

Supporting Information

The Role of Halogen Bond for the Catalytic Mechanism of Iso-Nazarov

Cyclization Reaction: A DFT Study

Yuanyuan Sun, Ying Li, Xiaoyan Li, Lingpeng Meng, Yanli Zeng*

College of Chemistry and Materials Science, Hebei Key Laboratory of Inorganic Nano-
materials, Hebei Normal University, Shijiazhuang, China, 050024

*E-mail address: yanlizeng@hebtu.edu.cn

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1. Structural Parameters

Table S1 C-C distances (in Å) along the reaction pathway in EtOAC solvent

	COM1	TS1	COM2
I ₂	3.088	1.761	1.605
IBr	3.067	1.781	1.604
ICl	3.068	1.799	1.597
ICl ₃	3.016	1.920	1.570

Table S2 O···I distances (in Å) along the reaction pathway in EtOAC solvent

	COM1	TS1	COM2
I ₂	2.783	2.280	2.205
IBr	2.566	2.249	2.194
ICl	2.490	2.217	2.161
ICl ₃	2.403	2.169	2.063

Table S3 Topological and energy properties of I···O interactions at the BCPs of the complexe I-XCOM1(X = I, Br, Cl) in EtOAC solvent (all values in a.u.)

	$\rho(r)$	$\nabla^2\rho(r)$	G_b	H_b	$-G_b/V_b$
I ₂ COM1	0.0239	0.0758	0.0184	0.0006	1.0337
IBrCOM1	0.0358	0.1078	0.0282	-0.0013	0.9570
IClCOM1	0.0413	0.1209	0.0330	-0.0028	0.9213
ICl ₃ COM1	0.0555	0.1287	0.0398	-0.0077	0.8379

Table S4 Gibbs free energy (in kcal·mol⁻¹) of the efficient carbon-carbon coupling, [1,2]-H shift process and direct hydrogen proton transfer process catalyzed by catalysts in EtOAC solvent

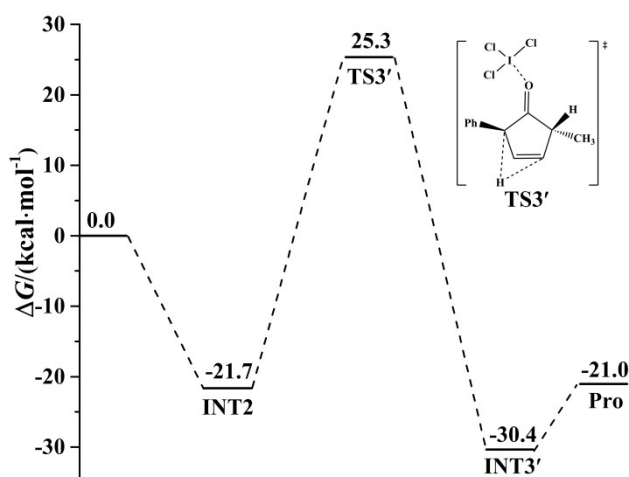
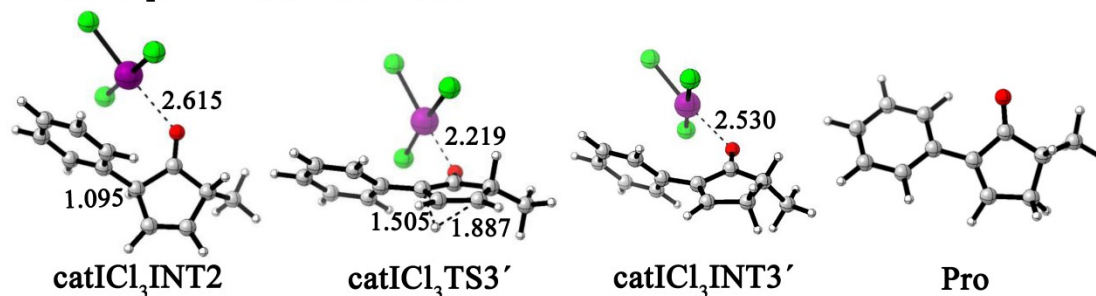
	COM1	TS1	INT1	TS2	INT2
I ₂	-1.1	27.2	26.4	30.6	-14.4
IBr	-3.7	21.1	20.2	24.2	-15.7
ICl	-4.8	17.3	15.7	21.4	-17.4
ICl ₃	-7.9	7.0	1.7	9.2	-21.7

Table S5 NPA charge (in e) of COM1 in EtOAc solvent

	I	O	C(1)	C(2)	C(3)	C(4)	C(5)
I ₂	0.0437	-0.5967	0.4125	-0.1026	-0.1313	-0.2340	-0.1617
IBr	0.2182	-0.6090	0.4249	-0.1428	-0.1162	-0.2377	-0.1537
ICl	0.3070	-0.6145	0.4298	-0.1461	-0.1083	-0.2431	-0.1410
ICl ₃	1.1845	-0.6410	0.4345	-0.1527	-0.0827	-0.2496	-0.1346

Table S6 Integral charge (in e) of the density difference between the region 1 and region 2 of COM1 in EtOAc solvent

	I ₂ COM1	IBrCOM1	IClCOM1	ICl ₃ COM1
region 1	0.0019	0.0076	0.0104	0.0081
region 2	-0.0503	-0.0506	-0.0568	-0.0817

**Fig. S1.** Potential energy curves of the direct proton transfer mechanism catalyzed by halogen bond catalyst ICl₃ in EtOAc solvent.**the direct proton transfer mechanism****Fig. S2.** Geometries and key bonds (in Å) of stationary points on the PES of the direct proton transfer mechanism catalyzed by ICl₃.

2. Energies and Cartesian Coordinates

Our initial configuration parameters and the coordination modes of the catalysts are based on the configuration coordinates given by Riveira and Gandon et al., which have been reported before (reference 38 in the manuscript).

2.1 Uncat

5-phenyl-2,4-pentadienal

Entropic correction (in solution) = -539.43289 Hartree

Sum of electronic and zero-point Energies = -539.403810 Hartree

Sum of electronic and thermal Free Energies = -539.443379 Hartree

C	-0.09339300	-0.15909600	-0.36544600
C	2.64237500	0.90393200	0.67647600
C	0.66936000	-1.23203600	-0.10002000
H	0.37915800	0.71680800	-0.80551800
C	-1.54621700	-0.05314100	-0.17272300
C	3.01391700	-0.31549000	-0.07135400
H	1.68989300	0.87292400	1.22985100
O	3.36002200	1.87931900	0.74668100
C	2.11115800	-1.28781900	-0.31700400
C	4.45755400	-0.43073800	-0.46516400
H	0.20448500	-2.15760300	0.22978700
C	-2.29965100	-1.02670700	0.49915200
C	-2.20864200	1.07294000	-0.67657200
H	2.48251000	-2.22302200	-0.73343000
H	5.11069000	-0.31893500	0.40407600
H	4.65635700	-1.39182800	-0.94011500
H	4.72284600	0.36747200	-1.16383800
C	-3.67160000	-0.87935800	0.64753600
H	-1.81171500	-1.90039100	0.91612300
C	-3.58335300	1.22127700	-0.52638800
H	-1.63520900	1.83688100	-1.19168300
C	-4.32006700	0.24408400	0.13478400
H	-4.23926500	-1.64059400	1.17047900
H	-4.07729900	2.10009400	-0.92469300
H	-5.39128100	0.35655600	0.25584700

Uncat-TS1

Imaginary frequency -615.64 cm⁻¹

Entropic correction (in solution) = -539.36739 Hartree

Sum of electronic and zero-point Energies = -539.340261 Hartree

Sum of electronic and thermal Free Energies = -539.377942 Hartree

C	-0.39774100	0.01811100	-0.75233600
C	-1.44196800	-0.70894700	0.25360700

C	-1.02821000	1.34066300	-0.96654400
H	-0.53494500	-0.59673600	-1.64764500
C	1.04315300	0.03552600	-0.34127400
C	-2.62302200	0.15395700	0.13769900
H	-1.22679400	-0.06592700	1.21614400
O	-1.45461500	-1.97480100	0.42310200
C	-2.30278400	1.38863200	-0.50035600
C	-3.93853600	-0.27240700	0.63787300
H	-0.48179200	2.19517000	-1.35284900
C	1.49855200	0.99016300	0.57316700
C	1.94044500	-0.91523500	-0.82820800
H	-2.96371000	2.24517600	-0.53840400
H	-4.60292900	0.56290600	0.85777200
H	-4.39554700	-0.88572500	-0.15141600
H	-3.82078700	-0.93044400	1.50140200
C	2.82736600	1.00276200	0.98150600
H	0.80243200	1.72296600	0.97403400
C	3.27026500	-0.90848000	-0.41588600
H	1.59227100	-1.66435800	-1.53160000
C	3.71755600	0.05212700	0.48621500
H	3.16818000	1.74973000	1.68944500
H	3.95692700	-1.65396800	-0.80062100
H	4.75316000	0.05837600	0.80615300

Uncat-INT1

Entropic correction (in solution) = -539.45428 Hartree

Sum of electronic and zero-point Energies = -539.426432 Hartree

Sum of electronic and thermal Free Energies = -539.464850 Hartree

C	-0.44076500	0.08778400	0.92374700
C	-1.33677200	0.75478400	-0.13959800
C	-1.14702300	-1.22396000	1.14920500
H	-0.45247100	0.72063400	1.81729300
C	0.98817000	-0.01571100	0.42653400
C	-2.41852700	-0.22949900	-0.58718100
H	-2.20433200	-0.51029900	-1.62649400
O	-1.21588500	1.88414100	-0.53249100
C	-2.19397900	-1.39297100	0.34229400
C	-3.81422500	0.39263600	-0.51746700
H	-0.80653700	-1.93870800	1.88946400
C	1.38220300	-1.05410700	-0.42008200
C	1.91886400	0.96654000	0.77017900
H	-2.83905200	-2.26466300	0.33974600
H	-4.56809000	-0.32821800	-0.84028000
H	-4.04716000	0.69956500	0.50533900
H	-3.87281300	1.26890400	-1.16534600

C	2.68414300	-1.11057200	-0.90938400
H	0.66851300	-1.82405400	-0.69504000
C	3.22035600	0.91111600	0.28093300
H	1.62026600	1.77722700	1.42672600
C	3.60705400	-0.12851300	-0.56037000
H	2.97745900	-1.92378900	-1.56372800
H	3.93292200	1.67936600	0.55918500
H	4.62137800	-0.17425100	-0.93980700

Uncat-TS2

Imaginary frequency -1061.37 cm⁻¹

Entropic correction (in solution) = -539.36214 Hartree

Sum of electronic and zero-point Energies = -539.334780 Hartree

Sum of electronic and thermal Free Energies = -539.372706 Hartree

C	0.39004500	0.33597100	-0.13771800
C	1.41038300	-0.67197600	-0.23539900
C	1.09304500	1.64493000	0.00770400
H	1.11761900	1.14719400	1.07771000
C	-1.04946400	0.15111600	-0.04022600
C	2.77068000	0.05249100	-0.28436200
H	3.00706500	0.01707000	-1.36639300
O	1.30774100	-1.89695400	-0.31559100
C	2.47680000	1.48283100	-0.05136200
C	3.88886000	-0.60206300	0.51295200
H	0.59574900	2.60500400	0.05264100
C	-1.93746900	1.24293600	-0.07030600
C	-1.60087600	-1.14076800	0.06461500
H	3.20598700	2.27382500	0.05979500
H	3.97862400	-1.65022500	0.22562200
H	4.84395600	-0.10415100	0.33630800
H	3.66541300	-0.55749400	1.58146200
C	-3.31068800	1.05271600	0.01482900
H	-1.55561900	2.25253500	-0.16939700
C	-2.97651500	-1.32154600	0.14077600
H	-0.93514300	-1.99344600	0.08088600
C	-3.84244300	-0.23056800	0.12072400
H	-3.97009800	1.91343400	-0.00965600
H	-3.37524300	-2.32713300	0.21983500
H	-4.91440400	-0.37739500	0.18254700

Uncat-Pro

Entropic correction (in solution) = -539.46642 Hartree

Sum of electronic and zero-point Energies = -539.438861 Hartree

Sum of electronic and thermal Free Energies = -539.476977 Hartree

C	0.40092100	0.41327700	-0.01581800
C	1.41278900	-0.60016200	-0.43020700

C	1.04536900	1.54569200	0.30863900
C	-1.05304700	0.17450600	0.01471400
C	2.79712200	0.03828300	-0.34726800
H	3.19906000	0.05269800	-1.36468700
O	1.19679900	-1.73984500	-0.77541800
C	2.53604200	1.46482100	0.15760800
C	3.71727000	-0.78779900	0.54933200
H	0.55311400	2.44429500	0.66676800
C	-1.94448400	1.20878800	-0.29480300
C	-1.56799900	-1.07849400	0.36541700
H	3.02618600	1.65593500	1.11815900
H	3.80230700	-1.80959000	0.17496500
H	4.71565600	-0.34681000	0.58541800
H	3.32273900	-0.82564600	1.56899800
C	-3.31751300	1.00072300	-0.24077900
H	-1.55567000	2.17684300	-0.59251600
C	-2.94303400	-1.28404800	0.41871600
H	-0.88968000	-1.88900800	0.60000000
C	-3.82152100	-0.24750000	0.11702700
H	-3.99466300	1.81098900	-0.48612700
H	-3.32840000	-2.25842400	0.69690000
H	-4.89226100	-0.41200000	0.15528600
H	2.89572400	2.23095500	-0.53528900

2.2 CatI₂

CatI₂

Entropic correction (in solution) = -595.29686 Hartree

Sum of electronic and zero-point Energies = -595.279868 Hartree

Sum of electronic and thermal Free Energies = -595.305554 Hartree

I	0.00000000	0.00000000	1.32792700
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I	0.00000000	0.00000000	-1.32792700
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CatI₂-COM1

Entropic correction (in solution) = -1134.73146 Hartree

Sum of electronic and zero-point Energies = -1134.690263 Hartree

Sum of electronic and thermal Free Energies = -1134.741618 Hartree

C	-3.55300200	0.35790400	0.23359300
C	-1.17368900	2.30498000	-0.06012200
C	-3.94736600	1.33252800	-0.60361400
H	-2.94426800	0.62773600	1.09451500
C	-3.91546100	-1.06259600	0.14814300
C	-2.33582600	3.20154800	-0.12261900
H	-1.27201000	1.31765500	-0.53654300
O	-0.10894900	2.63931200	0.43266700

C	-3.55331800	2.72852600	-0.46854700
C	-2.06910900	4.65439100	0.14305400
H	-4.66185400	1.11394900	-1.39297100
C	-4.51738800	-1.62731500	-0.98549600
C	-3.63865600	-1.89148500	1.24230900
H	-4.33896700	3.45828500	-0.65781200
H	-2.96831500	5.24934400	-0.01812900
H	-1.73704200	4.79449700	1.17541700
H	-1.27057300	5.03058500	-0.50122200
C	-4.84644600	-2.97537800	-1.01098200
H	-4.71906900	-1.01423500	-1.85648000
C	-3.96815000	-3.24223700	1.21618300
H	-3.16290500	-1.46645400	2.12021200
C	-4.57542100	-3.78793200	0.08977400
H	-5.30897300	-3.39861700	-1.89528300
H	-3.74785700	-3.86764500	2.07358800
H	-4.83049900	-4.84103100	0.06387900
I	1.87654300	0.70774100	0.16019100
I	3.67811600	-1.23748000	-0.19907000

CatI₂-TS1

Imaginary frequency -257.39 cm⁻¹

Entropic correction (in solution) = -1134.68646 Hartree

Sum of electronic and zero-point Energies = -1134.649386 Hartree

Sum of electronic and thermal Free Energies = -1134.696726 Hartree

C	3.00956800	0.57373300	0.37459200
C	2.35034100	-0.98174600	-0.12300700
C	4.22572100	0.53298200	-0.40500100
H	3.17865300	0.27519600	1.40975100
C	2.08051400	1.72324400	0.24274100
C	3.63930700	-1.66037700	-0.34403000
H	1.97071200	-0.63406700	-1.10208000
O	1.47094000	-1.53901100	0.67275400
C	4.64940000	-0.75484600	-0.66523500
C	3.77576300	-3.11536100	-0.16075800
H	4.69849700	1.42373200	-0.80849900
C	1.82567200	2.28160800	-1.01342700
C	1.40185100	2.21379000	1.35991400
H	5.60598400	-1.03013200	-1.09031000
H	4.70092600	-3.49435600	-0.59349200
H	3.78908600	-3.31533700	0.91873800
H	2.90313400	-3.63960400	-0.55723300
C	0.91670600	3.32406700	-1.14701600
H	2.32406800	1.88103500	-1.89243700
C	0.48922000	3.25419500	1.22599000

H	1.58262200	1.76868600	2.33296600
C	0.24554200	3.81004900	-0.02681400
H	0.71956300	3.74789700	-2.12480400
H	-0.03830800	3.62471000	2.09714200
H	-0.47350900	4.61406400	-0.13286400
I	-0.69183200	-0.94090300	0.26973400
I	-3.35319800	-0.19339500	-0.26495300

CatI₂-INT1

Entropic correction (in solution) = -1134.68770 Hartree

Sum of electronic and zero-point Energies = -1134.649854 Hartree

Sum of electronic and thermal Free Energies = -1134.697967 Hartree

C	2.90969300	0.39234200	0.51651800
C	2.29910900	-0.96895300	-0.07605500
C	4.27273900	0.35994900	-0.04577000
H	2.98030300	0.17104700	1.58854600
C	2.11815900	1.64381600	0.28209300
C	3.53067700	-1.74257500	-0.37409400
H	1.95276500	-0.65013700	-1.08641800
O	1.36374200	-1.61789500	0.64245600
C	4.63830200	-0.88965200	-0.47635200
C	3.51998000	-3.20152700	-0.48371500
H	4.89432600	1.24665300	-0.12775500
C	2.08483600	2.21844500	-0.99055200
C	1.36842000	2.21515800	1.30986600
H	5.61453500	-1.17951500	-0.84107700
H	4.41234000	-3.59050200	-0.97143700
H	3.48094200	-3.59214700	0.54390400
H	2.60176700	-3.54570200	-0.96526500
C	1.31570800	3.35124800	-1.23129900
H	2.64987800	1.76627600	-1.80224100
C	0.59368200	3.34507200	1.06872700
H	1.38020200	1.76269500	2.29605000
C	0.56640000	3.91444200	-0.20116500
H	1.29175700	3.78742300	-2.22318600
H	0.00554400	3.77617000	1.87044300
H	-0.04287500	4.79052900	-0.39058400
I	-0.70566000	-0.95487600	0.26880000
I	-3.39693700	-0.09467600	-0.24653300

CatI₂-TS2

Imaginary frequency -741.29 cm⁻¹

Entropic correction (in solution) = -1134.68101 Hartree

Sum of electronic and zero-point Energies = -1134.643773 Hartree

Sum of electronic and thermal Free Energies = -1134.691311 Hartree

C	-2.97908500	0.54843700	-0.52734300
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C	-2.45653200	-0.88722200	-0.24328200
C	-4.25250200	0.58878900	0.25374700
H	-3.22909000	0.52501700	-1.59582900
C	-2.00533500	1.66800700	-0.26062100
C	-3.53857500	-1.56789800	0.42413500
H	-2.19477800	-0.84263800	0.93413100
O	-1.53311600	-1.47904200	-0.95633000
C	-4.56640400	-0.61648000	0.77402800
C	-3.54929300	-3.01708700	0.68214700
H	-4.80090700	1.50835200	0.42333500
C	-1.69269300	2.01754400	1.05472600
C	-1.35101800	2.30714100	-1.31118100
H	-5.42145300	-0.85739900	1.39092500
H	-2.53884500	-3.42526700	0.65885200
H	-4.06067500	-3.26518000	1.61211300
H	-4.10651300	-3.47619600	-0.14536400
C	-0.72842600	2.98334200	1.31568900
H	-2.19271300	1.51450900	1.87903800
C	-0.38257300	3.27323200	-1.05143800
H	-1.58458900	2.03183800	-2.33437700
C	-0.06674500	3.60910200	0.26083300
H	-0.48480600	3.24105400	2.33991800
H	0.13075500	3.75598300	-1.87497600
H	0.69406000	4.35401900	0.46312100
I	0.65293400	-0.88684000	-0.40902900
I	3.26158600	-0.22020200	0.32735200

CatI₂-INT2

Entropic correction (in solution) = -1134.75276 Hartree

Sum of electronic and zero-point Energies = -1134.713752 Hartree

Sum of electronic and thermal Free Energies = -1134.763064 Hartree

C	3.15267600	0.55258500	0.67685600
C	2.93813900	-0.85607300	0.09903400
C	4.50397700	0.91584700	0.10890800
H	3.20203300	0.44914300	1.76806000
C	2.01929300	1.49193000	0.33150000
C	4.20174200	-1.31734700	-0.61910500
H	3.93165300	-1.60444300	-1.64154000
O	1.92428300	-1.50330200	0.19294500
C	5.05695800	-0.07874600	-0.58430000
C	4.82267100	-2.52718900	0.09099600
H	4.94733100	1.89095000	0.27224700
C	1.73063700	1.77426800	-1.00633100
C	1.22667500	2.05536400	1.32973200
H	6.02756400	-0.03461400	-1.06511900

H	4.13029100	-3.37104500	0.08194100
H	5.74276900	-2.82736600	-0.41414900
H	5.06472000	-2.28182400	1.12824600
C	0.65794400	2.59319200	-1.33830200
H	2.34499300	1.34012100	-1.79042100
C	0.15432000	2.88045200	0.99950500
H	1.44249500	1.83644800	2.37046200
C	-0.13590700	3.14589100	-0.33469400
H	0.43652500	2.79666700	-2.37985500
H	-0.45881900	3.30729700	1.78515000
H	-0.97593000	3.78029500	-0.59342800
I	-0.90378200	-0.82959100	0.12126300
I	-3.49630500	-0.24656500	-0.11348800

2.3 CatIBr

CatIBr

Entropic correction (in solution) = -2871.82620 Hartree

Sum of electronic and zero-point Energies = -2871.809210 Hartree

Sum of electronic and thermal Free Energies = -2871.834778 Hartree

I	0.00000000	0.00000000	0.98588200
Br	0.00000000	0.00000000	-1.49290700

CatIBr-COM1

Entropic correction (in solution) = -3411.26498 Hartree

Sum of electronic and zero-point Energies = -3411.224501 Hartree

Sum of electronic and thermal Free Energies = -3411.275196 Hartree

C	3.07519600	-0.61982800	0.26505800
C	0.43479600	-2.13783000	-0.09999200
C	3.34938300	-1.68714500	-0.50615800
H	2.37751100	-0.74145600	1.09163000
C	3.68424800	0.71081500	0.15326600
C	1.41218400	-3.22369600	-0.05549500
H	0.72389700	-1.20863000	-0.61103700
O	-0.70001600	-2.25834900	0.34780700
C	2.71122200	-2.98450400	-0.34911900
C	0.88254200	-4.59256800	0.25818800
H	4.14443800	-1.63318100	-1.24506300
C	4.42820800	1.11280000	-0.96524500
C	3.50682300	1.62021500	1.20325100
H	3.36313400	-3.84835300	-0.46775600
H	1.67160700	-5.33968100	0.17140500
H	0.48628600	-4.62005200	1.27690300
H	0.06133800	-4.85957100	-0.41129500
C	4.99236200	2.37967000	-1.01739500

H	4.55549300	0.43825600	-1.80429600
C	4.07170200	2.88960300	1.15009000
H	2.92274700	1.32269800	2.06809100
C	4.81862600	3.27196000	0.04042000
H	5.56290300	2.67798100	-1.88944400
H	3.92599800	3.57989100	1.97289200
H	5.25745400	4.26191500	-0.00607600
I	-2.28583400	-0.25884200	0.07872900
Br	-3.78592100	1.75196100	-0.21606500

CatIBr-TS1

Imaginary frequency -277.33 cm⁻¹

Entropic correction (in solution) = -3411.22549 Hartree

Sum of electronic and zero-point Energies = -3411.189343 Hartree

Sum of electronic and thermal Free Energies = -3411.235806 Hartree

C	2.64318300	0.56169700	0.40273500
C	1.96215800	-0.99837500	-0.12216000
C	3.86926900	0.49268900	-0.35293900
H	2.77397200	0.24363700	1.43705100
C	1.73654900	1.72484400	0.25391800
C	3.24728700	-1.69316600	-0.29724000
H	1.61377100	-0.63042400	-1.10360400
O	1.05405900	-1.53805100	0.65181300
C	4.27808400	-0.80494200	-0.59468900
C	3.35815200	-3.14912500	-0.09567400
H	4.36168200	1.37189800	-0.75827500
C	1.53495400	2.30359100	-1.00260800
C	1.02789100	2.21237700	1.35388100
H	5.24172500	-1.09800600	-0.99104600
H	4.29694400	-3.54142300	-0.48487800
H	3.32143000	-3.34219400	0.98428900
H	2.49905900	-3.66718900	-0.52834600
C	0.65053900	3.36445200	-1.15304300
H	2.05624900	1.90511300	-1.86901000
C	0.13939200	3.27099800	1.20274900
H	1.16723400	1.75146400	2.32635400
C	-0.04985700	3.84815000	-0.04983100
H	0.49498700	3.80465100	-2.13112700
H	-0.41184700	3.63948400	2.05997000
H	-0.75007900	4.66677500	-0.16950200
I	-1.07043200	-0.95135600	0.20658600
Br	-3.56429400	-0.26219000	-0.34874300

CatIBr-INT1

Entropic correction (in solution) = -3411.22691 Hartree

Sum of electronic and zero-point Energies = -3411.190064 Hartree

Sum of electronic and thermal Free Energies = -3411.237218 Hartree

C	2.57057700	0.28996600	0.51950800
C	1.86194600	-1.03223000	-0.04896600
C	3.92405800	0.15359900	-0.04983400
H	2.63302500	0.07760800	1.59379500
C	1.86603300	1.59019500	0.27510600
C	3.03362000	-1.89626400	-0.34013100
H	1.53263100	-0.70653100	-1.06239300
O	0.88664300	-1.59875400	0.68623800
C	4.19807700	-1.12542000	-0.46218300
C	2.91848300	-3.35235500	-0.42578000
H	4.60617100	0.99283900	-0.14917500
C	1.86501300	2.15382900	-1.00309500
C	1.16619500	2.22286100	1.30204400
H	5.14924700	-1.48886300	-0.82695100
H	3.77870600	-3.81163600	-0.91004500
H	2.85597600	-3.72262600	0.60817300
H	1.97606000	-3.63796600	-0.89885500
C	1.17856600	3.33743700	-1.24894000
H	2.38913500	1.65420800	-1.81427400
C	0.47470500	3.40454400	1.05581500
H	1.15284000	1.77928500	2.29225900
C	0.48057000	3.96352600	-0.21882900
H	1.17876900	3.76560700	-2.24462200
H	-0.07386200	3.88490800	1.85763700
H	-0.06347600	4.88085000	-0.41193000
I	-1.14116400	-0.89338000	0.23667600
Br	-3.62725000	-0.05104700	-0.34844600

CatIBr-TS2

Imaginary frequency -778.57 cm⁻¹

Entropic correction (in solution) = -3411.22058 Hartree

Sum of electronic and zero-point Energies = -3411.183394 Hartree

Sum of electronic and thermal Free Energies = -3411.230926 Hartree

C	-2.59271100	0.52391000	-0.58515700
C	-2.06997600	-0.89879500	-0.26321500
C	-3.90523800	0.55478700	0.13157800
H	-2.78844600	0.48956500	-1.66464500
C	-1.65139300	1.66222500	-0.28004100
C	-3.16363300	-1.58749000	0.36902200
H	-1.87811300	-0.85393800	0.93526900
O	-1.10364200	-1.48974600	-0.92061000
C	-4.22334300	-0.64613100	0.65653200
C	-3.16609100	-3.03370900	0.64733800
H	-4.47655700	1.46748800	0.25501200

C	-1.41021900	2.02638500	1.04599800
C	-0.96540200	2.31236200	-1.30323500
H	-5.10236100	-0.89385100	1.23576000
H	-2.15261100	-3.43433700	0.64834300
H	-3.69112500	-3.27098000	1.57262100
H	-3.70816300	-3.50833400	-0.18117200
C	-0.48771500	3.02124200	1.34549500
H	-1.93655200	1.51676700	1.84939900
C	-0.03847300	3.30750100	-1.00463600
H	-1.14361000	2.02475200	-2.33424000
C	0.20388900	3.66084700	0.31864100
H	-0.30076700	3.29177700	2.37831600
H	0.49942500	3.80035500	-1.80621400
H	0.93105900	4.43007600	0.55145300
I	1.01837800	-0.90462700	-0.32563400
Br	3.46927800	-0.30328500	0.42039100

CatIBr-INT2

Entropic correction (in solution) = -3411.28414 Hartree

Sum of electronic and zero-point Energies = -3411.246567 Hartree

Sum of electronic and thermal Free Energies = -3411.294484 Hartree

C	-2.60220000	0.47368700	-0.74436000
C	-2.45510700	-0.85146800	0.01385600
C	-4.03880100	0.83695800	-0.44758700
H	-2.47327000	0.24732800	-1.81090200
C	-1.56334400	1.49462800	-0.33854000
C	-3.81146000	-1.30558900	0.53400500
H	-3.72211800	-1.49756400	1.60890300
O	-1.42082300	-1.45388900	0.18949900
C	-4.67837800	-0.11071200	0.23629100
C	-4.26034600	-2.59448600	-0.16804500
H	-4.46829400	1.77414800	-0.78044700
C	-1.41728800	1.84416600	1.00632500
C	-0.71658300	2.06750100	-1.28532100
H	-5.71760100	-0.06303700	0.54056800
H	-3.56223400	-3.40668700	0.04246600
H	-5.25075700	-2.88652000	0.18597300
H	-4.31234700	-2.44514700	-1.24944800
C	-0.42404600	2.73360400	1.39870000
H	-2.07663200	1.40583900	1.75071700
C	0.27430300	2.96460400	-0.89535000
H	-0.82007600	1.79405200	-2.33050600
C	0.42813100	3.29221100	0.44786100
H	-0.31005300	2.98722100	2.44647400
H	0.93350700	3.39679700	-1.63964600

H	1.20725800	3.98059300	0.75449000
I	1.21706300	-0.84151200	0.02605500
Br	3.68644500	-0.40361100	-0.02750100

2.4 CatICI

CatICI

Entropic correction (in solution) = -757.83991 Hartree

Sum of electronic and zero-point Energies = -757.823759 Hartree

Sum of electronic and thermal Free Energies = -757.848211 Hartree

Cl	0.00000000	0.00000000	-1.77110700
I	0.00000000	0.00000000	0.56809100

CatICI-COM1

Entropic correction (in solution) = -1297.28051 Hartree

Sum of electronic and zero-point Energies = -1297.241388 Hartree

Sum of electronic and thermal Free Energies = -1297.290699 Hartree

C	-2.54714100	0.85865500	0.28641100
C	0.33075900	1.85314700	-0.08872300
C	-2.61852400	1.97663400	-0.45824000
H	-1.82491100	0.82287100	1.09995900
C	-3.39761400	-0.33054300	0.16195300
C	-0.41779900	3.10140000	0.00126800
H	-0.13678400	1.00471300	-0.60584200
O	1.48045200	1.75001200	0.33168100
C	-1.74199600	3.12222700	-0.28030200
C	0.36724700	4.33486700	0.34083800
H	-3.41203800	2.09416800	-1.19122000
C	-4.33724200	-0.49358800	-0.86630300
C	-3.25673100	-1.35174300	1.10953700
H	-2.21649900	4.09783800	-0.37223200
H	-0.26625300	5.22040300	0.29016500
H	0.77587200	4.25616900	1.35191400
H	1.21423700	4.46097300	-0.33775300
C	-5.11516100	-1.64032600	-0.93344100
H	-4.45871400	0.27571600	-1.62020400
C	-4.03495600	-2.50205000	1.04042900
H	-2.52722500	-1.23754700	1.90483200
C	-4.96779400	-2.64886100	0.01918600
H	-5.83742300	-1.75313600	-1.73380500
H	-3.91120700	-3.28249000	1.78224100
H	-5.57565800	-3.54431100	-0.03901200
I	2.68260600	-0.40640300	0.00568600
Cl	3.79862200	-2.50323500	-0.32232500

CatICI-TS1

Imaginary frequency -297.88 cm⁻¹

Entropic correction (in solution) = -1297.24519 Hartree

Sum of electronic and zero-point Energies = -1297.209294 Hartree

Sum of electronic and thermal Free Energies = -1297.255485 Hartree

C	2.14761000	0.75760200	0.44348900
C	1.64978200	-0.87343400	-0.12974600
C	3.39997800	0.81271500	-0.26386000
H	2.26227500	0.43013300	1.47653600
C	1.12989500	1.81968200	0.26948300
C	3.00662800	-1.42772500	-0.23049000
H	1.31421200	-0.52244700	-1.11968500
O	0.76237400	-1.50767700	0.59535100
C	3.95123600	-0.43670300	-0.48126900
C	3.26163100	-2.86346400	-0.00960300
H	3.81317200	1.73697300	-0.65707900
C	0.91176600	2.39217800	-0.98740200
C	0.33428000	2.21228400	1.34808300
H	4.95839900	-0.62724400	-0.82901600
H	4.25673800	-3.15206100	-0.34628400
H	3.19097100	-3.05606100	1.06872100
H	2.48890400	-3.47408000	-0.48220800
C	-0.07777900	3.35206000	-1.15883800
H	1.50229900	2.06563000	-1.83911100
C	-0.65891000	3.16966500	1.17563600
H	0.48814400	1.75433000	2.31983300
C	-0.86590600	3.74021400	-0.07715900
H	-0.24612400	3.78640300	-2.13738300
H	-1.27741900	3.46324300	2.01566400
H	-1.64754300	4.47844800	-0.21426400
I	-1.36176800	-1.11791200	0.09481300
Cl	-3.77474100	-0.67664400	-0.49609200

CatICI-INT1

Entropic correction (in solution) = -1297.24779 Hartree

Sum of electronic and zero-point Energies = -1297.210513 Hartree

Sum of electronic and thermal Free Energies = -1297.258072 Hartree

C	2.10726800	0.27445700	0.57749400
C	1.43515900	-1.03391400	-0.04405100
C	3.49747300	0.13457500	0.10059500
H	2.10016800	0.06308400	1.65417100
C	1.43321400	1.58425900	0.29403700
C	2.61622900	-1.90365000	-0.27756300
H	1.15850400	-0.70510300	-1.07114600
O	0.41939000	-1.61399500	0.63234200

C	3.79041900	-1.13946200	-0.31384200
C	2.49576100	-3.35635800	-0.39722700
H	4.19151700	0.96936800	0.06713900
C	1.51767900	2.15234800	-0.97911800
C	0.68160000	2.22288400	1.27972200
H	4.76131000	-1.50451800	-0.62043800
H	3.37691100	-3.81312300	-0.84485400
H	2.37966600	-3.74385900	0.62613900
H	1.57652600	-3.62671700	-0.92176300
C	0.86372500	3.34638600	-1.26082900
H	2.08338600	1.64954000	-1.75987600
C	0.02213600	3.41469000	0.99710600
H	0.60276800	1.77643200	2.26555400
C	0.11299000	3.97814700	-0.27228000
H	0.93080900	3.77822000	-2.25262700
H	-0.56784000	3.89940400	1.76620900
H	-0.40589900	4.90355100	-0.49385200
I	-1.55630400	-0.89775500	0.12690500
Cl	-3.91181000	-0.07055900	-0.49550800

CatICI-TS2

Imaginary frequency -772.96 cm⁻¹

Entropic correction (in solution) = -1297.23864 Hartree

Sum of electronic and zero-point Energies = -1297.202801 Hartree

Sum of electronic and thermal Free Energies = -1297.248965 Hartree

C	-2.12007600	0.66182300	-0.64396000
C	-1.71204600	-0.78971500	-0.29995500
C	-3.45355600	0.78768100	0.02262600
H	-2.27778400	0.63747000	-1.73016000
C	-1.10968700	1.72990100	-0.30651700
C	-2.86677400	-1.39904100	0.29925200
H	-1.57149700	-0.76059700	0.90960100
O	-0.75820800	-1.44854100	-0.91371500
C	-3.87066900	-0.38412100	0.54230700
C	-2.97611100	-2.83880300	0.59221800
H	-3.96738900	1.73723800	0.11613700
C	-0.92088400	2.11230600	1.02272100
C	-0.30867900	2.28776800	-1.30011500
H	-4.78510000	-0.56876200	1.08924200
H	-3.54566900	-3.28317900	-0.23420200
H	-1.99425000	-3.31107900	0.60986300
H	-3.52465700	-3.02481200	1.51574200
C	0.06545300	3.03290100	1.35539800
H	-1.53960000	1.67504700	1.80226000
C	0.68159700	3.20814200	-0.96785500

H	-0.44692500	1.98538000	-2.33290700
C	0.87224400	3.57911500	0.35917700
H	0.21112500	3.31844800	2.39078000
H	1.30902900	3.62808800	-1.74548800
H	1.64868300	4.28929100	0.61877100
I	1.33322700	-1.04596800	-0.20436900
Cl	3.65904700	-0.66033300	0.65175600

CatICI-INT2

Entropic correction (in solution) = -1297.30060 Hartree

Sum of electronic and zero-point Energies = -1297.263189 Hartree

Sum of electronic and thermal Free Energies = -1297.310922 Hartree

C	2.11691600	0.51658800	0.74363400
C	2.02592100	-0.79433500	-0.04454300
C	3.55042000	0.92406300	0.49020000
H	1.96988100	0.26218700	1.80177800
C	1.06186500	1.52084600	0.33769500
C	3.40719300	-1.20819800	-0.52749400
H	3.35710800	-1.39506000	-1.60560200
O	1.01314200	-1.41960700	-0.26825200
C	4.23312800	0.00540700	-0.19133500
C	3.86662600	-2.49014400	0.18190900
H	3.94408400	1.86733600	0.84889400
C	0.93010500	1.89187400	-1.00269200
C	0.19031100	2.06033500	1.28165800
H	5.27803500	0.08508700	-0.46798700
H	3.87792500	-2.34665300	1.26527300
H	3.19880700	-3.31969200	-0.05724300
H	4.87613700	-2.75193300	-0.14008900
C	-0.07284100	2.77116100	-1.39395400
H	1.60940300	1.48075600	-1.74470400
C	-0.81044000	2.94656900	0.89297100
H	0.28318600	1.76921200	2.32301400
C	-0.94876800	3.29711500	-0.44629200
H	-0.17504900	3.04264600	-2.43843500
H	-1.48844500	3.35341500	1.63454900
H	-1.73484100	3.97784300	-0.75215300
I	-1.57604100	-0.96897100	-0.03664800
Cl	-3.93375300	-0.70356000	0.08768000

2.5 CatICl₃

CatICl₃

Entropic correction (in solution) = -1678.208020 Hartree

Sum of electronic and zero-point Energies = -1678.186309 Hartree

Sum of electronic and thermal Free Energies = -1678.218734 Hartree

I	0.00000000	0.00000000	0.40712200
Cl	0.00000000	2.46406300	0.31684800
Cl	0.00000000	-2.46406300	0.31684800
Cl	0.00000000	0.00000000	-1.90295900

Cat[Cl₃]-COM1

Entropic correction (in solution) = -2217.653500 Hartree

Sum of electronic and zero-point Energies = -2217.609669 Hartree

Sum of electronic and thermal Free Energies = -2217.663613 Hartree

C	-2.83702300	1.08825200	0.23183500
C	0.04686700	1.93501300	-0.02287500
C	-2.84633200	2.25826000	-0.43832000
H	-2.15389400	0.97571800	1.07178900
C	-3.72366200	-0.05356200	-0.00626000
C	-0.60716600	3.21336800	0.15553800
H	-0.45185100	1.17722100	-0.63969900
O	1.17431700	1.70578900	0.43541000
C	-1.92083500	3.33830700	-0.16674600
C	0.23901700	4.35926100	0.62907700
H	-3.62509000	2.46310900	-1.16755000
C	-4.48089500	-0.19071100	-1.17856100
C	-3.80441900	-1.05461000	0.97013100
H	-2.33158400	4.34540700	-0.20874400
H	-0.32919400	5.28908800	0.60439400
H	0.57322900	4.18339100	1.65520800
H	1.13403300	4.46971500	0.01274600
C	-5.30935900	-1.28950700	-1.35516000
H	-4.41043100	0.55595500	-1.96153400
C	-4.63518700	-2.15473200	0.79221800
H	-3.21071500	-0.96177100	1.87362500
C	-5.39137200	-2.27336500	-0.36985300
H	-5.88680200	-1.38656500	-2.26725500
H	-4.68852200	-2.92025900	1.55750300
H	-6.03635000	-3.13247500	-0.51389200
I	2.11725500	-0.47321400	0.06353300
Cl	3.00485100	-2.64563900	-0.26927500
Cl	4.15665300	0.59275200	-0.86282300
Cl	-0.01854400	-1.39889700	0.99602600

Cat[Cl₃]-TS1

Imaginary frequency -335.86 cm⁻¹

Entropic correction (in solution) = -2217.629710 Hartree

Sum of electronic and zero-point Energies = -2217.588670 Hartree

Sum of electronic and thermal Free Energies = -2217.639908 Hartree

C	2.24101400	1.08240000	0.55046600
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C	1.94176400	-0.69320000	-0.11545400
C	3.53689700	1.18129900	-0.03306000
H	2.22578400	0.69633800	1.56802900
C	1.15316600	2.02421900	0.23101100
C	3.33114600	-1.09840900	0.03521900
H	1.71574000	-0.29179700	-1.10911800
O	1.00615500	-1.40163200	0.46509700
C	4.20641400	-0.03135400	-0.12102200
C	3.68385600	-2.49530100	0.37468300
H	3.91227300	2.10913500	-0.45475600
C	0.98318700	2.48941700	-1.07839000
C	0.22503600	2.37937200	1.21377500
H	5.26496100	-0.14498300	-0.31877800
H	4.74820900	-2.67818300	0.23159200
H	3.44237300	-2.66637500	1.43078800
H	3.08583300	-3.20270200	-0.20380500
C	-0.09978300	3.29753600	-1.39741500
H	1.68349800	2.18787800	-1.85249300
C	-0.86040700	3.18574200	0.89245100
H	0.34649300	2.00539400	2.22430300
C	-1.02578200	3.64076700	-0.41303400
H	-0.23535800	3.64361100	-2.41526500
H	-1.58391200	3.44586200	1.65613100
H	-1.88210100	4.25446300	-0.66767000
I	-1.06500100	-0.92607000	0.02843500
Cl	-3.43896900	-0.38686700	-0.44328500
Cl	-0.52351400	-1.32736700	-2.39928000
Cl	-1.34498800	-0.57040200	2.48067100

Cat[Cl₃]-INT1

Entropic correction (in solution) = -2217.638240 Hartree

Sum of electronic and zero-point Energies = -2217.595920 Hartree

Sum of electronic and thermal Free Energies = -2217.648418 Hartree

C	2.11618800	0.28532000	0.71423100
C	1.60938400	-1.00149800	-0.02984400
C	3.58433000	0.10187800	0.63526900
H	1.82075800	0.14879300	1.76446700
C	1.62218200	1.61476000	0.20174100
C	2.79060600	-1.90375200	-0.00332800
H	1.53061300	-0.71428000	-1.09891000
O	0.46759900	-1.61970300	0.42829100
C	3.94956300	-1.16906700	0.26942100
C	2.66977100	-3.34352100	-0.21591300
H	4.27904500	0.91162000	0.83672200
C	1.93262900	2.00924900	-1.10179000

C	0.84118900	2.44584600	1.00340100
H	4.95846500	-1.55406600	0.21354900
H	3.62979200	-3.82194800	-0.39874100
H	2.22816600	-3.75901800	0.70260100
H	1.94525400	-3.55358400	-1.00752200
C	1.46277200	3.21893100	-1.59978800
H	2.53157400	1.35941500	-1.73557800
C	0.36753500	3.65496000	0.50316300
H	0.58978400	2.13872500	2.01256500
C	0.67611900	4.04208600	-0.79743500
H	1.70203900	3.51452500	-2.61460600
H	-0.24943300	4.28981200	1.12825300
H	0.30024900	4.98051300	-1.18794100
I	-1.32237000	-0.65824700	0.07043800
Cl	-3.58187100	0.47238100	-0.36346500
Cl	-0.99029200	-1.29368100	-2.34316100
Cl	-1.34872500	-0.10969500	2.51549700

CatICl₃-TS2

Imaginary frequency -744.23 cm⁻¹

Entropic correction (in solution) = -2217.62617 Hartree

Sum of electronic and zero-point Energies = -2217.586178 Hartree

Sum of electronic and thermal Free Energies = -2217.636424 Hartree

C	2.11732000	0.99982500	0.81680900
C	1.92229900	-0.49070700	0.50664900
C	3.53861800	1.22374700	0.39943600
H	2.06041200	1.06126100	1.91202700
C	1.08445400	1.91813000	0.20598100
C	3.19759800	-1.02312700	0.15258500
H	2.04001100	-0.56882900	-0.71847100
O	0.91383800	-1.22612700	0.94361400
C	4.14204800	0.07616200	0.03792500
C	3.47934500	-2.45804800	-0.03998200
H	3.97664400	2.21330400	0.35252900
C	1.03025300	2.06812300	-1.18124700
C	0.12161000	2.53141300	1.00329600
H	5.15421900	-0.04966300	-0.32054700
H	3.94477800	-2.81351300	0.88785400
H	2.56112400	-3.02377400	-0.19526900
H	4.18605100	-2.61964000	-0.85415700
C	0.00340800	2.79756400	-1.76664300
H	1.78073800	1.59004100	-1.80624000
C	-0.90848100	3.26258400	0.41701300
H	0.16051600	2.41237500	2.08047200
C	-0.97421600	3.38743000	-0.96674400

H	-0.04322000	2.89537600	-2.84495300
H	-1.66626800	3.72061400	1.04201500
H	-1.78526600	3.94230400	-1.42379900
I	-1.05179200	-0.86112700	0.12022200
Cl	-3.31215300	-0.55238200	-0.87674800
Cl	0.03684900	-1.49829800	-2.08229600
Cl	-1.81063900	-0.24753500	2.39771400

CatICl₃-INT2

Entropic correction (in solution) = -2217.67542 Hartree

Sum of electronic and zero-point Energies = -2217.633810 Hartree

Sum of electronic and thermal Free Energies = -2217.685663 Hartree

C	2.42275300	0.69648900	0.68397100
C	2.31514800	-0.66282900	-0.01093200
C	3.80437100	1.14028200	0.26005600
H	2.39896100	0.49590100	1.76429600
C	1.27301400	1.61273000	0.33787500
C	3.67126800	-1.08012300	-0.54969100
H	3.55018200	-1.37967100	-1.59599900
O	1.30082200	-1.31645000	-0.14602000
C	4.46714200	0.19020600	-0.39755600
C	4.23199900	-2.26613500	0.24976500
H	4.18289100	2.12604700	0.50079600
C	0.99430000	1.90444900	-1.00063700
C	0.43727700	2.11496500	1.33440900
H	5.47942500	0.28255700	-0.77318800
H	4.31389200	-2.01285700	1.30952400
H	3.58560000	-3.13899200	0.14292800
H	5.22626500	-2.52200600	-0.12035800
C	-0.12615500	2.65469700	-1.33708800
H	1.64308900	1.51941200	-1.78301900
C	-0.68499600	2.86743600	0.99878000
H	0.64945500	1.89116600	2.37427300
C	-0.97530900	3.12735300	-0.33760500
H	-0.34742600	2.85605100	-2.37884800
H	-1.33866400	3.23730400	1.78059100
H	-1.85742800	3.69964000	-0.60106100
I	-1.24526000	-0.73534600	-0.01669000
Cl	-3.54694300	-0.33332300	0.03286500
Cl	-1.29181200	-0.69873100	-2.49705800
Cl	-1.21294600	-0.81187100	2.46682300

CatICl₃(a)—The indirect hydrogen proton transfer reaction pathway with H₂O

(a₁) One-step water co-catalyzed mechanism

H₂O

Entropic correction (in solution) = -76.411380 Hartree

Sum of electronic and zero-point Energies = -76.406339 Hartree

Sum of electronic and thermal Free Energies = -76.423983 Hartree

O	0.00000000	0.00000000	0.11764200
H	0.00000000	0.76109700	-0.47056700
H	0.00000000	-0.76109700	-0.47056700

Cat ICl₃-COM3-1

Entropic correction (in solution) = -2294.09090 Hartree

Sum of electronic and zero-point Energies = -2294.045059 Hartree

Sum of electronic and thermal Free Energies = -2294.101200 Hartree

C	2.33478000	0.70506200	0.68629000
C	2.22367700	-0.23602000	-0.51294600
C	3.60697100	1.45229200	0.35155100
H	2.50415600	0.05095100	1.55200200
C	1.08506700	1.51543600	0.91688700
C	3.55613900	-0.29831100	-1.23827900
H	3.36837500	-0.22093200	-2.31361400
O	1.22158300	-0.80673800	-0.89660700
C	4.26017200	0.91008100	-0.67517800
C	4.28197800	-1.62159200	-0.94797200
H	3.93094400	2.30996000	0.92823900
C	0.62148500	2.38478200	-0.07487300
C	0.33686400	1.34834500	2.08216700
H	5.20974900	1.25714100	-1.06513700
H	3.69059900	-2.46821000	-1.30310200
H	5.24352400	-1.62967800	-1.46469800
H	4.46106700	-1.73377200	0.12292500
C	-0.58966300	3.04833000	0.08273000
H	1.20109700	2.52132800	-0.98379000
C	-0.87671500	2.01189600	2.24123700
H	0.69345100	0.67541200	2.85497900
C	-1.34731800	2.85302800	1.23661100
H	-0.95177200	3.70396600	-0.70078900
H	-1.45918500	1.86095500	3.14304700
H	-2.29880600	3.35931200	1.35286500
I	-1.30024400	-0.60590800	-0.40231500
O	2.29391600	-2.36175400	1.63581600
H	2.49815200	-3.17859200	1.16983500
H	1.33093300	-2.35005500	1.70175100

Cl	-3.61411000	-0.54310300	-0.06513400
Cl	-1.04594900	-1.91045400	1.73496000
Cl	-1.55135000	0.62198700	-2.52128600

Cat ICl₃-TS3-1

Imaginary frequency -297.55 cm⁻¹

Entropic correction (in solution) = -2294.032880 Hartree

Sum of electronic and zero-point Energies = -2293.989518 Hartree

Sum of electronic and thermal Free Energies = -2294.043103 Hartree

C	1.99042100	0.39213400	-0.34987000
C	1.58643400	-0.81012100	0.19054300
C	3.24314500	0.13854700	-1.08377000
H	3.07857700	0.43446900	1.45711600
C	1.27657100	1.67965600	-0.32180300
C	2.56273100	-1.90326800	-0.19669200
H	2.01135200	-2.49724200	-0.94277500
O	0.51773000	-1.10756200	0.89245700
C	3.62656000	-1.15040700	-0.94558500
C	3.00226500	-2.83474400	0.93218900
H	3.77345100	0.90556600	-1.63784100
C	1.28130000	2.51980800	-1.44242700
C	0.56901200	2.08302600	0.81844900
H	4.50545700	-1.61187600	-1.37755200
H	2.12867800	-3.30154500	1.38899100
H	3.65020300	-3.62094300	0.54074800
H	3.54878800	-2.30280900	1.71509500
C	0.58816300	3.72487400	-1.42410100
H	1.80845100	2.21451500	-2.33989600
C	-0.12781300	3.28531600	0.83238600
H	0.55407600	1.44390500	1.69545500
C	-0.12100500	4.11075300	-0.28912100
H	0.59140800	4.35879100	-2.30350600
H	-0.68005500	3.57391300	1.71958300
H	-0.66794400	5.04632200	-0.28039100
I	-1.45310300	-0.69275000	0.10541000
O	4.04808300	0.25988300	1.64715100
H	4.37428900	-0.05132500	0.74541400
H	4.50558500	1.07973700	1.92828100
Cl	-3.75992300	-0.31526000	-0.78728100
Cl	-2.05126000	0.17645100	2.37450300
Cl	-0.63358500	-1.60164600	-2.08919300

Cat ICl₃-INT3-1

Entropic correction (in solution) = -2294.10330 Hartree

Sum of electronic and zero-point Energies = -2294.056438 Hartree

Sum of electronic and thermal Free Energies = -2294.113557 Hartree

C	2.08999700	0.72689500	-0.55542100
C	2.01885300	-0.63925900	-0.00978800
C	3.29156400	0.88293500	-1.13643300
H	3.53716400	1.64598100	1.80053300
C	0.98661500	1.69339300	-0.39915500
C	3.26641100	-1.39726400	-0.40163400
H	2.91828000	-2.05800900	-1.20751600
O	1.07511900	-1.13916100	0.59997200
C	4.17541400	-0.32022600	-1.00733600
C	3.86050800	-2.24454900	0.71600400
H	3.61878100	1.79951900	-1.61668500
C	0.34591100	2.24118000	-1.51299000
C	0.51863700	1.99775100	0.88383000
H	4.60511300	-0.61295100	-1.96837200
H	3.11664000	-2.94303300	1.10352300
H	4.70766800	-2.82062200	0.33811500
H	4.20360100	-1.60592500	1.53076800
C	-0.76050400	3.06721900	-1.34514700
H	0.69555000	1.98874200	-2.50798000
C	-0.58101000	2.83253900	1.04882300
H	1.00213200	1.55540600	1.74889600
C	-1.22954000	3.35821400	-0.06564600
H	-1.26462600	3.47447800	-2.21401100
H	-0.94400000	3.05468400	2.04559600
H	-2.09938000	3.99230000	0.06167500
I	-1.35371800	-0.76716900	0.09256800
O	3.62168000	0.72377900	2.06620200
H	5.00945800	-0.08347500	-0.33718900
H	3.63474900	0.74135200	3.02915400
Cl	-3.62677200	-0.64881100	-0.50541000
Cl	-1.92223600	-0.36424300	2.47480400
Cl	-0.71367500	-1.18332300	-2.28307800

(a₂) Two-step hydrogen bond/ halogen bond co-catalyzed mechanism

H₂O

Entropic correction (in solution) = -76.411380 Hartree

Sum of electronic and zero-point Energies = -76.406339 Hartree

Sum of electronic and thermal Free Energies = -76.423983 Hartree

O	0.00000000	0.00000000	0.11764200
H	0.00000000	0.76109700	-0.47056700
H	0.00000000	-0.76109700	-0.47056700

Cat ICl₃-COM3-2

Entropic correction (in solution) = -2294.090920 Hartree

Sum of electronic and zero-point Energies = -2294.045061 Hartree

Sum of electronic and thermal Free Energies = -2294.101220 Hartree

C	2.33464300	0.70521100	0.68615000
C	2.22361200	-0.23614500	-0.51288700
C	3.60694700	1.45223900	0.35141500
H	2.50387000	0.05124600	1.55200900
C	1.08499700	1.51578100	0.91640900
C	3.55613100	-0.29863500	-1.23811700
H	3.36841000	-0.22132900	-2.31346800
O	1.22153900	-0.80692700	-0.89649900
C	4.26022000	0.90977800	-0.67513400
C	4.28185000	-1.62193400	-0.94767800
H	3.93093200	2.31000100	0.92795500
C	0.62151400	2.38477600	-0.07570000
C	0.33677800	1.34927800	2.08177100
H	5.20987100	1.25668400	-1.06504900
H	4.46097200	-1.73400100	0.12322300
H	3.69037700	-2.46854300	-1.30267300
H	5.24337600	-1.63018800	-1.46443800
C	-0.58954900	3.04855100	0.08163600
H	1.20113900	2.52088700	-0.98467500
C	-0.87669800	2.01307000	2.24058600
H	0.69329000	0.67663400	2.85486700
C	-1.34720300	2.85385100	1.23561300
H	-0.95157300	3.70391000	-0.70215400
H	-1.45917200	1.86260400	3.14247200
H	-2.29861600	3.36032000	1.35167800
I	-1.30024900	-0.60609300	-0.40207400
Cl	-3.61412800	-0.54330500	-0.06499300
Cl	-1.55133800	0.62102200	-2.52149300
Cl	-1.04587700	-1.90977500	1.73572800
O	2.29404200	-2.36147500	1.63602700
H	1.33109300	-2.34966100	1.70245900
H	2.49794800	-3.17835700	1.16997200

Cat ICl₃-TS3-2

Imaginary frequency -465.41 cm⁻¹

Entropic correction (in solution) = -2294.04896 Hartree

Sum of electronic and zero-point Energies = -2294.007035 Hartree

Sum of electronic and thermal Free Energies = -2294.059244 Hartree

C	2.05105800	0.93831700	-0.13556500
C	1.96239400	-0.35968500	-0.63658300
C	3.46709500	1.36588300	-0.30190600
H	2.24872900	0.17814600	1.20843600
C	0.88260300	1.84911300	0.03072900
C	3.33722100	-0.83872700	-1.05997500

H	3.27072500	-1.00297500	-2.14504900
O	0.96018000	-1.17286600	-0.71772700
C	4.20594700	0.35998200	-0.78690200
C	3.76835100	-2.14509200	-0.38936100
H	3.81237900	2.35520400	-0.02829600
C	0.18034100	2.24488100	-1.11320700
C	0.41732700	2.26187100	1.28179200
H	5.27102500	0.37376600	-0.97761900
H	3.86316900	-2.01532400	0.69081400
H	3.03534000	-2.92944600	-0.58446400
H	4.73461600	-2.46618100	-0.78186500
C	-0.98739700	2.99136600	-1.00573900
H	0.54039600	1.93443900	-2.08859800
C	-0.75226300	3.00796900	1.39165500
H	0.95088500	1.98632400	2.18539300
C	-1.46422600	3.36179400	0.24917500
H	-1.53319400	3.26930100	-1.90020900
H	-1.11305700	3.30165800	2.37057100
H	-2.38477100	3.92716100	0.33627900
I	-1.13915800	-0.85572500	-0.13507800
Cl	-3.50744100	-0.65551900	0.44095800
Cl	-1.61932700	-0.51228800	-2.47375400
Cl	-0.47146000	-1.24934900	2.41149100
O	2.33598100	-0.35514400	2.21023900
H	1.41520600	-0.69422000	2.42840400
H	2.65382200	0.22524800	2.92274500

Cat ICl₃-INT3-2

Entropic correction (in solution) = -2294.052130 Hartree

Sum of electronic and zero-point Energies = -2294.010560 Hartree

Sum of electronic and thermal Free Energies = -2294.062421 Hartree

C	1.79832000	1.06256700	-0.55345600
C	1.59840500	-0.15805200	-1.13392000
C	3.24389800	1.21671500	-0.35910000
H	2.17439600	-0.95384300	1.89574300
C	0.78557600	2.05301800	-0.15731500
C	2.92210800	-0.84108300	-1.40139100
H	3.07802400	-0.81307300	-2.49075000
O	0.47531600	-0.78817500	-1.45928200
C	3.90990700	0.12335800	-0.80023700
C	2.99682900	-2.29997600	-0.94914900
H	3.69675000	2.11519400	0.04720800
C	-0.29312100	2.34065100	-1.00148900
C	0.87117600	2.71285100	1.07406100
H	4.98438400	0.00222500	-0.85272000

H	2.89686000	-2.40432700	0.13293000
H	2.19330600	-2.87396800	-1.41348200
H	3.95246900	-2.73639400	-1.24495800
C	-1.27965900	3.23805200	-0.60912500
H	-0.35457700	1.85331700	-1.96857500
C	-0.11102500	3.61708800	1.46262800
H	1.70381600	2.50268400	1.73850400
C	-1.19405600	3.87625300	0.62575700
H	-2.11514600	3.44034300	-1.26988500
H	-0.03677500	4.11343000	2.42353500
H	-1.96437500	4.57386300	0.93313100
I	-1.14309700	-0.90558500	-0.10933800
Cl	-3.14653900	-1.10097500	1.38651600
Cl	-2.52970100	-0.20748700	-1.91264400
Cl	0.57155100	-1.72783800	1.87134200
O	3.15337200	-0.56383000	1.96404900
H	3.20019300	0.09014000	2.68537800
H	3.43489900	-0.12912700	1.08853400

Cat ICl₃-TS4-2

Imaginary frequency -749.23 cm⁻¹

Entropic correction (in solution) = -2294.053010 Hartree

Sum of electronic and zero-point Energies = -2294.011056 Hartree

Sum of electronic and thermal Free Energies = -2294.063311 Hartree

C	1.72431300	1.21929100	-0.52445100
C	1.65683900	-0.03066900	-1.11821100
C	3.10725600	1.49302800	-0.28111000
H	2.49906700	-0.86274800	1.82286600
C	0.58956200	2.07823100	-0.14485700
C	3.04430200	-0.58161200	-1.34535600
H	3.26108400	-0.43724500	-2.41496700
O	0.61658800	-0.75438000	-1.42686100
C	3.91415000	0.42751700	-0.61701500
C	3.19469300	-2.06686900	-1.02286100
H	3.46126200	2.43023900	0.13746900
C	-0.43879800	2.33368900	-1.05806800
C	0.49817100	2.60979500	1.14577500
H	4.98755700	0.49564300	-0.74877100
H	2.89971100	-2.29966200	0.00222200
H	2.56430400	-2.65766700	-1.68832900
H	4.23219900	-2.37656400	-1.16112100
C	-1.54905300	3.07988900	-0.67936300
H	-0.36980900	1.93307700	-2.06405200
C	-0.60881100	3.36242900	1.52164600
H	1.28691200	2.40679600	1.86376300

C	-1.63943100	3.59165700	0.61259200
H	-2.34625900	3.25705700	-1.39237000
H	-0.67550500	3.75749600	2.52890800
H	-2.50865100	4.16663400	0.91016900
I	-1.07664800	-0.94297100	-0.09351300
Cl	-3.04464400	-1.27218200	1.36944900
Cl	-2.47399600	-0.42791600	-1.98106400
Cl	0.62698300	-1.48787900	1.89244900
O	3.46267400	-0.58241900	1.80876300
H	3.62579900	-0.00216900	2.57200400
H	3.70957300	-0.04167400	0.82667500

Cat ICl₃-INT4-2

Entropic correction (in solution) = -2294.104520 Hartree

Sum of electronic and zero-point Energies = -2294.058970 Hartree

Sum of electronic and thermal Free Energies = -2294.114817 Hartree

C	2.05398600	1.05969600	-0.48232400
C	1.94189100	-0.27337000	-1.08203800
C	3.35763900	1.30054400	-0.24765200
H	2.37742600	-0.39365600	2.11069000
C	0.87221900	1.88332900	-0.16241500
C	3.32322600	-0.83491200	-1.33971500
H	3.45917600	-0.83498100	-2.42710200
O	0.90236800	-0.89371500	-1.31390300
C	4.26045000	0.19329600	-0.68632000
C	3.45296700	-2.25987500	-0.80646800
H	3.73088100	2.20526600	0.22056000
C	-0.01968700	2.23949200	-1.17917700
C	0.58223300	2.22815600	1.15985400
H	5.03703100	0.56250800	-1.36073100
H	3.28790900	-2.27580200	0.27409700
H	2.72414100	-2.91829700	-1.28144400
H	4.45420500	-2.64558300	-1.00706200
C	-1.19670200	2.91321500	-0.87386800
H	0.20266700	1.97149000	-2.20708600
C	-0.60097000	2.89303800	1.46422600
H	1.26951100	1.94439200	1.94980500
C	-1.49577100	3.22710000	0.44983800
H	-1.88788200	3.17682200	-1.66593400
H	-0.82984600	3.14016600	2.49447000
H	-2.42287500	3.73449900	0.69074800
I	-1.25330800	-0.79013100	-0.07477400
Cl	-3.25112800	-0.92006500	1.16468900
Cl	-2.49834600	-0.37392400	-2.15308800
Cl	0.09949600	-1.23577700	2.01505800

O	3.30894900	-0.26015900	2.32557800
H	3.43546600	-0.74276300	3.14892900
H	4.75772400	-0.22835100	0.19286300

CatICl₃(b) – The direct proton transfer mechanism

CatICl₃-INT2

Entropic correction (in solution) = -2217.67542 Hartree

Sum of electronic and zero-point Energies = -2217.633810 Hartree

Sum of electronic and thermal Free Energies = -2217.685663 Hartree

C	2.42275300	0.69648900	0.68397100
C	2.31514800	-0.66282900	-0.01093200
C	3.80437100	1.14028200	0.26005600
H	2.39896100	0.49590100	1.76429600
C	1.27301400	1.61273000	0.33787500
C	3.67126800	-1.08012300	-0.54969100
H	3.55018200	-1.37967100	-1.59599900
O	1.30082200	-1.31645000	-0.14602000
C	4.46714200	0.19020600	-0.39755600
C	4.23199900	-2.26613500	0.24976500
H	4.18289100	2.12604700	0.50079600
C	0.99430000	1.90444900	-1.00063700
C	0.43727700	2.11496500	1.33440900
H	5.47942500	0.28255700	-0.77318800
H	4.31389200	-2.01285700	1.30952400
H	3.58560000	-3.13899200	0.14292800
H	5.22626500	-2.52200600	-0.12035800
C	-0.12615500	2.65469700	-1.33708800
H	1.64308900	1.51941200	-1.78301900
C	-0.68499600	2.86743600	0.99878000
H	0.64945500	1.89116600	2.37427300
C	-0.97530900	3.12735300	-0.33760500
H	-0.34742600	2.85605100	-2.37884800
H	-1.33866400	3.23730400	1.78059100
H	-1.85742800	3.69964000	-0.60106100
I	-1.24526000	-0.73534600	-0.01669000
Cl	-3.54694300	-0.33332300	0.03286500
Cl	-1.29181200	-0.69873100	-2.49705800
Cl	-1.21294600	-0.81187100	2.46682300

Cat ICl₃-TS3'

Imaginary frequency -1000.27 cm⁻¹

Entropic correction (in solution) = -2217.600520 Hartree

Sum of electronic and zero-point Energies = -2217.559193Hartree

Sum of electronic and thermal Free Energies = -2217.610711 Hartree

C	2.15539300	0.61856600	0.03535900
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C	1.83286300	-0.63692300	0.53263700
C	3.57460400	0.52232700	-0.49861500
H	3.50954200	0.73259500	0.68210800
C	1.33677500	1.83468400	0.01089400
C	2.96960400	-1.58851700	0.25481600
H	2.56883700	-2.06199600	-0.67497200
O	0.73057700	-1.05356000	1.06253800
C	4.04038500	-0.76827400	-0.33149100
C	3.29096800	-2.65909300	1.28473900
H	4.07405400	1.33572900	-1.00737300
C	1.36203400	2.68491400	-1.09999100
C	0.48111200	2.12585900	1.08045700
H	5.02281800	-1.13135700	-0.60255500
H	3.68125800	-2.19883800	2.19392800
H	2.38693800	-3.21370000	1.53513100
H	4.03464900	-3.35456800	0.89439200
C	0.53900300	3.80440900	-1.14141100
H	2.00921600	2.45459500	-1.93951500
C	-0.34595500	3.24034600	1.03030300
H	0.46057300	1.47122200	1.94483100
C	-0.31901100	4.08147900	-0.08008600
H	0.55786800	4.45369000	-2.00901000
H	-1.01328800	3.45095600	1.85804400
H	-0.96692600	4.94944200	-0.11891300
I	-1.20216300	-0.77881300	0.00671100
Cl	-3.36020200	-0.58361600	-1.15592000
Cl	0.00787600	-1.50911700	-2.08626700
Cl	-2.17485900	-0.06849500	2.17879000

Cat ICl₃-INT3'

Entropic correction (in solution) = -2217.689290 Hartree

Sum of electronic and zero-point Energies = -2217.647410Hartree

Sum of electronic and thermal Free Energies = -2217.699517 Hartree

C	2.30164400	0.84326300	-0.09773200
C	2.23485700	-0.59807500	0.18600000
C	3.53231000	1.11989800	-0.56293700
H	5.34676100	0.11282200	-0.03610000
C	1.14316900	1.73504600	0.10224300
C	3.59594100	-1.22148200	-0.03604600
H	3.46816700	-2.03385900	-0.75645100
O	1.24302500	-1.23225200	0.53877700
C	4.43659900	-0.07260200	-0.61462700
C	4.13939200	-1.78567200	1.27973600
H	3.85699600	2.11005600	-0.86578200
C	0.54796600	2.38819300	-0.97944300

C	0.57224400	1.84589800	1.37421300
H	4.74982400	-0.26605600	-1.64478100
H	4.25664600	-0.98735900	2.01786800
H	3.46236800	-2.53931200	1.68527800
H	5.11463100	-2.24648500	1.11385500
C	-0.62036500	3.12003200	-0.79473500
H	0.98048100	2.28742600	-1.96862900
C	-0.58921900	2.58720700	1.55824400
H	1.02967200	1.33376100	2.21479700
C	-1.19499200	3.21270600	0.47126900
H	-1.08964600	3.60742800	-1.64157700
H	-1.03177900	2.65951400	2.54483400
H	-2.11275100	3.77248200	0.61025600
I	-1.17044000	-0.77505800	-0.06589800
Cl	-3.39588100	-0.53970400	-0.78120600
Cl	-0.37762600	-0.76515800	-2.42986400
Cl	-1.90528900	-0.80812500	2.30469900

Pro

Entropic correction (in solution) = -539.46642 Hartree

Sum of electronic and zero-point Energies = -539.438861 Hartree

Sum of electronic and thermal Free Energies = -539.476977 Hartree

C	0.40092100	0.41327700	-0.01581800
C	1.41278900	-0.60016200	-0.43020700
C	1.04536900	1.54569200	0.30863900
C	-1.05304700	0.17450600	0.01471400
C	2.79712200	0.03828300	-0.34726800
H	3.19906000	0.05269800	-1.36468700
O	1.19679900	-1.73984500	-0.77541800
C	2.53604200	1.46482100	0.15760800
C	3.71727000	-0.78779900	0.54933200
H	0.55311400	2.44429500	0.66676800
C	-1.94448400	1.20878800	-0.29480300
C	-1.56799900	-1.07849400	0.36541700
H	3.02618600	1.65593500	1.11815900
H	3.80230700	-1.80959000	0.17496500
H	4.71565600	-0.34681000	0.58541800
H	3.32273900	-0.82564600	1.56899800
C	-3.31751300	1.00072300	-0.24077900
H	-1.55567000	2.17684300	-0.59251600
C	-2.94303400	-1.28404800	0.41871600
H	-0.88968000	-1.88900800	0.60000000
C	-3.82152100	-0.24750000	0.11702700
H	-3.99466300	1.81098900	-0.48612700
H	-3.32840000	-2.25842400	0.69690000

H	-4.89226100	-0.41200000	0.15528600
H	2.89572400	2.23095500	-0.53528900