SUPPORTING INFORMATION

In silico Acetylene [2+2+2] Cycloadditions Catalyzed by Rh/Cr Indenyl Fragments

Shah Masood Ahmad [1], Marco Dalla Tiezza [1] and Laura Orian [1,*]

[1] Dipartimento di Scienze Chimiche Universita' degli Studi di Padova, Via Marzolo 1, 35131-Padova (Italy); shahmasood.ahmad@studenti.unipd.it (S.M.A.); marco.dallatiezza@studenti.unipd.it (M.D.T.)

* Correspondence: laura.orian@unipd.it; Tel.: +39-0498275140 (L.O.)

Content

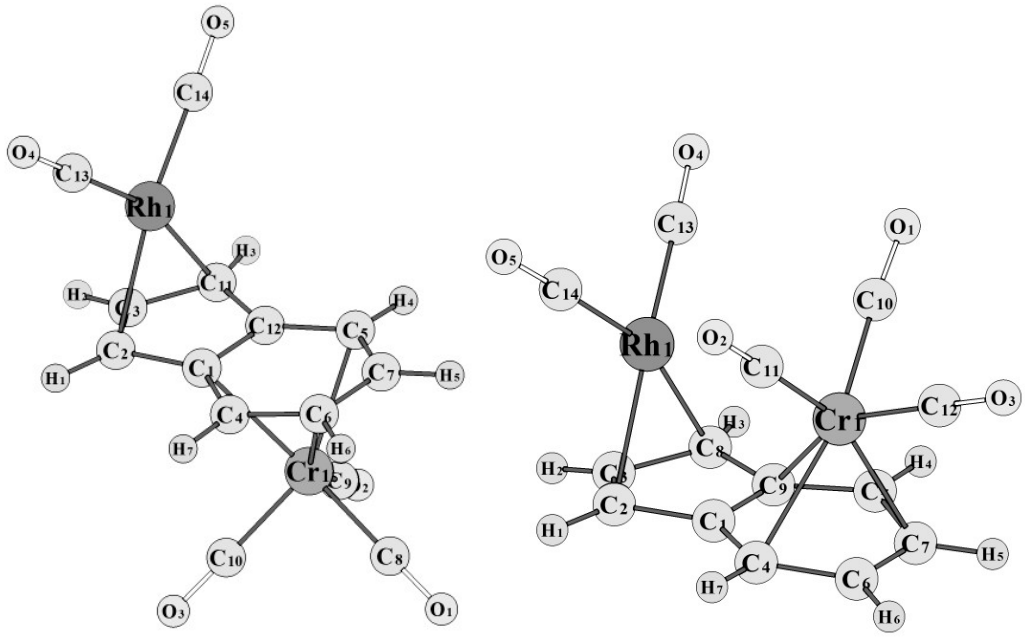


Figure S1. Optimized geometries of anti- and syn-[$Cr(CO)_3IndRh(CO)_2$]. Level of theory: ZORA-BLYP/TZ2P.

Table S1. Selected geometric parameters of the anti- and syn-[$Cr(CO)_3IndRh(CO)_2$], computed at ZORA-BLYP/TZ2P level of theory.

anti-[$Cr(CO)_3IndRh(CO)_2$]			**syn-[$Cr(CO)_3IndRh(CO)_2$]**		
Bond distances (Å)	Calc	Exp[20]	**Bond distances (Å)**	Calc	Exp[20]
Cr1-C12	2.36	2.28	Cr1-C9	2.49	2.37
Cr1-C5	2.29	2.25	Cr1-C5	2.30	2.24
Cr1-C7	2.26	2.23	Cr1-C7	2.24	2.18
Cr1-C6	2.26	2.22	Cr1-C6	2.24	2.19
Cr1-C4	2.29	2.23	Cr1-C4	2.31	2.25
Cr1-C1	2.36	2.26	Cr1-C1	2.48	2.40
Rh1-C11	2.30	2.21	Rh1-C2	2.28	2.20
Rh1-C3	2.26	2.23	Rh1-C3	2.21	2.19
Rh1-C2	2.30	2.23	Rh1-C8	2.29	2.25
Rh1-C1	2.62	2.41	Rh1-C9	2.69	2.58
Rh1-C12	2.62	2.45	Rh1-C1	2.69	2.54
Rh1-C13	1.89	1.85	Rh1-C13	1.89	1.87

Rh1-C14	1.89	1.86	Rh1-C14	1.89	1.88
Cr1-Rh1	4.77	4.47	Cr1-Rh1	3.30	3.08
Bond angles (°)			**Bond angles (°)**		
C8-Cr-C9	89.2	55.3	C12-Cr-C11	86.4	85.7
C10-Cr-C11	89.1	90.3	C10-Cr-C11	93.5	95.5
Cr1-C9-O2	179.0	177.1	Cr1-C10-O1	176.3	175.3
Cr1-C8-O1	179.1	178.3	Cr1-C12-O3	179.4	177.9
Cr1-C10-O3	179.1	179.2	Cr1-C11-O2	176.3	178.5
Rh1-C14-O5	178.4	172.5	Rh1-C13-O4	177.0	177.3
Rh1-C13-O4	178.4	177.3	Rh1-C14-O5	177.1	176.7
Other parameters			**Other parameters**		
ΔRh (Å) [a]	0.32	0.20	ΔRh (Å)	0.40	0.34
ΔCr (Å)	0.07	0.04	ΔCr (Å)	0.18	0.14
HA_{Rh} (°) [b]	11.7	11	HA_{Rh} (°)	13.7	11.8

[a] Δ is Basolo slippage parameter; [Eq. (1)]. [b] HA indicates the hinge angle, i.e. angle between the planes containing C1, C2, C3 and C3, C4, C5, C1 (Scheme 1 (b)).

Table S2. Cartesian coordinates (in Å) and ADF total energies (in kcal mol-1) of all the intermediates and the transition states along Path I catalyzed by anti-[$Cr(CO)_3$IndRh] fragment, computed at ZORA-BLYP/TZ2P level of theory.

anti-Ind-1

E= -4709.12 kcal mol^{-1}

C	-0.101707000000	0.073784000000	-0.721569000000
C	0.743258000000	-1.039092000000	-1.147626000000
C	1.099656000000	-1.807171000000	0.000589000000
Rh	2.532252000000	-0.082372000000	-0.000083000000
C	3.728037000000	0.983902000000	1.415549000000
C	3.681517000000	-0.225772000000	1.760419000000
C	3.676770000000	-0.216730000000	-1.764676000000
C	3.727916000000	0.990146000000	-1.410829000000
H	0.866851000000	-1.354711000000	-2.176823000000
H	1.543532000000	-2.794612000000	0.000956000000
H	0.867504000000	-1.352693000000	2.177702000000
H	4.110774000000	1.994387000000	-1.467010000000
H	3.874365000000	-1.041886000000	-2.428156000000
H	3.883274000000	-1.055290000000	2.417196000000
H	4.107661000000	1.988970000000	1.478591000000
C	-0.827149000000	1.070455000000	-1.436254000000
C	-0.827159000000	1.071541000000	1.435379000000
C	-1.475332000000	2.097669000000	-0.715037000000
C	-1.475282000000	2.098259000000	0.713405000000
H	-0.864402000000	1.058762000000	2.520480000000
H	-2.019138000000	2.870670000000	1.247653000000
H	-2.019209000000	2.869659000000	-1.249875000000
H	-0.864390000000	1.056861000000	-2.521345000000
C	-4.068369000000	0.847777000000	-0.001112000000
C	-2.886023000000	-1.065206000000	1.305977000000

C	-2.885290000000	-1.067421000000	-1.304318000000
O	-5.141555000000	1.310626000000	-0.001763000000
O	-3.199349000000	-1.824952000000	2.136056000000
O	-3.198135000000	-1.828591000000	-2.133277000000
Cr	-2.361194000000	0.144358000000	-0.000048000000
C	0.743405000000	-1.038088000000	1.148249000000
C	-0.101691000000	0.074314000000	0.721470000000
C	-2.945249000000	-1.038181000000	-1.315191000000
O	-5.033343000000	1.465997000000	-0.000577000000
O	-3.314378000000	-1.765237000000	2.151090000000
O	-3.315028000000	-1.767230000000	-2.149292000000
Cr	-2.337068000000	0.127972000000	-0.000119000000
C	0.731423000000	-1.227045000000	1.161146000000
C	-0.034170000000	-0.082987000000	0.732034000000

anti-Ind-TS (1, 2)

E=-4693.61 kcal mol^{-1} -447.22 cm^{-1}

C	-0.034123000000	-0.084252000000	-0.731582000000
C	0.731432000000	-1.229137000000	-1.158685000000
C	1.128239000000	-1.965074000000	0.001888000000
Rh	2.415212000000	-0.115669000000	0.000039000000
C	3.827353000000	1.239244000000	0.960971000000
C	3.797586000000	0.066662000000	1.503036000000
C	3.796301000000	0.066774000000	-1.504185000000
C	3.826622000000	1.239275000000	-0.961984000000
H	0.875619000000	-1.542042000000	-2.185214000000
H	1.612963000000	-2.933176000000	0.002739000000
H	0.875852000000	-1.537903000000	2.188262000000
H	3.905482000000	2.287302000000	-1.224960000000
H	4.123449000000	-0.558402000000	-2.319691000000
H	4.125339000000	-0.558767000000	2.318103000000
H	3.906578000000	2.287223000000	1.224017000000
C	-0.748844000000	0.938096000000	-1.439595000000
C	-0.748976000000	0.940566000000	1.438223000000
C	-1.318029000000	2.006443000000	-0.716972000000
C	-1.318128000000	2.007640000000	0.713699000000
H	-0.798929000000	0.925827000000	2.522611000000
H	-1.820762000000	2.810133000000	1.244215000000
H	-1.820592000000	2.808037000000	-1.248909000000
H	-0.798622000000	0.921540000000	-2.523968000000
C	-3.988489000000	0.938639000000	-0.000367000000
C	-2.944874000000	-1.036941000000	1.316246000000

anti-Ind-2

E= -4729.74 kcal mol^{-1}

C	-0.290362000000	0.351703000000	-0.930641000000
C	0.461053000000	-0.579892000000	-1.767746000000
C	1.061448000000	-1.536593000000	-0.940686000000
Rh	2.347025000000	0.155601000000	-0.293146000000
C	4.669724000000	0.302140000000	1.408725000000
C	3.397631000000	0.749223000000	1.355879000000
C	4.064762000000	-0.884382000000	-0.568517000000
C	5.043531000000	-0.616256000000	0.317170000000
H	0.461280000000	-0.579392000000	-2.850834000000
H	1.580770000000	-2.428721000000	-1.268173000000
H	1.084866000000	-1.773018000000	1.317029000000
H	6.047551000000	-1.038499000000	0.231797000000
H	4.158269000000	-1.551198000000	-1.427994000000
H	2.960803000000	1.409761000000	2.110623000000
H	5.382499000000	0.581524000000	2.187672000000
C	-1.107370000000	1.471734000000	-1.243627000000
C	-0.691026000000	0.721782000000	1.501972000000
C	-1.672599000000	2.221023000000	-0.181188000000
C	-1.439180000000	1.878733000000	1.181529000000
H	-0.560012000000	0.425364000000	2.538452000000
H	-1.900479000000	2.462925000000	1.970731000000
H	-2.304287000000	3.073271000000	-0.412109000000
H	-1.305874000000	1.745430000000	-2.274988000000
C	-4.121617000000	0.751249000000	-0.007294000000
C	-2.973209000000	-1.029848000000	1.473954000000

C	-2.816274000000	-1.196732000000	-1.135220000000
O	-5.206928000000	1.171592000000	-0.084842000000
O	-3.332209000000	-1.736810000000	2.328130000000
O	-3.073496000000	-2.011990000000	-1.926643000000
Cr	-2.389899000000	0.109631000000	0.123301000000
C	0.869124000000	-1.148547000000	0.457865000000
C	-0.069539000000	-0.024453000000	0.458634000000

anti-Ind-3

E= -5261.28 kcal mol^{-1}

C	0.266751000000	-0.070985000000	-0.544934000000
C	-0.408205000000	1.129369000000	-1.019786000000
C	-0.580979000000	1.998548000000	0.116552000000
Rh	-2.173808000000	0.347871000000	0.096461000000
C	-4.379247000000	1.415040000000	-1.433855000000
C	-3.599020000000	1.715384000000	-0.375635000000
C	-3.068320000000	-0.549221000000	-1.534014000000
C	-4.079013000000	0.152113000000	-2.090107000000
H	-0.519070000000	1.418833000000	-2.056739000000
H	-0.947329000000	3.016275000000	0.071006000000
H	-0.241159000000	1.699754000000	2.297343000000
H	-4.632333000000	-0.190678000000	-2.966275000000
H	-2.728720000000	-1.528464000000	-1.877114000000
H	-3.692430000000	2.596956000000	0.258182000000
H	-5.181589000000	2.074836000000	-1.769636000000
C	0.789827000000	-1.224369000000	-1.213069000000
C	0.970717000000	-1.028604000000	1.651631000000
C	1.278438000000	-2.300841000000	-0.442971000000
C	1.363486000000	-2.206441000000	0.980996000000
H	1.083800000000	-0.947377000000	2.728319000000
H	1.791793000000	-3.028734000000	1.545167000000
H	1.646565000000	-3.192891000000	-0.939764000000
H	0.768168000000	-1.288893000000	-2.296342000000
C	4.082674000000	-1.511246000000	0.013153000000
C	3.375658000000	0.641153000000	1.280159000000
C	3.181037000000	0.527130000000	-1.328265000000
O	5.050575000000	-2.164591000000	-0.025979000000
O	3.889076000000	1.359410000000	2.042837000000
O	3.570786000000	1.174322000000	-2.216906000000
Cr	2.538224000000	-0.505397000000	0.079324000000
C	-0.203236000000	1.309792000000	1.287496000000
C	0.373737000000	0.034453000000	0.902180000000
C	-3.381317000000	-1.115207000000	1.107485000000
C	-3.326914000000	-0.121892000000	1.867299000000
H	-3.558619000000	0.477820000000	2.729003000000
H	-3.739803000000	-2.066583000000	0.757414000000

anti-Ind-TS(3,4)

E= -5255.99 kcal mol^{-1} -328.373 cm^{-1}

C	0.358307000000	-0.252706000000	-0.690682000000
C	-0.283421000000	0.802694000000	-1.438374000000
C	-0.609433000000	1.863520000000	-0.529986000000
Rh	-2.112840000000	0.271524000000	-0.117595000000
C	-4.655520000000	1.587446000000	0.324109000000
C	-3.608006000000	1.102359000000	1.049352000000
C	-3.584025000000	0.567306000000	-1.532569000000
C	-4.645779000000	1.290084000000	-1.079274000000
H	-0.365028000000	0.847683000000	-2.517165000000
H	-0.973980000000	2.844943000000	-0.805008000000
H	-0.438711000000	2.005302000000	1.702247000000
H	-5.460541000000	1.595769000000	-1.737411000000
H	-3.444556000000	0.266842000000	-2.568880000000
H	-3.486165000000	1.254067000000	2.119801000000
H	-5.472849000000	2.140867000000	0.788934000000
C	0.971524000000	-1.490572000000	-1.074080000000
C	0.922087000000	-0.730553000000	1.698940000000
C	1.414210000000	-2.379100000000	-0.072626000000
C	1.389168000000	-2.001736000000	1.306287000000
H	0.954025000000	-0.433294000000	2.742679000000
H	1.794833000000	-2.679249000000	2.050878000000

H	1.838685000000	-3.337590000000	-0.353938000000
H	1.041024000000	-1.767235000000	-2.121587000000
C	4.163469000000	-1.423581000000	0.450078000000
C	3.314657000000	0.919804000000	1.168161000000
C	3.354912000000	0.238559000000	-1.371917000000
O	5.143304000000	-2.035534000000	0.630927000000
O	3.745900000000	1.798219000000	1.803792000000
O	3.811887000000	0.685639000000	-2.348041000000
Cr	2.607060000000	-0.481774000000	0.171246000000
C	-0.319788000000	1.418406000000	0.800052000000
C	0.333808000000	0.133086000000	0.717126000000
C	-3.397650000000	-1.362546000000	-0.409520000000
C	-3.427324000000	-1.063175000000	0.841298000000
H	-3.643869000000	-1.363102000000	1.852568000000
H	-3.597468000000	-2.072507000000	-1.193659000000

anti-Ind-4

E= -5329.93 kcal mol^{-1}

C	-0.475755000000	-0.220828000000	0.725234000000
C	0.426079000000	0.870092000000	1.147023000000
C	0.708150000000	1.702167000000	-0.000005000000
Rh	2.258865000000	0.322536000000	0.000000000000
C	3.584435000000	-1.527247000000	-0.703809000000
C	4.004302000000	-0.356294000000	-1.404727000000
C	4.004299000000	-0.356287000000	1.404735000000
C	3.584432000000	-1.527242000000	0.703822000000
H	0.501873000000	1.204517000000	2.176834000000
H	0.943076000000	2.760855000000	-0.000006000000
H	0.501878000000	1.204514000000	-2.176843000000
H	3.246816000000	-2.399285000000	1.255663000000
H	3.971047000000	-0.344295000000	2.490616000000
H	3.971053000000	-0.344308000000	-2.490608000000
H	3.246820000000	-2.399293000000	-1.255646000000
C	-1.207548000000	-1.182540000000	1.433517000000
C	-1.207552000000	-1.182539000000	-1.433525000000
C	-1.941750000000	-2.176351000000	0.705044000000
C	-1.941752000000	-2.176351000000	-0.705052000000
H	-1.236146000000	-1.176054000000	-2.519436000000
H	-2.520780000000	-2.918385000000	-1.245450000000
H	-2.520776000000	-2.918386000000	1.245443000000
H	-1.236139000000	-1.176056000000	2.519428000000
C	-4.058628000000	-0.203492000000	-1.291765000000
C	-2.758099000000	1.667578000000	0.000004000000
C	-4.058621000000	-0.203492000000	1.291768000000
O	-4.892106000000	-0.226930000000	-2.111536000000
O	-2.759846000000	2.835946000000	0.000007000000
O	-4.892094000000	-0.226930000000	2.111543000000
Cr	-2.733383000000	-0.190994000000	-0.000002000000
C	0.426081000000	0.870091000000	-1.147032000000
C	-0.475755000000	-0.220828000000	-0.725243000000
C	4.503151000000	0.774147000000	0.708051000000
C	4.503152000000	0.774143000000	-0.708048000000
H	4.863504000000	1.637676000000	-1.259349000000
H	4.863501000000	1.637684000000	1.259348000000

anti-Ind-5

E= -5850.18 kcal mol^{-1}

C	-0.497893000000	0.204018000000	1.448374000000
C	0.368153000000	0.449704000000	2.604082000000
C	1.713984000000	0.090718000000	2.240652000000
C	1.745706000000	-0.066231000000	0.827774000000
C	0.365096000000	-0.115353000000	0.335380000000
Rh	1.287997000000	2.107033000000	1.465055000000
C	1.297645000000	3.436506000000	3.128811000000
C	0.405878000000	3.857731000000	2.348403000000
C	3.104432000000	3.388952000000	0.494208000000
C	1.941937000000	3.552680000000	-0.311516000000
C	1.876370000000	2.889669000000	-1.571408000000
C	2.936312000000	2.115615000000	-2.016304000000
C	4.105547000000	1.983384000000	-1.227336000000

C	4.187420000000	2.606287000000	0.007312000000
H	2.547408000000	-0.036235000000	2.920174000000
H	0.008434000000	0.606294000000	3.614623000000
C	-1.910518000000	0.261130000000	1.264394000000
H	1.240925000000	4.355366000000	-0.105460000000
H	1.000402000000	3.031754000000	-2.200655000000
H	2.884770000000	1.629514000000	-2.988362000000
H	2.615522000000	-0.334528000000	0.240790000000
C	-0.197173000000	-0.372331000000	-0.948778000000
H	3.266218000000	4.035096000000	1.350696000000
H	4.944973000000	1.401037000000	-1.601583000000
H	5.094930000000	2.528001000000	0.602193000000
H	1.860122000000	3.425442000000	4.047804000000
H	-0.368728000000	4.550688000000	2.063635000000
C	-1.592316000000	-0.233235000000	-1.130825000000
C	-2.445420000000	0.088386000000	-0.031895000000
H	0.437502000000	-0.651217000000	-1.783988000000
H	-2.026668000000	-0.414872000000	-2.108857000000
H	-3.518202000000	0.146801000000	-0.185110000000
H	-2.567880000000	0.462607000000	2.104798000000
C	-2.582827000000	-2.882243000000	-0.313765000000
C	-1.705186000000	-2.556398000000	2.113047000000
C	-0.040068000000	-3.128966000000	0.190137000000
O	-3.398795000000	-3.550655000000	-0.817619000000
O	-1.953842000000	-3.016254000000	3.157466000000
O	0.770012000000	-3.951534000000	0.013140000000
Cr	-1.306142000000	-1.799969000000	0.46534100000

Table S3. Cartesian coordinates (in Å) and ADF total energies (in kcal mol-1) of all the intermediates and the transition states along Path I catalyzed by syn-[$Cr(CO)_3$IndRh] fragment, computed at ZORA-BLYP/TZ2P level of theory.

syn-Ind-1

E=-4708.53 kcal mol^{-1}

C	-0.094221000000	1.732326000000	0.756253000000
C	1.300310000000	1.781006000000	1.154561000000
C	2.091741000000	2.024483000000	-0.017834000000
Rh	1.667817000000	-0.128449000000	-0.057001000000
C	1.858576000000	-1.693823000000	-1.554668000000
C	2.862800000000	-0.951319000000	-1.636650000000
C	2.942097000000	-1.020083000000	1.420332000000
C	1.933407000000	-1.758439000000	1.357999000000
H	1.645702000000	1.857530000000	2.178905000000
H	3.130239000000	2.329974000000	-0.037182000000
H	1.534029000000	1.960153000000	-2.194339000000
H	1.298708000000	-2.585949000000	1.620692000000
H	3.898294000000	-0.695252000000	1.791097000000
H	3.798609000000	-0.608436000000	-2.041531000000
H	1.210865000000	-2.510191000000	-1.820334000000
C	-1.313979000000	1.695150000000	1.493232000000
C	-1.386984000000	1.763209000000	-1.367020000000
C	-2.537411000000	1.892534000000	0.810187000000
C	-2.573791000000	1.926533000000	-0.613946000000
H	-1.429708000000	1.742053000000	-2.451739000000
H	-3.524534000000	2.035974000000	-1.125380000000
H	-3.460687000000	1.976340000000	1.374130000000
H	-1.301472000000	1.622529000000	2.576502000000
Cr	-1.736354000000	-0.050200000000	0.030412000000
C	1.241259000000	1.835331000000	-1.158430000000
C	-0.131243000000	1.766547000000	-0.692216000000
C	-1.402582000000	-1.243222000000	-1.349816000000
O	-1.258237000000	-1.995350000000	-2.233543000000
C	-1.333741000000	-1.307048000000	1.333522000000
O	-1.146068000000	-2.099974000000	2.172328000000
C	-3.436516000000	-0.742118000000	0.057845000000

O	-4.521921000000	-1.177137000000	0.075512000000

O	-4.337590000000	-1.494008000000	0.000000000000

syn-Ind-TS (1,2)

E= -4693.35 kcal mol^{-1} -444.37 cm^{-1}

C	-0.186080000000	1.811021000000	0.730412000000
C	1.173867000000	1.974406000000	1.160852000000
C	1.989980000000	2.191853000000	0.000000000000
Rh	1.721119000000	-0.006503000000	0.000000000000
C	2.185000000000	-1.903486000000	-0.958930000000
C	2.806031000000	-0.897007000000	-1.483648000000
C	2.806031000000	-0.897007000000	1.483648000000
C	2.185000000000	-1.903486000000	0.958930000000
H	1.496445000000	2.084371000000	2.188872000000
H	3.015522000000	2.538591000000	0.000000000000
H	1.496445000000	2.084371000000	-2.188872000000
H	1.657204000000	-2.804586000000	1.246257000000
H	3.469079000000	-0.541119000000	2.255881000000
H	3.469079000000	-0.541119000000	-2.255881000000
H	1.657204000000	-2.804586000000	-1.246257000000
C	-1.424683000000	1.682081000000	1.432346000000
C	-1.424683000000	1.682081000000	-1.432346000000
C	-2.637407000000	1.768737000000	0.713964000000
C	-2.637407000000	1.768737000000	-0.713964000000
H	-1.438458000000	1.630097000000	-2.516937000000
H	-3.580806000000	1.784937000000	-1.250058000000
H	-3.580806000000	1.784937000000	1.250058000000
H	-1.438458000000	1.630097000000	2.516937000000
Cr	-1.664460000000	-0.121869000000	0.000000000000
C	1.173867000000	1.974406000000	-1.160852000000
C	-0.186080000000	1.811021000000	-0.730412000000
C	-1.179351000000	-1.305468000000	-1.346659000000
O	-0.924602000000	-2.059638000000	-2.202098000000
C	-1.179351000000	-1.305468000000	1.346659000000
O	-0.924602000000	-2.059638000000	2.202098000000
C	-3.295720000000	-0.962153000000	0.000000000000

syn-Ind-2

E=-4734.92 kcal mol^{-1}

C	-0.252915000000	1.721978000000	0.761704000000
C	1.207888000000	1.817066000000	0.822372000000
C	1.634727000000	2.356482000000	-0.462057000000
Rh	1.469169000000	0.122669000000	-0.449993000000
C	4.188932000000	-0.816441000000	-0.229503000000
C	3.463217000000	0.066005000000	-0.944390000000
C	2.154342000000	-1.217467000000	0.928289000000
C	3.462519000000	-1.524055000000	0.829134000000
H	1.782671000000	1.860105000000	1.740407000000
H	2.636106000000	2.708344000000	-0.674073000000
H	0.568705000000	2.689333000000	-2.385766000000
H	3.951511000000	-2.261681000000	1.469067000000
H	1.465055000000	-1.649371000000	1.655311000000
H	3.843331000000	0.640247000000	-1.792155000000
H	5.242195000000	-1.020258000000	-0.437534000000
C	-1.233801000000	1.360326000000	1.718367000000
C	-2.007997000000	1.926458000000	-0.987210000000
C	-2.608336000000	1.368687000000	1.351213000000
C	-2.976997000000	1.599601000000	0.003820000000
H	-2.315976000000	2.097999000000	-2.013858000000
H	-4.023813000000	1.541133000000	-0.277946000000
H	-3.366156000000	1.129346000000	2.089784000000
H	-0.944445000000	1.113542000000	2.735652000000
Cr	-1.551413000000	-0.154007000000	0.045778000000
C	0.540734000000	2.392619000000	-1.344534000000
C	-0.654956000000	2.049417000000	-0.605719000000
C	-0.403316000000	-1.026949000000	-1.136906000000
O	0.240404000000	-1.635215000000	-1.928453000000
C	-1.353954000000	-1.498082000000	1.299925000000
O	-1.274171000000	-2.332755000000	2.111495000000
C	-2.935075000000	-1.168005000000	-0.662708000000

O	-3.804757000000	-1.803827000000	-1.104767000000

syn-Ind-TS (2,3)

E= -5242.98 kcal mol^{-1} -47.554397 cm^{-1}

C	-0.575000000000	-2.137800000000	-0.379800000000
C	0.884500000000	-2.128800000000	-0.110600000000
C	0.987800000000	-2.516600000000	1.314600000000
Rh	1.143300000000	-0.033400000000	-0.109700000000
C	3.871000000000	-0.210400000000	-1.011300000000
C	3.158900000000	-0.174500000000	0.136500000000
C	1.728800000000	-0.093700000000	-2.032300000000
C	3.060800000000	-0.154700000000	-2.233700000000
H	1.574400000000	-2.558200000000	-0.835200000000
H	1.937800000000	-2.667400000000	1.816400000000
H	-0.451600000000	-2.798800000000	2.944900000000
H	3.506400000000	-0.120900000000	-3.229600000000
H	0.972100000000	-0.004700000000	-2.815300000000
H	3.605000000000	-0.203200000000	1.135200000000
H	4.961600000000	-0.250600000000	-1.045100000000
C	-1.324700000000	-1.932300000000	-1.560400000000
C	-2.662600000000	-2.256600000000	0.954900000000
C	-2.745200000000	-1.910900000000	-1.490900000000
C	-3.399900000000	-2.025900000000	-0.244500000000
H	-3.183200000000	-2.356400000000	1.902900000000
H	-4.481800000000	-1.945300000000	-0.199200000000
H	-3.326800000000	-1.743000000000	-2.392000000000
H	-0.824200000000	-1.785600000000	-2.512300000000
Cr	-1.932300000000	-0.287700000000	-0.085200000000
C	-0.241800000000	-2.604900000000	1.898700000000
C	-1.260500000000	-2.352100000000	0.883900000000
C	-0.785300000000	0.577000000000	1.111500000000
O	-0.180200000000	1.075400000000	1.995600000000
C	-1.734200000000	0.992000000000	-1.406100000000
O	-1.634100000000	1.794400000000	-2.249400000000
C	-3.304500000000	0.763200000000	0.597100000000
O	-4.173800000000	1.413300000000	1.017700000000
C	1.103300000000	3.686300000000	-0.820600000000
C	1.930500000000	3.695600000000	0.057000000000
H	2.670500000000	3.728000000000	0.827200000000
H	0.359900000000	3.669300000000	-1.593900000000

syn-Ind-3

E=-5259.27 kcal mol^{-1}

C	-0.226002000000	1.636642000000	0.728136000000
C	1.181896000000	1.904783000000	0.418304000000
C	1.140076000000	2.749982000000	-0.778332000000
Rh	1.689597000000	0.017871000000	-0.557889000000
C	4.360629000000	0.322460000000	0.491707000000
C	3.628706000000	0.688278000000	-0.583106000000
C	2.366399000000	-0.762135000000	1.159687000000
C	3.654115000000	-0.493448000000	1.465445000000
H	1.907958000000	2.071332000000	1.209472000000
H	2.023920000000	3.184911000000	-1.232662000000
H	-0.454183000000	3.401510000000	-2.152617000000
H	4.132296000000	-0.882449000000	2.366103000000
H	1.690363000000	-1.416667000000	1.710486000000
H	4.007633000000	1.255588000000	-1.435542000000
H	5.407833000000	0.603152000000	0.618376000000
C	-0.858869000000	0.967050000000	1.809338000000
C	-2.449900000000	2.102736000000	-0.287317000000
C	-2.270545000000	0.936360000000	1.886758000000
C	-3.053843000000	1.468532000000	0.826108000000
H	-3.065523000000	2.500580000000	-1.088699000000
H	-4.135429000000	1.384655000000	0.870367000000
H	-2.757955000000	0.447481000000	2.724090000000
H	-0.261080000000	0.507657000000	2.591294000000
Cr	-1.674635000000	-0.083520000000	-0.067253000000
C	-0.145519000000	2.888975000000	-1.248475000000
C	-1.039557000000	2.226672000000	-0.323158000000
C	-1.253864000000	-0.338675000000	-1.862382000000

O	-1.069688000000	-0.457419000000	-3.008713000000
C	-0.972549000000	-1.688993000000	0.526247000000
O	-0.616719000000	-2.726044000000	0.937063000000
C	-3.201109000000	-1.068420000000	-0.405994000000
O	-4.167740000000	-1.689068000000	-0.609900000000
C	1.623142000000	-1.975875000000	-1.467724000000
C	2.496574000000	-1.316108000000	-2.060730000000
H	3.331381000000	-1.111472000000	-2.705174000000
H	1.014567000000	-2.812623000000	-1.178946000000

syn-Ind-TS(3,4)

E= -5254.66 kcal mol^{-1} -325.80 cm^{-1}

C	-0.426855000000	1.594328000000	0.993930000000
C	0.976813000000	1.763815000000	1.286449000000
C	1.566559000000	2.452372000000	0.174908000000
Rh	1.654330000000	0.328243000000	-0.413385000000
C	4.518350000000	-0.077670000000	-0.341908000000
C	3.580128000000	0.654876000000	-1.001615000000
C	2.645717000000	-1.138822000000	0.658680000000
C	4.008290000000	-1.035376000000	0.594029000000
H	1.435286000000	1.623491000000	2.257302000000
H	2.543096000000	2.919813000000	0.175342000000
H	0.764215000000	2.973279000000	-1.855571000000
H	4.665357000000	-1.669710000000	1.190778000000
H	2.117444000000	-1.804666000000	1.338315000000
H	3.799899000000	1.416891000000	-1.748639000000
H	5.584956000000	0.020634000000	-0.550607000000
C	-1.526852000000	1.130998000000	1.775031000000
C	-1.965323000000	2.003117000000	-0.919885000000
C	-2.838605000000	1.261090000000	1.264754000000
C	-3.055981000000	1.697579000000	-0.076372000000
H	-2.141849000000	2.286165000000	-1.953426000000
H	-4.067474000000	1.744215000000	-0.466990000000
H	-3.686702000000	0.986975000000	1.883881000000
H	-1.368310000000	0.758530000000	2.782629000000
Cr	-1.777557000000	-0.151199000000	-0.112370000000
C	0.615536000000	2.499928000000	-0.892880000000
C	-0.647715000000	2.050546000000	-0.372590000000
C	-1.398926000000	-0.740284000000	-1.834373000000
O	-1.216477000000	-1.089211000000	-2.932372000000
C	-0.943270000000	-1.587531000000	0.715740000000
O	-0.476739000000	-2.507343000000	1.267831000000
C	-3.275446000000	-1.215250000000	-0.187884000000
O	-4.231336000000	-1.886525000000	-0.230128000000
C	1.849030000000	-1.684680000000	-1.216846000000
C	2.098329000000	-0.842261000000	-2.137290000000
H	2.216731000000	-0.586904000000	-3.174118000000
H	1.467005000000	-2.646183000000	-0.921631000000

syn-Ind-4

E=-5321.55 kcal mol^{-1}

C	1.353452000000	1.658522000000	-0.709514000000
C	0.175167000000	2.403426000000	-1.141536000000
C	-0.379063000000	3.072133000000	0.005318000000
Rh	-1.191721000000	1.070175000000	0.056433000000
C	-2.553241000000	-0.484989000000	-0.613390000000
C	-2.532630000000	-0.463518000000	0.815120000000
C	-4.072721000000	1.508368000000	-0.584973000000
C	-3.050326000000	0.698403000000	-1.253782000000
H	-0.049478000000	2.639591000000	-2.175284000000
H	-1.082955000000	3.894558000000	-0.002577000000
H	0.007780000000	2.730846000000	2.192407000000
H	-2.953053000000	0.769017000000	-2.334741000000
H	-4.798310000000	2.065218000000	-1.173384000000
H	-2.123961000000	-1.282080000000	1.398699000000
H	-2.162194000000	-1.321371000000	-1.183645000000
C	2.394832000000	0.996468000000	-1.418910000000
C	2.433646000000	1.058112000000	1.441332000000
C	3.527462000000	0.535009000000	-0.705764000000
C	3.546839000000	0.565907000000	0.718249000000

H	2.437757000000	1.036992000000	2.526975000000
H	4.404001000000	0.170902000000	1.253709000000
H	4.369872000000	0.116477000000	-1.246726000000
H	2.369655000000	0.928606000000	-2.502353000000
Cr	1.800594000000	-0.689101000000	0.056578000000
C	0.205789000000	2.452124000000	1.163832000000
C	1.372555000000	1.688874000000	0.732409000000
C	2.859590000000	-2.188208000000	0.076298000000
O	3.545225000000	-3.136490000000	0.088824000000
C	0.813848000000	-1.465269000000	1.416715000000
O	0.221537000000	-1.969549000000	2.291432000000
C	0.778867000000	-1.524209000000	-1.241540000000
O	0.164165000000	-2.066923000000	-2.076949000000
C	-4.052986000000	1.528466000000	0.771641000000
C	-3.012019000000	0.737729000000	1.434449000000
H	-2.882905000000	0.840601000000	2.509446000000
H	-4.761331000000	2.102999000000	1.364089000000

syn-Ind-5

E=-5847.20 kcal mol^{-1}

C	1.370114000000	1.870008000000	-0.371523000000
C	0.473471000000	2.840346000000	-0.998683000000
C	-0.219032000000	3.549276000000	0.047015000000
Rh	-1.356416000000	1.743848000000	-0.293685000000
C	-3.575441000000	1.993096000000	0.646786000000
C	-3.732604000000	3.062379000000	1.574624000000
C	-2.699345000000	0.603026000000	2.467782000000
C	-3.063078000000	0.742530000000	1.095240000000
H	0.559450000000	3.165119000000	-2.029521000000
H	-0.735196000000	4.496248000000	-0.046700000000
H	-0.467695000000	3.025834000000	2.216048000000
H	-3.187726000000	-0.154301000000	0.495778000000
H	-2.343598000000	-0.359939000000	2.820459000000
H	-4.174668000000	3.997093000000	1.235670000000
H	-4.078765000000	2.058656000000	-0.311006000000
C	2.463550000000	1.111443000000	-0.866245000000
C	1.722415000000	0.931477000000	1.891443000000
C	3.274340000000	0.397708000000	0.052717000000
C	2.905535000000	0.309599000000	1.425329000000
H	1.426300000000	0.822203000000	2.930430000000
H	3.511864000000	-0.275435000000	2.109113000000
H	4.167330000000	-0.108115000000	-0.299474000000
H	2.728133000000	1.141080000000	-1.918769000000
Cr	1.259901000000	-0.569645000000	0.159173000000
C	-0.066082000000	2.771648000000	1.242971000000
C	1.010549000000	1.806687000000	1.024315000000
C	2.112295000000	-2.195081000000	0.158995000000
O	2.666002000000	-3.225437000000	0.162821000000
C	-0.081242000000	-1.419949000000	1.110044000000
O	-0.884934000000	-2.018816000000	1.714332000000
C	0.497635000000	-1.089352000000	-1.447656000000
O	0.069193000000	-1.460986000000	-2.470278000000
C	-2.845529000000	1.661187000000	3.348160000000
C	-3.370007000000	2.900858000000	2.899550000000
H	-3.511108000000	3.715154000000	3.607801000000
H	-2.588166000000	1.533734000000	4.397853000000
C	-2.205137000000	0.736089000000	-2.008417000000
C	-2.339157000000	1.969739000000	-2.189839000000
H	-2.602601000000	2.855841000000	-2.741382000000
H	-2.277876000000	-0.300636000000	-2.28942000000

Table S4. Cartesian coordinates (in Å) and ADF total energies (in kcal mol-1) of all the intermediates and the transition states along Path I catalyzed by anti-[$Cr(CO)_3$IndRh] fragment, computed at ZORA-BLYP/TZ2P level of theory.

CO-anti-Ind-1

E= -5054.68 kcal mol^{-1}

C	1.777851000000	0.171665000000	-3.657102000000
C	1.596578000000	-0.313469000000	-2.326292000000
C	1.537711000000	0.599450000000	-1.259709000000
C	1.711409000000	2.016854000000	-1.512256000000
C	1.920720000000	2.490503000000	-2.820694000000
C	1.948054000000	1.552325000000	-3.897114000000
C	1.652031000000	2.703217000000	-0.223910000000
C	1.438112000000	1.787019000000	0.756200000000
C	1.305669000000	0.414388000000	0.206589000000
Rh	-0.703100000000	-0.373459000000	0.599371000000
C	-1.842906000000	1.385177000000	-0.036321000000
C	-1.851918000000	0.588457000000	-1.004313000000
C	-0.621079000000	-2.251150000000	-0.473891000000
C	-0.122805000000	-2.444632000000	0.669640000000
H	1.782542000000	3.772068000000	-0.091356000000
H	1.383427000000	2.004640000000	1.816801000000
H	1.883382000000	-0.367985000000	0.696990000000
H	-2.122146000000	0.280331000000	-1.998162000000
H	-2.076661000000	2.309577000000	0.459923000000
H	0.333472000000	-3.080060000000	1.409877000000
H	-0.926153000000	-2.611757000000	-1.441827000000
H	1.496492000000	-1.378865000000	-2.146123000000
H	1.832248000000	-0.530009000000	-4.483344000000
H	2.126644000000	1.902914000000	-4.908859000000
H	2.087750000000	3.546088000000	-3.013778000000
C	-0.582115000000	0.043514000000	2.487205000000
O	-0.688131000000	0.192308000000	3.630613000000
Cr	3.534941000000	0.889784000000	-2.424733000000
C	4.818190000000	1.801233000000	-3.411070000000
C	4.493401000000	-0.669437000000	-2.731747000000
C	4.546717000000	1.188491000000	-0.887542000000
O	5.174252000000	1.370877000000	0.076714000000
O	5.613370000000	2.378545000000	-4.039041000000
O	5.082424000000	-1.655795000000	-2.934297000000

CO-anti-Ind-TS(1,2)

E= -5040.78 kcal mol^{-1} -348.75 cm^{-1}

C	1.942823000000	-0.155180000000	-3.458847000000
C	1.774720000000	-0.426867000000	-2.066742000000
C	1.605675000000	0.644940000000	-1.171423000000
C	1.650094000000	2.011420000000	-1.656068000000
C	1.853177000000	2.275543000000	-3.025300000000
C	1.989332000000	1.176606000000	-3.927180000000
C	1.470837000000	2.891688000000	-0.503242000000
C	1.313007000000	2.130407000000	0.614466000000
C	1.334301000000	0.681435000000	0.296528000000
Rh	-0.620425000000	-0.344242000000	0.619759000000
C	-1.526751000000	1.258084000000	-0.438188000000
C	-2.079662000000	0.300355000000	-1.078704000000
C	-2.432110000000	-1.494868000000	-0.210392000000
C	-1.495444000000	-2.187646000000	0.330159000000
H	1.494455000000	3.975650000000	-0.548037000000
H	1.192075000000	2.511898000000	1.622953000000
H	1.988902000000	0.068600000000	0.914044000000
H	-2.499857000000	0.052437000000	-2.042191000000
H	-1.247458000000	2.295858000000	-0.552417000000
H	-1.345474000000	-3.160842000000	0.772587000000
H	-3.490757000000	-1.547186000000	-0.419639000000
H	1.769194000000	-1.452788000000	-1.710621000000
H	2.079707000000	-0.976378000000	-4.155180000000
H	2.158132000000	1.367939000000	-4.982359000000
H	1.922594000000	3.294671000000	-3.394168000000

C	-0.002286000000	-0.730311000000	2.319685000000
O	0.326312000000	-0.894427000000	3.422286000000
Cr	3.600617000000	0.923200000000	-2.358749000000
C	4.809904000000	1.808584000000	-3.450805000000
C	4.706889000000	-0.561884000000	-2.414099000000
C	4.534873000000	1.535193000000	-0.873387000000
O	5.108734000000	1.916023000000	0.067998000000
O	5.557953000000	2.368973000000	-4.150074000000
O	5.389984000000	-1.508097000000	-2.457631000000

CO-anti-Ind-2

E= -5097.75 kcal mol^{-1}

C	1.967814000000	-0.350767000000	0.293994000000
C	1.509981000000	0.007837000000	-1.018239000000
C	0.999324000000	1.388120000000	-0.946976000000
C	1.191782000000	1.849656000000	0.413536000000
C	1.809728000000	0.795438000000	1.139631000000
C	0.527571000000	2.029727000000	-2.148134000000
C	0.386022000000	1.265391000000	-3.321950000000
C	0.880645000000	-0.074980000000	-3.390322000000
C	1.516389000000	-0.674631000000	-2.285544000000
Rh	-0.375003000000	0.119283000000	0.606200000000
C	-1.015540000000	-0.622756000000	2.161583000000
O	-1.417275000000	-1.075266000000	3.148094000000
C	-2.135389000000	1.220193000000	0.411041000000
C	-3.095743000000	0.607610000000	-0.304057000000
H	0.984091000000	2.847087000000	0.778022000000
H	2.115985000000	0.849207000000	2.177595000000
H	2.435817000000	-1.287296000000	0.568171000000
H	-4.052211000000	1.081555000000	-0.534612000000
H	-2.226919000000	2.206949000000	0.863122000000
H	1.934324000000	-1.672958000000	-2.365955000000
H	0.826150000000	-0.611276000000	-4.332382000000
H	-0.033885000000	1.721806000000	-4.212525000000
H	0.197757000000	3.063050000000	-2.120742000000
C	-2.790306000000	-0.752853000000	-0.757108000000
C	-1.593682000000	-1.244321000000	-0.391960000000
H	-3.499095000000	-1.326592000000	-1.358211000000
H	-1.222101000000	-2.244606000000	-0.609941000000
Cr	2.575134000000	1.279179000000	-2.798395000000
C	3.073347000000	1.507544000000	-4.554559000000
C	4.231260000000	0.491462000000	-2.461040000000
C	3.304101000000	2.949842000000	-2.408313000000
O	3.373667000000	1.646679000000	-5.675208000000
O	3.750214000000	3.997226000000	-2.158972000000
O	5.260643000000	-0.009887000000	-2.244420000000

CO-anti-Ind-TS(2,3)

E= -5596.71 kcal mol^{-1} -57.794065cm^{-1}

C	1.767700000000	-0.065000000000	-3.503600000000
C	1.634100000000	-0.452700000000	-2.136100000000
C	1.554900000000	0.542000000000	-1.151800000000
C	1.663800000000	1.941800000000	-1.515700000000
C	1.811400000000	2.317200000000	-2.866400000000
C	1.843300000000	1.297800000000	-3.864600000000
C	1.619200000000	2.717600000000	-0.282900000000
C	1.498400000000	1.863400000000	0.780600000000
C	1.374500000000	0.460600000000	0.322100000000
Rh	-0.654900000000	0.300300000000	1.012500000000
C	-1.457300000000	0.882000000000	-0.834300000000
C	-1.967800000000	-0.141500000000	-1.552600000000
C	-1.778600000000	-1.469700000000	-0.963100000000
C	-1.146000000000	-1.521100000000	0.227100000000
H	1.706300000000	3.798200000000	-0.231600000000
H	1.540900000000	2.160000000000	1.824100000000
H	1.919200000000	-0.323300000000	0.844600000000
H	-2.483400000000	-0.023700000000	-2.509200000000
H	-1.536300000000	1.924100000000	-1.162400000000
H	-0.920900000000	-2.432400000000	0.779800000000
H	-2.139000000000	-2.377900000000	-1.454200000000

H	1.582700000000	-1.503600000000	-1.869600000000
H	1.837400000000	-0.827800000000	-4.272900000000
H	1.972500000000	1.571400000000	-4.907200000000
H	1.918300000000	3.360500000000	-3.149300000000
C	-0.113000000000	-0.515600000000	2.697100000000
O	0.125900000000	-1.129600000000	3.647400000000
Cr	3.515300000000	0.855300000000	-2.389500000000
C	4.722400000000	1.880000000000	-3.357600000000
C	4.558800000000	-0.632700000000	-2.769400000000
C	4.533500000000	1.148500000000	-0.858400000000
O	5.162300000000	1.332400000000	0.105800000000
O	5.473200000000	2.526800000000	-3.973500000000
O	5.203700000000	-1.573600000000	-3.012600000000
C	-3.494200000000	1.214800000000	1.657000000000
C	-2.984100000000	1.226900000000	2.752900000000
H	-2.606900000000	1.250700000000	3.751800000000
H	-3.929200000000	1.200100000000	0.681300000000

CO-anti-Ind-3

E= -5602.15 kcal mol^{-1}

C	1.776683000000	-0.194798000000	-3.465455000000
C	1.645454000000	-0.574363000000	-2.098694000000
C	1.534916000000	0.432020000000	-1.125183000000
C	1.608710000000	1.829494000000	-1.506426000000
C	1.745704000000	2.187668000000	-2.868957000000
C	1.782660000000	1.165896000000	-3.856283000000
C	1.560512000000	2.616688000000	-0.289686000000
C	1.467428000000	1.767097000000	0.792085000000
C	1.355125000000	0.366423000000	0.345236000000
Rh	-0.727825000000	0.430770000000	1.051564000000
C	-1.457434000000	0.762262000000	-0.886312000000
C	-1.849366000000	-0.354388000000	-1.542180000000
C	-1.693667000000	-1.595349000000	-0.797750000000
C	-1.197691000000	-1.493247000000	0.455550000000
H	1.625103000000	3.699269000000	-0.250661000000
H	1.558049000000	2.077484000000	1.827473000000
H	1.868806000000	-0.425148000000	0.885003000000
H	-2.271182000000	-0.349453000000	-2.549691000000
H	-1.558850000000	1.767132000000	-1.304666000000
H	-1.072131000000	-2.322992000000	1.149267000000
H	-1.979201000000	-2.563302000000	-1.218142000000
H	1.631972000000	-1.623479000000	-1.822124000000
H	1.873913000000	-0.965401000000	-4.224138000000
H	1.890390000000	1.427593000000	-4.903864000000
H	1.820107000000	3.230865000000	-3.163203000000
C	-0.146470000000	-0.234714000000	2.801503000000
O	0.136791000000	-0.793346000000	3.771192000000
Cr	3.496155000000	0.809078000000	-2.394208000000
C	4.641599000000	2.125750000000	-3.021793000000
C	4.617977000000	-0.448775000000	-3.166014000000
C	4.489950000000	0.704244000000	-0.825983000000
O	5.091803000000	0.640472000000	0.170743000000
O	5.352135000000	2.959008000000	-3.426080000000
O	5.313390000000	-1.243547000000	-3.662496000000
C	-3.019041000000	0.779432000000	1.304408000000
C	-2.465725000000	1.511262000000	2.125470000000
H	-2.273922000000	2.171057000000	2.947436000000
H	-3.702056000000	0.234597000000	0.686597000000

CO-anti-Ind-TS(3,b)

E= -5599.68 kcal mol^{-1} -270.092913cm^{-1}

C	1.731811000000	-0.164086000000	-3.438161000000
C	1.622342000000	-0.553559000000	-2.071000000000
C	1.540019000000	0.444903000000	-1.086639000000
C	1.611360000000	1.845581000000	-1.460005000000
C	1.724509000000	2.214054000000	-2.820511000000
C	1.742197000000	1.198936000000	-3.817273000000
C	1.583118000000	2.625112000000	-0.236120000000
C	1.503544000000	1.769233000000	0.838349000000

C	1.384855000000	0.370990000000	0.386135000000
Rh	-0.717930000000	0.376011000000	1.090431000000
C	-1.573108000000	0.788255000000	-0.811581000000
C	-1.837717000000	-0.343351000000	-1.534673000000
C	-1.617338000000	-1.581282000000	-0.841869000000
C	-1.092337000000	-1.501263000000	0.414663000000
H	1.646973000000	3.707396000000	-0.190814000000
H	1.586164000000	2.071731000000	1.876699000000
H	1.910143000000	-0.420013000000	0.915334000000
H	-2.199070000000	-0.323150000000	-2.564632000000
H	-1.677977000000	1.794649000000	-1.215773000000
H	-0.959474000000	-2.359509000000	1.072351000000
H	-1.869394000000	-2.546382000000	-1.287986000000
H	1.608403000000	-1.604827000000	-1.803179000000
H	1.810163000000	-0.929446000000	-4.204258000000
H	1.834959000000	1.468293000000	-4.864394000000
H	1.799305000000	3.259218000000	-3.107518000000
C	-0.160235000000	-0.280508000000	2.829816000000
O	0.113369000000	-0.796401000000	3.825945000000
Cr	3.476186000000	0.817711000000	-2.389846000000
C	4.617714000000	2.106224000000	-3.078582000000
C	4.572738000000	-0.474409000000	-3.140088000000
C	4.498920000000	0.758367000000	-0.838370000000
O	5.119977000000	0.721779000000	0.148044000000
O	5.324526000000	2.923580000000	-3.520505000000
O	5.250466000000	-1.292441000000	-3.623560000000
C	-2.948307000000	1.046735000000	0.873177000000
C	-2.372851000000	1.488922000000	1.902681000000
H	-2.468739000000	1.909943000000	2.888973000000
H	-3.826488000000	0.736607000000	0.338139000000

CO-anti-Ind-b

E= -5621.21 kcal mol^{-1}

C	1.731012000000	-0.123488000000	-3.412298000000
C	1.673132000000	-0.524947000000	-2.048033000000
C	1.621727000000	0.466020000000	-1.046424000000
C	1.663027000000	1.873042000000	-1.412076000000
C	1.736312000000	2.249404000000	-2.776164000000
C	1.721315000000	1.245206000000	-3.781176000000
C	1.635314000000	2.642295000000	-0.185821000000
C	1.583840000000	1.771648000000	0.883009000000
C	1.501053000000	0.384587000000	0.416627000000
Rh	-0.652540000000	0.235179000000	1.128113000000
C	-1.619358000000	0.715158000000	-0.756392000000
C	-2.176243000000	-0.538033000000	-1.295212000000
C	-2.109428000000	-1.645897000000	-0.485696000000
C	-1.419340000000	-1.483872000000	0.738901000000
H	1.676804000000	3.724866000000	-0.130760000000
H	1.660126000000	2.065611000000	1.924676000000
H	1.995253000000	-0.418063000000	0.958687000000
H	-2.641487000000	-0.578304000000	-2.283269000000
H	-1.131242000000	1.351772000000	-1.500317000000
H	-1.375079000000	-2.295788000000	1.467809000000
H	-2.571643000000	-2.599653000000	-0.748256000000
H	1.678105000000	-1.579854000000	-1.791137000000
H	1.786030000000	-0.881890000000	-4.187433000000
H	1.775174000000	1.523539000000	-4.828597000000
H	1.792897000000	3.297457000000	-3.057267000000
C	-0.239763000000	-0.195463000000	2.990758000000
O	-0.112416000000	-0.518253000000	4.091232000000
Cr	3.512703000000	0.861021000000	-2.426863000000
C	4.620886000000	2.206016000000	-3.056185000000
C	4.586224000000	-0.360871000000	-3.311229000000
C	4.592172000000	0.688683000000	-0.924390000000
O	5.249884000000	0.583004000000	0.033188000000
O	5.307118000000	3.058784000000	-3.463212000000
O	5.249498000000	-1.135978000000	-3.879260000000
C	-2.663124000000	1.496784000000	0.079485000000
C	-2.400028000000	1.287488000000	1.364278000000
H	-2.880094000000	1.651228000000	2.268238000000
H	-3.447827000000	2.112245000000	-0.373502000000

CO-anti-Ind-TS(b,h)

E= -5619.68 kcal mol^{-1} -227.823287 cm^{-1}

C	1.780857000000	-0.297697000000	-3.382157000000
C	1.753272000000	-0.666825000000	-2.011967000000
C	1.638846000000	0.345772000000	-1.029617000000
C	1.612954000000	1.742760000000	-1.429437000000
C	1.667108000000	2.087266000000	-2.808351000000
C	1.689698000000	1.063249000000	-3.786611000000
C	1.546885000000	2.538051000000	-0.226522000000
C	1.548041000000	1.683951000000	0.867931000000
C	1.525269000000	0.293035000000	0.426415000000
Rh	-0.666986000000	0.351455000000	1.155017000000
C	-1.700511000000	0.790617000000	-0.893049000000
C	-1.822518000000	-0.528211000000	-1.399683000000
C	-1.856589000000	-1.636038000000	-0.526383000000
C	-1.359764000000	-1.445075000000	0.748681000000
H	1.526238000000	3.621990000000	-0.194173000000
H	1.653126000000	2.005279000000	1.898916000000
H	1.990333000000	-0.505098000000	0.997694000000
H	-1.797754000000	-0.702951000000	-2.479198000000
H	-1.361385000000	1.539689000000	-1.611639000000
H	-1.324849000000	-2.254300000000	1.478740000000
H	-2.181794000000	-2.620114000000	-0.868979000000
H	1.828126000000	-1.712529000000	-1.729381000000
H	1.874935000000	-1.070360000000	-4.139378000000
H	1.722443000000	1.317332000000	-4.841089000000
H	1.669933000000	3.129880000000	-3.114800000000
C	-0.374297000000	-0.030188000000	2.976688000000
O	-0.232726000000	-0.310200000000	4.089952000000
Cr	3.513663000000	0.806636000000	-2.450009000000
C	4.544848000000	2.295140000000	-2.846732000000
C	4.632733000000	-0.183886000000	-3.538019000000
C	4.619271000000	0.427437000000	-1.005490000000
O	5.294430000000	0.190499000000	-0.083987000000
O	5.183830000000	3.237085000000	-3.108342000000
O	5.326622000000	-0.812029000000	-4.237245000000
C	-2.771405000000	1.359345000000	0.067571000000
C	-2.506270000000	1.236763000000	1.356618000000
H	-3.087773000000	1.525154000000	2.226206000000
H	-3.650381000000	1.830809000000	-0.385275000000

CO-anti-Ind-h

E= -5649.23 kcal mol^{-1}

C	1.308821000000	3.312495000000	2.277462000000
C	-0.056074000000	2.952830000000	2.523885000000
C	-1.122199000000	3.586721000000	1.758862000000
C	-0.795746000000	4.570333000000	0.770663000000
C	0.561422000000	4.815520000000	0.469758000000
C	1.608023000000	4.184805000000	1.210635000000
C	-2.376986000000	3.015236000000	2.205898000000
C	-2.084241000000	2.156945000000	3.321002000000
C	-0.685637000000	2.038325000000	3.466206000000
Rh	-1.451981000000	1.045224000000	1.379802000000
C	-1.739942000000	1.255962000000	-0.632446000000
C	-1.979321000000	0.387187000000	-1.633787000000
C	-0.360024000000	-0.461347000000	1.141166000000
O	0.354393000000	-1.364573000000	1.056079000000
C	-3.152334000000	-0.085146000000	1.376372000000
C	-3.549491000000	-1.121522000000	0.617037000000
C	-2.957577000000	-1.689358000000	-0.585002000000
C	-2.280438000000	-1.033714000000	-1.564165000000
H	-3.361671000000	3.345616000000	1.900636000000
H	-3.173298000000	-2.744996000000	-0.754363000000
H	-4.452304000000	-1.636111000000	0.965952000000
H	-2.005276000000	-1.613535000000	-2.446146000000
H	-1.917711000000	0.790863000000	-2.650535000000
H	-3.762852000000	0.196301000000	2.235771000000
H	-1.557260000000	2.303623000000	-0.892172000000
H	-2.821029000000	1.662306000000	3.941871000000

H	-0.166762000000	1.458457000000	4.219354000000
H	-1.580574000000	5.089857000000	0.229902000000
H	0.817398000000	5.535488000000	-0.301187000000
H	2.641435000000	4.433544000000	0.992320000000
H	2.107240000000	2.877446000000	2.870573000000
Cr	0.281669000000	5.308531000000	2.648255000000
C	0.839838000000	5.250457000000	4.422654000000
C	-1.204663000000	6.302027000000	3.170596000000
C	1.230235000000	6.877311000000	2.439701000000
O	1.193248000000	5.199991000000	5.532607000000
O	1.836718000000	7.864427000000	2.292819000000
O	-2.143597000000	6.914230000000	3.490115000000

CO-anti-Ind-TS(h,4)

E= -5647.57 kcal mol^{-1} -251.097861 cm^{-1}

C	1.304705000000	3.333070000000	2.139261000000
C	-0.043872000000	2.966473000000	2.446159000000
C	-1.145749000000	3.626124000000	1.768126000000
C	-0.877056000000	4.639773000000	0.795196000000
C	0.461384000000	4.904634000000	0.432506000000
C	1.545756000000	4.253660000000	1.097242000000
C	-2.375945000000	3.030103000000	2.264169000000
C	-2.035747000000	2.141429000000	3.335412000000
C	-0.625267000000	1.997976000000	3.374200000000
Rh	-1.484466000000	1.062986000000	1.390673000000
C	-1.990890000000	1.176012000000	-0.600529000000
C	-1.921264000000	0.262805000000	-1.602459000000
C	-0.396653000000	-0.463025000000	1.228461000000
O	0.343185000000	-1.351587000000	1.241057000000
C	-3.271952000000	0.102970000000	1.044288000000
C	-3.534760000000	-1.105454000000	0.490382000000
C	-2.765004000000	-1.796735000000	-0.512332000000
C	-2.024030000000	-1.167217000000	-1.478482000000
H	-3.374825000000	3.365569000000	2.012719000000
H	-2.913030000000	-2.872738000000	-0.600118000000
H	-4.469886000000	-1.588035000000	0.793296000000
H	-1.620110000000	-1.771615000000	-2.290098000000
H	-1.833260000000	0.650538000000	-2.622660000000
H	-4.040014000000	0.589334000000	1.648002000000
H	-2.101737000000	2.232706000000	-0.859696000000
H	-2.738807000000	1.640828000000	3.989621000000
H	-0.064437000000	1.404414000000	4.085548000000
H	-1.691268000000	5.173175000000	0.314545000000
H	0.673617000000	5.652761000000	-0.324627000000
H	2.566100000000	4.515382000000	0.836367000000
H	2.134030000000	2.876456000000	2.670589000000
Cr	0.287572000000	5.314593000000	2.641856000000
C	0.874599000000	5.173491000000	4.401463000000
C	-1.164425000000	6.318148000000	3.229979000000
C	1.264520000000	6.872020000000	2.474673000000
O	1.243108000000	5.068946000000	5.502990000000
O	1.888395000000	7.851568000000	2.352104000000
O	-2.084958000000	6.937214000000	3.589724000000

CO-anti-Ind-4

E= -5695.62 kcal/mol

H	-1.361731000000	2.786196000000	1.926957000000
H	-2.007291000000	0.179715000000	2.049412000000
C	0.476476000000	-1.555489000000	2.323673000000
H	-4.176736000000	1.320338000000	-0.948056000000
H	-4.554411000000	-0.943236000000	-0.004529000000
H	-2.799821000000	-2.699966000000	-0.222235000000
H	1.305448000000	2.971541000000	1.566302000000
C	2.661038000000	0.275129000000	1.959138000000
H	-2.133418000000	1.784845000000	-2.276536000000
H	-0.689956000000	-2.212666000000	-1.431378000000
H	-0.404725000000	-0.027561000000	-2.585694000000
C	2.906970000000	-1.114664000000	2.183358000000
C	1.831699000000	-2.009626000000	2.374961000000
H	3.492742000000	0.964107000000	1.845817000000
H	3.928094000000	-1.475643000000	2.250740000000

H	2.035956000000	-3.054412000000	2.587033000000
H	-0.338317000000	-2.253064000000	2.491240000000
C	0.577030000000	2.440254000000	-1.460565000000
O	1.124971000000	3.195128000000	-2.156637000000
C	1.332371000000	0.731233000000	1.883569000000
C	0.223873000000	-0.195885000000	2.065758000000
C	-3.405636000000	0.557551000000	-1.028625000000
C	-2.198779000000	0.861324000000	-1.709855000000
C	-1.207868000000	-0.148892000000	-1.864147000000
C	-3.617580000000	-0.710867000000	-0.506420000000
C	-2.623672000000	-1.707795000000	-0.632169000000
C	-1.437809000000	-1.434019000000	-1.300015000000
C	0.740189000000	2.047476000000	1.592743000000
C	-1.011677000000	0.574342000000	1.887054000000
C	-0.676934000000	1.953874000000	1.820820000000
Rh	-0.288788000000	1.326970000000	-0.241833000000
Cr	1.664669000000	-0.379895000000	3.926710000000
C	3.155517000000	0.170566000000	4.879008000000
C	0.628666000000	0.831027000000	4.878704000000
C	1.350112000000	-1.651558000000	5.237223000000
O	1.152971000000	-2.466211000000	6.050420000000
O	4.105840000000	0.512142000000	5.465673000000
O	-0.033515000000	1.600236000000	5.456094000000

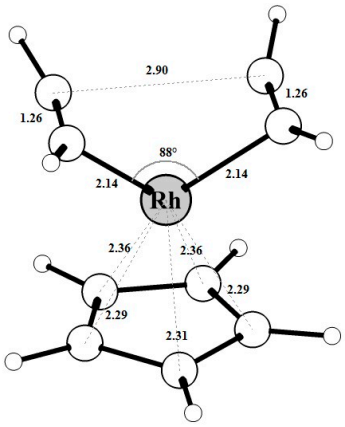
Acetylene

E= -508.77 kcal mol^{-1}

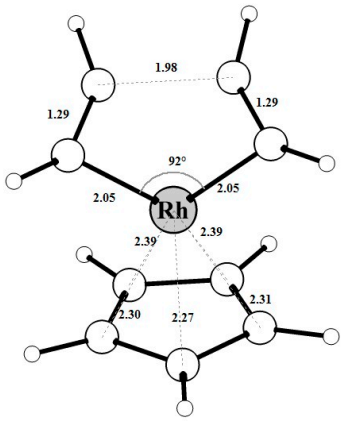
Benzene

E= -1666.21 kcal mol^{-1}

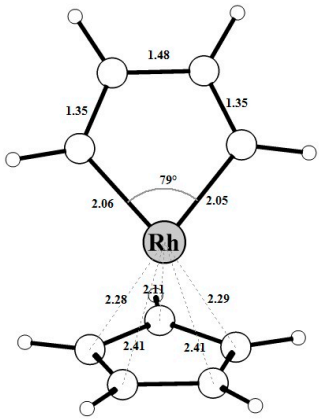
Figure S2. Optimized structures with relevant geometric parameters, i.e. bond lengths (Å) and angles (deg) of the intermediates and transition states along Path (I) for acetylene [2+2+2] cycloaddition catalyzed by CpRh fragment.



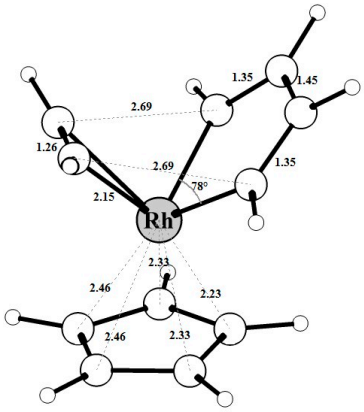
Cp-1



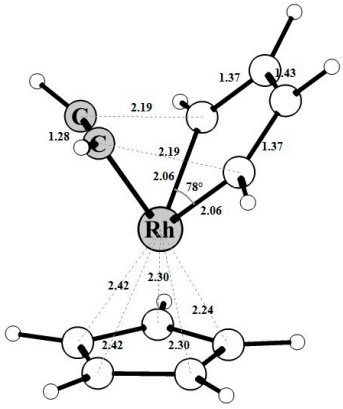
Cp-TS(1,2)



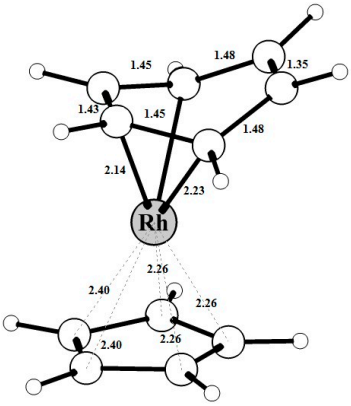
Cp-2



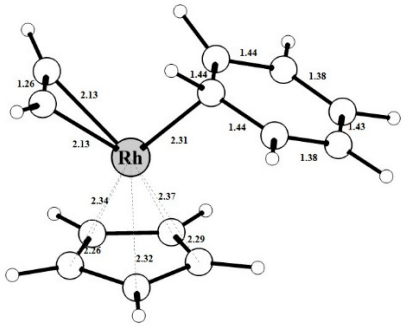
Cp-3



Cp-TS(3,4)

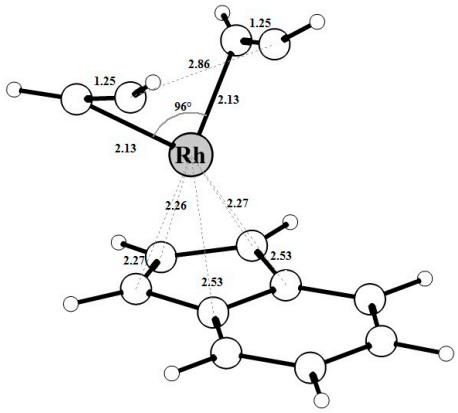


Cp-4

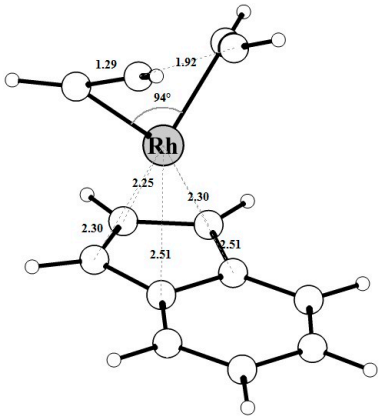


Cp-5

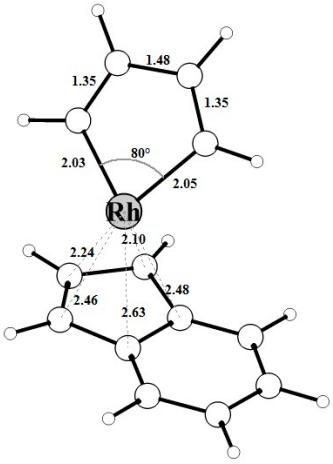
Figure S3. Optimized structures with relevant geometric parameters, i.e. bond lengths (Å) and angles (deg) of the intermediates and transition states along Path (I) for acetylene [2+2+2] cycloaddition catalyzed by IndRh fragment.



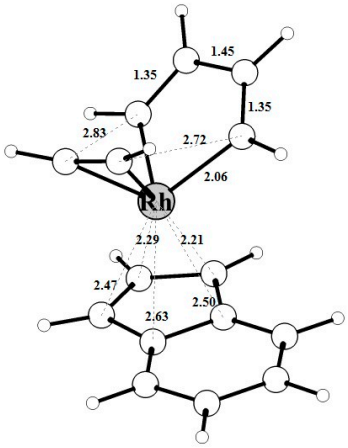
Ind-1



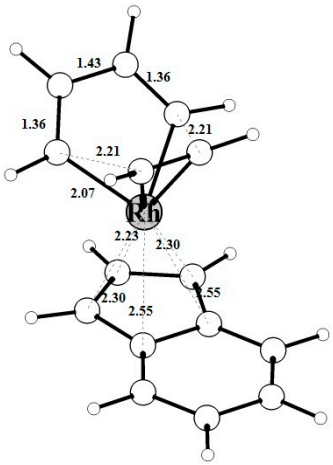
Ind-TS(1,2)



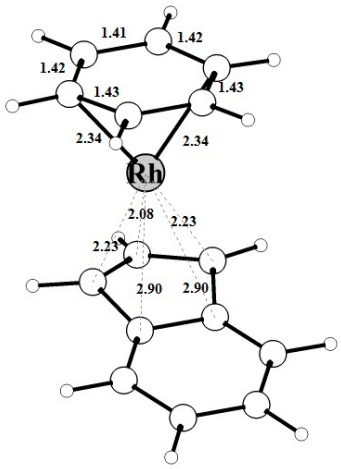
Ind-2



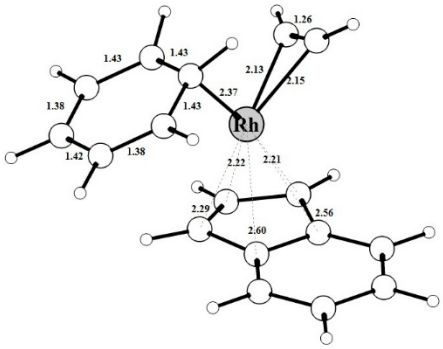
Ind-3



Ind-TS(3,4)

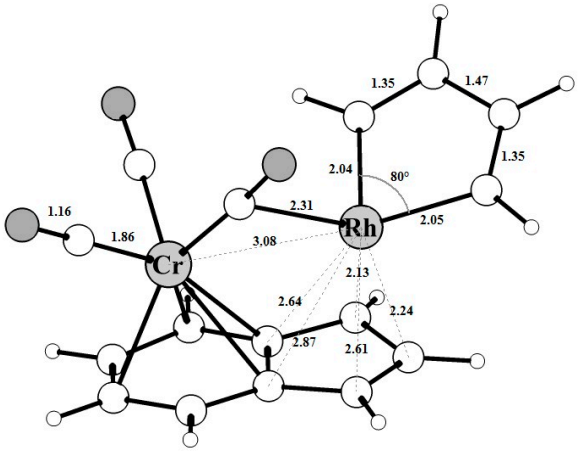


Ind-4

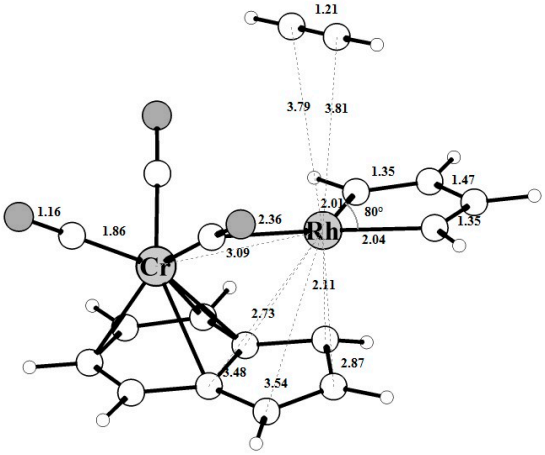


Ind-5

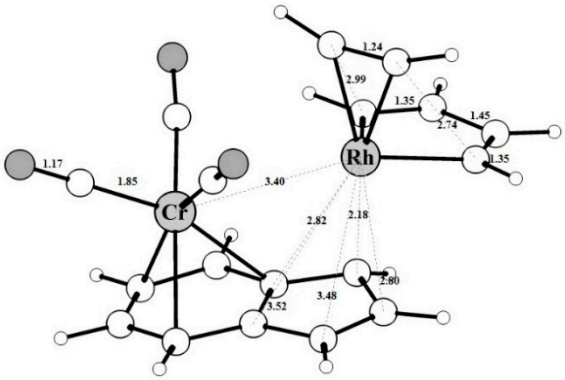
Figure S4. Optimized structures with relevant geometric parameters, i.e. bond lengths (Å) and angles (deg) of the intermediates and transition states along Path (I) for acetylene [2+2+2] cycloaddition catalyzed by syn-IndRh fragment.



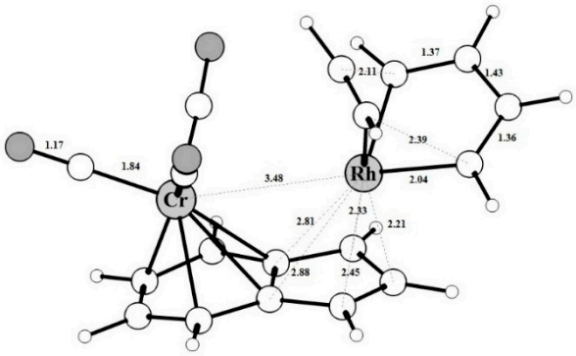
syn-Ind-2



syn-Ind-TS(2,3)

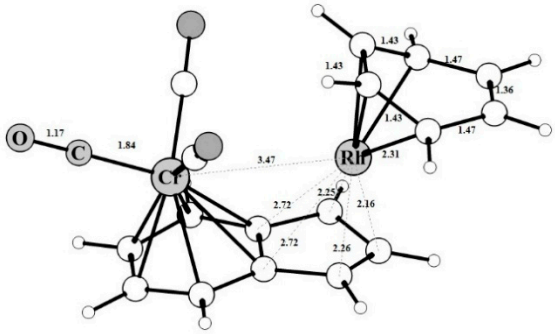


syn-Ind-3



syn-Ind-TS(3,4)

syn-Ind-4



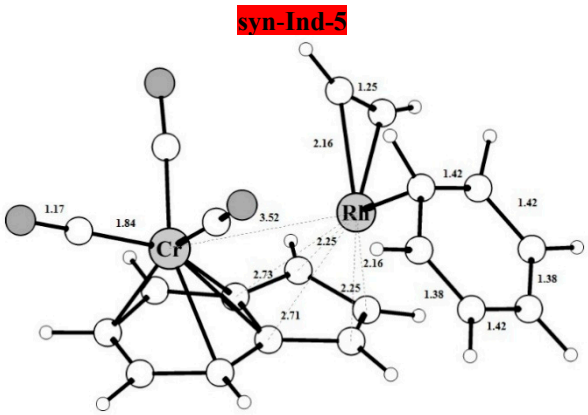
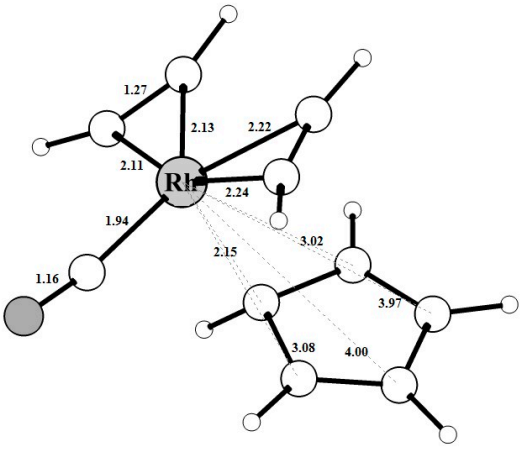
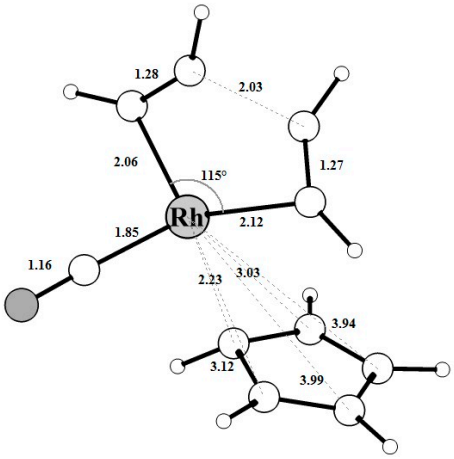


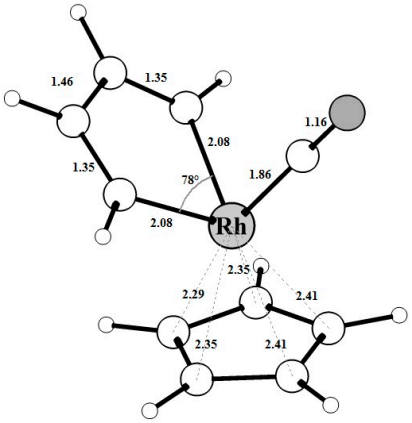
Figure S5. Optimized structures with relevant geometric parameters, i.e. bond lengths (Å) and angles (deg) of the intermediates and transition states along Path (II) for acetylene [2+2+2] cycloaddition catalyzed by CpRh(CO) fragment



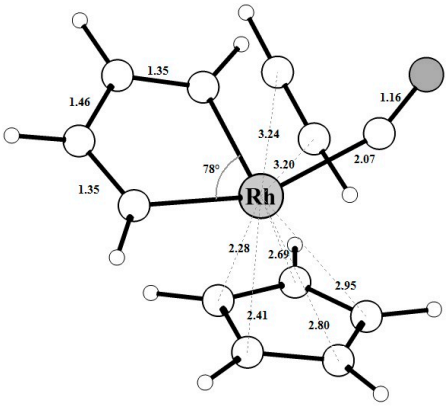
CO-Cp-1



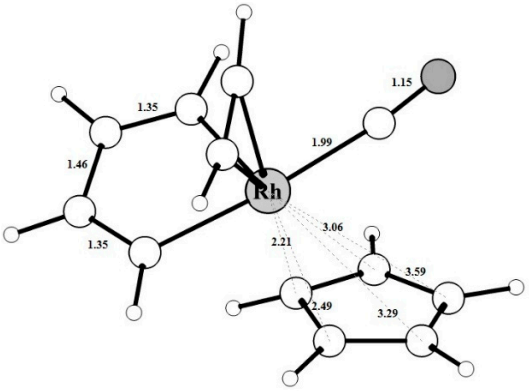
CO-Cp-TS(1,2)



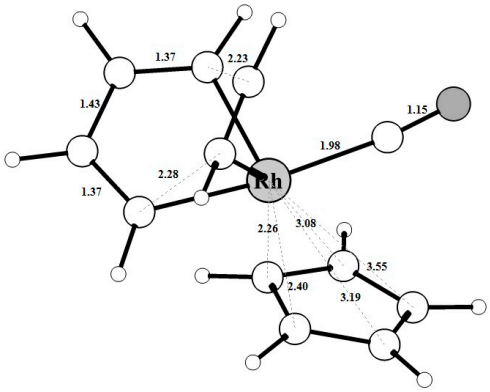
CO-Cp-2



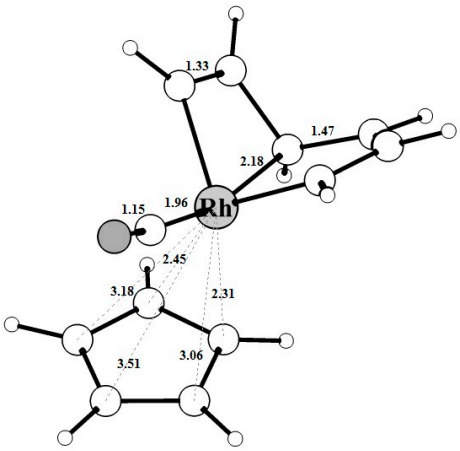
CO-Cp-TS(2,3)



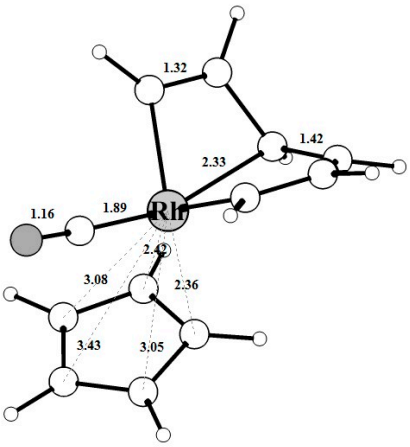
CO-Cp-3



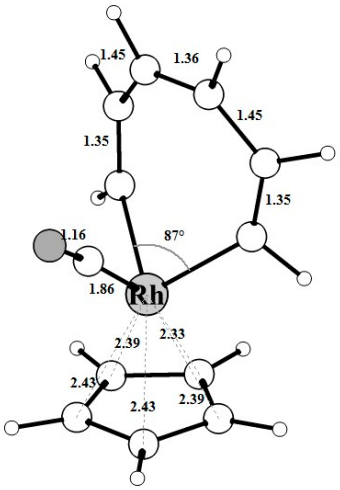
CO-Cp-TS(3,b)



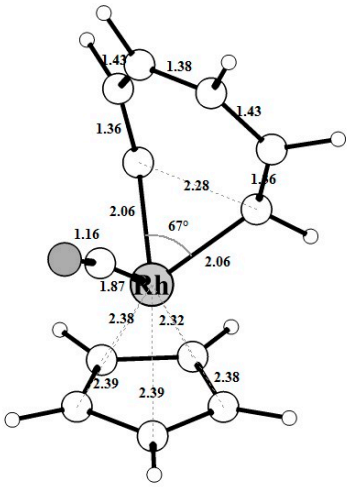
CO-Cp-b



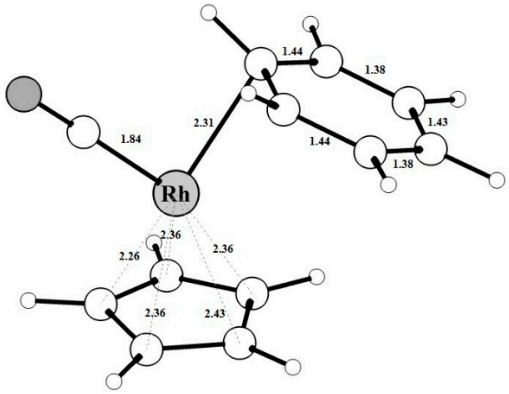
CO-Cp-TS(b,h)



CO-Cp-h

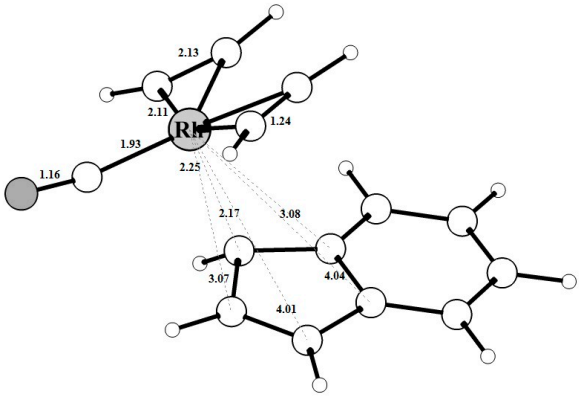


CO-Cp-TS(h,4)

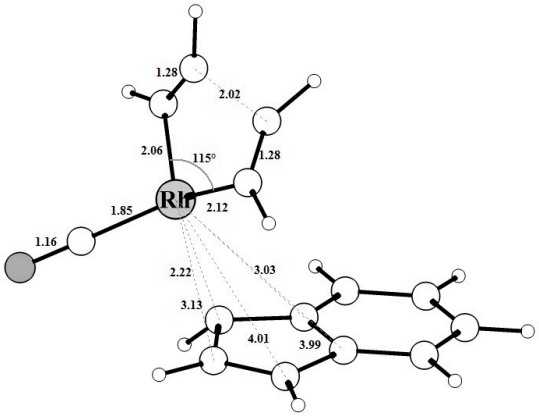


CO-Cp-4

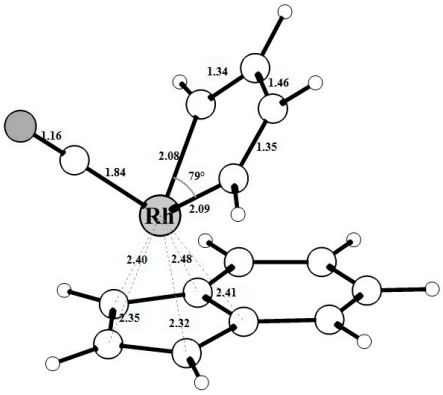
Figure S6. Optimized structures with relevant geometric parameters, i.e. bond lengths (Å) and angles (deg) of the intermediates and transition states along Path (II) for acetylene [2+2+2] cycloaddition catalyzed by IndRh(CO) fragment



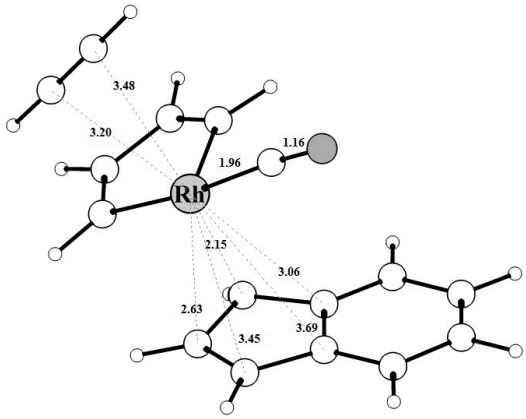
CO-Ind-1



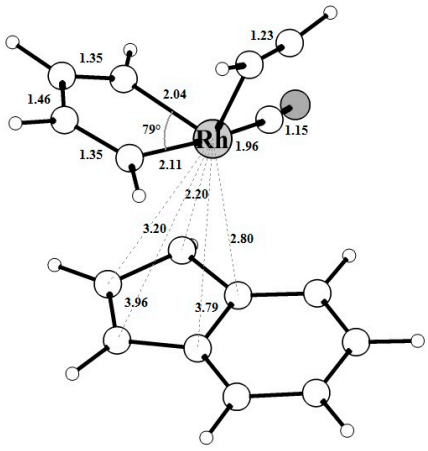
CO-Ind-TS(1,2)



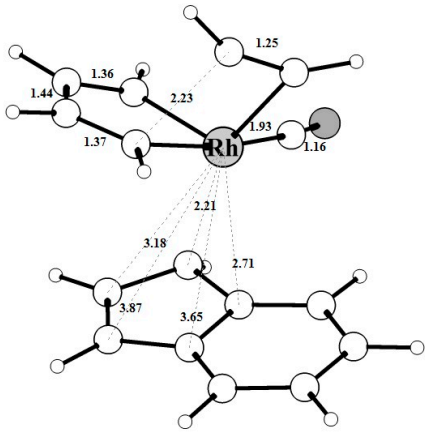
CO-Ind-2



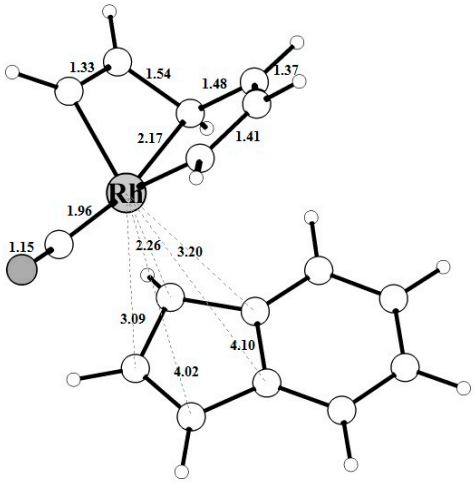
CO-Ind-TS(2,3)



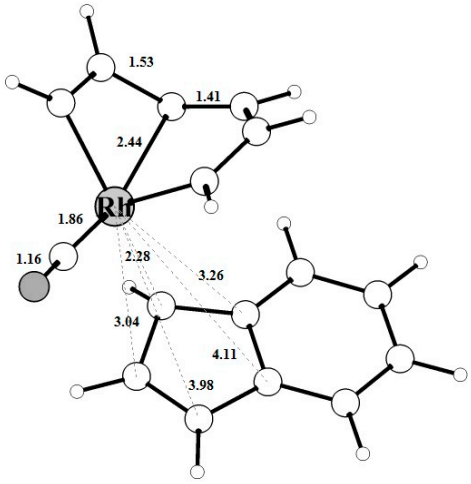
CO-Ind-3



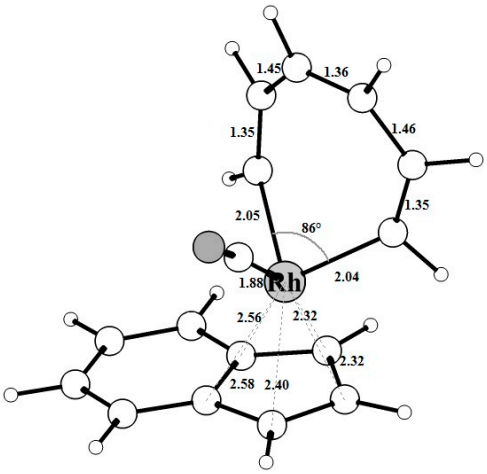
CO-Ind-TS(3,b)



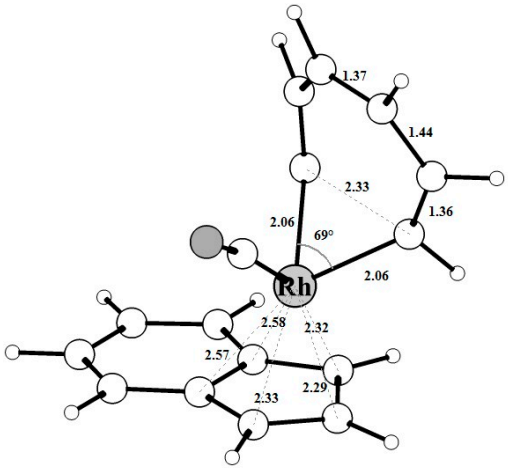
CO-Ind-b



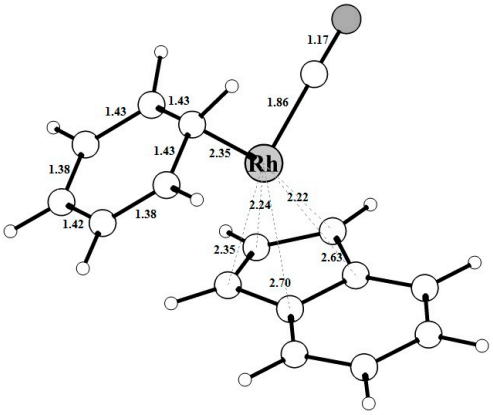
CO-Ind-TS(b,h)



CO-Ind-h

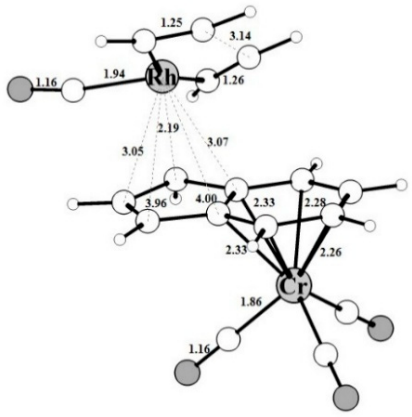


CO-Ind-TS(h,4)

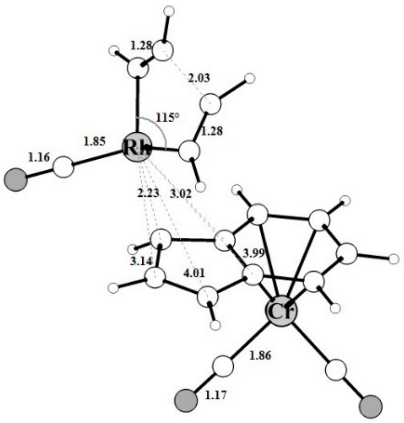


CO-Ind-4

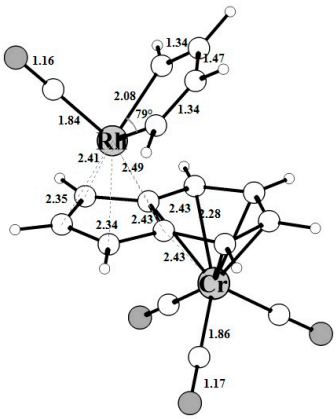
Figure S7. Optimized structures with relevant geometric parameters, i.e. bond lengths (Å) and angles (deg) of the intermediates and transition states along Path (II) for acetylene [2+2+2] cycloaddition catalyzed by anti-IndRh(CO) fragment.



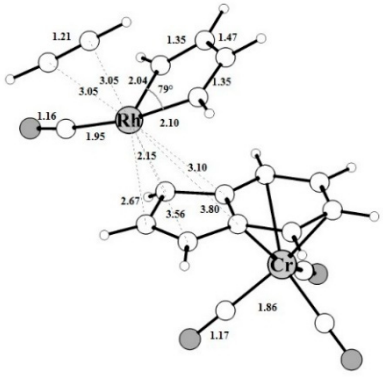
CO-anti-Ind-1



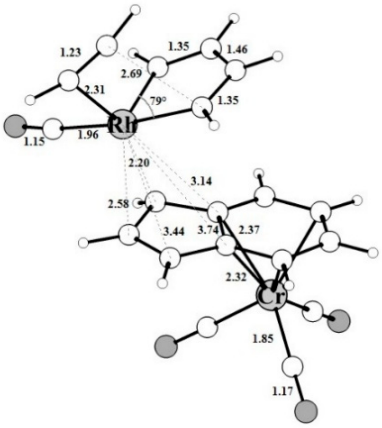
CO-anti-Ind-TS(1,2)



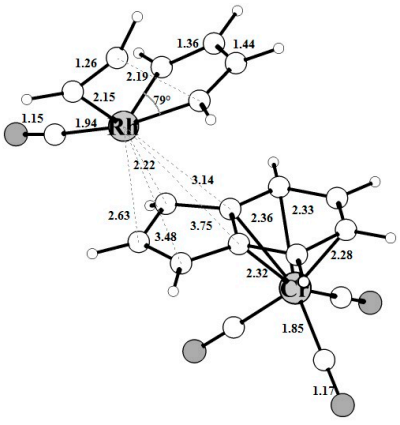
CO-anti-Ind-2



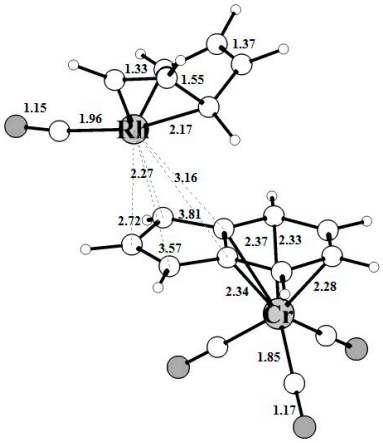
CO-anti-Ind-TS(2,3)



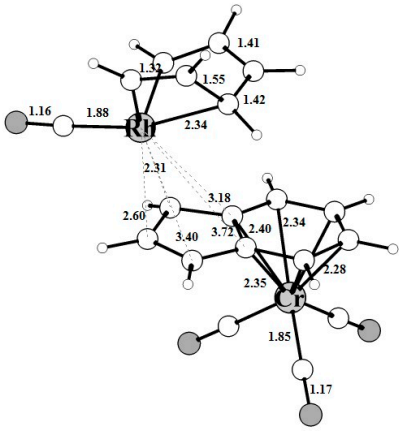
CO-anti-Ind-3



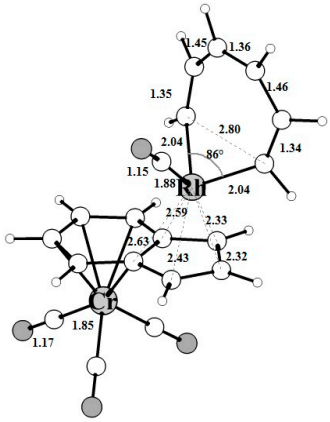
CO-anti-Ind-TS(3,b)



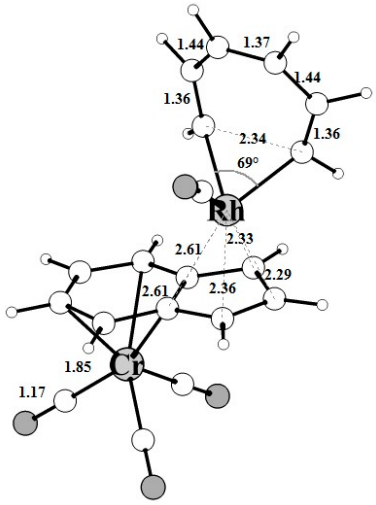
CO-anti-Ind-b



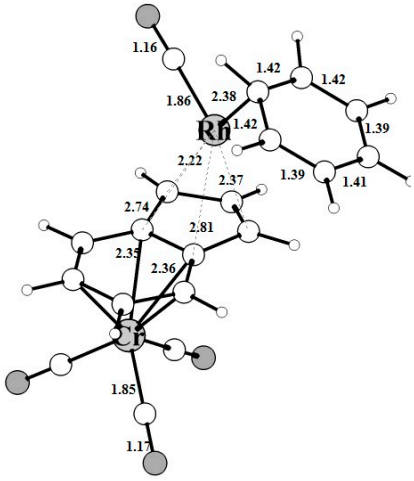
CO-anti-Ind-TS(b,h)



CO-anti-Ind-h



CO-anti-Ind-TS(h,4)



CO-anti-Ind-4