10.1071/CH19237_AC

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Supplementary Material

Elimination of ethene from 1,2-diiodoethane induced by N-heterocyclic carbene halogen bonding

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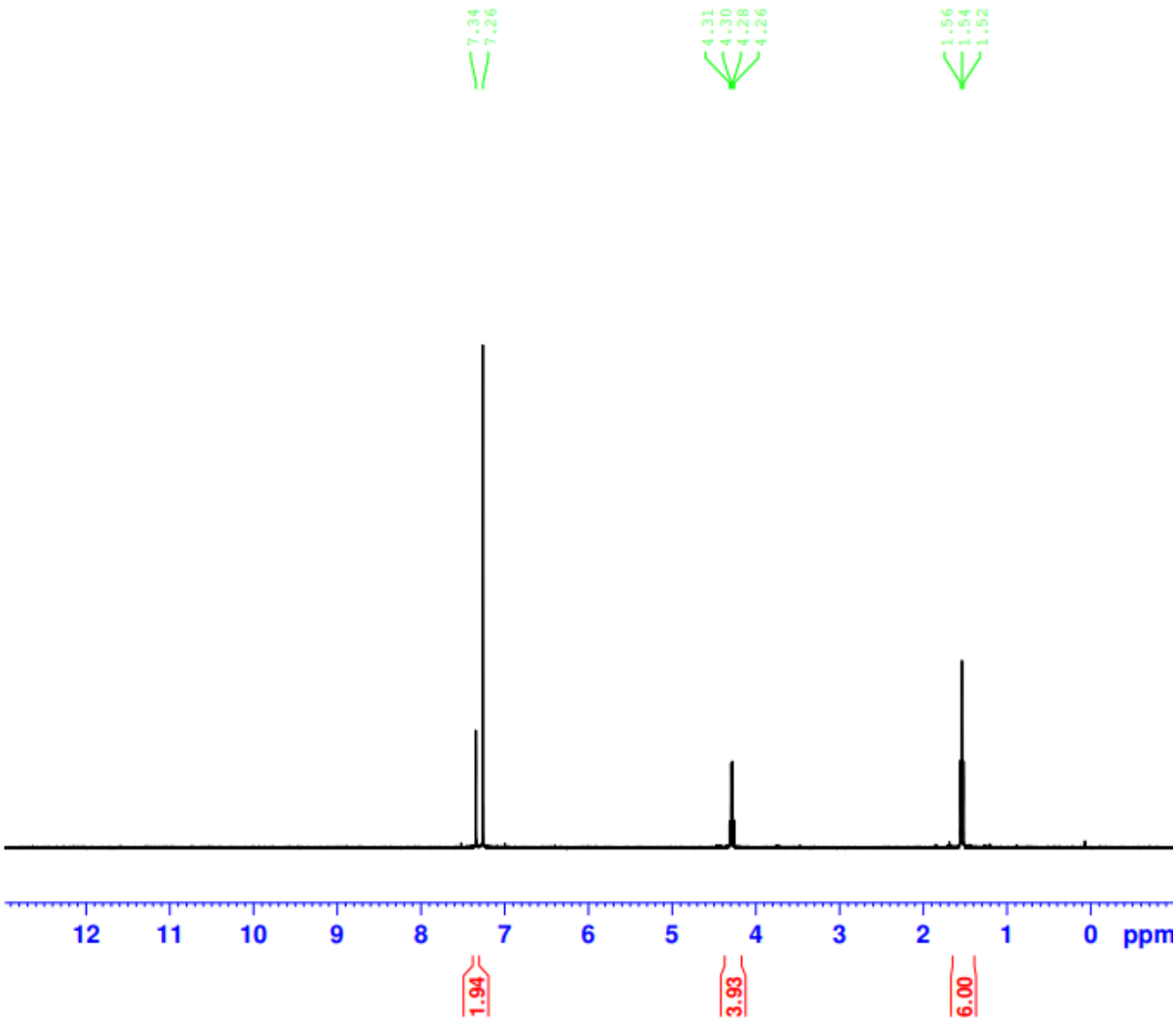

Figure S1. Proton-NMR spectrum of 1,3-diethyl-2-iodoimidazolium iodide in $CDCl_3$.

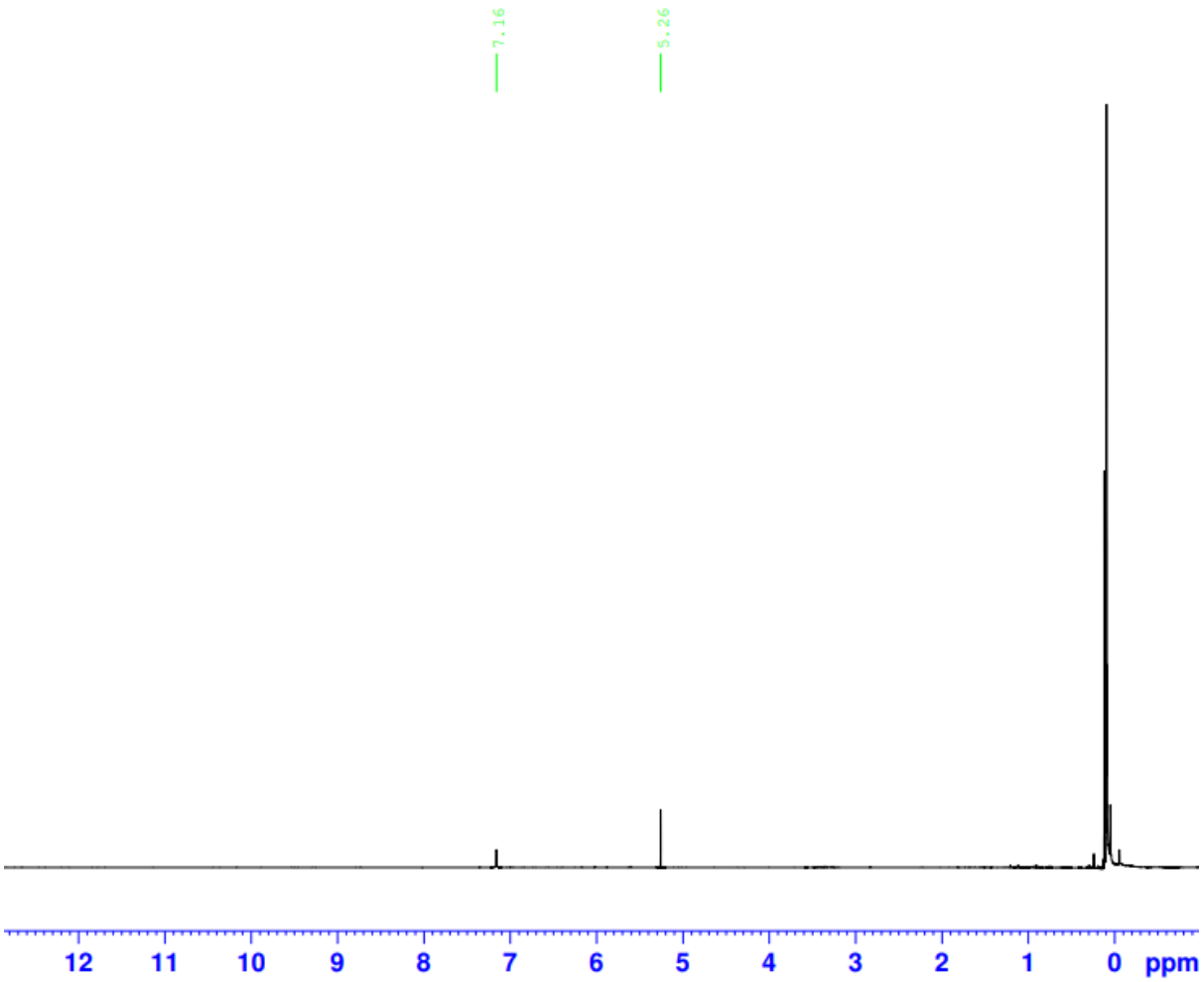

Figure S2. Proton-NMR spectrum of ethylene in C_6D_6.

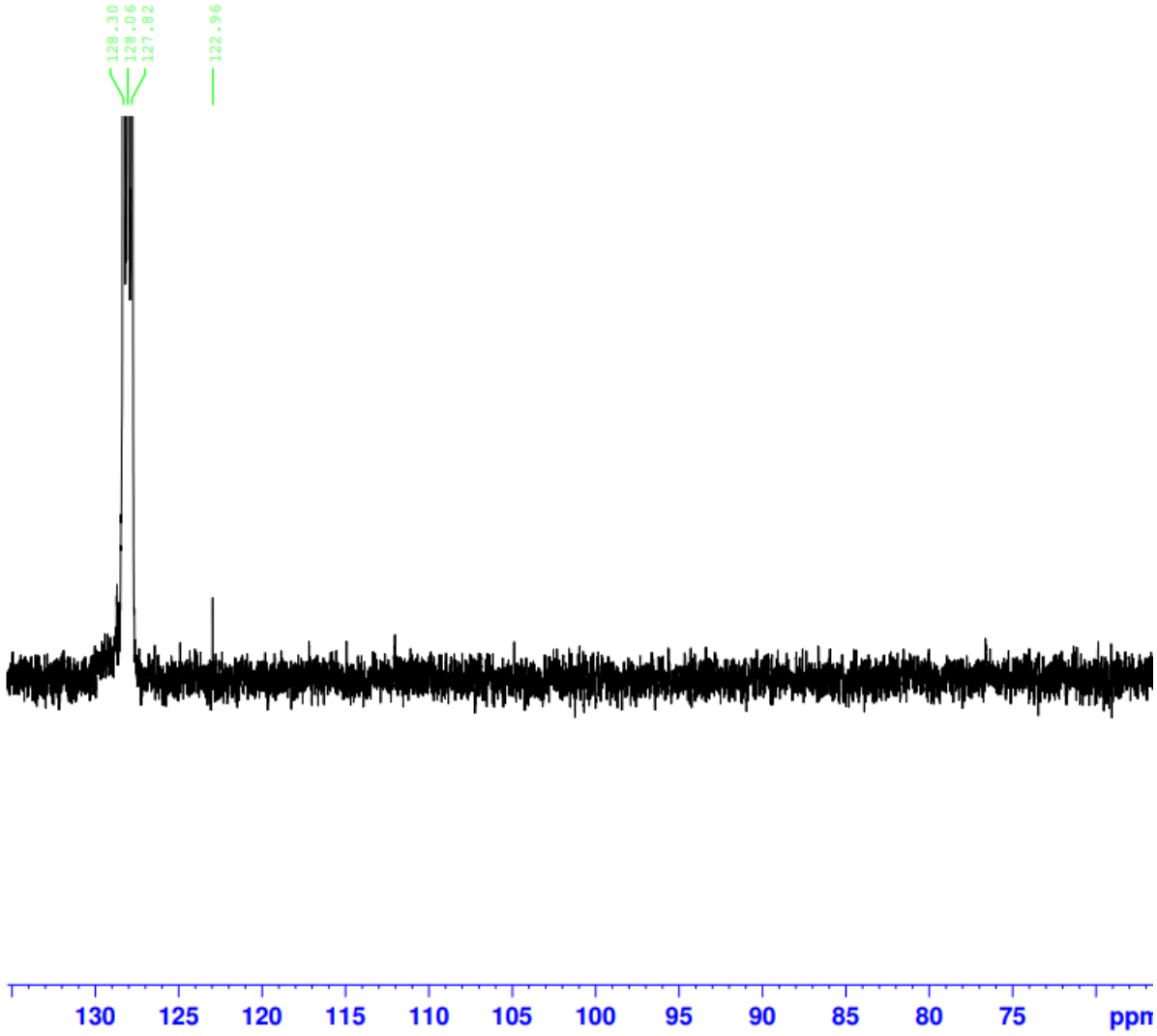

Figure S3. Carbon-NMR spectrum of ethylene in C_6D_6.

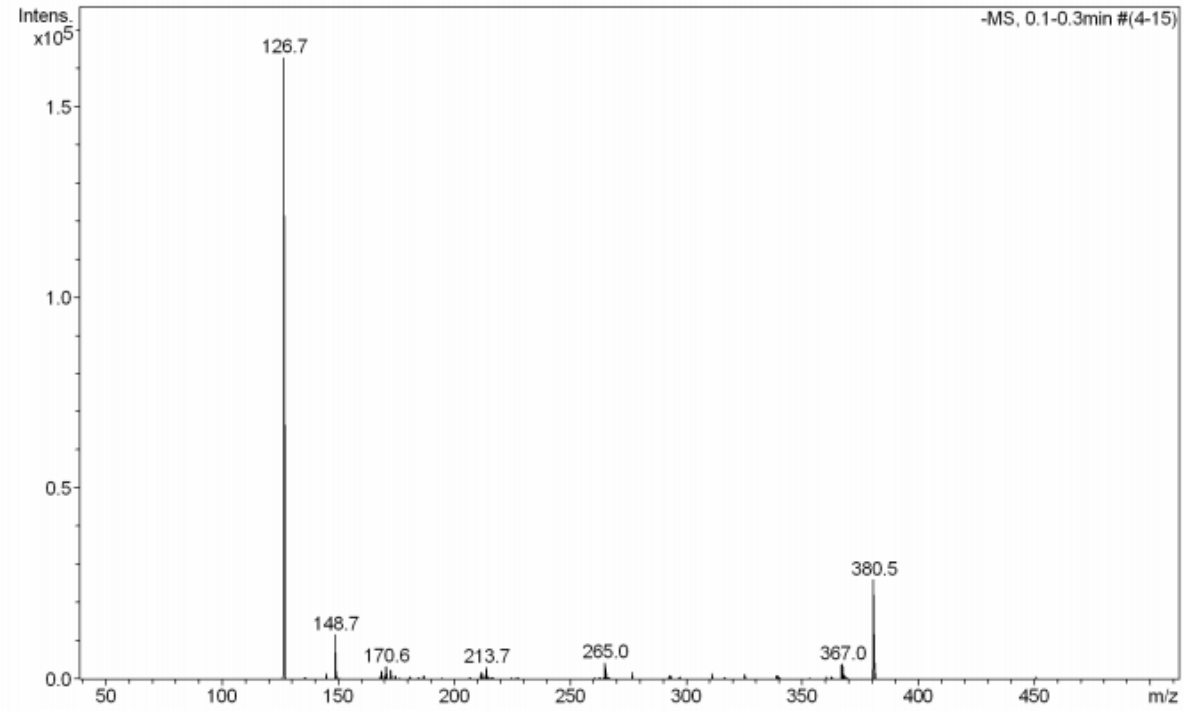

Figure S4. Negative ion mass spectrum of 1,3-diethyl-2-iodoimidazolium iodide.

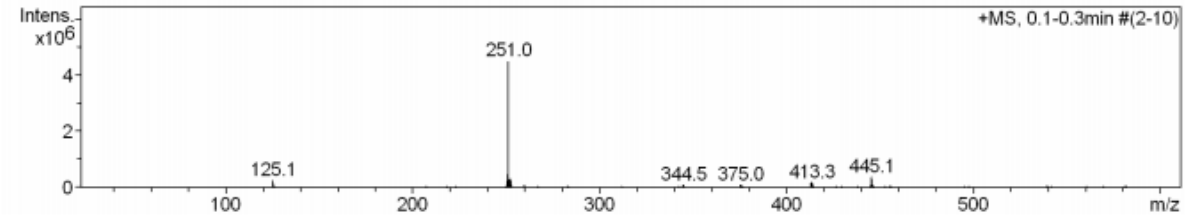

Figure S5. Positive ion mass spectrum of 1,3-diethyl-2-iodoimidazolium iodide.

Cartesian coordinates of B3LYP-D3(BJ/def2-TZVP (SMD, Acn) Optimized Geometries.

Unsaturated-NHC^{Me}
Electronic Energy = -304.9564862
Thermal Corr. to Free Energy = 0.095208

C	0.00000000	0.98002200	-0.00034100
C	0.67646900	-1.19747700	0.00005900
C	-0.67646900	-1.19747700	0.00000000
H	1.38325500	-2.00916500	0.00021100
H	-1.38325500	-2.00916500	0.00010600
N	1.06270900	0.13142900	-0.00004200
N	-1.06270900	0.13142900	-0.00003700
C	2.45181200	0.55523500	0.00009300
H	2.96310500	0.18129100	0.88801600
H	2.96359700	0.18001600	-0.88700100
H	2.48345700	1.64124200	-0.00067700
C	-2.45181200	0.55523500	0.00010700
H	-2.96359300	0.18004100	-0.88699900
H	-2.96310900	0.18126600	0.88801900
H	-2.48345700	1.64124200	-0.00063300

NHC-H
Electronic Energy = -305.459769781
Thermal Corr. to Free Energy = 0.109572

C	0.00000600	-0.86289100	0.00000000
C	-0.00002100	1.23395900	0.67910000
C	-0.00002100	1.23395900	-0.67910000
H	-0.00002000	2.04278900	1.38766000
H	-0.00002000	2.04278900	-1.38766000
N	-0.00002100	-0.08447100	1.08059000
N	-0.00002100	-0.08447100	-1.08059000
C	0.00002500	-0.55005100	2.46309000
H	0.89073900	-0.18088300	2.96752000
H	-0.89013100	-0.18001900	2.96785000
H	-0.00049800	-1.63611100	2.46345000
C	0.00002500	-0.55005100	-2.46309000
H	-0.89013100	-0.18001900	-2.96785000
H	0.89073900	-0.18088300	-2.96752000
H	-0.00049800	-1.63611100	-2.46345000
H	0.00001200	-1.93850100	0.00000000

Vinyliodide
Electronic Energy = -375.833432119
Thermal Corr. to Free Energy = 0.013933

C	-0.44685100	-2.42779800	0.00000000
H	-1.51124200	-2.22956500	0.00000000
H	-0.12954800	-3.46614200	0.00000000
C	0.46507400	-1.47305300	0.00000000
H	1.53145600	-1.65135800	0.00000000
I	0.00000000	0.58023000	0.00000000

1,2-diiodoethane
Electronic Energy = -674.284525039
Thermal Corr. to Free Energy = 0.023462

C	-0.51179000	0.54349100	0.00000000
H	-1.12500600	0.55911700	0.89353200
H	-1.12500600	0.55911700	-0.89353200
C	0.51179000	-0.54349100	0.00000000
H	1.12500600	-0.55911700	-0.89353200
H	1.12500600	-0.55911700	0.89353200
I	0.51179000	2.48162100	0.00000000
I	-0.51179000	-2.48162100	0.00000000

Elimination (Iodine) - TS
Electronic Energy = -979.217016445
Thermal Corr. to Free Energy = 0.128632

C	-2.69395100	-0.63537700	0.22373700
C	-4.67253200	-1.55316400	-0.33261300
C	-4.92761000	-0.47707400	0.44970700
H	-5.33447300	-2.25828300	-0.80415300
H	-5.85623000	-0.05847300	0.79610700
N	-3.29715200	-1.62978600	-0.45454300
N	-3.69967000	0.06742400	0.77839700
C	-2.59282300	-2.64293700	-1.22585300
H	-2.85788500	-3.63616700	-0.86507300
H	-2.85573300	-2.56047700	-2.28018300
H	-1.52414300	-2.48819800	-1.10711300
C	-3.51928800	1.24634400	1.61172700
H	-4.02807700	2.09941500	1.16395700
H	-3.92559800	1.06585500	2.60660700
H	-2.45697800	1.46029300	1.68538700
C	0.06109000	-0.07643100	0.56476700
C	0.88200900	-1.11655200	0.04395700
I	0.13628300	1.79578900	-0.50258300
I	3.29629900	-0.80690500	0.25604700
H	-1.22884000	-0.40701900	0.38068700
H	0.17778000	0.15226900	1.61969700
H	0.87732900	-1.27494200	-1.02629300
H	0.84238700	-2.03746200	0.61716700

S_N2 (Iodine) - TS
Electronic Energy = -979.238695749
Thermal Corr. to Free Energy = 0.134204

C	-3.34206500	0.02744500	-0.09310400
C	-5.44700800	0.78252200	-0.34066600
C	-5.49159600	-0.56906200	-0.38668700
H	-6.22576400	1.52047000	-0.42175600
H	-6.31709600	-1.24720000	-0.51385200
N	-4.11927500	1.12674200	-0.15901400
N	-4.18962300	-1.01136300	-0.23313100
C	-3.64781800	2.50032700	-0.06629300
H	-3.85968500	3.02848400	-0.99559300
H	-4.14811700	3.00656600	0.75844400
H	-2.57677900	2.49184400	0.10972400
C	-3.81230900	-2.41675000	-0.21360600
H	-4.24853700	-2.90692800	0.65647800
H	-4.16927300	-2.90507400	-1.11945100
H	-2.73027500	-2.48831500	-0.16507700
C	1.43772700	-0.21525900	0.87131100
C	2.08027500	0.08109700	-0.36694800
I	-0.88051200	-0.07474500	0.30402300
I	4.55302100	0.03361600	-0.17193700
H	1.53691000	0.52756300	1.65499100
H	1.53429600	-1.23309600	1.23246400
H	2.03074000	1.09982200	-0.72658900
H	2.02961300	-0.66384700	-1.14936100

Halogen bonding (iodine) - TS
Electronic Energy = -979.222025491
Thermal Corr. to Free Energy = 0.136279

C	2.00672300	-1.31476500	0.42274000
C	4.09267300	-1.07360300	-0.42838800
C	4.03213200	-0.34184900	0.70880800
H	4.89736300	-1.23441700	-1.12455400
H	4.77385900	0.26213500	1.20181200
N	2.84709900	-1.65631700	-0.58191300
N	2.75106300	-0.50158200	1.20743200
C	2.48808200	-2.51487700	-1.69822500
H	2.56554700	-1.96554700	-2.63682300
H	3.15156000	-3.37882600	-1.73487300
H	1.46525800	-2.85366400	-1.56044100
C	2.28631500	0.12302900	2.43495500
H	2.86885400	-0.23960900	3.28223300
H	2.38863100	1.20524900	2.36514500
H	1.24118300	-0.12921700	2.58492500
C	-0.10068400	0.01971900	-1.06979300
H	-0.90078200	0.07173700	-1.79869400
H	0.82802800	-0.20062100	-1.58284300
C	-0.38397700	-0.96053800	0.02144600
H	-0.30590700	-0.70258300	1.05607300
H	-0.40082100	-2.00464700	-0.23642400
I	0.13903200	2.04042700	-0.33923900
I	-2.93691000	-0.85830200	0.21577800

NHC-iodoethane adduct
Electronic Energy = -681.33966547

Thermal Corr. to Free Energy = 0.145763

C	0.78805300	-1.64961300	0.00000000
C	0.78220300	-3.76095700	0.67843900
C	0.78220300	-3.76095700	-0.67843900
H	0.78350200	-4.56849800	1.38794400
H	0.78350200	-4.56849800	-1.38794400
N	0.78220300	-2.44332400	1.08043900
N	0.78220300	-2.44332400	-1.08043900
C	0.77849100	-1.98378300	2.46697200
H	0.73383700	-2.85740400	3.10984900
H	1.68904300	-1.42468800	2.67363000
H	-0.09085300	-1.35420000	2.64373800
C	0.77849100	-1.98378300	-2.46697200
H	1.68904300	-1.42468800	-2.67363000
H	0.73383700	-2.85740400	-3.10984900
H	-0.09085300	-1.35420000	-2.64373800
C	0.74925300	-0.16502800	0.00000000
H	1.27464200	0.20491800	-0.87910800
H	1.27464200	0.20491800	0.87910800
C	-0.69451400	0.32694800	0.00000000
H	-1.23326100	0.02180400	-0.89093700
H	-1.23326100	0.02180400	0.89093700
I	-0.77452400	2.49105100	0.00000000

NHC-iodine adduct

Electronic Energy = -602.653993729

Thermal Corr. to Free Energy = 0.094221

N	-1.37160500	-1.08523200	-0.00002000
C	-2.68821500	-0.67829700	-0.00000400
C	-2.68821500	0.67829700	-0.00000100
N	-1.37160500	1.08523200	-0.00002000
C	-0.58352200	0.00000000	0.00000000
H	-3.49589500	-1.38765500	-0.00001700
H	-3.49589500	1.38765500	-0.00001300
C	-0.91848100	-2.47221900	0.00003000
C	-0.91848100	2.47221900	0.00002900
H	-1.79615700	-3.11095400	-0.00031400
H	-0.32286400	-2.66314600	0.89037700
H	-0.32226100	-2.66301300	-0.88993900
H	-1.79615700	3.11095400	-0.00031300
H	-0.32226200	2.66301300	-0.88994000
H	-0.32286200	2.66314600	0.89037500
I	1.46902500	0.00000000	-0.00000500

Ethene

Electronic Energy = -78.6293597755

Thermal Corr. to Free Energy = 0.02996

C	0.00000000	0.00000000	0.66309400
C	0.00000000	0.00000000	-0.66309400
H	0.00000000	0.92267500	-1.23311500
H	0.00000000	-0.92267500	-1.23311500
H	0.00000000	-0.92267500	1.23311500
H	0.00000000	0.92267500	1.23311500

1,2-dibromoethane

Electronic Energy = -5227.04881659

Thermal Corr. to Free Energy = 0.026303

C	-0.49705900	0.56255300	0.00000000
H	-1.11412200	0.58190200	0.89230200
H	-1.11412200	0.58190200	-0.89230200
C	0.49705900	-0.56255300	0.00000000
H	1.11412200	-0.58190200	-0.89230200
H	1.11412200	-0.58190200	0.89230200
Br	0.49705900	2.28131400	0.00000000
Br	-0.49705900	-2.28131400	0.00000000

Elimination (bromine) - TS

Electronic Energy = -5531.97952656

Thermal Corr. to Free Energy = 0.131564

C	-2.21474400	-0.30373000	0.14271000
C	-4.19978300	-1.29531300	-0.21973400
C	-4.43931900	-0.12064600	0.41110400
H	-4.87041800	-2.06075500	-0.56896800
H	-5.36033600	0.34136000	0.72075300
N	-2.82835600	-1.38548400	-0.37047700
N	-3.20636100	0.46746600	0.62444700
C	-2.14012100	-2.49854200	-1.00715900
H	-2.36451300	-3.42526900	-0.47996100
H	-2.45811900	-2.58830300	-2.04545500
H	-1.07069300	-2.31187200	-0.97242500
C	-3.00893000	1.75554900	1.27134900
H	-3.49520600	2.54120800	0.69372900
H	-3.42769700	1.73501600	2.27685300
H	-1.94323100	1.95731500	1.32645500
C	0.55693500	0.18613900	0.48571000
C	1.33706900	-0.95824000	0.12811800
Br	0.76994900	1.73939200	-0.71571500
Br	3.50224000	-0.81804500	0.38208300
H	-0.81042200	-0.10970200	0.29974600
H	0.69051900	0.55519700	1.49859900
H	1.31830200	-1.24730800	-0.91530800
H	1.16155900	-1.79921500	0.79270800

S_N2 (bromine) - TS

Electronic Energy = -5531.98146568

Thermal Corr. to Free Energy = 0.134079

C	-2.64335800	-0.01483000	-0.05984800
C	-4.78832400	0.57716900	-0.29877800
C	-4.73844700	-0.77480000	-0.26296000
H	-5.61745100	1.25369000	-0.40859600
H	-5.51542200	-1.51523600	-0.33622900
N	-3.48461400	1.02576800	-0.17346300
N	-3.40560700	-1.11899300	-0.11624200
C	-3.10440300	2.43117200	-0.14082100
H	-3.61672200	2.96051200	-0.94180900
H	-3.37831800	2.86988300	0.81844600
H	-2.03106500	2.51064000	-0.28240500
C	-2.92313500	-2.48926700	-0.01502500
H	-3.19138300	-2.90828600	0.95451600
H	-3.37093000	-3.08788700	-0.80602800
H	-1.84324100	-2.49210100	-0.12499400
C	1.80246400	0.22560400	0.88845800
C	2.42403200	-0.06927000	-0.33795600
H	1.85150500	1.24808300	1.24432600
H	1.85436000	-0.52191700	1.67138700
H	2.39839800	0.67760100	-1.11871300
H	2.39814600	-1.08941600	-0.69356800
Br	-0.45073500	0.07876400	0.29556500
Br	4.79704100	-0.03784000	-0.19804500

Halogen bonding (bromine) - TS

Electronic Energy = -5531.983602

Thermal Corr. to Free Energy = 0.137962

C	1.66059200	-0.78322500	0.39767900
C	3.78375600	-0.78087200	-0.39204800
C	3.74471000	0.06003900	0.66700800
H	4.59547800	-1.07148100	-1.03594600
H	4.51502000	0.65212400	1.12965300
N	2.50231300	-1.28416400	-0.53611200
N	2.44117200	0.04055500	1.13328200
C	2.12422800	-2.23190500	-1.57192400
H	2.22217500	-1.77426200	-2.55676200
H	2.76615200	-3.11114400	-1.52243300
H	1.09319800	-2.53372400	-1.41416700
C	1.98635400	0.84257800	2.25733200
H	2.69414100	0.75014500	3.08028100
H	1.90486300	1.89112300	1.97075500
H	1.01660100	0.48163200	2.58438900
C	-0.63816100	0.10787800	-1.06045600
H	-1.53421100	0.03258000	-1.66471700
H	0.22697000	-0.12760900	-1.66831700
C	-0.72109300	-0.75225200	0.16086000
H	-0.66456400	-0.34634500	1.14705000
H	-0.61145900	-1.81260000	0.03697200
Br	-0.46739700	2.02125700	-0.62019300
Br	-3.08892000	-0.96693200	0.41968800

Vinylbromide

Electronic Energy = -2652.21784689

Thermal Corr. to Free Energy = 0.015276

C	-0.44283600	-2.08803600	0.00000000
H	-1.50909400	-1.90252700	0.00000000
H	-0.10828800	-3.11925500	0.00000000
C	0.45787300	-1.12505800	0.00000000
H	1.52715700	-1.28109200	0.00000000
Br	0.00000000	0.73089800	0.00000000

NHC-bromoethane adduct

Electronic Energy = -2957.72239578

Thermal Corr. to Free Energy = 0.150129

C	-1.28519600	0.00000000	0.28595800
C	-3.30189600	0.67846600	-0.33412600
C	-3.30189400	-0.67847000	-0.33412900
H	-4.07352400	1.38814000	-0.57064000
H	-4.07352000	-1.38814500	-0.57064600
N	-2.04119900	1.08045100	0.04760600
N	-2.04119800	-1.08045200	0.04760700
C	-1.60381300	2.46774700	0.18081200
H	-2.37060300	3.10379500	-0.25096400
H	-1.47122100	2.71489500	1.23278200
H	-0.66789000	2.60978100	-0.35469200
C	-1.60380700	-2.46774700	0.18081300
H	-1.47119900	-2.71488900	1.23278200
H	-2.37060300	-3.10379800	-0.25094900
H	-0.66789200	-2.60978200	-0.35470500
C	0.14569200	0.00000100	0.68183200
H	0.34583400	-0.87966400	1.29190500
H	0.34583400	0.87966600	1.29190500
C	1.03172900	0.00000100	-0.55886500
H	0.88585300	-0.88983300	-1.16314200
H	0.88585300	0.88983500	-1.16314200
Br	2.93699900	0.00000100	-0.04716500

NHC-bromine adduct

Electronic Energy = -2879.02826671

Thermal Corr. to Free Energy = 0.096703

N	-0.00002700	0.98162700	1.08918100
C	-0.00002700	2.29687700	0.67854200
C	-0.00002700	2.29687700	-0.67854200
N	-0.00002700	0.98162700	-1.08918100
C	-0.00002500	0.20474700	0.00000000
H	-0.00003600	3.10435500	1.38817100
H	-0.00003600	3.10435500	-1.38817100
C	0.00000200	0.52662800	2.47763200
C	0.00000200	0.52662800	-2.47763200
H	-0.00016800	1.40621400	3.11316200
H	0.89335200	-0.06288600	2.67425100
H	-0.89316300	-0.06318400	2.67419300
H	-0.00016800	1.40621400	-3.11316200
H	-0.89316300	-0.06318400	-2.67419300
H	0.89335200	-0.06288600	-2.67425100
Br	0.00002500	-1.64635200	0.00000000

DMAP

Electronic Energy = -382.449484751

Thermal Corr. to Free Energy = 0.125991

C	-1.94708100	-1.13399100	0.00365100
C	-0.56755400	-1.19682800	0.00358000
C	0.18511900	0.00000100	-0.00011600
C	-0.56755700	1.19682900	-0.00366200
C	-1.94708300	1.13399000	-0.00356100
N	-2.66169300	-0.00000200	0.00008500
H	-2.51532800	-2.05892800	0.00707200
H	-0.08540600	-2.16232300	0.00750800
H	-0.08541100	2.16232400	-0.00759600
H	-2.51533300	2.05892600	-0.00687900
N	1.54080800	0.00000100	-0.00024600
C	2.27249500	-1.25524500	-0.00669400
H	3.33737300	-1.04240700	-0.02478900
H	2.05577700	-1.85160600	0.88462700
H	2.02819300	-1.85663600	-0.88709600
C	2.27249300	1.25524600	0.00683400
H	3.33738100	1.04239800	0.02427300
H	2.05537500	1.85223000	-0.88395900
H	2.02858300	1.85602100	0.88777900

S_N2 (DMAP-Iodine) - TS

Electronic Energy = -1056.71646254

Thermal Corr. to Free Energy = 0.162257

C	-1.10537000	0.41953600	-1.13638200
H	-2.03472400	0.46012300	-1.69043900
H	-0.27591700	0.51045600	-1.83002700
C	-0.97605200	-0.81036800	-0.30503900
H	-0.85026900	-0.77567100	0.75790900
H	-0.82787500	-1.74933000	-0.81028100
I	-1.06326200	2.22710100	0.04660200
I	-3.46807600	-1.42544600	0.15477000
C	2.05760200	-0.80084100	-1.27588700
C	3.43217700	-0.74685400	-1.21381100
C	4.06991700	-0.58659800	0.04090500
C	3.21383700	-0.49513900	1.16534400
C	1.84949900	-0.56156100	0.98903000
N	1.26522100	-0.70847000	-0.20374200
H	1.56267800	-0.91963400	-2.23395800
H	4.00052000	-0.82733300	-2.12704700
H	3.60685500	-0.36904000	2.16195000
H	1.18748900	-0.48792500	1.84468600
N	5.41480800	-0.52335800	0.15684100
C	6.25617400	-0.58555400	-1.02783500
H	7.29658100	-0.52145400	-0.72412900
H	6.11281800	-1.52467900	-1.56876600
H	6.04486500	0.24085300	-1.71250700
C	6.03118700	-0.33767800	1.46104500
H	7.11073700	-0.33865900	1.34337500
H	5.73313700	0.61240900	1.91401100
H	5.76000800	-1.14467100	2.14656200

DMAP-etI

Electronic Energy = -758.790879676

Thermal Corr. to Free Energy = 0.180146

C	1.32550100	-1.15001600	0.47905400
C	2.65782300	-1.20086200	0.20579100
C	3.40285500	-0.00052500	0.03349800
C	2.67270400	1.21390100	0.16476600
C	1.33931900	1.18903400	0.43701100
N	0.66393600	0.02604600	0.60016200
H	0.73390900	-2.04277500	0.61785400
H	3.12503300	-2.16894700	0.13215500
H	3.15109300	2.17272000	0.05220600
H	0.75790100	2.09330300	0.53955700
N	4.71158800	-0.01261000	-0.23258300
C	5.42529500	-1.27685100	-0.38469100
H	6.45667400	-1.06665800	-0.64760900
H	5.41034100	-1.85010800	0.54486900
H	4.98111500	-1.88140300	-1.17757800
C	5.45004800	1.23855700	-0.37448500
H	6.49787800	1.00926700	-0.53687200
H	5.08150200	1.81703900	-1.22449700
H	5.36348500	1.84631200	0.52813100
C	-0.79104000	0.03683900	0.83957100
H	-1.03206200	-0.82571500	1.45571100
H	-1.02970100	0.94137900	1.39314200
C	-1.52892700	-0.00927100	-0.48347000
H	-1.32717700	0.86404300	-1.09589500
H	-1.32118400	-0.91995300	-1.03668100
I	-3.66413100	-0.00617700	-0.14377000

DMAP-I

Electronic Energy = -680.092335912

Thermal Corr. to Free Energy = 0.12645

C	0.15166800	-1.17547500	-0.00780800
C	1.51309400	-1.20670800	-0.00719400
C	2.26667000	-0.00000300	-0.00001200
C	1.51307500	1.20668600	0.00719800
C	0.15165400	1.17542500	0.00781500
N	-0.52717000	-0.00002800	-0.00000200
H	-0.44048700	-2.07712900	-0.01519400
H	1.99380400	-2.17115600	-0.01543800
H	1.99376200	2.17114400	0.01546300

H	-0.44052200	2.07706600	0.01521600
N	3.60128800	0.00001100	-0.00003500
C	4.34187000	-1.25819500	0.01356800
H	5.40346200	-1.03755600	0.04843100
H	4.08127300	-1.85355700	0.89066100
H	4.13457800	-1.84373500	-0.88467900
C	4.34185000	1.25822900	-0.01354800
H	5.40343700	1.03761600	-0.04875100
H	4.08101100	1.85377800	-0.89043700
H	4.13479100	1.84357100	0.88488300
I	-2.59515500	0.00000600	0.00000000