.896582	2.204164	-0.147484
14	7	0	2.101778	0.383970	0.038241
15	6	0	2.154058	2.672578	0.444231
16	1	0	2.534404	3.542409	-0.099355
17	1	0	1.991345	2.979166	1.486152
18	6	0	3.056086	1.450603	0.331327
19	1	0	3.787083	1.542583	-0.483270
20	1	0	3.607299	1.235008	1.251928
21	6	0	2.515943	-0.973926	-0.130870
22	6	0	3.232976	-3.647777	-0.473086
23	6	0	2.432469	-1.849457	0.963409
24	6	0	3.041431	-1.389002	-1.366133
25	6	0	3.376357	-2.732659	-1.514495
26	6	0	2.782449	-3.182619	0.760310
27	1	0	3.761967	-3.071501	-2.473284
28	1	0	2.698914	-3.876708	1.593560
29	6	0	-0.235847	3.069433	-0.176047
30	6	0	-2.484842	4.709334	-0.280347

31	6	0	-0.494087	3.791991	-1.344641
32	6	0	-1.077971	3.137519	0.941577
33	6	0	-2.195265	3.965642	0.865129
34	6	0	-1.624470	4.609586	-1.372697
35	1	0	-2.868034	4.017303	1.718494
36	1	0	-1.846518	5.169278	-2.278395
37	6	0	0.371941	3.608596	-2.551690
38	1	0	1.426463	3.806999	-2.336424
39	1	0	0.065033	4.269504	-3.363734
40	1	0	0.318384	2.575448	-2.914780
41	6	0	-0.840251	2.274049	2.140209
42	1	0	-1.000649	1.216811	1.896768
43	1	0	-1.516696	2.537408	2.954978
44	1	0	0.183603	2.353320	2.518530
45	6	0	3.319059	-0.421156	-2.475792
46	1	0	4.361324	-0.081957	-2.427789
47	1	0	2.673327	0.457342	-2.443440
48	1	0	3.172819	-0.888442	-3.450477
49	6	0	2.045727	-1.377771	2.331434
50	1	0	1.483981	-0.444120	2.307668
51	1	0	2.942895	-1.220248	2.942753
52	1	0	1.427618	-2.117587	2.842861
53	6	0	-3.692155	5.595668	-0.325924
54	1	0	-3.919629	5.916735	-1.344003
55	1	0	-3.543815	6.497888	0.276607
56	1	0	-4.575560	5.091327	0.074932
57	6	0	3.545350	-5.098080	-0.678312
58	1	0	2.665180	-5.638872	-1.042060
59	1	0	3.855795	-5.580531	0.251061
60	1	0	4.335886	-5.241453	-1.418125
61	6	0	-1.976788	0.691421	-1.124494
62	1	0	-2.043501	1.783282	-1.097600
63	6	0	-6.481752	-0.213319	0.812189
64	1	0	-6.108459	-0.514500	1.792171

65	6	0	-7.679200	0.356423	0.724400
66	1	0	-8.087720	0.673453	-0.231989
67	1	0	-8.301358	0.522947	1.597083
68	1	0	-5.357795	-1.544817	-0.409451

Heptadiene-derived η^2-complex 11b

Energy: -2175.173473

1	44	0	-0.408964	-0.741531	0.206990
2	17	0	-0.627399	-1.180287	-2.177652
3	17	0	-0.132200	-0.674073	2.612525
4	6	0	-3.125543	0.252607	-0.535740
5	1	0	-3.668682	1.202650	-0.448819
6	6	0	-3.346511	-2.251860	-0.195688
7	1	0	-4.069315	-3.037986	0.065839
8	1	0	-3.031379	-2.440121	-1.227817
9	6	0	-4.043640	-0.900867	-0.085362
10	1	0	-4.951875	-0.891507	-0.696016
11	1	0	-4.363247	-0.733477	0.951572
12	1	0	-2.851146	0.096852	-1.583587
13	6	0	0.951564	0.714575	0.030324
14	7	0	0.872074	2.056086	-0.081398
15	7	0	2.262698	0.377804	0.078577
16	6	0	2.194065	2.696024	-0.000637
17	1	0	2.300098	3.457389	-0.777964
18	1	0	2.316262	3.187871	0.972299
19	6	0	3.146282	1.517026	-0.173822
20	1	0	3.562717	1.461409	-1.188888
21	1	0	3.979587	1.528998	0.534470
22	6	0	2.667476	-0.993659	0.003129
23	6	0	3.243646	-3.719360	-0.130648
24	6	0	2.999286	-1.678679	1.183148
25	6	0	2.721793	-1.621918	-1.254714
26	6	0	2.993876	-2.986705	-1.291008
27	6	0	3.268722	-3.044409	1.087499
28	1	0	3.011808	-3.488849	-2.255684
29	1	0	3.506628	-3.593046	1.996107
30	6	0	-0.329188	2.824515	-0.131897
31	6	0	-2.673738	4.326593	-0.259300

32	6	0	-0.935065	3.037082	-1.378712
33	6	0	-0.860993	3.355914	1.049998
34	6	0	-2.034670	4.103565	0.959309
35	6	0	-2.106450	3.789950	-1.415299
36	1	0	-2.465665	4.512799	1.870265
37	1	0	-2.589893	3.958445	-2.375200
38	6	0	-0.354431	2.445209	-2.622961
39	1	0	0.711002	2.676992	-2.725467
40	1	0	-0.866736	2.818884	-3.511251
41	1	0	-0.438585	1.351487	-2.617871
42	6	0	-0.219236	3.079769	2.373340
43	1	0	-0.040608	2.007185	2.516589
44	1	0	-0.848794	3.428280	3.193630
45	1	0	0.748141	3.584344	2.472062
46	6	0	2.582789	-0.848814	-2.529661
47	1	0	3.563861	-0.474442	-2.848682
48	1	0	1.906198	0.001170	-2.436305
49	1	0	2.192145	-1.478185	-3.329707
50	6	0	3.143819	-0.974292	2.495715
51	1	0	2.607581	-0.026366	2.517418
52	1	0	4.204457	-0.780358	2.697810
53	1	0	2.758427	-1.581625	3.316324
54	6	0	-3.956911	5.097300	-0.327287
55	1	0	-4.816037	4.424434	-0.425549
56	1	0	-3.981155	5.765945	-1.191298
57	1	0	-4.116994	5.697419	0.570432
58	6	0	3.469931	-5.198582	-0.194384
59	1	0	2.516775	-5.738156	-0.213822
60	1	0	4.027167	-5.560791	0.671944
61	1	0	4.015332	-5.486795	-1.095992
62	6	0	-0.986396	-2.970382	0.388626
63	1	0	-0.269449	-3.229540	1.165560
64	1	0	-0.827023	-3.372267	-0.608430
65	6	0	-2.180326	-2.396249	0.724465

66	1	0	-2.344370	-2.135051	1.770888
67	6	0	-1.913021	0.295528	0.323504
68	1	0	-1.993979	0.942194	1.213862

Octadiene-derived 14e Propagating Carbene 10c

Energy: -2214.44627021

1	44	0	1.447375	1.978688	-0.238018
2	17	0	0.932421	0.574984	1.560570
3	17	0	2.261567	2.204467	-2.409467
4	6	0	-1.260388	2.094739	-0.854193
5	1	0	-1.657438	2.549660	-1.774717
6	1	0	-0.955410	1.073249	-1.130093
7	6	0	-4.638496	1.127001	0.860150
8	1	0	-4.196192	0.740105	1.789181
9	1	0	-4.994354	2.139244	1.089171
10	6	0	-2.352213	2.028559	0.219296
11	1	0	-1.915557	1.620387	1.139756
12	1	0	-2.677927	3.049641	0.461166
13	6	0	-3.545887	1.188335	-0.205562
14	1	0	-3.969815	1.583789	-1.137887
15	1	0	-3.207864	0.170218	-0.439989
16	6	0	2.666503	3.143804	0.691082
17	7	0	2.570179	4.451845	1.047500
18	7	0	3.892341	2.705488	1.102608
19	6	0	3.725614	4.907335	1.827155
20	1	0	4.078211	5.876196	1.461562
21	1	0	3.446564	5.033265	2.881888
22	6	0	4.731687	3.783112	1.622677
23	1	0	5.508449	4.046249	0.892229
24	1	0	5.229979	3.475391	2.546871
25	6	0	4.435975	1.430587	0.750680
26	6	0	5.403116	-1.084992	0.034524
27	6	0	4.361829	0.380999	1.679306
28	6	0	5.073772	1.270849	-0.491229
29	6	0	5.529945	-0.000258	-0.831428
30	6	0	4.840577	-0.868199	1.290596
31	1	0	6.002333	-0.142917	-1.800567
32	1	0	4.765897	-1.696462	1.991413
33	6	0	1.384615	5.241069	1.019028
34	6	0	-0.935852	6.778698	0.933062
35	6	0	1.178554	6.097085	-0.067948

36	6	0	0.449327	5.114812	2.053509
37	6	0	-0.702044	5.898188	1.989606
38	6	0	0.011220	6.858747	-0.088933
39	1	0	-1.444051	5.805132	2.779604
40	1	0	-0.169353	7.520344	-0.933280
41	6	0	2.148663	6.113182	-1.207631
42	1	0	3.171876	6.314798	-0.875153
43	1	0	1.879516	6.868650	-1.947355
44	1	0	2.172397	5.137912	-1.708726
45	6	0	0.633458	4.099005	3.137529
46	1	0	0.561556	3.080731	2.735589
47	1	0	-0.126081	4.208310	3.913127
48	1	0	1.613739	4.170982	3.618585
49	6	0	5.347560	2.430421	-1.400007
50	1	0	6.349153	2.832771	-1.203184
51	1	0	4.626492	3.240992	-1.286288
52	1	0	5.318403	2.124349	-2.446453
53	6	0	3.844556	0.588283	3.069619
54	1	0	3.164975	1.437833	3.137322
55	1	0	4.678154	0.760162	3.761764
56	1	0	3.303677	-0.291477	3.422374
57	6	0	-2.167621	7.631308	0.902437
58	1	0	-2.494371	7.832654	-0.120148
59	1	0	-1.985733	8.602140	1.376006
60	1	0	-2.996357	7.164415	1.438682
61	6	0	5.851343	-2.452721	-0.379611
62	1	0	5.064569	-2.967215	-0.941299
63	1	0	6.091411	-3.077880	0.482804
64	1	0	6.729962	-2.412431	-1.027418
65	6	0	-7.048832	0.676633	0.336864
66	1	0	-7.844692	0.005914	0.031880
67	1	0	-7.332057	1.705991	0.542292
68	6	0	-5.790590	0.266967	0.459666
69	1	0	-5.550124	-0.774156	0.238777
70	6	0	-0.099001	2.894920	-0.370013
71	1	0	-0.295997	3.943212	-0.126119

Octadiene-derived η^2-complex 11c

Energy: -2214.4567771

1	44	0	-0.238614	-0.791504	-0.114933
2	17	0	0.054953	-1.451097	2.203568
3	17	0	-0.508643	-0.472410	-2.509704
4	6	0	-3.079571	0.252244	-0.459654
5	1	0	-3.357011	1.292785	-0.236058
6	1	0	-2.932478	0.172501	-1.539589
7	6	0	-2.945786	-2.607167	-1.193269
8	1	0	-3.146842	-3.605700	-1.604397
9	1	0	-2.555294	-2.028677	-2.039533
10	6	0	-4.193876	-0.687802	0.042457
11	1	0	-4.043654	-0.857178	1.116791
12	1	0	-5.161774	-0.183890	-0.037665
13	6	0	-4.269319	-2.026650	-0.696760
14	1	0	-4.773757	-2.756539	-0.052272
15	1	0	-4.915892	-1.913023	-1.573929
16	6	0	0.940549	0.815623	-0.039360
17	7	0	0.686770	2.143036	-0.061018
18	7	0	2.280486	0.649957	-0.119017
19	6	0	1.923763	2.936121	0.000742
20	1	0	1.880454	3.775638	-0.697730
21	1	0	2.058413	3.345769	1.011480
22	6	0	2.990441	1.908523	-0.354499
23	1	0	3.305140	1.975968	-1.404894
24	1	0	3.883991	1.977367	0.271330
25	6	0	2.899136	-0.639949	-0.111972
26	6	0	3.983242	-3.205477	0.001542
27	6	0	3.346986	-1.141388	1.124398
28	6	0	3.062843	-1.359859	-1.303288
29	6	0	3.591282	-2.652073	-1.211705
30	6	0	3.875658	-2.424069	1.156345
31	1	0	3.709671	-3.231130	-2.125191
32	1	0	4.205369	-2.831257	2.109231
33	6	0	-0.580385	2.752360	0.182905
34	6	0	-3.035311	3.985008	0.659238
35	6	0	-1.283401	3.305124	-0.894458

36	6	0	-1.069010	2.812741	1.496840
37	6	0	-2.304327	3.422123	1.706780
38	6	0	-2.507124	3.919869	-0.629409
39	1	0	-2.701007	3.465688	2.718846
40	1	0	-3.067448	4.348796	-1.457246
41	6	0	-0.754420	3.197588	-2.288780
42	1	0	0.255470	3.611257	-2.377890
43	1	0	-1.394865	3.729921	-2.994077
44	1	0	-0.690617	2.148471	-2.599218
45	6	0	-0.297094	2.214521	2.630676
46	1	0	-0.208660	1.125298	2.535360
47	1	0	-0.776433	2.428000	3.587453
48	1	0	0.725079	2.605100	2.677195
49	6	0	2.785738	-0.765880	-2.649774
50	1	0	3.732179	-0.542177	-3.156021
51	1	0	2.196263	0.148409	-2.599177
52	1	0	2.229617	-1.457257	-3.286120
53	6	0	3.264731	-0.302897	2.360635
54	1	0	2.231765	-0.018272	2.574064
55	1	0	3.852829	0.616745	2.260524
56	1	0	3.643905	-0.847186	3.226862
57	6	0	-4.344080	4.665487	0.922811
58	1	0	-4.932217	4.779677	0.010149
59	1	0	-4.191218	5.667571	1.337438
60	1	0	-4.947155	4.113675	1.648276
61	6	0	4.511978	-4.604699	0.079583
62	1	0	3.787890	-5.272024	0.558329
63	1	0	5.427360	-4.656844	0.675136
64	1	0	4.728303	-5.011600	-0.909880
65	6	0	-0.556385	-3.030571	-0.542353
66	1	0	0.152865	-3.377491	0.205426
67	1	0	-0.292463	-3.137889	-1.592430
68	6	0	-1.847717	-2.756561	-0.186233
69	1	0	-2.106052	-2.797794	0.872720
70	6	0	-1.841620	-0.026188	0.316721
71	1	0	-1.983144	0.174962	1.396508

Metallocyclobutane 12b from heptadiene

Energy: -2175.171237 au

1	44	0	-0.057572	0.782994	0.141920
2	17	0	-0.886641	0.494102	2.400702
3	17	0	0.613455	1.141175	-2.166701
4	6	0	-1.141214	2.438952	0.087749
5	1	0	-1.361913	2.782863	-0.924787
6	1	0	-1.973980	2.464203	0.789550
7	6	0	1.379806	1.828665	0.909777
8	1	0	1.471694	1.655268	1.987216
9	6	0	0.193557	2.948979	0.636143
10	1	0	-0.000460	3.280261	1.661283
11	6	0	2.628367	2.336824	0.220679
12	1	0	2.745084	1.876269	-0.763435
13	1	0	3.514435	2.093000	0.813987
14	6	0	0.915953	3.960704	-0.253627
15	1	0	0.744320	3.690316	-1.299464
16	1	0	0.509660	4.963837	-0.095964
17	6	0	2.397472	3.844863	0.081482
18	1	0	3.042591	4.305668	-0.671517
19	1	0	2.607203	4.342845	1.036627
20	6	0	-0.277674	-1.190186	-0.272772
21	7	0	-1.438226	-1.831011	-0.462122
22	7	0	0.738686	-2.051839	-0.419098
23	6	0	-1.240969	-3.248576	-0.800534
24	1	0	-1.799568	-3.882793	-0.106181
25	1	0	-1.613838	-3.448801	-1.811365
26	6	0	0.275632	-3.421539	-0.678272
27	1	0	0.565893	-4.081793	0.147426
28	1	0	0.734465	-3.808967	-1.592860
29	6	0	2.116318	-1.672650	-0.343347
30	6	0	4.752008	-0.789828	-0.185001
31	6	0	2.836695	-1.473571	-1.528467
32	6	0	2.698721	-1.496568	0.920580
33	6	0	4.016300	-1.047071	0.971235
34	6	0	4.152530	-1.027340	-1.420081

35	1	0	4.479721	-0.896317	1.943855
36	1	0	4.718066	-0.843622	-2.330868
37	6	0	-2.721425	-1.242305	-0.223253
38	6	0	-5.159344	-0.004105	0.298660
39	6	0	-3.339327	-1.454220	1.018444
40	6	0	-3.311632	-0.461308	-1.224326
41	6	0	-4.530411	0.153328	-0.933517
42	6	0	-4.554894	-0.821616	1.254385
43	1	0	-5.000216	0.769022	-1.697246
44	1	0	-5.033309	-0.954465	2.222028
45	6	0	-2.719918	-2.331735	2.061846
46	1	0	-3.065125	-2.051002	3.057897
47	1	0	-1.630377	-2.252224	2.065808
48	1	0	-2.988386	-3.384492	1.907958
49	6	0	-2.667676	-0.284093	-2.564105
50	1	0	-3.385171	0.104707	-3.288758
51	1	0	-2.271170	-1.226218	-2.954255
52	1	0	-1.818170	0.406736	-2.530185
53	6	0	1.935171	-1.784186	2.175640
54	1	0	1.448562	-2.764160	2.135817
55	1	0	1.140858	-1.051459	2.357742
56	1	0	2.598448	-1.777368	3.042171
57	6	0	2.233103	-1.742618	-2.871677
58	1	0	1.155667	-1.568365	-2.876368
59	1	0	2.419589	-2.777472	-3.184913
60	1	0	2.667309	-1.090069	-3.630595
61	6	0	-6.452631	0.688740	0.601854
62	1	0	-7.209070	-0.012475	0.965449
63	1	0	-6.857201	1.193242	-0.277452
64	1	0	-6.321660	1.442854	1.384219
65	6	0	6.141209	-0.236842	-0.099919
66	1	0	6.657548	-0.572838	0.802120
67	1	0	6.121418	0.858660	-0.068499
68	1	0	6.745455	-0.519889	-0.964261

Metallocyclobutane fragmentation transition structure 13b from heptadiene

Energy: -2175.149707 au

1	44	0	0.148615	0.711667	0.255523
2	17	0	-0.449634	0.290168	2.573759
3	17	0	0.731699	1.153416	-2.065504
4	6	0	-1.247738	1.887007	0.145282
5	1	0	-1.399093	2.498713	-0.754714
6	1	0	-1.987145	1.990610	0.950598
7	6	0	1.659144	2.091891	0.987264
8	1	0	1.994687	1.458359	1.808977
9	6	0	0.506551	2.893014	1.143923
10	1	0	-0.073124	2.853518	2.060503
11	6	0	2.641409	2.758600	0.056351
12	1	0	3.073348	2.074296	-0.679199
13	1	0	3.473055	3.139567	0.667312
14	6	0	0.666724	4.164962	0.347466
15	1	0	-0.236327	4.500437	-0.167748
16	1	0	0.907306	4.948942	1.079558
17	6	0	1.847741	3.900858	-0.594355
18	1	0	1.479138	3.571781	-1.566112
19	1	0	2.454725	4.795100	-0.754125
20	6	0	-0.321122	-1.184994	-0.277898
21	7	0	-1.501117	-1.816088	-0.386354
22	7	0	0.663970	-2.058945	-0.563463
23	6	0	-1.333960	-3.180356	-0.915756
24	1	0	-1.963066	-3.886982	-0.369456
25	1	0	-1.632240	-3.208811	-1.971858
26	6	0	0.159447	-3.425307	-0.727155
27	1	0	0.377213	-4.017905	0.172156
28	1	0	0.628415	-3.917408	-1.582817
29	6	0	2.037779	-1.690949	-0.408789
30	6	0	4.638124	-0.722144	-0.128038
31	6	0	2.797197	-1.427742	-1.561771
32	6	0	2.581403	-1.562615	0.879251
33	6	0	3.879219	-1.053121	0.988827
34	6	0	4.088933	-0.942912	-1.393554
35	1	0	4.307370	-0.930625	1.981480
36	1	0	4.678085	-0.709562	-2.277430
37	6	0	-2.785376	-1.208821	-0.219312

38	6	0	-5.272413	-0.012261	0.147964
39	6	0	-3.472490	-1.427604	0.981641
40	6	0	-3.324354	-0.436751	-1.255380
41	6	0	-4.569452	0.156596	-1.042707
42	6	0	-4.713313	-0.816082	1.141885
43	1	0	-5.002418	0.761033	-1.836851
44	1	0	-5.255465	-0.969285	2.072345
45	6	0	-2.881438	-2.275502	2.063001
46	1	0	-3.579900	-2.393374	2.893041
47	1	0	-1.965943	-1.817985	2.451703
48	1	0	-2.621417	-3.277186	1.704083
49	6	0	-2.590533	-0.247738	-2.545339
50	1	0	-3.222677	0.247522	-3.284505
51	1	0	-2.265852	-1.201936	-2.973510
52	1	0	-1.682400	0.352344	-2.420032
53	6	0	1.875329	-2.049334	2.108808
54	1	0	2.291310	-3.018563	2.408853
55	1	0	0.800367	-2.166031	1.975261
56	1	0	2.009447	-1.363395	2.947496
57	6	0	2.249788	-1.681166	-2.930757
58	1	0	1.171206	-1.524296	-2.970719
59	1	0	2.460577	-2.710523	-3.246896
60	1	0	2.706034	-1.013743	-3.663013
61	6	0	-6.594322	0.659902	0.363860
62	1	0	-6.488518	1.539799	1.007222
63	1	0	-7.310130	-0.004723	0.854212
64	1	0	-7.034716	0.996931	-0.576568
65	6	0	6.005684	-0.128352	0.016978
66	1	0	6.420933	-0.306705	1.010685
67	1	0	5.979182	0.956405	-0.134564
68	1	0	6.702929	-0.532690	-0.720754

Metallocyclobutane 12c from octadiene

Energy: -2214.462541 au

1	44	0	0.045934	0.672910	-0.092661

2	17	0	0.810124	0.446981	-2.388788
3	17	0	-0.612906	0.997309	2.210462
4	6	0	1.104751	2.316188	-0.028251
5	1	0	1.929370	2.372360	-0.738749
6	1	0	1.321651	2.679006	0.979204
7	6	0	-1.420502	1.743474	-0.820207
8	1	0	-1.532570	1.574831	-1.897809
9	6	0	-0.250427	2.839794	-0.591279
10	1	0	-0.019589	3.135520	-1.620169
11	6	0	-2.719449	2.079573	-0.140028
12	1	0	-3.462666	1.324775	-0.415890
13	1	0	-2.619805	2.047650	0.946592
14	6	0	-0.818823	3.968250	0.268652
15	1	0	-0.979590	3.579841	1.280150
16	1	0	-0.064605	4.756219	0.357838
17	6	0	-3.171274	3.467374	-0.608093
18	1	0	-3.376752	3.427771	-1.684176
19	6	0	-2.108089	4.543170	-0.313112
20	1	0	-1.868494	5.093619	-1.230183
21	6	0	0.403582	-1.300527	0.152384
22	7	0	1.611404	-1.885456	0.150018
23	7	0	-0.545384	-2.249004	0.202240
24	6	0	1.506611	-3.340696	0.337740
25	1	0	2.175414	-3.866346	-0.347397
26	1	0	1.791817	-3.605564	1.365041
27	6	0	0.030908	-3.593787	0.053570
28	1	0	-0.140734	-3.962448	-0.966154
29	1	0	-0.434198	-4.293492	0.751674
30	6	0	-1.949651	-1.980630	0.277712
31	6	0	-4.660277	-1.384087	0.492212
32	6	0	-2.546808	-1.975955	1.545734
33	6	0	-2.683672	-1.740564	-0.892012
34	6	0	-4.038745	-1.440815	-0.754203
35	6	0	-3.902273	-1.669158	1.626880
36	1	0	-4.621408	-1.239068	-1.650657
37	1	0	-4.374685	-1.641162	2.605997
38	6	0	2.849108	-1.170016	0.128916
39	6	0	5.195392	0.332056	0.027184

40	6	0	3.606456	-1.166188	-1.054361
41	6	0	3.272333	-0.491466	1.279457
42	6	0	4.445542	0.261162	1.196410
43	6	0	4.767460	-0.402209	-1.080840
44	1	0	4.782122	0.799915	2.079487
45	1	0	5.350472	-0.370751	-1.998569
46	6	0	3.199223	-1.970699	-2.249530
47	1	0	2.114638	-2.058678	-2.331637
48	1	0	3.626705	-2.980469	-2.206883
49	1	0	3.557532	-1.507210	-3.169994
50	6	0	2.521468	-0.557494	2.573066
51	1	0	1.907095	-1.457150	2.654592
52	1	0	1.835482	0.287147	2.693452
53	1	0	3.215069	-0.541513	3.417000
54	6	0	-2.049044	-1.821930	-2.245924
55	1	0	-2.701123	-1.389627	-3.007194
56	1	0	-1.865991	-2.863644	-2.534131
57	1	0	-1.090045	-1.297106	-2.295971
58	6	0	-1.744148	-2.274088	2.772160
59	1	0	-2.374648	-2.271087	3.662341
60	1	0	-0.963685	-1.520477	2.912277
61	1	0	-1.255475	-3.252851	2.713179
62	6	0	6.434656	1.170428	-0.048910
63	1	0	6.293596	2.023036	-0.720884
64	1	0	7.282912	0.600923	-0.439141
65	1	0	6.715784	1.565408	0.929011
66	6	0	-6.099003	-0.985029	0.610284
67	1	0	-6.557528	-1.381099	1.518702
68	1	0	-6.687016	-1.324856	-0.245303
69	1	0	-6.196519	0.105871	0.651935
70	1	0	-4.123340	3.717568	-0.130188
71	1	0	-2.500424	5.289903	0.383716

Metallocyclobutane fragmentation transition structure 13c from octadiene

Energy: -2214.445284 au

1	6	0	0.414892	-1.328147	0.340542
2	7	0	-0.564124	-2.204849	0.644999
3	7	0	1.599251	-1.950156	0.469200
4	6	0	-0.047550	-3.563553	0.836529
5	1	0	-0.520098	-4.047541	1.694666
6	1	0	-0.249237	-4.172974	-0.055430
7	6	0	1.439983	-3.299083	1.036349
8	1	0	1.724477	-3.294154	2.096803
9	1	0	2.082936	-4.014852	0.518602
10	6	0	2.880628	-1.340654	0.293946
11	6	0	5.363797	-0.142525	-0.089745
12	6	0	3.572921	-1.582821	-0.899305
13	6	0	3.410896	-0.541831	1.313893
14	6	0	4.654178	0.052127	1.093364
15	6	0	4.812663	-0.971191	-1.067575
16	1	0	5.080648	0.677510	1.874703
17	1	0	5.359955	-1.143353	-1.991719
18	6	0	-1.942542	-1.865543	0.471410
19	6	0	-4.582415	-1.022546	0.158841
20	6	0	-2.709241	-1.579396	1.614741
21	6	0	-2.490910	-1.810064	-0.819663
22	6	0	-3.811263	-1.365988	-0.945586
23	6	0	-4.021028	-1.158239	1.431392
24	1	0	-4.244544	-1.298758	-1.941343
25	1	0	-4.616704	-0.908018	2.306089
26	6	0	-2.135774	-1.738973	2.987316
27	1	0	-2.163641	-2.789028	3.303043
28	1	0	-2.705091	-1.162652	3.717898
29	1	0	-1.099550	-1.397688	3.029814
30	6	0	-1.760238	-2.299694	-2.033054
31	1	0	-1.905438	-1.631764	-2.884383
32	1	0	-2.145187	-3.285467	-2.320097
33	1	0	-0.683614	-2.381596	-1.888229
34	6	0	2.667606	-0.325634	2.594366
35	1	0	2.349391	-1.271375	3.045587
36	1	0	1.755414	0.263624	2.447662
37	1	0	3.290306	0.195036	3.324029
38	6	0	2.983324	-2.448398	-1.967303

39	1	0	2.101388	-1.966907	-2.403556
40	1	0	2.663659	-3.421151	-1.578988
41	1	0	3.703172	-2.629380	-2.767129
42	6	0	-5.968596	-0.480982	-0.006575
43	1	0	-5.969799	0.611061	0.086906
44	1	0	-6.648888	-0.864331	0.757718
45	1	0	-6.384893	-0.723111	-0.986312
46	6	0	6.684130	0.529649	-0.315031
47	1	0	7.123997	0.880448	0.620581
48	1	0	6.576101	1.400684	-0.970029
49	1	0	7.401205	-0.139887	-0.796637
50	44	0	-0.048694	0.554483	-0.227559
51	17	0	-0.627310	1.162470	2.050202
52	17	0	0.521874	0.091115	-2.545673
53	6	0	1.377869	1.702221	-0.191082
54	1	0	2.081369	1.781406	-1.030131
55	1	0	1.593674	2.313365	0.695433
56	6	0	-1.533464	1.923001	-1.042112
57	1	0	-1.663012	1.416781	-1.999125
58	6	0	-0.414155	2.783989	-0.966918
59	1	0	0.175624	2.861621	-1.878186
60	6	0	-0.449275	3.969389	-0.028251
61	1	0	0.243774	4.736808	-0.385081
62	1	0	-0.116025	3.675818	0.973277
63	6	0	-2.799280	2.167434	-0.256061
64	1	0	-3.062025	1.281386	0.334042
65	1	0	-3.596749	2.258256	-1.008616
66	6	0	-2.781994	3.409010	0.638756
67	1	0	-3.805716	3.778545	0.759895
68	1	0	-2.425088	3.129874	1.634298
69	6	0	-1.877845	4.500313	0.087074
70	1	0	-2.232378	4.836302	-0.897337
71	1	0	-1.895445	5.378040	0.740372

Basis Set Details.

The calculations were carried out using a locally modified version of GAUSSIAN 03.[1]

Ru has the SDD pseudopotential and SDD basis set. In addition it has an f-function with exponent 0.57800.

C, N, Cl and H have the 6-311G** basis set.

The functional is M06-L and the solvation model is COSMO (with the default Klamt radii and DCM as solvent).

The frequencies are with the B1 basis set.

Ru has the LANL2DZ pseudo potential and LANL2DZ basis set with an addition f-function of exponent 0.57800.

C, N, Cl and H have the 6-31G* basis set

(The frequencies were used to provide thermodynamic corrections to the solvation energies)

Reference

1. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *Gaussian 03, Revision D.02,* Gaussian Inc., Wallingford, CT, 2004.