Supplementary Material (ESI) for Chemical Communications
This journal is (c) The Royal Society of Chemistry 2008

SUPPORTING INFORMATION

Novel $^{\oplus}N(\leftarrow L)_2$ Species with two Lone Pairs on Nitrogen: Systems Isoelectronic to Carbodicarbenes

*Dhilon S. Patel and Prasad V. Bharatam**

Table S1: Absolute Energies of **IVa-e, 1 and 3** and their corresponding transition states (a.u, ZPE corrected values, which have been scaled by a factor of 0.9806 for B3LYP) at B3LYP/6-31+G* and G2MP2 level of theory

	B3LYP/6-31+G*	**G2MP2**
IVa	-132.993995674	-132.815394
IVa -TS	-132.930241957	-132.749650
IVb_1	-188.372388419	-188.126301
IVb_2	-188.364734061	-188.120730
IVb-TS	-188.372068447	-
IVc	-243.743491246	-243.436226
IVc -TS1	-243.730972678	-243.419396
IVc -TS2	-243.737222470	-243.428090
IVd_2	-243.764546838	-243.450639
IVd_1	-243.754882278	-243.440748
IVd -TS1	-243.754382140	-243.438761
IVd -TS2	-243.733914805	-243.419413
IVe	-299.127074784	-298.749297
IVe -TS	-299.112914075	-298.734070
1	-354.486918480	-354.045202
1-TS1	-354.472485441	-354.035260
1-TS2	-354.478313428	-
3	-506.864268439	-506.171746
3-TS1	-506.846513602	-
3-TS2	-506.854539205	-

Table S2: Relative Energies of **IIIa-e, 1 and 3** and their corresponding transition states at B3LYP/6-31+G* and G2MP2 level of theory

Relative Energies			**Charge on central N**
	B3LYP/6-31+G*	**G2MP2**	
IVa	**0.00**	**0.00**	-0.40651
IVa -TS	40.01	41.25	
IVb_1	**0.00**	**0.00**	-0.56571
IVb_2	4.80	3.50	-0.61429
IVb-TS	0.20	-	
IVc	**0.00**	**0.00**	-0.57678
IVc -TS1	7.86	10.56	
IVc -TS2	3.93	5.11	
IVd_2	**0.00**	**0.00**	-0.70669
IVd_1	6.06	6.21	-0.70350
IVd -TS1	6.38	7.45	
IVd -TS2	19.22	19.59	
IVe	**0.00**	**0.00**	-0.72695
IVe -TS	8.89	9.56	
1	**0.00**	**0.00**	-0.77210
1-TS1	9.06	6.24	
1-TS2	5.40	-	
3	**0.00**	**0.00**	-0.6150
3-TS1	11.14	-	
3-TS2	6.11	-	

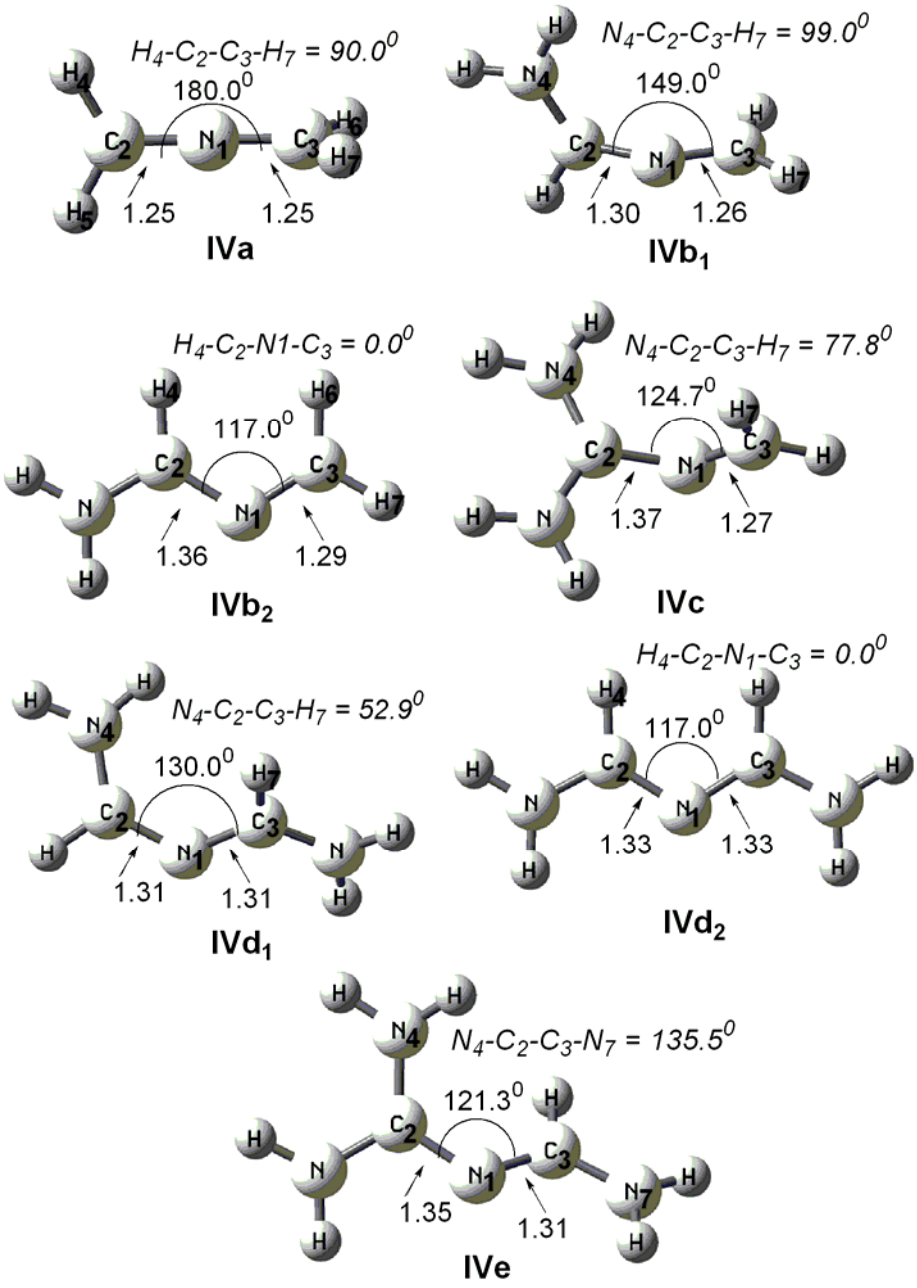


Figure S1: 3D structures for **IVa-e.** Angles are in degrees and distances in angstrom.

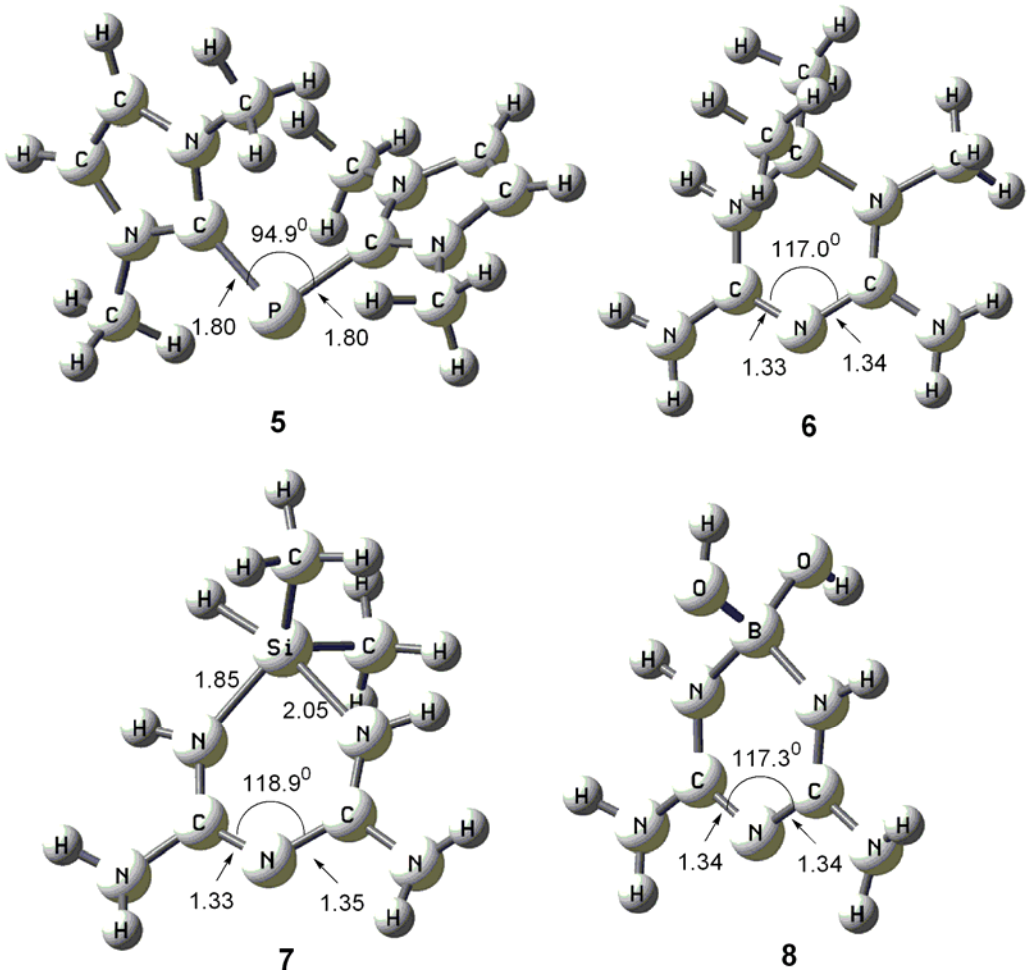


Figure S2: 3D structures for **5-8.** Angles are in degrees and distances in angstrom.

This journal is (c) The Royal Society of Chemistry 2008

Geometries and Absolute Energies (**E**) (a.u, ZPE corrected values, which have been scaled by a factor of 0.9806) at B3LYP/6-31+G* level of theory. In case of proton affinity calculation total **E** value includes enthalpy correction also.

IVa

E = -132.993995674

N	-0.000033	-0.000111	-0.000097
H	-1.789502	-0.667333	-0.675812
H	-1.789210	0.667527	0.676004
C	-1.250624	0.000042	0.000034
H	1.789364	-0.676629	0.666712
C	1.250660	0.000038	0.000032
H	1.789361	0.676735	-0.666622

IVb$_1$

E = -188.372388419

N	-1.613699	-0.344379	0.018670
H	2.000113	-0.432809	1.155527
N	0.633232	0.168155	-0.263613
H	-2.558557	0.003285	0.144753
H	-0.797296	1.536821	0.258370
C	-0.589857	0.486185	0.053323
C	1.780931	-0.196282	0.109678
H	2.576562	-0.280387	-0.631056
H	-1.503987	-1.332753	-0.191001

IVb$_2$

E = -188.364734061

N	1.672492	-0.114556	0.000112
H	-1.934432	1.151408	0.000559
N	-0.587507	-0.470335	-0.000174
H	2.503942	0.473031	0.000170
H	0.374858	1.474361	-0.000387
C	0.476074	0.384176	-0.000158
C	-1.761038	0.068253	0.000127
H	-2.628233	-0.590286	-0.000016
H	1.798753	-1.128849	0.000296

IVc

E = -243.743491246

H	2.887202	-0.006135	-0.196234
H	-0.540831	2.029366	-0.116223
H	-2.045345	-1.224432	0.245866
N	-1.038339	1.166891	0.072748
H	-0.556701	-2.028490	-0.110208
N	0.882882	-0.006696	-0.507076
N	-1.047738	-1.161630	0.075725
H	1.832278	0.008301	1.354401
H	-2.035495	1.238051	0.242370
C	-0.418787	-0.000157	-0.079423
C	1.898997	-0.000944	0.261131

IVd$_1$

E = -243.754882278

H	1.563741	-1.436267	-0.431082
N	-0.044140	0.649656	-0.011124
H	1.825996	1.441229	0.289837
C	-0.979539	-0.206173	0.314611
N	1.978420	-0.554529	-0.145696
N	-2.199284	-0.140745	-0.191097
H	2.992392	-0.515604	-0.116344
C	1.258280	0.535963	0.076857
H	-2.942464	-0.738699	0.150641
H	-2.434293	0.557435	-0.891513
H	-0.822784	-0.967512	1.085071

IVd$_2$

E = -243.764546838

H	-2.335186	-1.252530	-0.000195
N	0.000032	-0.316147	-0.000093
H	-1.162533	1.471454	0.000319
C	1.129761	0.376771	-0.000079
N	-2.293164	-0.236002	0.000045
N	2.293184	-0.235970	0.000057
H	-3.166719	0.278667	0.000159
C	-1.129815	0.376826	-0.000005
H	3.166695	0.278762	0.000132
H	2.335260	-1.252492	0.000246
H	1.162441	1.471397	-0.000226

IVe

E = -299.127074784

C	0.955220	-0.039526	-0.052217
N	-0.308406	-0.475508	-0.223921
N	1.901499	-0.964515	0.120363
N	1.292337	1.264449	-0.077737
C	-1.328039	0.195019	0.245733
H	2.891528	-0.755143	0.122494
H	1.620858	-1.935594	0.183096
H	2.253153	1.570253	0.023828
H	0.652083	1.943847	-0.466303
N	-2.575623	-0.140139	-0.053981
H	-3.365334	0.334574	0.364815
H	-2.761171	-0.918985	-0.678882
H	-1.222853	1.038079	0.936791

1

E = -354.486918480

C	-1.182351	-0.112845	0.057746
N	-2.249983	-0.824182	-0.333017
N	-0.000151	-0.718155	-0.000725
C	1.182333	-0.112991	-0.057914
N	2.249372	-0.824722	0.333565
N	1.382656	1.159280	-0.493007
N	-1.381918	1.159345	0.493135
H	-3.202550	-0.506064	-0.216854
H	-2.099020	-1.759407	-0.689011
H	3.202107	-0.506704	0.218507
H	2.097890	-1.760233	0.688576
H	2.321300	1.502565	-0.658731
H	0.657701	1.610570	-1.036413
H	-0.656800	1.609979	1.036729
H	-2.320349	1.503350	0.658542

2

E = -433.053916349

C	1.850802	0.155461	0.027377
N	0.606174	0.517016	-0.239119
N	2.216702	-0.956660	0.724009
N	2.832432	0.958598	-0.422712
C	-0.469438	-0.279026	-0.186007
H	3.171798	-1.071402	1.040027
H	1.518591	-1.445181	1.269479

H	3.808053	0.821532	-0.198790
H	2.577058	1.765057	-0.976751
N	-0.386499	-1.632692	-0.372452
N	-1.674757	0.263641	0.031121
H	-1.223445	-2.177654	-0.531787
H	0.440011	-1.991325	-0.834422
C	-2.898337	-0.544770	-0.021753
C	-1.836782	1.690161	0.348157
H	-3.034581	-0.996815	-1.011655
H	-2.898092	-1.323437	0.750149
H	-3.749382	0.110107	0.164360
H	-0.870302	2.186142	0.305741
H	-2.261670	1.796797	1.351771
H	-2.513864	2.145905	-0.380698

3

E = -506.864268439

C	1.169721	-0.382472	-0.005581
C	-1.169718	-0.382473	0.005527
N	2.332648	-0.986664	0.349697
N	1.528730	0.883357	-0.390980
N	-1.528676	0.883438	0.390807
N	-2.332664	-0.986656	-0.349687
C	3.414681	-0.130785	0.164023
C	2.918681	1.035802	-0.310067
C	-2.918682	1.035810	0.310146
C	-3.414705	-0.130799	-0.163892
H	2.365669	-1.937708	0.695126
H	0.913530	1.516036	-0.885516
H	-0.913539	1.515918	0.885681
H	-2.365717	-1.937732	-0.695023
H	3.409495	1.956503	-0.584200
H	4.426241	-0.427126	0.393216
H	-3.409488	1.956515	0.584279
H	-4.426282	-0.427152	-0.393000
N	-0.000006	-1.005725	-0.000051

4

E = -490.333371327

C	0.000000	1.078934	0.000000
C	-1.196559	0.420860	0.032618
C	1.196559	0.420861	-0.032617
N	-2.410675	0.952786	0.461716
N	-1.575009	-0.863113	-0.414911
N	1.575009	-0.863112	0.414912
N	2.410674	0.952786	-0.461716
C	-3.479375	0.112980	0.164719
C	-2.967617	-1.008081	-0.396596
C	2.967617	-1.008081	0.396595
C	3.479375	0.112980	-0.164720
H	-2.466741	1.916101	0.756231
H	-4.499427	0.368470	0.407783
H	-3.459457	-1.907018	-0.736811
H	-0.963842	-1.396625	-1.016134
H	0.963843	-1.396625	1.016136
H	3.459457	-1.907018	0.736810
H	4.499427	0.368470	-0.407785
H	2.466741	1.916101	-0.756232

5

E = -793.446524991

C	1.302112	0.343920	0.247275
C	-1.302147	0.343648	-0.247099
N	2.565408	0.440926	-0.267383
N	1.325444	-0.771993	1.042116
N	-1.324994	-0.772518	-1.041604
N	-2.565705	0.440717	0.266919
C	3.356196	-0.582554	0.198017
C	2.570410	-1.358503	1.007121
C	-2.570024	-1.358980	-1.007205
C	-3.356212	-0.582943	-0.198603
H	4.396836	-0.680833	-0.077387
H	2.801064	-2.258932	1.559214
H	-2.800346	-2.259574	-1.559166
H	-4.396974	-0.681216	0.076340
P	-0.000188	1.558509	0.000309
C	0.228802	-1.212922	1.898056
H	-0.215872	-0.333555	2.369640
H	-0.529885	-1.748145	1.321654
H	0.639548	-1.874298	2.662241
C	-0.228099	-1.213358	-1.897271
H	0.216309	-0.334012	-2.369152
H	0.530731	-1.748149	-1.320660
H	-0.638548	-1.875138	-2.661266
C	3.019052	1.512827	-1.152692
H	2.218744	1.746686	-1.857065
H	3.261914	2.405294	-0.572468
H	3.903867	1.164611	-1.686022
C	-3.019832	1.512742	1.151814
H	-2.219668	1.747096	1.856190
H	-3.262948	2.404943	0.571282
H	-3.904572	1.164397	1.685185

6

E = -510.449642401

C	1.724335	-0.060599	-0.123510
C	-0.055952	1.355771	0.017986
N	3.051956	-0.230532	-0.216815
N	0.891956	-1.101768	-0.338150
N	-0.950710	0.366045	-0.223834
N	-0.465859	2.633481	0.094656
H	3.644822	0.585364	-0.134015
H	0.246548	3.340023	0.227594
H	3.490542	-1.134324	-0.323451
H	-1.432742	2.911285	0.166035
N	1.264389	1.157033	0.151705
C	-0.655321	-1.308421	1.593160
H	-1.700043	-1.212713	1.907491
H	-0.327292	-2.328108	1.821046
H	-0.049880	-0.610691	2.180415
C	-1.289622	-2.063715	-0.743998
H	-0.807330	-3.040792	-0.630233
H	-2.315349	-2.185590	-0.389320
H	-1.295076	-1.800202	-1.805856
H	1.259726	-2.011701	-0.588124
C	-0.519353	-1.031455	0.085796
C	-2.374693	0.682273	-0.389151
H	-2.846883	0.963947	0.561075
H	-2.487495	1.492109	-1.115179
H	-2.898035	-0.181546	-0.792122

7

E = -723.400232005

C	1.444239	-1.005494	-0.015708
C	1.058472	1.270030	0.001291
N	2.397531	-1.996691	-0.072424
N	0.149785	-1.377970	-0.034291
N	-0.252997	1.158981	-0.000192
N	1.677903	2.501386	-0.053562
H	3.341173	-1.689259	0.123174
H	2.666880	2.492414	0.158841
H	2.162259	-2.924063	0.253952
H	1.170353	3.313761	0.269235
N	1.924768	0.230808	0.020079
C	-2.252341	0.078787	1.642137
H	-2.317549	1.168380	1.754145
H	-3.258655	-0.346146	1.746737
H	-1.651597	-0.297919	2.481841
C	-2.314670	0.151678	-1.590906
H	-1.751130	-0.195155	-2.468287
H	-3.326102	-0.266782	-1.669180
H	-2.381668	1.244744	-1.661918
H	0.011111	-2.381565	-0.106228
Si	-1.479258	-0.489957	-0.002980
H	-2.108846	-1.895926	-0.029826
H	-0.739748	2.051301	-0.048921

8

E = -530.151766617

C	0.938109	-1.145781	-0.017240
C	0.937796	1.145991	-0.017469
N	1.694786	-2.293457	-0.042494
N	-0.386881	-1.218452	-0.054553
N	-0.387249	1.218246	-0.055211
N	1.694224	2.293830	-0.042558
H	2.670736	-2.160998	0.188298
H	2.670021	2.161493	0.188909
H	-0.800765	-2.144889	-0.046678
H	1.282173	-3.152258	0.295818
H	1.281355	3.152411	0.295953
H	-0.801441	2.144536	-0.047357
N	1.635828	0.000202	0.000930
B	-1.382343	-0.000105	0.018941
O	-2.325737	-0.000615	-1.079271
O	-2.106364	0.000229	1.261256
H	-1.886901	-0.000258	-1.940651
H	-3.057049	-0.000266	1.080583

9

E = -506.490252304

C	1.171101	-0.380808	-0.000262
C	-1.115245	-0.450282	-0.000155
N	2.384748	-1.017818	0.000115
N	1.347773	0.947324	-0.000309
N	-1.363273	0.900429	-0.000095
N	-2.360503	-1.036983	-0.000089
C	3.380516	-0.051532	0.000341
C	2.715986	1.146209	0.000088
C	-2.733921	1.142607	0.000182
C	-3.357838	-0.061481	0.000245
H	2.498168	-2.021133	0.000276
H	-0.568317	1.543032	-0.000485
H	-2.486035	-2.037835	0.000502
H	3.136893	2.142730	0.000040
H	4.430259	-0.303777	0.000552
H	-3.140440	2.141854	0.000375
H	-4.406531	-0.312932	0.000481
N	0.015884	-1.110126	-0.000246

10

E = -489.789601855

C	1.194769	-0.419993	-0.037257
C	-1.151328	-0.514079	-0.134315
N	2.445064	-1.018708	0.041147
N	1.393355	0.936205	-0.050330
N	-1.397606	0.887829	-0.216331
N	-2.474416	-1.054334	-0.095094
C	3.433984	-0.049496	0.097286
C	2.749151	1.142985	0.035855
C	-2.724151	1.155089	0.104513
C	-3.387518	-0.026741	0.194694
H	2.541401	-2.022393	0.092112
H	-0.589880	1.487288	-0.048674
H	-2.548326	-1.975485	0.316611
H	3.168449	2.144601	0.043263
H	4.487908	-0.285238	0.155971
H	-3.114053	2.164239	0.153808
H	-4.446375	-0.214669	0.310249
C	0.007776	-1.213646	-0.057290

IVa-TS

E = -132.930241957 NIMAG = 1

N	-0.000003	-0.544002	0.000021
H	-2.065987	-0.370078	-0.000243
H	-1.131867	1.266754	0.000408
C	-1.116485	0.167894	-0.000010
H	2.065932	-0.370156	0.000192
C	1.116482	0.167896	-0.000018
H	1.131955	1.266756	-0.000339

IVb-TS N-inversion

E = -188.372068447 NIMAG = 1

N	1.650203	-0.335749	-0.000064
H	-2.377313	-0.304641	-0.942980
N	-0.621709	0.120087	-0.000097
H	2.589410	0.044067	0.000087
H	0.806090	1.555779	0.000249
C	0.606413	0.484014	0.000107
C	-1.838457	-0.173059	0.000026
H	-2.376908	-0.305603	0.943128
H	1.551526	-1.345693	-0.000154

IVc-TS1 N-inversion

E = -243.730972678 NIMAG = 1

H	2.667087	-0.167304	0.925313
H	-0.633868	-2.044375	0.050609
H	-2.089450	1.191123	0.306599
N	-1.129201	-1.163134	0.013114
H	-0.633838	2.044373	-0.050673
N	0.853327	0.000007	-0.000023

N	-1.129192	1.163133	-0.013123
H	2.667166	0.167284	-0.925280
H	-2.089480	-1.191085	-0.306503
C	-0.446651	-0.000001	0.000008
C	2.104625	-0.000008	0.000018

IVc-TS2 C-N rotation

E = -243.73722247 NIMAG = 1

H	-2.052750	1.012036	0.001275
H	-0.228752	1.940236	-0.000541
H	2.437336	-0.495387	0.000421
N	0.570134	1.319244	-0.000019
H	1.295891	-1.812683	0.000183
N	-0.789441	-0.686546	-0.000452
N	1.474187	-0.812764	0.000215
H	-2.816228	-0.682730	0.000010
H	1.479291	1.769478	-0.000206
C	0.428765	-0.002411	-0.000131
C	-1.911923	-0.076004	0.000238

IVd-TS1 N-inversion

E = -243.754382140 NIMAG = 1

H	1.978565	-1.419607	0.164071
N	-0.015895	0.230415	-0.145839
H	1.599955	1.501303	-0.271432
C	-1.155251	0.095403	0.430358
N	2.198868	-0.437546	0.030566
N	-2.274009	-0.213577	-0.220862
H	3.176432	-0.182689	-0.054408
C	1.250202	0.479735	-0.104162
H	-3.153638	-0.290146	0.273947
H	-2.281642	-0.341635	-1.227259
H	-1.252126	0.226898	1.510857

IVd-TS2 C-N rotation

E = -243.733914805 NIMAG = 1

H	2.024045	-1.221304	-0.000010
H	-2.620428	0.953236	0.000032
H	2.620428	0.953235	0.000053
H	-1.027502	1.579306	-0.000020
H	1.027503	1.579306	-0.000054
C	-1.206920	-0.500074	0.000023
N	1.622129	0.760934	0.000017
N	-1.622128	0.760934	-0.000018
C	1.206920	-0.500074	-0.000008
H	-2.024045	-1.221304	0.000083
N	0.000000	-1.039238	-0.000024

IVe-TS N-inversion

E = -299.112914075 NIMAG = 1

C	0.943428	-0.014528	0.032156
N	-0.263182	-0.450424	0.254252
N	1.937537	-0.901568	-0.171078
N	1.244934	1.307605	-0.010119
C	-1.504203	-0.187689	0.485282
H	2.866705	-0.616506	-0.447175
H	1.727734	-1.890400	-0.170917
H	2.206716	1.621665	0.003619
H	0.548727	1.993058	0.246771
N	-2.420634	0.062912	-0.446146
H	-3.401539	0.133224	-0.199418
H	-2.180564	0.092708	-1.432200
H	-1.893721	-0.250119	1.506331

1-TS1 N-inversion

E = -354.472485441 NIMAG = 2

C	-1.287219	-0.000164	-0.000022
N	-0.000001	-0.002853	-0.002323
N	-1.995525	-0.887807	-0.742153
N	-1.990068	0.890054	0.744337
C	1.287221	-0.000720	-0.000662
H	-2.991398	-0.784576	-0.883855
H	-1.504078	-1.509669	-1.368590
H	-2.985873	0.790349	0.889061
H	-1.494682	1.510196	1.369365
N	1.992400	0.889210	-0.743178
N	1.993191	-0.888597	0.743365
H	2.988265	0.788021	-0.886519
H	1.498683	1.508731	-1.370159
H	2.988994	-0.786801	0.886523
H	1.500089	-1.511001	1.367939

1-TS2 C-N rotation

E = -354.478313428 NIMAG = 1

C	1.250241	-0.083266	-0.070857
N	-0.020434	-0.348887	-0.231004
N	2.015822	-0.893360	0.686064
N	1.839980	0.970327	-0.683862
C	-1.251977	-0.014176	0.001889
H	3.023095	-0.810870	0.729042
H	1.593446	-1.707222	1.111698
H	2.846521	1.072063	-0.723070
H	1.308182	1.498074	-1.362834
N	-1.628378	1.060574	0.741362
N	-2.225204	-0.809699	-0.509104
H	-2.574285	1.143233	1.091803
H	-0.926295	1.600187	1.228619
H	-3.187542	-0.503127	-0.560039
H	-1.945212	-1.560369	-1.125612

3-TS1 N-inversion

E = -506.846513602 NIMAG = 2

C	1.286378	-0.000288	-0.001138
C	3.459460	0.476518	-0.478351
C	3.458505	-0.476554	0.480976
H	4.273731	0.975572	-0.979716
H	4.271770	-0.975463	0.984118
C	-1.286386	-0.000247	-0.001149
C	-3.459741	-0.479092	-0.474988
C	-3.458238	0.480385	0.477932
H	-4.274298	-0.981088	-0.972938
H	-4.271214	0.983065	0.977777
N	-2.121407	0.768812	0.763363
H	-1.789100	1.446389	1.435802
N	-2.123843	-0.768618	-0.763555
H	-1.793567	-1.446238	-1.436960
N	2.121858	-0.763699	0.768467
H	1.789960	-1.437024	1.445366

N	2.123409	0.763466	-0.768712
H	1.792783	1.436238	-1.446785
N	-0.000006	-0.000785	-0.003328

3-TS2 C-N rotation

E = -506.854539205 NIMAG = 1

C	-1.253529	-0.146034	-0.025874
C	-3.501975	-0.468877	-0.051519
C	-3.287522	0.856617	0.135758
H	-4.422121	-1.027032	-0.126841
H	-3.979147	1.674899	0.260848
C	1.255274	-0.170850	-0.024354
C	3.282482	0.865284	-0.085791
C	3.504964	-0.455615	0.120429
H	3.968720	1.692228	-0.180361
H	4.425141	-1.004292	0.246458
N	2.262383	-1.075666	0.154394
H	2.083726	-2.061269	0.295016
N	1.899972	1.033915	-0.164468
H	1.437685	1.905335	-0.381260
N	-1.903397	1.048185	0.142398
H	-1.445044	1.931904	0.312783
N	-2.255768	-1.074302	-0.143707
H	-2.064602	-2.056481	-0.289431
N	-0.003550	-0.494766	-0.067061

1-H+

E = -354.519950181

C	1.252157	-0.075026	-0.086316
N	2.281101	-0.745571	0.403450
N	-0.000002	-0.679587	-0.000013
C	-1.252157	-0.075021	0.086314
N	-2.281113	-0.745562	-0.403436
N	-1.382347	1.114366	0.657545
N	1.382359	1.114362	-0.657546
H	3.241552	-0.478816	0.194667
H	2.166682	-1.533756	1.036189
H	-3.241559	-0.478791	-0.194649
H	-2.166710	-1.533765	-1.036154
H	-2.268654	1.614903	0.633319
H	-0.677927	1.493738	1.283549
H	0.677964	1.493719	-1.283587
H	2.268662	1.614907	-0.633288
H	-0.000005	-1.697921	-0.000036

2-H+

E = -433.044540701

C	-1.914312	-0.128028	0.036258
N	-0.622322	-0.430029	-0.354804
N	-2.145523	0.754600	0.999278
N	-2.901826	-0.770679	-0.573439
C	0.538208	0.348662	-0.211395
H	-3.090316	1.059483	1.219092
H	-1.413974	1.085990	1.618696
H	-3.853099	-0.750629	-0.214143
H	-2.766708	-1.274257	-1.445313
N	0.416397	1.676187	-0.340391
N	1.684368	-0.256299	0.020759
H	1.189413	2.296513	-0.121832
H	-0.339680	2.086701	-0.879122
C	2.973737	0.460909	-0.149244
C	1.792459	-1.656755	0.500630
H	2.910957	1.164973	-0.981976
H	3.250168	0.974219	0.778062
H	3.738940	-0.280412	-0.383794
H	0.855854	-1.992179	0.946829
H	2.568480	-1.687548	1.268923
H	2.086232	-2.311430	-0.326342
H	-0.494468	-1.336622	-0.796401

3-H+

E = -506.892275887

C	1.230734	0.388765	0.037016
C	-1.230738	0.388748	-0.037138
N	2.278150	0.655282	-0.763628
N	1.633984	-0.566900	0.895375
N	-1.633943	-0.567270	-0.895124
N	-2.278191	0.655585	0.763351
C	3.363529	-0.127211	-0.402115
C	2.950929	-0.913049	0.632669
C	-2.950901	-0.913317	-0.632339
C	-3.363550	-0.127063	0.402108
H	2.274291	1.330675	-1.524603
H	1.080868	-0.937160	1.663423
H	-1.080788	-0.937848	-1.662989
H	-2.274378	1.331301	1.524038
H	3.470234	-1.672116	1.200216
H	4.316456	-0.058706	-0.907341
H	-3.470176	-1.672615	-1.199603
H	-4.316499	-0.058359	0.907265
N	-0.000004	1.029752	-0.000162
H	-0.000007	2.048457	-0.000308

6-H+

E = -510.408457897

C	1.741477	-0.129748	-0.159829
C	-0.150121	1.358586	0.046965
N	3.052997	-0.240928	-0.313346
N	0.880529	-1.115245	-0.359205
N	-0.986496	0.358139	-0.191352
N	-0.513245	2.635846	0.114952
H	3.664181	0.568144	-0.377274
H	0.160868	3.394254	0.076822
H	3.497978	-1.145974	-0.441404
H	-1.487763	2.912497	0.167807
N	1.199710	1.074958	0.222184
C	-0.603730	-1.301433	1.635975
H	-1.640417	-1.217208	1.976902
H	-0.258860	-2.315010	1.862717
H	0.006503	-0.593383	2.205796
C	-1.316286	-2.097149	-0.668735
H	-0.846979	-3.075493	-0.518071
H	-2.337576	-2.192716	-0.294496
H	-1.333763	-1.878085	-1.740904
H	1.189658	-1.968969	-0.817150
C	-0.530984	-1.052814	0.124670
C	-2.403879	0.653359	-0.516188
H	-2.970374	0.890702	0.390754
H	-2.446339	1.481092	-1.228255
H	-2.849382	-0.213174	-0.996881

H	1.798941	1.779130	0.643857

7-H+

E = -723.545874449

C	-1.069811	1.264845	-0.106715
C	-1.337170	-1.207819	-0.067016
N	-1.819639	2.390863	-0.102894
N	0.227264	1.314650	-0.357223
N	-0.099806	-1.425126	-0.291570
N	-2.375270	-2.100805	0.046026
H	-2.821696	2.362758	-0.238947
H	-3.295028	-1.840267	-0.291646
H	-1.384862	3.304002	-0.130806
H	-2.154507	-3.079851	-0.090201
N	-1.755677	0.119423	0.184445
C	1.784966	-0.325621	1.830723
H	2.812468	-0.267528	2.212792
H	1.167075	0.290642	2.495648
H	1.445116	-1.361302	1.902832
C	2.527976	-0.646585	-1.327088
H	2.024899	-0.428330	-2.276312
H	3.582703	-0.369210	-1.439425
H	2.473054	-1.726079	-1.158088
H	0.504352	2.231801	-0.702025
Si	1.780519	0.344689	0.080059
H	2.570598	1.613793	0.131491
H	0.104317	-2.388852	-0.552449
H	-2.629623	0.230826	0.685402

8-H+

E = -530.340349054

C	-0.868307	1.222224	-0.064432
C	-0.868978	-1.221874	-0.064494
N	-1.657093	2.312918	0.017513
N	0.422001	1.238287	-0.231575
N	0.421335	-1.238525	-0.231719
N	-1.658518	-2.312048	0.017585
H	-2.652713	2.266800	-0.156858
H	-2.653904	-2.265208	-0.158062
H	0.857818	2.147709	-0.363114
H	-1.245363	3.237510	0.015827
H	-1.247357	-3.236902	0.015091
H	0.856684	-2.148188	-0.363174
N	-1.515381	0.000348	0.057225
B	1.433121	-0.000334	0.031137
O	2.508721	-0.000335	-0.878430
O	1.818658	-0.000740	1.384709
H	2.283775	-0.000251	-1.818583
H	2.781137	-0.000694	1.495142
H	-2.427403	0.000525	0.498165

1-BH3

E = -381.093381273

C	1.177332	-0.225549	0.055722
N	2.263020	0.413637	-0.352380
N	-0.006099	0.455853	0.026998
C	-1.212789	-0.174773	-0.062719
N	-2.303372	0.513330	0.249750
N	-1.343722	-1.467109	-0.437582
N	1.277949	-1.509049	0.474393
H	3.196754	0.058403	-0.189279
H	2.154173	1.371436	-0.684516
H	-3.234397	0.158065	0.074081
H	-2.187542	1.496909	0.490053
H	-2.269032	-1.855889	-0.574756
H	-0.595087	-1.934671	-0.932464
H	0.580017	-1.882816	1.106431
H	2.194748	-1.935858	0.545543
B	0.133778	2.135527	0.061177
H	0.842326	2.362334	1.007061
H	0.614234	2.430176	-1.013400
H	-0.966779	2.609575	0.179085

2-BH3

E = -459.662065324

C	-1.755316	-0.214946	-0.222082
N	-0.621676	0.319253	0.275497
N	-1.796460	-1.390209	-0.887898
N	-2.875704	0.494710	-0.087424
C	0.570862	-0.372590	0.296651
H	-2.669572	-1.759160	-1.239647
H	-0.996506	-2.005200	-0.920681
H	-3.759141	0.196084	-0.476563
H	-2.828706	1.382133	0.405936
N	0.599604	-1.582155	0.908216
N	1.658568	0.141890	-0.249026
H	1.461757	-2.105549	0.998169
H	-0.096518	-1.762437	1.623182
C	2.991046	-0.420186	0.028772
C	1.621727	1.344552	-1.102481
H	3.098915	-0.638738	1.095573
H	3.174080	-1.321773	-0.567310
H	3.738635	0.326880	-0.238391
H	0.598408	1.571315	-1.391391
H	2.227757	1.149473	-1.991114
H	2.029730	2.193888	-0.547816
B	-0.659949	1.758449	1.126805
H	0.461873	1.906647	1.540509
H	-1.003038	2.611246	0.338274
H	-1.458166	1.557539	2.016536

3-BH3

E = -533.477493174

C	1.171699	0.138847	0.003509
C	-1.191152	0.169090	-0.019151
N	2.347374	0.712739	-0.308327
N	1.453228	-1.145944	0.356232
N	-1.484613	-1.114267	-0.372039
N	-2.361039	0.741204	0.322199
C	3.387947	-0.191268	-0.135352
C	2.836875	-1.354199	0.288226
C	-2.867961	-1.319829	-0.282022
C	-3.407777	-0.158640	0.158054
H	2.400311	1.684764	-0.604846
H	0.810003	-1.759633	0.840434
H	-0.853754	-1.722585	-0.878922
H	-2.416397	1.720434	0.589384
H	3.280944	-2.305202	0.537476
H	4.414372	0.075053	-0.333961
H	-3.318771	-2.268210	-0.529168
H	-4.429643	0.110158	0.375998

N	-0.002673	0.808757	-0.009599
B	0.100705	2.470998	0.004845
H	0.676210	2.744773	1.029571
H	0.719367	2.755137	-1.000654
H	-1.029896	2.888897	-0.048397

6-BH3

E = -537.064764101

C	1.115478	-1.088659	-0.229744
C	0.388140	1.116414	-0.060739
N	2.113115	-1.936377	-0.462155
N	-0.163667	-1.478741	-0.351288
N	-0.896826	0.746894	-0.238030
N	0.744476	2.398455	-0.075786
H	3.062289	-1.589500	-0.339457
H	1.731423	2.610669	0.057301
H	1.962955	-2.934278	-0.530990
H	0.074726	3.151202	-0.014100
N	1.393606	0.197940	0.094268
C	-1.395010	-0.757821	1.681043
H	-2.187031	-0.094318	2.043614
H	-1.655563	-1.782952	1.963000
H	-0.460304	-0.488216	2.182131
C	-2.545202	-1.119478	-0.548971
H	-2.663722	-2.194348	-0.374216
H	-3.434134	-0.641463	-0.132070
H	-2.504281	-0.942882	-1.628198
H	-0.378536	-2.390474	-0.736079
C	-1.269531	-0.646192	0.152297
C	-1.921583	1.777152	-0.458639
H	-2.135795	2.340839	0.458273
H	-1.592316	2.457469	-1.248819
H	-2.840912	1.308580	-0.800352
B	2.938094	0.711413	0.363924
H	3.340932	1.129136	-0.698770
H	2.860989	1.555858	1.224891
H	3.560136	-0.238072	0.773679

7-BH3

E = -750.029935652

C	-1.070335	-1.138370	-0.106424
C	-0.820779	1.209156	-0.066876
N	-1.929188	-2.178290	-0.229470
N	0.244253	-1.384989	-0.183829
N	0.487572	1.132162	-0.105517
N	-1.474709	2.395484	-0.199960
H	-2.902301	-1.998350	-0.002847
H	-2.462403	2.399944	0.033411
H	-1.585076	-3.119427	-0.103677
H	-0.958600	3.246268	-0.026298
N	-1.627943	0.091125	0.056895
C	2.790054	0.326541	-1.414192
H	3.817981	-0.056168	-1.399588
H	2.339089	0.010191	-2.364765
H	2.831041	1.423399	-1.423649
C	2.332806	0.132790	1.783046
H	1.638396	-0.278876	2.528331
H	3.331644	-0.253471	2.021143
H	2.336920	1.222054	1.910904
H	0.449591	-2.368544	-0.333471
Si	1.820916	-0.426016	0.041655
H	2.514068	-1.795929	0.029623
H	0.926827	2.037464	-0.251936
B	-3.242707	0.229799	0.255856
H	-3.763454	0.207964	-0.840526
H	-3.611035	-0.687952	0.962932
H	-3.472352	1.257519	0.857812

8-BH3

E = -556.782067289

C	0.616707	-1.175603	-0.039880
C	0.616600	1.175723	-0.039857
N	1.338500	-2.319042	-0.108147
N	-0.703688	-1.208043	-0.097144
N	-0.703800	1.208004	-0.097082
N	1.338220	2.319288	-0.108153
H	2.327479	-2.245413	0.110186
H	2.327238	2.245792	0.110063
H	-1.122938	-2.131195	-0.135397
H	0.878248	-3.198079	0.080208
H	0.877849	3.198235	0.080346
H	-1.123154	2.131108	-0.135361
N	1.320121	0.000096	0.037388
B	-1.701954	-0.000072	0.038667
O	-2.694265	-0.000089	-1.007918
O	-2.344614	-0.000132	1.318576
H	-2.307516	-0.000100	-1.894077
H	-3.305678	-0.000193	1.205517
B	2.950843	-0.000087	0.108064
H	3.307466	0.975430	0.737971
H	3.306965	-0.974676	0.739741
H	3.375309	-0.001183	-1.027731

$^{\oplus}$N(←PMe$_3$)$_2$ Optimized at MP2(full)/6-31+G*

E = -974.459240606

P	-1.515545	0.000934	0.072924
P	1.515459	-0.000951	0.072945
N	-0.000022	-0.000119	0.575522
C	2.574818	-0.226922	1.507557
H	2.389355	0.577768	2.223552
H	2.339461	-1.180415	1.987069
H	3.629500	-0.217873	1.217539
C	2.015793	1.545730	-0.718791
H	1.832777	2.380281	-0.036436
H	3.080022	1.522313	-0.972927
H	1.442030	1.707889	-1.635607
C	1.916690	-1.320086	-1.099099
H	1.653392	-2.289617	-0.667209
H	1.361680	-1.184787	-2.032035
H	2.986456	-1.315954	-1.330305
C	-1.917257	1.322233	-1.096497
H	-1.654314	2.290988	-0.662656
H	-1.362165	1.188987	-2.029682
H	-2.987015	1.318163	-1.327741
C	-2.015050	-1.544415	-0.721927
H	-1.441279	-1.704389	-1.639126
H	-1.831501	-2.380225	-0.041259
H	-3.079307	-1.521088	-0.975951
C	-2.574871	0.223568	1.508086
H	-2.389031	-0.582520	2.222409
H	-2.339769	1.176156	1.989519
H	-3.629582	0.214755	1.218186

Protonated $^{\oplus}N(\leftarrow PMe_3)_2$ Optimized at MP2(full)/6-31+G*
E = -974.670515172

P	1.567116	-0.006129	0.055802
P	-1.567127	0.006119	0.055797
N	-0.000010	0.000025	0.727456
C	-2.640795	0.519405	1.394329
H	-2.596942	-0.195127	2.222687
H	-2.366836	1.517365	1.748716
H	-3.673284	0.549420	1.028554
C	-2.027589	-1.629937	-0.518654
H	-1.949869	-2.352577	0.299123
H	-3.066284	-1.607379	-0.868624
H	-1.394825	-1.951886	-1.349959
C	-1.636734	1.175303	-1.302865
H	-1.371556	2.179106	-0.959289
H	-0.985754	0.876343	-2.129480
H	-2.663090	1.200220	-1.687747
C	1.636796	-1.175221	-1.302944
H	1.371705	-2.179068	-0.959430
H	0.985738	-0.876255	-2.129496
H	2.663135	-1.200019	-1.687878
C	2.027609	1.629950	-0.518544
H	1.394998	1.951893	-1.349965
H	1.949724	2.352572	0.299233
H	3.066368	1.607421	-0.868331
C	2.640733	-0.519468	1.394356
H	2.596806	0.195002	2.222765
H	2.366835	-1.517477	1.748653
H	3.673242	-0.549394	1.028626
H	0.000004	-0.000383	1.751606

1 Optimized at CCSD/6-31G*
E = -353.5669437

C	-1.175176	-0.115050	0.056059
N	-2.246901	-0.825045	-0.304132
N	0.000002	-0.743269	0.000014
C	1.175178	-0.115044	-0.056056
N	2.246908	-0.825038	0.304126
N	1.358648	1.173680	-0.442988
N	-1.358653	1.173686	0.442974
H	-3.196264	-0.497927	-0.182338
H	-2.101119	-1.773568	-0.627227
H	3.196269	-0.497920	0.182315
H	2.101131	-1.773566	0.627206
H	2.297638	1.507864	-0.630501
H	0.631175	1.614885	-0.993536
H	-0.631218	1.614844	0.993614
H	-2.297651	1.507844	0.630496

1-H+ Optimized at CCSD/6-31G*
E = -353.7721099

C	1.247828	-0.076126	-0.085982
N	2.277916	-0.751068	0.385375
N	0.000010	-0.685674	0.000083
C	-1.247832	-0.076144	0.086033
N	-2.277865	-0.751105	-0.385410
N	-1.366711	1.123580	0.633088
N	1.366652	1.123599	-0.633050
H	3.236909	-0.469402	0.185175
H	2.166187	-1.550390	1.005824
H	-3.236883	-0.469468	-0.185284
H	-2.166059	-1.550429	-1.005845
H	-2.258541	1.616868	0.619535
H	-0.657243	1.504644	1.253692
H	0.657131	1.504671	-1.253587
H	2.258484	1.616886	-0.619573
H	0.000019	-1.705091	-0.000848

1-BH3 Optimized at CCSD/6-31G*
E = -380.078473

C	-1.171556	-0.236379	-0.060999
N	-2.273310	0.389462	0.310278
N	0.001352	0.462570	-0.003139
C	1.210583	-0.160984	0.068308
N	2.289985	0.514927	-0.289487
N	1.348838	-1.449768	0.450787
N	-1.244976	-1.524927	-0.461267
H	-3.195338	0.002681	0.146437
H	-2.194074	1.347189	0.647825
H	3.223800	0.166495	-0.108596
H	2.177447	1.487044	-0.564967
H	2.282677	-1.823307	0.582642
H	0.626602	-1.882066	1.014638
H	-0.511533	-1.901101	-1.050945
H	-2.159983	-1.944166	-0.590028
B	-0.155428	2.150849	-0.024784
H	-0.826280	2.377670	-1.001081
H	-0.682545	2.423981	1.034372
H	0.948980	2.629668	-0.080430

BH3 Optimized at CCSD/6-31G*
E = - -26.4832385

B	0.000000	0.000219	0.000000
H	1.196172	-0.020594	0.000000
H	-0.614654	-1.025858	0.000000
H	-0.581518	1.045359	0.000000

Full reference for ref. 20 is given as:

Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.

Reference for B3LYP level of theory:

(a) Becke, A. D. J. Chem. Phys. 1993, 98, 5648-5652. (b) Lee, C.; Yang, W.; Parr, R. G., Phys. Rev. 1988, 37B, 785-789. (c) Perdew, J. P.; Wang, Y. Phys. Rev. 1992, 45B, 13244-13249.

Reference for MP2 (full) level of theory:

(a) Moller, C.; Plesset, M. S. Phys. Rev. 1934, 46, 618-622. (b) Krishan, R.; Frisch, M. J.; Pople, J. A. J. Chem. Phys. 1980, 72, 4244-4245.

Calculation of Absolute Proton Affinity:

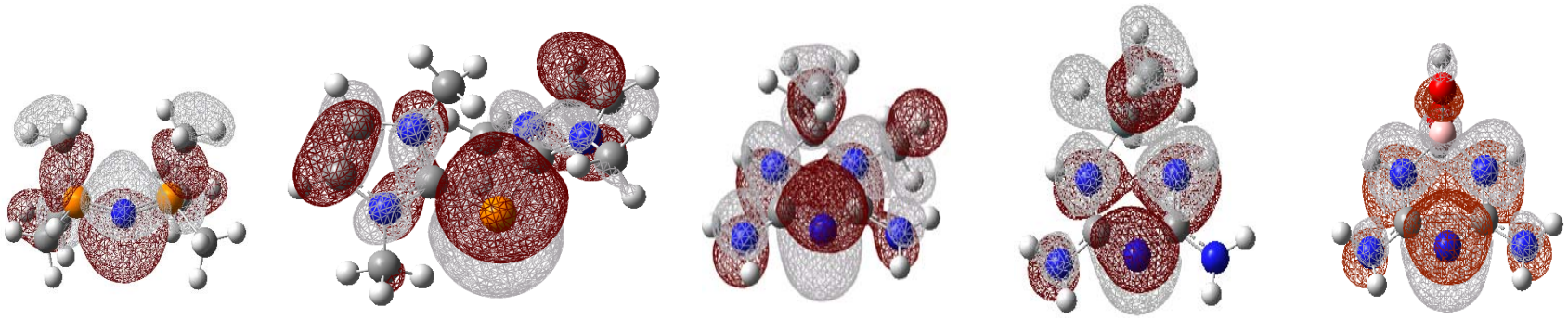
APA is the absolute proton affinity of a molecule (eq. 1).

$$APA = -\Delta H_{298} = H_{298}(B) + H_{298}(H^+) - H_{298}(BH^+)$$

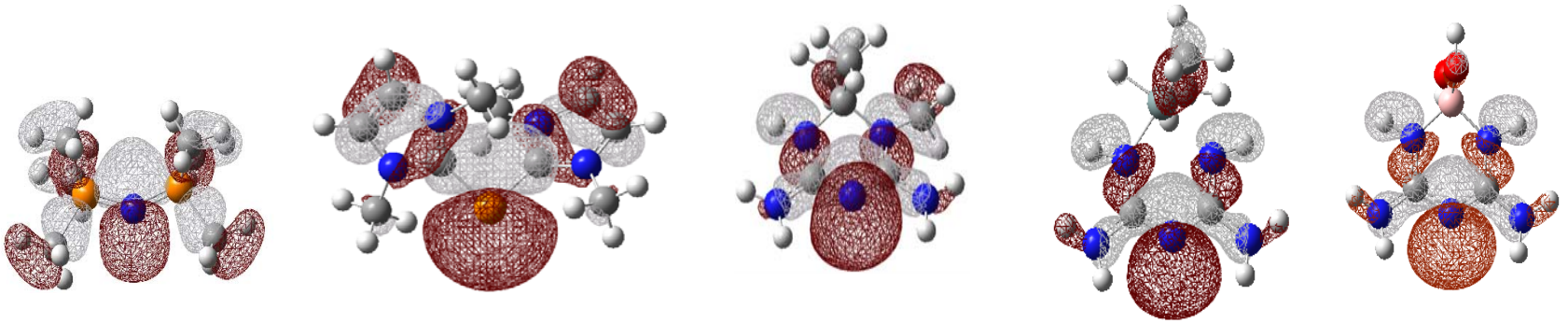
equation (1) gives the negative of enthalpy change ($-\Delta H_{298}$), which includes the changes in total energy, in zero-point energy (ZPE), in vibrational energy on going from 0 to 298.15K, and in rotational and translational energy, and a work term (RT = 0.592 kcal/mol).[15c] For H^+, only the translational energy term is not equal to zero ($H_{298}\,H^+$ = 3/2RT = 0.899kcal/mol at 298.15K) and a work term (RT = 0.592 kcal/mol).

Vertical ionization energies were calculated using equation

$$E_{deprot} = \left[E(B) - E(BH^-)\right] + \left[ZPE(B) - ZPE(BH^-)\right]$$

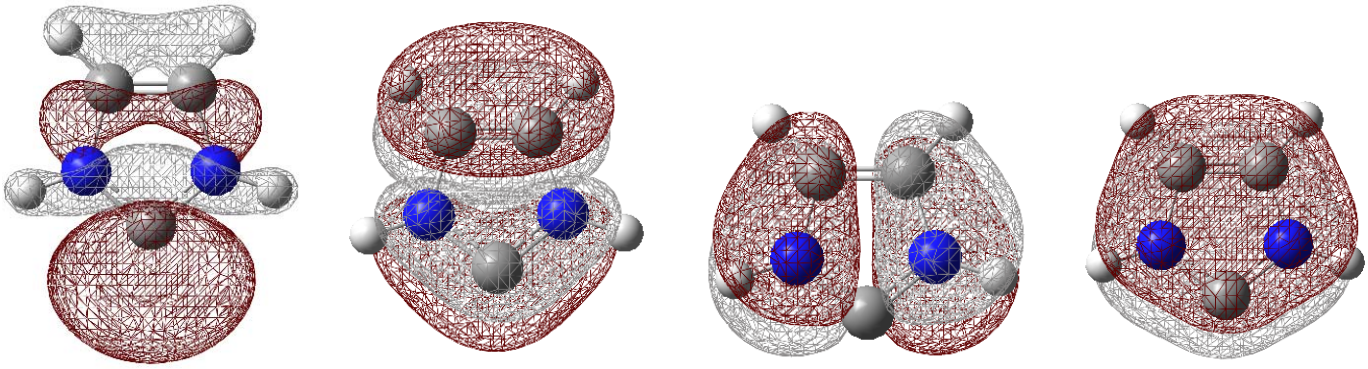


HOMO of $^{\oplus}N(\leftarrow PMe_3)_2$ **HOMO of 5** **HOMO of 6** **HOMO of 7** **HOMO of 8**



HOMO -1 of $^{\oplus}N(\leftarrow PMe_3)_2$ **HOMO -3 of 5** **HOMO -3 of 6** **HOMO -4of 7** **HOMO -4 of 8**

Figure S3: Molecular orbital showing presence of π and σ two lone pairs on central nitrogen of $^{\oplus}N(\leftarrow PMe_3)_2$ and **5-8**.



(A) HOMO **(B) HOMO-1** **(C) HOMO-2** **(D) HOMO-3**

Fig. S4: Representative MOs of the N-Heterocyclic carbine (NHC) calculated at B3LYP/6-31+G*

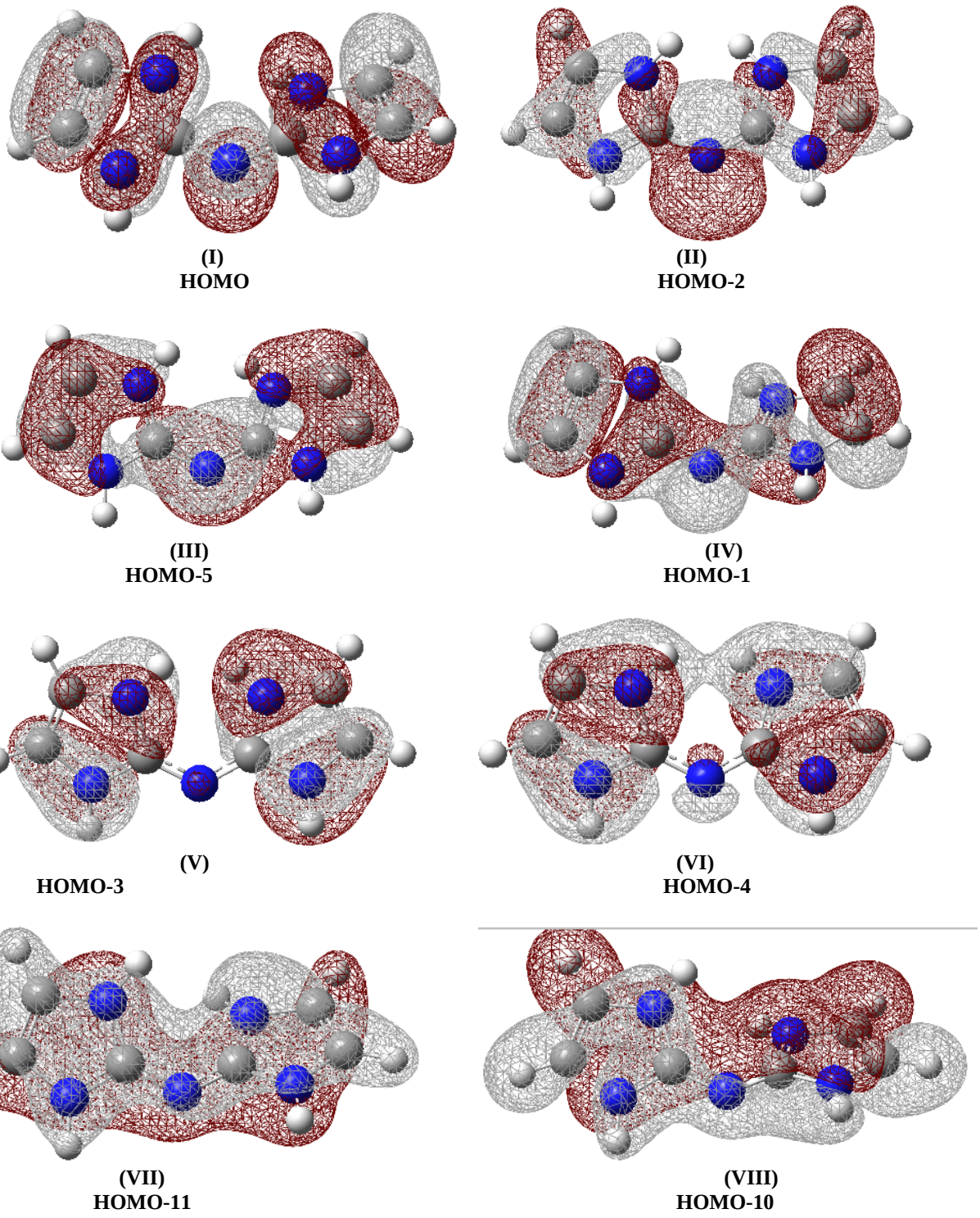


Fig. S5: Representative MOs of the compd. **3** in comparison to NHC calculated at B3LYP/6-31+G*. In this figure MO No. **VII** is the most stable full π-type bonding orbital while MO No. **VIII** is π-type anti-bonding orbital between two **D**. MO No. **III** is the π-type bonding orbital while MO No. **IV** π-type anti-bonding orbital between two **B**. MO No. **V** is the π-type bonding orbital while MO No. **VI** π-type anti-bonding orbital between two **C**. MO No. **I** is over and above π-type molecular orbital which is present in compd. **3** (one of the representative of title compounds). These analyses strongly support the presence of two lone pair in the title compounds.

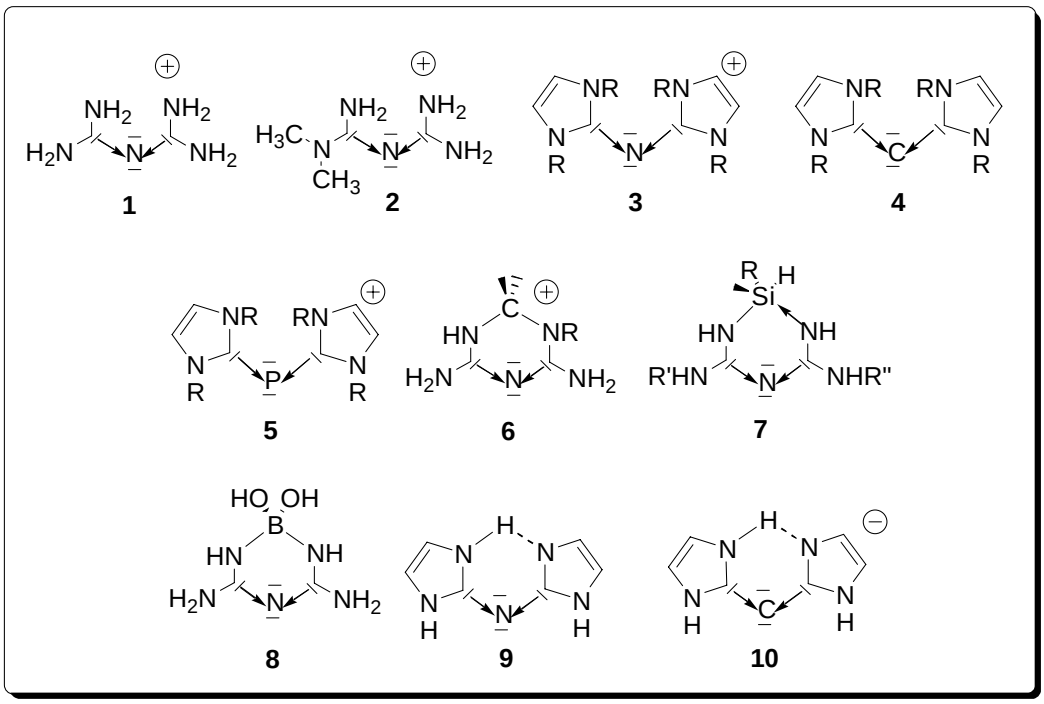


Fig. S6: In structures **1-10,** the carbons next to the central nitrogen would ordinarily be assumed to have a hydrogen attached, so as to satisfy the valence of carbon. Indeed there is no hydrogen, to avoid any possible confusion, structures **1-10** have been redrawn here in the best way. However, it should be noted that the representation of these systems as given in the main text became acceptable over a period of the past 3-4 years.