# Supporting Information for "Theoretical Prediction of New Noble-Gas Molecules FNgBNR (Ng = Ar, Kr, and Xe; R = H, $CH_3$,CCH, $CHCH_2$, F, and OH)"

**Jien-Lian Chen, Chang-Yu Yang, Hsiao-Jing Lin, and Wei-Ping Hu***
*Department of Chemistry and Biochemistry, National Chung Cheng University*
*Chia-Yi, Taiwan 621*

E-mail: chewph@ccu.edu.tw

Fax: 886-5-272-1040

12 Tables, 3 Figures.

Submitted to *Physical Chemistry Chemical Physic*, March 2013

Table S1 The calculated geometries (in Å) of FArBNR at various methods.

| | F–Ar | Ar–B | B–N | N–R |
|---|---|---|---|---|
| | | FArBNH | | |
| MP2/aug-cc-pVDZ | 2.041 | 1.794 | 1.244 | 1.004 |
| MP2/aug-cc-pVTZ | 2.009 | 1.775 | 1.236 | 0.995 |
| B3LYP/aug-cc-pVDZ | 2.024 | 1.831 | 1.229 | 1.000 |
| B3LYP/aug-cc-pVTZ | 2.018 | 1.816 | 1.225 | 0.994 |
| MPW1PW91/aug-cc-pVDZ | 2.000 | 1.807 | 1.228 | 0.998 |
| MPW1PW91/aug-cc-pVTZ | 1.991 | 1.796 | 1.223 | 0.992 |
| CCSD(T)/aug-cc-pVTZ | 2.019 | 1.791 | 1.234 | 0.996 |
| | | FArBNCH$_3$ | | |
| MP2/aug-cc-pVDZ | 2.058 | 1.790 | 1.246 | 1.431 |
| MP2/aug-cc-pVTZ | 2.024 | 1.773 | 1.239 | 1.419 |
| B3LYP/aug-cc-pVDZ | 2.039 | 1.829 | 1.229 | 1.421 |
| B3LYP/aug-cc-pVTZ | 2.032 | 1.815 | 1.225 | 1.415 |
| MPW1PW91/aug-cc-pVDZ | 2.014 | 1.805 | 1.228 | 1.412 |
| MPW1PW91/aug-cc-pVTZ | 2.004 | 1.796 | 1.224 | 1.407 |
| | | FArBNCCH | | |
| MP2/aug-cc-pVDZ | 2.023 | 1.800 | 1.254 | 1.320 |
| MP2/aug-cc-pVTZ | 1.991 | 1.780 | 1.247 | 1.308 |
| B3LYP/aug-cc-pVDZ | 2.012 | 1.833 | 1.242 | 1.306 |
| B3LYP/aug-cc-pVTZ | 2.006 | 1.817 | 1.237 | 1.300 |
| MPW1PW91/aug-cc-pVDZ | 1.987 | 1.808 | 1.240 | 1.303 |
| MPW1PW91/aug-cc-pVTZ | 1.977 | 1.797 | 1.236 | 1.297 |
| | | FArBNCHCH$_2$ | | |
| MP2/aug-cc-pVDZ | 2.046 | 1.792 | 1.251 | 1.388 |
| MP2/aug-cc-pVTZ | 2.014 | 1.774 | 1.244 | 1.376 |
| B3LYP/aug-cc-pVDZ | 2.029 | 1.830 | 1.235 | 1.377 |
| B3LYP/aug-cc-pVTZ | 2.022 | 1.816 | 1.231 | 1.370 |
| MPW1PW91/aug-cc-pVDZ | 2.004 | 1.806 | 1.234 | 1.371 |
| MPW1PW91/aug-cc-pVTZ | 1.995 | 1.796 | 1.230 | 1.365 |
| | | FArBNF | | |
| MP2/aug-cc-pVDZ | 2.021 | 1.806 | 1.239 | 1.312 |
| MP2/aug-cc-pVTZ | 1.992 | 1.785 | 1.230 | 1.299 |
| B3LYP/aug-cc-pVDZ | 2.014 | 1.843 | 1.225 | 1.307 |
| B3LYP/aug-cc-pVTZ | 2.007 | 1.827 | 1.219 | 1.303 |
| MPW1PW91/aug-cc-pVDZ | 1.989 | 1.816 | 1.222 | 1.294 |

| | | | | |
|---|---|---|---|---|
| MPW1PW91/aug-cc-pVTZ | 1.982 | 1.805 | 1.217 | 1.290 |
| | | FArBNOH | | |
| MP2/aug-cc-pVDZ | 2.044 | 1.797 | 1.242 | 1.336 |
| MP2/aug-cc-pVTZ | 2.068 | 1.808 | 1.242 | 1.336 |
| B3LYP/aug-cc-pVDZ | 2.030 | 1.836 | 1.227 | 1.331 |
| B3LYP/aug-cc-pVTZ | 2.024 | 1.820 | 1.222 | 1.328 |
| MPW1PW91/aug-cc-pVDZ | 2.006 | 1.811 | 1.225 | 1.319 |
| MPW1PW91/aug-cc-pVTZ | 1.998 | 1.800 | 1.220 | 1.316 |

Table S2 The calculated geometries (in Å) of FKrBNR at various methods.

| | F–Kr | Kr–B | B–N | N–R |
|---|---|---|---|---|
| | | FKrBNH | | |
| MP2/aug-cc-pVDZ | 2.082 | 1.961 | 1.248 | 1.003 |
| MP2/aug-cc-pVTZ | 2.059 | 1.937 | 1.240 | 0.995 |
| B3LYP/aug-cc-pVDZ | 2.084 | 1.995 | 1.233 | 1.000 |
| B3LYP/aug-cc-pVTZ | 2.075 | 1.983 | 1.228 | 0.993 |
| MPW1PW91/aug-cc-pVDZ | 2.058 | 1.971 | 1.231 | 0.997 |
| MPW1PW91/aug-cc-pVTZ | 2.047 | 1.964 | 1.227 | 0.992 |
| CCSD(T)/aug-cc-pVTZ | 2.064 | 1.953 | 1.238 | 0.995 |
| | | $FKrBNCH_3$ | | |
| MP2/aug-cc-pVDZ | 2.097 | 1.958 | 1.250 | 1.430 |
| MP2/aug-cc-pVTZ | 2.073 | 1.934 | 1.242 | 1.417 |
| B3LYP/aug-cc-pVDZ | 2.095 | 1.993 | 1.233 | 1.420 |
| B3LYP/aug-cc-pVTZ | 2.087 | 1.982 | 1.228 | 1.414 |
| MPW1PW91/aug-cc-pVDZ | 2.070 | 1.970 | 1.231 | 1.411 |
| MPW1PW91/aug-cc-pVTZ | 2.059 | 1.962 | 1.227 | 1.406 |
| | | FKrBNCCH | | |
| MP2/aug-cc-pVDZ | 2.068 | 1.966 | 1.258 | 1.319 |
| MP2/aug-cc-pVTZ | 2.045 | 1.940 | 1.250 | 1.307 |
| B3LYP/aug-cc-pVDZ | 2.071 | 1.995 | 1.245 | 1.306 |
| B3LYP/aug-cc-pVTZ | 2.062 | 1.983 | 1.241 | 1.299 |
| MPW1PW91/aug-cc-pVDZ | 2.045 | 1.972 | 1.244 | 1.302 |
| MPW1PW91/aug-cc-pVTZ | 2.033 | 1.964 | 1.239 | 1.296 |
| | | $FKrBNCHCH_2$ | | |
| MP2/aug-cc-pVDZ | 2.086 | 1.960 | 1.255 | 1.386 |
| MP2/aug-cc-pVTZ | 2.063 | 1.935 | 1.247 | 1.373 |
| B3LYP/aug-cc-pVDZ | 2.086 | 1.994 | 1.239 | 1.375 |
| B3LYP/aug-cc-pVTZ | 2.078 | 1.982 | 1.234 | 1.368 |
| MPW1PW91/aug-cc-pVDZ | 2.059 | 1.970 | 1.237 | 1.369 |
| MPW1PW91/aug-cc-pVTZ | 2.050 | 1.962 | 1.233 | 1.363 |
| | | FKrBNF | | |
| MP2/aug-cc-pVDZ | 2.066 | 1.971 | 1.243 | 1.315 |
| MP2/aug-cc-pVTZ | 2.045 | 1.945 | 1.234 | 1.302 |
| B3LYP/aug-cc-pVDZ | 2.073 | 2.002 | 1.228 | 1.310 |
| B3LYP/aug-cc-pVTZ | 2.064 | 1.990 | 1.222 | 1.306 |
| MPW1PW91/aug-cc-pVDZ | 2.048 | 1.978 | 1.226 | 1.297 |

| | | | | |
|---|---|---|---|---|
| MPW1PW91/aug-cc-pVTZ | 2.037 | 1.970 | 1.220 | 1.293 |
| | | FKrBNOH | | |
| MP2/aug-cc-pVDZ | 2.085 | 1.963 | 1.247 | 1.339 |
| MP2/aug-cc-pVTZ | 2.063 | 1.938 | 1.238 | 1.328 |
| B3LYP/aug-cc-pVDZ | 2.088 | 1.998 | 1.230 | 1.333 |
| B3LYP/aug-cc-pVTZ | 2.079 | 1.985 | 1.225 | 1.330 |
| MPW1PW91/aug-cc-pVDZ | 2.062 | 1.973 | 1.229 | 1.321 |
| MPW1PW91/aug-cc-pVTZ | 2.052 | 1.965 | 1.224 | 1.318 |

Table S3 The calculated geometries (in Å) of FXeBNR at various methods.

| | F–Xe | Xe–B | B–N | N–R |
|---|---|---|---|---|
| | | FXeBNH | | |
| MP2/aug-cc-pVDZ | 2.153 | 2.154 | 1.253 | 1.003 |
| MP2/aug-cc-pVTZ | 2.129 | 2.131 | 1.244 | 0.994 |
| B3LYP/aug-cc-pVDZ | 2.161 | 2.187 | 1.237 | 0.999 |
| B3LYP/aug-cc-pVTZ | 2.145 | 2.179 | 1.232 | 0.993 |
| MPW1PW91/aug-cc-pVDZ | 2.137 | 2.165 | 1.235 | 0.997 |
| MPW1PW91/aug-cc-pVTZ | 2.118 | 2.161 | 1.231 | 0.991 |
| CCSD(T)/aug-cc-pVTZ | 2.128 | 2.148 | 1.242 | 0.994 |
| | | $FXeBNCH_3$ | | |
| MP2/aug-cc-pVDZ | 2.163 | 2.150 | 1.255 | 1.428 |
| MP2/aug-cc-pVTZ | 2.139 | 2.128 | 1.246 | 1.416 |
| B3LYP/aug-cc-pVDZ | 2.171 | 2.184 | 1.236 | 1.418 |
| B3LYP/aug-cc-pVTZ | 2.154 | 2.177 | 1.232 | 1.412 |
| MPW1PW91/aug-cc-pVDZ | 2.145 | 2.163 | 1.235 | 1.410 |
| MPW1PW91/aug-cc-pVTZ | 2.126 | 2.159 | 1.231 | 1.404 |
| | | FXeBNCCH | | |
| MP2/aug-cc-pVDZ | 2.142 | 2.152 | 1.263 | 1.317 |
| MP2/aug-cc-pVTZ | 2.118 | 2.129 | 1.254 | 1.305 |
| B3LYP/aug-cc-pVDZ | 2.149 | 2.185 | 1.250 | 1.304 |
| B3LYP/aug-cc-pVTZ | 2.132 | 2.178 | 1.245 | 1.298 |
| MPW1PW91/aug-cc-pVDZ | 2.124 | 2.163 | 1.248 | 1.301 |
| MPW1PW91/aug-cc-pVTZ | 2.105 | 2.159 | 1.244 | 1.295 |
| | | $FXeBNCHCH_2$ | | |
| MP2/aug-cc-pVDZ | 2.155 | 2.150 | 1.260 | 1.383 |
| MP2/aug-cc-pVTZ | 2.131 | 2.128 | 1.251 | 1.371 |
| B3LYP/aug-cc-pVDZ | 2.162 | 2.184 | 1.243 | 1.373 |
| B3LYP/aug-cc-pVTZ | 2.146 | 2.177 | 1.238 | 1.366 |
| MPW1PW91/aug-cc-pVDZ | 2.137 | 2.163 | 1.242 | 1.367 |
| MPW1PW91/aug-cc-pVTZ | 2.118 | 2.159 | 1.237 | 1.361 |
| | | FXeBNF | | |
| MP2/aug-cc-pVDZ | 2.142 | 2.158 | 1.248 | 1.318 |
| MP2/aug-cc-pVTZ | 2.118 | 2.135 | 1.238 | 1.304 |
| B3LYP/aug-cc-pVDZ | 2.151 | 2.192 | 1.232 | 1.313 |
| B3LYP/aug-cc-pVTZ | 2.134 | 2.184 | 1.227 | 1.308 |
| MPW1PW91/aug-cc-pVDZ | 2.126 | 2.169 | 1.230 | 1.300 |

| | | | | |
|---|---|---|---|---|
| MPW1PW91/aug-cc-pVTZ | 2.108 | 2.165 | 1.225 | 1.295 |
| | | FXeBNOH | | |
| MP2/aug-cc-pVDZ | 2.155 | 2.153 | 1.251 | 1.342 |
| MP2/aug-cc-pVTZ | 2.130 | 2.130 | 1.242 | 1.331 |
| B3LYP/aug-cc-pVDZ | 2.164 | 2.187 | 1.235 | 1.336 |
| B3LYP/aug-cc-pVTZ | 2.148 | 2.178 | 1.230 | 1.332 |
| MPW1PW91/aug-cc-pVDZ | 2.139 | 2.164 | 1.233 | 1.323 |
| MPW1PW91/aug-cc-pVTZ | 2.121 | 2.160 | 1.228 | 1.319 |

Table S4 The calculated three-body dissociation energies (in kcal/mol) of FNgBNR → F + Ng + BNR

| | Ar | Kr | Xe |
|---|---|---|---|
| | | R=H | |
| MP2/aug-cc-pVDZ | 12.2 | 32.0 | 58.2 |
| MP2/aug-cc-pVTZ | 20.3 | 41.0 | 67.1 |
| B3LYP/aug-cc-pVDZ | 15.3 | 31.1 | 53.2 |
| B3LYP/aug-cc-pVTZ | 16.9 | 33.1 | 55.4 |
| MPW1PW91/aug-cc-pVDZ | 11.6 | 28.6 | 51.6 |
| MPW1PW91/aug-cc-pVTZ | 12.9 | 30.3 | 53.5 |
| CCSD(T)/aug-cc-pVTZ | 10.1 | 30.7 | 66.4 |
| CCSD(T)/aug-cc-pVQZ[a] | 11.5 | 31.8 | 59.6 |
| | | R=$CH_3$ | |
| MP2/aug-cc-pVDZ | 19.3 | 35.1 | 61.0 |
| MP2/aug-cc-pVTZ | 23.6 | 44.0 | 69.8 |
| B3LYP/aug-cc-pVDZ | 17.2 | 32.5 | 54.0 |
| B3LYP/aug-cc-pVTZ | 18.7 | 34.4 | 56.2 |
| MPW1PW91/aug-cc-pVDZ | 11.6 | 29.9 | 52.5 |
| MPW1PW91/aug-cc-pVTZ | 14.6 | 31.5 | 54.4 |
| CCSD(T)/aug-cc-pVTZ[b] | 11.3 | 32.6 | 58.6 |
| | | R=CCH | |
| MP2/aug-cc-pVDZ | 17.0 | 37.9 | 65.5 |
| MP2/aug-cc-pVTZ | 23.6 | 45.5 | 72.9 |
| B3LYP/aug-cc-pVDZ | 13.0 | 29.7 | 52.7 |
| B3LYP/aug-cc-pVTZ | 14.5 | 31.5 | 54.8 |
| MPW1PW91/aug-cc-pVDZ | 9.0 | 26.9 | 51.1 |
| MPW1PW91/aug-cc-pVTZ | 10.3 | 28.5 | 52.9 |
| CCSD(T)/aug-cc-pVTZ[b] | 8.5 | 30.3 | 58.0 |
| | | R=$CHCH_2$ | |
| MP2/aug-cc-pVDZ | 17.0 | 39.3 | 65.8 |
| MP2/aug-cc-pVTZ | 26.4 | 47.4 | 73.9 |
| B3LYP/aug-cc-pVDZ | 15.5 | 31.3 | 53.3 |
| B3LYP/aug-cc-pVTZ | 17.0 | 33.2 | 55.5 |
| MPW1PW91/aug-cc-pVDZ | 9.0 | 28.6 | 51.7 |
| MPW1PW91/aug-cc-pVTZ | 12.9 | 30.3 | 53.6 |
| CCSD(T)/aug-cc-pVTZ[b] | 8.5 | 32.2 | 58.8 |
| | | R=F | |

| | | | |
|---|---|---|---|
| MP2/aug-cc-pVDZ | 15.8 | 31.3 | 58.6 |
| MP2/aug-cc-pVTZ | 18.7 | 40.4 | 67.6 |
| B3LYP/aug-cc-pVDZ | 12.7 | 29.3 | 52.2 |
| B3LYP/aug-cc-pVTZ | 14.5 | 31.5 | 54.6 |
| MPW1PW91/aug-cc-pVDZ | 13.4 | 26.8 | 50.7 |
| MPW1PW91/aug-cc-pVTZ | 10.6 | 28.7 | 52.9 |
| CCSD(T)/aug-cc-pVTZ[b] | 12.2 | 28.8 | 56.2 |
| | | R=OH | |
| MP2/aug-cc-pVDZ | 14.3 | 34.3 | 60.8 |
| MP2/aug-cc-pVTZ | 22.4 | 43.4 | 69.9 |
| B3LYP/aug-cc-pVDZ | 15.4 | 31.3 | 53.4 |
| B3LYP/aug-cc-pVTZ | 17.2 | 33.5 | 55.8 |
| MPW1PW91/aug-cc-pVDZ | 11.7 | 28.8 | 51.9 |
| MPW1PW91/aug-cc-pVTZ | 13.2 | 30.6 | 54.1 |
| CCSD(T)/aug-cc-pVTZ[b] | 10.1 | 31.0 | 57.7 |

[a]Single-point energies using the CCSD(T)/aptz geometry.

[b]Single-point energies using the MPW1PW91/apdz geometry.

**CCSD(T)/CBS calculation of the H–C bond energies**

Table S4 Calculated hemolytic bond dissociation energies [a] (in kcal/mol)

| | H–CCH | H–CN |
|---|---|---|
| CCSD(T)/aug-cc-pVQZ | 139.4 | 132.8 |
| CCSD(T)/aug-cc-pV5Z | 139.7 | 133.0 |
| CCSD(T)/CBS | 140.9 | 133.3 |
| exp.[b] | 136.8 | 129.4 |

[a] Born-Oppenheimer energies, not including zero-point and thermal energies.
[b]Obtained using the heats of formation from NIST Chemistry WebBook (Ref. S1) and the calculated zero-point and thermal energies at the CCSD(T)/aptz level.

**Comparison of the bond energies of RCC–H , RNB–H and RNB–NgF**

As seen in the following table, the bond energies are fairly constant regardless the identities of the R groups for all five types of molecules listed in the following table with the only exception of HCCOH. The bond energies of H–CCR are ~20 kcal/mol higher than those of H–BNR. The bond energies of F–Ng–BNR are significantly lower. It is interesting to note that the bond energies are predicted to be slightly more sensitive to the identities R groups for FNgBNR. It is difficult to say whether the trends in bond energies parallel or not among these five series of molecules since the bond energies in a series are all similar and the differences were probably within the calculation errors.

Table S5 The calculated bond dissociation energies (in kcal/mol) by CCSD(T)/aug-cc-pVQZ level.

| | R=H[a] | R=$CH_3$[b] | R=CCH[b] | R=$CHCH_2$[b] | R=F[b] | R=OH[b] |
|---|---|---|---|---|---|---|
| H–BNR | 116.3 | 116.3 | 117.8 | 117.3 | 116.6 | 116.4 |
| H–CCR | 139.5 | 140.1 | 141.1 | 138.5 | 140.8 | 132.9 |
| F–Ar–BNR | 11.5 | 13.6 | 9.8 | 12.6 | 8.5 | 11.5 |
| F–Kr–BNR | 31.8 | 33.5 | 31.1 | 33.0 | 29.7 | 31.9 |
| F–Xe–BNR | 59.8 | 61.1 | 60.3 | 61.3 | 58.0 | 60.0 |

[a]Single-point energies using the CCSD(T)/aptz geometry.
[b]Single-point energies using the MPW1PW91/apdz geometry.

**Comparison of the bond lengths of RNBH, RCCH, and RNBNgF.**

As seen in the following tables, the H–B bonds are ~0.1 Å longer than the H–C bonds. The H–B distance is almost independent of the R groups while the H–C distances show slightly more variation. The B–N distances are 0.02-0.03 Å longer than the C–C distances. Both bonds show only very small variations (< 0.02 Å) with different R groups. The C–R and N–R bonds show much stronger dependence on the identities of the R groups. Most importantly, the BN–CCH bond was predicted to be very short (1.30 Å), similar to a double bond, but the CC–CCH bond was predicted to be considerably longer (1.37 Å). Also the BN–$CH_3$ (1.41 Å) and BN–$CHCH_2$ (1.36 Å) bonds are significantly shorter than the CC–$CH_3$ (1.46 Å) and CC–$CHCH_2$ (1.42 Å) bonds. However, the BN–F (1.30 Å) and BN–OH (1.33 Å) bonds were predicted to be slightly longer (by 0.02 A) than the CC–F (1.28 Å) and CC–OH (1.31 Å) bonds. It is obvious that although CC and BN are isoelectronic, *the nature of these two types of double bonds is different* and makes the trends in the relative bond lengths between the BN–R and CC–R not very uniform. On the other hand, the bond length trends of BN–R or CC–R within each series are quite similar.

If we compare the N–R bond lengths in HBNR and FNgBNR (see Figure 2), we found the *trends parallel*. The N–H bonds of course are both the shortest (~1.00 Å). For other R groups, the N–F and N–CCH bonds are the shortest N–R bonds in both HBNR and FNgBNR with bond length around 1.30 Å. The N–$CH_3$ are the longest N–C bonds in both HBNR and FNgBNR with bond length around 1.41 Å. In addition, for both sets of molecules, the N–$CHCH_2$ bond lengths (~1.37 A) are between the N–CCH and N–$CH_3$. These trends indicated that in FNgBNR molecules the FNg– part does not seem to have significant effects on the bonding properties of the BN–R.

Table S6 The calculated geometries (in Å) of HBNR.

| | R(H–B) | R(B–N) | R(N–R) |
|---|---|---|---|
| R=H[a] | 1.170 | 1.244 | 0.993 |
| R=$CH_3$[b] | 1.173 | 1.238 | 1.408 |
| R=CCH[b] | 1.171 | 1.249 | 1.301 |
| R=$CHCH_2$[b] | 1.173 | 1.243 | 1.364 |
| R=F[b] | 1.173 | 1.231 | 1.304 |
| R=OH[b] | 1.173 | 1.234 | 1.328 |

[a]The calculated geometries were obtained at the CCSD(T)/aptz level.

[b]The calculated geometries were obtained at theMPW1PW91/apdz level.

Table S7 The calculated geometries (in Å) of HCCR.

| | R(H–C) | R(C–C) | R(C–R) |
|---|---|---|---|
| R=H[a] | 1.064 | 1.210 | 1.064 |
| R=$CH_3$[b] | 1.075 | 1.222 | 1.460 |
| R=CCH[b] | 1.069 | 1.215 | 1.370 |
| R=$CHCH_2$[b] | 1.069 | 1.214 | 1.424 |
| R=F[b] | 1.062 | 1.203 | 1.283 |
| R=OH[b] | 1.068 | 1.208 | 1.307 |

[a]The calculated geometries were obtained at the CCSD(T)/aptz level.

[b]The calculated geometries were obtained at theMPW1PW91/apdz level.

Table S8 Calculated reaction energies (in kcal/mol) of FNgBNR → Ng + FBNR

| | Ar | Kr | Xe |
|---|---|---|---|
| | | R=H | |
| MPW1PW91/apdz | –142.3 | –125.3 | –102.2 |
| MP2/apdz | –146.1 | –126.3 | –100.0 |
| CCSD(T)/aptz[a] | –148.9 | –128.2 | –101.8 |
| | | $R=CH_3$ | |
| MPW1PW91/apdz | –139.1 | –122.6 | –100.0 |
| MP2/apdz | –142.4 | –123.1 | –97.2 |
| CCSD(T)/aptz[a] | –145.4 | –125.1 | –99.1 |
| | | R=CCH | |
| MPW1PW91/apdz | –144.1 | –126.2 | –102.0 |
| MP2/apdz | –147.6 | –126.6 | –99.1 |
| CCSD(T)/aptz[a] | –150.7 | –128.9 | –101.2 |
| | | $R=CHCH_2$ | |
| MPW1PW91/apdz | –141.3 | –124.3 | –101.2 |
| MP2/apdz | –144.6 | –124.6 | –98.1 |
| CCSD(T)/aptz[a] | –147.6 | –126.7 | –100.0 |
| | | R=F | |
| MPW1PW91/apdz | –140.4 | –122.6 | –98.7 |
| MP2/apdz | –144.7 | –123.8 | –96.5 |
| CCSD(T)/aptz[a] | –147.4 | –125.8 | –98.3 |
| | | R=OH | |
| MPW1PW91/apdz | –138.2 | –121.1 | –98.0 |
| MP2/apdz | –142.2 | –122.1 | –95.6 |
| CCSD(T)/aptz[a] | –145.0 | –124.0 | –97.3 |

[a]Single-point energies using the MPW1PW91/apdz geometry. The level of theory is the same as the CCSD(T)/aptz in Table 2 and approximately the same as the CCSD(T)/aptz in Table 1 in which the geometry was also calculated at the CCSD(T)/aptz level.

Table S9 Calculated barrier heights (in kcal/mol) of FNgBNR → Ng + FBNR

| | Ar | Kr | Xe |
|---|---|---|---|
| | | R=H | |
| MP2/apdz | 15.0 | 23.7 | 33.3 |
| MP2/aptz | 15.4 | 23.3 | 31.5 |
| B3LYP/apdz | 20.4 | 27.9 | 35.8 |
| B3LYP/aptz | 19.5 | 26.8 | 33.8 |
| MPW1PW91/apdz | 20.7 | 28.5 | 36.6 |
| MPW1PW91/aptz | 19.9 | 27.5 | 34.7 |
| CCSD(T)/aptz | 15.9 | 23.9 | 32.5 |
| CCSD(T)/apqz[a] | 16.0 | 24.1 | 32.3 |
| CCSD(T)/ap5z[a] | 16.1 | 24.1 | 32.7 |
| | | R=$CH_3$ | |
| MP2/apdz | 13.9 | 22.4 | 32.0 |
| MP2/aptz | 14.5 | 22.2 | 30.3 |
| B3LYP/apdz | 19.1 | 26.6 | 34.5 |
| B3LYP/aptz | 18.4 | 25.6 | 32.7 |
| MPW1PW91/apdz | 19.5 | 27.2 | 35.4 |
| MPW1PW91/aptz | 18.9 | 26.4 | 33.7 |
| CCSD(T)/aptz[b] | 14.8 | 22.7 | 31.2 |
| | | R=CCH | |
| MP2/apdz | 16.0 | 25.0 | 34.7 |
| MP2/aptz | 16.5 | 24.6 | 32.6 |
| B3LYP/apdz | 21.0 | 28.9 | 36.9 |
| B3LYP/aptz | 20.2 | 27.7 | 34.9 |
| MPW1PW91/apdz | 21.4 | 29.5 | 37.8 |
| MPW1PW91/aptz | 20.7 | 28.5 | 35.9 |
| CCSD(T)/aptz[b] | 16.0 | 25.1 | 33.5 |
| | | R=$CHCH_2$ | |
| MP2/apdz | 14.4 | 23.0 | 32.8 |
| MP2/aptz | 14.9 | 22.8 | 30.9 |
| B3LYP/apdz | 19.6 | 27.3 | 35.2 |
| B3LYP/aptz | 18.9 | 26.2 | 33.4 |
| MPW1PW91/apdz | 20.2 | 27.9 | 36.2 |
| MPW1PW91/aptz | 19.4 | 27.0 | 34.4 |
| CCSD(T)/aptz[b] | 15.3 | 23.4 | 41.3 |
| | | R=F | |

| | | | |
|---|---|---|---|
| MP2/apdz | 16.3 | 25.4 | 35.2 |
| MP2/aptz | 16.7 | 24.8 | 33.2 |
| B3LYP/apdz | 21.8 | 29.6 | 37.5 |
| B3LYP/aptz | 20.9 | 28.4 | 35.6 |
| MPW1PW91/apdz | 22.1 | 30.1 | 38.3 |
| MPW1PW91/aptz | 21.3 | 29.0 | 36.4 |
| CCSD(T)/aptz[b] | 17.0 | 25.5 | 34.2 |
| | | R=OH | |
| MP2/apdz | 19.4 | 27.2 | 35.5 |
| MP2/aptz | 14.5 | 22.3 | 30.7 |
| B3LYP/apdz | 19.1 | 26.7 | 34.7 |
| B3LYP/aptz | 18.3 | 25.6 | 32.9 |
| MPW1PW91/apdz | 14.0 | 22.6 | 32.4 |
| MPW1PW91/aptz | 18.7 | 26.3 | 33.8 |
| CCSD(T)/aptz[b] | 14.8 | 22.9 | 31.6 |

[a]Single-point energies using the CCSD(T)/aptz geometry.

[b]Single-point energies using the MPW1PW91/apdz geometry.

**Stability comparison of the FNgBNH and FNgNBH**

Table S10 Calculated Relative Energies (kcal/mol) by CCSD(T)/aug-cc-pVQZ level.[a]

| | FNgBNH | FNgNBH |
|---|---|---|
| Ng= Ar | 0.0 | 41.4 |
| Ng= Kr | 0.0 | 31.0 |
| Ng= Xe | 0.0 | 19.1 |

[a]Single-point energies using the CCSD(T)/aptz geometry for FNgBNH and using MPW1PW91/apdz geometry for FNgNBH.

Table S11 Calculated bond dissociation energies and barrier heights (in kcal/mol) of FNgBNH and FNgNBH isomers

| | FNgBNH | | FNgNBH | |
|---|---|---|---|---|
| | three-body dissociation energy[a] | Barrier height[b] | three-body dissociation energy[b] | Barrier height[b] |
| Ng=Ar | 11.5 | 15.7 | –9.9 | NA[c] |
| Ng=Kr | 31.8 | 23.8 | 20.7 | 48.6 |
| Ng=Xe | 59.6 | 32.4 | 60.5 | 60.5 |

[a]CCSD(T)/apqz single-point energies using the CCSD(T)/aptz geometry.

[b]CCSD(T)/aptz single-point energies using the MPW1PW91/apdz geometry.

[c]In CCSD(T)/aptz single-point energy calculations, the energy of transitions state was lower than that of the reactant.

Table S12 Calculated atomic charges[a] of FNgCCH by ChelpG and NBO (in parentheses) methods, in atomic unit, *e*.

| | F | Ng | C | C | H |
|---|---|---|---|---|---|
| FArCCH | –0.493 (–0.629) | 0.542 (0.722) | –0.057 (–0.122) | –0.253 (–0.212) | 0.261 (0.241) |
| FKrCCH | –0.484 (–0.667) | 0.594 (0.884) | –0.104 (–0.239) | –0.273 (–0.217) | 0.268 (0.239) |
| FXeCCH | –0.451 (–0.710) | 0.609 (1.071) | –0.151 (–0.380) | –0.259 (–0.216) | 0.253 (0.234) |

[a]Using electron density calculated at the MP2/aug-cc-pVTZ level

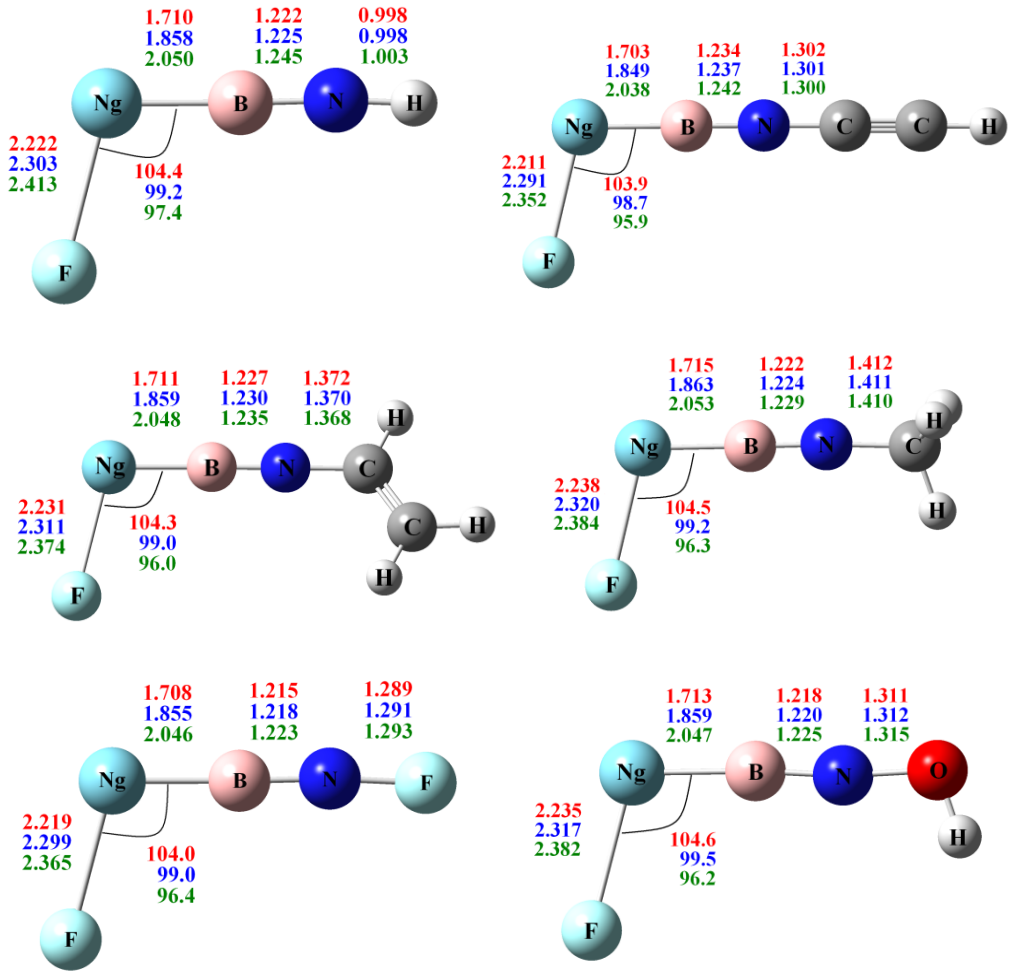


**Figure S1** Calculated geometry of the transition states of the two-body dissociation of FNgBNR at the MPW1PW91/aug-cc-pVDZ level. The values in red, blue, and green colors are for Ng = Ar, Kr, and Xe, respectively. The bond lengths are in angstroms, and the bond angles in degrees.

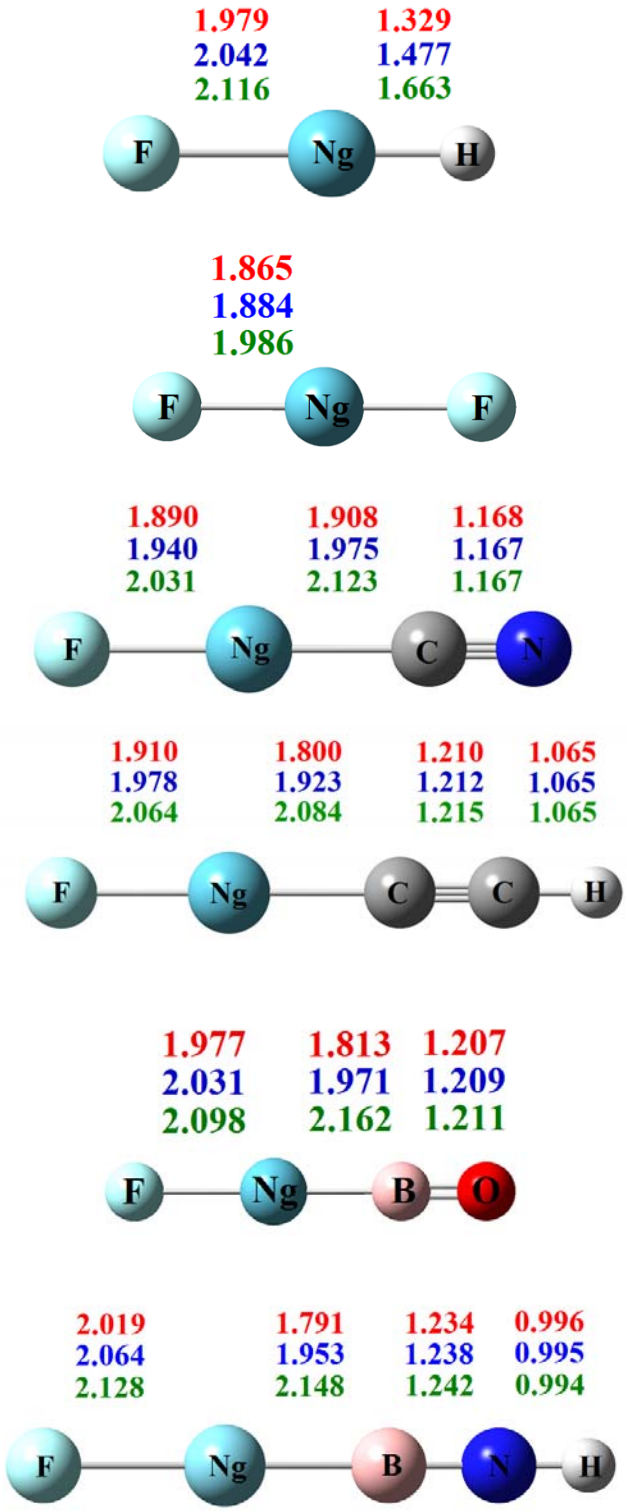


**Figure S2** Calculated geometry of the FNgY at the CCSD(T)/aug-cc-pVTZ level. From top Y= BNH, H, CN, and CCH. The values in red, blue, and green colors are for Ng = Ar, Kr, and Xe, respectively. The bond lengths are in angstroms. All of molecules are linear. The experimental bond length of $KrF_2$ and $XeF_2$ were 1.875 and 1.977 Å, respectively.

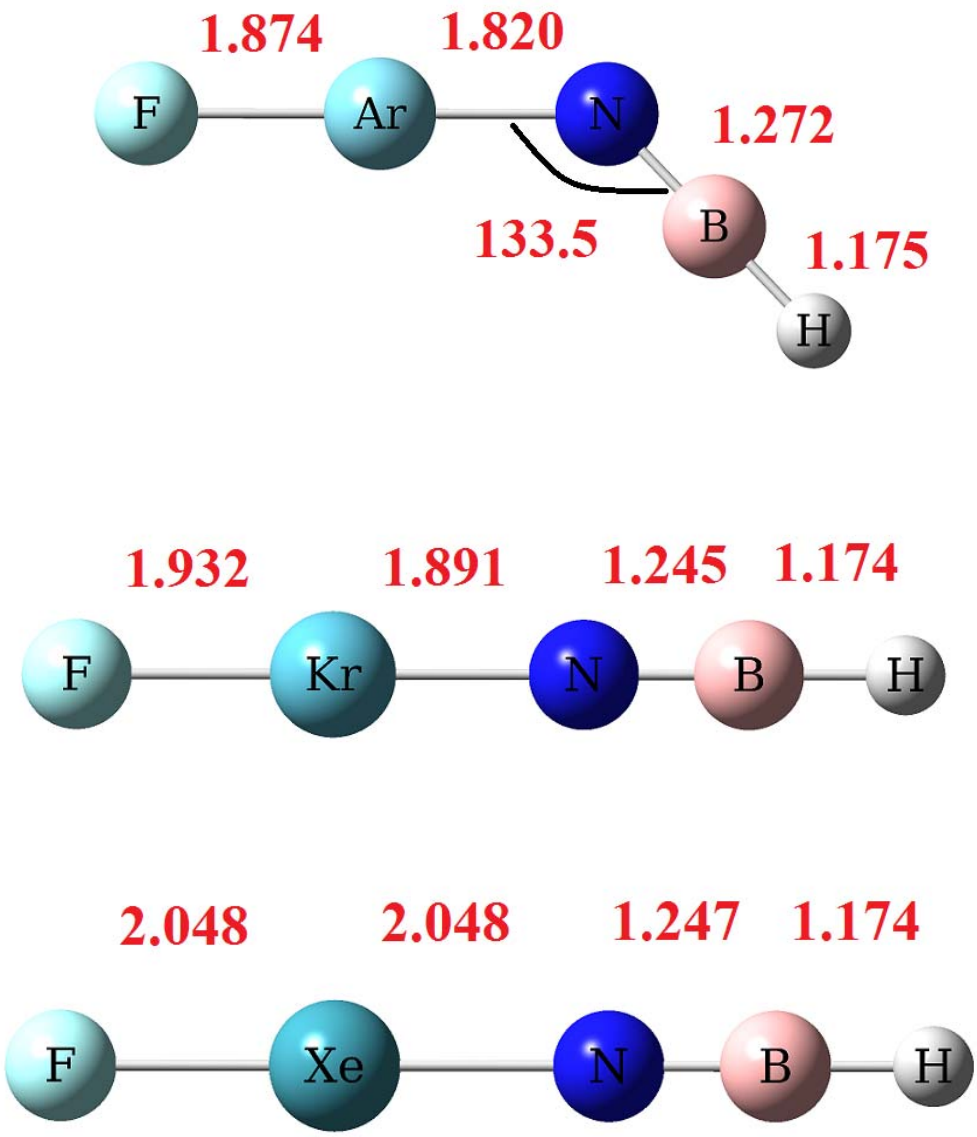


**Figure S3** Calculated geometry of the FNgNBH at the MPW1PW91/aug-cc-pVDZ level. The bond lengths are in angstroms, and the bond angles in degrees.

## References

S1. The NIST Chemistry WebBook, http://webbook.nist.gov/chemistry/