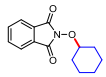
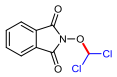
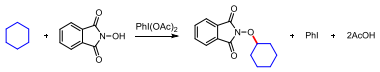
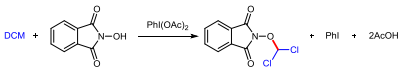
## The calculated results and XYZ co-ordinates for all optimized structures

**Supplementary Table 4**. The calculated results

| | Sum of electronic and zero-point Energies= (Hatree) | Sum of electronic and thermal Enthalpies= (Hatree) | Sum of electronic and thermal Free Energies= (Hatree) | BDE (kJ/mol) | ΔH (kJ/mol) | ΔrG (kJ/mol) |
|---|---|---|---|---|---|---|
| NHPI | -587.945664 | -587.935491 | -587.980161 | - | - | - |
| PINO radical | -587.331633 | -587.322099 | -587.366246 | - | - | - |
| Cyclohexane | -235.650608 | -235.644013 | -235.677687 | - | - | - |
| Cyclohexane radical | -234.99982 | -234.992855 | -235.029591 | - | - | - |
| DCM | -959.618621 | -959.614026 | -959.644938 | - | - | - |
| DCM radical | -958.962118 | -958.957469 | -958.989551 | - | - | - |
| H radical | -0.500273 | -0.497912 | -0.510927 | - | - | - |
| $PhI(OAc)_2$ | -699.488887 | -699.471004 | -699.538385 | - | - | - |
|  | -822.407933 | -822.391989 | -822.451542 | - | - | - |
|  | -1546.372479 | -1546.358995 | -1546.413432 | - | - | - |
| PhI | -242.883837 | -242.87709 | -242.915565 | - | - | - |
| AcOH | -228.943942 | -228.938451 | -228.971058 | - | - | - |
| | | Cyclohexane-H—> Cyclohexane radical + H | | 402.3 | - | - |
| | | DCM—> DCM radical+ H | | 416.5 | - | - |
| | |  | | - | -250.7 | -296.6 |
| | |  | | - | -242.8 | -282.6 |

Data presented here correspond to:

Atomic number, $x_i$, $y_i$, $z_i$

**(NHPI)**

| | | | |
|---|---|---|---|
| C | 1.689545 | 1.425491 | -0.000960 |
| C | 0.503597 | 0.703402 | 0.004604 |
| C | 0.503401 | -0.703251 | 0.004835 |
| C | 1.689242 | -1.425630 | -0.000651 |
| C | 2.894160 | -0.701793 | -0.012868 |
| C | 2.894301 | 0.701320 | -0.012987 |
| H | 1.681102 | 2.509654 | 0.000358 |

| | | | |
|---|---|---|---|
| H | 1.680548 | -2.509798 | 0.000568 |
| H | 3.838624 | -1.235316 | -0.023023 |
| H | 3.838894 | 1.234612 | -0.023144 |
| C | -0.904077 | -1.187949 | 0.020220 |
| C | -0.903844 | 1.188124 | 0.020045 |
| O | -1.347477 | 2.338114 | -0.001249 |
| O | -1.347916 | -2.337761 | -0.001568 |
| O | -3.055583 | -0.000051 | -0.177925 |
| H | -3.511318 | -0.000146 | 0.694459 |
| N | -1.673999 | 0.000043 | 0.094756 |

**(PINO radical)**

| | | | |
|---|---|---|---|
| C | -1.642142 | 1.425548 | -0.000177 |
| C | -0.452993 | 0.704546 | -0.000288 |
| C | -0.453004 | -0.704568 | -0.000020 |
| C | -1.642173 | -1.425510 | 0.000183 |
| C | -2.845471 | -0.702327 | 0.000230 |
| C | -2.845475 | 0.702413 | 0.000077 |
| H | -1.633617 | 2.509573 | -0.000328 |
| H | -1.633741 | -2.509536 | 0.000183 |
| H | -3.790060 | -1.235318 | 0.000394 |
| H | -3.790073 | 1.235382 | 0.000155 |
| C | 0.938872 | -1.201964 | -0.000180 |
| C | 0.938838 | 1.202036 | -0.000034 |
| O | 1.381331 | 2.347111 | -0.000102 |
| O | 1.381117 | -2.347237 | -0.000388 |
| O | 3.058641 | -0.000100 | 0.000439 |
| N | 1.757151 | 0.000095 | 0.000178 |

**(Cyclohexane)**

| | | | |
|---|---|---|---|
| C | 1.275087 | 0.736172 | 0.231032 |
| H | 1.332324 | -0.769218 | -1.330010 |
| H | 1.332324 | 0.769218 | 1.330010 |
| H | 2.168066 | 1.251733 | -0.146260 |
| C | 0.000000 | 1.472343 | -0.231032 |
| H | 0.000000 | 2.503467 | 0.146260 |
| H | 0.000000 | 1.538436 | -1.330010 |
| C | -1.275087 | 0.736172 | 0.231032 |
| H | -1.332324 | 0.769218 | 1.330010 |
| H | -2.168066 | 1.251733 | -0.146260 |
| C | -1.275087 | -0.736172 | -0.231032 |
| H | -2.168066 | -1.251733 | 0.146260 |
| H | -1.332324 | -0.769218 | -1.330010 |
| C | -0.000000 | -1.472343 | 0.231032 |

| | | | |
|---|---|---|---|
| H | -0.000000 | -2.503467 | -0.146260 |
| H | 2.168066 | -1.251733 | 0.146260 |
| H | 0.000000 | -1.538436 | 1.330010 |
| C | 1.275087 | -0.736172 | -0.231032 |

**(Cyclohexane radical)**

| | | | |
|---|---|---|---|
| C | -0.049197 | -0.796716 | 1.294743 |
| H | -1.087854 | 1.112979 | 1.304587 |
| H | 0.990420 | -1.131485 | 1.489417 |
| H | -0.645373 | -1.165426 | 2.139234 |
| C | -0.541232 | -1.375215 | -0.000000 |
| H | -1.084313 | -2.317028 | -0.000000 |
| C | -0.049197 | -0.796716 | -1.294743 |
| H | 0.990420 | -1.131485 | -1.489417 |
| H | -0.645373 | -1.165426 | -2.139234 |
| C | -0.049197 | 0.753899 | -1.272576 |
| H | 0.451872 | 1.139953 | -2.169843 |
| H | -1.087854 | 1.112979 | -1.304587 |
| C | 0.631760 | 1.295961 | 0.000000 |
| H | 0.611025 | 2.393854 | 0.000000 |
| H | 0.451872 | 1.139953 | 2.169843 |
| H | 1.692710 | 1.000456 | -0.000000 |
| C | -0.049197 | 0.753899 | 1.272576 |

**(DCM)**

| | | | |
|---|---|---|---|
| C | -0.000000 | 0.000000 | 0.804765 |
| H | -0.907756 | 0.000000 | 1.397554 |
| H | 0.907756 | -0.000000 | 1.397554 |
| Cl | -0.000000 | 1.543100 | -0.224226 |
| Cl | -0.000000 | -1.543100 | -0.224226 |

**(DCM radical)**

| | | | |
|---|---|---|---|
| C | 0.013325 | 0.735059 | -0.000000 |
| H | -0.533020 | 1.668377 | -0.000000 |
| Cl | 0.013325 | -0.178786 | 1.535188 |
| Cl | 0.013325 | -0.178786 | -1.535188 |

**($PhI(OAc)_2$)**

| | | | |
|---|---|---|---|
| C | 0.984695 | -3.333566 | 0.710456 |
| C | 0.998103 | -1.929902 | 0.719527 |
| C | 0.000186 | -1.285807 | -0.000007 |
| C | -0.997553 | -1.930186 | -0.719534 |
| C | -0.983736 | -3.333845 | -0.710456 |
| C | 0.000582 | -4.030400 | -0.000003 |
| H | 1.747783 | -3.869923 | 1.264132 |

| | | | |
|---|---|---|---|
| H | 1.756412 | -1.370499 | 1.253536 |
| H | -1.756036 | -1.370983 | -1.253507 |
| H | -1.746675 | -3.870422 | -1.264121 |
| H | 0.000737 | -5.115221 | -0.000007 |
| I | -0.000121 | 0.920128 | 0.000025 |
| O | 2.055465 | 0.778865 | 0.706861 |
| C | 3.220877 | 0.938927 | -0.001846 |
| O | 4.287456 | 0.611186 | 0.526153 |
| O | -2.055702 | 0.778272 | -0.706829 |
| C | -3.221163 | 0.938351 | 0.001780 |
| O | -4.287700 | 0.610636 | -0.526322 |
| C | -3.133441 | 1.528039 | 1.394004 |
| H | -2.559086 | 0.877388 | 2.063419 |
| H | -2.641741 | 2.507185 | 1.378072 |
| H | -4.141294 | 1.642400 | 1.793307 |
| C | 3.133020 | 1.528771 | -1.393990 |
| H | 2.558621 | 0.878192 | -2.063435 |
| H | 2.641293 | 2.507895 | -1.377865 |
| H | 4.140831 | 1.643237 | -1.793349 |

**(PhI)**

| | | | |
|---|---|---|---|
| C | -2.670326 | -1.210447 | 0.000000 |
| C | -1.268986 | -1.217902 | 0.000003 |
| C | -0.583641 | -0.000029 | -0.000009 |
| C | -1.268966 | 1.217887 | -0.000004 |
| C | -2.670277 | 1.210476 | 0.000006 |
| C | -3.372225 | 0.000013 | -0.000003 |
| H | -3.207051 | -2.153877 | 0.000004 |
| H | -0.728230 | -2.156631 | 0.000003 |
| H | -0.728145 | 2.156579 | -0.000004 |
| H | -3.207016 | 2.153899 | 0.000011 |
| H | -4.457212 | 0.000051 | -0.000005 |
| H | 1.572343 | -0.000000 | 0.000000 |

**(AcOH)**

| | | | |
|---|---|---|---|
| C | 1.397411 | -0.132856 | 0.000019 |
| H | 1.674025 | -0.719187 | -0.882210 |
| H | 1.673594 | -0.721031 | 0.881056 |
| H | 1.938063 | 0.813218 | 0.000978 |
| C | -0.078072 | 0.131749 | 0.000014 |
| O | -0.629071 | 1.234473 | 0.000002 |
| O | -0.800684 | -1.048470 | 0.000027 |
| H | -1.763680 | -0.854376 | -0.000252 |