Halogen bond catalysis of the [4+2] cycloaddition reaction of 2-alkenylindoles: catalytic modes and stereoselectivity

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Table S1. The I···C5 and I···C6 distances (in Å) in COM1a-endo catalysed by I_2, IBr, and ICl.

endo	I···C5	I···C6
COM1a(I_2)-endo	3.181	3.093
COM1a(IBr)-endo	2.969	2.821
COM1a(ICl)-endo	2.821	2.642

Table S2. The I···C5 and I···C6 distances (in Å) in COM1a-exo catalysed by I_2, IBr, and ICl.

exo	I···C5	I···C6
COM1a(I_2)-exo	3.184	3.077
COM1a(IBr)-exo	2.966	2.811
COM1a(ICl)-exo	2.816	2.639

Table S3-S88. Calculated Gibbs free energy and XYZ coordinates.

Table S3. Calculated Gibbs free energy and XYZ coordinates for all atoms in **COM1-endo** without catalysts.

G= -882.0114 Hartree

C	2.93146200	-0.08696000	0.71080100
C	2.71452500	-1.10025200	-0.25653300
C	3.71374900	-1.34454200	-1.21454400
C	4.86628800	-0.58249100	-1.19021700
C	5.05368000	0.42785700	-0.22541500
C	4.09371600	0.68861500	0.73529500
C	0.89760100	-0.97806300	1.08542500
C	1.41811400	-1.64922100	0.00184800
H	3.57798400	-2.11745400	-1.96247600
H	5.64235800	-0.75994100	-1.92506700
H	5.96734600	1.00981100	-0.23706700
H	4.23344500	1.46344200	1.47982300
H	0.93663200	-2.45336400	-0.53284300
C	-0.39124300	-1.08552900	1.76165200
H	-0.53275200	-0.43380800	2.61947200
C	-1.38017000	-1.89017800	1.37809600

H	-2.32633100	-1.90704400	1.90430600
H	-1.28289300	-2.54235100	0.51681800
N	1.82442400	-0.05201000	1.51769200
C	-2.57799900	-0.06001600	-0.87339200
C	-3.01169600	0.91573000	0.05919300
C	-4.31839900	0.83134400	0.56858500
C	-5.13835000	-0.19735200	0.14536700
C	-4.68673500	-1.15295100	-0.78790900
C	-3.40791600	-1.09680100	-1.31042000
C	-0.86146400	1.34121000	-0.48522200
C	-1.90604500	1.79269100	0.28718700
H	-4.67443700	1.56302300	1.28500800
H	-6.14766900	-0.27376700	0.53178600
H	-5.35571600	-1.94539500	-1.10149400
H	-3.05710800	-1.83167000	-2.02573700
H	-1.87658000	2.64125000	0.95289100
C	0.50526500	1.83119000	-0.63793000
H	1.20860500	1.13566700	-1.09223300
C	0.92821300	3.03385500	-0.25199100
H	0.25500300	3.76021900	0.19047600
N	-1.27723300	0.22944100	-1.18921600
H	-0.67012500	-0.33485100	-1.76369100
H	1.65101400	0.63480700	2.23507400
H	1.96532200	3.32060400	-0.37362400

Table S4. Calculated Gibbs free energy and XYZ coordinates for all atoms in **TS1-endo** without catalysts.

G= -881.9603 Hartree Frequency =-568.46 cm^{-1}

C	3.50580500	-0.25054600	-0.34316200
C	2.63931400	0.87227800	-0.32953600
C	3.18859700	2.14281100	-0.09930500
C	4.55313700	2.26161000	0.10529900
C	5.39252100	1.13372300	0.08251500
C	4.88143100	-0.13495600	-0.14416600
C	1.40617200	-0.98538600	-0.73063100
C	1.31602200	0.38048400	-0.57698600
H	2.55088600	3.01965500	-0.08511900
H	4.98557600	3.23899900	0.28389100
H	6.45660500	1.25778500	0.24410300
H	5.52583400	-1.00619100	-0.16379300
H	0.40636200	0.95984300	-0.62084400
C	0.35579500	-1.97176000	-0.91170400
H	0.66301300	-2.98843300	-1.12763200

C	-0.92253300	-1.54338000	-1.29461200
H	-1.56059600	-2.24655000	-1.81650600
H	-1.04077600	-0.51550900	-1.61764200
N	2.72817900	-1.35916900	-0.58221600
C	-2.85743900	0.88169200	0.65566500
C	-3.21189200	-0.28888500	-0.04751800
C	-4.30067700	-0.26604800	-0.91787500
C	-5.01166400	0.91665300	-1.07553200
C	-4.63824100	2.07302700	-0.37630700
C	-3.55976800	2.07575000	0.49762700
C	-1.39846400	-0.73045400	1.29140500
C	-2.22906800	-1.31037600	0.29210400
H	-4.58434100	-1.15862400	-1.46450600
H	-5.86115700	0.95047800	-1.74636200
H	-5.20464800	2.98576700	-0.51833000
H	-3.27566800	2.97045700	1.03844200
H	-2.46933100	-2.36356300	0.29850100
C	-0.24588100	-1.32920600	1.80004800
H	0.45439600	-0.73198300	2.37361600
C	0.13277100	-2.54888500	1.28362800
H	-0.60586700	-3.25489200	0.92865700
N	-1.77618300	0.59091400	1.46186800
H	-1.23915200	1.27125900	1.97583800
H	3.06684900	-2.30480700	-0.65937900
H	1.09242000	-2.97478900	1.55375900

Table S5. Calculated Gibbs free energy and XYZ coordinates for all atoms in **1-endo** without catalysts.

G= -882.0295 Hartree

C	3.81918100	-0.23734800	-0.36374100
C	3.13605100	0.92313800	0.07290000
C	3.88654600	2.04232400	0.46360100
C	5.26760700	1.97859900	0.40778600
C	5.92468500	0.81507000	-0.03441200
C	5.21256000	-0.30554300	-0.42653100
C	1.60291300	-0.64816900	-0.47317900
C	1.73162800	0.63401700	-0.00719300
H	3.38861300	2.94331300	0.80379800
H	5.85725800	2.83674300	0.70751600
H	7.00742700	0.79605000	-0.06809700
H	5.71580500	-1.20296100	-0.76694700
H	0.92267000	1.29384400	0.26350800
C	0.39675300	-1.51988700	-0.66904800

H	0.64347800	-2.24602000	-1.45019600
C	-0.83887900	-0.70301200	-1.12672600
H	-1.00787700	-0.84451000	-2.19621100
H	-0.66059600	0.36237700	-0.97392000
N	2.86336000	-1.17254300	-0.68196900
C	-3.58919400	0.38982400	0.79144500
C	-3.26455700	-0.11012900	-0.47922700
C	-3.97233600	0.30697800	-1.58955600
C	-5.00817000	1.23443300	-1.43081700
C	-5.31690300	1.72466800	-0.16591500
C	-4.61471000	1.30938900	0.96705100
C	-1.79213900	-0.98156200	1.14331600
C	-2.10900100	-1.07151100	-0.33705100
H	-3.72571500	-0.07623900	-2.57400600
H	-5.56871000	1.57252900	-2.29326100
H	-6.11892200	2.44468500	-0.05246200
H	-4.86043200	1.69411600	1.94952100
H	-2.41197100	-2.09418000	-0.59610600
C	-0.69077400	-1.55621300	1.63163100
H	-0.39071800	-1.47301800	2.66845100
C	0.12521100	-2.33720400	0.63535400
H	-0.40659400	-3.25251700	0.34590700
N	-2.76136500	-0.18700200	1.75004100
H	-2.66190100	0.18020400	2.68297100
H	3.04700200	-2.09334200	-1.04818000
H	1.07838800	-2.65142500	1.06308300

Table S6. Calculated Gibbs free energy and XYZ coordinates for all atoms in **COM1-exo** without catalysts.

G= -882.0089 Hartree

C	-3.32449700	-0.31028600	0.41258600
C	-2.54748700	0.87175400	0.51613000
C	-3.09762300	2.08500700	0.06755300
C	-4.37298300	2.08710600	-0.46396700
C	-5.12516700	0.89881900	-0.55951300
C	-4.61531800	-0.31081800	-0.12449800
C	-1.33104900	-0.86097200	1.30357200
C	-1.29284400	0.49575500	1.09065400
H	-2.52564400	3.00328200	0.13765300
H	-4.80705700	3.01556900	-0.81510300
H	-6.12202900	0.93442400	-0.98225100
H	-5.19243900	-1.22521900	-0.19639100
H	-0.45917700	1.14168100	1.31797900

C	-0.32126600	-1.77324000	1.82868800
H	-0.67562100	-2.75493600	2.13298400
C	0.97192600	-1.47282800	1.94085500
H	1.36305600	-0.51269200	1.61846200
H	1.67549800	-2.18527000	2.35361100
N	-2.56850200	-1.33817000	0.91338900
C	3.32477000	-0.31029900	-0.41336600
C	2.54720000	0.87152100	-0.51518600
C	3.09740700	2.08466500	-0.06638800
C	4.37346300	2.08689600	0.46345500
C	5.12626100	0.89884700	0.55715100
C	4.61631300	-0.31069100	0.12198400
C	1.33053400	-0.86106700	-1.30258200
C	1.29208700	0.49549500	-1.08863600
H	2.52497200	3.00276100	-0.13509700
H	4.80762200	3.01528300	0.81468700
H	6.12368200	0.93456900	0.97855900
H	5.19388700	-1.22491400	0.19248600
H	0.45789800	1.14131200	-1.31432200
C	0.32060900	-1.77324100	-1.82759800
H	0.67471800	-2.75513300	-2.13152800
C	-0.97244900	-1.47237100	-1.94007900
H	-1.36309900	-0.51188900	-1.61813200
N	2.56849300	-1.33812600	-0.91386400
H	-2.83387600	-2.31036800	0.91512700
H	2.83466100	-2.31009700	-0.91761000
H	-1.67631500	-2.18461100	-2.35267200

Table S7. Calculated Gibbs free energy and XYZ coordinates for all atoms in **TS1-exo** without catalysts.

G= -881.9604 Hartree Frequency = -575.66 cm^{-1}

C	3.87654600	0.31206300	0.32855900
C	3.30784900	-0.92813500	-0.05703000
C	4.14696900	-1.91476200	-0.59660200
C	5.49876600	-1.64840900	-0.73490400
C	6.04013400	-0.41123700	-0.34299700
C	5.23803600	0.58339400	0.19453500
C	1.66281000	0.39326800	0.77463400
C	1.90577400	-0.85079500	0.22931300
H	3.73969300	-2.87260600	-0.90015800
H	6.15424500	-2.40426900	-1.15100700
H	7.10191000	-0.23220900	-0.46254300

H	5.65231600	1.53767400	0.49835500
H	1.17102900	-1.62461000	0.06809600
C	0.41580300	1.01735500	1.17334200
H	0.47907900	1.97169500	1.67885200
C	-0.75063200	0.24941300	1.28127600
H	-0.64585400	-0.82806700	1.35142000
H	-1.57506700	0.64689200	1.86269800
N	2.85485900	1.09158200	0.81823000
C	-4.01107000	0.27802800	-0.21222900
C	-2.95392000	-0.65325900	-0.27457000
C	-3.21766800	-2.00832400	-0.08046300
C	-4.52292900	-2.41027300	0.17059800
C	-5.56031600	-1.46915000	0.23545900
C	-5.32361600	-0.11473700	0.04650600
C	-2.13062500	1.45164000	-0.67885300
C	-1.72419900	0.10096700	-0.48581500
H	-2.41406300	-2.73518600	-0.12589000
H	-4.74535400	-3.45954800	0.31986100
H	-6.57062700	-1.80552700	0.43579300
H	-6.12805100	0.60915600	0.09556400
H	-0.86293700	-0.31857400	-0.99197600
C	-1.24952900	2.53205700	-0.77146400
H	-1.62589500	3.53782600	-0.61516300
C	0.10085400	2.27830000	-0.77783600
H	0.49317200	1.36181100	-1.19826500
N	-3.49313600	1.53332300	-0.45547600
H	2.95451100	2.02650700	1.18053900
H	-4.01380100	2.39463300	-0.41041900
H	0.80940000	3.09562800	-0.70378800

Table S8. Calculated Gibbs free energy and XYZ coordinates for all atoms in **1-exo** without catalysts.

G= -882.0300 Hartree

C	-3.89624900	-0.32501900	0.21151700
C	-3.32510400	0.92875000	-0.11252000
C	-4.16653100	1.96272700	-0.54870900
C	-5.52661700	1.72664100	-0.64595900
C	-6.07235500	0.47282800	-0.31392600
C	-5.26809600	-0.56766600	0.11923900
C	-1.67000700	-0.46403700	0.55028500
C	-1.91052900	0.81135300	0.11148900
H	-3.75468500	2.93226500	-0.80517900
H	-6.18608100	2.51770500	-0.98242000

H	-7.14134300	0.31869900	-0.39933400
H	-5.68592100	-1.53437100	0.37486100
H	-1.16938100	1.58008000	-0.04204300
C	-0.39098900	-1.18221500	0.86518800
H	-0.53581400	-1.71967400	1.80733100
C	0.79172400	-0.20832900	1.05753700
H	0.43087900	0.78254500	1.33944200
H	1.42403700	-0.56330000	1.87381800
N	-2.86711200	-1.14921200	0.60313500
C	4.03195400	-0.22211700	-0.33673500
C	2.95934200	0.64030000	-0.06315200
C	3.19715700	1.96097300	0.26325400
C	4.51688300	2.42247700	0.32374700
C	5.57117100	1.55572400	0.05397400
C	5.34716300	0.21938700	-0.28313600
C	2.16723400	-1.53928000	-0.48794200
C	1.67128200	-0.13454500	-0.20034600
H	2.37075600	2.63145600	0.47421500
H	4.71818300	3.45456400	0.58179500
H	6.59020700	1.92108700	0.10495500
H	6.17259400	-0.44983700	-0.49385400
H	1.07012000	0.23980200	-1.03972800
C	1.32912100	-2.57675500	-0.45050300
H	1.65816100	-3.59910100	-0.59047900
C	-0.12953400	-2.25386000	-0.25127400
H	-0.55111600	-1.85854100	-1.18397600
N	3.54792200	-1.48633800	-0.66340800
H	-2.96946200	-2.10091100	0.91871000
H	4.12773200	-2.31045800	-0.66839700
H	-0.69665600	-3.15719100	-0.01997800

Table S9. Calculated Gibbs free energy and XYZ coordinates for all atoms in **COM1a-endo** catalysed by I_2.

G= -1473.2985 Hartree

I	-2.33268100	-0.61282600	-0.02335500
C	1.46853500	3.01986300	-0.57146800
C	1.51716500	2.85656300	0.83522800
C	1.80888000	3.97301500	1.63774500
C	2.03759200	5.19223200	1.03030400
C	1.97889200	5.33117600	-0.37193300
C	1.69382100	4.25343200	-1.18921500
C	1.07925600	0.85398100	-0.10993600
C	1.26421100	1.47586000	1.10316900

H	1.85356600	3.87495500	2.71643400
H	2.26375800	6.06084600	1.63695600
H	2.16079400	6.30236200	-0.81624600
H	1.65195000	4.35744700	-2.26700700
H	1.23432600	0.99629300	2.06942900
C	0.81991500	-0.53910600	-0.44229600
H	0.84765800	-0.79146200	-1.49930600
C	0.58906500	-1.50999600	0.45244600
H	0.46433000	-2.53886400	0.13676600
H	0.57640500	-1.31005000	1.51894800
N	1.19665200	1.79162900	-1.11470700
C	3.57028100	-2.38124300	0.71035900
C	3.65591200	-2.48126700	-0.70059300
C	3.37863700	-3.71712100	-1.30774700
C	3.03263500	-4.79340200	-0.51165800
C	2.96278900	-4.67100400	0.89066100
C	3.23186500	-3.46871200	1.51951100
C	4.09142600	-0.34593200	-0.10078800
C	3.99272900	-1.18029500	-1.19023700
H	3.43161400	-3.82188800	-2.38553100
H	2.81428900	-5.75110400	-0.96881400
H	2.69295700	-5.53488000	1.48616000
H	3.17285000	-3.36870100	2.59706200
H	4.14725400	-0.89549000	-2.21943400
C	4.37565900	1.08188900	0.00265200
H	4.43935900	1.48030000	1.01165900
C	4.52662500	1.90495800	-1.03274700
H	4.45025900	1.55359300	-2.05638400
N	3.84399600	-1.07892900	1.04179200
H	3.82237800	-0.69456000	1.97339700
H	1.12330600	1.58874900	-2.09936900
H	4.71447800	2.96036200	-0.88082600
I	-4.98055300	-0.11521500	-0.04012100

Table S10. Calculated Gibbs free energy and XYZ coordinates for all atoms in **TS1a-endo** catalysed by I_2.

G= -1473.2628 Hartree Frequency = -401.71 cm^{-1}

I	2.04637800	-0.35666000	0.35861100
C	-1.17293600	3.44012200	0.16543000
C	-1.72917400	2.76711700	-0.95081100
C	-2.38598200	3.51994000	-1.93754800
C	-2.47231500	4.89193200	-1.78717600

C	-1.91168100	5.53846100	-0.66912500
C	-1.25472700	4.82540600	0.31882000
C	-0.78120500	1.23880400	0.41829000
C	-1.46355300	1.37166500	-0.76947700
H	-2.81292000	3.03096400	-2.80581300
H	-2.97506800	5.48409600	-2.54230100
H	-1.99374100	6.61509000	-0.58191000
H	-0.81789400	5.32105500	1.17745800
H	-1.74491600	0.56880500	-1.43331800
C	-0.33309600	0.04373700	1.11753300
H	-0.08354400	0.17184200	2.16670000
C	-0.79544500	-1.22178500	0.70128400
H	-0.41101600	-2.10058300	1.20430300
H	-1.01751300	-1.36457300	-0.35152200
N	-0.59669900	2.48715600	0.97021500
C	-3.86269100	-2.16602300	-0.60252000
C	-3.07394000	-2.74471600	0.40919100
C	-2.70571300	-4.08788500	0.30412600
C	-3.14559100	-4.81070500	-0.79419900
C	-3.93201400	-4.21229500	-1.79178300
C	-4.30114700	-2.87847900	-1.71517000
C	-3.46857700	-0.54974400	0.92010100
C	-2.73776800	-1.68437200	1.34340400
H	-2.09448600	-4.55492300	1.06751100
H	-2.87830900	-5.85584000	-0.88841700
H	-4.25611200	-4.80430100	-2.63858100
H	-4.90579500	-2.41136500	-2.48240100
H	-2.44796300	-1.84053600	2.37151500
C	-3.60034100	0.74281500	1.56006000
H	-4.10817500	1.51746100	0.99380200
C	-3.11367600	1.00339000	2.77570400
H	-2.60752900	0.24692900	3.36495800
N	-4.07895300	-0.84017500	-0.25273600
H	-4.59913400	-0.17205800	-0.80451300
H	-0.12813000	2.66393300	1.84504000
H	-3.21611800	1.98816100	3.21289100
I	4.84564800	-0.51498800	-0.39624400

Table S11. Calculated Gibbs free energy and XYZ coordinates for all atoms in **INT1a-endo** catalysed by I_2.

G= -1473.2885 Hartree

I	1.91829400	-0.12761200	0.30657200
C	-1.51215200	3.32449500	0.13751500

C	-2.05627600	2.65721900	-0.98470300
C	-2.87012400	3.37535300	-1.87395700
C	-3.11448300	4.71332700	-1.62289900
C	-2.55844100	5.35710200	-0.50138600
C	-1.74982400	4.67612000	0.39190900
C	-0.83016500	1.18269300	0.21090400
C	-1.60445700	1.29592700	-0.91801700
H	-3.29144700	2.88958900	-2.74652700
H	-3.73774600	5.28187200	-2.30233400
H	-2.76414000	6.40771000	-0.33656800
H	-1.31508600	5.17137600	1.25175300
H	-1.82101300	0.51059500	-1.62575500
C	-0.21682100	-0.01106300	0.83164800
H	-0.18659300	0.09801700	1.91625400
C	-0.88908900	-1.31088200	0.42413800
H	-0.26847900	-2.15666600	0.72175100
H	-0.97990900	-1.35591200	-0.66312600
N	-0.77224700	2.40055300	0.84221200
C	-3.98335500	-2.39797500	-0.38054800
C	-2.86664100	-2.80105500	0.34376600
C	-2.41430500	-4.10353900	0.22539900
C	-3.12084700	-4.97144300	-0.60803400
C	-4.23987900	-4.54182800	-1.32199800
C	-4.69676400	-3.23003200	-1.22312300
C	-3.35883600	-0.55620800	0.79325400
C	-2.29636200	-1.59936800	1.05693200
H	-1.54147200	-4.44633000	0.76757500
H	-2.79260500	-5.99842300	-0.70488500
H	-4.76287500	-5.23767500	-1.96522300
H	-5.56159200	-2.88240500	-1.77318900
H	-2.17925000	-1.74370700	2.13426800
C	-3.56515700	0.72897000	1.41983500
H	-4.28213300	1.39098400	0.94512600
C	-2.96062500	1.07653100	2.55807400
H	-2.25957800	0.42214100	3.06390000
N	-4.22768200	-1.04058800	-0.05922400
H	-5.03951400	-0.52281000	-0.38301900
H	-0.21957800	2.59561700	1.66359600
H	-3.17224800	2.03100300	3.02258500
I	5.37609000	-0.42259200	-0.34844600

Table S12. Calculated Gibbs free energy and XYZ coordinates for all atoms in **TS2a-**

endo catalysed by I_2.

G= -1473.2520 Hartree Frequency = -472.70 cm^{-1}

I	2.05671900	-0.41354400	0.43830900
C	-0.74350200	3.41899700	0.10919100
C	-1.52229800	2.75151700	-0.86900200
C	-2.12697500	3.50814000	-1.88273400
C	-1.94412800	4.88132000	-1.89874100
C	-1.16362500	5.52048600	-0.92046300
C	-0.55175200	4.79958200	0.09419200
C	-0.71260500	1.21311800	0.58552200
C	-1.48810400	1.35442300	-0.54617700
H	-2.72439000	3.02182900	-2.64568400
H	-2.40518200	5.47501500	-2.67902700
H	-1.03503800	6.59545400	-0.96031800
H	0.05318300	5.29009800	0.84765700
H	-1.96447900	0.55492600	-1.09291300
C	-0.46027400	0.02130300	1.35797800
H	0.13967100	0.07474800	2.25698000
C	-1.02823800	-1.26705400	0.84861600
H	-0.45429400	-2.11672800	1.21686000
H	-0.96080300	-1.28389100	-0.23991100
N	-0.27702900	2.46267300	0.98339200
C	-4.32076300	-1.68180100	-0.37127100
C	-3.23989200	-2.41980100	0.12321900
C	-2.93780500	-3.65122100	-0.43343600
C	-3.73117300	-4.12710000	-1.47802300
C	-4.80439300	-3.37535400	-1.95693800
C	-5.11945100	-2.13324800	-1.41125400
C	-3.44151100	-0.40984700	1.28908900
C	-2.56768800	-1.61468500	1.19763800
H	-2.09969800	-4.23346100	-0.06784700
H	-3.51053300	-5.08838600	-1.92447100
H	-5.40524600	-3.76164000	-2.77104800
H	-5.94903100	-1.54546200	-1.78402700
H	-2.54152100	-2.13576400	2.15795500
C	-3.15484100	0.64004200	2.15018500
H	-3.62988400	1.60439100	2.01692500
C	-2.05467600	0.47936400	2.97249900
H	-1.78634800	-0.49640200	3.35554900
N	-4.41287700	-0.48964600	0.35645200
H	-5.08507300	0.24183400	0.17430400
H	0.35150800	2.63223700	1.75272200
H	-1.66847100	1.32405000	3.53110200

I	4.66379300	-0.85840100	-0.55688000

Table S13. Calculated Gibbs free energy and XYZ coordinates for all atoms in **2a-endo** catalysed by I_2.

G= -1473.3202 Hartree

I	1.77278600	-0.23023200	-0.00580800
C	-0.35004500	2.97292000	0.14244900
C	-0.65338300	2.05298300	-0.88415200
C	-0.56031600	2.46576600	-2.21963200
C	-0.16824700	3.76541900	-2.48868800
C	0.13770100	4.66306900	-1.44970500
C	0.05357300	4.28179800	-0.12112900
C	-0.91244800	1.02176500	1.12525600
C	-0.98937000	0.80826300	-0.24002500
H	-0.78890700	1.77597400	-3.02369600
H	-0.09176000	4.10090900	-3.51581700
H	0.44557100	5.67254100	-1.69384400
H	0.28953600	4.97076900	0.68105400
H	-1.35992800	-0.08858800	-0.71545800
C	-1.21666800	0.10950200	2.27891000
H	-0.31813800	0.04714100	2.90279700
C	-1.57191700	-1.30842300	1.81119000
H	-1.42290800	-1.97996100	2.65782900
H	-0.87988800	-1.63334100	1.03055100
N	-0.52778000	2.31773800	1.34519100
C	-4.35869300	-1.12017600	-0.61002700
C	-3.28446400	-1.87208600	-0.11369500
C	-2.68122600	-2.83172300	-0.90285600
C	-3.15164100	-3.03369300	-2.20567000
C	-4.21927800	-2.28256800	-2.68656000
C	-4.84257300	-1.31471500	-1.89553700
C	-3.85291200	-0.17012100	1.39799500
C	-3.03295900	-1.44568500	1.31506800
H	-1.84873000	-3.41502000	-0.52321600
H	-2.68332300	-3.77551600	-2.84027600
H	-4.57472000	-2.44451800	-3.69737400
H	-5.66896700	-0.72791100	-2.27820900
H	-3.53569900	-2.17648800	1.96250900
C	-3.61696600	0.79884300	2.28122800
H	-4.21883500	1.69961100	2.30725200
C	-2.37625100	0.68642000	3.13249300
H	-2.51641600	0.02927900	3.99887900

N	-4.79958100	-0.21704900	0.36440400
H	-5.26837100	0.63264900	0.08493500
H	-0.31985900	2.70705200	2.25219500
H	-2.10527400	1.66682800	3.52911700
I	4.34130200	-1.11413700	-0.01471800

Table S14. Calculated Gibbs free energy and XYZ coordinates for all atoms in **COM1a-exo** catalysed by I_2.

G= -1473.2968 Hartree

C	1.88807800	2.92191200	-0.72595000
C	1.69038600	2.83907500	0.67496000
C	2.00081300	3.95466800	1.47116300
C	2.49665500	5.09209100	0.86451600
C	2.68834700	5.14993300	-0.53156500
C	2.38684600	4.07221700	-1.34346900
C	1.14614700	0.85265100	-0.24824200
C	1.21767400	1.51959000	0.95169000
H	1.85939100	3.91628400	2.54526000
H	2.74349600	5.95834300	1.46650900
H	3.07809300	6.05799600	-0.97571400
H	2.53459200	4.11405100	-2.41615300
H	0.96740700	1.10844300	1.91740000
C	0.76632600	-0.51677600	-0.55971000
H	0.73139000	-0.77833200	-1.61485800
C	0.50675600	-1.46396200	0.35300800
H	0.57590600	-1.26130800	1.41626100
H	0.28626700	-2.48198400	0.05361200
N	1.54152100	1.70878900	-1.25866300
C	3.31886100	-2.69756000	-0.65811900
C	3.37860200	-2.63208800	0.75642600
C	2.93173500	-3.73419300	1.50369600
C	2.43568100	-4.83960400	0.83787000
C	2.38089400	-4.87912900	-0.56973700
C	2.82269000	-3.81390300	-1.33499700
C	4.10255900	-0.66375700	-0.08509000
C	3.88317900	-1.33621200	1.09275800
H	2.96486600	-3.71020300	2.58707500
H	2.08190500	-5.69330000	1.40344600
H	1.98714600	-5.76065100	-1.06128900
H	2.77977400	-3.84084600	-2.41757000
H	4.06369700	-0.94629200	2.08229300
C	4.56810800	0.69433300	-0.34769900
H	4.84594500	0.91376200	-1.37574700

C	4.63999400	1.65578600	0.57054300
H	4.33824800	1.48259600	1.59754600
N	3.77072400	-1.49560000	-1.13858200
H	1.57826300	1.46746700	-2.23645100
H	3.84367700	-1.24529600	-2.11210700
H	4.97597800	2.65314300	0.31413500
I	-5.00230200	0.14147800	0.02850900
I	-2.37361700	-0.45273500	-0.03653300

Table S15. Calculated Gibbs free energy and XYZ coordinates for all atoms in **TS1a-exo** catalysed by I_2.

G= -1473.2630 Hartree Frequency = -384.81 cm^{-1}

C	0.25052600	3.86489100	0.21781000
C	-0.49208400	3.63128100	-0.96511200
C	-0.69022100	4.69239100	-1.86249700
C	-0.15126400	5.93027200	-1.56472800
C	0.58666000	6.13811600	-0.38364500
C	0.79710600	5.11335700	0.52212600
C	-0.39130500	1.70629600	0.21790400
C	-0.89033900	2.25441200	-0.94188800
H	-1.25457300	4.53940200	-2.77515600
H	-0.29443500	6.75700300	-2.24996500
H	0.99885400	7.11921400	-0.18097200
H	1.36627600	5.27013600	1.43054700
H	-1.46099800	1.73522300	-1.69690000
C	-0.50577300	0.35643400	0.75527500
H	-0.41685200	0.27042500	1.83354700
C	-1.28906000	-0.60302400	0.08448700
H	-1.31048300	-0.57349200	-0.99974800
H	-1.38265500	-1.59359800	0.51550600
N	0.28562700	2.68326800	0.91904500
C	-4.33700600	-2.18755800	0.24832700
C	-3.88534400	-1.21024700	-0.65726800
C	-3.96017600	-1.46393300	-2.02959100
C	-4.49162200	-2.67224400	-2.45067300
C	-4.93566200	-3.63398800	-1.52755500
C	-4.86311100	-3.40986600	-0.16238700
C	-3.61087800	-0.44218400	1.47630500
C	-3.33471600	-0.12268900	0.12904400
H	-3.61493300	-0.72849900	-2.74712300
H	-4.56598600	-2.88384600	-3.51006100

H	-5.34150900	-4.56998100	-1.89055300
H	-5.19924500	-4.14926300	0.55391000
H	-3.18903600	0.89042800	-0.22065900
C	-3.33346200	0.32021500	2.67336400
H	-3.56548700	-0.15513000	3.62123800
C	-2.79892600	1.54457900	2.64534100
H	-2.57278400	2.05238300	1.71333600
N	-4.14985300	-1.68346600	1.52778400
H	0.79655500	2.52349700	1.77360400
H	-4.37549100	-2.17403600	2.38164900
H	-2.59014600	2.07826000	3.56386300
I	4.34189300	-1.88076800	-0.17743500
I	1.67664400	-0.80311500	0.23796900

Table S16. Calculated Gibbs free energy and XYZ coordinates for all atoms in **INT1a-exo** catalysed by I_2.

G= -1473.2904 Hartree

C	-0.51160300	3.81061900	0.18702900
C	-1.22699000	3.46134600	-0.98210000
C	-1.68168700	4.48080200	-1.83240200
C	-1.40972800	5.79537400	-1.50266800
C	-0.69122500	6.11953200	-0.33572500
C	-0.23407100	5.13726600	0.52433400
C	-0.66378700	1.56579000	0.11322300
C	-1.31003600	2.02806400	-1.00559400
H	-2.22973200	4.23791000	-2.73538100
H	-1.74896100	6.59311900	-2.15217800
H	-0.48951900	7.15937500	-0.10885600
H	0.32274300	5.38437000	1.42013800
H	-1.77131100	1.42343900	-1.77194900
C	-0.44176100	0.18540200	0.59831400
H	-0.51025200	0.14610300	1.68419100
C	-1.32714900	-0.86077800	-0.05828000
H	-1.15224000	-0.85812800	-1.13659100
H	-1.05279500	-1.85367900	0.30303300
N	-0.19981500	2.64111200	0.84216400
C	-4.16249300	-2.65366400	0.29118900
C	-3.56514100	-1.79783000	-0.62807600
C	-3.61088900	-2.10977600	-1.97577700
C	-4.28052000	-3.27227400	-2.35767600
C	-4.87545700	-4.11155700	-1.41410500
C	-4.82554400	-3.81686900	-0.05452300
C	-3.31945600	-0.95559800	1.53575900

C	-2.87626300	-0.68921200	0.12291100
H	-3.14635300	-1.46901800	-2.71578900
H	-4.33824600	-3.53116600	-3.40721000
H	-5.38361300	-5.00886800	-1.74271300
H	-5.27979100	-4.46086200	0.68702300
H	-3.17558100	0.31388500	-0.19234400
C	-3.13826300	-0.13639100	2.71067800
H	-3.33307600	-0.60116200	3.67113100
C	-2.83272000	1.16163200	2.61926200
H	-2.67507200	1.65486600	1.66541700
N	-3.96891300	-2.09002800	1.57671400
H	0.41050300	2.56633800	1.64221100
H	-4.34484300	-2.49151800	2.43140400
H	-2.75350800	1.77090800	3.51086600
I	5.01945800	-1.39178900	-0.19954700
I	1.65490900	-0.39849000	0.25012800

Table S17. Calculated Gibbs free energy and XYZ coordinates for all atoms in **TS2a-exo** catalysed by I_2.

G= -1473.2537 Hartree Frequency = -487.28 cm^{-1}

C	0.81500100	3.75153600	0.25151300
C	0.04289500	3.59045200	-0.92520200
C	0.05400100	4.61274200	-1.88500300
C	0.81990800	5.74342400	-1.65498300
C	1.58106000	5.87888500	-0.48103600
C	1.58954900	4.88638400	0.48683800
C	-0.21635700	1.74684500	0.36840500
C	-0.60568400	2.31441400	-0.82716700
H	-0.52742900	4.51537700	-2.79475900
H	0.83697700	6.53832300	-2.39098900
H	2.17280200	6.77368800	-0.33012900
H	2.17639600	4.98710000	1.39217400
H	-1.24867100	1.85913100	-1.56484100
C	-0.62090600	0.49454100	0.96894400
H	-0.23065900	0.21875400	1.93954900
C	-1.55896100	-0.39145200	0.21695600
H	-1.26369500	-0.44870300	-0.83310200
H	-1.54833400	-1.40825800	0.61170700
N	0.62336300	2.62746800	1.02390400
C	-4.78146700	-1.54496800	0.19348800
C	-3.93768900	-0.81901800	-0.65320400
C	-3.96343100	-1.05502500	-2.01748200

C	-4.84161200	-2.01847700	-2.51341300
C	-5.67328000	-2.73466300	-1.65161100
C	-5.65828000	-2.51126700	-0.27713600
C	-3.64561500	-0.12426100	1.55274700
C	-3.09030600	0.08683700	0.18789400
H	-3.31310700	-0.50324800	-2.68704800
H	-4.87754700	-2.21576600	-3.57728200
H	-6.34529600	-3.48101200	-2.05709200
H	-6.30264300	-3.06755900	0.39200400
H	-3.09041600	1.13296900	-0.13311300
C	-3.07419400	0.45864700	2.67311100
H	-3.24016900	0.03792600	3.65794600
C	-2.12202500	1.43997400	2.44864900
H	-2.21606100	2.11374800	1.60694800
N	-4.56772100	-1.10936600	1.50696900
H	1.10322900	2.42411600	1.88681200
H	-5.02207600	-1.49814200	2.32094900
H	-1.52235500	1.81083100	3.27248500
I	1.62344200	-0.91435400	0.37212600
I	3.95002800	-2.35450100	-0.31933700

Table S18. Calculated Gibbs free energy and XYZ coordinates for all atoms in **2a-exo** catalysed by I_2.

G= -1473.3203 Hartree

C	-1.44089600	3.19000300	-0.18731800
C	-1.09380500	2.65166800	1.07070300
C	-1.79962200	3.06578500	2.20818900
C	-2.81861700	3.99005500	2.05981300
C	-3.15139300	4.50918400	0.79527800
C	-2.47127500	4.11713200	-0.34510400
C	0.24894400	1.72972800	-0.51494300
C	-0.02566200	1.71309100	0.83935600
H	-1.55171600	2.66504400	3.18420000
H	-3.37355600	4.32092400	2.92924500
H	-3.95650600	5.22910200	0.71216100
H	-2.72653700	4.51374900	-1.32031800
H	0.52045900	1.16176900	1.58939100
C	1.30732000	1.03634300	-1.32176700
H	0.80873500	0.54700800	-2.16438800
C	2.04507700	-0.05275600	-0.51338900
H	1.42734900	-0.41718300	0.30971700

H	2.24200900	-0.90899600	-1.16132800
N	-0.60163400	2.61931600	-1.12213000
C	5.49087700	-0.65253600	-0.07266000
C	4.28943200	-0.58291200	0.64839800
C	4.09325400	-1.39170400	1.75054000
C	5.10256700	-2.28306500	2.13080200
C	6.28744000	-2.34516000	1.40439300
C	6.50349700	-1.52953000	0.29181000
C	4.21608800	0.87323800	-1.20446900
C	3.40074900	0.45273000	0.00384900
H	3.16618700	-1.34005900	2.31177900
H	4.96079600	-2.92644700	2.98997900
H	7.06280800	-3.04022300	1.70462900
H	7.42937500	-1.58205400	-0.26826100
H	3.23663800	1.30767800	0.67357500
C	3.66866700	1.61964500	-2.16555200
H	4.19711400	1.88852600	-3.07167100
C	2.27288800	2.12615000	-1.90934700
H	2.30664000	2.95447500	-1.19031000
N	5.46662200	0.26848100	-1.11763000
H	-0.64911100	2.77700000	-2.11731100
H	6.11043700	0.23541800	-1.89207900
H	1.83810400	2.53386700	-2.82354100
I	-1.81070400	-0.62744900	0.09875900
I	-3.54509500	-2.64720600	-0.37288500

Table S19. Calculated Gibbs free energy and XYZ coordinates for all atoms in **COM1b-endo** catalysed by I_2.

G= -1473.3012 Hartree

C	0.25100400	2.60396500	-0.54711600
C	0.09707200	2.14317400	0.78091700
C	-0.34859900	3.03872500	1.76524100
C	-0.61667000	4.34568300	1.40291100
C	-0.45371300	4.78323800	0.07408100
C	-0.02042600	3.92227600	-0.91831100
C	0.85309000	0.43300600	-0.51059800
C	0.46661700	0.75510500	0.78413800
H	-0.47983700	2.70807700	2.78901400
H	-0.95964400	5.04975700	2.15124200
H	-0.67325900	5.81419200	-0.17524400
H	0.10500700	4.25505000	-1.94164300
H	0.55033500	0.10749800	1.64378400
C	1.38071900	-0.80484200	-1.07130400

H	1.71138900	-0.75669500	-2.10437100
C	1.50131400	-1.93936000	-0.38482400
H	1.93614500	-2.82276900	-0.83537600
H	1.18415700	-2.01687500	0.64987200
N	0.70143000	1.54304400	-1.29847300
C	4.31383600	-1.21160200	0.80832200
C	4.86520900	-1.25997900	-0.49660900
C	5.38796400	-2.47712900	-0.96523300
C	5.35339000	-3.58431300	-0.13894400
C	4.80977100	-3.50866000	1.15980900
C	4.28682200	-2.32686200	1.65106200
C	4.07212200	0.82233500	-0.12404800
C	4.70140300	0.04117800	-1.06524600
H	5.81067800	-2.54368100	-1.96133800
H	5.75321900	-4.52854500	-0.48881400
H	4.80179400	-4.39428200	1.78383500
H	3.86482200	-2.26663200	2.64748700
H	4.98697900	0.35797200	-2.05635200
C	3.63349700	2.21423400	-0.16801100
H	2.90841900	2.50739500	0.58910300
C	4.04452200	3.11021500	-1.06375200
H	4.77775300	2.86097300	-1.82329400
N	3.84463700	0.06054000	1.00423300
H	3.37527600	0.39420100	1.83166800
H	0.92215600	1.57650100	-2.28224100
H	3.65578800	4.12077000	-1.05499800
I	-4.71853100	-1.31233000	-0.22493500
I	-2.21594600	-0.35277000	0.16573600

Table S20. Calculated Gibbs free energy and XYZ coordinates for all atoms in **TS1b-endo** catalysed by I_2.

G= -1473.2623 Hartree Frequency = -429.33 cm^{-1}

C	-0.86486800	3.46828800	-0.57677600
C	-0.70629300	2.66512400	0.55933200
C	-1.25984100	3.06451700	1.76663400
C	-1.95482300	4.27197300	1.81466000
C	-2.10921900	5.05435000	0.66935700
C	-1.56775700	4.66189500	-0.55319800
C	0.44760500	1.73064000	-1.24215100
C	0.01700300	1.43993500	0.14546900
H	-1.16360200	2.44432500	2.65022100
H	-2.38903400	4.60315100	2.74957200
H	-2.66177700	5.98393600	0.72825100

H	-1.68906700	5.26360600	-1.44497200
H	0.77183400	1.03325900	0.80834000
C	1.33907400	1.01526400	-2.02843600
H	1.54542200	1.37565800	-3.02968300
C	1.97823800	-0.14372200	-1.55842100
H	2.38217400	-0.81922400	-2.30340000
H	1.56102700	-0.65445000	-0.69482300
N	-0.20002900	2.85177900	-1.64198200
C	3.94617300	-1.23589200	1.02721400
C	4.19425300	-1.16525800	-0.35315700
C	4.63261300	-2.30431300	-1.02960200
C	4.82321400	-3.47038800	-0.30413000
C	4.56749900	-3.51807300	1.07521500
C	4.12053100	-2.40257700	1.76571500
C	3.51114100	0.88823600	0.40075700
C	3.81061800	0.17090300	-0.79226400
H	4.82508600	-2.27600500	-2.09567700
H	5.17166100	-4.36320100	-0.80790900
H	4.71931000	-4.44654500	1.61119600
H	3.91583900	-2.43736400	2.82835800
H	4.22861000	0.65733000	-1.66143300
C	3.14946500	2.27275800	0.54822700
H	2.86796700	2.61165900	1.54053300
C	3.09469000	3.11348400	-0.49277100
H	3.39231100	2.81057400	-1.48900300
N	3.52828000	0.02500200	1.44101700
H	3.27927500	0.26787300	2.39029800
H	-0.11733000	3.24712300	-2.56738500
H	2.76876600	4.13763600	-0.35973700
I	-3.56216800	-2.68663100	-0.06394500
I	-1.48919300	-0.27638100	0.01684900

Table S21. Calculated Gibbs free energy and XYZ coordinates for all atoms in **INT1b-endo** catalysed by I_2.

G= -1473.2728 Hartree

C	0.90056500	3.62306500	0.68538700
C	0.85558900	2.82319500	-0.46414600
C	1.47853100	3.23866900	-1.62797500
C	2.13493100	4.47048700	-1.63659000
C	2.17481600	5.25475400	-0.48509300
C	1.56081400	4.84331900	0.69778100
C	-0.44529700	1.85654100	1.24109600
C	0.12425500	1.56635400	-0.12421100

H	1.46570000	2.61157900	-2.51244500
H	2.62399700	4.81428100	-2.53908400
H	2.69573100	6.20457500	-0.50422900
H	1.59865400	5.45232200	1.59248600
H	-0.61509500	1.24187200	-0.85125800
C	-1.42880100	1.19720000	1.88063600
H	-1.75152900	1.55547000	2.85358900
C	-2.07354100	-0.03130900	1.34858000
H	-2.19247400	-0.76651300	2.14711100
H	-1.47318400	-0.51003600	0.57202800
N	0.20960900	2.98498300	1.71088600
C	-4.19587400	-1.31128400	-0.94486200
C	-4.11738200	-1.19511900	0.43955900
C	-4.45442500	-2.27917700	1.23258500
C	-4.87895600	-3.44821600	0.60276600
C	-4.94921200	-3.53799400	-0.78898300
C	-4.60301900	-2.46085800	-1.59877500
C	-3.50839500	0.81646700	-0.56900600
C	-3.54909800	0.15477200	0.77493300
H	-4.39548400	-2.22217400	2.31283300
H	-5.15540300	-4.30566900	1.20295900
H	-5.27488600	-4.46228000	-1.24851800
H	-4.64724600	-2.52091800	-2.67829400
H	-4.13274700	0.72333100	1.50073600
C	-3.16253500	2.17439200	-0.88659000
H	-2.98067700	2.41219500	-1.92941200
C	-3.07507900	3.11840600	0.05936400
H	-3.30023700	2.91360300	1.09753200
N	-3.80573100	-0.06893900	-1.49438900
H	-3.79085600	0.12890000	-2.49013400
H	-0.02082700	3.42565500	2.58741600
H	-2.79593100	4.13267000	-0.19943900
I	3.58574300	-2.99390000	-0.00375000
I	1.51969100	-0.14729100	-0.02357200

Table S22. Calculated Gibbs free energy and XYZ coordinates for all atoms in **TS2b-endo** catalysed by I_2.

G= -1473.2670 Hartree Frequency = -245.93 cm^{-1}

C	-1.92727300	3.27065800	-0.63150400
C	-1.68729800	2.54445300	0.54065800
C	-2.47572200	2.75586500	1.65948400
C	-3.49156400	3.70959500	1.59155000

C	-3.71997600	4.42080100	0.41429200
C	-2.94132400	4.21079000	-0.72325700
C	-0.08443600	1.99950700	-1.08059200
C	-0.58156600	1.58336200	0.26702900
H	-2.31199700	2.18324600	2.56511000
H	-4.11429900	3.89324700	2.45784200
H	-4.51909400	5.15112400	0.37812100
H	-3.12024400	4.76250800	-1.63777000
H	0.19934400	1.49694100	1.01959400
C	1.09663300	1.64741400	-1.68291200
H	1.28085500	2.03629000	-2.68008100
C	1.95535800	0.52111100	-1.22406400
H	2.06804400	-0.20302100	-2.03393000
H	1.51436800	-0.01507400	-0.38232300
N	-0.99562400	2.87650000	-1.59658000
C	4.46154900	-0.28734500	0.93215200
C	4.24614300	-0.29907400	-0.44609300
C	4.71186200	-1.36003500	-1.20405500
C	5.39295100	-2.39013900	-0.55637900
C	5.59601100	-2.35823700	0.82377100
C	5.13052000	-1.29973200	1.59957500
C	3.36325200	1.64918900	0.49080900
C	3.44243900	0.91513500	-0.81041500
H	4.54924000	-1.39250900	-2.27495600
H	5.76500000	-3.22923600	-1.13022600
H	6.12278900	-3.17307700	1.30428200
H	5.28139900	-1.27240500	2.67115700
H	3.87747900	1.50825500	-1.61725800
C	2.62470300	2.82524000	0.66002300
H	2.29792400	3.12247500	1.64922800
C	2.15825800	3.45300700	-0.46686900
H	2.68382400	3.38087700	-1.40840100
N	3.89848000	0.89298600	1.45212300
H	3.87578400	1.12758900	2.43615400
H	-0.92587900	3.27829900	-2.51926800
H	1.44228600	4.26364800	-0.38773800
I	-2.55096900	-3.63376700	-0.07600600
I	-1.40959600	-0.48651600	0.10775000

Table S23. Calculated Gibbs free energy and XYZ coordinates for all atoms in **2b-endo** catalysed by I_2.

G= -1473.3202 Hartree

C	-1.53252000	3.19074100	-0.30258400

C	-1.04527600	2.70911100	0.93201700
C	-1.68801700	3.09485500	2.11615700
C	-2.78376000	3.93578900	2.03587400
C	-3.25635400	4.39843100	0.79386700
C	-2.64172500	4.03267400	-0.39145400
C	0.23450900	1.85460100	-0.74103700
C	0.06906500	1.84759300	0.63126400
H	-1.33233200	2.73649100	3.07518800
H	-3.29123500	4.24385400	2.94194300
H	-4.11886600	5.05315200	0.76475000
H	-3.00465700	4.38656200	-1.34899800
H	0.71705000	1.36219100	1.34425300
C	1.29156300	1.25599200	-1.62222900
H	0.80822800	0.98616700	-2.56677500
C	1.92321100	-0.01755300	-1.00590500
H	1.51907000	-0.90928000	-1.48896700
H	1.67098600	-0.09410400	0.05322500
N	-0.72976600	2.66225500	-1.29181400
C	5.02039200	-0.37376500	0.63878100
C	4.16814900	-1.03962200	-0.25546300
C	4.09122900	-2.41877700	-0.24398100
C	4.86793600	-3.13781100	0.67117800
C	5.70716500	-2.46494900	1.55353600
C	5.79984100	-1.07188800	1.55138000
C	3.96530800	1.29515500	-0.51651200
C	3.46023200	-0.00933600	-1.10189300
H	3.43350400	-2.93812700	-0.93275200
H	4.81469700	-4.21895400	0.69390000
H	6.30370000	-3.03003000	2.26013000
H	6.45673100	-0.55475200	2.24034100
H	3.75746300	-0.09118500	-2.15526000
C	3.41428000	2.45381500	-0.88600800
H	3.69673000	3.40735000	-0.45854800
C	2.35883000	2.35133100	-1.95485200
H	2.81495400	2.07688000	-2.91398700
N	4.94326800	1.00038800	0.42766800
H	5.29348200	1.67955900	1.08431000
H	-0.86964300	2.78730900	-2.28300400
H	1.85714000	3.30736300	-2.11014800
I	-3.29308400	-2.72720300	-0.16287400
I	-1.62325300	-0.61519900	0.09564000

Table S24. Calculated Gibbs free energy and XYZ coordinates for all atoms in **COM1b-exo** catalysed by I_2.

G= -1473.2988 Hartree

C	-0.07195600	2.99278100	-0.32399300
C	0.18798800	2.16264600	0.79136600
C	-0.01551200	2.67255200	2.08311000
C	-0.46233300	3.97312000	2.22166600
C	-0.71720500	4.78116100	1.09620700
C	-0.52843100	4.30553700	-0.18873600
C	0.64758100	1.00735100	-1.10737700
C	0.61901500	0.89471900	0.27468500
H	0.17387700	2.05371200	2.95243100
H	-0.62263700	4.38259900	3.21156100
H	-1.06910700	5.79530700	1.24078300
H	-0.72617000	4.92349800	-1.05612700
H	0.97382100	0.04567500	0.83866600
C	1.06132200	0.05209600	-2.12788300
H	0.81808800	0.31162300	-3.15440700
C	1.70662800	-1.08151900	-1.85744900
H	1.98249900	-1.35387500	-0.84305200
H	1.98441900	-1.76655400	-2.64870500
N	0.20910600	2.26028500	-1.45447000
C	4.71165000	-1.61968600	-0.20482700
C	4.12763600	-1.10763000	0.98155500
C	3.91661000	-1.97944600	2.06390400
C	4.27778500	-3.30678900	1.93507400
C	4.85359400	-3.79374100	0.74413200
C	5.07851500	-2.96210200	-0.33749100
C	4.27464000	0.56502600	-0.52991500
C	3.86957900	0.28049000	0.75178100
H	3.47431700	-1.61270000	2.98321400
H	4.11725400	-3.98959800	2.76067500
H	5.12421700	-4.84046500	0.67532400
H	5.52133100	-3.33387400	-1.25385700
H	3.44103200	0.98801300	1.44472200
C	4.20447300	1.80283000	-1.29845100
H	4.82618000	1.84962900	-2.18905500
C	3.43184100	2.83957000	-0.97606500
H	2.77867200	2.81512300	-0.10876400
N	4.80436000	-0.58029500	-1.09392700
H	0.12610700	2.59438800	-2.40250100
H	5.12491000	-0.65479100	-2.04650300
H	3.43087400	3.74164400	-1.57522100
I	-4.50807300	-1.50189700	-0.07343900
I	-2.05069100	-0.35816100	-0.01973400

Table S25. Calculated Gibbs free energy and XYZ coordinates for all atoms in **TS1b-exo** catalysed by I_2.

G= -1473.2609 Hartree Frequency = -439.53 cm^{-1}

C	-1.19558000	3.49181800	-0.35155800
C	-1.19682300	2.65809900	0.77299700
C	-1.99492600	2.97528400	1.86217500
C	-2.77298100	4.13022000	1.80473200
C	-2.76509100	4.94337500	0.67028200
C	-1.97361600	4.63531300	-0.43437500
C	0.31828000	1.84851300	-0.81189200
C	-0.31624100	1.50398500	0.47920100
H	-2.01893300	2.33240400	2.73429300
H	-3.39841600	4.39643300	2.64751000
H	-3.38509800	5.83099400	0.64489600
H	-1.96417100	5.26384700	-1.31599600
H	0.33435500	1.13255800	1.26377900
C	1.36040200	1.20221100	-1.46445700
H	1.73083100	1.63458200	-2.38539700
C	1.95023200	0.03676100	-0.94663400
H	1.36385400	-0.56262600	-0.25732900
H	2.56833000	-0.55544100	-1.61338900
N	-0.29410300	2.96239600	-1.28086800
C	5.00011900	-1.18599700	-0.00052700
C	3.82733500	-0.98604000	0.74617900
C	3.30266500	-2.04027000	1.49472900
C	3.97550000	-3.25283300	1.48830400
C	5.14801300	-3.42929000	0.73722700
C	5.67963700	-2.40010100	-0.02454500
C	4.37605900	0.95532900	-0.33965300
C	3.35547500	0.36009300	0.45081600
H	2.39236200	-1.91329200	2.06917500
H	3.58967500	-4.08138400	2.06874300
H	5.64642600	-4.39050200	0.75030200
H	6.58087300	-2.53429900	-0.60964700
H	2.74199400	0.93987700	1.12558100
C	4.43506100	2.29488900	-0.86364900
H	5.23291100	2.52006400	-1.56377100
C	3.52525700	3.22544400	-0.55145200
H	2.73920900	3.04167200	0.17098300
N	5.29153800	0.01137400	-0.64709100
H	-0.09379000	3.37426600	-2.18075400
H	6.07690800	0.15681500	-1.26628800
H	3.56775400	4.21265100	-0.99400100
I	-3.48503000	-2.83401200	-0.38387000

I	-1.66440000	-0.32477700	0.08008900

Table S26. Calculated Gibbs free energy and XYZ coordinates for all atoms in **INT1b-exo** catalysed by I_2.

G= -1473.2712 Hartree

C	4.26590500	0.28912700	0.52519400
C	3.44475600	-0.25037000	-0.47018800
C	3.96485400	-1.11962100	-1.41206900
C	5.32121800	-1.44409300	-1.35140200
C	6.12811100	-0.90472400	-0.35138800
C	5.61533000	-0.02837700	0.60427000
C	2.17975500	1.17380300	0.94764000
C	2.05804700	0.28073300	-0.27534800
H	3.32403000	-1.55332900	-2.17181500
H	5.74552200	-2.12530800	-2.07776100
H	7.17731700	-1.17197300	-0.31012600
H	6.24597800	0.38792200	1.38020400
H	1.69867000	0.82786400	-1.14694900
C	1.24896500	1.93280500	1.55708400
H	1.58785100	2.55893300	2.37545700
C	-0.22680800	1.89526100	1.30800300
H	-0.61143800	0.88371100	1.45310200
H	-0.73704200	2.52639900	2.03869200
N	3.51752900	1.14069800	1.32674600
C	-2.93853400	3.17475700	-0.30174400
C	-2.22290400	1.98376000	-0.22915500
C	-2.90421300	0.77809700	-0.19451000
C	-4.29732200	0.81472300	-0.25480500
C	-4.99271900	2.02323500	-0.33293300
C	-4.31967200	3.24199300	-0.35521800
C	-0.75783300	3.80038700	-0.27653600
C	-0.75741200	2.30891200	-0.11820500
H	-2.38685000	-0.17397200	-0.12658500
H	-4.84531700	-0.11935900	-0.23819600
H	-6.07443200	2.01572900	-0.37476500
H	-4.84755300	4.18545600	-0.41073600
H	-0.15658700	1.82318900	-0.89024500
C	0.36652700	4.69782300	-0.33235400
H	0.16171000	5.75409700	-0.19771000
C	1.60700900	4.26345800	-0.57727300
H	1.82422700	3.21981300	-0.76017900
N	-1.99557500	4.23128000	-0.31516900
H	3.84070700	1.50521600	2.20896000

H	-2.24505200	5.21376400	-0.37749100
H	2.43574300	4.95879800	-0.62360500
I	-2.42736600	-3.26464400	0.15716400
I	0.55020500	-1.29744900	-0.07198800

Table S27. Calculated Gibbs free energy and XYZ coordinates for all atoms in **TS2b-exo** catalysed by I_2.

G= -1473.2632 Hartree Frequency = -283.41 cm^{-1}

C	-1.60945300	3.48048600	-0.41902800
C	-1.52853800	2.64892600	0.70346600
C	-2.38151600	2.85046500	1.77612000
C	-3.30193300	3.89661900	1.71054300
C	-3.37382800	4.71097500	0.58084500
C	-2.52735300	4.51463300	-0.50955600
C	0.12574600	2.05558800	-0.85302900
C	-0.49615200	1.61240300	0.43003700
H	-2.34098700	2.20033600	2.64248400
H	-3.97343500	4.07285300	2.54124400
H	-4.10172100	5.51229500	0.54565700
H	-2.58254000	5.14613400	-1.38752700
H	0.20375700	1.38503600	1.23047800
C	1.29997000	1.61978200	-1.42004300
H	1.56287900	2.03498000	-2.38555300
C	1.98930800	0.36937900	-0.98242700
H	1.26655800	-0.39303700	-0.68735600
H	2.57044300	-0.04486300	-1.80763700
N	-0.63758500	3.07622700	-1.33837200
C	5.01336900	-0.70144200	0.14383400
C	3.67273100	-0.83116300	0.50949100
C	3.19352200	-2.05464900	0.94679200
C	4.08228500	-3.12699600	1.01675300
C	5.42002100	-2.97495400	0.64880000
C	5.91409600	-1.75231100	0.20114500
C	4.12092000	1.36496400	-0.14024000
C	2.98884800	0.47915200	0.26014600
H	2.15299900	-2.17762600	1.22481000
H	3.72925800	-4.09198600	1.35724000
H	6.08938500	-3.82395100	0.70975100
H	6.95036200	-1.63038600	-0.08696900
H	2.43120200	0.85628000	1.12017100
C	3.92974100	2.68980600	-0.54882600
H	4.65917600	3.17245500	-1.18798000
C	2.70358900	3.25366800	-0.30637100

H	2.10805700	2.94318800	0.53978100
N	5.23040300	0.62982000	-0.25724300
H	-0.47034900	3.52409600	-2.22708900
H	6.11377200	0.98292700	-0.60159400
H	2.43427200	4.20528300	-0.74957000
I	-2.93781200	-3.30018000	-0.31934100
I	-1.52190600	-0.36865600	0.09081700

Table S28. Calculated Gibbs free energy and XYZ coordinates for all atoms in **2b-exo** catalysed by I_2.

G= -1473.3241 Hartree

C	3.28005300	0.49789600	0.71676400
C	3.30844300	0.74709000	-0.67738300
C	4.00776400	-0.13851800	-1.50915900
C	4.63408500	-1.23797300	-0.94732000
C	4.58043000	-1.47620600	0.43812400
C	3.90584800	-0.61391400	1.29012500
C	2.02968500	2.32977800	0.30905400
C	2.50435600	1.91431400	-0.90575600
H	4.04214800	0.02868300	-2.57958000
H	5.17005500	-1.93326600	-1.58189200
H	5.07448300	-2.34851100	0.84862000
H	3.86429400	-0.79429900	2.35817400
H	2.27409800	2.36460300	-1.85834400
C	1.09236100	3.44754900	0.67398600
H	1.60415100	4.09307700	1.39586100
C	-0.17825600	2.87605800	1.34651400
H	0.07266000	2.34123900	2.26627900
H	-0.84609500	3.70027400	1.61309200
N	2.50482800	1.47714900	1.28855800
C	-2.98623400	1.43539200	-0.52056100
C	-2.22083100	1.36371200	0.65308600
C	-2.71999500	0.73265200	1.77479800
C	-4.00212100	0.17302100	1.72589800
C	-4.74904000	0.24301500	0.55461100
C	-4.25240000	0.87392500	-0.58981500
C	-1.12020400	2.67490600	-0.95221300
C	-0.86485500	1.95140700	0.35264100
H	-2.12606900	0.66793800	2.68051200
H	-4.41219300	-0.31846100	2.59938500
H	-5.74022200	-0.19463500	0.52562800
H	-4.84059000	0.92424600	-1.49841500

H	-0.18838300	1.11114800	0.13919600
C	-0.40905500	3.71848500	-1.37803700
H	-0.67462600	4.22505700	-2.30060900
C	0.71640200	4.29862800	-0.55201800
H	1.60776700	4.45754400	-1.16638100
N	-2.26048400	2.08697500	-1.52588800
H	2.31602000	1.56619900	2.27461300
H	-2.74453600	2.55438500	-2.27857500
H	0.41705200	5.29313600	-0.20208700
I	-1.69324000	-2.20465000	-0.48853000
I	0.82684300	-1.71147400	0.25467800

Table S29. Calculated Gibbs free energy and XYZ coordinates for all atoms in **COM1a-endo** catalysed by IBr.

G= -1594.6947 Hartree

I	-2.66097200	-0.28645000	-0.01556800
C	1.52753800	2.91733100	-0.55440200
C	1.58986600	2.72985400	0.84871200
C	2.10151700	3.76576500	1.65068000
C	2.52431500	4.93157200	1.04510800
C	2.44708700	5.09715700	-0.35453400
C	1.94979600	4.09984700	-1.17042500
C	0.77443200	0.85112800	-0.09788900
C	1.10450100	1.41389700	1.11434600
H	2.16149400	3.64646700	2.72635900
H	2.92068800	5.73843300	1.64950600
H	2.78524600	6.02659100	-0.79661500
H	1.89332500	4.22280200	-2.24536200
H	1.02515200	0.93210800	2.07676100
C	0.27364500	-0.47069400	-0.42574300
H	0.25465000	-0.73129200	-1.48088600
C	-0.11472300	-1.39516900	0.47741500
H	-0.37127000	-2.40015600	0.16411700
H	-0.06940600	-1.19994500	1.54340500
N	1.02800100	1.76547200	-1.09959200
C	2.64886200	-2.75505900	0.70260300
C	2.66070800	-2.87279700	-0.70961200
C	2.11693100	-4.02773700	-1.29565100
C	1.59012900	-5.01038000	-0.47794900
C	1.60015200	-4.87515100	0.92503500
C	2.13028500	-3.75171400	1.53340800
C	3.52673700	-0.86233900	-0.14638100

C	3.22736400	-1.66421900	-1.22361600
H	2.10687000	-4.14205300	-2.37367400
H	1.16483300	-5.90420800	-0.91830800
H	1.18437400	-5.66616100	1.53742500
H	2.13354300	-3.64177500	2.61155900
H	3.39468000	-1.41688700	-2.26047900
C	4.08155000	0.48523500	-0.06745100
H	4.26117000	0.86622100	0.93439800
C	4.34404200	1.26155400	-1.11662900
H	4.16202800	0.92760400	-2.13267600
N	3.18305100	-1.52976700	1.01133800
H	3.27680200	-1.14799100	1.93962900
H	0.87625200	1.60044000	-2.08239500
H	4.73629600	2.26186600	-0.98353100
Br	-5.11345600	0.41003900	-0.06881400

Table S30. Calculated Gibbs free energy and XYZ coordinates for all atoms in **TS1a-endo** catalysed by IBr.

G= -1594.6638 Hartree Frequency = -387.04 cm^{-1}

I	-2.66097200	-0.28645000	-0.01556800
C	1.52753800	2.91733100	-0.55440200
C	1.58986600	2.72985400	0.84871200
C	2.10151700	3.76576500	1.65068000
C	2.52431500	4.93157200	1.04510800
C	2.44708700	5.09715700	-0.35453400
C	1.94979600	4.09984700	-1.17042500
C	0.77443200	0.85112800	-0.09788900
C	1.10450100	1.41389700	1.11434600
H	2.16149400	3.64646700	2.72635900
H	2.92068800	5.73843300	1.64950600
H	2.78524600	6.02659100	-0.79661500
H	1.89332500	4.22280200	-2.24536200
H	1.02515200	0.93210800	2.07676100
C	0.27364500	-0.47069400	-0.42574300
H	0.25465000	-0.73129200	-1.48088600
C	-0.11472300	-1.39516900	0.47741500
H	-0.37127000	-2.40015600	0.16411700
H	-0.06940600	-1.19994500	1.54340500
N	1.02800100	1.76547200	-1.09959200
C	2.64886200	-2.75505900	0.70260300
C	2.66070800	-2.87279700	-0.70961200

C	2.11693100	-4.02773700	-1.29565100
C	1.59012900	-5.01038000	-0.47794900
C	1.60015200	-4.87515100	0.92503500
C	2.13028500	-3.75171400	1.53340800
C	3.52673700	-0.86233900	-0.14638100
C	3.22736400	-1.66421900	-1.22361600
H	2.10687000	-4.14205300	-2.37367400
H	1.16483300	-5.90420800	-0.91830800
H	1.18437400	-5.66616100	1.53742500
H	2.13354300	-3.64177500	2.61155900
H	3.39468000	-1.41688700	-2.26047900
C	4.08155000	0.48523500	-0.06745100
H	4.26117000	0.86622100	0.93439800
C	4.34404200	1.26155400	-1.11662900
H	4.16202800	0.92760400	-2.13267600
N	3.18305100	-1.52976700	1.01133800
H	3.27680200	-1.14799100	1.93962900
H	0.87625200	1.60044000	-2.08239500
H	4.73629600	2.26186600	-0.98353100
Br	-5.11345600	0.41003900	-0.06881400

Table S31. Calculated Gibbs free energy and XYZ coordinates for all atoms in **INT1a-endo** catalysed by IBr.

G= -1594.6903 Hartree

I	2.34240700	-0.27785700	0.26044700
C	-0.91539200	3.36210100	0.17948200
C	-1.45637200	2.74763900	-0.97375100
C	-2.21591500	3.52317700	-1.86287300
C	-2.41122900	4.86323100	-1.58119600
C	-1.85954800	5.45329000	-0.42852700
C	-1.10385000	4.71499200	0.46577900
C	-0.32541500	1.19120400	0.21247500
C	-1.06407200	1.36683400	-0.93239600
H	-2.63381300	3.07928200	-2.75906000
H	-2.99214700	5.47519200	-2.26046700
H	-2.02617600	6.50682900	-0.24000300
H	-0.67156500	5.16787400	1.35002500
H	-1.29176400	0.61135400	-1.66867100
C	0.22546000	-0.04102700	0.81774700
H	0.26922300	0.05564700	1.90335500
C	-0.52259500	-1.29852600	0.40897400

H	0.05195100	-2.17822600	0.70117600
H	-0.62244800	-1.33662700	-0.67797900
N	-0.23411100	2.38910800	0.87753200
C	-3.63219200	-2.30087700	-0.38770300
C	-2.54623000	-2.71909200	0.37354000
C	-2.14409100	-4.04191700	0.31405800
C	-2.86955500	-4.91359800	-0.49884200
C	-3.95731700	-4.46852400	-1.25064100
C	-4.36276500	-3.13688800	-1.21148400
C	-2.96006900	-0.44249000	0.73386600
C	-1.94023600	-1.51337700	1.04944600
H	-1.29554900	-4.39725600	0.88602400
H	-2.58112500	-5.95574500	-0.54945200
H	-4.49620400	-5.16784800	-1.87675000
H	-5.20264200	-2.77833800	-1.79189700
H	-1.83028500	-1.62367100	2.13124900
C	-3.13548100	0.86927900	1.31187100
H	-3.82739200	1.53366700	0.80459600
C	-2.53844300	1.24042200	2.44687400
H	-1.86291000	0.58609900	2.98611000
N	-3.82831400	-0.92384900	-0.12196600
H	-4.61013800	-0.38626000	-0.48569500
H	0.30679200	2.54039600	1.71573500
H	-2.73113900	2.21590400	2.87451600
Br	5.50710200	-0.74896500	-0.49301900

Table S32. Calculated Gibbs free energy and XYZ coordinates for all atoms in **TS2a-endo** catalysed by IBr.

G= -1594.6515 Hartree Frequency = -494.94 cm^{-1}

I	2.37413500	-0.73427000	0.29132100
C	-0.02209500	3.34259400	0.12259000
C	-0.91099600	2.77256900	-0.82235000
C	-1.48581500	3.60181500	-1.79581800
C	-1.16605200	4.94950800	-1.80616500
C	-0.27702100	5.49132900	-0.86209600
C	0.30796100	4.69694400	0.11246500
C	-0.19020000	1.13812300	0.57080500
C	-1.00119300	1.37359200	-0.51797200
H	-2.16608300	3.18995000	-2.53273700
H	-1.60264000	5.59899600	-2.55542100
H	-0.04198800	6.54829200	-0.89736600
H	0.99624400	5.11193400	0.83920800
H	-1.58171000	0.63419100	-1.04869800

C	-0.02321500	-0.08834600	1.31739200
H	0.63438600	-0.11422000	2.17728700
C	-0.73762600	-1.30686600	0.80959600
H	-0.24249200	-2.21473000	1.15265500
H	-0.69827100	-1.31555500	-0.28047200
N	0.38685900	2.33046500	0.96241300
C	-4.11536600	-1.28780100	-0.27829500
C	-3.09564900	-2.15928300	0.11919700
C	-2.95435100	-3.38416300	-0.51070400
C	-3.84464300	-3.71976500	-1.53148000
C	-4.85507600	-2.83725100	-1.91287200
C	-5.00923300	-1.59998100	-1.29174500
C	-3.01948800	-0.20030300	1.38549600
C	-2.29118700	-1.49019700	1.19726900
H	-2.16535500	-4.06843900	-0.22017100
H	-3.74907800	-4.67331700	-2.03513800
H	-5.53420700	-3.11556500	-2.70936000
H	-5.79155200	-0.91286700	-1.58913000
H	-2.29826200	-2.05877500	2.13118200
C	-2.56924100	0.76818800	2.26661800
H	-2.93973600	1.78409400	2.20592700
C	-1.43662300	0.44861600	3.00152700
H	-1.27243700	-0.56352600	3.34862400
N	-4.04319900	-0.13186300	0.50836300
H	-4.63133000	0.68056900	0.38836500
H	1.07083500	2.42208200	1.69710300
H	-0.92759900	1.22082600	3.56686400
Br	4.71111800	-1.36239300	-0.76614000

Table S33. Calculated Gibbs free energy and XYZ coordinates for all atoms in **2a-endo** catalysed by IBr.

G= -1594.7175 Hartree

I	1.99356400	-0.49165500	-0.00203400
C	0.24697700	2.85950000	0.13659700
C	-0.06656000	1.93640500	-0.87944500
C	0.06484700	2.32061200	-2.21799500
C	0.50561300	3.60310300	-2.49835800
C	0.82386300	4.50481600	-1.46833800
C	0.70229700	4.14783000	-0.13510900
C	-0.41244900	0.95528300	1.15206400
C	-0.44849500	0.70630000	-0.22118000
H	-0.17040200	1.62516300	-3.01491800
H	0.61182000	3.91979900	-3.52865500

H	1.17149800	5.49885500	-1.72159400
H	0.94776400	4.84009500	0.66102500
H	-0.91658900	-0.15163400	-0.68237200
C	-0.80855100	0.08399200	2.31055500
H	0.07725100	-0.06478100	2.93755300
C	-1.31053600	-1.29111400	1.85029700
H	-1.25757400	-1.96022300	2.71000100
H	-0.64353900	-1.70767100	1.09222700
N	0.01818000	2.22961900	1.35028100
C	-4.00690300	-0.80260900	-0.63136900
C	-3.03200400	-1.66598500	-0.11220700
C	-2.51894000	-2.68693100	-0.88824100
C	-2.98015300	-2.83879000	-2.20104500
C	-3.94957400	-1.97748500	-2.70446000
C	-4.48147100	-0.94606800	-1.92687800
C	-3.43987000	0.09398400	1.38454400
C	-2.76624200	-1.26595000	1.32167300
H	-1.76276200	-3.35612800	-0.49100000
H	-2.58134600	-3.62806200	-2.82573800
H	-4.29858800	-2.10196100	-3.72276100
H	-5.23073800	-0.27390100	-2.32741500
H	-3.36251800	-1.93305100	1.95823200
C	-3.11360600	1.03449900	2.27069700
H	-3.61246300	1.99627900	2.28709200
C	-1.91022300	0.78489200	3.14720900
H	-2.13717700	0.14375100	4.00679500
N	-4.36503800	0.14689500	0.33342800
H	-4.73864800	1.03987900	0.04572700
H	0.21651200	2.63170500	2.25459000
H	-1.54162200	1.72731200	3.55633900
Br	4.32600300	-1.60460100	-0.02878300

Table S34. Calculated Gibbs free energy and XYZ coordinates for all atoms in **COM1a-exo** catalysed by IBr.

G= -1594.6937 Hartree

C	1.82130700	2.77404100	-0.69195300
C	1.71151700	2.69100600	0.71874500
C	2.23363300	3.73361000	1.50476100
C	2.84220400	4.80125100	0.87709300
C	2.94151500	4.86138700	-0.52972300
C	2.43486300	3.85643800	-1.33078800
C	0.82524800	0.82426500	-0.18552300
C	1.07696500	1.44773700	1.01472400

H	2.16265000	3.69189700	2.58553600
H	3.25150000	5.61114200	1.46871600
H	3.42421900	5.71525100	-0.98973600
H	2.51173800	3.90085000	-2.41055000
H	0.84735600	1.05281600	1.99226100
C	0.23571600	-0.46744700	-0.47907800
H	0.17579200	-0.74468300	-1.52901500
C	-0.18165900	-1.35545600	0.44835000
H	-0.08248100	-1.15393000	1.50911000
H	-0.50819300	-2.34712600	0.15759700
N	1.27110900	1.63486600	-1.21279100
C	2.36677900	-2.98519600	-0.69115000
C	2.49989200	-2.92414500	0.71862500
C	1.90340600	-3.92893200	1.49822900
C	1.19396600	-4.93427700	0.86801700
C	1.07016700	-4.97026500	-0.53546400
C	1.65542500	-4.00180300	-1.33253300
C	3.50994900	-1.11190200	-0.17718800
C	3.23191600	-1.73152900	1.01712400
H	1.98893500	-3.90619700	2.57872300
H	0.72337100	-5.71106200	1.45867700
H	0.50829200	-5.77251700	-0.99839500
H	1.56120100	-4.02678200	-2.41190100
H	3.51899000	-1.37296600	1.99323900
C	4.18243000	0.14813100	-0.47659300
H	4.44206300	0.31434000	-1.51905300
C	4.45925300	1.08642300	0.42664900
H	4.18584000	0.96882800	1.46936500
N	2.99344700	-1.87905500	-1.20541500
H	1.19049300	1.41959100	-2.19414600
H	3.07179200	-1.65373800	-2.18479200
H	4.94595300	2.01159600	0.14320000
I	-2.67270900	-0.13330100	-0.00260900
Br	-5.09156500	0.68276900	-0.00077400

Table S35. Calculated Gibbs free energy and XYZ coordinates for all atoms in **TS1a-exo** catalysed by IBr.

G= -1594.6646 Hartree Frequency = -374.92 cm^{-1}

C	2.08492500	3.14154200	0.22255000
C	1.31407200	3.23543200	-0.96126000
C	1.56843400	4.28775200	-1.85505300
C	2.56536200	5.19629500	-1.55231600

C	3.32126300	5.08094100	-0.36973800
C	3.09298400	4.05702100	0.53219200
C	0.61899100	1.43343000	0.21405000
C	0.38855300	2.14062600	-0.94312200
H	0.99300200	4.38100700	-2.76883200
H	2.77408500	6.01129100	-2.23476100
H	4.09782800	5.80745500	-0.16324600
H	3.67476200	3.96494900	1.44136600
H	-0.34234800	1.90153400	-1.70049300
C	-0.03566700	0.24243200	0.74651700
H	0.00126900	0.12982800	1.82558100
C	-1.14051800	-0.31345400	0.07294600
H	-1.15980600	-0.26633000	-1.01057400
H	-1.64388300	-1.17040600	0.50614800
N	1.63428200	2.04569800	0.91928000
C	-4.56653300	-0.51387200	0.26786300
C	-3.77506700	0.20140200	-0.65018400
C	-3.96048300	-0.00749000	-2.02024000
C	-4.93165500	-0.90790700	-2.42618800
C	-5.71066800	-1.61059700	-1.49102200
C	-5.53972900	-1.42823300	-0.12872600
C	-3.18966100	0.80202600	1.47309900
C	-2.83235900	0.98498400	0.12222700
H	-3.36048700	0.52795600	-2.74701500
H	-5.09568600	-1.07768800	-3.48301700
H	-6.45878800	-2.31004700	-1.84267100
H	-6.13470400	-1.97000200	0.59602200
H	-2.28086000	1.84272200	-0.23732900
C	-2.61922600	1.39342700	2.66454700
H	-3.01635900	1.05206000	3.61539400
C	-1.64111300	2.30237300	2.62805900
H	-1.23562700	2.67312100	1.69214500
N	-4.17765500	-0.12286300	1.54071300
H	2.03380800	1.68992700	1.77416100
H	-4.56834200	-0.47912100	2.40154700
H	-1.23117500	2.71160100	3.54265600
I	1.42996900	-1.69072700	0.19834000
Br	3.28277500	-3.64514100	-0.23475100

Table S36. Calculated Gibbs free energy and XYZ coordinates for all atoms in **INT1a-exo** catalysed by IBr.

G= -1594.6909 Hartree

C	2.08492500	3.14154200	0.22255000
C	1.31407200	3.23543200	-0.96126000
C	1.56843400	4.28775200	-1.85505300
C	2.56536200	5.19629500	-1.55231600
C	3.32126300	5.08094100	-0.36973800
C	3.09298400	4.05702100	0.53219200
C	0.61899100	1.43343000	0.21405000
C	0.38855300	2.14062600	-0.94312200
H	0.99300200	4.38100700	-2.76883200
H	2.77408500	6.01129100	-2.23476100
H	4.09782800	5.80745500	-0.16324600
H	3.67476200	3.96494900	1.44136600
H	-0.34234800	1.90153400	-1.70049300
C	-0.03566700	0.24243200	0.74651700
H	0.00126900	0.12982800	1.82558100
C	-1.14051800	-0.31345400	0.07294600
H	-1.15980600	-0.26633000	-1.01057400
H	-1.64388300	-1.17040600	0.50614800
N	1.63428200	2.04569800	0.91928000
C	-4.56653300	-0.51387200	0.26786300
C	-3.77506700	0.20140200	-0.65018400
C	-3.96048300	-0.00749000	-2.02024000
C	-4.93165500	-0.90790700	-2.42618800
C	-5.71066800	-1.61059700	-1.49102200
C	-5.53972900	-1.42823300	-0.12872600
C	-3.18966100	0.80202600	1.47309900
C	-2.83235900	0.98498400	0.12222700
H	-3.36048700	0.52795600	-2.74701500
H	-5.09568600	-1.07768800	-3.48301700
H	-6.45878800	-2.31004700	-1.84267100
H	-6.13470400	-1.97000200	0.59602200
H	-2.28086000	1.84272200	-0.23732900
C	-2.61922600	1.39342700	2.66454700
H	-3.01635900	1.05206000	3.61539400
C	-1.64111300	2.30237300	2.62805900
H	-1.23562700	2.67312100	1.69214500
N	-4.17765500	-0.12286300	1.54071300
H	2.03380800	1.68992700	1.77416100
H	-4.56834200	-0.47912100	2.40154700
H	-1.23117500	2.71160100	3.54265600
I	1.42996900	-1.69072700	0.19834000
Br	3.28277500	-3.64514100	-0.23475100

Table S37. Calculated Gibbs free energy and XYZ coordinates for all atoms in **TS2a-exo** catalysed by IBr.

G= -1594.6531 Hartree Frequency = -505.71 cm^{-1}

C	2.20820600	3.00956000	0.27929400
C	1.39988100	3.14435700	-0.87570100
C	1.71556500	4.14317400	-1.80798800
C	2.80747300	4.96181300	-1.57291000
C	3.59775200	4.80604600	-0.42088600
C	3.30981600	3.82952600	0.51982000
C	0.59725100	1.43215200	0.37318400
C	0.38176700	2.13635600	-0.79196400
H	1.11386900	4.26798200	-2.70103600
H	3.06175800	5.73486200	-2.28814700
H	4.44773300	5.45950400	-0.26564100
H	3.91818000	3.70591700	1.40794200
H	-0.39011500	1.93612700	-1.51907700
C	-0.17448400	0.34867700	0.95015400
H	0.13395900	-0.08337900	1.89388900
C	-1.35261300	-0.17233500	0.18751000
H	-1.10060800	-0.27203100	-0.87068600
H	-1.64870600	-1.16012500	0.54287400
N	1.68547800	1.97728600	1.02693000
C	-4.77463600	-0.26849600	0.22668200
C	-3.76293400	0.19355400	-0.62100100
C	-3.89038800	0.04120600	-1.99141200
C	-5.03749700	-0.57452000	-2.49241200
C	-6.03408300	-1.03214900	-1.62976200
C	-5.92076000	-0.88751800	-0.24918400
C	-3.22218000	0.65978600	1.60041700
C	-2.65743200	0.75184600	0.22411000
H	-3.11449100	0.39238600	-2.66274800
H	-5.15583700	-0.70148600	-3.56100800
H	-6.91544300	-1.51027600	-2.03925200
H	-6.69314100	-1.24246100	0.42146400
H	-2.34520500	1.76270700	-0.05588100
C	-2.46815300	0.98085900	2.71496700
H	-2.72932500	0.59270900	3.69216100
C	-1.25535600	1.61809500	2.48036600
H	-1.16667400	2.34323000	1.68131000
N	-4.40884000	0.01650400	1.54800500
H	2.09775600	1.59926100	1.86561100
H	-4.94769300	-0.24884800	2.36006500

H	-0.54853500	1.74400500	3.29302900
I	1.49026000	-1.65075300	0.27259700
Br	3.12168900	-3.58624700	-0.46533600

Table S38. Calculated Gibbs free energy and XYZ coordinates for all atoms in **2a-exo** catalysed by IBr.

G= -1594.7176 Hartree

C	-2.23850100	2.65757300	-0.12996500
C	-1.88695800	2.05138800	1.09226700
C	-2.70336300	2.24451600	2.21233500
C	-3.83629700	3.02875900	2.07937500
C	-4.17277100	3.61784900	0.84807900
C	-3.38256500	3.44023600	-0.27548900
C	-0.33190900	1.49982800	-0.48287300
C	-0.68502800	1.28783100	0.84695600
H	-2.45300700	1.78486800	3.16113000
H	-4.47915800	3.19141800	2.93572200
H	-5.06870900	4.22220000	0.77616300
H	-3.64056900	3.89157500	-1.22575900
H	-0.06796400	0.80663100	1.59024400
C	0.87522800	1.07512300	-1.26650000
H	0.51669100	0.59270300	-2.18096300
C	1.75657100	0.05843300	-0.50624700
H	1.19061900	-0.45377900	0.27350200
H	2.09320300	-0.71155300	-1.20278100
N	-1.26949400	2.30897200	-1.05516800
C	5.24628500	-0.03653500	-0.03382600
C	4.04067500	-0.21736200	0.66028700
C	3.95963000	-1.14399900	1.68127900
C	5.09042900	-1.90147300	2.00564100
C	6.27848000	-1.71540600	1.30598600
C	6.37799800	-0.77832500	0.27574000
C	3.76468900	1.37284500	-1.05855900
C	3.00957900	0.72324100	0.08535800
H	3.02986700	-1.28685000	2.22181600
H	5.04033400	-2.63497900	2.80040100
H	7.14836100	-2.30873200	1.56224800
H	7.30623400	-0.63797800	-0.26478500
H	2.70619700	1.47877600	0.82259000
C	3.11849100	2.11512000	-1.95985200
H	3.60590400	2.54628500	-2.82504100
C	1.65812100	2.36763400	-1.69072300
H	1.54969400	3.09866800	-0.87921100

N	5.09106800	0.96044500	-0.99453900
H	-1.29010900	2.55161500	-2.03464500
H	5.74530500	1.10591000	-1.74693300
H	1.17567800	2.80742800	-2.56507600
I	-1.86456700	-1.10282900	-0.00933000
Br	-3.07629300	-3.28468100	-0.58605100

Table S39. Calculated Gibbs free energy and XYZ coordinates for all atoms in **COM1b-endo** catalysed by IBr.

G= -1594.6980 Hartree

C	-0.44607700	2.46010700	-0.84303300
C	-0.65721000	2.05539500	0.48940100
C	-1.26378500	2.94281100	1.38404400
C	-1.63970400	4.19380000	0.92324300
C	-1.43247300	4.57088800	-0.41502700
C	-0.83499400	3.70911700	-1.32039400
C	0.41957800	0.38832000	-0.64010900
C	-0.14788200	0.70751400	0.60491900
H	-1.43629000	2.65452600	2.41424100
H	-2.10783200	4.89557400	1.60257700
H	-1.74598000	5.55380300	-0.74438000
H	-0.66875200	3.99651000	-2.35141200
H	0.07004000	0.18466800	1.52394000
C	1.14802400	-0.79395900	-1.07365100
H	1.59605900	-0.74287600	-2.06077100
C	1.30586900	-1.88187300	-0.32196700
H	1.88996700	-2.72243500	-0.67586100
H	0.86824000	-1.96147700	0.66784200
N	0.20984600	1.42577900	-1.48868800
C	4.06890200	-0.99799600	0.83533700
C	4.48447100	-0.63057300	-0.46820000
C	5.14771200	-1.58339600	-1.25935600
C	5.37751200	-2.84343300	-0.73959800
C	4.96508400	-3.18118300	0.56545700
C	4.30930800	-2.26678100	1.36921400
C	3.39651800	1.11867400	0.46140000
C	4.05128600	0.71537300	-0.67950000
H	5.47092800	-1.33232000	-2.26324200
H	5.88689000	-3.58735500	-1.34032200
H	5.16503900	-4.17616700	0.94443900
H	3.98428100	-2.52415400	2.37039100
H	4.20373500	1.31409500	-1.56415600
C	2.72687700	2.37037000	0.80005600

H	2.33060800	2.43825200	1.81018100
C	2.55352200	3.39273700	-0.03542400
H	2.91754900	3.36271000	-1.05702100
N	3.41372900	0.08102100	1.37184100
H	3.01160400	0.12075100	2.29539600
H	0.46237500	1.41744000	-2.46652200
H	2.02647700	4.28482400	0.27921900
I	-2.36198000	-0.70892300	0.14798200
Br	-4.55143500	-2.08075700	-0.12087300

Table S40. Calculated Gibbs free energy and XYZ coordinates for all atoms in **TS1b-endo** catalysed by IBr.

G= -1594.6638 Hartree Frequency = -424.77 cm^{-1}

C	2.34429400	-2.55262700	-0.58480400
C	1.90167500	-1.86606900	0.55208300
C	2.58606700	-2.00713700	1.74980300
C	3.69900500	-2.84603400	1.78758200
C	4.12912400	-3.51560800	0.64135500
C	3.45800200	-3.37676200	-0.57210700
C	0.44559000	-1.47291200	-1.23165100
C	0.74685000	-1.02513800	0.15092800
H	2.26798200	-1.46710500	2.63402100
H	4.24259400	-2.97278000	2.71533200
H	5.00194300	-4.15480200	0.69189400
H	3.78989600	-3.89330000	-1.46401600
H	-0.09998100	-0.96389900	0.82522400
C	-0.66140300	-1.16740300	-2.01037400
H	-0.71979000	-1.58844900	-3.00771000
C	-1.69590800	-0.34053100	-1.54365600
H	-2.33217100	0.12018300	-2.29036600
H	-1.50624800	0.29785700	-0.68511900
N	1.47352100	-2.25481100	-1.63882400
C	-3.93659300	-0.05195500	1.02640900
C	-4.13661500	-0.23776900	-0.35091500
C	-4.97608900	0.63376200	-1.04546400
C	-5.60053400	1.65090300	-0.33997200
C	-5.38532200	1.81812800	1.03710800
C	-4.54598900	0.97223600	1.74479900
C	-2.71646000	-1.85548400	0.43401800
C	-3.26776500	-1.33058200	-0.76886700
H	-5.13850500	0.51407500	-2.11015200
H	-6.26343400	2.33293500	-0.85738800
H	-5.88248400	2.62722600	1.55725900
H	-4.37093200	1.10207200	2.80533300

H	-3.46237400	-1.95415300	-1.62905800
C	-1.84906800	-2.99062200	0.60381700
H	-1.47216200	-3.18259800	1.60373600
C	-1.46137100	-3.75759400	-0.42332700
H	-1.84049400	-3.60570800	-1.42629700
N	-3.06677400	-1.04742000	1.45970500
H	-2.73766000	-1.15275300	2.40976100
H	1.54349000	-2.65044500	-2.56508300
H	-0.76725200	-4.57489900	-0.27164600
I	1.43539000	1.13729300	0.01077300
Br	2.29599300	3.99773700	-0.09695500

Table S41. Calculated Gibbs free energy and XYZ coordinates for all atoms in **INT1b-endo** catalysed by IBr.

G= -1594.6754 Hartree

C	-2.46560100	-2.58788400	0.69000200
C	-2.10069800	-1.88239400	-0.46435100
C	-2.84979000	-2.00399800	-1.62154700
C	-3.95947400	-2.85112600	-1.61948400
C	-4.31291500	-3.54446200	-0.46347200
C	-3.57385700	-3.42253400	0.71327400
C	-0.50550300	-1.53324200	1.22971600
C	-0.91148400	-1.03989900	-0.13581100
H	-2.58380600	-1.44140200	-2.50945500
H	-4.55438300	-2.96235400	-2.51705500
H	-5.18207400	-4.19127300	-0.47365300
H	-3.85550600	-3.95940300	1.61064000
H	-0.10816600	-1.06039100	-0.86740900
C	0.66257300	-1.33064100	1.86799200
H	0.80952600	-1.78409300	2.84372500
C	1.75058300	-0.46970100	1.33676400
H	2.14957100	0.16092600	2.13378200
H	1.39955800	0.20454500	0.55279400
N	-1.56284800	-2.29212600	1.70668000
C	4.22558800	-0.15827500	-0.93883800
C	4.09688500	-0.22778100	0.44504300
C	4.83267000	0.63582500	1.23931600
C	5.69401000	1.53471300	0.61190400
C	5.80549800	1.58210200	-0.77923300
C	5.06330500	0.72962100	-1.59047800
C	2.73669900	-1.82731800	-0.56773900
C	3.03227900	-1.23536300	0.77634000
H	4.74658500	0.61443100	2.31898400

H	6.28510200	2.21321400	1.21366800
H	6.47722900	2.29678000	-1.23699900
H	5.13533800	0.76188500	-2.66968500
H	3.33300500	-1.98842500	1.50686300
C	1.86795200	-2.92578000	-0.88719900
H	1.60837300	-3.07014800	-1.93079700
C	1.39577300	-3.74730200	0.05950700
H	1.68109900	-3.65032600	1.09835200
N	3.37286400	-1.14023900	-1.49106600
H	3.28708400	-1.31844000	-2.48676100
H	-1.53666300	-2.77374300	2.59145800
H	0.72476900	-4.55752200	-0.19922200
I	-1.47445000	1.09628400	-0.03957100
Br	-2.20708200	4.29319700	0.00567200

Table S42. Calculated Gibbs free energy and XYZ coordinates for all atoms in **TS2b-endo** catalysed by IBr.

G= -1594.6682 Hartree Frequency = -245.28 cm^{-1}

C	2.76313200	-2.36663500	-0.61897900
C	2.35326200	-1.70159400	0.54215500
C	3.17149200	-1.69390800	1.65950800
C	4.39099500	-2.36919800	1.60082200
C	4.78604900	-3.02183900	0.43379200
C	3.97708100	-3.02955200	-0.70204800
C	0.66587100	-1.59070900	-1.08104000
C	1.04743400	-1.04072800	0.25625700
H	2.87361100	-1.16353000	2.55668100
H	5.04139900	-2.37835300	2.46623800
H	5.74085700	-3.53247500	0.40442000
H	4.28336700	-3.53420800	-1.60986900
H	0.26895100	-1.13748700	1.00996200
C	-0.56590100	-1.54733400	-1.68320100
H	-0.65404500	-1.98797400	-2.67207400
C	-1.67337400	-0.66029400	-1.23397200
H	-1.97281200	-0.00643200	-2.05591700
H	-1.37148500	-0.01163200	-0.41013100
N	1.76289700	-2.22915300	-1.58601700
C	-4.28094000	-0.44718100	0.94288400
C	-4.08903800	-0.41682700	-0.43857500
C	-4.81238700	0.47483400	-1.21241300
C	-5.72277000	1.31858000	-0.57712400
C	-5.89693600	1.27281500	0.80657800
C	-5.17387700	0.38434100	1.59809200
C	-2.74320700	-2.06293900	0.52512700

C	-3.01257100	-1.40195300	-0.78903900
H	-4.67419500	0.51882200	-2.28638800
H	-6.29913100	2.02264700	-1.16353500
H	-6.60578400	1.94231600	1.27736100
H	-5.30271400	0.34758000	2.67216100
H	-3.29356600	-2.10360100	-1.57668200
C	-1.73853800	-3.02007600	0.70627900
H	-1.34216100	-3.20863500	1.69669300
C	-1.14364800	-3.54052800	-0.41418000
H	-1.67694700	-3.61518600	-1.35105400
N	-3.43805700	-1.43873600	1.47922300
H	-3.35312400	-1.64117500	2.46727400
H	1.79216100	-2.65788300	-2.49858900
H	-0.25049600	-4.14957100	-0.32991400
I	1.36088200	1.16146900	0.06871200
Br	1.78807700	4.26224300	-0.09761000

Table S43. Calculated Gibbs free energy and XYZ coordinates for all atoms in **2b-endo** catalysed by IBr.

G= -1594.6937 Hartree

C	2.33842200	-2.55635700	-0.27826300
C	1.81262200	-2.07294500	0.93604700
C	2.52425200	-2.28370900	2.12238800
C	3.72861600	-2.96354300	2.06100000
C	4.23920800	-3.42984400	0.83690000
C	3.55539600	-3.23181700	-0.35126700
C	0.38333800	-1.53069600	-0.75789700
C	0.58126900	-1.38875700	0.61367300
H	2.13964700	-1.91730900	3.06688000
H	4.29263600	-3.13784700	2.96906400
H	5.18720200	-3.95353400	0.82231400
H	3.94791700	-3.58790200	-1.29584900
H	-0.14979300	-1.02260400	1.31767600
C	-0.77504000	-1.17196600	-1.64246700
H	-0.35549700	-0.82654700	-2.59287700
C	-1.66011300	-0.04838500	-1.04602900
H	-1.47009400	0.89403200	-1.56268900
H	-1.41422200	0.11757900	0.00392200
N	1.44304800	-2.21582600	-1.27718900
C	-4.72369500	-0.34168800	0.67077000
C	-4.05679200	0.47475700	-0.25518800
C	-4.28168600	1.83762700	-0.26677100
C	-5.17552500	2.38897400	0.65778900

C	-5.82783000	1.56813300	1.57235300
C	-5.61537400	0.18848000	1.59332200
C	-3.35859100	-1.76542700	-0.48686500
C	-3.16026600	-0.39450900	-1.10364600
H	-3.76876200	2.47350300	-0.98034500
H	-5.35819800	3.45609900	0.66303300
H	-6.51678100	2.00464500	2.28594300
H	-6.12753100	-0.44578300	2.30667400
H	-3.49054000	-0.40037200	-2.15014500
C	-2.57920800	-2.78454100	-0.85726100
H	-2.63927000	-3.76994900	-0.41361700
C	-1.59287600	-2.47103800	-1.95048300
H	-2.11510300	-2.30075200	-2.89968100
N	-4.35436600	-1.67073800	0.47817800
H	-4.53690500	-2.39759800	1.15164000
H	1.58325600	-2.38156700	-2.26310400
H	-0.90758700	-3.30275000	-2.11697300
I	1.64786300	1.12716300	0.05401400
Br	2.76015300	3.42367100	-0.22829100

Table S44. Calculated Gibbs free energy and XYZ coordinates for all atoms in **COM1b-exo** catalysed by IBr.

G= -1594.6970 Hartree

C	-0.85296200	2.81348900	-0.36285500
C	-0.54718300	2.00240100	0.75006400
C	-0.85175300	2.46408000	2.03673100
C	-1.44314200	3.70777700	2.17058000
C	-1.74531900	4.49735700	1.04596900
C	-1.45840100	4.06299400	-0.23664700
C	0.13010400	0.94646700	-1.15247700
C	0.03513600	0.78728000	0.23519900
H	-0.62963400	1.85597700	2.90560500
H	-1.68226500	4.08342500	3.15785300
H	-2.21238100	5.46421700	1.18709700
H	-1.69032200	4.66636600	-1.10554300
H	0.55353300	0.02956400	0.80246600
C	0.72147500	0.07947500	-2.16210500
H	0.54838200	0.35800700	-3.19719100
C	1.44644700	-0.99773200	-1.86462300
H	1.65136800	-1.28605700	-0.83791700
H	1.86567900	-1.61943100	-2.64576700
N	-0.43566900	2.13681000	-1.49306500
C	4.40902200	-1.14783700	-0.19463100

C	3.75565500	-0.77721000	1.00792700
C	3.64113400	-1.72701600	2.03794800
C	4.16125500	-2.99191800	1.84288100
C	4.80351100	-3.33858300	0.63678600
C	4.93719800	-2.42688800	-0.39405100
C	3.71157700	0.98228100	-0.40907000
C	3.33220500	0.57995700	0.84905100
H	3.14879400	-1.46815900	2.96840500
H	4.07617600	-3.73436900	2.62712100
H	5.19907100	-4.33977500	0.51556500
H	5.43117600	-2.69139900	-1.32151600
H	2.81696300	1.19114000	1.57418000
C	3.49589200	2.24213900	-1.11217100
H	4.09649500	2.40210500	-2.00396100
C	2.62104600	3.17205300	-0.73037300
H	1.98901700	3.03649600	0.14224200
N	4.38204000	-0.05711400	-1.02504000
H	-0.53661100	2.47027300	-2.44045100
H	4.72147500	-0.03845100	-1.97395800
H	2.51279600	4.09698600	-1.28295600
I	-2.17722600	-0.75322300	-0.03879600
Br	-4.28310500	-2.24849600	-0.09580500

Table S45. Calculated Gibbs free energy and XYZ coordinates for all atoms in **TS1b -exo** catalysed by IBr.

G= -1594.6628 Hartree Frequency = -433.75 cm^{-1}

C	-2.22086800	2.81189700	-0.38129200
C	-2.05603700	1.98245300	0.73360900
C	-2.93771500	2.08121900	1.79922400
C	-3.96735300	3.01844400	1.72833500
C	-4.12103200	3.82923700	0.60307800
C	-3.24710800	3.73780200	-0.47850900
C	-0.34387800	1.58679000	-0.80940700
C	-0.91528500	1.07437900	0.45837000
H	-2.83302500	1.43535200	2.66315100
H	-4.66252300	3.11295600	2.55303200
H	-4.93428400	4.54350200	0.56606800
H	-3.36392500	4.36537100	-1.35328700
H	-0.21099500	0.88009300	1.26122900
C	0.84192800	1.22512700	-1.43483700
H	1.12542800	1.76041700	-2.33251900
C	1.67996500	0.21753700	-0.92801000

H	1.23885000	-0.52660200	-0.27208200
H	2.43655000	-0.18648600	-1.59254000
N	-1.19070900	2.52992900	-1.28566800
C	4.94912500	-0.19840500	-0.01033900
C	3.76445400	-0.38032400	0.72260100
C	3.54365300	-1.59176900	1.37870400
C	4.52000000	-2.57339300	1.29759700
C	5.69793300	-2.36838100	0.56244400
C	5.93242600	-1.17816200	-0.10874400
C	3.76944700	1.71428700	-0.20433000
C	2.94649500	0.80766300	0.51700200
H	2.63226200	-1.76000600	1.94041600
H	4.37191800	-3.51777100	1.80603600
H	6.43799500	-3.15747100	0.51582600
H	6.83716700	-1.01790100	-0.68179400
H	2.19852000	1.14731100	1.21914300
C	3.46956900	3.05694700	-0.62652700
H	4.18599100	3.54021900	-1.28250200
C	2.33898100	3.68145200	-0.27665300
H	1.62519000	3.23637800	0.40602300
N	4.90646500	1.07925200	-0.55993600
H	-1.06608000	2.99577000	-2.17300100
H	5.62241000	1.48046700	-1.14976100
H	2.11734900	4.67574400	-0.64329900
I	-1.75535500	-1.00921800	0.01974500
Br	-2.81724200	-3.71405300	-0.48089400

Table S46. Calculated Gibbs free energy and XYZ coordinates for all atoms in **INT1b-exo** catalysed by IBr.

G= -1594.6726 Hartree

C	-3.96333900	-0.94130900	0.50990300
C	-3.28136200	-0.22251500	-0.47731400
C	-3.98081300	0.51507700	-1.41500500
C	-5.37583000	0.52533100	-1.35903900
C	-6.04377900	-0.18946900	-0.36674100
C	-5.34976300	-0.93553800	0.58529400
C	-1.73259400	-1.33333600	0.93963400
C	-1.81064300	-0.42940600	-0.27975300
H	-3.45130500	1.08811200	-2.16813600
H	-5.94011500	1.09928100	-2.08283600
H	-7.12634000	-0.16531600	-0.32854400

H	-5.87240900	-1.48842200	1.35621500
H	-1.33811600	-0.88303200	-1.15160200
C	-0.65754400	-1.86104900	1.55570400
H	-0.85137500	-2.54737000	2.37303600
C	0.77374200	-1.49206300	1.31582600
H	0.92332800	-0.42248800	1.47545100
H	1.40910000	-2.00368500	2.04184400
N	-3.04497700	-1.60916800	1.30861200
C	3.70764500	-2.08310300	-0.31745300
C	2.73169500	-1.09529400	-0.22768700
C	3.10996400	0.23693200	-0.18439900
C	4.47243000	0.52878700	-0.25323100
C	5.43260900	-0.48050200	-0.34943900
C	5.06543800	-1.82327100	-0.38094400
C	1.73682400	-3.20728600	-0.28128300
C	1.38492500	-1.75879200	-0.11291000
H	2.38696900	1.04311200	-0.10175300
H	4.78422100	1.56567400	-0.22788500
H	6.48175500	-0.21786000	-0.39762800
H	5.80062600	-2.61504200	-0.44951200
H	0.68334300	-1.42486600	-0.88080500
C	0.85651600	-4.34627100	-0.32787400
H	1.30633400	-5.32363600	-0.19189800
C	-0.45370900	-4.21984100	-0.56189200
H	-0.91490700	-3.25860600	-0.74396800
N	3.04101200	-3.33230200	-0.33380200
H	-3.28152800	-2.05107200	2.18287400
H	3.51695500	-4.22644700	-0.40572300
H	-1.09348700	-5.09265700	-0.59882000
I	-0.68961200	1.43750400	-0.06176200
Br	1.69770500	3.80012500	0.24803000

Table S47. Calculated Gibbs free energy and XYZ coordinates for all atoms in **TS2b -exo** catalysed by IBr.

G= -1594.6648 Hartree Frequency = -281.89 cm^{-1}

C	2.67583200	-2.58509900	-0.40656000
C	2.37650200	-1.76797800	0.68859400
C	3.26600000	-1.67851200	1.74649300
C	4.44466700	-2.42316500	1.69407200
C	4.72989900	-3.22692300	0.59088900
C	3.84802200	-3.31986100	-0.48493900
C	0.60374900	-1.72447700	-0.85279100

C	1.08574600	-1.07869400	0.40675700
H	3.05434700	-1.03358100	2.59155000
H	5.14945600	-2.36968500	2.51411900
H	5.65480600	-3.79001800	0.56488200
H	4.06761300	-3.94227500	-1.34336000
H	0.35842000	-1.05495800	1.21551900
C	-0.64924100	-1.65644600	-1.41399700
H	-0.79656500	-2.17311800	-2.35488500
C	-1.65859200	-0.63080000	-1.01503000
H	-1.17858800	0.32187300	-0.78631000
H	-2.35141200	-0.44980800	-1.83814600
N	1.61813600	-2.50924100	-1.31640700
C	-4.83457100	-0.38402500	0.17513700
C	-3.57545200	0.13376700	0.48244800
C	-3.44731900	1.46418100	0.84506600
C	-4.59881100	2.24876100	0.90082900
C	-5.84894400	1.71068600	0.59156100
C	-5.99163300	0.37654100	0.21883600
C	-3.40544800	-2.13180200	-0.04792600
C	-2.55780300	-0.94567500	0.26789200
H	-2.47647000	1.88723900	1.07678900
H	-4.52191900	3.29075300	1.18385600
H	-6.72758100	2.34173100	0.63970500
H	-6.95900500	-0.04403000	-0.02404700
H	-1.89722000	-1.10425800	1.12281900
C	-2.86262700	-3.37212800	-0.40373100
H	-3.44644900	-4.07033100	-0.99144800
C	-1.52390600	-3.56329500	-0.18074000
H	-1.01816700	-3.05446400	0.62716000
N	-4.67887800	-1.74330200	-0.15566500
H	1.58199800	-3.01287000	-2.19010200
H	-5.43442100	-2.34986400	-0.44722900
H	-1.01071100	-4.42496500	-0.59154400
I	1.48143000	1.09985400	0.02168200
Br	1.95442400	4.10965300	-0.41803300

Table S48. Calculated Gibbs free energy and XYZ coordinates for all atoms in **2b-exo** catalysed by IBr.

G= -1594.7191 Hartree

C	2.99596900	0.73471500	0.71818200
C	3.02450700	1.10322400	-0.64985800
C	3.84140500	0.37886600	-1.52837500
C	4.57717900	-0.68851900	-1.04069900

C	4.51842700	-1.05246300	0.31607900
C	3.72954900	-0.34822900	1.21617300
C	1.53778000	2.42823300	0.42096400
C	2.08778200	2.17997700	-0.80744600
H	3.88050900	0.64066300	-2.57945800
H	5.20356700	-1.26116000	-1.71365300
H	5.09808100	-1.89723500	0.66787600
H	3.68833200	-0.62084900	2.26463500
H	1.82097600	2.67491100	-1.72775800
C	0.43831700	3.36373200	0.84153800
H	0.83242400	4.02191800	1.62319800
C	-0.73851000	2.55084500	1.43274800
H	-0.42410500	1.99448400	2.31973700
H	-1.53441600	3.23697700	1.73600300
N	2.09785300	1.56309200	1.34353900
C	-3.23793700	0.82049700	-0.61754500
C	-2.48877200	0.77981200	0.56794300
C	-2.89286200	-0.01357000	1.62255600
C	-4.06485000	-0.76840200	1.49496500
C	-4.79666100	-0.72516200	0.31304500
C	-4.39356500	0.06823900	-0.76500300
C	-1.59734600	2.38190600	-0.89946000
C	-1.24708000	1.60751500	0.35308900
H	-2.30946900	-0.05398600	2.53652500
H	-4.40111700	-1.38943600	2.31591700
H	-5.70194800	-1.31426500	0.22262500
H	-4.96893300	0.09661300	-1.68267700
H	-0.43713500	0.91077100	0.09502500
C	-1.05402500	3.55452600	-1.22625700
H	-1.38210300	4.08394200	-2.11523900
C	-0.04579700	4.23719800	-0.32950200
H	0.81983900	4.57736300	-0.90609300
N	-2.61869600	1.66694100	-1.54625700
H	1.87174300	1.53861200	2.32554900
H	-3.16292100	2.10757100	-2.27345500
H	-0.50104000	5.14455700	0.08336700
I	0.93584700	-1.74501700	0.16681000
Br	-1.30020900	-2.57638300	-0.54893800

Table S49. Calculated Gibbs free energy and XYZ coordinates for all atoms in **COM1a-endo** catalysed by ICl.

G= -1637.8490 Hartree

C	2.99596900	0.73471500	0.71818200
C	3.02450700	1.10322400	-0.64985800

C	3.84140500	0.37886600	-1.52837500
C	4.57717900	-0.68851900	-1.04069900
C	4.51842700	-1.05246300	0.31607900
C	3.72954900	-0.34822900	1.21617300
C	1.53778000	2.42823300	0.42096400
C	2.08778200	2.17997700	-0.80744600
H	3.88050900	0.64066300	-2.57945800
H	5.20356700	-1.26116000	-1.71365300
H	5.09808100	-1.89723500	0.66787600
H	3.68833200	-0.62084900	2.26463500
H	1.82097600	2.67491100	-1.72775800
C	0.43831700	3.36373200	0.84153800
H	0.83242400	4.02191800	1.62319800
C	-0.73851000	2.55084500	1.43274800
H	-0.42410500	1.99448400	2.31973700
H	-1.53441600	3.23697700	1.73600300
N	2.09785300	1.56309200	1.34353900
C	-3.23793700	0.82049700	-0.61754500
C	-2.48877200	0.77981200	0.56794300
C	-2.89286200	-0.01357000	1.62255600
C	-4.06485000	-0.76840200	1.49496500
C	-4.79666100	-0.72516200	0.31304500
C	-4.39356500	0.06823900	-0.76500300
C	-1.59734600	2.38190600	-0.89946000
C	-1.24708000	1.60751500	0.35308900
H	-2.30946900	-0.05398600	2.53652500
H	-4.40111700	-1.38943600	2.31591700
H	-5.70194800	-1.31426500	0.22262500
H	-4.96893300	0.09661300	-1.68267700
H	-0.43713500	0.91077100	0.09502500
C	-1.05402500	3.55452600	-1.22625700
H	-1.38210300	4.08394200	-2.11523900
C	-0.04579700	4.23719800	-0.32950200
H	0.81983900	4.57736300	-0.90609300
N	-2.61869600	1.66694100	-1.54625700
H	1.87174300	1.53861200	2.32554900
H	-3.16292100	2.10757100	-2.27345500
H	-0.50104000	5.14455700	0.08336700
I	0.93584700	-1.74501700	0.16681000
Br	-1.30020900	-2.57638300	-0.54893800

Table S50. Calculated Gibbs free energy and XYZ coordinates for all atoms in **TS1a-endo** catalysed by ICl.

G= -1637.8217 Hartree Frequency = -386.64 cm^{-1}

I	1.91170700	-2.11385700	0.08646800
C	1.82372100	2.85625300	0.16778900
C	0.92966400	2.72100800	-0.92289400
C	0.83725200	3.76481800	-1.85791700
C	1.61841200	4.89174000	-1.68237400
C	2.50017200	5.00369900	-0.58992700
C	2.61703400	3.99171200	0.34646600
C	0.78658600	0.87110900	0.36396000
C	0.28639500	1.44968100	-0.77822000
H	0.16686400	3.68273500	-2.70584800
H	1.55823000	5.70356200	-2.39711600
H	3.10067300	5.89883300	-0.48227500
H	3.29847400	4.07413200	1.18467000
H	-0.45550700	1.02206800	-1.43484100
C	0.43657100	-0.38608800	1.01862800
H	0.74290000	-0.47950200	2.05661300
C	-0.72164100	-1.08495700	0.62010400
H	-0.95939200	-2.02099000	1.10901800
H	-1.05305400	-1.00223500	-0.40976300
N	1.72095400	1.71329100	0.92341600
C	-3.76860900	0.15370800	-0.49618000
C	-3.49544200	-0.83711800	0.46662800
C	-4.05421600	-2.10945600	0.31527900
C	-4.87223500	-2.34718100	-0.77762000
C	-5.13098600	-1.34335700	-1.72577100
C	-4.58133000	-0.07755500	-1.60353800
C	-2.40832600	1.09006900	1.03913000
C	-2.55536900	-0.26227200	1.40785700
H	-3.85501300	-2.89005500	1.04010500
H	-5.32079600	-3.32417500	-0.90769500
H	-5.77204400	-1.56367300	-2.57022600
H	-4.77560000	0.69835900	-2.33363000
H	-2.36560000	-0.63059300	2.40447300
C	-1.67309900	2.15132600	1.70057500
H	-1.58440900	3.08976600	1.16139100
C	-1.10609900	2.00704600	2.89973000
H	-1.18298000	1.08367200	3.46283500
N	-3.09474200	1.30258900	-0.11021200
H	-3.08981200	2.17371800	-0.62219400
H	2.23514000	1.52124500	1.76907500
H	-0.55154400	2.81978900	3.35059200
Cl	3.72639900	-3.76226400	-0.78944900

Table S51. Calculated Gibbs free energy and XYZ coordinates for all atoms in **INT1a-**

endo catalysed by ICl.

G= -1637.8503 Hartree

I	1.91170700	-2.11385700	0.08646800
C	1.82372100	2.85625300	0.16778900
C	0.92966400	2.72100800	-0.92289400
C	0.83725200	3.76481800	-1.85791700
C	1.61841200	4.89174000	-1.68237400
C	2.50017200	5.00369900	-0.58992700
C	2.61703400	3.99171200	0.34646600
C	0.78658600	0.87110900	0.36396000
C	0.28639500	1.44968100	-0.77822000
H	0.16686400	3.68273500	-2.70584800
H	1.55823000	5.70356200	-2.39711600
H	3.10067300	5.89883300	-0.48227500
H	3.29847400	4.07413200	1.18467000
H	-0.45550700	1.02206800	-1.43484100
C	0.43657100	-0.38608800	1.01862800
H	0.74290000	-0.47950200	2.05661300
C	-0.72164100	-1.08495700	0.62010400
H	-0.95939200	-2.02099000	1.10901800
H	-1.05305400	-1.00223500	-0.40976300
N	1.72095400	1.71329100	0.92341600
C	-3.76860900	0.15370800	-0.49618000
C	-3.49544200	-0.83711800	0.46662800
C	-4.05421600	-2.10945600	0.31527900
C	-4.87223500	-2.34718100	-0.77762000
C	-5.13098600	-1.34335700	-1.72577100
C	-4.58133000	-0.07755500	-1.60353800
C	-2.40832600	1.09006900	1.03913000
C	-2.55536900	-0.26227200	1.40785700
H	-3.85501300	-2.89005500	1.04010500
H	-5.32079600	-3.32417500	-0.90769500
H	-5.77204400	-1.56367300	-2.57022600
H	-4.77560000	0.69835900	-2.33363000
H	-2.36560000	-0.63059300	2.40447300
C	-1.67309900	2.15132600	1.70057500
H	-1.58440900	3.08976600	1.16139100
C	-1.10609900	2.00704600	2.89973000
H	-1.18298000	1.08367200	3.46283500
N	-3.09474200	1.30258900	-0.11021200
H	-3.08981200	2.17371800	-0.62219400
H	2.23514000	1.52124500	1.76907500
H	-0.55154400	2.81978900	3.35059200
Cl	3.72639900	-3.76226400	-0.78944900

Table S52. Calculated Gibbs free energy and XYZ coordinates for all atoms in **TS2a-endo** catalysed by ICl.

G= -1637.8067 Hartree Frequency = -525.72 cm^{-1}

I	2.35751300	-1.65152600	0.03018100
C	1.37771100	2.95146500	0.14721900
C	0.32102300	2.74122300	-0.77250900
C	0.00132100	3.76162000	-1.67934100
C	0.72850800	4.94007300	-1.65009100
C	1.77695400	5.12317600	-0.73210400
C	2.11703700	4.13285000	0.17668400
C	0.54130500	0.88901100	0.51184700
C	-0.19390500	1.42545800	-0.52135300
H	-0.80070900	3.62520600	-2.39595400
H	0.49156600	5.73430700	-2.34785500
H	2.33118800	6.05401700	-0.73554900
H	2.92662600	4.27031000	0.88366500
H	-0.99891300	0.93632300	-1.04853800
C	0.34203700	-0.36961600	1.20203400
H	1.00384300	-0.65484200	2.01146300
C	-0.73863100	-1.27869600	0.68426500
H	-0.52613900	-2.31490600	0.94530300
H	-0.75897100	-1.22410100	-0.40506400
N	1.47763000	1.81735400	0.92256800
C	-4.00387900	-0.18494300	-0.15521800
C	-3.27934800	-1.34498400	0.13888400
C	-3.56262800	-2.52133000	-0.53389100
C	-4.57560800	-2.51726700	-1.49373600
C	-5.28688000	-1.35045200	-1.77226700
C	-5.01283900	-0.15803200	-1.10609600
C	-2.52869200	0.43063100	1.45704800
C	-2.24489300	-1.00924200	1.17574600
H	-3.00707400	-3.42782100	-0.32243300
H	-4.81108300	-3.42792200	-2.02975700
H	-6.06794800	-1.36783500	-2.52244100
H	-5.56311400	0.74921500	-1.32232400
H	-2.37148400	-1.59665400	2.08931800
C	-1.74728400	1.16447100	2.32975200
H	-1.78155800	2.24697200	2.32768300
C	-0.72367600	0.46686600	2.96325700
H	-0.87653700	-0.55585700	3.28468400
N	-3.53094600	0.85291900	0.65709600
H	-3.85052600	1.80970500	0.60824200

H	2.18357000	1.65073300	1.62246200
H	0.03449900	1.01333400	3.51269900
Cl	4.23658800	-2.84911100	-1.11962600

Table S53. Calculated Gibbs free energy and XYZ coordinates for all atoms in **2a-endo** catalysed by ICl.

G= -1637.8732 Hartree

I	2.08063000	-1.12222000	0.01524300
C	1.21928200	2.52374900	0.09950700
C	0.72702500	1.66025200	-0.89457700
C	0.94354600	1.96895500	-2.23970300
C	1.64399900	3.12421900	-2.54715900
C	2.13809300	3.96637900	-1.53771100
C	1.93684100	3.67892700	-0.19666300
C	0.16038300	0.83920500	1.16482700
C	0.09576900	0.54776500	-0.20846700
H	0.57425700	1.31523800	-3.02074500
H	1.81971600	3.38356300	-3.58387100
H	2.68758600	4.85835600	-1.81208700
H	2.31722000	4.32525900	0.58458900
H	-0.59195400	-0.16218500	-0.64632200
C	-0.44395000	0.12068700	2.33833900
H	0.37372900	-0.20203200	2.99165100
C	-1.24179200	-1.11815600	1.91008400
H	-1.36344600	-1.74466700	2.79445300
H	-0.67394700	-1.70930500	1.18867700
N	0.85050100	1.99023400	1.32964300
C	-3.70012900	-0.11632300	-0.66412500
C	-2.95893600	-1.15966800	-0.09167700
C	-2.67567500	-2.29733400	-0.82220800
C	-3.13168800	-2.38634800	-2.14250100
C	-3.86898900	-1.34602200	-2.69851600
C	-4.16824100	-0.19395100	-1.96745000
C	-2.98252300	0.70078600	1.33707400
C	-2.63975900	-0.77876800	1.33697700
H	-2.10040800	-3.10656900	-0.38461500
H	-2.90939500	-3.26673100	-2.73215300
H	-4.21561100	-1.42420100	-3.72220000
H	-4.73657700	0.61591300	-2.40872600
H	-3.38815100	-1.26677700	1.97521400
C	-2.46397200	1.57507000	2.19944900
H	-2.72994100	2.62508100	2.17178300
C	-1.36874800	1.09050400	3.11881800

H	-1.75391900	0.55490400	3.99382700
N	-3.85054400	0.92435400	0.26084200
H	-4.00703600	1.86795100	-0.06300300
H	1.11970000	2.36971600	2.22631400
H	-0.79979700	1.93893100	3.50321100
Cl	3.98715800	-2.72332100	0.00216500

Table S54. Calculated Gibbs free energy and XYZ coordinates for all atoms in **COM1a-exo** catalysed by ICl.

G= -1637.8473 Hartree

C	-2.54385100	-1.90936800	-0.66821800
C	-2.44946000	-1.82773300	0.74393300
C	-3.41993300	-2.47379700	1.53172300
C	-4.43498600	-3.16337300	0.90314000
C	-4.50935500	-3.23045600	-0.50610100
C	-3.57254400	-2.61023100	-1.30806400
C	-0.76774800	-0.63186300	-0.16432800
C	-1.31802700	-1.01315600	1.03890200
H	-3.36826400	-2.42363700	2.61313000
H	-5.19098800	-3.66595800	1.49398900
H	-5.32022300	-3.78229100	-0.96609800
H	-3.63079200	-2.65933700	-2.38866800
H	-0.96235100	-0.72518700	2.01608600
C	0.36275700	0.22085000	-0.45375300
H	0.54197500	0.45426100	-1.50043500
C	1.15922500	0.80305200	0.48291700
H	0.96621800	0.67406400	1.54159200
H	1.88157400	1.55760500	0.19504700
N	-1.51241700	-1.18114600	-1.19186600
C	-0.27161400	3.43467600	-0.70314600
C	-0.45494800	3.44973700	0.70227100
C	0.53386000	4.03999100	1.50703300
C	1.65888100	4.57167900	0.90487100
C	1.82166700	4.53933800	-0.49487600
C	0.86091700	3.97551800	-1.31638700
C	-2.19339900	2.35248100	-0.23690700
C	-1.68120500	2.76260100	0.97023900
H	0.41956100	4.06427100	2.58479700
H	2.43208300	5.02291900	1.51491400
H	2.71470000	4.96585000	-0.93538700
H	0.98445100	3.94823100	-2.39272300
H	-2.13208500	2.59160800	1.93524600
C	-3.38485300	1.57594600	-0.56479900

H	-3.67014200	1.55781900	-1.61368800
C	-4.10160300	0.89022400	0.32351000
H	-3.82856000	0.86200100	1.37253100
N	-1.34130900	2.76777100	-1.24405100
H	-1.30485800	-1.08363300	-2.17355200
H	-1.49789800	2.61513200	-2.22807200
H	-4.97194200	0.32030000	0.02234900
I	2.69641400	-1.28776500	0.00468300
Cl	4.42594300	-3.04032700	-0.02586000

Table S55. Calculated Gibbs free energy and XYZ coordinates for all atoms in **TS1a-exo** catalysed by ICl.

G= -1637.8218 Hartree Frequency = -373.78 cm^{-1}

C	-2.54385100	-1.90936800	-0.66821800
C	-2.44946000	-1.82773300	0.74393300
C	-3.41993300	-2.47379700	1.53172300
C	-4.43498600	-3.16337300	0.90314000
C	-4.50935500	-3.23045600	-0.50610100
C	-3.57254400	-2.61023100	-1.30806400
C	-0.76774800	-0.63186300	-0.16432800
C	-1.31802700	-1.01315600	1.03890200
H	-3.36826400	-2.42363700	2.61313000
H	-5.19098800	-3.66595800	1.49398900
H	-5.32022300	-3.78229100	-0.96609800
H	-3.63079200	-2.65933700	-2.38866800
H	-0.96235100	-0.72518700	2.01608600
C	0.36275700	0.22085000	-0.45375300
H	0.54197500	0.45426100	-1.50043500
C	1.15922500	0.80305200	0.48291700
H	0.96621800	0.67406400	1.54159200
H	1.88157400	1.55760500	0.19504700
N	-1.51241700	-1.18114600	-1.19186600
C	-0.27161400	3.43467600	-0.70314600
C	-0.45494800	3.44973700	0.70227100
C	0.53386000	4.03999100	1.50703300
C	1.65888100	4.57167900	0.90487100
C	1.82166700	4.53933800	-0.49487600
C	0.86091700	3.97551800	-1.31638700
C	-2.19339900	2.35248100	-0.23690700
C	-1.68120500	2.76260100	0.97023900
H	0.41956100	4.06427100	2.58479700
H	2.43208300	5.02291900	1.51491400
H	2.71470000	4.96585000	-0.93538700
H	0.98445100	3.94823100	-2.39272300

H	-2.13208500	2.59160800	1.93524600
C	-3.38485300	1.57594600	-0.56479900
H	-3.67014200	1.55781900	-1.61368800
C	-4.10160300	0.89022400	0.32351000
H	-3.82856000	0.86200100	1.37253100
N	-1.34130900	2.76777100	-1.24405100
H	-1.30485800	-1.08363300	-2.17355200
H	-1.49789800	2.61513200	-2.22807200
H	-4.97194200	0.32030000	0.02234900
I	2.69641400	-1.28776500	0.00468300
Cl	4.42594300	-3.04032700	-0.02586000

Table S56. Calculated Gibbs free energy and XYZ coordinates for all atoms in **INT1a-exo** catalysed by ICl.

G= -1637.8502 Hartree

C	-2.54385100	-1.90936800	-0.66821800
C	-2.44946000	-1.82773300	0.74393300
C	-3.41993300	-2.47379700	1.53172300
C	-4.43498600	-3.16337300	0.90314000
C	-4.50935500	-3.23045600	-0.50610100
C	-3.57254400	-2.61023100	-1.30806400
C	-0.76774800	-0.63186300	-0.16432800
C	-1.31802700	-1.01315600	1.03890200
H	-3.36826400	-2.42363700	2.61313000
H	-5.19098800	-3.66595800	1.49398900
H	-5.32022300	-3.78229100	-0.96609800
H	-3.63079200	-2.65933700	-2.38866800
H	-0.96235100	-0.72518700	2.01608600
C	0.36275700	0.22085000	-0.45375300
H	0.54197500	0.45426100	-1.50043500
C	1.15922500	0.80305200	0.48291700
H	0.96621800	0.67406400	1.54159200
H	1.88157400	1.55760500	0.19504700
N	-1.51241700	-1.18114600	-1.19186600
C	-0.27161400	3.43467600	-0.70314600
C	-0.45494800	3.44973700	0.70227100
C	0.53386000	4.03999100	1.50703300
C	1.65888100	4.57167900	0.90487100
C	1.82166700	4.53933800	-0.49487600
C	0.86091700	3.97551800	-1.31638700
C	-2.19339900	2.35248100	-0.23690700
C	-1.68120500	2.76260100	0.97023900

H	0.41956100	4.06427100	2.58479700
H	2.43208300	5.02291900	1.51491400
H	2.71470000	4.96585000	-0.93538700
H	0.98445100	3.94823100	-2.39272300
H	-2.13208500	2.59160800	1.93524600
C	-3.38485300	1.57594600	-0.56479900
H	-3.67014200	1.55781900	-1.61368800
C	-4.10160300	0.89022400	0.32351000
H	-3.82856000	0.86200100	1.37253100
N	-1.34130900	2.76777100	-1.24405100
H	-1.30485800	-1.08363300	-2.17355200
H	-1.49789800	2.61513200	-2.22807200
H	-4.97194200	0.32030000	0.02234900
I	2.69641400	-1.28776500	0.00468300
Cl	4.42594300	-3.04032700	-0.02586000

Table S57. Calculated Gibbs free energy and XYZ coordinates for all atoms in **TS2a-exo** catalysed by ICl.

G=-1637.8087 Hartree Frequency = -539.92 cm^{-1}

C	-3.09459400	-1.94996300	0.31800800
C	-2.33934000	-2.36119800	-0.80663700
C	-2.89574500	-3.30037400	-1.68675600
C	-4.16485700	-3.79177600	-1.43100300
C	-4.89761200	-3.36445900	-0.30998000
C	-4.37395500	-2.43872800	0.57873100
C	-1.12919600	-0.84333400	0.36077000
C	-1.09396500	-1.64881800	-0.75616100
H	-2.33961500	-3.63283200	-2.55581700
H	-4.60529500	-4.51608800	-2.10566000
H	-5.88972300	-3.76411900	-0.13813800
H	-4.93640000	-2.10451000	1.44240900
H	-0.29078400	-1.70268500	-1.47512900
C	-0.10400100	0.03453300	0.89903400
H	-0.30615200	0.60406000	1.79868300
C	1.17847900	0.18533000	0.13559000
H	0.96882200	0.27954700	-0.93221600
H	1.71337900	1.08632900	0.43887500
N	-2.32716800	-1.04509100	1.01808800
C	4.50945100	-0.60565500	0.28689400
C	3.42730400	-0.83840600	-0.56771100
C	3.61668900	-0.81395100	-1.93903300
C	4.89539800	-0.55650900	-2.43416300

C	5.96161700	-0.32487800	-1.56481600
C	5.78782200	-0.34514700	-0.18291800
C	2.74180200	-0.99889900	1.65869300
C	2.19787500	-1.03444700	0.26939400
H	2.78855900	-0.98996100	-2.61623300
H	5.06264100	-0.53406800	-3.50352500
H	6.94614500	-0.12520200	-1.96970900
H	6.61393100	-0.16735100	0.49402800
H	1.64347000	-1.94986900	0.04014600
C	1.90790400	-1.03141500	2.75880900
H	2.24081700	-0.66114000	3.72083000
C	0.57084200	-1.33757900	2.51094400
H	0.31682100	-2.08549100	1.76988400
N	4.05804800	-0.69698200	1.60913800
H	-2.63550800	-0.51994900	1.82145000
H	4.63172800	-0.52212300	2.42165700
H	-0.16030300	-1.21879900	3.30326700
I	-1.18189700	2.32608800	0.07702900
Cl	-2.20291900	4.44883300	-0.76553300

Table S58. Calculated Gibbs free energy and XYZ coordinates for all atoms in **2a-exo** catalysed by ICl.

G= -1637.8721 Hartree

C	-3.09459400	-1.94996300	0.31800800
C	-2.33934000	-2.36119800	-0.80663700
C	-2.89574500	-3.30037400	-1.68675600
C	-4.16485700	-3.79177600	-1.43100300
C	-4.89761200	-3.36445900	-0.30998000
C	-4.37395500	-2.43872800	0.57873100
C	-1.12919600	-0.84333400	0.36077000
C	-1.09396500	-1.64881800	-0.75616100
H	-2.33961500	-3.63283200	-2.55581700
H	-4.60529500	-4.51608800	-2.10566000
H	-5.88972300	-3.76411900	-0.13813800
H	-4.93640000	-2.10451000	1.44240900
H	-0.29078400	-1.70268500	-1.47512900
C	-0.10400100	0.03453300	0.89903400
H	-0.30615200	0.60406000	1.79868300
C	1.17847900	0.18533000	0.13559000
H	0.96882200	0.27954700	-0.93221600
H	1.71337900	1.08632900	0.43887500
N	-2.32716800	-1.04509100	1.01808800
C	4.50945100	-0.60565500	0.28689400

C	3.42730400	-0.83840600	-0.56771100
C	3.61668900	-0.81395100	-1.93903300
C	4.89539800	-0.55650900	-2.43416300
C	5.96161700	-0.32487800	-1.56481600
C	5.78782200	-0.34514700	-0.18291800
C	2.74180200	-0.99889900	1.65869300
C	2.19787500	-1.03444700	0.26939400
H	2.78855900	-0.98996100	-2.61623300
H	5.06264100	-0.53406800	-3.50352500
H	6.94614500	-0.12520200	-1.96970900
H	6.61393100	-0.16735100	0.49402800
H	1.64347000	-1.94986900	0.04014600
C	1.90790400	-1.03141500	2.75880900
H	2.24081700	-0.66114000	3.72083000
C	0.57084200	-1.33757900	2.51094400
H	0.31682100	-2.08549100	1.76988400
N	4.05804800	-0.69698200	1.60913800
H	-2.63550800	-0.51994900	1.82145000
H	4.63172800	-0.52212300	2.42165700
H	-0.16030300	-1.21879900	3.30326700
I	-1.18189700	2.32608800	0.07702900
Cl	-2.20291900	4.44883300	-0.76553300

Table S59. Calculated Gibbs free energy and XYZ coordinates for all atoms in **COM1b-endo** catalysed by ICl.

G= -1637.8529 Hartree

C	-3.09459400	-1.94996300	0.31800800
C	-2.33934000	-2.36119800	-0.80663700
C	-2.89574500	-3.30037400	-1.68675600
C	-4.16485700	-3.79177600	-1.43100300
C	-4.89761200	-3.36445900	-0.30998000
C	-4.37395500	-2.43872800	0.57873100
C	-1.12919600	-0.84333400	0.36077000
C	-1.09396500	-1.64881800	-0.75616100
H	-2.33961500	-3.63283200	-2.55581700
H	-4.60529500	-4.51608800	-2.10566000
H	-5.88972300	-3.76411900	-0.13813800
H	-4.93640000	-2.10451000	1.44240900
H	-0.29078400	-1.70268500	-1.47512900
C	-0.10400100	0.03453300	0.89903400
H	-0.30615200	0.60406000	1.79868300
C	1.17847900	0.18533000	0.13559000
H	0.96882200	0.27954700	-0.93221600

H	1.71337900	1.08632900	0.43887500
N	-2.32716800	-1.04509100	1.01808800
C	4.50945100	-0.60565500	0.28689400
C	3.42730400	-0.83840600	-0.56771100
C	3.61668900	-0.81395100	-1.93903300
C	4.89539800	-0.55650900	-2.43416300
C	5.96161700	-0.32487800	-1.56481600
C	5.78782200	-0.34514700	-0.18291800
C	2.74180200	-0.99889900	1.65869300
C	2.19787500	-1.03444700	0.26939400
H	2.78855900	-0.98996100	-2.61623300
H	5.06264100	-0.53406800	-3.50352500
H	6.94614500	-0.12520200	-1.96970900
H	6.61393100	-0.16735100	0.49402800
H	1.64347000	-1.94986900	0.04014600
C	1.90790400	-1.03141500	2.75880900
H	2.24081700	-0.66114000	3.72083000
C	0.57084200	-1.33757900	2.51094400
H	0.31682100	-2.08549100	1.76988400
N	4.05804800	-0.69698200	1.60913800
H	-2.63550800	-0.51994900	1.82145000
H	4.63172800	-0.52212300	2.42165700
H	-0.16030300	-1.21879900	3.30326700
I	-1.18189700	2.32608800	0.07702900
Cl	-2.20291900	4.44883300	-0.76553300

Table S60. Calculated Gibbs free energy and XYZ coordinates for all atoms in **TS1b-endo** catalysed by ICl.

G= -1637.8241 Hartree Frequency = -411.27 cm^{-1}

C	2.98013800	-1.62884000	-0.58458400
C	2.41280500	-1.01582600	0.53770700
C	3.12581400	-0.95925000	1.72477200
C	4.39686800	-1.53102700	1.76700300
C	4.94883700	-2.13056800	0.63459000
C	4.24807700	-2.18704100	-0.56878400
C	0.88184800	-1.01771000	-1.22986500
C	1.09117300	-0.46478200	0.13645000
H	2.70782800	-0.47028400	2.59700100
H	4.96703700	-1.50155100	2.68691800
H	5.94178400	-2.55966200	0.68763400
H	4.67547900	-2.64957800	-1.44964600

H	0.26250200	-0.60516000	0.82198700
C	-0.27324600	-0.99147700	-1.99786300
H	-0.24658300	-1.45323300	-2.97830800
C	-1.45895200	-0.39366800	-1.54550600
H	-2.18915700	-0.11753400	-2.29702600
H	-1.41218500	0.29864900	-0.70965700
N	2.05008400	-1.56902600	-1.62987300
C	-3.70599200	-0.49335000	1.03204700
C	-3.86679300	-0.78791200	-0.33155300
C	-4.88186800	-0.15853800	-1.05369300
C	-5.71142500	0.73051100	-0.38826700
C	-5.53173200	1.01019700	0.97571300
C	-4.52345500	0.40639700	1.70986000
C	-2.12031000	-2.01073100	0.50693400
C	-2.78153000	-1.68275800	-0.70887100
H	-5.02031200	-0.36465400	-2.10849600
H	-6.51062000	1.22320100	-0.92759200
H	-6.19248600	1.71536800	1.46406900
H	-4.37700200	0.62533000	2.75990500
H	-2.83007400	-2.36918800	-1.54145900
C	-1.02250100	-2.91808900	0.71608500
H	-0.61174700	-2.98021400	1.71931500
C	-0.47529500	-3.62352300	-0.28189500
H	-0.87866700	-3.60002100	-1.28667000
N	-2.63539700	-1.24898000	1.49864200
H	-2.28876200	-1.23228800	2.44817900
H	2.19201700	-1.97558500	-2.54338400
H	0.38147700	-4.26137300	-0.10338900
I	1.24271500	1.77190200	-0.03736900
Cl	1.36870700	4.65770300	-0.15540600

Table S61. Calculated Gibbs free energy and XYZ coordinates for all atoms in **INT1b-endo** catalysed by ICl.

G= -1637.8346 Hartree

C	-2.97429900	-1.72280900	0.67907300
C	-2.48065600	-1.09414800	-0.47172000
C	-3.22125800	-1.09848400	-1.64037000
C	-4.45471500	-1.75240100	-1.65339800
C	-4.93435100	-2.37255700	-0.50142600
C	-4.20363300	-2.36631700	0.68679800
C	-0.87433900	-1.00732500	1.24484200
C	-1.17286900	-0.45777300	-0.12729200
H	-2.85350000	-0.59191600	-2.52571800

H	-5.04614100	-1.76960100	-2.55996800
H	-5.89719300	-2.86885000	-0.52403600
H	-4.58194300	-2.84568900	1.58129800
H	-0.37346700	-0.61790100	-0.84607500
C	0.30517000	-1.00614800	1.89347600
H	0.36403600	-1.47113700	2.87296800
C	1.53240200	-0.36287500	1.35788800
H	2.04577600	0.18556800	2.15012600
H	1.31000200	0.36133100	0.57116100
N	-2.05169100	-1.57184600	1.71014500
C	3.99961100	-0.54707200	-0.94465700
C	3.87384200	-0.56783600	0.44117300
C	4.76320300	0.15954200	1.21444600
C	5.76885600	0.87356700	0.56445900
C	5.87276400	0.87662500	-0.82818600
C	4.97838400	0.16165500	-1.61861800
C	2.23522300	-1.90943900	-0.53256600
C	2.64660500	-1.35803100	0.79785500
H	4.68513600	0.17269200	2.29496800
H	6.48089800	1.44155100	1.14950900
H	6.65952600	1.44828400	-1.30330200
H	5.04186100	0.16303500	-2.69898800
H	2.81276300	-2.14210100	1.53831700
C	1.18035400	-2.83835400	-0.82699000
H	0.89328900	-2.95135500	-1.86680800
C	0.57360800	-3.54431200	0.13613000
H	0.87860900	-3.48205200	1.17232000
N	2.97753100	-1.36691500	-1.47294900
H	2.85105600	-1.54383200	-2.46464700
H	-2.11627200	-2.05136100	2.59414100
H	-0.23456700	-4.22399500	-0.10594000
I	-1.37618800	1.73699600	-0.04003800
Cl	-1.58507100	4.87675400	0.01216500

Table S62. Calculated Gibbs free energy and XYZ coordinates for all atoms in **TS2b-endo** catalysed by ICl.

G= -1637.8282 Hartree Frequency = -244.88 cm^{-1}

C	3.16100300	-1.60304000	-0.61851400
C	2.67459900	-0.98541800	0.53901800
C	3.49255300	-0.85580600	1.64862000
C	4.79114900	-1.36260100	1.58608800
C	5.26133100	-1.96954400	0.42250000
C	4.45227100	-2.09805600	-0.70596300
C	0.97425800	-1.12377800	-1.06889800

C	1.28751200	-0.51007100	0.25995600
H	3.13314600	-0.36051000	2.54329300
H	5.44308200	-1.27568700	2.44602600
H	6.27546600	-2.34865100	0.38989200
H	4.81684400	-2.56783200	-1.61104200
H	0.53742200	-0.71182900	1.02225100
C	-0.25423200	-1.25744200	-1.66417200
H	-0.28134000	-1.72109900	-2.64623400
C	-1.47204500	-0.52249000	-1.22620300
H	-1.85453600	0.07518400	-2.05646200
H	-1.26227200	0.17070600	-0.41012200
N	2.14332600	-1.61366300	-1.57678400
C	-4.09040700	-0.63433200	0.94257600
C	-3.90148500	-0.60015200	-0.43910700
C	-4.73856800	0.17249300	-1.22625400
C	-5.75645200	0.89412800	-0.60364400
C	-5.92536800	0.84681200	0.78066200
C	-5.08926900	0.07750300	1.58544400
C	-2.34439200	-2.03027000	0.55213800
C	-2.69888400	-1.43396900	-0.77321300
H	-4.60636400	0.21885000	-2.30084100
H	-6.42200300	1.50419900	-1.20085100
H	-6.71948700	1.42100000	1.24111400
H	-5.21227400	0.04029900	2.66014600
H	-2.87826900	-2.17954000	-1.55050700
C	-1.21694700	-2.83443100	0.75197900
H	-0.80377300	-2.94932400	1.74695400
C	-0.55105100	-3.28618300	-0.35838100
H	-1.06672600	-3.45110000	-1.29328100
N	-3.12141200	-1.49218900	1.49490500
H	-3.00977600	-1.66061200	2.48635300
H	2.22331100	-2.03827100	-2.48822300
H	0.41748000	-3.76430900	-0.26211200
I	1.28911600	1.70407000	0.04725200
Cl	1.26235500	4.68962700	-0.17384400

Table S63. Calculated Gibbs free energy and XYZ coordinates for all atoms in **2b-endo** catalysed by ICl.

G= -1637.8722 Hartree

C	2.93669700	-1.79624000	-0.27080900
C	2.36298900	-1.33672600	0.92814200
C	3.11552100	-1.37155200	2.10544000
C	4.41036500	-1.86011000	2.04749900

C	4.96782500	-2.30306700	0.83641800
C	4.24194200	-2.27532700	-0.34357800
C	0.83474300	-1.12843500	-0.76211200
C	1.03346600	-0.86079400	0.59981500
H	2.69439800	-1.01890200	3.03930400
H	5.00885500	-1.89859700	2.94927700
H	5.98557500	-2.67310500	0.82444000
H	4.66804700	-2.61344800	-1.27996900
H	0.24682900	-0.63751700	1.30399900
C	-0.39054500	-1.03545300	-1.62296400
H	-0.06372200	-0.68642800	-2.60755000
C	-1.44911800	-0.05169300	-1.06478900
H	-1.42948400	0.88154500	-1.62995600
H	-1.22645800	0.20736700	-0.02862500
N	1.97886600	-1.65772800	-1.26551700
C	-4.40378900	-0.75628800	0.71734200
C	-3.89554100	0.09933600	-0.27148400
C	-4.35557300	1.39821700	-0.36898700
C	-5.32763800	1.84603200	0.53199500
C	-5.82202300	0.98740400	1.50879800
C	-5.37052400	-0.32918500	1.61736600
C	-2.81617200	-1.99524100	-0.36725800
C	-2.86571500	-0.65581500	-1.07662700
H	-3.96540900	2.06433300	-1.13095500
H	-5.69436000	2.86281800	0.47038800
H	-6.57368200	1.34387100	2.20328600
H	-5.76001800	-0.99300300	2.37962300
H	-3.19496900	-0.78918100	-2.11499300
C	-1.87047600	-2.88390800	-0.68413800
H	-1.75062300	-3.83226000	-0.17648900
C	-0.96823100	-2.47936000	-1.81923600
H	-1.52375700	-2.46923200	-2.76446800
N	-3.80550800	-2.00955400	0.60741500
H	-3.86202300	-2.71479700	1.32469700
H	2.13066100	-1.85629200	-2.24426900
H	-0.14935600	-3.18780300	-1.94761000
I	1.57900400	1.65993500	-0.02072300
Cl	2.19703200	4.02554700	-0.37118100

Table S64. Calculated Gibbs free energy and XYZ coordinates for all atoms in **COM1b-exo** catalysed by ICl.

G= -1637.8528 Hartree

C	-1.44529000	2.10645700	-0.86614100

C	-1.47910700	1.59491400	0.44248100
C	-2.24685500	2.24529900	1.41072300
C	-2.94750100	3.38294800	1.04232200
C	-2.90639200	3.87130700	-0.27395600
C	-2.15614600	3.23785300	-1.25248000
C	-0.06805500	0.32009700	-0.83523100
C	-0.64611600	0.40482100	0.45559800
H	-2.29083900	1.86735100	2.42520100
H	-3.54395000	3.90530300	1.78010900
H	-3.47285100	4.75808600	-0.52965600
H	-2.12042200	3.60745000	-2.26947100
H	-0.18136300	-0.01906100	1.33360600
C	0.92036200	-0.60632500	-1.35951500
H	1.25275100	-0.43159300	-2.37767300
C	1.42646200	-1.60965600	-0.64271500
H	1.10572700	-1.80145800	0.37529300
H	2.18665200	-2.26427700	-1.05140000
N	-0.58197700	1.30463400	-1.60188800
C	4.16373300	-0.00291100	-0.40139000
C	3.74368500	-0.27134400	0.92557000
C	4.18696000	-1.44962400	1.55075400
C	5.00898200	-2.31076300	0.84986900
C	5.41277600	-2.02261300	-0.47005200
C	5.00000000	-0.86896000	-1.11131100
C	2.77822300	1.65278600	0.23986700
C	2.87205900	0.79501100	1.31025800
H	3.87892800	-1.68057100	2.56413400
H	5.35312500	-3.22493000	1.31834200
H	6.05928800	-2.71875900	-0.99060200
H	5.30649900	-0.64643100	-2.12661600
H	2.37178200	0.91304200	2.25898700
C	1.99858700	2.87113700	0.04542500
H	2.16114800	3.39515000	-0.89319500
C	1.11382600	3.35061200	0.91840800
H	0.91598100	2.85131100	1.86074900
N	3.56953400	1.17012600	-0.78525500
H	-0.40039900	1.40771300	-2.59082300
H	3.68121800	1.61448600	-1.68304900
H	0.55086200	4.25199300	0.71000400
I	-2.33367000	-1.45235300	0.10881500
Cl	-4.02492200	-3.31056800	-0.06129500

Table S65. Calculated Gibbs free energy and XYZ coordinates for all atoms in **TS1b-exo** catalysed by ICl.

G= -1637.8212 Hartree Frequency = -417.86 cm^{-1}

C	2.88024000	-2.03959700	-0.29296800
C	2.56781400	-1.16707500	0.75384200
C	3.45872700	-1.00892300	1.80389000
C	4.64680100	-1.73849000	1.78554600
C	4.94395300	-2.59709400	0.72654900
C	4.06136000	-2.76163300	-0.33912800
C	0.80606900	-1.22728600	-0.78887100
C	1.27181000	-0.51316600	0.43047500
H	3.24025000	-0.32393600	2.61472400
H	5.35285200	-1.63084900	2.59929500
H	5.87770600	-3.14565900	0.72930900
H	4.28639400	-3.42527600	-1.16460300
H	0.54109400	-0.42460400	1.22945300
C	-0.42514100	-1.13734100	-1.42513600
H	-0.60345200	-1.77316400	-2.28316000
C	-1.43262200	-0.27286100	-0.97043900
H	-1.14030800	0.57190700	-0.35529300
H	-2.25744200	-0.05646900	-1.64126900
N	1.81141500	-2.03241900	-1.19792400
C	-4.69061600	-0.29405700	0.04292900
C	-3.52727600	0.04829800	0.75200500
C	-3.45578900	1.28411100	1.39658400
C	-4.55387300	2.12790800	1.32881600
C	-5.70814400	1.76332900	0.61772500
C	-5.79566400	0.54745000	-0.04208700
C	-3.26978600	-2.03316600	-0.16759500
C	-2.56456600	-1.02134900	0.53542200
H	-2.56333100	1.57606400	1.93772800
H	-4.52172900	3.08817900	1.82789300
H	-6.54631900	2.44784900	0.58014400
H	-6.68051500	0.26519700	-0.59835300
H	-1.74958400	-1.24541000	1.20856600
C	-2.80146900	-3.32823600	-0.59094200
H	-3.45979700	-3.90846400	-1.22953900
C	-1.59302600	-3.79564300	-0.25829300
H	-0.93144600	-3.25217800	0.40538600
N	-4.48909900	-1.55791600	-0.50223700
H	1.77733800	-2.58754100	-2.04114900
H	-5.15858300	-2.05449600	-1.07359300
H	-1.24908400	-4.75524000	-0.62290100
I	1.67814300	1.63536400	-0.14842000

Cl	2.15737500	4.35771100	-0.83207100

Table S66. Calculated Gibbs free energy and XYZ coordinates for all atoms in **INT1b-exo** catalysed by ICl.

G= -1637.8329 Hartree

C	-3.71495000	-1.11294300	0.49972100
C	-3.12857600	-0.28747500	-0.46498900
C	-3.91552600	0.38768600	-1.37998100
C	-5.30146300	0.22800400	-1.32346700
C	-5.87446800	-0.59184300	-0.35351600
C	-5.09161900	-1.27741400	0.57485000
C	-1.45168700	-1.24197900	0.91973500
C	-1.64231500	-0.32121800	-0.27493300
H	-3.46189500	1.04271100	-2.11561600
H	-5.93365600	0.75161700	-2.02910500
H	-6.95187400	-0.69967200	-0.31414000
H	-5.54125800	-1.91322200	1.32753200
H	-1.12593700	-0.69631500	-1.15934300
C	-0.31970100	-1.65005900	1.52485000
H	-0.42783000	-2.38052400	2.31953600
C	1.05475300	-1.09585500	1.30873600
H	1.06756900	-0.02257800	1.50768500
H	1.74677200	-1.54971600	2.02137900
N	-2.71937700	-1.68941700	1.27771700
C	4.04875600	-1.24204600	-0.30248500
C	2.95137800	-0.39303500	-0.19928100
C	3.15235700	0.97527000	-0.11110600
C	4.46623200	1.44348100	-0.14841200
C	5.55083400	0.57062900	-0.25696400
C	5.36176500	-0.80674900	-0.33428900
C	2.24192800	-2.61421700	-0.33476100
C	1.70207400	-1.23066000	-0.12315000
H	2.32782600	1.67584700	-0.01979700
H	4.64099800	2.51063200	-0.08815500
H	6.55747500	0.96838500	-0.27935100
H	6.19300000	-1.49590900	-0.41314700
H	0.96722200	-0.96524700	-0.88618700
C	1.51809400	-3.85483500	-0.43861600
H	2.09081100	-4.77155400	-0.34698300
C	0.20244800	-3.88918700	-0.67490800
H	-0.38080700	-2.98891900	-0.81342200

N	3.55183600	-2.56611500	-0.36889200
H	-2.89771700	-2.16905400	2.14609700
H	4.14290900	-3.38622800	-0.46153500
H	-0.31784500	-4.83535100	-0.75602300
I	-0.74914100	1.65585800	-0.01200100
Cl	1.19527200	4.17529500	0.35251000

Table S67. Calculated Gibbs free energy and XYZ coordinates for all atoms in **TS2b-exo** catalysed by ICl.

G= -1637.8250 Hartree Frequency = -277.57 cm^{-1}

C	3.09920100	-1.85379100	-0.38440500
C	2.70653000	-1.04191600	0.68454400
C	3.58221200	-0.80572400	1.73068900
C	4.84455300	-1.39906400	1.69300500
C	5.22262100	-2.19817200	0.61502600
C	4.35379500	-2.43842200	-0.44889000
C	0.93088300	-1.28054900	-0.83584800
C	1.33717300	-0.52769400	0.39255900
H	3.29532200	-0.16358000	2.55542100
H	5.54094600	-1.22992600	2.50448100
H	6.21061100	-2.64181700	0.59946000
H	4.64611100	-3.05831400	-1.28730200
H	0.61906400	-0.57140500	1.20882400
C	-0.32587100	-1.39854200	-1.37899600
H	-0.41313300	-1.96396300	-2.29919000
C	-1.45949100	-0.50384900	-0.99823400
H	-1.10633100	0.50683700	-0.78842200
H	-2.16861600	-0.42956700	-1.82405900
N	2.03403700	-1.94368100	-1.28503900
C	-4.64704900	-0.67694200	0.18151700
C	-3.47562900	0.02371800	0.47320500
C	-3.54034100	1.36892400	0.79577700
C	-4.79233800	1.98232700	0.82794100
C	-5.95169300	1.26269200	0.53452400
C	-5.90114800	-0.08858700	0.20167300
C	-2.98328500	-2.20974700	0.01264500
C	-2.31384700	-0.90627600	0.29199100
H	-2.64105800	1.93324500	1.01463800
H	-4.86606400	3.03251100	1.07988600
H	-6.91139000	1.76336700	0.56383500
H	-6.79745100	-0.65008500	-0.02946100
H	-1.64206800	-0.94393900	1.15232000
C	-2.26806200	-3.37087800	-0.30285200

H	-2.74166600	-4.16339500	-0.86941500
C	-0.91682400	-3.36060400	-0.07403300
H	-0.49374000	-2.75811300	0.71672900
N	-4.29825700	-2.00954100	-0.10731300
H	2.05213100	-2.48486600	-2.13652400
H	-4.95888900	-2.72591200	-0.37928800
H	-0.28363600	-4.15341300	-0.45486900
I	1.45524700	1.65367200	-0.08407700
Cl	1.55134900	4.54522800	-0.65856000

Table S68. Calculated Gibbs free energy and XYZ coordinates for all atoms in **2b-exo** catalysed by ICl.

G= -1637.8730 Hartree

C	2.83592200	0.99689700	0.56327100
C	2.55602000	1.42743000	-0.76092600
C	3.42113000	1.03624200	-1.79398800
C	4.51564000	0.24560600	-1.49180900
C	4.77707600	-0.16860400	-0.17233200
C	3.94632100	0.19926900	0.87282600
C	0.94922500	2.22939100	0.61154100
C	1.35378100	2.20743200	-0.69706100
H	3.22866800	1.34712500	-2.81411100
H	5.18653200	-0.06495000	-2.28347900
H	5.64096100	-0.78953000	0.03013200
H	4.14416300	-0.11430500	1.89121500
H	0.82945500	2.66802900	-1.52034200
C	-0.28599200	2.79298100	1.25075000
H	0.01433200	3.25482800	2.19689900
C	-1.27192700	1.64198900	1.56882900
H	-0.79269200	0.89705600	2.21027100
H	-2.13628100	2.04399900	2.10523200
N	1.84743300	1.50768400	1.37162800
C	-3.71746700	0.27571000	-0.76374300
C	-2.81398000	-0.03342800	0.26407700
C	-2.97506400	-1.18191800	1.01296300
C	-4.06389200	-2.02043000	0.74531700
C	-4.95745100	-1.69987700	-0.27084200
C	-4.79664500	-0.54836500	-1.04630200
C	-2.31847400	2.07492600	-0.64480800
C	-1.72825800	1.01332500	0.25891200
H	-2.26773000	-1.43147600	1.79718300
H	-4.20853600	-2.92141200	1.32833000
H	-5.79745600	-2.35488800	-0.47060100

H	-5.49379500	-0.30818000	-1.84011900
H	-0.85210600	0.58385700	-0.24503500
C	-1.95914900	3.35801900	-0.61537900
H	-2.45334100	4.08130900	-1.25654200
C	-0.94936000	3.87953500	0.37946300
H	-0.16642900	4.45399300	-0.12588200
N	-3.32839800	1.46038300	-1.40196100
H	1.78785900	1.38081600	2.37039300
H	-4.01245500	2.02627400	-1.88244500
H	-1.45716600	4.58886700	1.04243500
I	1.28615800	-1.66146200	0.09624200
Cl	-0.24107800	-3.43630400	-0.17920900

Table S69. Calculated Gibbs free energy and XYZ coordinates for all atoms in **COM1c-endo** catalysed by ICl.

G= -1868.7955 Hartree

I	2.72105600	-2.19396600	-0.58617200
C	-2.22277400	-1.17712600	1.55920500
C	-1.21273500	-0.67216400	2.41666100
C	-1.48970800	-0.53491100	3.78972200
C	-2.74159100	-0.88125500	4.25343100
C	-3.73522900	-1.37312500	3.37896900
C	-3.49351900	-1.53070800	2.02875500
C	-0.41228800	-0.73716500	0.30812700
C	-0.07174400	-0.40449200	1.59964100
H	-0.72986600	-0.16257200	4.46697000
H	-2.97181100	-0.77882600	5.30685600
H	-4.70690500	-1.63660100	3.77890500
H	-4.25046300	-1.91483900	1.35572300
H	0.89196100	-0.03848600	1.92149200
C	0.33058500	-0.58865700	-0.93031900
H	-0.07460800	-1.09482200	-1.80342300
C	1.42775300	0.19085000	-1.06885900
H	1.88496700	0.33234300	-2.03973300
H	1.80485100	0.79081900	-0.24653200
N	-1.69976800	-1.23374400	0.29498600
C	1.32645500	3.47554000	0.73944700
C	1.42920600	3.87035400	-0.61867100
C	2.56095200	4.59655700	-1.02942000
C	3.53838500	4.89397700	-0.10047100
C	3.41693300	4.48546100	1.24387700
C	2.31483400	3.77564900	1.68232000
C	-0.49637500	2.71882400	-0.34529500
C	0.26130800	3.38374200	-1.28350600

H	2.66221600	4.91373000	-2.06096100
H	4.41692000	5.45011800	-0.40450100
H	4.20295100	4.73420400	1.94656400
H	2.21740000	3.46349300	2.71530600
H	0.00480300	3.51596600	-2.32300600
C	-1.72788200	1.95959200	-0.46535100
H	-2.19934600	1.66421000	0.47050900
C	-2.23271400	1.53412900	-1.63134600
H	-1.70118800	1.76968400	-2.55033900
N	0.14459600	2.79451400	0.87651500
H	-0.17632600	2.32947800	1.71266700
H	-2.22947200	-1.43871100	-0.54083000
Cl	4.29294800	-3.98352500	-0.15115300
C	-3.40961000	0.66972900	-1.77507900
C	-3.55443500	-0.08672300	-2.94553400
C	-4.37318400	0.52721800	-0.76590000
C	-4.61236900	-0.97662600	-3.09611400
H	-2.82219100	0.02155100	-3.73887100
C	-5.43081600	-0.35840000	-0.91892300
H	-4.30008700	1.11859600	0.13974600
C	-5.55299700	-1.11850400	-2.08136100
H	-4.70284500	-1.55636400	-4.00684800
H	-6.16851700	-0.45170500	-0.13039800
H	-6.38099400	-1.80712500	-2.19712800

Table S70. Calculated Gibbs free energy and XYZ coordinates for all atoms in **TS1c-endo** catalysed by ICl.

G= -1868.7708 Hartree Frequency = -384.71 cm^{-1}

I	2.13172300	-2.46625200	-0.43857900
C	-2.18778900	-1.01674500	1.58087100
C	-1.35189000	-0.25958700	2.43763900
C	-1.82180200	0.07776200	3.71781000
C	-3.08678200	-0.33197500	4.09622500
C	-3.90177200	-1.08051200	3.22429000
C	-3.46577000	-1.43481100	1.95956500
C	-0.28466700	-0.56659600	0.47153900
C	-0.14519200	0.00679000	1.71318600
H	-1.19891100	0.64832600	4.39721200
H	-3.46102200	-0.07862400	5.08075300
H	-4.88738200	-1.38798100	3.55231000
H	-4.08922900	-2.01065400	1.28568100
H	0.71137900	0.56074100	2.06530800

C	0.60767800	-0.54913800	-0.68531000
H	0.16228300	-0.84525500	-1.63099100
C	1.68217700	0.36214600	-0.72888200
H	2.34288500	0.35223500	-1.58616400
H	2.13560000	0.68115800	0.20381900
N	-1.50836100	-1.19575200	0.40121200
C	1.78342400	3.59495700	0.55940400
C	2.21104300	3.12221600	-0.69724000
C	3.53054100	3.34730500	-1.10007200
C	4.37378000	4.04180200	-0.24765800
C	3.92659300	4.50281600	1.00182600
C	2.62618300	4.28469200	1.42797100
C	0.01629100	2.55932400	-0.38765500
C	1.10392600	2.38568700	-1.26905900
H	3.88282400	2.98852500	-2.06000700
H	5.39745300	4.23216100	-0.54516500
H	4.61257200	5.03842100	1.64620200
H	2.27948600	4.63577200	2.39201400
H	0.99369100	2.13775000	-2.31350900
C	-1.34292100	2.09517600	-0.50550500
H	-1.96299900	2.18881000	0.38097300
C	-1.81913000	1.52720500	-1.62704000
H	-1.17762400	1.48749200	-2.50404000
N	0.45259700	3.23706000	0.70561400
H	-0.11250400	3.41734000	1.52345200
H	-1.87418000	-1.65640700	-0.41817700
Cl	3.47258900	-4.67634000	-0.17076100
C	-3.14863100	0.93925400	-1.79833800
C	-3.55110300	0.54498000	-3.08042600
C	-4.02886400	0.73295000	-0.72553900
C	-4.80061000	-0.02559400	-3.29160700
H	-2.87627500	0.69323800	-3.91672000
C	-5.27424700	0.16200800	-0.93699600
H	-3.73344200	0.99470500	0.28388900
C	-5.66634800	-0.21763100	-2.22057100
H	-5.09608400	-0.32189100	-4.29068100
H	-5.93891800	0.00326700	-0.09600200
H	-6.63927000	-0.66605000	-2.38089000

Table S71. Calculated Gibbs free energy and XYZ coordinates for all atoms in **INT1c-endo** catalysed by ICl.

G= -1868.8012 Hartree

I	2.13172300	-2.46625200	-0.43857900

C	-2.18778900	-1.01674500	1.58087100
C	-1.35189000	-0.25958700	2.43763900
C	-1.82180200	0.07776200	3.71781000
C	-3.08678200	-0.33197500	4.09622500
C	-3.90177200	-1.08051200	3.22429000
C	-3.46577000	-1.43481100	1.95956500
C	-0.28466700	-0.56659600	0.47153900
C	-0.14519200	0.00679000	1.71318600
H	-1.19891100	0.64832600	4.39721200
H	-3.46102200	-0.07862400	5.08075300
H	-4.88738200	-1.38798100	3.55231000
H	-4.08922900	-2.01065400	1.28568100
H	0.71137900	0.56074100	2.06530800
C	0.60767800	-0.54913800	-0.68531000
H	0.16228300	-0.84525500	-1.63099100
C	1.68217700	0.36214600	-0.72888200
H	2.34288500	0.35223500	-1.58616400
H	2.13560000	0.68115800	0.20381900
N	-1.50836100	-1.19575200	0.40121200
C	1.78342400	3.59495700	0.55940400
C	2.21104300	3.12221600	-0.69724000
C	3.53054100	3.34730500	-1.10007200
C	4.37378000	4.04180200	-0.24765800
C	3.92659300	4.50281600	1.00182600
C	2.62618300	4.28469200	1.42797100
C	0.01629100	2.55932400	-0.38765500
C	1.10392600	2.38568700	-1.26905900
H	3.88282400	2.98852500	-2.06000700
H	5.39745300	4.23216100	-0.54516500
H	4.61257200	5.03842100	1.64620200
H	2.27948600	4.63577200	2.39201400
H	0.99369100	2.13775000	-2.31350900
C	-1.34292100	2.09517600	-0.50550500
H	-1.96299900	2.18881000	0.38097300
C	-1.81913000	1.52720500	-1.62704000
H	-1.17762400	1.48749200	-2.50404000
N	0.45259700	3.23706000	0.70561400
H	-0.11250400	3.41734000	1.52345200
H	-1.87418000	-1.65640700	-0.41817700
Cl	3.47258900	-4.67634000	-0.17076100
C	-3.14863100	0.93925400	-1.79833800
C	-3.55110300	0.54498000	-3.08042600
C	-4.02886400	0.73295000	-0.72553900
C	-4.80061000	-0.02559400	-3.29160700

H	-2.87627500	0.69323800	-3.91672000
C	-5.27424700	0.16200800	-0.93699600
H	-3.73344200	0.99470500	0.28388900
C	-5.66634800	-0.21763100	-2.22057100
H	-5.09608400	-0.32189100	-4.29068100
H	-5.93891800	0.00326700	-0.09600200
H	-6.63927000	-0.66605000	-2.38089000

Table S72. Calculated Gibbs free energy and XYZ coordinates for all atoms in **TS2c-endo** catalysed by ICl.

G= -1868.7579 Hartree Frequency = -467.85 cm^{-1}

I	0.41131700	2.91703400	-0.19757200
C	2.57161100	-0.73057800	1.47406900
C	1.48762900	-1.16664800	2.27751300
C	1.76715400	-1.80565800	3.49485300
C	3.08713100	-2.00022300	3.86692900
C	4.14485200	-1.56829300	3.04771700
C	3.90171600	-0.92882200	1.84131800
C	0.65738900	-0.20698900	0.39946100
C	0.28434000	-0.82295400	1.57762100
H	0.95891900	-2.14422200	4.13337000
H	3.31243300	-2.49294000	4.80531800
H	5.16715400	-1.73569400	3.36488200
H	4.71335000	-0.59286600	1.20638900
H	-0.72861100	-1.00227700	1.90364600
C	-0.16682500	0.25481900	-0.69691300
H	0.31361300	0.63345500	-1.59168600
C	-1.64315300	0.43386100	-0.48312700
H	-1.99819300	1.35188200	-0.95150500
H	-1.84732900	0.52308100	0.58594000
N	2.03806000	-0.14580100	0.35138000
C	-4.16047200	-1.76567700	0.37785000
C	-3.98040500	-0.62241100	-0.40899000
C	-4.96312500	0.35149200	-0.44509700
C	-6.12252800	0.16324600	0.30888900
C	-6.28363000	-0.98186400	1.08814700
C	-5.30250900	-1.96997300	1.13806000
C	-2.14070100	-2.04660100	-0.62956700
C	-2.62201400	-0.69775500	-1.04449300
H	-4.83607200	1.24360300	-1.04787300
H	-6.90343900	0.91282800	0.29055600
H	-7.18952100	-1.10941300	1.66814300
H	-5.42810600	-2.85898000	1.74329800

H	-2.64732600	-0.58907500	-2.13071400
C	-0.90199000	-2.51867200	-0.98365100
H	-0.48497100	-3.38994600	-0.49479300
C	-0.12958300	-1.71449900	-1.84124400
H	-0.64272500	-1.16219700	-2.62067000
N	-3.03861500	-2.58783000	0.23298300
H	-2.90432800	-3.46364100	0.71650800
H	2.56747200	0.19715700	-0.43584600
Cl	0.89064300	5.29079400	0.26168100
C	1.28793400	-1.96649600	-2.09295500
C	1.90475700	-1.39114700	-3.21263800
C	2.07252700	-2.70419600	-1.19610700
C	3.26399500	-1.55901900	-3.43820100
H	1.30738400	-0.80673600	-3.90517500
C	3.43127000	-2.87306200	-1.42270800
H	1.63001900	-3.10324600	-0.29006700
C	4.03076000	-2.30274900	-2.54330400
H	3.72677500	-1.11039300	-4.30877500
H	4.02734700	-3.43470700	-0.71357200
H	5.09254000	-2.43136200	-2.71579300

Table S73. Calculated Gibbs free energy and XYZ coordinates for all atoms in **2c-endo** catalysed by ICl.

G= -1868.8108 Hartree

I	0.24505400	2.66754700	-0.17247200
C	3.03686000	0.22683200	0.00026700
C	2.29490700	0.58130000	1.14191600
C	2.95903800	1.11446000	2.25067600
C	4.33429500	1.26610800	2.18703500
C	5.05503200	0.90927600	1.03431900
C	4.41758700	0.38952200	-0.08022400
C	0.88555000	-0.28902000	-0.43346600
C	0.90312400	0.31077900	0.83593300
H	2.40766400	1.40138400	3.13815600
H	4.86783600	1.66945000	3.03893900
H	6.12949500	1.04404300	1.01733100
H	4.96643900	0.11159000	-0.97167500
H	0.08968100	0.25303500	1.54420900
C	-0.20929400	-1.02896400	-1.13806100
H	0.02638900	-1.01919100	-2.20648700
C	-1.59693400	-0.38534300	-0.91624100

H	-1.83039700	0.29048300	-1.74103300
H	-1.59512700	0.21572300	-0.00532600
N	2.14345900	-0.27536500	-0.93255500
C	-4.37552300	-1.50645600	0.92543100
C	-4.04318000	-0.90928100	-0.29916800
C	-4.90350500	-0.00108400	-0.88507600
C	-6.10281000	0.31483200	-0.23809800
C	-6.41960100	-0.28454800	0.97702100
C	-5.56266600	-1.20757800	1.57917200
C	-2.30214800	-2.32623900	0.41952300
C	-2.70179400	-1.44011700	-0.74277400
H	-4.65096900	0.46477100	-1.83148900
H	-6.78476800	1.02862500	-0.68248100
H	-7.35034300	-0.03173900	1.47105400
H	-5.81493200	-1.67127500	2.52497800
H	-2.79467700	-2.03199800	-1.66252400
C	-1.06408200	-2.82499800	0.48981900
H	-0.71613900	-3.43214200	1.31581600
C	-0.18837100	-2.56951500	-0.70989900
H	-0.62767400	-3.07817700	-1.57728300
N	-3.36733700	-2.39115300	1.30497400
H	-3.29313500	-2.78418200	2.22975200
H	2.40119700	-0.67427800	-1.82449500
Cl	-0.28791100	4.96581500	-0.91161800
C	1.22970400	-3.07256200	-0.57176400
C	1.91249000	-3.53005300	-1.69945700
C	1.91970800	-2.98374800	0.63921100
C	3.26041900	-3.87064500	-1.62777700
H	1.38406300	-3.61249200	-2.64452800
C	3.26649900	-3.32073000	0.71416300
H	1.40953200	-2.61595100	1.52307900
C	3.94301600	-3.76004200	-0.42033700
H	3.77536700	-4.22437400	-2.51326900
H	3.79104200	-3.23047100	1.65818500
H	4.99329700	-4.01918300	-0.36219200

Table S74. Calculated Gibbs free energy and XYZ coordinates for all atoms in **COM1c-exo** catalysed by ICl.

G= -1868.7947 Hartree

C	-1.76583900	-1.96566200	0.18410300

C	-1.51106500	-1.60433100	1.53189300
C	-2.34187500	-2.11963600	2.54478100
C	-3.36662800	-2.97454200	2.19397100
C	-3.58999400	-3.33312800	0.84619800
C	-2.80200800	-2.83651800	-0.17192700
C	0.01477500	-0.59858400	0.21077300
C	-0.37656400	-0.73860900	1.52306000
H	-2.16930300	-1.85453800	3.58135000
H	-4.01025700	-3.38576700	2.96214100
H	-4.40250400	-4.00864100	0.60691700
H	-2.98032000	-3.10257000	-1.20664000
H	0.08373800	-0.25815700	2.37254200
C	1.11595300	0.14774700	-0.36252300
H	1.07240000	0.34294400	-1.43104400
C	2.15767000	0.64766700	0.35339900
H	2.20543700	0.52574500	1.42958300
H	2.87855000	1.31330800	-0.10519700
N	-0.83569900	-1.33156800	-0.59360500
C	1.30360800	3.65109700	-0.38091200
C	1.02005800	3.44359900	0.99331500
C	2.01329100	3.74396800	1.94176900
C	3.23489000	4.21928900	1.50510200
C	3.49316600	4.41714400	0.13311300
C	2.53474200	4.14134900	-0.82548500
C	-0.76754600	2.77838500	-0.21872000
C	-0.29963000	2.90162300	1.06922000
H	1.82359600	3.59324900	2.99845200
H	4.01110800	4.44772000	2.22539100
H	4.46092100	4.79366300	-0.17537600
H	2.73156100	4.29089100	-1.88051200
H	-0.84314200	2.63311700	1.96161200
C	-2.02247900	2.25345400	-0.73146800
H	-2.28732300	2.54672200	-1.74397800
C	-2.82216700	1.43951700	-0.02839800
H	-2.48908400	1.11267100	0.95452700
N	0.20129600	3.24801200	-1.08837200
H	-0.75088000	-1.42142900	-1.59455400
H	0.11232600	3.26817300	-2.09237000
I	3.29443400	-1.63058500	-0.41850500
Cl	4.75133400	-3.56785500	-0.80679300
C	-4.11625800	0.90212400	-0.46351500
C	-4.79093400	1.35709600	-1.60603800
C	-4.70746700	-0.11094200	0.29926700
C	-6.00602300	0.80086600	-1.97750700

H	-4.37322500	2.16180400	-2.19992400
C	-5.92521600	-0.66797200	-0.07289900
H	-4.19491600	-0.47571000	1.18404400
C	-6.57858400	-0.21586100	-1.21360200
H	-6.51568700	1.16613100	-2.86127500
H	-6.35792700	-1.45908400	0.52847800
H	-7.52916900	-0.64565100	-1.50591400

Table S75. Calculated Gibbs free energy and XYZ coordinates for all atoms in **TS1c-exo** catalysed by ICl.

G= -1868.7717 Hartree Frequency = -378.05 cm^{-1}

C	-1.76583900	-1.96566200	0.18410300
C	-1.51106500	-1.60433100	1.53189300
C	-2.34187500	-2.11963600	2.54478100
C	-3.36662800	-2.97454200	2.19397100
C	-3.58999400	-3.33312800	0.84619800
C	-2.80200800	-2.83651800	-0.17192700
C	0.01477500	-0.59858400	0.21077300
C	-0.37656400	-0.73860900	1.52306000
H	-2.16930300	-1.85453800	3.58135000
H	-4.01025700	-3.38576700	2.96214100
H	-4.40250400	-4.00864100	0.60691700
H	-2.98032000	-3.10257000	-1.20664000
H	0.08373800	-0.25815700	2.37254200
C	1.11595300	0.14774700	-0.36252300
H	1.07240000	0.34294400	-1.43104400
C	2.15767000	0.64766700	0.35339900
H	2.20543700	0.52574500	1.42958300
H	2.87855000	1.31330800	-0.10519700
N	-0.83569900	-1.33156800	-0.59360500
C	1.30360800	3.65109700	-0.38091200
C	1.02005800	3.44359900	0.99331500
C	2.01329100	3.74396800	1.94176900
C	3.23489000	4.21928900	1.50510200
C	3.49316600	4.41714400	0.13311300
C	2.53474200	4.14134900	-0.82548500
C	-0.76754600	2.77838500	-0.21872000
C	-0.29963000	2.90162300	1.06922000
H	1.82359600	3.59324900	2.99845200
H	4.01110800	4.44772000	2.22539100
H	4.46092100	4.79366300	-0.17537600
H	2.73156100	4.29089100	-1.88051200

H	-0.84314200	2.63311700	1.96161200
C	-2.02247900	2.25345400	-0.73146800
H	-2.28732300	2.54672200	-1.74397800
C	-2.82216700	1.43951700	-0.02839800
H	-2.48908400	1.11267100	0.95452700
N	0.20129600	3.24801200	-1.08837200
H	-0.75088000	-1.42142900	-1.59455400
H	0.11232600	3.26817300	-2.09237000
I	3.29443400	-1.63058500	-0.41850500
Cl	4.75133400	-3.56785500	-0.80679300
C	-4.11625800	0.90212400	-0.46351500
C	-4.79093400	1.35709600	-1.60603800
C	-4.70746700	-0.11094200	0.29926700
C	-6.00602300	0.80086600	-1.97750700
H	-4.37322500	2.16180400	-2.19992400
C	-5.92521600	-0.66797200	-0.07289900
H	-4.19491600	-0.47571000	1.18404400
C	-6.57858400	-0.21586100	-1.21360200
H	-6.51568700	1.16613100	-2.86127500
H	-6.35792700	-1.45908400	0.52847800
H	-7.52916900	-0.64565100	-1.50591400

Table S76. Calculated Gibbs free energy and XYZ coordinates for all atoms in **INT1c-exo** catalysed by ICl.

G= -1868.8036 Hartree

C	2.68632200	1.13147200	1.10060200
C	2.08659600	0.65005500	2.28858000
C	2.88435500	0.48432800	3.43202600
C	4.22920800	0.79688200	3.35940300
C	4.80234800	1.28070400	2.16667300
C	4.04284000	1.45621700	1.02405400
C	0.51637100	0.72192200	0.66469100
C	0.70335000	0.40698400	1.98738300
H	2.45027700	0.11811700	4.35517100
H	4.85620600	0.67470900	4.23424500
H	5.85816900	1.52238500	2.14539800
H	4.48047100	1.82166300	0.10269900
H	-0.05262200	0.05218100	2.67126600
C	-0.67846900	0.61365400	-0.20254800
H	-0.38024500	0.29712400	-1.20180400
C	-1.78641700	-0.27696600	0.33797800
H	-2.14404400	0.11133800	1.29501700

H	-2.63303300	-0.24251200	-0.35061900
N	1.71317900	1.15033900	0.13123900
C	-3.07017900	-3.29861600	-0.18793300
C	-2.73711900	-2.49549000	0.89870500
C	-3.61933600	-2.38651300	1.95881600
C	-4.80984400	-3.11290200	1.90255900
C	-5.11836500	-3.91336600	0.80264300
C	-4.24589000	-4.02030900	-0.27789600
C	-1.00731700	-2.48225200	-0.68038700
C	-1.44171500	-1.78951600	0.58894000
H	-3.39453900	-1.75860000	2.81245000
H	-5.50928500	-3.05124300	2.72650700
H	-6.05217900	-4.46046700	0.78498900
H	-4.47500200	-4.63459300	-1.13906700
H	-0.68403500	-1.87639000	1.36910500
C	0.24596500	-2.40444200	-1.35652500
H	0.28907600	-2.79844600	-2.36584500
C	1.35913800	-1.97177200	-0.71621500
H	1.27212300	-1.66585100	0.32351900
N	-1.99792800	-3.23623900	-1.10877200
H	1.82822200	1.50187800	-0.80770800
H	-1.96124400	-3.78262200	-1.96330000
I	-1.53003700	2.60488600	-0.56873700
Cl	-2.82325900	5.43468100	-1.21440500
C	2.70259500	-1.90174000	-1.26224700
C	2.98287100	-2.09392000	-2.62515700
C	3.75497800	-1.61391300	-0.38086300
C	4.28469900	-2.00365500	-3.08598400
H	2.18273400	-2.29638500	-3.32693100
C	5.05961700	-1.52683200	-0.84668500
H	3.54233700	-1.45204600	0.67083300
C	5.32471500	-1.72221200	-2.19788300
H	4.49536500	-2.14549900	-4.13850600
H	5.86288000	-1.29845600	-0.15728600
H	6.34107000	-1.65032400	-2.56582400

Table S77. Calculated Gibbs free energy and XYZ coordinates for all atoms in **TS2c-exo** catalysed by ICl.

G= -1868.7584 Hartree Frequency = -500.62 cm^{-1}

C	2.98978800	-0.37860200	1.56556500
C	2.08686900	-0.42951700	2.65666900
C	2.60157000	-0.61925100	3.94796900

C	3.96914200	-0.75881300	4.11348400
C	4.84423500	-0.71331500	3.01348200
C	4.36760000	-0.52284300	1.72598000
C	0.90285100	-0.12202700	0.74899700
C	0.76888400	-0.26587200	2.11541400
H	1.93555800	-0.65799800	4.80245500
H	4.37615700	-0.90654900	5.10667700
H	5.90931300	-0.82760900	3.17520900
H	5.03688800	-0.48493100	0.87445500
H	-0.15756400	-0.23164700	2.66788000
C	-0.12081500	-0.01409000	-0.27087300
H	0.17506200	0.05590500	-1.31024500
C	-1.54204800	0.22030200	0.14745500
H	-1.57619800	0.89471100	1.00648900
H	-2.11408400	0.68904500	-0.65432700
N	2.24408700	-0.18629100	0.42683500
C	-4.61923500	-1.28461800	0.00545100
C	-3.76022900	-0.76431900	0.97973800
C	-4.27918500	-0.05704000	2.05034200
C	-5.66119700	0.11905300	2.13191800
C	-6.50163000	-0.40440300	1.14972200
C	-5.99518000	-1.11745100	0.06517700
C	-2.53172900	-1.92023000	-0.63903100
C	-2.34791700	-1.08060500	0.58291000
H	-3.62472400	0.35350600	2.81124700
H	-6.08538100	0.66824700	2.96285300
H	-7.57165200	-0.25547900	1.22860500
H	-6.64865000	-1.52356200	-0.69679400
H	-1.77097300	-1.57970500	1.36725000
C	-1.46582500	-2.36430300	-1.37890900
H	-1.59611000	-2.73737300	-2.38795400
C	-0.18335800	-2.18166700	-0.82137600
H	-0.08262300	-2.30579700	0.25262600
N	-3.85331100	-1.95804700	-0.95054900
H	2.61043600	-0.14021500	-0.51170300
H	-4.22764800	-2.39082800	-1.78185500
I	0.35448700	2.63282200	-0.81543200
Cl	0.75122400	5.03122500	-1.23915500
C	1.04448400	-2.45216000	-1.57554000
C	2.17833100	-2.92201100	-0.90093700
C	1.12507600	-2.21741100	-2.95477500
C	3.35983400	-3.16641200	-1.58944700
H	2.12756100	-3.08763300	0.17038000
C	2.30764800	-2.45690000	-3.64071300

H	0.26325600	-1.82586000	-3.48469500
C	3.42680400	-2.93371100	-2.96035700
H	4.22807400	-3.53352800	-1.05563500
H	2.36143900	-2.26551500	-4.70548700
H	4.34918000	-3.11791700	-3.49777200

Table S78. Calculated Gibbs free energy and XYZ coordinates for all atoms in **2c-exo** catalysed by ICl.

G= -1868.8125 Hartree

C	-2.83881600	0.70963700	1.18442500
C	-2.32194400	-0.43250300	1.82234600
C	-3.10844700	-1.10841000	2.76017400
C	-4.37758700	-0.62394300	3.02934600
C	-4.87739600	0.51429700	2.37385700
C	-4.11821100	1.19808400	1.43832100
C	-0.75483100	0.39589600	0.37581600
C	-1.00472100	-0.66088600	1.26322900
H	-2.73230900	-1.99284000	3.26036200
H	-5.00101100	-1.13106400	3.75536800
H	-5.87644600	0.86336300	2.60401600
H	-4.49849400	2.07448500	0.92809000
H	-0.25208700	-1.32673900	1.65762400
C	0.49237600	0.77140800	-0.37256100
H	0.21351800	0.90677300	-1.42129900
C	1.58055800	-0.32273700	-0.30388400
H	1.14608300	-1.29866600	-0.08458500
H	2.05869200	-0.40771800	-1.28118300
N	-1.86065200	1.17961300	0.32077300
C	5.02015800	-0.10689600	0.43186600
C	3.88645700	-0.88367500	0.71101400
C	4.01164700	-2.24221000	0.92708100
C	5.27985000	-2.82849800	0.85551900
C	6.39562700	-2.04646300	0.57384300
C	6.28579500	-0.67127200	0.35926900
C	3.26673100	1.35402100	0.30968900
C	2.67656800	0.01938100	0.71602000
H	3.13851100	-2.84847000	1.14374100
H	5.39303200	-3.89300700	1.01710800
H	7.37327400	-2.51055600	0.51811900
H	7.15793200	-0.06724500	0.14054100
H	2.23550800	0.08343500	1.71986800

C	2.47306200	2.37206300	-0.02984100
H	2.84842900	3.32496000	-0.38196000
C	0.98481100	2.18017000	0.16431300
H	0.77072800	2.18211900	1.24135000
N	4.64855600	1.22754400	0.27424500
H	-1.95830100	1.97967100	-0.28979300
H	5.25094900	1.92172300	-0.13893000
I	-1.65415500	-2.20748000	-0.80868100
Cl	-2.34919400	-3.78358400	-2.56747400
C	0.19784500	3.31766000	-0.45449600
C	-0.60018800	4.15101700	0.32947700
C	0.26773600	3.55595700	-1.82998700
C	-1.32376000	5.19261000	-0.24698000
H	-0.66076300	3.97720100	1.39898000
C	-0.45186500	4.59472800	-2.40835000
H	0.89690900	2.92416300	-2.44968300
C	-1.25299800	5.41515200	-1.61750600
H	-1.94017000	5.82913100	0.37666200
H	-0.38788600	4.76520200	-3.47642500
H	-1.81567700	6.22382300	-2.06795400

Table S79. Calculated Gibbs free energy and XYZ coordinates for all atoms in **COM1d-endo** catalysed by ICl.

G= -1868.7989 Hartree

C	-2.83881600	0.70963700	1.18442500
C	-2.32194400	-0.43250300	1.82234600
C	-3.10844700	-1.10841000	2.76017400
C	-4.37758700	-0.62394300	3.02934600
C	-4.87739600	0.51429700	2.37385700
C	-4.11821100	1.19808400	1.43832100
C	-0.75483100	0.39589600	0.37581600
C	-1.00472100	-0.66088600	1.26322900
H	-2.73230900	-1.99284000	3.26036200
H	-5.00101100	-1.13106400	3.75536800
H	-5.87644600	0.86336300	2.60401600
H	-4.49849400	2.07448500	0.92809000
H	-0.25208700	-1.32673900	1.65762400
C	0.49237600	0.77140800	-0.37256100
H	0.21351800	0.90677300	-1.42129900
C	1.58055800	-0.32273700	-0.30388400
H	1.14608300	-1.29866600	-0.08458500
H	2.05869200	-0.40771800	-1.28118300
N	-1.86065200	1.17961300	0.32077300

C	5.02015800	-0.10689600	0.43186600
C	3.88645700	-0.88367500	0.71101400
C	4.01164700	-2.24221000	0.92708100
C	5.27985000	-2.82849800	0.85551900
C	6.39562700	-2.04646300	0.57384300
C	6.28579500	-0.67127200	0.35926900
C	3.26673100	1.35402100	0.30968900
C	2.67656800	0.01938100	0.71602000
H	3.13851100	-2.84847000	1.14374100
H	5.39303200	-3.89300700	1.01710800
H	7.37327400	-2.51055600	0.51811900
H	7.15793200	-0.06724500	0.14054100
H	2.23550800	0.08343500	1.71986800
C	2.47306200	2.37206300	-0.02984100
H	2.84842900	3.32496000	-0.38196000
C	0.98481100	2.18017000	0.16431300
H	0.77072800	2.18211900	1.24135000
N	4.64855600	1.22754400	0.27424500
H	-1.95830100	1.97967100	-0.28979300
H	5.25094900	1.92172300	-0.13893000
I	-1.65415500	-2.20748000	-0.80868100
Cl	-2.34919400	-3.78358400	-2.56747400
C	0.19784500	3.31766000	-0.45449600
C	-0.60018800	4.15101700	0.32947700
C	0.26773600	3.55595700	-1.82998700
C	-1.32376000	5.19261000	-0.24698000
H	-0.66076300	3.97720100	1.39898000
C	-0.45186500	4.59472800	-2.40835000
H	0.89690900	2.92416300	-2.44968300
C	-1.25299800	5.41515200	-1.61750600
H	-1.94017000	5.82913100	0.37666200
H	-0.38788600	4.76520200	-3.47642500
H	-1.81567700	6.22382300	-2.06795400

Table S80. Calculated Gibbs free energy and XYZ coordinates for all atoms in **TS1d-endo** catalysed by ICl.

G= -1868.7756 Hartree Frequency = -401.60 cm^{-1}

C	2.64757200	0.66918500	-0.49103100
C	1.82736000	0.89340500	0.62018500
C	2.39364300	1.26678200	1.82738600
C	3.78102500	1.40078900	1.89838900
C	4.57844100	1.19060200	0.77401600
C	4.02183300	0.82277900	-0.44994800

C	0.54750800	0.11140200	-1.17171800
C	0.41575500	0.70100300	0.19022600
H	1.77212500	1.45791700	2.69448400
H	4.24372700	1.68463300	2.83537800
H	5.65234600	1.31004000	0.85099600
H	4.63893900	0.64464900	-1.32162900
H	-0.24669400	0.17128200	0.86559300
C	-0.43957600	-0.47961800	-1.95176600
H	-0.16082600	-0.85016900	-2.93217200
C	-1.75503900	-0.63609100	-1.50281000
H	-2.52033900	-0.81585300	-2.24810000
H	-2.09766400	-0.05532300	-0.65110400
N	1.83466300	0.25095300	-1.55347600
C	-3.57734500	-2.06103000	1.04948100
C	-3.52246900	-2.38344000	-0.31721900
C	-4.70626600	-2.45362600	-1.05403800
C	-5.90573800	-2.21335500	-0.40232200
C	-5.93702600	-1.89038800	0.96363600
C	-4.77409300	-1.80483100	1.71270600
C	-1.39807900	-2.38310700	0.54589700
C	-2.11795500	-2.48718400	-0.67751300
H	-4.68633700	-2.69533800	-2.11027400
H	-6.83603700	-2.27121900	-0.95326200
H	-6.88976600	-1.70123000	1.44222500
H	-4.79458800	-1.54987100	2.76466600
H	-1.75342500	-3.05410200	-1.52088900
C	0.00973100	-2.46242300	0.77181800
H	0.35834300	-2.23457100	1.77419900
C	0.88584500	-2.70578900	-0.22795100
H	0.49328200	-2.96098000	-1.20792500
N	-2.27530900	-2.06352100	1.53268800
H	-2.01321100	-1.85800200	2.48671900
H	2.18749900	-0.04786000	-2.45163600
I	-0.57116400	2.70358000	-0.05172500
Cl	-1.87163100	5.29145900	-0.30713100
C	2.34180200	-2.64653200	-0.13728700
C	3.02327800	-2.37107700	1.05855800
C	3.08594300	-2.82129700	-1.31066100
C	4.40447500	-2.27948400	1.07323000
H	2.47447200	-2.21899500	1.97997900
C	4.47236400	-2.72237300	-1.29603700
H	2.56642600	-3.03573100	-2.23915400
C	5.13363100	-2.45187500	-0.10374600
H	4.91802000	-2.05924900	2.00105500

H	5.03401500	-2.85928200	-2.21212000
H	6.21394700	-2.37183500	-0.08773100

Table S81. Calculated Gibbs free energy and XYZ coordinates for all atoms in **INT1d-endo** catalysed by ICl.

G= -1868.7884 Hartree

C	2.83358900	0.46821700	-0.73392200
C	2.13021200	0.82333600	0.42408600
C	2.81284600	1.20728500	1.56334200
C	4.20979000	1.22002200	1.53815300
C	4.89606000	0.87249400	0.37698000
C	4.21878700	0.49266000	-0.78225300
C	0.63535900	0.04741200	-1.22174700
C	0.66752100	0.71396300	0.13178600
H	2.27188000	1.49953800	2.45663700
H	4.76167900	1.51417200	2.42208500
H	5.97955800	0.89488400	0.36998100
H	4.75486800	0.21564800	-1.68189200
H	0.08247000	0.19178800	0.88473200
C	-0.41256200	-0.54351500	-1.82961100
H	-0.25449100	-1.00044600	-2.80289100
C	-1.79217900	-0.57725000	-1.27531700
H	-2.51194400	-0.30961000	-2.05213500
H	-1.92887900	0.14219500	-0.46481000
N	1.92431700	0.10913600	-1.72630400
C	-3.90576300	-1.99780900	0.95117400
C	-3.75181000	-1.93358900	-0.43096700
C	-4.86365000	-1.74867100	-1.23459200
C	-6.11217700	-1.64778400	-0.62168000
C	-6.24137200	-1.71714500	0.76625400
C	-5.13063800	-1.89269900	1.58715700
C	-1.68068600	-2.28684700	0.59148100
C	-2.28590900	-1.99878900	-0.75387800
H	-4.76806200	-1.68462100	-2.31216500
H	-6.99606000	-1.50830600	-1.23090600
H	-7.22216800	-1.62937600	1.21596100
H	-5.22211200	-1.94259600	2.66444800
H	-2.03081300	-2.75274400	-1.50084200
C	-0.31482900	-2.49919400	0.89351600
H	-0.00731900	-2.42316400	1.93080300
C	0.58184300	-2.73374500	-0.10183400
H	0.20077600	-2.92642000	-1.09812200

N	-2.62721100	-2.19380800	1.51393300
H	-2.45289700	-2.27737300	2.50877000
H	2.19401500	-0.34140600	-2.58668900
I	-0.26969500	2.70568600	0.02735400
Cl	-1.73925500	5.50374200	-0.03309700
C	2.02645200	-2.77497200	0.02128900
C	2.69750100	-2.40428500	1.19813900
C	2.77607800	-3.13375200	-1.10800300
C	4.08032300	-2.40930000	1.24189400
H	2.13880400	-2.08524300	2.06982200
C	4.16282700	-3.14100000	-1.06083600
H	2.25928100	-3.40631800	-2.02229100
C	4.81391600	-2.77907000	0.11417000
H	4.59245600	-2.10556200	2.14606600
H	4.73442900	-3.42167400	-1.93667800
H	5.89677900	-2.77145200	0.15093300

Table S82. Calculated Gibbs free energy and XYZ coordinates for all atoms in **TS2d-endo** catalysed by ICl.

G= -1868.7815 Hartree Frequency = -228.51 cm^{-1}

C	2.83358900	0.46821700	-0.73392200
C	2.13021200	0.82333600	0.42408600
C	2.81284600	1.20728500	1.56334200
C	4.20979000	1.22002200	1.53815300
C	4.89606000	0.87249400	0.37698000
C	4.21878700	0.49266000	-0.78225300
C	0.63535900	0.04741200	-1.22174700
C	0.66752100	0.71396300	0.13178600
H	2.27188000	1.49953800	2.45663700
H	4.76167900	1.51417200	2.42208500
H	5.97955800	0.89488400	0.36998100
H	4.75486800	0.21564800	-1.68189200
H	0.08247000	0.19178800	0.88473200
C	-0.41256200	-0.54351500	-1.82961100
H	-0.25449100	-1.00044600	-2.80289100
C	-1.79217900	-0.57725000	-1.27531700
H	-2.51194400	-0.30961000	-2.05213500
H	-1.92887900	0.14219500	-0.46481000
N	1.92431700	0.10913600	-1.72630400
C	-3.90576300	-1.99780900	0.95117400
C	-3.75181000	-1.93358900	-0.43096700

C	-4.86365000	-1.74867100	-1.23459200
C	-6.11217700	-1.64778400	-0.62168000
C	-6.24137200	-1.71714500	0.76625400
C	-5.13063800	-1.89269900	1.58715700
C	-1.68068600	-2.28684700	0.59148100
C	-2.28590900	-1.99878900	-0.75387800
H	-4.76806200	-1.68462100	-2.31216500
H	-6.99606000	-1.50830600	-1.23090600
H	-7.22216800	-1.62937600	1.21596100
H	-5.22211200	-1.94259600	2.66444800
H	-2.03081300	-2.75274400	-1.50084200
C	-0.31482900	-2.49919400	0.89351600
H	-0.00731900	-2.42316400	1.93080300
C	0.58184300	-2.73374500	-0.10183400
H	0.20077600	-2.92642000	-1.09812200
N	-2.62721100	-2.19380800	1.51393300
H	-2.45289700	-2.27737300	2.50877000
H	2.19401500	-0.34140600	-2.58668900
I	-0.26969500	2.70568600	0.02735400
Cl	-1.73925500	5.50374200	-0.03309700
C	2.02645200	-2.77497200	0.02128900
C	2.69750100	-2.40428500	1.19813900
C	2.77607800	-3.13375200	-1.10800300
C	4.08032300	-2.40930000	1.24189400
H	2.13880400	-2.08524300	2.06982200
C	4.16282700	-3.14100000	-1.06083600
H	2.25928100	-3.40631800	-2.02229100
C	4.81391600	-2.77907000	0.11417000
H	4.59245600	-2.10556200	2.14606600
H	4.73442900	-3.42167400	-1.93667800
H	5.89677900	-2.77145200	0.15093300

Table S83. Calculated Gibbs free energy and XYZ coordinates for all atoms in **2d-endo** catalysed by ICl.

G= -1868.8108 Hartree

C	3.03695500	0.22702100	0.00001400
C	2.29506000	0.58147800	1.14169000
C	2.95924000	1.11456300	2.25044700
C	4.33450900	1.26616500	2.18675700
C	5.05518800	0.90935400	1.03400800
C	4.41768000	0.38964000	-0.08052500
C	0.88561800	-0.28886300	-0.43364700
C	0.90323000	0.31104400	0.83574500

H	2.40790800	1.40146700	3.13795900
H	4.86809800	1.66945000	3.03865700
H	6.12965600	1.04407100	1.01697700
H	4.96646000	0.11167600	-0.97201000
H	0.08989600	0.25305700	1.54413000
C	-0.20925500	-1.02888600	-1.13812600
H	0.02634100	-1.01912900	-2.20657200
C	-1.59695100	-0.38537500	-0.91627000
H	-1.83049700	0.29042000	-1.74106600
H	-1.59519400	0.21571700	-0.00537300
N	2.14350300	-0.27532400	-0.93270800
C	-4.37548600	-1.50665800	0.92540500
C	-4.04316200	-0.90947100	-0.29920100
C	-4.90352500	-0.00132400	-0.88511900
C	-6.10286700	0.31451600	-0.23816000
C	-6.41964300	-0.28488500	0.97694900
C	-5.56265100	-1.20784700	1.57913300
C	-2.30202000	-2.32626400	0.41956100
C	-2.70172100	-1.44021900	-0.74276800
H	-4.65099900	0.46453700	-1.83153100
H	-6.78487000	1.02825900	-0.68255900
H	-7.35040800	-0.03212400	1.47096200
H	-5.81487500	-1.67152500	2.52496000
H	-2.79456100	-2.03216200	-1.66248300
C	-1.06390500	-2.82490400	0.48987800
H	-0.71593200	-3.43199800	1.31589500
C	-0.18821700	-2.56942600	-0.70986800
H	-0.62750800	-3.07815400	-1.57722000
N	-3.36718000	-2.39116600	1.30501500
H	-3.29322400	-2.78471300	2.22958700
H	2.40115000	-0.67367300	-1.82492500
I	0.24491300	2.66739700	-0.17238200
Cl	-0.28861500	4.96578400	-0.91135900
C	1.22987400	-3.07239600	-0.57166700
C	1.91271900	-3.52993900	-1.69931400
C	1.91982600	-2.98343600	0.63931300
C	3.26065700	-3.87042200	-1.62755300
H	1.38430200	-3.61250300	-2.64437800
C	3.26664800	-3.32032000	0.71434600
H	1.40963100	-2.61558000	1.52314600
C	3.94321800	-3.75966900	-0.42010000
H	3.77567000	-4.22421500	-2.51298500
H	3.79114200	-3.22994900	1.65838200
H	4.99351800	-4.01872300	-0.36192000

Table S84. Calculated Gibbs free energy and XYZ coordinates for all atoms in **COM1d-exo** catalysed by ICl.

G= -1868.8005 Hartree

C	-1.85317900	0.84752500	0.73970100
C	-1.27002100	1.00421400	-0.52880600
C	-2.06142000	1.44049900	-1.59558700
C	-3.39908400	1.70657600	-1.35692100
C	-3.95864300	1.55251900	-0.07670000
C	-3.19456400	1.12136300	0.99361800
C	0.31337300	0.25086300	0.94602200
C	0.14134800	0.68818000	-0.38965000
H	-1.63289300	1.57444900	-2.58175400
H	-4.03091900	2.04028200	-2.17117800
H	-5.01029700	1.76321900	0.07251300
H	-3.62200400	0.98722900	1.97942100
H	0.79857600	0.38827100	-1.19237900
C	1.49193300	-0.27494500	1.61502600
H	1.34818600	-0.63066400	2.63054200
C	2.69325100	-0.33109000	1.03944600
H	2.86080300	0.02767400	0.02998300
H	3.54707500	-0.74276600	1.56284300
N	-0.86232300	0.38333800	1.59605400
C	2.76074100	-3.44503600	0.30129700
C	2.69914600	-2.82782900	-0.97393200
C	3.89549200	-2.61192000	-1.68050500
C	5.09029000	-3.00237000	-1.10824900
C	5.12628000	-3.61742900	0.16031800
C	3.96807400	-3.84931400	0.87894500
C	0.60695600	-2.94466400	-0.12708100
C	1.32531000	-2.52868600	-1.22575500
H	3.87710400	-2.14058300	-2.65651900
H	6.01957600	-2.83728900	-1.63996400
H	6.08052500	-3.91353400	0.57895900
H	3.99312100	-4.32134400	1.85399200
H	0.91752100	-2.05321900	-2.10419800
C	-0.80239600	-2.82578000	0.20420900
H	-1.09578400	-3.23196000	1.16881300
C	-1.71795700	-2.24934600	-0.58688100
H	-1.40524600	-1.87366600	-1.55871700
N	1.48007100	-3.51216200	0.78153400

H	-0.98139400	0.23030400	2.58779900
H	1.21172200	-3.89241400	1.67547000
I	1.16478700	2.98444500	-0.04087800
Cl	2.19382800	5.27406100	0.13470200
C	-3.13985600	-2.06736400	-0.27535200
C	-4.00644100	-1.66219600	-1.29515300
C	-3.66831400	-2.25729200	1.01004900
C	-5.36043800	-1.46507600	-1.04870600
H	-3.60813000	-1.49369300	-2.28993700
C	-5.01766300	-2.05790700	1.25738700
H	-3.01769100	-2.54488900	1.82816000
C	-5.87156600	-1.66146600	0.22836400
H	-6.01364300	-1.15027100	-1.85408600
H	-5.40796500	-2.20602700	2.25755100
H	-6.92518800	-1.50415200	0.42555200

Table S85. Calculated Gibbs free energy and XYZ coordinates for all atoms in **TS1d-exo** catalysed by ICl.

G= -1868.7707 Hartree Frequency = -429.31 cm^{-1}

C	-1.85317900	0.84752500	0.73970100
C	-1.27002100	1.00421400	-0.52880600
C	-2.06142000	1.44049900	-1.59558700
C	-3.39908400	1.70657600	-1.35692100
C	-3.95864300	1.55251900	-0.07670000
C	-3.19456400	1.12136300	0.99361800
C	0.31337300	0.25086300	0.94602200
C	0.14134800	0.68818000	-0.38965000
H	-1.63289300	1.57444900	-2.58175400
H	-4.03091900	2.04028200	-2.17117800
H	-5.01029700	1.76321900	0.07251300
H	-3.62200400	0.98722900	1.97942100
H	0.79857600	0.38827100	-1.19237900
C	1.49193300	-0.27494500	1.61502600
H	1.34818600	-0.63066400	2.63054200
C	2.69325100	-0.33109000	1.03944600
H	2.86080300	0.02767400	0.02998300
H	3.54707500	-0.74276600	1.56284300
N	-0.86232300	0.38333800	1.59605400
C	2.76074100	-3.44503600	0.30129700
C	2.69914600	-2.82782900	-0.97393200
C	3.89549200	-2.61192000	-1.68050500
C	5.09029000	-3.00237000	-1.10824900
C	5.12628000	-3.61742900	0.16031800

C	3.96807400	-3.84931400	0.87894500
C	0.60695600	-2.94466400	-0.12708100
C	1.32531000	-2.52868600	-1.22575500
H	3.87710400	-2.14058300	-2.65651900
H	6.01957600	-2.83728900	-1.63996400
H	6.08052500	-3.91353400	0.57895900
H	3.99312100	-4.32134400	1.85399200
H	0.91752100	-2.05321900	-2.10419800
C	-0.80239600	-2.82578000	0.20420900
H	-1.09578400	-3.23196000	1.16881300
C	-1.71795700	-2.24934600	-0.58688100
H	-1.40524600	-1.87366600	-1.55871700
N	1.48007100	-3.51216200	0.78153400
H	-0.98139400	0.23030400	2.58779900
H	1.21172200	-3.89241400	1.67547000
I	1.16478700	2.98444500	-0.04087800
Cl	2.19382800	5.27406100	0.13470200
C	-3.13985600	-2.06736400	-0.27535200
C	-4.00644100	-1.66219600	-1.29515300
C	-3.66831400	-2.25729200	1.01004900
C	-5.36043800	-1.46507600	-1.04870600
H	-3.60813000	-1.49369300	-2.28993700
C	-5.01766300	-2.05790700	1.25738700
H	-3.01769100	-2.54488900	1.82816000
C	-5.87156600	-1.66146600	0.22836400
H	-6.01364300	-1.15027100	-1.85408600
H	-5.40796500	-2.20602700	2.25755100
H	-6.92518800	-1.50415200	0.42555200

Table S86. Calculated Gibbs free energy and XYZ coordinates for all atoms in **INT1d-exo** catalysed by ICl.

G= -1868.7830 Hartree

C	2.60423600	1.56357100	-0.29495600
C	1.68979500	1.85871400	0.72390500
C	2.07449900	2.63762500	1.80083800
C	3.38890900	3.10587400	1.85799500
C	4.28849600	2.80368000	0.83774400
C	3.91126400	2.02780600	-0.25900700
C	0.71248000	0.38306700	-0.83376500
C	0.37989700	1.22757100	0.37195900
H	1.36383000	2.88404500	2.58171600

H	3.70858400	3.71254600	2.69560800
H	5.30333300	3.17938300	0.89224800
H	4.61279600	1.79257300	-1.05012700
H	-0.09288400	0.67326200	1.17999000
C	-0.02653600	-0.59510300	-1.39122800
H	0.39523000	-1.13753300	-2.23032400
C	-1.40331800	-0.95305800	-0.94410100
H	-1.97539800	-0.05980700	-0.68172800
H	-1.94354600	-1.44885700	-1.75261200
N	1.98482100	0.75395300	-1.24077800
C	-3.15751300	-3.59558900	0.22576500
C	-2.98900300	-2.24501200	0.52256000
C	-4.09394300	-1.46768500	0.82538900
C	-5.34638800	-2.08142900	0.84159500
C	-5.48976700	-3.43779300	0.54581000
C	-4.38857800	-4.22794800	0.22573800
C	-0.91937200	-3.23673500	0.08590900
C	-1.54121900	-1.89374000	0.33332700
H	-3.99181800	-0.41127400	1.04446900
H	-6.22324300	-1.49451700	1.08341900
H	-6.47506600	-3.88600400	0.56181900
H	-4.49245700	-5.27907000	-0.01062100
H	-1.09603900	-1.39004100	1.19343500
C	0.46025500	-3.51928200	-0.07737100
H	0.74009900	-4.47431700	-0.50709000
C	1.38202400	-2.58625600	0.27447300
H	1.03278800	-1.70177900	0.79418400
N	-1.88078400	-4.13670300	-0.04291500
H	2.47279800	0.29978500	-1.99707800
H	-1.71369900	-5.11361800	-0.25659200
I	-1.12249200	2.75996300	-0.14659900
Cl	-3.33823400	4.85759500	-0.83237000
C	2.81604200	-2.62651700	0.05828400
C	3.57771000	-1.54789700	0.53179500
C	3.45831700	-3.66660900	-0.63265900
C	4.94898700	-1.50510400	0.32144600
H	3.08736600	-0.73794400	1.06302500
C	4.82699200	-3.62401800	-0.83566300
H	2.88795300	-4.50429600	-1.01522300
C	5.57363000	-2.54376100	-0.36136200
H	5.52359700	-0.66320800	0.68744600
H	5.31859000	-4.42842300	-1.36828600
H	6.64357300	-2.51504400	-0.52830600

Table S87. Calculated Gibbs free energy and XYZ coordinates for all atoms in **TS2d-exo** catalysed by ICl.

G= -1868.7784 Hartree Frequency = -215.35 cm^{-1}

C	2.60423600	1.56357100	-0.29495600
C	1.68979500	1.85871400	0.72390500
C	2.07449900	2.63762500	1.80083800
C	3.38890900	3.10587400	1.85799500
C	4.28849600	2.80368000	0.83774400
C	3.91126400	2.02780600	-0.25900700
C	0.71248000	0.38306700	-0.83376500
C	0.37989700	1.22757100	0.37195900
H	1.36383000	2.88404500	2.58171600
H	3.70858400	3.71254600	2.69560800
H	5.30333300	3.17938300	0.89224800
H	4.61279600	1.79257300	-1.05012700
H	-0.09288400	0.67326200	1.17999000
C	-0.02653600	-0.59510300	-1.39122800
H	0.39523000	-1.13753300	-2.23032400
C	-1.40331800	-0.95305800	-0.94410100
H	-1.97539800	-0.05980700	-0.68172800
H	-1.94354600	-1.44885700	-1.75261200
N	1.98482100	0.75395300	-1.24077800
C	-3.15751300	-3.59558900	0.22576500
C	-2.98900300	-2.24501200	0.52256000
C	-4.09394300	-1.46768500	0.82538900
C	-5.34638800	-2.08142900	0.84159500
C	-5.48976700	-3.43779300	0.54581000
C	-4.38857800	-4.22794800	0.22573800
C	-0.91937200	-3.23673500	0.08590900
C	-1.54121900	-1.89374000	0.33332700
H	-3.99181800	-0.41127400	1.04446900
H	-6.22324300	-1.49451700	1.08341900
H	-6.47506600	-3.88600400	0.56181900
H	-4.49245700	-5.27907000	-0.01062100
H	-1.09603900	-1.39004100	1.19343500
C	0.46025500	-3.51928200	-0.07737100
H	0.74009900	-4.47431700	-0.50709000
C	1.38202400	-2.58625600	0.27447300
H	1.03278800	-1.70177900	0.79418400
N	-1.88078400	-4.13670300	-0.04291500
H	2.47279800	0.29978500	-1.99707800
H	-1.71369900	-5.11361800	-0.25659200

I	-1.12249200	2.75996300	-0.14659900
Cl	-3.33823400	4.85759500	-0.83237000
C	2.81604200	-2.62651700	0.05828400
C	3.57771000	-1.54789700	0.53179500
C	3.45831700	-3.66660900	-0.63265900
C	4.94898700	-1.50510400	0.32144600
H	3.08736600	-0.73794400	1.06302500
C	4.82699200	-3.62401800	-0.83566300
H	2.88795300	-4.50429600	-1.01522300
C	5.57363000	-2.54376100	-0.36136200
H	5.52359700	-0.66320800	0.68744600
H	5.31859000	-4.42842300	-1.36828600
H	6.64357300	-2.51504400	-0.52830600

Table S88. Calculated Gibbs free energy and XYZ coordinates for all atoms in **2d-exo** catalysed by ICl.

G= -1868.8123 Hartree

C	2.60423600	1.56357100	-0.29495600
C	1.68979500	1.85871400	0.72390500
C	2.07449900	2.63762500	1.80083800
C	3.38890900	3.10587400	1.85799500
C	4.28849600	2.80368000	0.83774400
C	3.91126400	2.02780600	-0.25900700
C	0.71248000	0.38306700	-0.83376500
C	0.37989700	1.22757100	0.37195900
H	1.36383000	2.88404500	2.58171600
H	3.70858400	3.71254600	2.69560800
H	5.30333300	3.17938300	0.89224800
H	4.61279600	1.79257300	-1.05012700
H	-0.09288400	0.67326200	1.17999000
C	-0.02653600	-0.59510300	-1.39122800
H	0.39523000	-1.13753300	-2.23032400
C	-1.40331800	-0.95305800	-0.94410100
H	-1.97539800	-0.05980700	-0.68172800
H	-1.94354600	-1.44885700	-1.75261200
N	1.98482100	0.75395300	-1.24077800
C	-3.15751300	-3.59558900	0.22576500
C	-2.98900300	-2.24501200	0.52256000
C	-4.09394300	-1.46768500	0.82538900
C	-5.34638800	-2.08142900	0.84159500
C	-5.48976700	-3.43779300	0.54581000

C	-4.38857800	-4.22794800	0.22573800
C	-0.91937200	-3.23673500	0.08590900
C	-1.54121900	-1.89374000	0.33332700
H	-3.99181800	-0.41127400	1.04446900
H	-6.22324300	-1.49451700	1.08341900
H	-6.47506600	-3.88600400	0.56181900
H	-4.49245700	-5.27907000	-0.01062100
H	-1.09603900	-1.39004100	1.19343500
C	0.46025500	-3.51928200	-0.07737100
H	0.74009900	-4.47431700	-0.50709000
C	1.38202400	-2.58625600	0.27447300
H	1.03278800	-1.70177900	0.79418400
N	-1.88078400	-4.13670300	-0.04291500
H	2.47279800	0.29978500	-1.99707800
H	-1.71369900	-5.11361800	-0.25659200
I	-1.12249200	2.75996300	-0.14659900
Cl	-3.33823400	4.85759500	-0.83237000
C	2.81604200	-2.62651700	0.05828400
C	3.57771000	-1.54789700	0.53179500
C	3.45831700	-3.66660900	-0.63265900
C	4.94898700	-1.50510400	0.32144600
H	3.08736600	-0.73794400	1.06302500
C	4.82699200	-3.62401800	-0.83566300
H	2.88795300	-4.50429600	-1.01522300
C	5.57363000	-2.54376100	-0.36136200
H	5.52359700	-0.66320800	0.68744600
H	5.31859000	-4.42842300	-1.36828600
H	6.64357300	-2.51504400	-0.52830600