

Supporting information belonging to the paper:

The role of β -H elimination in Rh Mediated Carbene Insertion Polymerization

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S1. Calculated energies

Table S1-1: Calculated energies (B3LYP/TZVP//B3LYP/SVP), for more details see text. The free energy correction terms G_{corr} (298 K, 0.1 MPa) include the zero vibrational energies ($E_{\text{vib},0}$), but not the SCF-energies and the Truton entropic correction term.

	E_{SCF} (a.u.)	E_{SCF} (Solvent, a.u.)	$E_{\text{vib},0}$ (a.u.)	G_{corr} (kJ/mol)
A	-1263.78980	-1263.80517	0.43160	992.83
A – β -H agostic complex	-1263.76991	-1263.78616	0.42965	986.77
A_TS	-1263.75443	-1263.77008	0.42603	977.71
B - N coordinated	-1640.35201	-1640.37548	0.51016	1148.50
B - C coordinated	-1640.34777	-1640.37029	0.50974	1174.12
B_TS	-1640.32853	-1640.35078	0.50724	1166.38
C	-1530.85095	-1530.87289	0.49913	1150.78
D	-1263.75574	-1263.77173	0.42731	979.84
E	-423.03616	-423.04254	0.18831	406.56
E - dimer	-846.14267	-846.14924	0.37751	878.70
E - tetramer	-1692.32697	-1692.33072	0.75774	1824.28
<i>Activation of MDA</i>				
F - N coordinated	-799.63887	-799.65212	0.26671	586.22
F - C coordinated	-799.62560	-799.63644	0.26589	584.02
F_TS	-799.61127	-799.62218	0.26362	577.98
G	-690.13520	-690.14633	0.25532	586.51
<i>Insertion of DMM</i>				
H_dmm	-957.32074	-957.33479	0.32852	739.42
H_TS_dmm	-957.32033	-957.33405	0.32779	739.16
I	-957.36189	-957.37361	0.33242	786.11
<i>Insertion of DMF</i>				
H_dmf	-957.33392	-957.34762	0.32917	740.99
H_TS_dmf	-957.32889	-957.34213	0.32755	737.90
(Z)-trimethyl but-1-ene-1,2,3-tricarboxylate	-840.69237	-840.70809	0.23703	505.07
dmf	-534.26083	-534.27198	0.13820	267.62
dmm	-534.25120	-534.26331	0.13800	266.67
mda	-376.56942	-376.57814	0.07646	117.65
N ₂	-109.51486	-109.51571	0.00567	-33.53

S2. Calculated structures

Pictures of the lowest conformers of the calculated compounds (see scheme 3). Carbon (grey) and hydrogen (light grey) atoms are not labelled.

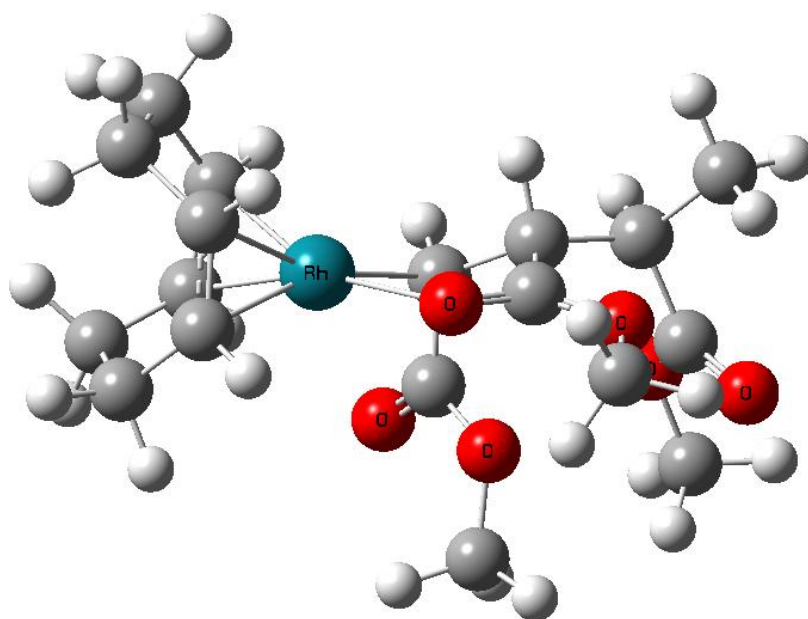


Figure S2-1: A.

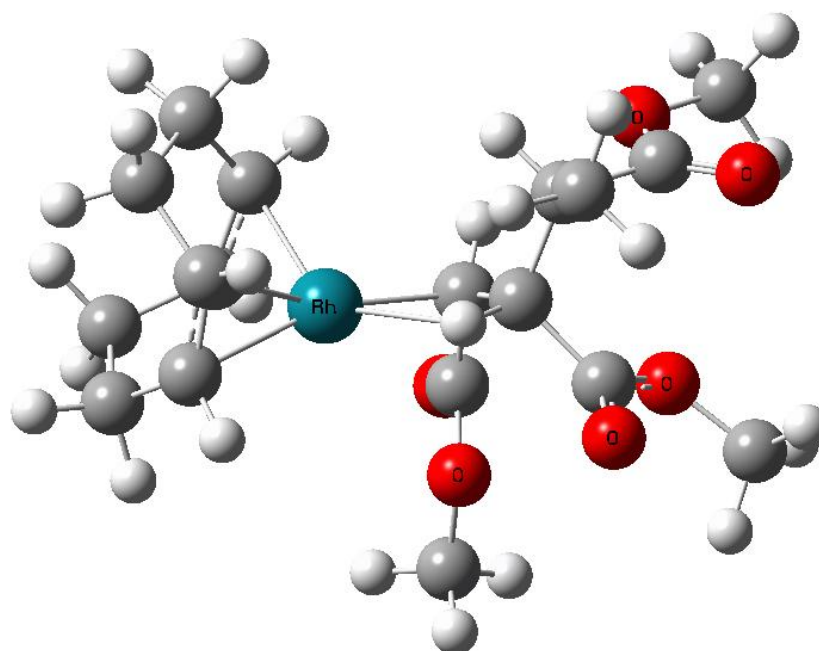


Figure S2-2: A β -H agnostic complex.

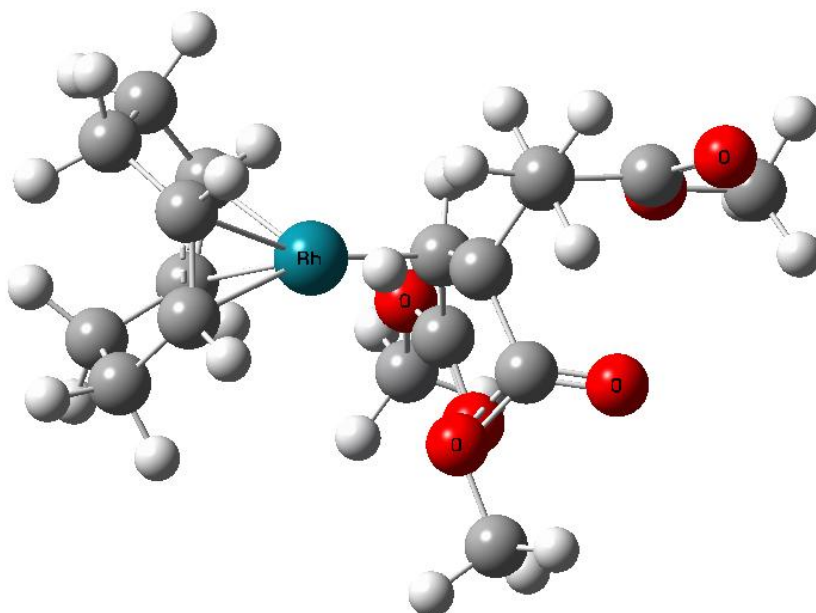


Figure S2-3: **A_TS**.

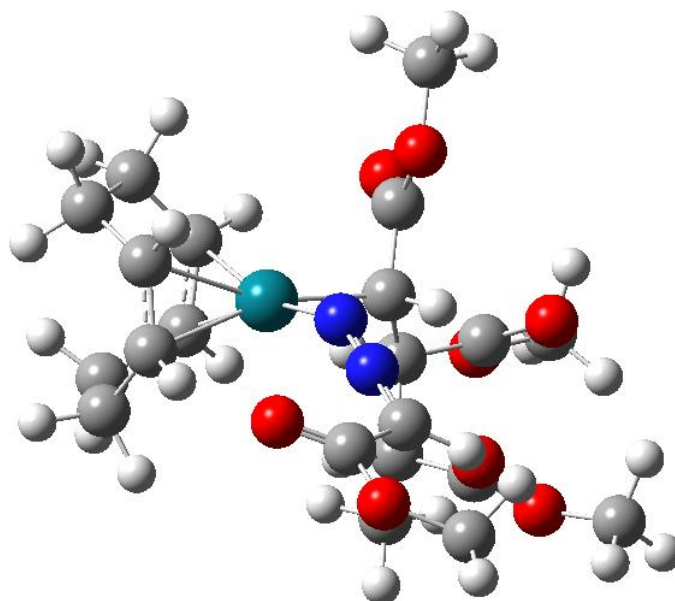


Figure S2-4: **B – N** coordinated

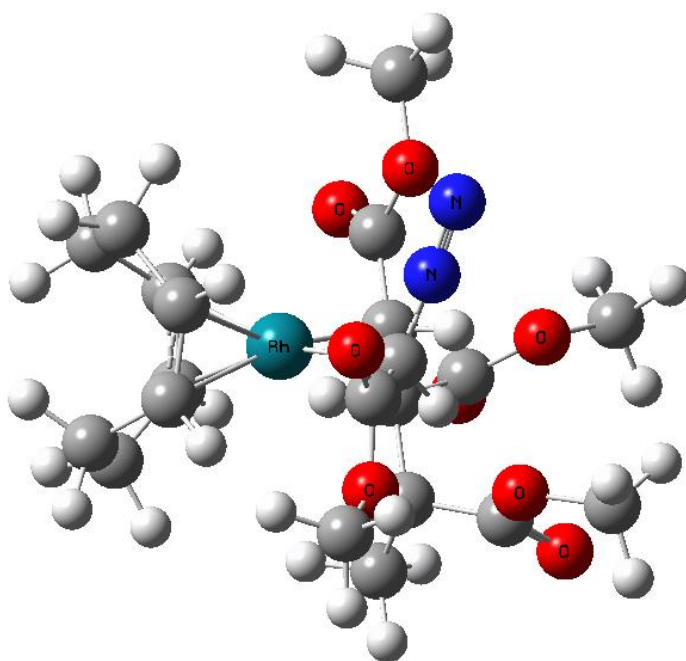


Figure S2-5: **B** - C coordinated

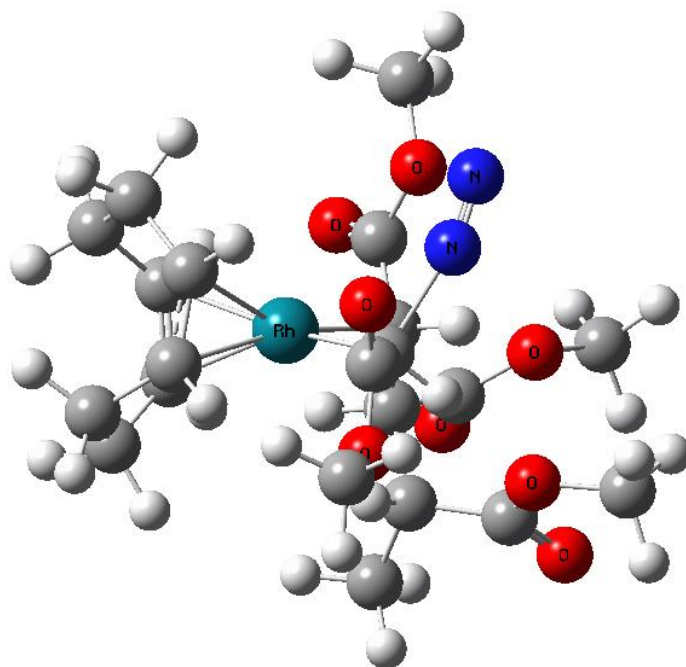


Figure S2-6: **B_TS**.

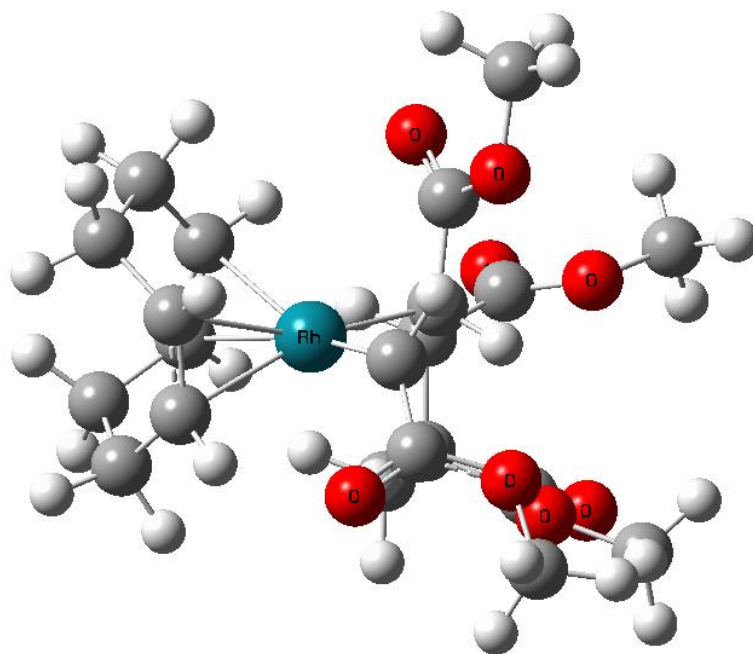


Figure S2-7: **C.**

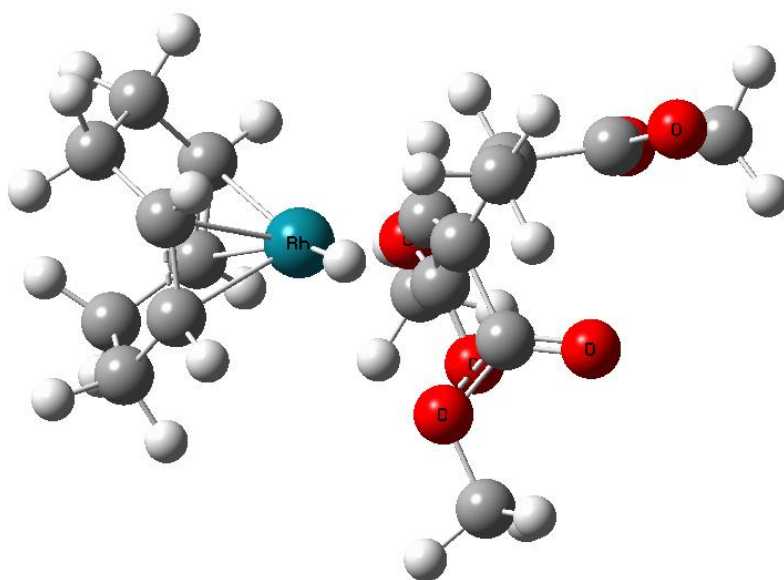


Figure S2-8: **D.**

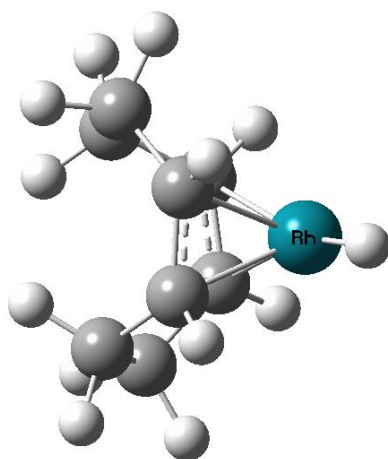


Figure S2-9: **E.**

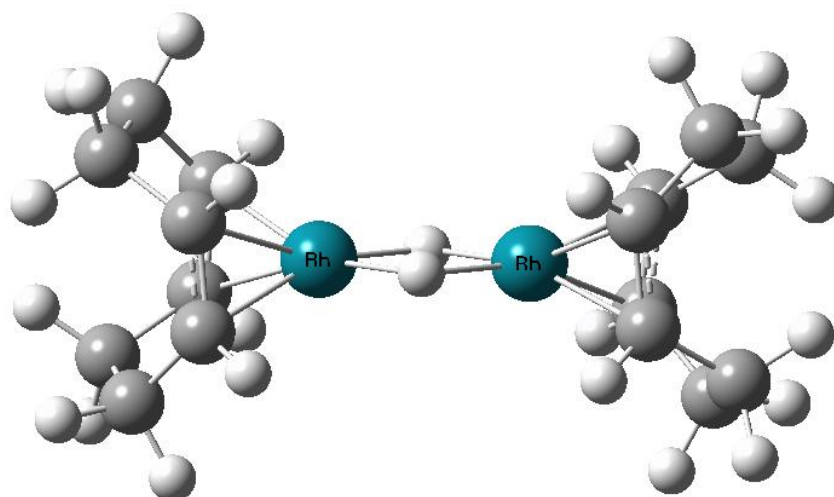


Figure S2-10: E dimer.

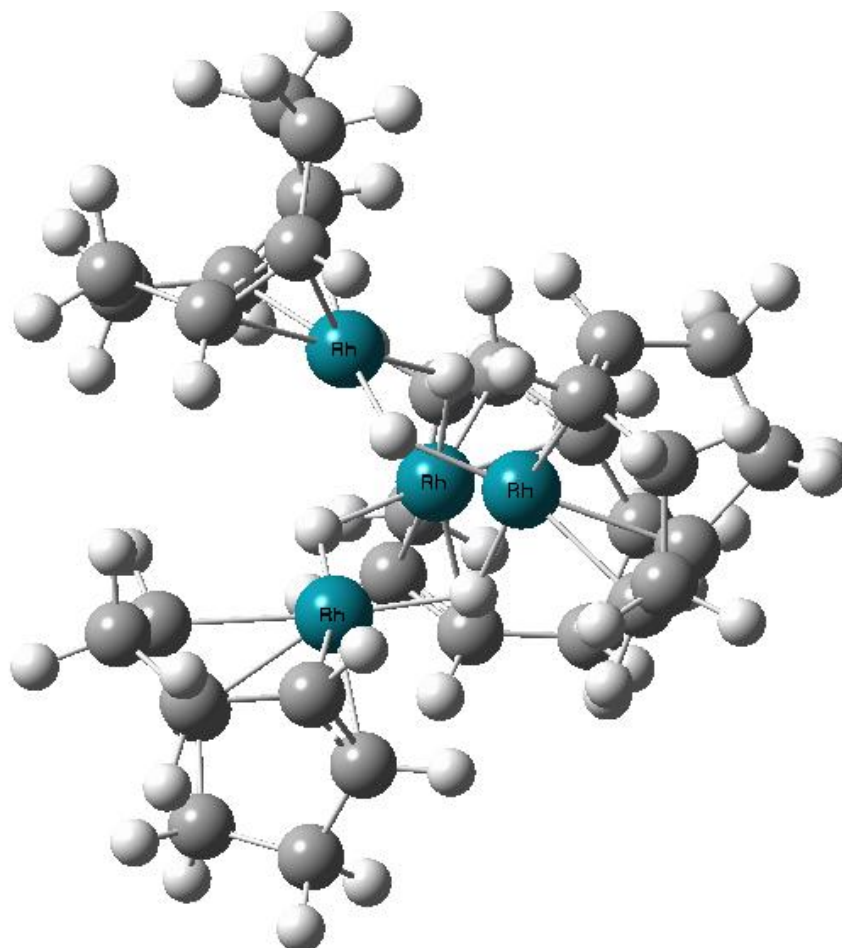


Figure S2-11: E tetramer.

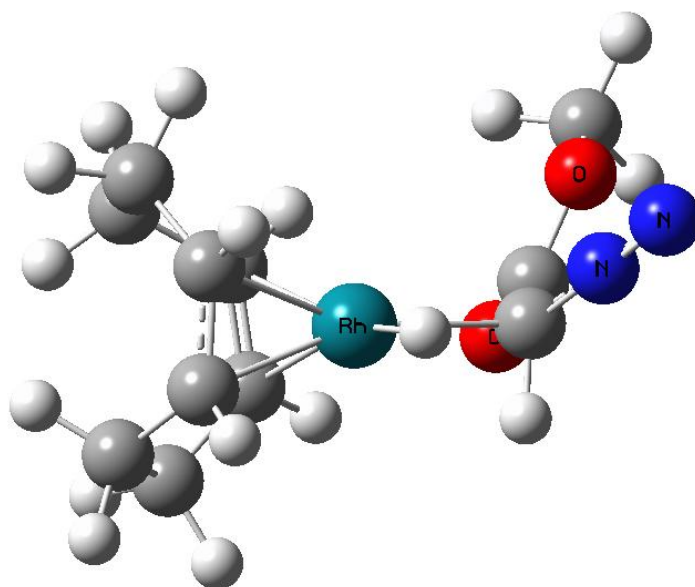


Figure S2-12: F – coordination of MDA via the carbon.

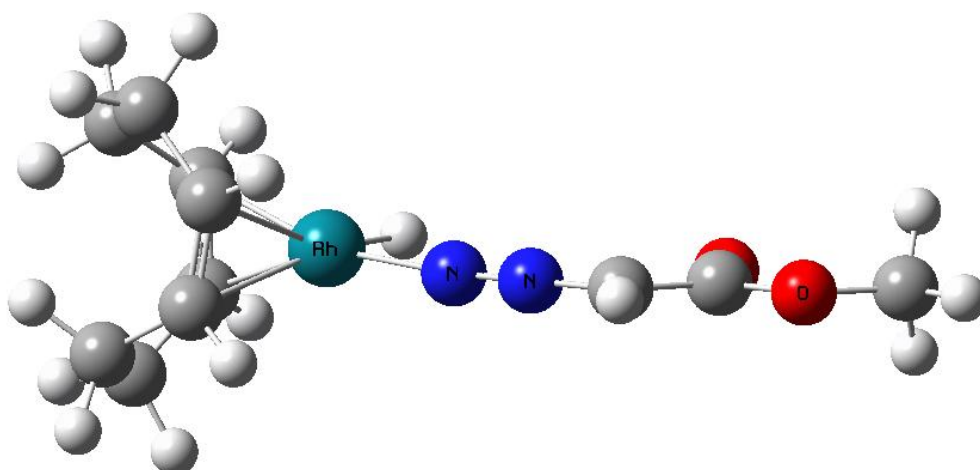


Figure S2-13: F – coordination of MDA via the terminal nitrogen.

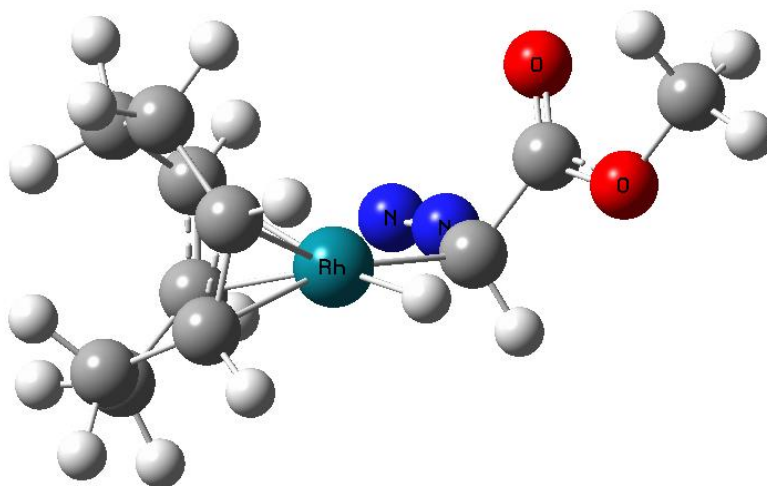


Figure S2-14: F_TS.

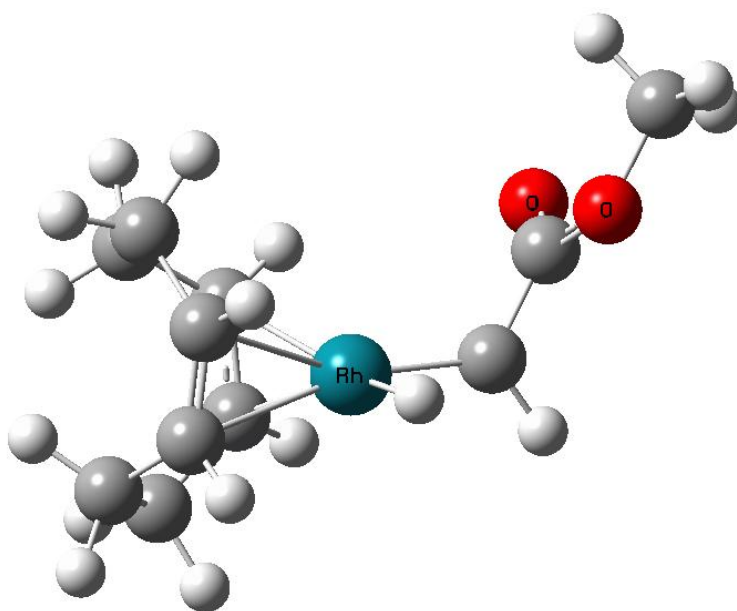


Figure S2-15: **G**.

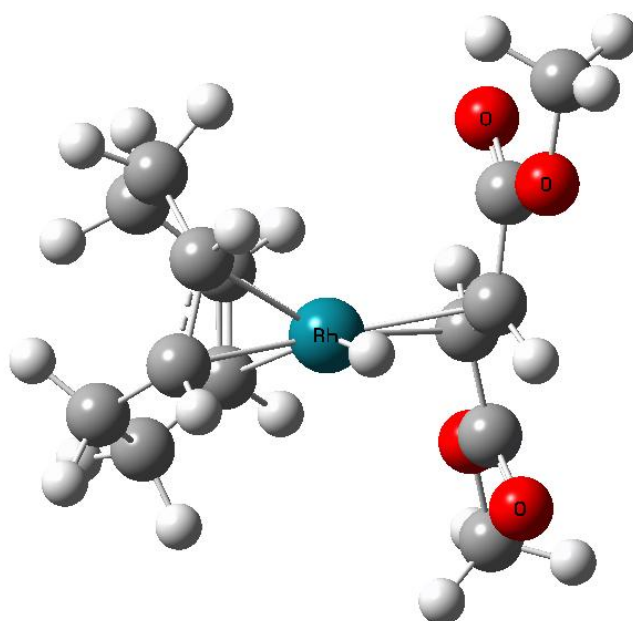


Figure S2-16: **H** – DMF coordinated.

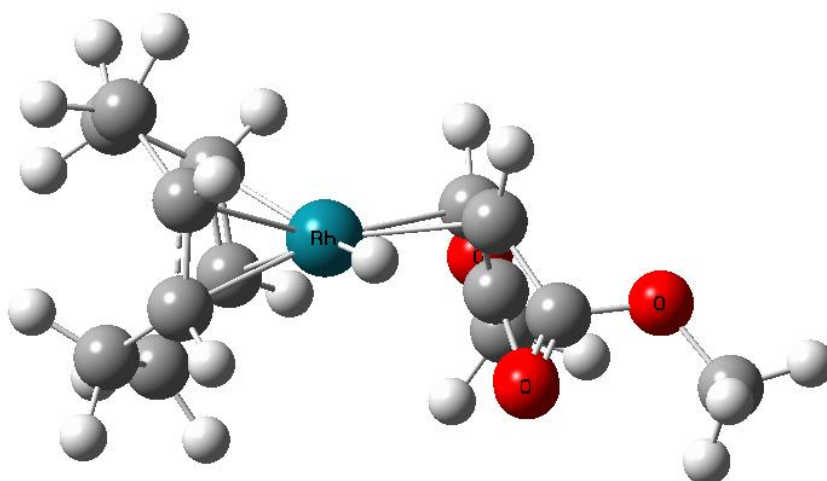


Figure S2-17: **H** – DMM coordinated.

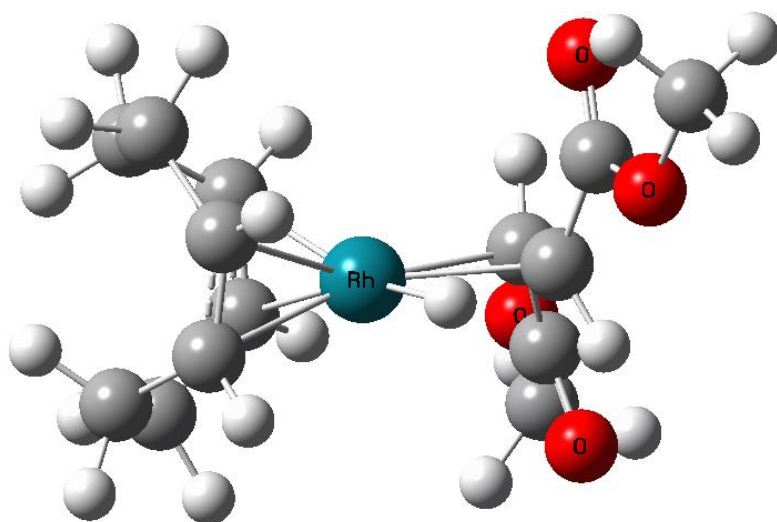


Figure S2-18: **H_TS** – insertion of DMF.

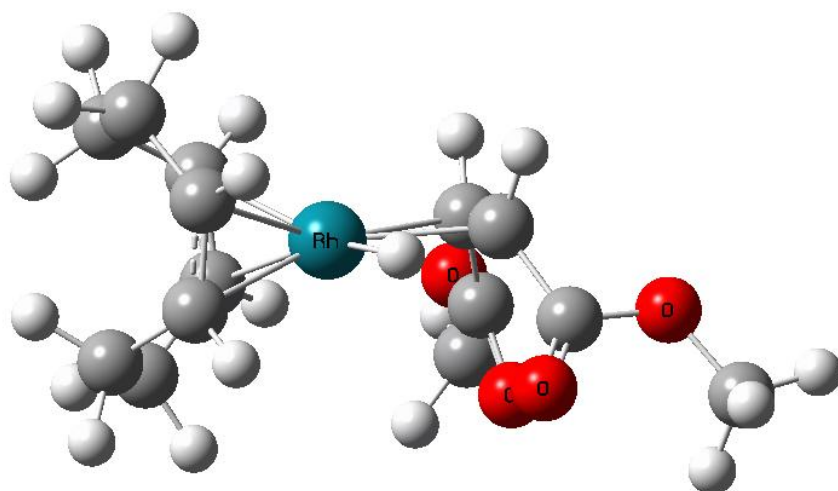


Figure S2-19: **H_TS** – insertion of DMM.

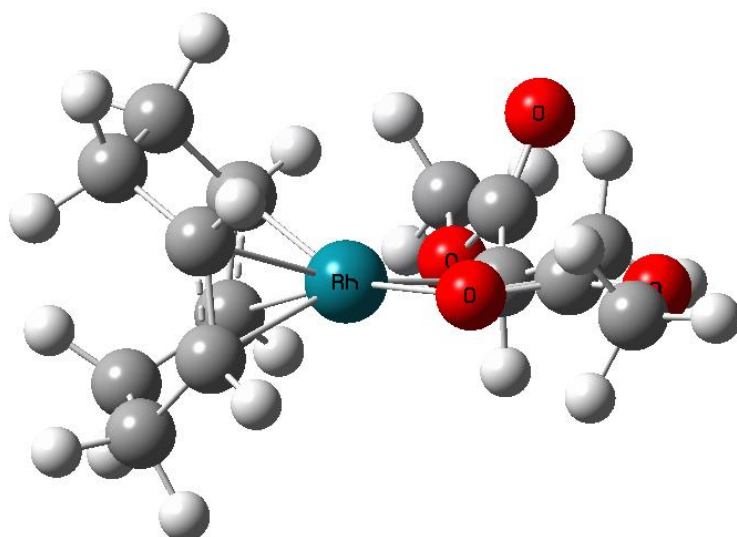


Figure S2-20: **I**.

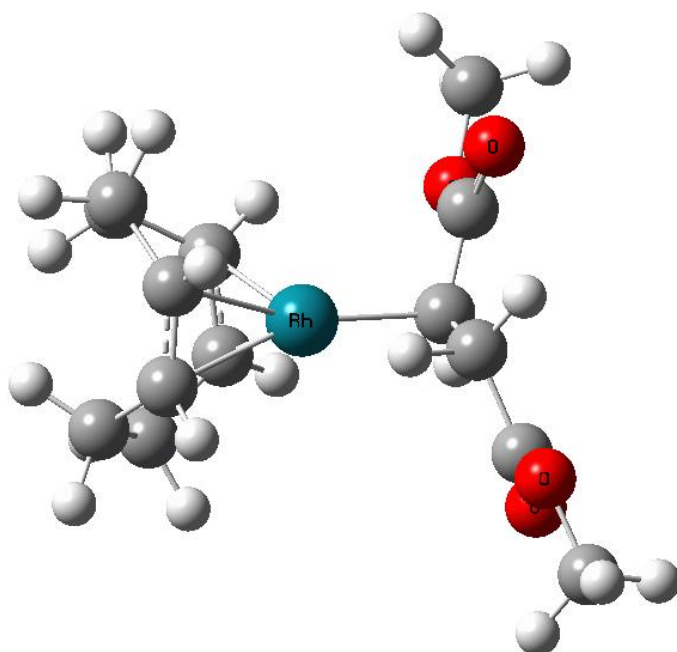


Figure S2-21: I – β -H agnostic complex after insertion of DMF.

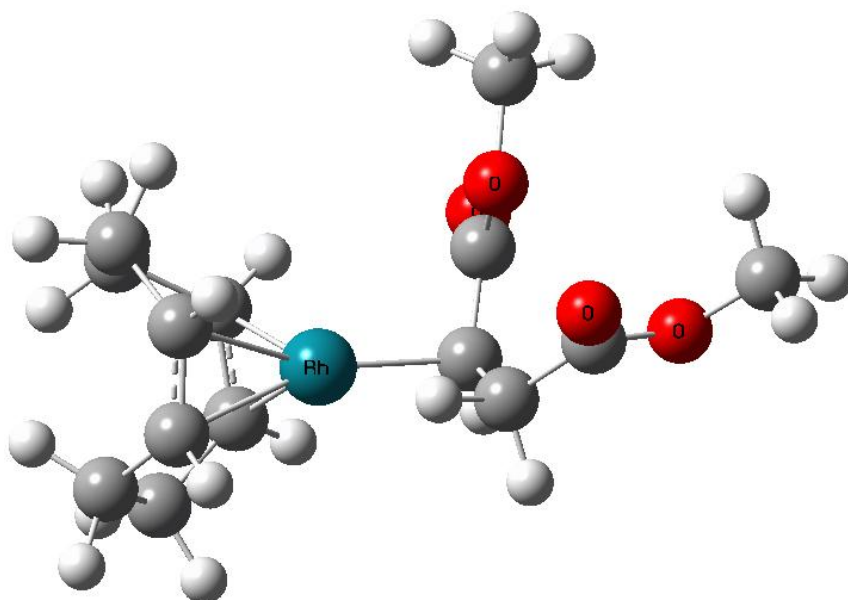


Figure S2-22: I – β -H agnostic complex after insertion of DMM.

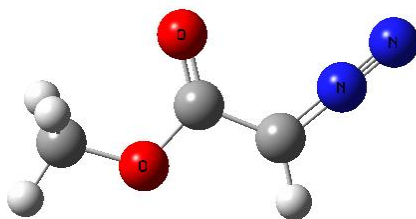


Figure S2-23: MDA.

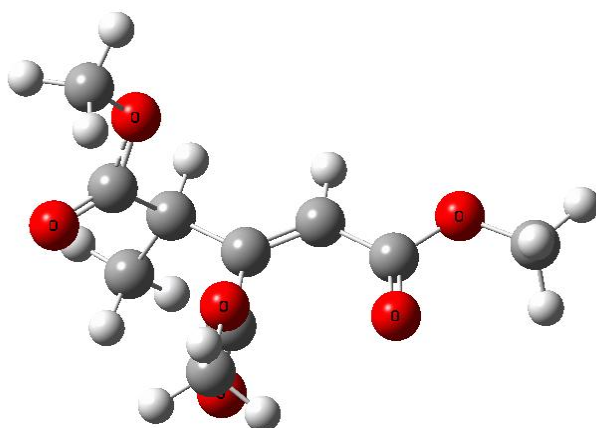


Figure S2-24: (Z)-trimethyl but-1-ene-1,2,3-tricarboxylate.

S3. Structures (xyz in Å) (B3LYP/TZVP//B3LYP/SVP)

<u>A</u>			
Rh	-0.0951288	0.1942870	1.3858504
C	-0.4767765	-1.5697758	2.5208935
H	-0.5015265	-2.3926430	1.7971530
C	-1.6078254	-0.7212234	2.5531278
H	-2.4415419	-0.9889175	1.8927141
C	-2.0088723	0.1911047	3.6985925
H	-2.5384406	-0.3832847	4.4849677
H	-2.7482607	0.9090277	3.3051888
C	-0.8236404	0.9725238	4.3124854
H	-0.3664146	0.3940123	5.1303141
H	-1.2037222	1.8955819	4.7791435
C	0.2371614	1.3336400	3.2813303
H	0.2573050	2.3810074	2.9591532
C	1.3637467	0.5630632	2.9975975
H	2.1972782	1.0671640	2.4924852
C	1.7048066	-0.7826734	3.6098237
H	2.4915892	-1.2369584	2.9857564
H	2.1545065	-0.6537677	4.6144796
C	0.4999866	-1.7501280	3.6821922
H	0.8741398	-2.7861401	3.6760229
H	-0.0301372	-1.6323062	4.6412115
C	-0.8863673	-0.4971794	-0.4856715
C	0.1058163	-1.5305304	-0.8388363
O	0.0527771	-2.7142299	-0.5713812
O	1.2004687	-0.9971896	-1.4834640
C	2.2921555	-1.8780598	-1.7148540
H	2.9977947	-1.3358043	-2.3587173
H	1.9588182	-2.8042282	-2.2059159
H	2.7840720	-2.1522189	-0.7669073
H	-1.8733838	-0.9632711	-0.3764512
C	-0.9610660	0.7735383	-1.3612473
H	-1.7268452	1.4052415	-0.8707874
C	-1.4901559	0.6145193	-2.8228699
H	-2.3871005	-0.0133067	-2.7064923
C	-1.9076125	1.9441880	-3.4687900
H	-2.5665232	2.5134194	-2.7929292
H	-2.4631872	1.7624967	-4.4023567
H	-1.0325475	2.5595435	-3.7137223
C	0.3030784	1.5722984	-1.1248666
O	0.8249832	2.2128769	-2.1459925
C	2.0400645	2.9441810	-1.9357977
H	2.8274073	2.2732032	-1.5636721
H	1.8823632	3.7540210	-1.2084462
H	2.3139736	3.3508786	-2.9161281
O	0.7905128	1.6543390	0.0079864
C	-0.5749098	-0.1574603	-3.7713452
O	0.2612808	0.3229900	-4.4962690
O	-0.8645274	-1.4739174	-3.7528003
C	-0.1052088	-2.3061438	-4.6276423
H	-0.4361143	-3.3341883	-4.4347072
H	0.9718992	-2.2079343	-4.4281489
H	-0.2885418	-2.0344455	-5.6791616

A (β -H agostic complex)

Rh	0.1994234	0.0615516	1.3089909
C	-1.4253297	-0.1056173	2.6489495
H	-2.1838802	-0.7320048	2.1637028

C	-1.3205815	1.2333861	2.1721024
H	-2.0345119	1.5335181	1.3953421
C	-0.7227878	2.3995711	2.9371302
H	-1.4565832	2.7986265	3.6656876
H	-0.5483680	3.2134853	2.2140291
C	0.6065451	2.0619335	3.6549758
H	0.4068287	1.7056491	4.6777543
H	1.1955547	2.9855008	3.7721922
C	1.4425008	1.0282176	2.9116187
H	2.3293938	1.4096059	2.3915741
C	1.3844444	-0.3445005	3.1412884
H	2.2358861	-0.9439003	2.7924617
C	0.4566553	-1.0495502	4.1140744
H	0.4831282	-2.1245091	3.8718956
H	0.8423176	-0.9667934	5.1492188
C	-1.0088396	-0.5552331	4.0493710
H	-1.6737351	-1.3696851	4.3775545
H	-1.1696563	0.2648552	4.7680982
C	-0.7372561	-0.2125237	-0.5467273
C	-1.1272691	-1.6300682	-0.4391035
O	-2.2531769	-2.0655982	-0.3351896
O	-0.0260961	-2.4504280	-0.3742187
C	-0.2839934	-3.8416888	-0.2148675
H	0.6939971	-4.3401635	-0.2279876
H	-0.9158220	-4.2191345	-1.0338011
H	-0.7999090	-4.0420090	0.7374805
H	-1.5961332	0.4148128	-0.8001153
C	0.5737846	0.1761760	-1.2065426
H	1.4004553	0.1937621	-0.4166735
C	0.5683680	1.6309250	-1.7937188
H	0.0165863	2.2423925	-1.0633590
C	1.9796782	2.1947595	-1.9822733
H	2.5226734	2.1993653	-1.0244728
H	1.9377620	3.2282824	-2.3580716
H	2.5551382	1.5986028	-2.7039794
C	1.1636975	-0.8064677	-2.2239237
O	0.2311054	-1.2139494	-3.0999502
C	0.6867011	-2.0283738	-4.1811362
H	1.1966638	-2.9265480	-3.8023502
H	1.3835184	-1.4630406	-4.8181600
H	-0.2080723	-2.3069085	-4.7516064
O	2.3254581	-1.1238010	-2.2793274
C	-0.2072797	1.6969704	-3.1087661
O	0.2903745	1.6581677	-4.2075371
O	-1.5311601	1.8140783	-2.9006155
C	-2.3601688	1.8114868	-4.0650340
H	-3.3908949	1.9239873	-3.7066069
H	-2.2494308	0.8650944	-4.6155889
H	-2.0930404	2.6418473	-4.7360294

A TS

Rh	-0.0633620	0.4019688	1.0852013
C	-0.4611749	-1.1965495	2.6508484
H	-0.3315435	-2.1292629	2.0944388
C	-1.6353434	-0.4925529	2.4074928
H	-2.3462850	-0.9515514	1.7118360
C	-2.1992643	0.6338988	3.2466574
H	-2.7754238	0.2228777	4.0993311
H	-2.9320552	1.1745657	2.6255750
C	-1.1364755	1.6323201	3.7586486
H	-0.7201236	1.2893460	4.7182039
H	-1.6309440	2.5921681	3.9781856

C	-0.0078317	1.8768494	2.7644193
H	-0.0214581	2.8559847	2.2755809
C	1.2010159	1.1759471	2.7228733
H	2.0449626	1.6692939	2.2284929
C	1.5948932	0.0029737	3.5949163
H	2.4243320	-0.5171947	3.0882676
H	2.0082371	0.3620092	4.5584602
C	0.4517615	-1.0053819	3.8526717
H	0.8932150	-1.9784166	4.1211822
H	-0.1410799	-0.6972545	4.7274853
C	-0.6440371	-0.6608235	-0.6730790
C	-0.1383000	-2.0496644	-0.7402127
O	0.9447411	-2.4219055	-1.1393488
O	-1.0790216	-2.9207294	-0.2913805
C	-0.7298573	-4.3016352	-0.3435554
H	-1.6070070	-4.8538329	0.0179447
H	0.1418375	-4.5151030	0.2950875
H	-0.4843424	-4.6073633	-1.3724404
H	-1.7330552	-0.5963409	-0.7522596
C	0.1058293	0.4722209	-1.1457611
H	0.6361822	1.4972189	0.1589329
C	-0.6668552	1.5674873	-1.9098284
H	-1.6629102	1.6265739	-1.4376245
C	-0.0256096	2.9563244	-1.8790602
H	0.0411153	3.3296323	-0.8463473
H	-0.6209347	3.6615915	-2.4744222
H	0.9839109	2.9349295	-2.3167840
C	1.4849259	0.2215541	-1.7399280
O	2.4464595	0.0125846	-0.8366182
C	3.7006042	-0.4401541	-1.3521063
H	4.0856132	0.2536092	-2.1140994
H	3.5758746	-1.4383811	-1.7979500
H	4.3830761	-0.4883329	-0.4943741
O	1.6742374	0.2478236	-2.9336877
C	-0.9403362	1.1565748	-3.3686661
O	-0.8577445	1.9032266	-4.3108905
O	-1.3709423	-0.1127651	-3.4701661
C	-1.6016903	-0.5922842	-4.7944524
H	-1.9744572	-1.6190245	-4.6877917
H	-0.6640759	-0.5862085	-5.3710580
H	-2.3412503	0.0331193	-5.3174975

B – N coordinated

Rh	-1.2636685	0.0155921	0.5725182
C	-2.3669881	-1.6222711	-0.3486342
H	-1.7326080	-2.0039397	-1.1538949
C	-3.0406549	-0.4189667	-0.6157526
H	-2.8815167	0.0278597	-1.6024119
C	-4.2593896	0.1058349	0.1143193
H	-5.1791887	-0.3367084	-0.3170993
H	-4.3255940	1.1866706	-0.0922993
C	-4.2240448	-0.1211595	1.6416583
H	-4.6487815	-1.1053494	1.8924686
H	-4.8797558	0.6176155	2.1292640
C	-2.8260012	-0.0000117	2.2286947
H	-2.6181350	0.9288420	2.7708137
C	-1.9429223	-1.0541815	2.4364883
H	-1.1386400	-0.8883833	3.1629103
C	-2.1682223	-2.5008327	2.0533162
H	-1.1860352	-3.0008226	2.0653354
H	-2.7741183	-3.0146856	2.8253839
C	-2.8118523	-2.6780253	0.6622342

H	-2.5523357	-3.6745970	0.2709905
H	-3.9097208	-2.6700266	0.7433051
C	-0.1057778	0.5944499	-1.1959500
C	-0.9310555	1.6073982	-1.8947968
O	-1.5835685	1.4275368	-2.9092646
O	-0.9155891	2.8122921	-1.2664712
C	-1.6940298	3.8428379	-1.8626989
H	-1.5431385	4.7378901	-1.2448458
H	-2.7631538	3.5763781	-1.8835373
H	-1.3693875	4.0363735	-2.8972078
H	0.7724040	1.1024411	-0.7836914
C	0.3514743	-0.5339976	-2.1270021
H	-0.5116925	-1.1104814	-2.4871674
C	1.3067991	-1.5508006	-1.4112179
H	0.8240946	-1.7711698	-0.4455734
C	1.4916549	-2.8548362	-2.1968947
H	0.5165333	-3.3432346	-2.3495208
H	2.1414428	-3.5577010	-1.6517924
H	1.9376249	-2.6788870	-3.1854407
C	1.0259148	0.0393028	-3.3754893
O	0.7171463	-0.6609246	-4.4822338
C	1.2749688	-0.1837205	-5.7066731
H	2.3752838	-0.1874402	-5.6654587
H	0.9369286	0.8437113	-5.9106593
H	0.9194719	-0.8635182	-6.4914862
O	1.7713254	0.9909823	-3.3845180
C	2.6255255	-0.8785573	-1.0466053
O	2.8180484	-0.2274231	-0.0417029
O	3.5688133	-1.0626896	-1.9817684
C	4.7867627	-0.3352297	-1.8221413
H	5.2607028	-0.5671840	-0.8563998
H	4.5902575	0.7461467	-1.8777145
H	5.4373849	-0.6438028	-2.6500151
C	2.2425636	0.7547013	2.8760360
H	3.1726797	0.7935291	2.3110260
N	1.1568359	0.8597138	2.1744196
N	0.1659646	0.9652230	1.6111286
C	2.0674813	0.4798890	4.3157592
O	0.9857807	0.3114933	4.8292120
O	3.1870815	0.4127432	5.0698584
C	4.4821385	0.6199354	4.5263650
H	4.5865764	1.6265398	4.0867728
H	4.7346842	-0.1403449	3.7676568
H	5.1846030	0.5262704	5.3653229

B – C coordinated

Rh	1.0513263	-0.1831343	0.4480406
C	0.8683824	-1.9354628	1.6866812
H	-0.1820919	-2.2377499	1.6975910
C	1.2101231	-0.8480592	2.5160771
H	0.3829381	-0.3860327	3.0623622
C	2.5958763	-0.6035234	3.1065771
H	3.0904144	-1.5672124	3.3088455
H	2.4813395	-0.1182782	4.0887069
C	3.4872889	0.2834288	2.2109590
H	4.5570006	0.1202929	2.4486877
H	3.2890627	1.3427624	2.4423898
C	3.2425115	0.0917960	0.7279963
H	3.5090891	0.9561960	0.1089614
C	3.0782077	-1.1266113	0.0731871
H	3.1830464	-1.1303348	-1.0154637
C	3.1747812	-2.4934744	0.7341174

H	3.6173665	-3.2073333	0.0209712
H	3.8738574	-2.4499049	1.5832730
C	1.8019413	-3.0227896	1.1939757
H	1.3059664	-3.5279881	0.3483235
H	1.9281265	-3.7991408	1.9745364
C	-1.0859129	0.3290218	0.5641101
C	-1.2180757	1.1281868	1.8002724
O	-1.6364001	0.7414483	2.8761805
O	-0.7770897	2.4128856	1.6364180
C	-0.8280721	3.2467612	2.7884534
H	-0.4869333	4.2394662	2.4654356
H	-0.1713328	2.8660705	3.5872106
H	-1.8520111	3.3076059	3.1885907
C	1.0837376	1.0993351	-1.4940120
H	0.1436211	0.6599482	-1.8533928
C	2.2926310	0.9825883	-2.3563540
O	3.2481297	1.7230245	-2.3241272
O	2.1819949	-0.0786535	-3.1719845
C	3.2923813	-0.3231612	-4.0419136
H	3.4592717	0.5351150	-4.7100643
H	3.0290212	-1.2152963	-4.6229605
H	4.2103285	-0.4999303	-3.4610504
H	-1.2644120	0.9958573	-0.2887153
C	-2.0898550	-0.8300990	0.5164001
H	-1.9068911	-1.5127757	1.3559922
N	0.9380109	2.3511206	-1.0064714
N	0.8708969	3.3916546	-0.5954916
C	-1.9781113	-1.6974047	-0.7867304
H	-0.8972981	-1.8013640	-0.9773643
C	-2.6162370	-3.0824091	-0.6277385
H	-2.1323544	-3.6297612	0.1957893
H	-2.5042706	-3.6763393	-1.5481589
H	-3.6881216	-3.0011120	-0.4014245
C	-3.5486979	-0.4156183	0.7231123
O	-3.8216968	0.7932648	0.1860329
C	-5.1836931	1.2150444	0.2536081
H	-5.2147344	2.2247625	-0.1759249
H	-5.5359442	1.2310982	1.2958987
H	-5.8262547	0.5341567	-0.3256744
O	-4.3864228	-1.0987261	1.2585237
C	-2.5868627	-0.9862825	-1.9879834
O	-3.7111123	-1.1397928	-2.3942503
O	-1.7193691	-0.1276914	-2.5873829
C	-2.2384444	0.6024353	-3.7034234
H	-1.4085685	1.2112935	-4.0848756
H	-3.0748822	1.2457244	-3.3912706
H	-2.5967732	-0.0841979	-4.4844298

B TS

Rh	1.0918972	-0.1389095	0.3652186
C	1.0079365	-1.9859746	1.7708518
H	-0.0490622	-2.2598214	1.7384440
C	1.3471954	-0.9233160	2.5797193
H	0.5176860	-0.4057877	3.0708112
C	2.7422086	-0.5815786	3.0719141
H	3.3308049	-1.5012518	3.2057797
H	2.6558653	-0.1332447	4.0745622
C	3.4925578	0.4074082	2.1520400
H	4.5771372	0.3810524	2.3779515
H	3.1671724	1.4348635	2.3860463
C	3.2664375	0.1850812	0.6715169
H	3.5214972	1.0493344	0.0484402

C	3.1484274	-1.0450413	0.0235909
H	3.2915653	-1.0493082	-1.0594506
C	3.2848844	-2.4177182	0.6714617
H	3.7233127	-3.1119753	-0.0631875
H	4.0080887	-2.3733650	1.5000607
C	1.9442426	-3.0033821	1.1587558
H	1.4208501	-3.4653000	0.3057597
H	2.1246221	-3.8251077	1.8798325
C	-1.0595661	0.3474266	0.5209034
C	-1.1594812	1.1122198	1.7806148
O	-1.4809459	0.6746078	2.8725040
O	-0.8144525	2.4268851	1.6289345
C	-0.8495317	3.2254928	2.8056223
H	-0.5948932	4.2470049	2.4922666
H	-0.1214521	2.8710541	3.5532828
H	-1.8485328	3.2078581	3.2683073
C	1.0408168	0.7337316	-1.4321996
H	0.1045721	0.5649609	-1.9849537
C	2.2150888	0.8690487	-2.3605543
O	3.0600663	1.7335035	-2.3465607
O	2.2241359	-0.1744691	-3.2095620
C	3.3402406	-0.2578441	-4.1022824
H	3.3807157	0.6272803	-4.7548518
H	3.1848469	-1.1658532	-4.6973362
H	4.2846316	-0.3228646	-3.5407609
H	-1.2934205	1.0206741	-0.3120176
C	-2.0207143	-0.8511155	0.5020920
H	-1.7533075	-1.5546864	1.3004839
N	0.7676013	2.4988497	-1.1321333
N	0.6491053	3.4757432	-0.6292370
C	-1.9773323	-1.6727882	-0.8347056
H	-0.9136504	-1.7188412	-1.1178724
C	-2.5344543	-3.0915984	-0.6671710
H	-1.9561575	-3.6385059	0.0937067
H	-2.4753519	-3.6532058	-1.6125341
H	-3.5852302	-3.0691393	-0.3476465
C	-3.4756370	-0.5051618	0.8321175
O	-3.8377393	0.7074185	0.3614240
C	-5.2068742	1.0662892	0.5438465
H	-5.3118456	2.0875465	0.1549087
H	-5.4807736	1.0321599	1.6089167
H	-5.8618595	0.3774475	-0.0116598
O	-4.2407125	-1.2404355	1.4064483
C	-2.7234110	-0.9592753	-1.9554849
O	-3.8779896	-1.1448663	-2.2505825
O	-1.9490195	-0.0605055	-2.6142340
C	-2.5993204	0.6843695	-3.6472203
H	-1.8359803	1.3467654	-4.0756684
H	-3.4311570	1.2750741	-3.2348358
H	-2.9983543	0.0120900	-4.4214340
<u>C</u>			
Rh	1.3316843	-0.1071868	-0.1100309
C	1.4466152	1.6498784	-1.8758812
H	0.4474433	2.0772705	-1.7638239
C	1.5328357	0.4153216	-2.4606132
H	0.6081602	-0.0525259	-2.8136647
C	2.7994936	-0.3087880	-2.8587741
H	3.0975697	-0.0024053	-3.8805407
H	2.5525111	-1.3800579	-2.9324596
C	3.9856720	-0.1273500	-1.8861809
H	4.5422015	0.7919895	-2.1253478

H	4.6967994	-0.9522912	-2.0494665
C	3.5911523	-0.1160990	-0.4139213
H	3.9166620	-0.9932194	0.1541806
C	3.2342868	1.0003078	0.3468867
H	3.3179444	0.8891296	1.4323750
C	3.1282049	2.4296335	-0.1296926
H	2.4649848	2.9641762	0.5706716
H	4.1161450	2.9230758	-0.0377564
C	2.5912863	2.5913472	-1.5657498
H	2.2395913	3.6272209	-1.6981260
H	3.4009979	2.4550605	-2.2965844
C	-0.8320567	-0.5167012	-0.3831635
H	-1.2105745	-0.7811924	0.6067463
C	1.3310590	-1.1494506	1.4114173
H	1.1974613	-2.2394726	1.2767380
C	1.5687912	-0.7578373	2.8218707
O	2.6055852	-0.2790353	3.2328450
O	0.5132043	-1.0288604	3.6067569
C	0.6498295	-0.6890625	4.9909106
H	1.5078517	-1.2125677	5.4387330
H	-0.2827160	-1.0040712	5.4752040
H	0.7970121	0.3947159	5.1154102
C	-0.7814796	-1.7304107	-1.2336175
O	-0.8999800	-1.7594506	-2.4467368
O	-0.5792507	-2.8721867	-0.5182233
C	-0.5196619	-4.0786450	-1.2705826
H	-0.3930637	-4.8905296	-0.5418050
H	0.3284241	-4.0706309	-1.9746243
H	-1.4425994	-4.2307914	-1.8514178
C	-1.6801219	0.6059649	-0.9916434
C	-1.8488215	1.8374149	-0.0331593
H	-0.8530366	2.0103793	0.4050804
C	-3.0636057	0.1508111	-1.4688423
O	-3.6578321	0.6381698	-2.3987996
O	-3.5780828	-0.8252393	-0.6948631
C	-4.9154752	-1.2248522	-0.9942094
H	-5.1551739	-2.0389228	-0.2981745
H	-4.9943278	-1.5733948	-2.0348970
H	-5.6082203	-0.3819633	-0.8480966
H	-1.2200710	0.9916016	-1.9110026
C	-2.3296644	3.0951851	-0.7655460
H	-1.6297408	3.3643851	-1.5721927
H	-2.3987781	3.9487092	-0.0729116
H	-3.3207263	2.9397340	-1.2131779
C	-2.7942803	1.5170094	1.1193372
O	-3.9808426	1.7421383	1.1257702
O	-2.1562098	0.9313193	2.1526917
C	-2.9746428	0.5208777	3.2480812
H	-2.3033280	0.0196756	3.9558093
H	-3.7586109	-0.1734244	2.9096028
H	-3.4587797	1.3886330	3.7222941

D

Rh	-0.0450001	0.4864010	1.0617193
C	-0.4231693	-1.2292070	2.5968823
H	-0.2321486	-2.1293084	2.0078094
C	-1.6168905	-0.5737200	2.3475267
H	-2.2836290	-1.0383104	1.6141359
C	-2.2501680	0.5058479	3.1975623
H	-2.8342874	0.0470199	4.0197972
H	-2.9852487	1.0345853	2.5691481
C	-1.2456871	1.5297306	3.7686158

H	-0.8341700	1.1715499	4.7246373
H	-1.7875608	2.4580421	4.0103519
C	-0.1078778	1.8612952	2.8103037
H	-0.1474841	2.8638600	2.3741241
C	1.1346981	1.2155062	2.7696030
H	1.9674929	1.7736893	2.3288984
C	1.5663097	0.0291179	3.6027436
H	2.4203899	-0.4394324	3.0869908
H	1.9568525	0.3722697	4.5815803
C	0.4635988	-1.0320004	3.8149250
H	0.9415124	-1.9930411	4.0631380
H	-0.1534546	-0.7723523	4.6884044
C	-0.6235106	-0.6767199	-0.6674165
C	-0.0971210	-2.0624400	-0.7087335
O	0.9854539	-2.4295307	-1.1089171
O	-1.0297936	-2.9354810	-0.2475400
C	-0.6711614	-4.3149881	-0.2864944
H	-1.5428462	-4.8691168	0.0846303
H	0.2048891	-4.5149782	0.3503921
H	-0.4279325	-4.6287676	-1.3133273
H	-1.7151945	-0.6349070	-0.7174908
C	0.0846648	0.4510572	-1.1630815
H	0.6362466	1.7189683	0.3687615
C	-0.7074702	1.5273988	-1.9263409
H	-1.7075670	1.5656780	-1.4601086
C	-0.1050489	2.9338419	-1.9077212
H	-0.0668152	3.3245263	-0.8810306
H	-0.7093217	3.6101779	-2.5272950
H	0.9124463	2.9322087	-2.3265979
C	1.4824656	0.2562179	-1.7186790
O	2.4255069	0.0267734	-0.7993771
C	3.7015958	-0.3755033	-1.3008995
H	4.0919699	0.3605033	-2.0193165
H	3.6131468	-1.3542787	-1.7960638
H	4.3624571	-0.4493469	-0.4281581
O	1.7078905	0.3329365	-2.9050733
C	-0.9688934	1.1003603	-3.3840146
O	-0.9264797	1.8445681	-4.3306937
O	-1.3389740	-0.1896828	-3.4805283
C	-1.5615086	-0.6795254	-4.8021340
H	-1.8781517	-1.7246460	-4.6924435
H	-0.6341562	-0.6234004	-5.3923893
H	-2.3401491	-0.0938696	-5.3144256

E

Rh	0.0580661	-1.0140345	0.0994185
C	0.0241434	0.2564072	-1.5549132
C	-1.2909371	0.1260720	-0.9946432
C	1.2452663	0.6618725	1.0314536
C	-0.0435335	0.7877291	1.5275082
C	0.9057075	1.4956827	-1.3826922
C	1.8311135	1.4264609	-0.1424718
C	-1.9835117	1.1511705	-0.1161424
C	-1.0822240	1.7589737	0.9894075
H	-0.2491846	0.3498329	2.5125185
H	1.9814412	0.1570932	1.6725033
H	-1.7203236	2.1010459	1.8199312
H	-0.5781079	2.6624167	0.6116638
H	-2.4150918	1.9626097	-0.7362941
H	-2.8443783	0.6482827	0.3548617
H	2.1213599	2.4496567	0.1672538
H	0.2714509	2.3965680	-1.3372509

H	1.5314705	1.6208254	-2.2805448
H	0.2181282	-0.3202750	-2.4664848
H	2.7701461	0.9239996	-0.4263965
H	-1.9882496	-0.5239498	-1.5370212
H	-0.3320174	-2.2339527	-0.8484366

E_dimer

Rh	0.0026606	0.0000292	1.3401549
Rh	-0.0023911	0.0001174	-1.3401370
C	0.6336468	-1.3948716	2.9014508
C	-0.7637995	-1.4347646	2.7631692
C	-1.7694544	-0.7546104	3.6707275
C	-1.3826601	0.6978095	4.0295909
C	-0.6351517	1.3951269	2.8984024
C	0.7630316	1.4343992	2.7678619
C	1.7633314	0.7543211	3.6813695
C	1.3743357	-0.6981000	4.0374754
C	0.6348613	1.3951865	-2.8983223
C	-0.7633472	1.4343139	-2.7674847
C	-1.7638449	0.7541856	-3.6806816
C	-1.3745176	-0.6979811	-4.0374447
C	-0.6336661	-1.3949783	-2.9017443
C	0.7637380	-1.4347766	-2.7636107
C	1.7691541	-0.7544401	-3.6712614
C	1.3823243	0.6980873	-4.0296752
H	0.0004323	1.1898189	-0.0002222
H	0.0003681	-1.1895393	0.0001826
H	1.2045936	-2.1616712	2.3667069
H	-1.1796360	-2.2479517	2.1564237
H	-2.7365434	-0.7488191	3.1420499
H	-1.9311965	-1.3513078	4.5906335
H	-2.2968357	1.2670522	4.2626043
H	-0.7771732	0.7198314	4.9494989
H	-1.2029096	2.1621930	2.3607335
H	1.1822598	2.2471762	2.1628748
H	2.7336256	0.7486384	3.1585740
H	1.9194124	1.3508810	4.6023166
H	2.2869449	-1.2675605	4.2760363
H	0.7631697	-0.7202970	4.9536104
H	1.2025668	2.1624139	-2.3608502
H	-1.1825046	2.2471023	-2.1624772
H	-2.7338767	0.7479774	-3.1574176
H	-1.9205865	1.3510102	-4.6013445
H	-2.2871277	-1.2675053	-4.2758735
H	-0.7636426	-0.7198462	-4.9537606
H	-1.2045814	-2.1616631	-2.3668325
H	1.1796604	-2.2478054	-2.1567337
H	2.7364014	-0.7488516	-3.1428780
H	1.9305772	-1.3508951	-4.5913688
H	2.2964297	1.2674136	-4.2627168
H	0.7767136	0.7202607	-4.9494921

E_tetramer

Rh	-0.8506888	1.6278619	0.4522947
Rh	-0.8724534	-1.6577194	0.1668928
Rh	1.4127245	-0.1037042	1.2226781
Rh	0.2854352	0.1434531	-1.8440901
C	-1.6358025	2.7466012	2.1642766
C	-2.5454405	1.7310361	1.8222099
C	-3.8245916	1.9202649	1.0315390
C	-3.6581897	2.8148685	-0.2188707
C	-2.2736141	2.7112418	-0.8499383

C	-1.1953639	3.5477719	-0.5278272
C	-1.1962296	4.6474223	0.5164998
C	-1.8452473	4.2253845	1.8518818
C	-2.4125690	-2.8336064	-0.8041999
C	-3.0367753	-2.0530860	0.1857568
C	-3.5108417	-2.5822415	1.5353508
C	-2.4379894	-2.4629548	2.6438002
C	-1.0166061	-2.6084660	2.1371799
C	-0.5687448	-3.5741713	1.2267878
C	-1.4337130	-4.6909699	0.6545798
C	-2.0781277	-4.3090222	-0.6954550
C	3.4704552	-0.7546544	0.7842426
C	2.9347994	-1.5274460	1.8305159
C	3.2354861	-1.3556147	3.3074319
C	3.2035758	0.1167152	3.7704852
C	2.1846414	0.9517837	3.0031698
C	2.4739888	1.7059147	1.8579593
C	3.8111514	1.7588575	1.1456234
C	4.4785874	0.3745163	0.9695488
C	2.1256689	0.8610862	-2.8163290
C	1.0226850	1.6066126	-3.2683230
C	0.3105490	1.4291660	-4.5956060
C	0.0371522	-0.0485839	-4.9483724
C	-0.2287275	-0.9044355	-3.7151700
C	0.7490161	-1.6383791	-3.0291133
C	2.2327098	-1.6441879	-3.3377272
C	2.8154783	-0.2391951	-3.6163882
H	-0.1753895	0.5233382	1.5724703
H	-1.1412547	-0.5191177	-1.0836983
H	0.4573370	1.3892154	-0.6793433
H	0.8490933	-1.3610116	0.2112269
H	-0.9507833	2.5353386	2.9922327
H	-2.5146229	0.8123181	2.4170452
H	-4.6296067	2.3183094	1.6822899
H	-4.1658875	0.9217477	0.7147297
H	-3.8729733	3.8660748	0.0326235
H	-4.4159239	2.5290692	-0.9658715
H	-2.2240480	2.1908499	-1.8117420
H	-0.4066391	3.6490366	-1.2807260
H	-1.6852847	5.5596049	0.1198441
H	-0.1458743	4.9276596	0.6996292
H	-2.9228208	4.4547701	1.8453449
H	-1.4194667	4.8312068	2.6679275
H	-2.4841596	-2.4676599	-1.8351849
H	-3.5077275	-1.1235321	-0.1490011
H	-4.4080527	-2.0228483	1.8462001
H	-3.8382638	-3.6292921	1.4317355
H	-2.5181416	-1.4706302	3.1164295
H	-2.6390498	-3.1951166	3.4514389
H	-0.2570348	-2.1117268	2.7508021
H	0.5114618	-3.7470241	1.1836831
H	-0.8150628	-5.5924664	0.5174554
H	-2.2093840	-4.9716520	1.3846007
H	-1.3758484	-4.5497253	-1.5101722
H	-2.9795269	-4.9273532	-0.8817853
H	3.4326309	-1.1917438	-0.2183834
H	2.5615890	-2.5234061	1.5654105
H	2.4764494	-1.9261003	3.8674673
H	4.2094816	-1.8198365	3.5632556
H	2.9622851	0.1522203	4.8451061
H	4.2029655	0.5708889	3.6774714
H	1.2914961	1.2368913	3.5692579

H	1.7968903	2.5344633	1.6245320
H	3.6350295	2.2009271	0.1515539
H	4.5017046	2.4535825	1.6646100
H	5.1450635	0.4090052	0.0924217
H	5.1328975	0.1528596	1.8279096
H	2.7225436	1.3046037	-2.0135104
H	0.8754799	2.5923075	-2.8121143
H	-0.6496320	1.9666139	-4.5291404
H	0.8760858	1.9235647	-5.4110556
H	-0.8343301	-0.1044969	-5.6202843
H	0.8792992	-0.4697055	-5.5198803
H	-1.2677689	-1.2226486	-3.5814448
H	0.4043337	-2.4864577	-2.4273716
H	2.7460861	-2.0794002	-2.4651635
H	2.4525526	-2.3253968	-4.1844165
H	3.8899356	-0.2422636	-3.3716575
H	2.7596067	-0.0089538	-4.6925793

F' – N coordinated

Rh	0.3346613	0.8420286	0.1115959
C	1.0469053	2.7119033	0.9764093
C	1.5082754	2.6007801	-0.3467358
C	-1.6772703	1.9501986	0.2892898
C	-1.2846009	2.1145792	-1.0255699
C	-0.0916751	3.6202922	1.4350670
C	-1.4776654	2.9353816	1.4220253
C	0.9302924	3.2902158	-1.5651448
C	-0.6154670	3.3535452	-1.5954550
N	-0.2967337	-0.9809355	-0.1897532
N	-0.6657297	-2.0652851	-0.2709908
C	-1.0056000	-3.3179426	-0.3483844
C	-0.0104345	-4.3438811	-0.0169757
O	1.1318302	-4.1418521	0.3272883
O	-0.5559670	-5.5737854	-0.1521739
C	0.3070588	-6.6706314	0.1393573
H	1.1889355	-6.6649732	-0.5202425
H	0.6569273	-6.6305621	1.1828588
H	-0.2859849	-7.5791325	-0.0272839
H	-2.0236027	-3.5619101	-0.6563649
H	-1.6775937	1.4022682	-1.7586161
H	-2.3889554	1.1442270	0.5025028
H	-0.9417546	3.4842365	-2.6398122
H	-0.9709614	4.2467397	-1.0597099
H	1.3504431	4.3120693	-1.6582723
H	1.2846447	2.7406429	-2.4528472
H	-2.2782753	3.7015839	1.4076760
H	-0.1088113	4.5341579	0.8202694
H	0.1189858	3.9599775	2.4616424
H	1.7516260	2.4201154	1.7614850
H	-1.6108813	2.3818799	2.3654983
H	2.5380689	2.2527964	-0.4826687
H	1.7084004	0.1952412	0.5638926

F – C coordinated

Rh	0.6430719	0.4667074	0.1515825
C	0.8472518	2.5963748	0.3302369
C	0.9508991	2.2100680	-1.0271223
C	-1.4977096	0.9553019	0.7897839
C	-1.5423319	0.8025021	-0.5842783
C	-0.3776516	3.2692695	0.9469318
C	-1.3974320	2.2686788	1.5399750
C	-0.1322692	2.3412852	-2.0793067

C	-1.5457613	1.9422546	-1.5899464
H	-1.8513342	-0.1767499	-0.9657613
H	-1.8004467	0.0914298	1.3906705
H	-2.1538658	1.6496684	-2.4615357
H	-2.0552873	2.8159059	-1.1542265
H	-0.1537113	3.3726809	-2.4862470
H	0.1519644	1.6937618	-2.9259753
H	-2.3960252	2.7450362	1.6090377
H	-0.8665473	3.9131465	0.1974559
H	-0.0475255	3.9502747	1.7476308
H	1.7898249	2.7803334	0.8567743
H	-1.1083872	2.0352551	2.5780417
H	1.9627806	2.1485935	-1.4441968
H	2.2330181	0.3446258	0.2344521
C	0.5795701	-1.7183451	0.7168117
C	-0.6811856	-2.4556776	0.4453558
O	-0.5606861	-3.2918039	-0.6041498
O	-1.6982012	-2.3023099	1.0778740
C	-1.7319515	-4.0276657	-0.9687613
H	-2.0670236	-4.6652208	-0.1368664
H	-1.4461944	-4.6431417	-1.8307470
H	-2.5509189	-3.3449030	-1.2415979
N	1.6933636	-2.2673992	0.1896128
N	2.5973436	-2.7530581	-0.2655541
H	0.7348565	-1.3212418	1.7334860

F TS

Rh	0.4237128	0.2479780	-0.2327032
C	0.8329573	2.1640784	-1.2903125
C	-0.3231087	1.5753465	-1.8135968
C	0.0483086	1.6766840	1.4613099
C	-1.2018517	1.3617265	0.9464443
C	0.8549462	3.3427822	-0.3225241
C	0.8656727	2.9184312	1.1641366
C	-1.7556806	1.9437462	-1.4871540
C	-2.0131016	2.2424236	0.0093500
H	-1.7552592	0.5530036	1.4375043
H	0.3722653	1.1272039	2.3544492
H	-3.0846136	2.0949066	0.2190911
H	-1.8117035	3.3027904	0.2275570
H	-2.0826495	2.8044120	-2.1048960
H	-2.3900215	1.0963951	-1.7957261
H	0.5320067	3.7614603	1.8017873
H	0.0001013	4.0072270	-0.5248626
H	1.7526663	3.9502267	-0.5199501
H	1.7649940	1.9826700	-1.8342577
H	1.9040730	2.7070778	1.4678465
H	-0.2095047	1.0048024	-2.7416995
H	1.2442637	-0.5099146	-1.3820875
C	0.6798626	-1.5765174	0.5699862
C	-0.1248522	-2.6979685	-0.0363363
O	0.5825029	-3.3206918	-0.9911265
O	-1.2560735	-2.9945172	0.2727019
C	-0.1186293	-4.2983680	-1.7600592
H	-0.5188988	-5.0935345	-1.1128310
H	0.6121669	-4.7107751	-2.4669174
H	-0.9558002	-3.8365124	-2.3062929
H	1.7197479	-1.8638393	0.7864707
N	0.0995461	-1.6529251	2.1933262
N	-0.3059081	-1.2311068	3.1381829

G

Rh	0.3080015	0.1193556	-0.4829294
C	-0.2420721	2.2967718	-1.2338923
C	-1.4072436	1.6009083	-0.9895377
C	1.0600639	1.3803289	1.2267813
C	-0.2058275	0.9337533	1.5940197
C	0.3841576	3.3314444	-0.3132451
C	1.4181335	2.7429195	0.6739664
C	-2.2678485	1.6669037	0.2519829
C	-1.4774875	1.7681680	1.5772481
H	-0.2491201	0.0059981	2.1741676
H	1.9147872	0.8036684	1.5970299
H	-2.1299037	1.4323627	2.3989565
H	-1.2374302	2.8189109	1.8005963
H	-2.9832082	2.5097070	0.1744724
H	-2.8841779	0.7536765	0.2735041
H	1.5917226	3.4555463	1.5046461
H	-0.4052657	3.8670495	0.2358137
H	0.8857159	4.0944987	-0.9297885
H	0.1540601	2.2588255	-2.2527935
H	2.3883016	2.6434123	0.1601903
H	-1.8701350	1.0931013	-1.8413158
H	0.1823808	-0.3353315	-2.0244096
C	1.0742259	-1.5550287	-0.2515154
C	0.3593575	-2.7265044	0.3054740
O	-0.2577842	-3.4853165	-0.6114913
O	0.3547823	-2.9571992	1.4969073
C	-0.9644112	-4.6260570	-0.1173646
H	-0.2875311	-5.3045315	0.4244785
H	-1.3828685	-5.1287398	-0.9982061
H	-1.7719831	-4.3205566	0.5656850
H	2.1379638	-1.7635777	-0.4729195

H (DMM)

Rh	-0.4645601	-0.6160992	-0.2250190
C	-1.2734198	-2.2066167	1.1056381
C	-1.6063028	-2.4992028	-0.2227651
C	1.4922110	-1.5646129	0.4751607
C	1.2228262	-2.1177436	-0.7652534
C	-0.1745642	-2.8941019	1.9068856
C	1.1865581	-2.1687196	1.8284466
C	-0.9116920	-3.4893926	-1.1325275
C	0.6287932	-3.4949679	-1.0096358
H	1.6993931	-1.6417578	-1.6280975
H	2.1970459	-0.7282503	0.4930551
H	1.0561277	-3.9051796	-1.9385025
H	0.9447960	-4.1811466	-0.2091842
H	-1.3082212	-4.5098529	-0.9592620
H	-1.1888615	-3.2337216	-2.1684449
H	2.0018502	-2.8546217	2.1326788
H	-0.0721762	-3.9399919	1.5783522
H	-0.4852494	-2.9437727	2.9624627
H	-2.0354367	-1.6952761	1.7013562
H	1.1967467	-1.3466019	2.5625424
H	-2.6165228	-2.2303960	-0.5490696
H	-1.9082008	-0.0169234	-0.0806383
C	-0.8808706	1.3834945	-0.9471783
C	0.5084764	1.1340147	-1.0882597
C	1.4877312	1.7426948	-0.1609000
C	-1.4364774	2.4221751	0.0113088
O	2.7605128	1.5090122	-0.5694835
O	-1.1539775	3.6502888	-0.4615349

C	3.7905516	2.0770306	0.2371624
C	-1.5560569	4.7445067	0.3614267
O	1.2334192	2.3718667	0.8438864
O	-2.0988759	2.2229601	0.9969095
H	-1.4807764	1.3175388	-1.8622676
H	0.9055480	0.8374565	-2.0623517
H	-1.2897381	5.6561646	-0.1889455
H	-2.6391937	4.7165058	0.5561989
H	-1.0227343	4.7114247	1.3239054
H	4.7398643	1.8127322	-0.2463697
H	3.6847959	3.1712581	0.2965518
H	3.7599658	1.6728630	1.2611481

H TS (DMM)

Rh	-0.4277138	-0.6198098	-0.2427188
C	-1.2881914	-2.1505777	1.1316040
C	-1.6452371	-2.4608002	-0.1845054
C	1.4816806	-1.5931082	0.4616495
C	1.1799936	-2.1606495	-0.7685799
C	-0.2016960	-2.8552094	1.9342924
C	1.1800675	-2.1718255	1.8273342
C	-0.9898755	-3.4917095	-1.0787331
C	0.5521998	-3.5298632	-0.9787919
H	1.6653567	-1.7183303	-1.6446884
H	2.2126953	-0.7785316	0.4571296
H	0.9563327	-3.9666493	-1.9059636
H	0.8653019	-4.2081593	-0.1703841
H	-1.4066270	-4.4979779	-0.8733199
H	-1.2769989	-3.2561229	-2.1167284
H	1.9781893	-2.8789733	2.1283452
H	-0.1329750	-3.9092576	1.6238757
H	-0.5021376	-2.8767690	2.9938545
H	-2.0207170	-1.5920787	1.7221601
H	1.2261563	-1.3416648	2.5509125
H	-2.6472818	-2.1605164	-0.5089781
H	-1.8331913	0.1112039	-0.1619013
C	-0.9046979	1.3845709	-0.9380569
C	0.4951221	1.1438107	-1.0924211
C	1.4700229	1.7501397	-0.1618946
C	-1.4499913	2.4333833	0.0182958
O	2.7450324	1.5278645	-0.5710071
O	-1.1571038	3.6565841	-0.4558386
C	3.7701558	2.0912788	0.2444166
C	-1.5435715	4.7560657	0.3682198
O	1.2119953	2.3672257	0.8504269
O	-2.1149335	2.2366755	1.0028328
H	-1.4948198	1.3490804	-1.8618768
H	0.8861895	0.8830486	-2.0794180
H	-1.2739220	5.6641662	-0.1862352
H	-2.6252550	4.7370754	0.5714801
H	-1.0020485	4.7196851	1.3258862
H	4.7218369	1.8391038	-0.2410867
H	3.6582833	3.1840748	0.3183389
H	3.7411057	1.6736001	1.2630598

H (DMF)

Rh	-0.3187046	-0.1687469	0.4175423
C	-1.9313807	-1.3712318	1.3250978
C	-2.4923419	-0.3900388	0.4906871
C	0.0474598	-2.1729139	-0.6767946
C	-0.7061678	-1.4316570	-1.5637380
C	-1.8016334	-2.8531085	0.9800106

C	-0.4673408	-3.2180449	0.2916816
C	-3.0257102	-0.5809748	-0.9112188
C	-2.2008708	-1.5541609	-1.7833913
H	-0.1628789	-0.8463867	-2.3114379
H	1.1315773	-2.1677069	-0.8286317
H	-2.4198915	-1.3471746	-2.8428276
H	-2.5205805	-2.5920727	-1.6071191
H	-4.0816374	-0.9152723	-0.8706287
H	-3.0402829	0.4090895	-1.3950849
H	-0.5590214	-4.1963710	-0.2204316
H	-2.6536244	-3.1674476	0.3571857
H	-1.8843486	-3.4389838	1.9089397
H	-1.9063668	-1.1415899	2.3944003
H	0.3053354	-3.3590624	1.0645902
H	-2.8659512	0.5149471	0.9824226
H	-0.5620106	0.7110737	1.6873379
C	0.8789492	1.6740346	0.3412387
C	1.5066283	0.6981433	-0.4494838
C	2.6902864	-0.0217827	0.0822148
C	0.0283060	2.7141944	-0.3047278
O	3.2650548	-0.7902114	-0.8763995
O	-0.3430992	3.6567993	0.5850165
C	4.4280149	-1.5167161	-0.4826170
C	-1.1686171	4.7048007	0.0841604
O	3.1152579	0.0365711	1.2145256
O	-0.2880125	2.7473528	-1.4741512
H	1.2921513	1.9218974	1.3202930
H	1.3907889	0.7253853	-1.5348963
H	-1.3457793	5.3855386	0.9266138
H	-0.6715478	5.2388495	-0.7403804
H	-2.1254078	4.3072994	-0.2900923
H	4.7713940	-2.0534454	-1.3762813
H	5.2133871	-0.8343258	-0.1230334
H	4.1949722	-2.2290247	0.3242790

H TS (DMF)

Rh	-0.3170099	-0.2868363	0.2191494
C	-1.5816685	-1.7460566	1.3356310
C	-2.3497850	-1.1327304	0.3408739
C	0.6973405	-2.1726270	-0.3981424
C	-0.1675131	-1.8178340	-1.4303033
C	-1.0040222	-3.1545331	1.2549899
C	0.4332906	-3.1956059	0.6867984
C	-2.6928144	-1.7088892	-1.0167559
C	-1.5230187	-2.4523036	-1.7019573
H	0.2640397	-1.2462717	-2.2589818
H	1.7473985	-1.8869723	-0.5202963
H	-1.6991898	-2.4621152	-2.7893313
H	-1.5072588	-3.5088714	-1.3932894
H	-3.5720396	-2.3789840	-0.9385122
H	-3.0109236	-0.8710539	-1.6583528
H	0.6681120	-4.2145002	0.3199312
H	-1.6701869	-3.7971398	0.6585405
H	-0.9963204	-3.5936939	2.2652606
H	-1.6611376	-1.3289431	2.3448045
H	1.1477326	-2.9997436	1.5029008
H	-3.0007554	-0.3086494	0.6541238
H	-0.8356378	0.9393541	1.1387258
C	0.2952697	1.8382543	0.4024647
C	1.1874374	1.1017751	-0.4401245
C	2.5144691	0.7323513	0.0996435
C	-0.6527317	2.8206679	-0.2319143

O	3.2985705	0.1735634	-0.8567028
O	-1.1910032	3.6312128	0.6983101
C	4.6102849	-0.2052071	-0.4467068
C	-2.1196299	4.6067931	0.2260094
O	2.8902783	0.8822119	1.2434524
O	-0.9051985	2.8978649	-1.4101638
H	0.6739666	2.1466663	1.3818705
H	1.1093963	1.2196076	-1.5239122
H	-2.4249560	5.1891090	1.1044670
H	-1.6520089	5.2626431	-0.5242699
H	-2.9958189	4.1231982	-0.2338909
H	5.1065232	-0.6083684	-1.3390412
H	5.1681867	0.6616123	-0.0596612
H	4.5733328	-0.9699522	0.3453638

I

Rh	0.1452191	-0.0767794	-0.4267948
C	1.1017558	0.8502560	-2.2243218
H	0.3003980	1.4473233	-2.6743329
C	1.0249936	-0.5339813	-2.3836993
H	0.1815389	-0.9186579	-2.9707861
C	2.1504438	-1.5269156	-2.1594872
H	2.8381389	-1.5445425	-3.0283086
H	1.6976680	-2.5309455	-2.1151361
C	2.9394512	-1.2729288	-0.8549079
H	3.7901007	-0.5990787	-1.0463347
H	3.3844660	-2.2216269	-0.5142195
C	2.0669012	-0.7012012	0.2622723
H	1.9016845	-1.3600238	1.1208122
C	1.8915324	0.6807240	0.5078975
H	1.6428271	0.9716124	1.5335188
C	2.4725355	1.8202940	-0.3086061
H	1.9230593	2.7345537	-0.0290011
H	3.5269433	2.0036513	-0.0195272
C	2.3614147	1.6100169	-1.8354572
H	2.3631812	2.5911547	-2.3368647
H	3.2495090	1.0807343	-2.2152864
C	-2.4212950	-0.0079416	1.1034699
H	-3.2085245	-0.5537907	1.6545959
C	-0.9932930	-0.5048014	1.3562393
H	-0.9314803	-1.6052433	1.3617950
C	-0.4521743	0.0399095	2.6149778
O	-0.7859864	1.0774830	3.1577047
O	0.5308327	-0.7476844	3.1425120
C	1.1300524	-0.2795204	4.3448438
H	1.6158383	0.6987749	4.1989518
H	1.8787212	-1.0310415	4.6292382
H	0.3813742	-0.1691657	5.1451415
C	-2.7537516	-0.0075872	-0.3527546
O	-1.8882559	0.0136820	-1.2342255
O	-4.0415063	-0.0108117	-0.6534075
C	-4.4064313	0.0341177	-2.0396275
H	-5.5027453	0.0317314	-2.0605495
H	-4.0101640	-0.8430295	-2.5719901
H	-4.0148079	0.9462441	-2.5133259
H	-2.4941209	1.0409729	1.4480642

I (β -H agostic complex after insertion of DMM)

Rh	0.1818018	0.6776271	-0.3020998
C	-0.3852515	2.3439889	-1.6978242
C	-1.5299975	1.8602645	-1.0677245
C	1.2206902	2.2381764	0.6844902

C	-0.0059548	2.0004309	1.3563472
C	0.3503120	3.6166107	-1.3008603
C	1.4968073	3.3655347	-0.2909054
C	-2.2136606	2.4698356	0.1422577
C	-1.2347196	2.9021780	1.2597949
H	0.0555576	1.3816401	2.2597689
H	2.1219067	1.8175977	1.1465690
H	-1.7662783	2.8870065	2.2243213
H	-0.9208742	3.9479417	1.1115193
H	-2.8500327	3.3252634	-0.1586122
H	-2.9048696	1.7111345	0.5445431
H	1.7301247	4.2998483	0.2577432
H	-0.3668891	4.3446497	-0.8905930
H	0.7676926	4.0886242	-2.2044701
H	-0.1664311	1.9573500	-2.7002483
H	2.4158504	3.1064132	-0.8423746
H	-2.1405423	1.1409603	-1.6291088
H	1.9978376	-1.5352571	-1.4303056
C	1.0535076	-1.5600366	-0.8649832
C	1.2545747	-0.9394417	0.4967265
C	0.5287954	-2.9883189	-0.9439914
C	0.4794265	-1.3885282	1.6684280
O	0.7641502	-1.1767591	2.8280196
O	1.0744338	-3.9377801	-0.4452081
O	-0.5854312	-3.0711448	-1.6949765
O	-0.6753563	-2.0310436	1.3147063
C	-1.4930030	-2.4859440	2.3879335
C	-1.1422772	-4.3768787	-1.8467333
H	2.2894839	-0.7170151	0.7731696
H	0.3220552	-0.9341649	-1.5031716
H	-0.9442720	-3.1968396	3.0249102
H	-1.8254897	-1.6450187	3.0163381
H	-2.3589826	-2.9799115	1.9279613
H	-2.0164454	-4.2641275	-2.5003618
H	-1.4461405	-4.7842887	-0.8702421
H	-0.4118002	-5.0654895	-2.2986073

I (β -H agostic complex after insertion of DMF)

Rh	0.2839826	0.4199512	-0.2060068
C	2.2165982	1.5280981	-0.4885239
C	1.3261340	1.8934421	-1.4964337
C	0.2155583	1.5657594	1.5770616
C	-0.6064480	2.1829092	0.6014653
C	2.5141785	2.3621787	0.7502570
C	1.6169860	2.0000562	1.9591415
C	0.4628327	3.1404495	-1.5212382
C	-0.2332371	3.4444748	-0.1731886
H	-1.6799183	1.9779527	0.6818836
H	-0.2927575	0.9684809	2.3435516
H	-1.1461592	4.0293534	-0.3686473
H	0.4045455	4.0904172	0.4508673
H	1.0545057	4.0174982	-1.8503870
H	-0.3065675	2.9905997	-2.2959537
H	1.5751832	2.8508557	2.6681627
H	2.4130472	3.4313377	0.5075695
H	3.5691384	2.2211639	1.0350407
H	2.9542396	0.7543590	-0.7316266
H	2.0780643	1.1684395	2.5168859
H	1.4403956	1.3945384	-2.4676857
H	0.6433387	-1.3256064	-1.0617577
C	-0.1597262	-1.9644467	-0.5030761
C	-1.0173262	-1.1161029	0.3777593

C	0.6515040	-3.0449746	0.1906249
C	-2.3618474	-0.8099647	-0.1453461
O	-2.7383811	-0.9791488	-1.2907384
O	0.6404363	-3.2892615	1.3703881
O	1.4084200	-3.7123171	-0.7006116
O	-3.1649692	-0.2645735	0.8051507
C	-4.4767392	0.0953102	0.3839435
C	2.2270047	-4.7598273	-0.1778912
H	-0.9776375	-1.3387027	1.4485478
H	-0.7079470	-2.3805663	-1.3644414
H	-4.4461432	0.8789366	-0.3903714
H	-5.0125805	-0.7728137	-0.0303561
H	-4.9946942	0.4695994	1.2769103
H	2.7640558	-5.1852008	-1.0348820
H	1.6110903	-5.5319876	0.3081327
H	2.9400585	-4.3673010	0.5636558

MDA

N	-2.9598153	-0.2495313	-0.0002650
N	-1.9440256	0.2513372	0.0000546
C	-0.7599697	0.8076521	0.0001536
C	0.4136412	-0.0667831	0.0001021
O	0.3973677	-1.2771006	0.0001774
O	1.5400863	0.6788876	0.0000159
C	2.7669387	-0.0486107	-0.0002084
H	2.8443888	-0.6928705	0.8894728
H	2.8488020	-0.6846041	-0.8954960
H	3.5669804	0.7027704	0.0050699
H	-0.7140693	1.8959076	0.0002452

DMF

C	0.5493948	-0.0020687	0.3837404
C	-0.5493714	-0.0067828	-0.3835720
C	-1.9088289	-0.0025596	0.2227468
C	1.9088352	-0.0001062	-0.2228752
O	-2.8567204	-0.0020529	-0.7323190
O	2.8567548	-0.0014929	0.7322777
C	-4.2098524	0.0052277	-0.2775526
C	4.2099765	0.0029622	0.2776609
O	-2.1492751	0.0016600	1.4075936
O	2.1490822	0.0027488	-1.4076995
H	0.4678711	0.0003711	1.4737807
H	4.8360299	0.0008884	1.1786098
H	4.4187681	-0.8866313	-0.3366508
H	4.4149988	0.8980406	-0.3299127
H	-4.8360690	0.0037004	-1.1783972
H	-4.4202763	-0.8833632	0.3375809
H	-4.4131187	0.9013565	0.3291128
H	-0.4675199	-0.0084107	-1.4735547

DMM

C	-1.3900062	-0.3881933	0.6613410
C	-0.1450264	0.0313834	1.3577141
O	0.8220200	0.5351548	0.8334961
O	-0.2324153	-0.2113306	2.6794132
C	0.9006515	0.1588346	3.4643613
H	1.7987513	-0.3882445	3.1379380
H	1.1020907	1.2377209	3.3762667
H	0.6529513	-0.0999583	4.5014797
H	-2.2189082	-0.7098257	1.2962874
H	-2.4807269	-0.6420093	-1.1230353
C	-1.5212234	-0.3657699	-0.6724922

C	-0.4826804	0.1118399	-1.6480179
O	-0.5912496	1.1441490	-2.2606547
O	0.5102571	-0.7698189	-1.8030496
C	1.5874055	-0.3605465	-2.6490445
H	1.2226605	-0.0981765	-3.6536993
H	2.0965328	0.5133088	-2.2149192
H	2.2759680	-1.2132237	-2.7008784

(Z)-trimethyl but-1-ene-1,2,3-tricarboxylate

C	-0.9937151	-1.1527080	0.4968849
C	-0.4360130	-2.4332039	-0.0000466
O	0.7139965	-2.6273255	-0.3267458
O	-1.3881585	-3.3854888	-0.0427679
C	-0.9709850	-4.6725824	-0.4959396
H	-1.8592857	-5.3152694	-0.4536740
H	-0.1753769	-5.0761326	0.1494856
H	-0.5862804	-4.6197831	-1.5263202
H	-2.0541759	-1.1504689	0.7602976
C	-0.2560915	-0.0370438	0.6320844
C	-0.8421567	1.2626961	1.1645814
H	-1.9255536	1.1023102	1.2757171
C	-0.2279481	1.6925442	2.5053350
H	-0.3550826	0.8977947	3.2551125
H	-0.7237697	2.6048455	2.8709217
H	0.8441271	1.9039015	2.4004432
C	1.2246084	-0.0084138	0.3270082
O	1.4495665	0.2349803	-0.9690244
C	2.8224221	0.2816647	-1.3696226
H	3.2950947	-0.6988027	-1.2078426
H	3.3696997	1.0443207	-0.7960188
H	2.8195796	0.5323196	-2.4376005
O	2.0787352	-0.1004137	1.1716730
C	-0.6618214	2.3580292	0.1059957
O	0.2007109	3.1998787	0.1197010
O	-1.5847784	2.2475386	-0.8624021
C	-1.4731263	3.1653059	-1.9525775
H	-2.3007567	2.9324779	-2.6340396
H	-0.5078696	3.0388991	-2.4662121
H	-1.5488506	4.2048984	-1.5987633

S4. Polymerisation of D-EDA in comparison to EDA

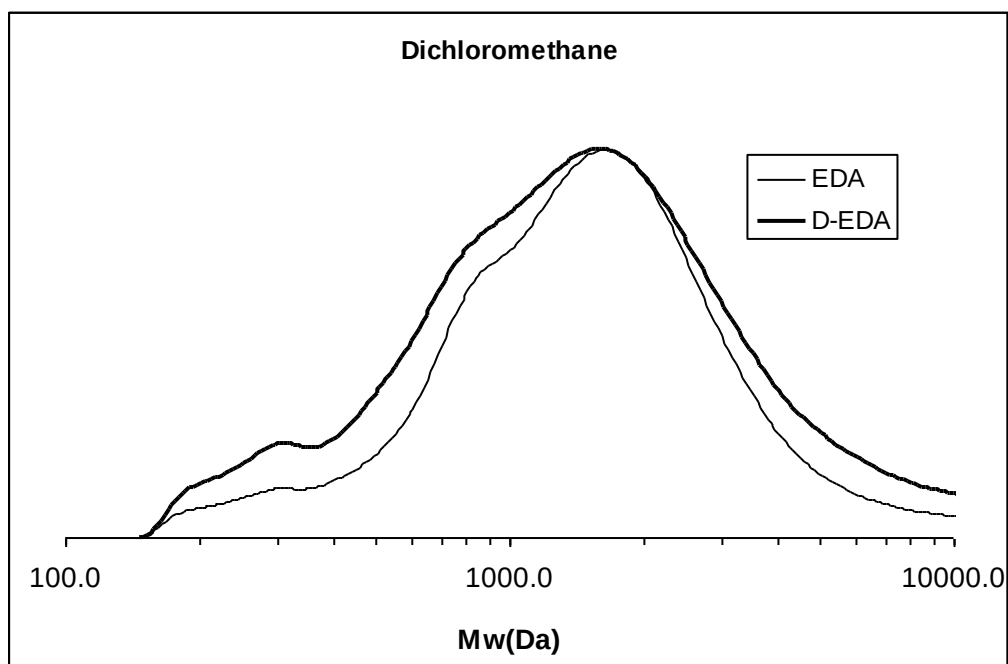


Figure S4-1: SEC traces of the oligomers formed in dichloromethane.

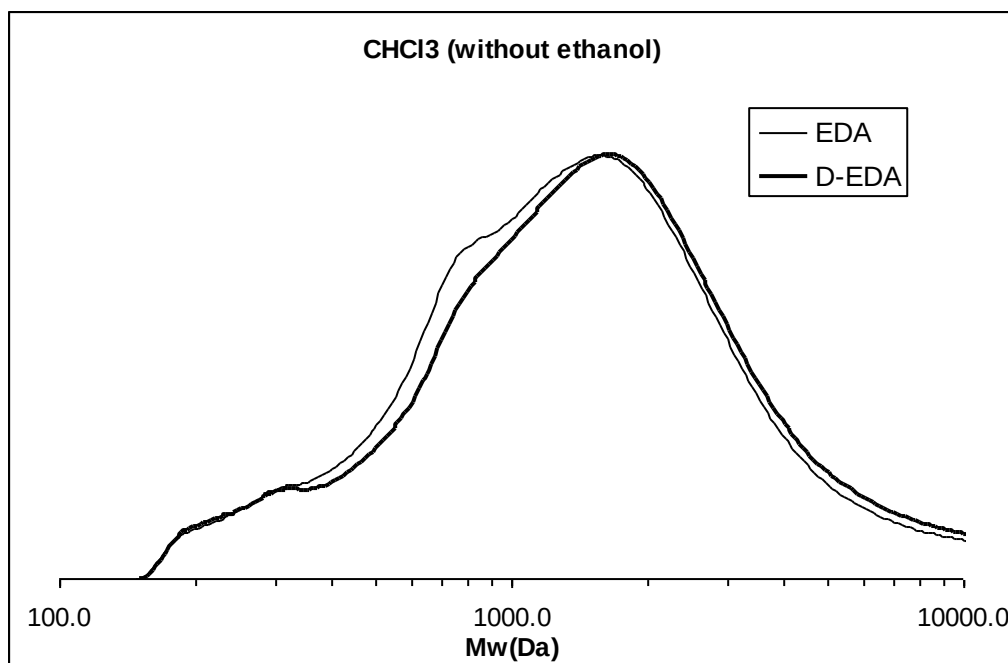


Figure S4-2: SEC traces of the oligomers formed in chloroform without ethanol as stabilizing agent.

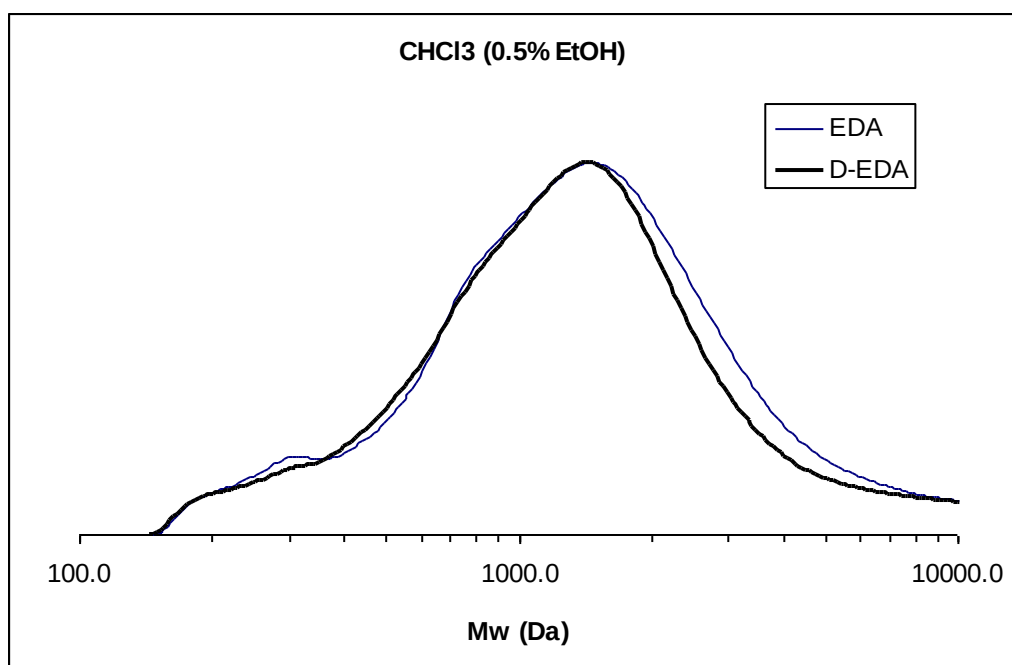


Figure S4-3: SEC traces of the oligomers formed in chloroform with 0.5% ethanol as stabilizing agent.

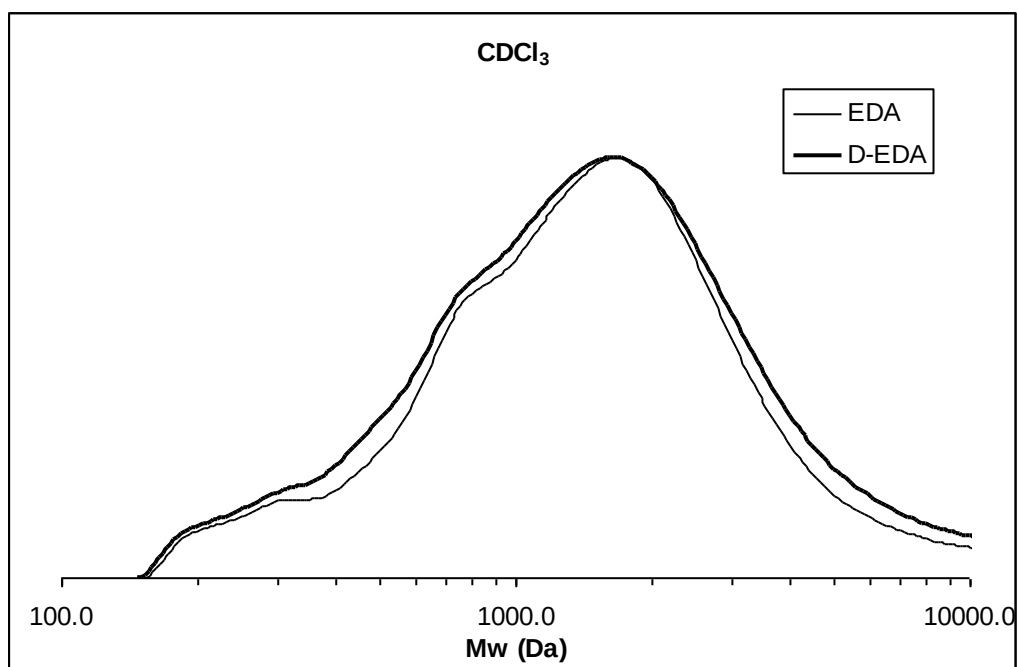


Figure S4-4: SEC traces of the oligomers formed in deuterated chloroform.

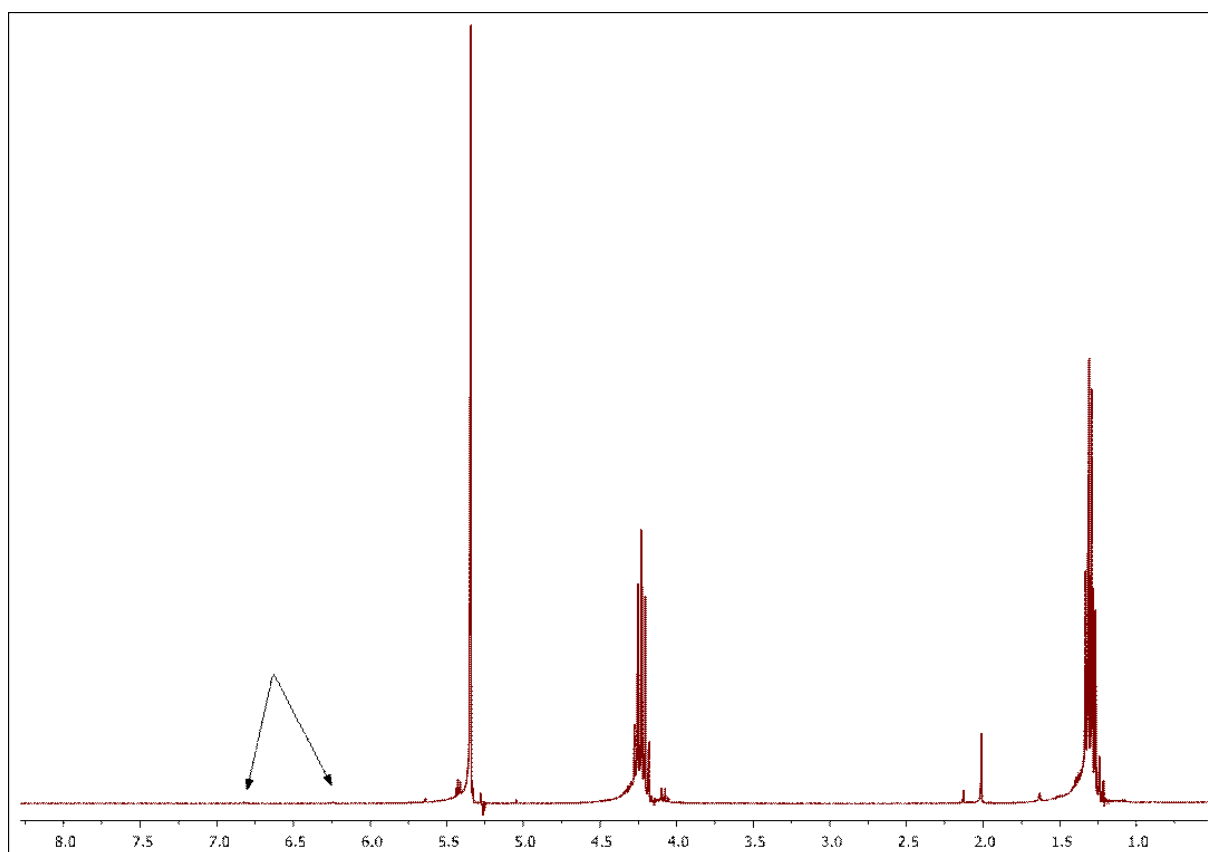


Figure S4-5: NMR (300 MHz, CD_2Cl_2) of the dimers that are formed in the polymerisation of D-EDA as side products. The arrows show the residual signals of the olefinic protons.

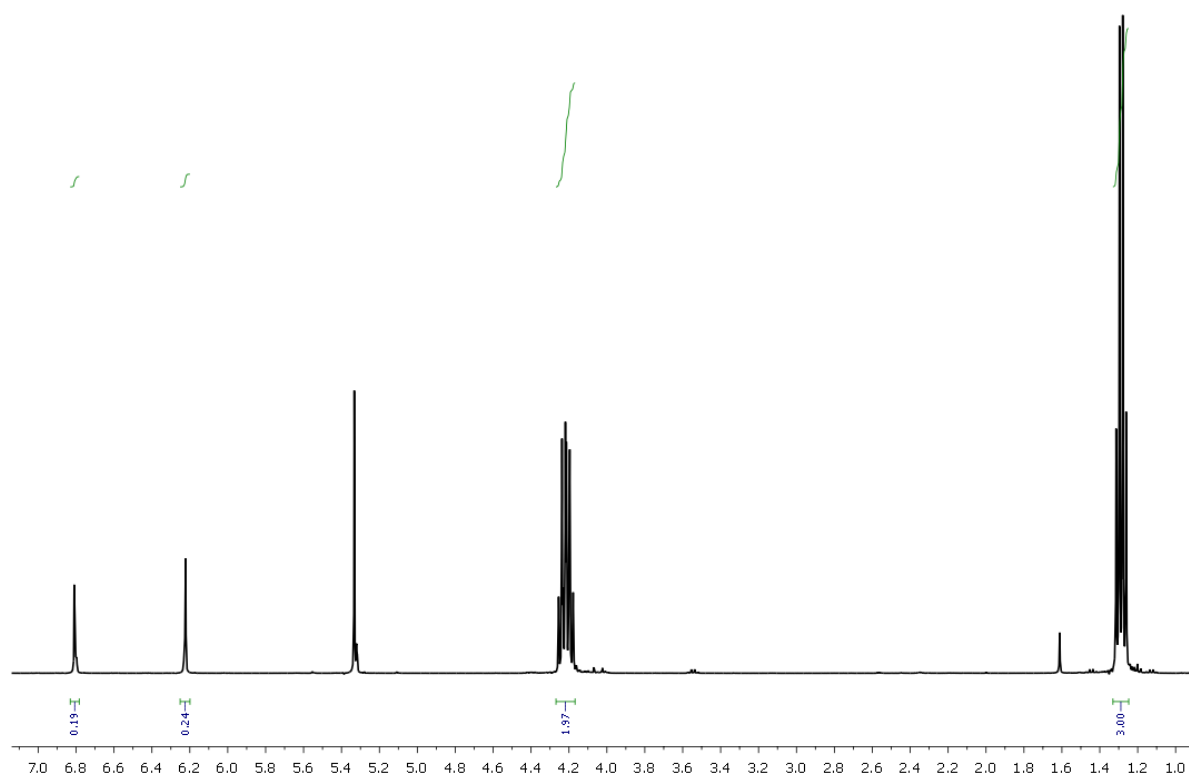


Figure S4-6: NMR (300 MHz, CD_2Cl_2) of the dimers that are formed in the polymerisation of 50% D-EDA and 50% EDA as side products.

Polymerisation experiments with added olefins

Table S0-1: Polymerisation of EDA^a with varying amounts of dimethyl fumarate (yields in %, M_w and M_n in kDa).

Entry	equ. DMF	Solvent	Polymer				Oligomer			
			yield	M_w	M_n	M_w/M_n	yield	M_w	M_n	M_w/M_n
1	0	DCM	29	190	63	3.0	43	2.4	1.2	2.0
2	1	DCM	28	200	63	3.2	45	3.2	1.4	2.3
3	5	DCM	25	220	80	2.7	49	3.2	1.3	2.4
4	10	DCM	26	240	78	3.1	48	2.7	1.2	2.2
5	25	DCM	24	220	70	3.2	48	2.3	1.1	2.1

a) Standard conditions: 0.04 mmol [Rh(cod)(L-pro)], 5 ml dichloromethane, 2 mmol EDA and 0 – 25 equivalents of dimethyl fumarate relative to catalyst concentration.

Table S0-2: Polymerisation of EDA^a with varying amounts of maleic anhydride (yields in %, M_w and M_n in kDa).

Entry	equ. MA	Solvent	Polymer				Oligomer			
			yield	M_w	M_n	M_w/M_n	yield	M_w	M_n	M_w/M_n
1	0	DCM	28	190	63	3.0	46	2.2	1.3	1.7
2	1	DCM	15	190	53	3.5	43	2.7	1.2	2.2
3	5	DCM	8	120	39	3.1	36	2.9	1.0	2.4
4	10	DCM	7	130	35	3.7	36	2.4	1.0	2.4
5	25	DCM	3	110	33	3.3	nd ^b			

a) Standard conditions: 0.04 mmol [Rh(cod)(L-pro)], 5 ml dichloromethane, 2 mmol EDA and 0 – 25 equivalents of maleic anhydride relative to catalyst concentration. b) Because of the high amount of cycloaddition products, the oligomeric fraction was not analyzed further.

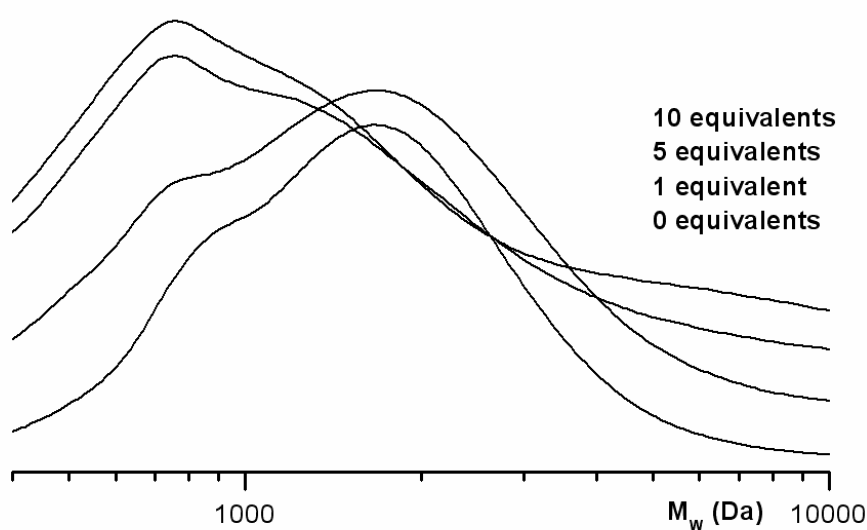
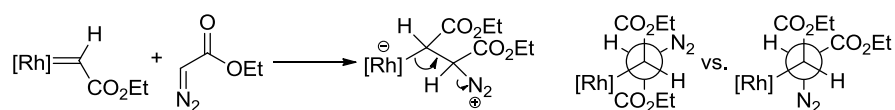


Figure S0-1: Molecular weight distribution of the oligomer fraction after addition of varying amounts of maleic anhydride (0, 1, 5, 10 equivalents relative to catalyst concentration). The peaks on the left side are caused by the different olefins and their cycloaddition products with EDA; the ones on the right side present the actual oligomers. The SEC trace off the oligomer when 25 equivalents are added is not clear and therefore excluded.

S5. Formation of the dimers

In the text the question arose if the the decreased formation of dimers using deuterated EDA could be explained by a KIE in a rate limiting β -H elimination step from a Rh-CH(COOEt)-CH₂(COOEt) species. In our view, there are reasons that speak against this possibility.

Firstly, in the transitions state, the *cis* or *trans* arrangement of the ester groups is already present rendering the formation of maleate unfavourable. The DFT calculations predict a difference in energy of more than 20 kJ mol⁻¹. That means, we should observe exclusively or at least mainly diethyl fumarate as side product if this is the only pathway towards the dimers. This is not the case; instead, both dimers are formed in roughly equal amounts. The proposed chain transfer could explain this result by the fast consumption of the fumarate afterwards – however we do not find any experimental evidence for this (*vide infra*). More likely is the formation of the dimers by nucleophilic attack of EDA at an intermediate electrophilic carbene. This mechanism is proposed for EDA dimerisation as a competing pathway in the Rh(II) catalyzed cyclopropanation.¹ In this case, the steric demand of the present diazo group is comparable to the ester groups (see Scheme S5-1).



Scheme S5-1: The formation of the dimers can be explained by nucleophilic attack of EDA at an intermediate carbene complex.

Secondly, the hydride complex [$\{\text{Rh}(\text{cod})\text{H}\}_4$] (Ref 2) gives the same product distribution as $[\text{Rh}(\text{cod})(\text{L-pro})]$. It further catalyzes the isomerisation of diethyl maleate to diethyl fumarate – without that the insertion product can be detected.

We also investigated the deuterium content of the dimers. In the case of 100% D-EDA, the dimers exhibit the same deuterium content as the used substrate (see Figure S4-5). If we use a mixture of 50% EDA and 50% D-EDA, the dimers have a deuterium content of 45% (see Figure S4-6), which is within the experimental error. In case of β -H elimination, the KIE will lead to an increase of ²H in the dimer because the hydrogen will be transferred to the metal preferable. However, if after two monomer insertions the formed hydride complex eliminates again dimer, the deuterium content of the product will not alter in comparison to the substrate. These experiments are therefore only of weak evidence.

The formation of *cis* and *trans* products being the strongest argument, we believe that experimental evidence speaks against a KIE in the dimer formation. It seems more likely, that D-EDA supports the catalyst activation process and leads therefore to a higher selectivity.

¹ Doyle, M.P.; McKervey, M.A.; Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*; John Wiley & Sons: New York, 1998.

² Kulzick, M.; Price, R. T.; Muetterties, E. L.; Day, V. W. *Organometallics* **1982**, *1*, 1256.