

Supplementary Material

Hydrogen and halogen rearrangements in imidazoles: Hydrogen, fluorine, chlorine and bromine shifts

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Table S1. Optimized geometries of the stationary points (Å), Enthalpy (au) and number of imaginary frequencies obtained with the G4 method.**1 (X=F)**

G4 Enthalpy=-325.231394
NIMAG= 0
N,0.,0.0132524472,-1.1019540421
C,0.,-1.0829944239,-0.3045361437
N,0.,-0.6974010504,0.9543614629
C,0.,0.6770985203,0.936072025
C,0.,1.157424672,-0.3505204241
H,0.,-2.0870163906,-0.6962548325
H,0.,1.2497969995,1.8505261706
H,0.,2.1346365507,-0.8000001831
F,0.,-0.0080383639,-2.4570985512

2 (X=F)

G4 Enthalpy=-325.289643
NIMAG= 0
N,0.5475678992,0.5857105666,1.1985799714
C,0.1158763296,1.3123032024,0.
N,0.5475678992,0.5857105666,-1.1985799714
C,1.0402184982,-0.5028171283,-0.7471500664
C,1.0402184982,-0.5028171283,0.7471500664
H,-0.9850306123,1.3188567075,0.
H,1.4133099823,-1.2949861481,-1.389715697
H,1.4133099823,-1.2949861481,1.389715697
F,0.5741053908,2.5800110784,0.

3 (X=F)

G4 Enthalpy=-325.318289
NIMAG= 0
N,-1.055115153,-0.0746453273,0.
C,0.0920271441,0.6495372433,0.
N,1.1695689401,-0.0662600684,0.
C,0.7035628988,-1.3723222481,0.
C,-0.6607844799,-1.4069163201,0.
H,-1.9919054546,0.2913047047,0.
H,1.3903304304,-2.2038726684,0.
H,-1.3770094964,-2.2106043014,0.
F,0.0333792205,1.9637846457,0.

4 (X=F)

G4 Enthalpy=-325.284815
NIMAG= 0
N,-0.0265626814,-0.1112485037,-1.227393515
C,0.0108603012,-1.048212653,-0.3617306858
N,0.0002131225,-0.6751859728,1.0354367457
C,-0.0497983511,0.6027819478,0.9983400483

C,0.021423438,1.1093893814,-0.4352161558
H,0.043891134,-2.1022672853,-0.6147131321
H,-0.0708564203,1.2251856721,1.8871986235
H,1.0093560463,1.5720986017,-0.5992551012
F,-0.9413568692,2.0061426318,-0.7733629777

5 (X=F)

G4 Enthalpy=-325.309723

NIMAG= 0

N,1.0520824871,-0.1375854124,0.
C,0.5609614131,-1.4183457465,0.
N,-0.7477842644,-1.4340659736,0.
C,-1.1499114695,-0.1121828835,0.
C,-0.0453030976,0.6844135919,0.
H,1.2109731942,-2.2799218254,0.
H,-2.1870723759,0.1793041851,0.
H,2.0129627184,0.1618686494,0.
F,0.1126168246,1.995330535,0.

6 (X=F)

G4 Enthalpy=-325.317385

NIMAG= 0

N,1.1520492545,0.0028494038,0.
C,0.7897071052,-1.2645014542,0.
N,-0.5612464699,-1.400094235,0.
C,-1.1103352822,-0.1299350388,0.
C,-0.0144150205,0.690083412,0.
H,1.4590073238,-2.1108981199,0.
H,-2.1692824172,0.0551180942,0.
H,-1.0763491977,-2.2640974757,0.
F,-0.017590716,2.0109961336,0.

7 (X=F)

G4 Enthalpy=-325.300094

NIMAG= 0

N,1.1888932039,-0.0787632618,0.
C,0.6130344951,-1.3815111584,0.
N,-0.6667710911,-1.4858734727,0.
C,-1.1356439606,-0.104931648,0.
C,0.1546874018,0.6659827706,0.
H,1.2779113599,-2.2381859927,0.
H,-1.751094414,0.107858606,-0.8819942207
H,-1.751094414,0.107858606,0.8819942207
F,0.1994350789,1.9742528711,0.

8 (X=F)

G4 Enthalpy=-325.299870

NIMAG= 0

N,1.1415030046,-0.2058417677,0.
C,0.4390777839,-1.4809764699,0.
N,-1.0096030984,-1.2601087366,0.
C,-1.1387390541,0.0137879917,0.
C,0.1965798754,0.6421259424,0.
H,0.7175781364,-2.0686702652,-0.8829177428
H,-2.0933324186,0.5287522178,0.
H,0.7175781364,-2.0686702652,0.8829177428
F,0.3669076845,1.9456639927,0.

TS1 (X=F)

G4 Enthalpy=-325.175189

NIMAG= 1

N,0.26449331,0.43590409,1.1294329624
C,-0.1505409019,1.0599746265,-0.1319634675
N,0.2933000144,0.463193467,-1.2017355953
C,1.0870691435,-0.5378633842,-0.6807323692
C,1.1254602661,-0.5134079671,0.7076977652
H,-0.8781676596,1.8563004672,-0.1131552296
H,1.551855439,-1.2620024625,-1.3405921113
H,1.6365888183,-1.1674006225,1.3957058409
F,1.0627573,1.9963269056,1.0129890745

TS2 (X=F)

G4 Enthalpy=-325.235262

NIMAG= 1

N,0.4944848505,0.7197101786,1.086719487
C,0.3698181044,1.3977464017,-0.1725174404
N,0.7770421347,0.6879050596,-1.2320068597
C,1.1058911173,-0.5010201462,-0.69875022
C,0.9172280354,-0.507183083,0.6852874834
H,-0.6507403946,0.9220336258,0.4640438525
H,1.4366447258,-1.3189377319,-1.3251031699
H,0.9872415577,-1.3240439708,1.3874658156
F,0.2695337363,2.7107752349,-0.1951389484

TS3 (X=F)

G4 Enthalpy=-325.148795

NIMAG= 2.2171

N,0.3172684897,-0.1045710459,-1.1514840897
C,-0.0814367322,-1.0861456931,-0.3220672844
N,-0.1548972872,-0.7193155476,0.9641382152
C,0.0734717088,0.6246675174,1.0140244731
C,0.3390624978,1.0684402808,-0.2575128166
H,-0.2223844275,-2.1009988417,-0.6601012723
H,0.0443707303,1.1753933411,1.9399748906
H,0.6854104115,2.0158995636,-0.6349924809
F,-1.0695790214,0.9196005356,-1.5248566751

TS4 (X=F)

G4 Enthalpy=-325.222165

NIMAG= 1

N,0.0352655325,-0.789966601,-1.1649002761

C,-0.26549192,-1.4048757463,0.

N,0.0352655325,-0.789966601,1.1649002761

C,0.5906798921,0.3541958301,0.754137766

C,0.5906798921,0.3541958301,-0.754137766

H,-0.7278863419,-2.3871015467,0.

H,1.0759716196,1.0522272927,1.4210947997

H,1.0759716196,1.0522272927,-1.4210947997

F,-0.5709378649,1.4352714753,0.

TS5 (X=F)

G4 Enthalpy=-325.247518

NIMAG= 1

N,-0.2018423659,-0.0858950624,-1.1839455746

C,0.0349302828,-1.0604976485,-0.2986957591

N,0.1440658905,-0.7160266382,1.0012549919

C,-0.0768818058,0.6135293498,0.9960354411

C,-0.2681300462,1.0093041765,-0.4016037665

H,0.1752841913,-2.0855500479,-0.6181805986

H,-0.1083470572,1.2490367097,1.8702728014

H,0.887725478,1.1742490938,0.1750585028

F,-0.6813117074,2.1809476472,-0.8446507386

TS6 (X=F)

G4 Enthalpy=-325.229356

NIMAG= 1

N,-0.1403175893,-0.0596265081,-1.2128835891

C,0.0658156019,-1.0538636993,-0.3180632325

N,0.0727631276,-0.6953883432,0.9747054691

C,-0.1087167581,0.633152154,0.9884383566

C,-0.2069435708,1.090142756,-0.3328633289

H,0.27059835,-2.0622584407,-0.648535295

H,-0.1391298121,1.2177735215,1.8958533264

H,0.8429595901,0.7451619288,-0.9956559748

F,-0.6701014394,2.2417986008,-0.7852454616

TS7 (X=F)

G4 Enthalpy=-325.239057

NIMAG= 1

N,1.1187951548,0.0843315382,-0.4153742449

C,0.720572835,-1.2699403033,-0.0768729702

N,-0.5835628089,-1.3770812247,0.223966798

C,-1.060121439,-0.1243893196,0.1349348449

C,-0.028841826,0.7455619427,-0.21216738

H,1.3600458846,-2.0954221523,-0.3587432757

H,-2.092800601,0.1198050021,0.339378814
H,1.4640296852,-0.5039826311,0.6639766848
F,-0.0785914546,2.059932268,-0.2990992709

TS8 (X=F)

G4 Enthalpy=-325.245475
NIMAG= 2.1884
N,1.0584142205,-0.1335963614,0.2337901967
C,0.6132118654,-1.3697343241,-0.0576483898
N,-0.7798443585,-1.406061818,-0.4154543729
C,-1.1625361252,-0.1208202827,-0.240260473
C,-0.0286156632,0.6171119464,0.105447235
H,1.2545128386,-2.2053720131,-0.3048431664
H,-2.190597598,0.19289687,-0.3242849463
H,-0.3221746815,-1.8975090141,0.6811000519
F,0.009174082,1.9126057171,0.3221538647

1 (X=Cl)

G4 Enthalpy=-685.534267
NIMAG= 0
N,0.,0.0114083117,-1.0855862259
C,0.,-1.0773194855,-0.2583526457
N,0.,-0.6959043645,0.9945835837
C,0.,0.6823931308,0.975598424
C,0.,1.1530954517,-0.3080627762
H,0.,-2.0854445084,-0.6412820888
H,0.,1.2547028556,1.8903632818
H,0.,2.1339347231,-0.7502116609
Cl,0.,-0.0201071536,-2.7864544102

2 (X=Cl)

G4 Enthalpy=-685.551756
NIMAG= 0
N,0.4808136972,0.5137049684,1.1968600531
C,0.0514251017,1.2306437728,0.
N,0.4808136972,0.5137049684,-1.1968600531
C,1.0505957263,-0.539481259,-0.7435388543
C,1.0505957263,-0.539481259,0.7435388543
H,-1.0388211215,1.3165660075,0.
H,1.4660152698,-1.3061009532,-1.3900744212
H,1.4660152698,-1.3061009532,1.3900744212
Cl,0.6996904923,2.9035302705,0.

3 (X=Cl)

G4 Enthalpy=-685.581173
NIMAG= 0
N,-1.0497584541,-0.1200939225,0.
C,0.0971716453,0.6117415483,0.
N,1.1714233727,-0.1249040325,0.

C,0.7015508261,-1.4231284781,0.
C,-0.6662077143,-1.4467912189,0.
H,-1.9864082438,0.2469557481,0.
H,1.3828500488,-2.2595353209,0.
H,-1.3869926999,-2.2469491833,0.
Cl,0.0404252693,2.3327105197,0.

4 (X=Cl)

G4 Enthalpy=-685.551226

NIMAG= 0

N,0.0868899355,-0.1482651945,-1.2139442604
C,0.0143187095,-1.0839538614,-0.3440530553
N,-0.0489558848,-0.7073798672,1.0427920859
C,-0.0041987714,0.5718913036,1.0046924015
C,0.1231758286,1.0669759558,-0.4190674448
H,-0.002162819,-2.1372838371,-0.6005690693
H,-0.0380002561,1.2025787005,1.8862183509
H,1.062615916,1.6002671239,-0.5940042562
Cl,-1.1965129383,2.2138534964,-0.8527609025

5 (X=Cl)

G4 Enthalpy=-685.578712

NIMAG= 0

N,1.0456146968,-0.1818111052,0.
C,0.5632629472,-1.4588482695,0.
N,-0.7490394848,-1.4817905577,0.
C,-1.1495161668,-0.1657870179,0.
C,-0.0500009521,0.6488683698,0.
H,1.2148223809,-2.3195014577,0.
H,-2.1882215422,0.1230295651,0.
H,2.0068865658,0.1167617786,0.
Cl,0.1257169852,2.3578938145,0.

6 (X=Cl)

G4 Enthalpy=-685.581701

NIMAG= 0

N,1.1590909089,-0.0518620065,0.
C,0.7898107547,-1.3143497722,0.
N,-0.565259827,-1.4438886039,0.
C,-1.1022844319,-0.1747934236,0.
C,-0.0083972177,0.6505977084,0.
H,1.4541109736,-2.1648976724,0.
H,-2.1607226934,0.0161013968,0.
H,-1.0849960171,-2.3057585191,0.
Cl,-0.0298078702,2.3783716126,0.

7 (X=Cl)

G4 Enthalpy=-685.561178

NIMAG= 0

N,1.1646649039,-0.4385762272,0.
C,0.6903316863,-1.785067106,0.
N,-0.5774668726,-1.9781672417,0.
C,-1.1458530096,-0.6372485166,0.
C,0.0793888731,0.2386625528,0.
H,1.4188493295,-2.5882151002,0.
H,-1.7765936834,-0.4726897091,-0.8815858029
H,-1.7765936834,-0.4726897091,0.8815858029
Cl,0.0187234062,1.957581737,0.

8 (X=Cl)

G4 Enthalpy=-685.560657

NIMAG= 0

N,1.1378100807,-0.2039087081,0.
C,0.4353754935,-1.4815525564,0.
N,-1.0084522137,-1.2588018236,0.
C,-1.1396165985,0.0141249765,0.
C,0.195223236,0.6536570329,0.
H,0.7210094701,-2.0663062406,-0.8831837768
H,-2.0931405583,0.5305547625,0.
H,0.7210094701,-2.0663062406,0.8831837768
Cl,0.4260372001,2.3662283474,0.

TS1 (X=Cl)

G4 Enthalpy=-685.481929

NIMAG= 1

N,0.267070237,0.4063645237,1.1019676277
C,-0.1444328868,1.0333050815,-0.1507334863
N,0.3122844382,0.4304730283,-1.2253993595
C,1.0766137881,-0.5779445837,-0.7117732338
C,1.1030396858,-0.5547035572,0.6871606225
H,-0.934305819,1.7688877666,-0.143350689
H,1.5204593954,-1.3193965976,-1.3657417526
H,1.6213554504,-1.2017578793,1.3771429192
Cl,1.1707314406,2.3457973377,1.2083742219

TS2 (X=Cl)

G4 Enthalpy=-685.499276

NIMAG= 1

N,0.4889777796,0.664364698,1.0869616513
C,0.363720726,1.3536335997,-0.1772386869
N,0.7741014437,0.6304284448,-1.2328579503
C,1.1150180166,-0.5514624292,-0.6971563383
C,0.9183441601,-0.5562231029,0.6862109339
H,-0.6416956201,0.9000549779,0.4785155635
H,1.4605137774,-1.3656336772,-1.3206582343
H,1.003277761,-1.3690634433,1.3920226048
Cl,0.2248858232,3.080886501,-0.2157995436

TS3 (X=Cl)

G4 Enthalpy=-685.465003

NIMAG= 1

N,0.3178221228,-0.1150603264,-1.1161969906

C,-0.037802364,-1.101255552,-0.2869417609

N,-0.0982554909,-0.7372980901,1.0079728322

C,0.0841169563,0.601998392,1.0474455779

C,0.3346702658,1.0568706632,-0.2357980275

H,-0.1952622526,-2.1137819116,-0.6259463575

H,0.057163189,1.1576852647,1.9716121446

H,0.7636769717,1.9805428613,-0.5887833732

Cl,-1.2948430284,1.0632688091,-1.806241085

TS4 (X=Cl)

G4 Enthalpy=-685.512959

NIMAG= 1

N,0.0469311532,-0.823680577,-1.1622471956

C,-0.2433750228,-1.4488843752,-0.0000250647

N,0.0472127529,-0.8238198209,1.1622015588

C,0.6043362314,0.3196223716,0.753454551

C,0.6041536806,0.3197126009,-0.7534982247

H,-0.6848683841,-2.4398831934,-0.0000309403

H,1.1472587244,0.9825529934,1.4119587969

H,1.1469163296,0.9827223137,-1.4120546047

Cl,-0.8290475037,1.8078649128,0.0002411084

TS5 (X=Cl)

G4 Enthalpy=-685.512996

NIMAG= 1

N,-0.2060059548,-0.0885908712,-1.1849538156

C,0.0354678786,-1.0627631375,-0.2985692804

N,0.1523696698,-0.714722062,0.9973664375

C,-0.0634915318,0.6155203499,0.9901339988

C,-0.2762299079,1.0150044301,-0.4073658148

H,0.1707396831,-2.0885053163,-0.6183716993

H,-0.1103146964,1.2496616085,1.8648137176

H,0.868730289,1.1852586372,0.1902672701

Cl,-0.8039179296,2.5599674313,-0.985906194

TS6 (X=Cl)

G4 Enthalpy=-685.497928

NIMAG= 1

N,-0.1094847068,-0.1084379989,-1.1980877761

C,0.0833338746,-1.096810676,-0.2997452323

N,0.0750719166,-0.7389006782,0.9945510133

C,-0.0909519283,0.5883214206,1.001759866

C,-0.17843442,1.058352486,-0.3190339947

H,0.2762369406,-2.1094491597,-0.6259395117
H,-0.1297638829,1.1731457837,1.9092763831
H,0.8484539716,0.7184530651,-1.0025802071
Cl,-0.7875342655,2.5722177273,-0.8944502703

TS7 (X=Cl)

G4 Enthalpy=-685.504714

NIMAG= 1

N,1.1191834756,0.0834964924,-0.4202517597
C,0.7212985705,-1.2649106791,-0.0793438355
N,-0.5843073112,-1.3717494918,0.2270478171
C,-1.0563279768,-0.1215459835,0.1340672448
C,-0.0272995418,0.7578524979,-0.2171039937
H,1.3599302845,-2.0936058037,-0.3558421691
H,-2.0892424716,0.1240927318,0.3376031678
H,1.4627717378,-0.5105473721,0.6665239217
Cl,-0.1031560769,2.4762743082,-0.3218376335

TS8 (X=Cl)

G4 Enthalpy=-685.507421

NIMAG= 1

N,1.0598522304,-0.135994299,0.2330630547
C,0.6123445457,-1.3708661696,-0.0601468683
N,-0.7834032405,-1.4039358287,-0.4154272146
C,-1.1589978163,-0.1183787384,-0.2395996394
C,-0.0274279082,0.6257475892,0.1080917765
H,1.2528910593,-2.2078185526,-0.3059551317
H,-2.1860179614,0.1988469142,-0.3271599039
H,-0.3154676184,-1.8847390024,0.685771395
Cl,0.0105965094,2.3263281972,0.3949092218

1 (X=Br)

G4 Enthalpy=-2799.090655

NIMAG= 0

N,0.,0.0101891535,-1.0719099687
C,0.,-1.0760772431,-0.2412214058
N,0.,-0.694397765,1.0112662508
C,0.,0.6844629542,0.9924209755
C,0.,1.1515880988,-0.2917531699
H,0.,-2.0861046445,-0.6195546179
H,0.,1.2569007371,1.9071295658
H,0.,2.1335248822,-0.731832563
Br,0.,-0.0233272122,-2.9239495849

2 (X=Br)

G4 Enthalpy=-2799.101035

NIMAG= 0

N,0.4545212827,0.4875469143,1.1943564214
C,0.0220546815,1.1939730114,0.

N,0.4545212827,0.4875469143,-1.1943564214
C,1.0536015241,-0.5523326122,-0.7422127149
C,1.0536015241,-0.5523326122,0.7422127149
H,-1.0620806718,1.3217439599,0.
H,1.4874310089,-1.3070956392,-1.3901548102
H,1.4874310089,-1.3070956392,1.3901548102
Br,0.7560622141,3.0150312638,0.

3 (X=Br)

G4 Enthalpy=-2799.128405

NIMAG= 0

N,-1.0493734002,-0.1368246969,0.
C,0.0978996045,0.5950506388,0.
N,1.1707265921,-0.1441569407,0.
C,0.7006815244,-1.4416708465,0.
C,-0.6677551287,-1.4630646171,0.
H,-1.9860795006,0.2302202083,0.
H,1.3811571976,-2.278848418,0.
H,-1.3894036252,-2.2625609988,0.
Br,0.0462007861,2.4718613309,0.

4 (X=Br)

G4 Enthalpy=-2799.101456

NIMAG= 0

N,0.132220447,-0.1597486274,-1.2060827281
C,0.0139159012,-1.0955400925,-0.3381220977
N,-0.0690753378,-0.7172857611,1.0440592143
C,0.0125486236,0.5618718455,1.0071985122
C,0.1686896515,1.0484875783,-0.4109946236
H,-0.0244086983,-2.1474652602,-0.5975337551
H,-0.0229412142,1.1935021465,1.8876523696
H,1.082905743,1.617119336,-0.5932777724
Br,-1.2966853959,2.277742655,-0.8835952695

5 (X=Br)

G4 Enthalpy=-2799.127000

NIMAG= 0

N,1.0448498878,-0.198573596,0.
C,0.563166767,-1.4747567464,0.
N,-0.7497608419,-1.4989278571,0.
C,-1.1504252987,-0.1838532766,0.
C,-0.0514879531,0.6322947676,0.
H,1.21506997,-2.3352381419,0.
H,-2.1898239995,0.1027078479,0.
H,2.0063551306,0.0993250515,0.
Br,0.1315817677,2.495837071,0.

6 (X=Br)

G4 Enthalpy=-2799.129243
NIMAG= 0
N,1.1597111354,-0.0705990647,0.
C,0.789444322,-1.3326401267,0.
N,-0.5662851261,-1.4605422618,0.
C,-1.1011350693,-0.1910125841,0.
C,-0.0073539551,0.63385071,0.
H,1.452938764,-2.1839324681,0.
H,-2.1596210765,0.0001239552,0.
H,-1.0871466036,-2.3218831433,0.
Br,-0.029007811,2.5161557035,0.

7 (X=Br)

G4 Enthalpy=-2799.108043
NIMAG= 0
N,1.1632081819,-0.4570987436,0.
C,0.6889991975,-1.8037758418,0.
N,-0.5791823127,-1.9954423537,0.
C,-1.14628851,-0.6549647408,0.
C,0.0799083396,0.2215149539,0.
H,1.4165815505,-2.6077138973,0.
H,-1.7770647475,-0.489509176,-0.881368737
H,-1.7770647475,-0.489509176,0.881368737
Br,0.0263539982,2.1000896553,0.

8 (X=Br)

G4 Enthalpy=-2799.107561
NIMAG= 0
N,1.1339215948,-0.2203324302,0.
C,0.4316013733,-1.4990734398,0.
N,-1.0116455041,-1.2768592529,0.
C,-1.143265376,-0.0041126682,0.
C,0.1923325715,0.6366173598,0.
H,0.7180580728,-2.0833395242,-0.8832558259
H,-2.0966523819,0.5119566642,0.
H,0.7180580728,-2.0833395242,0.8832558259
Br,0.4528471569,2.5061723654,0.

TS1 (X=Br)

G4 Enthalpy=-2799.046430
NIMAG= 1
N,0.2678941038,0.3978510638,1.0935461789
C,-0.1435039677,1.0229837418,-0.1550668464
N,0.3141297122,0.4176021413,-1.2321331055
C,1.0730314579,-0.5919391622,-0.7217719502
C,1.0956490307,-0.568518157,0.6797158456
H,-0.9483667463,1.742794131,-0.1516734634
H,1.5167024992,-1.3337770073,-1.3749706965
H,1.6126816208,-1.2165745074,1.3701003231

Br,1.204598019,2.4606028761,1.2699005845

TS2 (X=Br)

G4 Enthalpy=-2799.047537

NIMAG= 1

N,0.4873248033,0.6453683915,1.0857978179
C,0.3622987325,1.3340258896,-0.1785213943
N,0.7733459807,0.6109316951,-1.232709593
C,1.1186284113,-0.5701280451,-0.6963064084
C,0.9196078761,-0.5749604949,0.6862916612
H,-0.6414735507,0.8915535989,0.4867353033
H,1.4698805761,-1.3824260525,-1.3190799283
H,1.0084994985,-1.3864707916,1.393220711
Br,0.2090315396,3.2190913779,-0.2254281694

TS3 (X=Br)

G4 Enthalpy=-2799.032151

NIMAG= 1

N,0.3198214248,-0.1187654627,-1.1044124571
C,-0.0248827569,-1.1057373898,-0.2750276822
N,-0.0864798718,-0.743162276,1.0223190151
C,0.0895477421,0.5947059571,1.058471133
C,0.3367635039,1.0511505229,-0.2278026862
H,-0.1825973749,-2.1187085532,-0.6133769463
H,0.0639984917,1.1520746083,1.9820207707
H,0.7844049137,1.9690953991,-0.5739109858
Br,-1.3692897028,1.1123173045,-1.9011572012

TS4 (X=Br)

G4 Enthalpy=-2799.072042

NIMAG= 1

N,0.0548405282,-0.836796081,-1.1614005385
C,-0.2362909252,-1.4639412563,-0.0000269346
N,0.0551218339,-0.8369354056,1.1613513452
C,0.61382865,0.3053892955,0.7520626936
C,0.6136464814,0.3054795197,-0.7521101914
H,-0.6777431302,-2.4546907885,-0.0000328986
H,1.1649186586,0.9630310652,1.4094469554
H,1.1645772533,0.9632001558,-1.4095490188
Br,-0.913381043,1.931470768,0.0002587325

TS5 (X=Br)

G4 Enthalpy=-2799.061442

NIMAG= 1

N,-0.2016917664,-0.1049624093,-1.1780121182
C,0.0412236921,-1.0798475159,-0.2910937895
N,0.1608932412,-0.7305104457,1.0031173415
C,-0.054314155,0.6010350829,0.9950970224

C,-0.2740535136,0.9981216719,-0.4019992232
H,0.1742393894,-2.1059701275,-0.6107846732
H,-0.1056648152,1.233786921,1.8704604981
H,0.8694361683,1.1757548215,0.202294109
Br,-0.8427207407,2.6834230711,-1.041664547

TS6 (X=Br)

G4 Enthalpy=-2799.046895

NIMAG= 1

N,-0.0984429372,-0.1235010122,-1.1911639487
C,0.088970802,-1.1128805788,-0.2929204787
N,0.0758352107,-0.7554267368,1.0012924829
C,-0.0849605884,0.5727133444,1.0081825682
C,-0.1679184843,1.043793153,-0.3120160228
H,0.278543078,-2.1263559244,-0.6186866985
H,-0.1254541701,1.1558639541,1.9166741317
H,0.8527794133,0.7075548736,-1.0066965632
Br,-0.832424824,2.6951308971,-0.9389152006

TS7 (X=Br)

G4 Enthalpy=-2799.052468

NIMAG= 1

N,1.1191293778,0.0661938922,-0.4207186612
C,0.722470482,-1.2820369053,-0.0770734185
N,-0.5829420907,-1.3886406363,0.2311074637
C,-1.0556200087,-0.1389110411,0.1355160158
C,-0.0273696442,0.7408348486,-0.2183745795
H,1.3615707876,-2.1113264136,-0.3511034165
H,-2.0889548327,0.1050585289,0.3387748552
H,1.4641888092,-0.5265025183,0.6668911523
Br,-0.1096221903,2.6146869449,-0.3341566514

TS8 (X=Br)

G4 Enthalpy=-2799.054532

NIMAG= 1

N,1.0592148406,-0.1538290241,0.2284445374
C,0.6112257453,-1.3892823595,-0.063216917
N,-0.7854295709,-1.4214624924,-0.4170235167
C,-1.1595295549,-0.1350816567,-0.2422734476
C,-0.0273117713,0.6086239958,0.1038120148
H,1.2510875004,-2.2271326412,-0.3080088996
H,-2.1865237618,0.1818405465,-0.3309742319
H,-0.315531401,-1.8986577811,0.6852487109
Br,0.0171677737,2.4641715225,0.4175384397

9 (X=H)

G4 Enthalpy=-193.964230

NIMAG= 0

C,0.,0.,1.2174064352

C,1.1795650264,0.,0.2823499242
C,0.734284318,0.,-0.987265308
C,-0.734284318,0.,-0.987265308
C,-1.1795650264,0.,0.2823499242
H,0.,-0.8757950048,1.882736765
H,0.,0.8757950048,1.882736765
H,2.2095950377,0.,0.6126960853
H,1.3445444626,0.,-1.8820488092
H,-1.3445444626,0.,-1.8820488092
H,-2.2095950377,0.,0.6126960853

TS9 (X=H)

G4 Enthalpy=-193.922242

NIMAG= 1

C,0.0599801296,0.954413354,-0.745765565
C,0.0599801296,0.954413354,0.745765565
C,0.0254749735,-0.3936213978,1.1470595386
C,0.0077429132,-1.1939200232,0.
C,0.0254749735,-0.3936213978,-1.1470595386
H,0.2115166376,1.8365183776,-1.3517351831
H,-0.9933509259,1.1847411317,0.
H,0.2115166376,1.8365183776,1.3517351831
H,-0.0283361,-0.7367413611,2.1701291126
H,-0.0713734658,-2.2738855651,0.
H,-0.0283361,-0.7367413611,-2.1701291126

9 (X=F)

G4 Enthalpy=-293.179003

NIMAG= 0

C,0.3714544964,-0.7677429553,0.0000000007
C,0.108035877,0.1302047122,1.1881423889
C,-0.1186284958,1.3724590055,0.7405782941
C,-0.1186284958,1.3724590042,-0.7405782965
C,0.108035877,0.1302047101,-1.1881423891
H,0.1665936416,-0.2116591405,2.2119144931
H,-0.2779822613,2.2566991737,1.3450745865
H,-0.2779822613,2.2566991713,-1.3450745905
H,0.1665936416,-0.2116591443,-2.2119144927
H,1.4417972214,-1.0405609507,0.0000000009
F,-0.3474560105,-1.9448052758,0.0000000017

9 (X=Cl)

G4 Enthalpy=-653.447898

NIMAG= 0

C,0.5976690225,-0.2774928015,0.0000000004
C,0.2160454977,0.568355295,1.18602954
C,-0.2433240977,1.746223487,0.7387860887
C,-0.2433240977,1.7462234849,-0.7387860937
C,0.2160454977,0.5683552915,-1.1860295417

H,0.3356452323,0.2378076679,2.2073945301
H,-0.5681576958,2.5810962532,1.3467007342
H,-0.5681576958,2.5810962494,-1.3467007416
H,0.3356452323,0.2378076615,-2.2073945308
H,1.6661736446,-0.5162335148,0.0000000007
Cl,-0.2313002677,-1.9009938187,0.0000000027

9 (X=Br)

G4 Enthalpy=-2766.998653

NIMAG= 0

C,0.7010445268,0.3197733796,0.0000000006
C,0.2600553587,1.1289946907,1.1850763731
C,-0.3061865328,2.2611058466,0.7381437172
C,-0.3061865328,2.2611058493,-0.738143709
C,0.2600553587,1.128994695,-1.185076369
H,0.4120451199,0.8125320774,2.2064506897
H,-0.7050764036,3.0624981112,1.3468492368
H,-0.7050764036,3.0624981162,-1.3468492257
H,0.4120451199,0.8125320854,-2.2064506868
H,1.7713139618,0.1007894997,0.0000000002
Br,-0.1288443466,-1.4905973637,-0.0000000027

10 (X=F)

G4 Enthalpy=-293.185892

NIMAG= 0

C,0.1607469443,-0.8322813407,0.1307424804
C,0.1544115402,-0.1029148551,1.2559047726
C,0.0875859886,1.3100634101,0.8543043863
C,0.0548895457,1.4154782785,-0.4868868432
C,0.0990934707,0.0351967296,-1.0918228989
H,0.191238943,-0.4764125804,2.2688339798
H,0.0686247316,2.1307740989,1.5604787808
H,0.0050648208,2.3236173597,-1.0703128618
H,-0.7843816176,-0.1893825355,-1.7044111437
H,0.9714434894,-0.1168887715,-1.7415180999
F,0.2131153735,-2.1549514637,0.0246874579

10 (X=Cl)

G4 Enthalpy=-653.453520

NIMAG= 0

C,0.1596570766,-0.8061583468,0.1302143985
C,0.1526452052,-0.0630535387,1.2501952083
C,0.0859866253,1.3497780613,0.856217138
C,0.0534587504,1.4509538448,-0.4852800461
C,0.0976622027,0.0714205208,-1.0887843142
H,0.1893411633,-0.4321020193,2.2655878867
H,0.0670812221,2.1695464956,1.5631919379
H,0.0036131603,2.3583735634,-1.0710981255
H,-0.7853583744,-0.1484316236,-1.7032735492

H,0.9690901335,-0.0759946465,-1.7403512369
Cl,0.2286565755,-2.532033901,0.0233808797

10 (X=Br)

G4 Enthalpy=-2767.001645

NIMAG= 0

C,0.1611492484,-0.8461580992,0.1226766651
C,0.1542996418,-0.1060238349,1.2445316307
C,0.0876989295,1.3082469639,0.8561024667
C,0.0550296353,1.4129663315,-0.4851635664
C,0.0990265167,0.0357244111,-1.0939648383
H,0.1909997534,-0.4750822704,2.2601016597
H,0.0690003571,2.1248936458,1.5667647354
H,0.0051662563,2.3221311296,-1.0684147391
H,-0.7840240029,-0.1800802771,-1.7096967847
H,0.9700983424,-0.1076567921,-1.7467675791
Br,0.2363426057,-2.7264012376,0.0073456506

11 (X=F)

G4 Enthalpy=-293.187692

NIMAG= 0

C,0.0425317383,-0.3120350511,0.
C,-1.1867935748,0.4818603177,0.
C,-0.8378786615,1.779125503,0.
C,0.6657554111,1.893058875,0.
C,1.1368082179,0.4637198693,0.
H,-2.1817776828,0.057457164,0.
H,-1.5025570383,2.6321161954,0.
H,1.025559586,2.4498686526,0.8770387622
H,1.025559586,2.4498686526,-0.8770387622
H,2.1673049722,0.1440587051,0.
F,0.0040308373,-1.6406649203,0.

11 (X=Cl)

G4 Enthalpy=-653.453760

NIMAG= 0

C,0.0398086125,-0.2814668495,0.
C,-1.187721152,0.5214472424,0.
C,-0.8380052659,1.8183505259,0.
C,0.6642587686,1.9327966853,0.
C,1.1307309948,0.5019538188,0.
H,-2.183077668,0.0991428528,0.
H,-1.5048084762,2.6698197796,0.
H,1.0314168421,2.4849328991,0.8770055396
H,1.0314168421,2.4849328991,-0.8770055396
H,2.1627624623,0.1850923589,0.
Cl,0.0117614282,-2.0185682507,0.

11 (X=Br)

G4 Enthalpy=-2767.001715
NIMAG= 0
C,0.0394333293,-0.2676994565,0.
C,-1.1885450938,0.5356119023,0.
C,-0.8380958573,1.832441035,0.
C,0.6639696996,1.9465617053,0.
C,1.1295108616,0.5155547435,0.
H,-2.1846582792,0.1152258314,0.
H,-1.5053536875,2.6835844582,0.
H,1.0329350728,2.4974902837,0.8771039146
H,1.0329350728,2.4974902837,-0.8771039146
H,2.1623973041,0.2008403351,0.
Br,0.0140149667,-2.1586671623,0.

TS9 (X=F)

G4 Enthalpy=-293.100167
NIMAG= 1
C,0.552936962,-0.4635480451,0.7569214669
C,0.094432557,0.7796314058,1.1694993953
C,-0.1878284239,1.5139148527,0.
C,0.094432557,0.7796314058,-1.1694993953
C,0.552936962,-0.4635480451,-0.7569214669
H,-0.0406631735,1.111620369,2.1862882531
H,-0.5794193011,2.5265028903,0.
H,-0.0406631735,1.111620369,-2.1862882531
H,1.0125092083,-1.2293449552,-1.3630098292
H,1.0125092083,-1.2293449552,1.3630098292
F,-0.7266680054,-1.5051785198,0.

TS10 (X=F)

G4 Enthalpy=-293.134924
NIMAG= 1
C,0.1079916839,-0.7890033936,0.1178125314
C,-0.0483839047,0.0700889236,1.2196651
C,-0.1041123499,1.3706108346,0.7110750079
C,-0.0065117615,1.3628091664,-0.6873516405
C,0.1192933803,0.0299230382,-1.1174519132
H,-0.0801505619,-0.2411782527,2.2522437148
H,-0.1434566809,2.2642753792,1.3204830677
H,0.0612317925,2.2285452714,-1.3291767828
H,0.1125131548,-0.3874300448,-2.1133161632
H,1.2136985412,-0.4485446012,-0.4904835151
F,-0.0102800637,-2.1177980107,0.1165005901

TS11 (X=F)

G4 Enthalpy=-293.140193
NIMAG= 2.2656
C,0.2329471502,-0.8053106406,0.0862515514
C,0.1570166942,-0.0266742434,1.2374975632
C,0.0712698543,1.3195332808,0.8603212827

C,0.0853371667,1.4048219115,-0.5422061984
C,0.1895359114,0.0031140951,-1.059216624
H,0.1034946424,-0.4151130846,2.2449271913
H,-0.0381830437,2.1589364622,1.5313862197
H,0.1892297198,2.2809977486,-1.1649604159
H,-0.9169500264,0.7063421432,-1.0091357001
H,0.3754335586,-0.2737424188,-2.0855464434
F,0.2761268125,-2.1380373439,0.0570799533

TS12 (X=F)

G4 Enthalpy=-293.144715

NIMAG= 1

C,-0.0425134824,-0.2762596653,0.
C,-0.0344330998,0.5014353204,-1.1576070025
C,-0.0382884718,1.8458432868,-0.742651101
C,-0.0382884718,1.8458432868,0.742651101
C,-0.0344330998,0.5014353204,1.1576070025
H,0.0214417523,0.1390532062,-2.1721022366
H,-0.1921552443,2.728770516,-1.3462719889
H,-0.1921552443,2.728770516,1.3462719889
H,1.0252856594,2.0861559236,0.
H,0.0214417523,0.1390532062,2.1721022366
F,0.0180443186,-1.6058506078,0.

TS9 (X=Cl)

G4 Enthalpy=-653.396882

NIMAG= 1

C,0.5771149947,-0.4309021632,0.7594707955
C,0.1060825819,0.8065779629,1.1662846368
C,-0.1704289146,1.5488861512,0.
C,0.1060825819,0.8065779629,-1.1662846368
C,0.5771149947,-0.4309021632,-0.7594707955
H,-0.0342469708,1.1365339349,2.1835067703
H,-0.5389775482,2.5691727224,0.
H,-0.0342469708,1.1365339349,-2.1835067703
H,1.0834031821,-1.1728258801,-1.357677891
H,1.0834031821,-1.1728258801,1.357677891
Cl,-1.0107857315,-1.8648698073,0.

TS10 (X=Cl)

G4 Enthalpy=-653.404469

NIMAG= 1.2560

C,0.1115561055,-0.7975299122,0.1185469116
C,-0.0481941202,0.0705615681,1.2164411134
C,-0.1042872194,1.3714887296,0.7129570745
C,0.0006822031,1.3631510296,-0.6846918762
C,0.1292032644,0.0324089606,-1.1159902802
H,-0.0764963354,-0.2394978322,2.2496330215
H,-0.1535184793,2.2638763008,1.323624095
H,0.0560088831,2.228740574,-1.3285740647

H,0.1167362132,-0.382323607,-2.1127001117
H,1.2036281978,-0.4620847262,-0.5049676776
Cl,-0.0512487627,-2.5307669049,0.1253029044

TS11 (X=Cl)

G4 Enthalpy=-653.409024

NIMAG= 2.6053

C,0.2337735599,-0.8111401035,0.0848559456
C,0.1564633279,-0.0235720044,1.2359095029
C,0.0705083436,1.3207688199,0.8622345804
C,0.090607441,1.4033628621,-0.5424317013
C,0.1954880106,0.007178147,-1.0556706133
H,0.1056367099,-0.4100474307,2.2442129351
H,-0.0411816907,2.1603723355,1.5326724484
H,0.1848805611,2.2804834032,-1.1663116221
H,-0.9144574781,0.705207702,-1.0097868107
H,0.3714737816,-0.2698945101,-2.0839664829
Cl,0.2835169032,-2.5475846909,0.045656348

TS12 (X=Cl)

G4 Enthalpy=-653.411076

NIMAG= 1

C,-0.0384190581,-0.2792845925,0.
C,-0.0358529366,0.5046700832,-1.1559006671
C,-0.0425904512,1.848979947,-0.7438187557
C,-0.0425904512,1.848979947,0.7438187557
C,-0.0358529366,0.5046700832,1.1559006671
H,0.0146037829,0.1442026019,-2.1713502609
H,-0.1853743684,2.7324419162,-1.349612435
H,-0.1853743684,2.7324419162,1.349612435
H,1.0193817888,2.0711806834,0.
H,0.0146037829,0.1442026019,2.1713502609
Cl,0.0522445056,-2.0176900973,0.

TS9 (X=Br)

G4 Enthalpy=-2766.957765

NIMAG= 1

C,0.585832792,-0.4206674245,0.7590756296
C,0.1108416365,0.815618736,1.1650846285
C,-0.1661903888,1.5599518958,0.
C,0.1108416365,0.815618736,-1.1650846285
C,0.585832792,-0.4206674245,-0.7590756296
H,-0.0280709184,1.1455926283,2.1826894515
H,-0.5321649988,2.5808844465,0.
H,-0.0280709184,1.1455926283,-2.1826894515
H,1.1018101177,-1.1559394082,-1.3576400967
H,1.1018101177,-1.1559394082,1.3576400967
Br,-1.0979564888,-1.9780886321,0.

TS10 (X=Br)

G4 Enthalpy=-2766.953602

NIMAG= 1.2269

C,0.1134270575,-0.7837651904,0.1195445062
C,-0.0466412891,0.084454816,1.2161747477
C,-0.1043510887,1.3861074531,0.7125293833
C,0.0030836091,1.3774662376,-0.6842283035
C,0.1344448368,0.0461178443,-1.1153712404
H,-0.073648734,-0.2227318388,2.2502763781
H,-0.1571572187,2.2781902108,1.3234601543
H,0.0546574152,2.242699078,-1.3290566645
H,0.1188858168,-0.3666229459,-2.1128529167
H,1.2047761963,-0.452319212,-0.5120967111
Br,-0.0634066511,-2.6715722727,0.1312017767

TS11 (X=Br)

G4 Enthalpy=-2766.957578

NIMAG= 2.6899

C,0.2355148099,-0.7974651219,0.085500943
C,0.1564796569,-0.0095342874,1.2363021932
C,0.068987154,1.334777196,0.8624234932
C,0.0899365263,1.4165452187,-0.5424695887
C,0.1961967591,0.0206277004,-1.0548635962
H,0.106764922,-0.3931616238,2.2457368093
H,-0.0439759507,2.1744091323,1.5326880541
H,0.1816242702,2.2937317788,-1.1668806301
H,-0.9148875996,0.7169547527,-1.0107013348
H,0.3717051741,-0.2544048121,-2.0838536823
Br,0.2883637478,-2.6873454035,0.0434918694

TS12 (X=Br)

G4 Enthalpy=-2766.959227

NIMAG= 1

C,-0.0406963512,-0.264961171,0.
C,-0.0369916662,0.5184505837,-1.1558825582
C,-0.0429995353,1.8632074951,-0.7438794866
C,-0.0429995353,1.8632074951,0.7438794866
C,-0.0369916662,0.5184505837,1.1558825582
H,0.0114075027,0.1605622791,-2.1723156072
H,-0.1829575451,2.7466989831,-1.3504050461
H,-0.1829575451,2.7466989831,1.3504050461
H,1.0189520871,2.0797349469,0.
H,0.0114075027,0.1605622791,2.1723156072
Br,0.0596060415,-2.1578173666,0.

Table S2. Experimental values of the atomic heat of formation, ΔH_f° gas, used in this article

Atom	ΔH_f° gas (kJ/mol)
H	218.00
C	716.68
N	472.68
F	79.38
Cl	121.30
Br	111.87

Source: NIST Chemistry WebBook, NIST Standard Reference Database Number 69, <https://webbook.nist.gov/chemistry/>, visited on 10/10/2023

Table S3. Average ΔH for compounds **1-8** and Bond dissociation energies, BDE, of model compounds (kJ mol^{-1})

Bonds	ΔH	BDE	Csp ²	Csp ³
Csp ² - F	-204.0	-467.4	1	0
Csp ² - Cl	-100.9	-352.3	1	0
Csp ² - Br	-77.2	-292.9	1	0
Csp ³ - F	-146.6	-517.6	0	1
Csp ³ - Cl	-45.2	-396.5	0	1
Csp ³ - Br	-27.8	-333.2	0	1
N-F	0.0	-286.6	0	0
N-Cl	0.0	-253.1	0	0
N-Br	0.0	----	0	0

Source of the BDE: Luo, Y. R. Comprehensive Handbook of Chemical Bond Energies, CRC Press, Taylor & Francis Group, Boca Raton, USA

$$\Delta H = (188 \pm 25) + (0.70 \pm 0.08) \text{ BDE} - (57 \pm 16) \text{ Csp}^2 + (28 \pm 18) \text{ Csp}^3, n = 8, R^2 = 0.975 \text{ (Eq. 17)}$$

Figure S1. Evolution of $-H_{\text{BCP}}$ (au) with the interatomic distances (\AA). The fitted exponential relationships are indicated.

