**Composite high-level *ab initio* and DFT calculations of the adiabatic electron affinities of the *m-* and *p-*monosubstituted benzaldehydes**

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**Supplementary Materials**

* 1. **Statistical analysis**

The statistical descriptors are calculated as follows:

(S1)

(S2)

(S3)

(S4)

(S5)

(S6)

**Correlation between experimental and calculated results**

The different correlation graphs have been plotted by using origin software (excel can be also used). A scattered plot has been generated. Then Fit linear was applied to fit the scattered point to a linear relationship. The determination coefficient (R2), slope and intercept of the general linear equation (y=ax+b) (a=slope and b = intercept) were obtained. If R2 is very close to unity (1), this means these the calculated results are highly correlated with the experimental data and the mathematical model (equation) is valid.

**Supplementary Tables**

Table S1. Zero-point energies and total electronic energies of the 12 *m-* and *p-*monosubstituted benzaldehyde as calculated using G4, G3B3, CBS-Q and CBS-QB3 methods. All values are in Hartree.

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Species | G4 | |  | G3B3 | |  | CBS-Q | |  | CBS-QB3 | |
| ZPE | E (Hartree) |  | ZPE | E (Hartree) |  | ZPE | E (Hartree) |  | ZPE | E (Hartree) |
|  | H | | | | | | | | | | |
| Neutral | 0.108022 | -345.378587 |  | 0.105819 | -345.323522 |  | 0.108017 | -344.973548 |  | 0.108418 | -344.968454 |
| Anion | 0.104022 | -345.394857 |  | 0.101924 | -345.336415 |  | 0.102924 | -344.986059 |  | 0.104332 | -344.981802 |
|  | 3-Me | | | | | | | | | | |
| Neutral | 0.134755 | -384.660381 |  | 0.132253 | -384.598826 |  | 0.134702 | -384.219889 |  | 0.135291 | -384.197869 |
| Anion | 0.130878 | -384.676895 |  | 0.128473 | -384.611416 |  | 0.129830 | -384.230041 |  | 0.131260 | -384.211315 |
|  | 4-Me | | | | | | | | | | |
| Neutral | 0.134799 | -384.660899 |  | 0.132197 | -384.599266 |  | 0.134766 | -384.201389 |  | 0.135270 | -384.198082 |
| Anion | 0.130690 | -384.674650 |  | 0.128236 | -384.608629 |  | 0.129667 | -384.213783 |  | 0.131028 | -384.209046 |
|  | 3-Ome | | | | | | | | | | |
| Neutral | 0.139990 | -459.844120 |  | 0.137266 | -459.770562 |  | 0.140366 | -459.334293 |  | 0.140348 | -459.326489 |
| Anion | 0.135388 | -459.855714 |  | 0.133478 | -459.784168 |  | 0.135588 | -459.351439 |  | 0.136352 | -459.341334 |
|  | 3-Cl | | | | | | | | | | |
| Neutral | 0.098568 | -804.866863 |  | 0.096504 | -804.789601 |  | 0.098808 | -804.160493 |  | 0.098868 | -804.129830 |
| Anion | 0.094806 | -804.894304 |  | 0.092848 | -804.813431 |  | 0.094075 | -804.187549 |  | 0.095099 | -804.155088 |
|  | 4-Cl | | | | | | | | | | |
| Neutral | 0.098579 | -804.867549 |  | 0.096511 | -804.790227 |  | 0.098804 | -804.163606 |  | 0.098884 | -804.130356 |
| Anion | 0.094953 | -804.892253 |  | 0.092919 | -804.811307 |  | 0.094189 | -804.188513 |  | 0.095143 | -804.153289 |
|  | 3-F | | | | | | | | | | |
| Neutral | 0.099978 | -444.602528 |  | 0.097855 | -444.529992 |  | 0.100227 | -444.145053 |  | 0.100184 | -444.135203 |
| Anion | 0.096184 | -444.627074 |  | 0.094233 | -444.550574 |  | 0.095563 | -444.167659 |  | 0.096400 | -444.157022 |
|  | 4-F | | | | | | | | | | |
| Neutral | 0.100059 | -444.603765 |  | 0.097932 | -444.531183 |  | 0.100280 | -444.152244 |  | 0.100284 | -444.135877 |
| Anion | 0.096013 | -444.620567 |  | 0.094034 | -444.544043 |  | 0.095172 | -444.168429 |  | 0.096192 | -444.150563 |
|  | 3-CN | | | | | | | | | | |
| Neutral | 0.106640 | -437.600668 |  | 0.104349 | -437.532458 |  | 0.107013 | -437.089009 |  | 0.107019 | -437.089009 |
| Anion | 0.102935 | -437.641236 |  | 0.100790 | -437.569208 |  | 0.102231 | -437.141388 |  | 0.103308 | -437.127448 |
|  | 4-CN | | | | | | | | | | |
| Neutral | 0.106573 | -437.600557 |  | 0.104294 | -437.532246 |  | 0.106949 | -437.108646 |  | 0.106965 | -437.089224 |
| Anion | 0.104014 | -437.648825 |  | 0.101818 | -437.577121 |  | 0.103320 | -437.140008 |  | 0.104293 | -437.135360 |
|  | 3-NO2 | | | | | | | | | | |
| Neutral | 0.110649 | -549.831532 |  | 0.108270 | -549.742298 |  | 0.111106 | -549.285645 |  | 0.110818 | -549.257588 |
| Anion | 0.107417 | -549.885686 |  | 0.105210 | -549.791604 |  | 0.106455 | -549.345537 |  | 0.107595 | -549.311279 |
|  | 4-NO2 | | | | | | | | | | |
| Neutral | 0.110546 | -549.830913 |  | 0.108161 | -549.741598 |  | 0.111598 | -549.283761 |  | 0.110738 | -549.257159 |
| Anion | 0.108419 | -549.895115 |  | 0.106115 | -549.801464 |  | 0.107099 | -549.342245 |  | 0.108507 | -549.321655 |

Table S2. Zero-point energies and total electronic energies and of the 12 m-and p-monosubstituted benzaldehyde as calculated using B3LYP method. All values are in Hartree.

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | | 6-31+G(d,p) | | 6-311++G(2df,2p) | |  | 6-31+G(d,p) | | 6-311++G(2df,2p) | |
| Species | | ZPE | E (Hartree) | ZPE | E (Hartree) |  | ZPE | E (Hartree) | ZPE | E (Hartree) |
|  | **H** | | | | |  | **3-F** | | | |
| Neutral | | 0.109782 | -345.597961 | 0.109651 | -345.690830 |  | 0.101428 | -444.836968 | 0.101337 | -444.963034 |
| Anion | | 0.105878 | -345.613958 | 0.105590 | -345.707496 | 0.097699 | -444.862726 | 0.097612 | -444.988835 |
|  | | **3-CH3** | | | |  | **4-F** | | | |
| Neutral | | 0.137047 | -384.919093 | 0.136763 | -385.021172 |  | 0.101507 | -444.838512 | 0.101442 | -444.964689 |
| Anion -a | | 0.133130 | -384.934453 | 0.132965 | -385.037405 | 0.097356 | -444.857368 | 0.097248 | -444.983259 |
|  | | **4-CH3** | | | |  | **3-CN** | | | |
| Neutral | | 0.137010 | -384.919910 | 0.136832 | -385.021995 |  | 0.108233 | -437.839606 | 0.108156 | -437.959819 |
| Anion -a | | 0.132793 | -384.932892 | 0.132706 | -385.035575 | 0.104622 | -437.882218 | 0.104627 | -438.003147 |
|  | | **3-OCH3** | | | |  | **4-CN** | | | |
| Neutral | | 0.141431 | -460.121654 | 0.142019 | -460.254920 |  | 0.108184 | -437.839502 | 0.108107 | -437.959725 |
| Anion -a | | 0.137703 | -460.140874 | 0.138086 | -460.272107 | 0.105413 | -437.891719 | 0.105469 | -438.012497 |
|  | | **3Cl** | | | |  | **3-NO2** | | | |
| Neutral | | 0.100114 | -805.190796 | 0.100059 | -805.316412 |  | 0.112124 | -550.104213 | 0.111965 | -550.263881 |
| Anion -a | | 0.096413 | -805.219575 | 0.096377 | -805.345699 | 0.109138 | -550.167457 | 0.108966 | -550.325780 |
|  | | **4-Cl** | | | |  | **4-NO2** | | | |
| Neutral | | 0.100116 | -805.191728 | 0.100100 | -805.317425 |  | 0.112029 | -550.103293 | 0.111909 | -550.262973 |
| Anion -a | | 0.096341 | -805.218106 | 0.096390 | -805.344347 | 0.109843 | -550.178143 | 0.109753 | -550.336617 |

Table S3. Zero-point energies and total electronic energies of the 12 m-and p-monosubstituted benzaldehyde as calculated using CAM-B3LYP method. All values are in Hartree.

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | | 6-31+G(d,p) | | 6-311++G(2df,2p) | |  | 6-31+G(d,p) | | 6-311++G(2df,2p) | |
| Species | | ZPE | E (Hartree) | ZPE | E (Hartree) |  | ZPE | E (Hartree) | ZPE | E (Hartree) |
|  | **H** | | | | |  | **3F** | | | |
| Neutral | | 0.11116 | -345.41070 | 0.11096 | -345.50557 |  | 0.10280 | -444.63288 | 0.10265 | -444.76143 |
| Anion | | 0.10736 | -345.42441 | 0.10724 | -345.52000 | 0.09918 | -444.65673 | 0.09906 | -444.78545 |
|  | | **3-CH3** | | | |  | **4-F** | | | |
| Neutral | | 0.13869 | -384.70659 | 0.13838 | -384.81081 |  | 0.10285 | -444.63443 | 0.10273 | -444.76311 |
| Anion -a | | 0.13492 | -384.71958 | 0.13469 | -384.82476 | 0.09884 | -444.65112 | 0.09870 | -444.77959 |
|  | | **4-CH3** | | | |  | **3-CN** | | | |
| Neutral | | 0.13868 | -384.70739 | 0.13843 | -384.81163 |  | 0.10975 | -437.61132 | 0.10961 | -437.73435 |
| Anion -a | | 0.13459 | -384.71772 | 0.13436 | -384.82267 | 0.10613 | -437.65055 | 0.10610 | -437.77461 |
|  | | **3-OCH3** | | | |  | **4-CN** | | | |
| Neutral | | 0.14405 | -459.89433 | 0.14372 | -460.02518 |  | 0.10972 | -437.61108 | 0.10957 | -437.73411 |
| Anion -a | | 0.13967 | -459.90662 | 0.14001 | -460.04080 | 0.10694 | -437.66017 | 0.10698 | -437.78410 |
|  | | **3-Cl** | | | |  | **3-NO2** | | | |
| Neutral | | 0.10151 | -805.00671 | 0.10139 | -805.13479 |  | 0.11388 | -549.85403 | 0.11367 | -550.01737 |
| Anion -a | | 0.09793 | -805.03321 | 0.09784 | -805.16190 | 0.11098 | -549.91394 | 0.11075 | -550.07578 |
|  | | **4-Cl** | | | |  | **4-NO2** | | | |
| Neutral | | 0.10151 | -805.00753 | 0.10143 | -805.13568 |  | 0.11381 | -549.85306 | 0.11364 | -550.01642 |
| Anion -a | | 0.09790 | -805.03192 | 0.09787 | -805.16066 | 0.11158 | -549.92378 | 0.11148 | -550.08595 |

Table S4. Zero-point energies and total electronic energies of the 12 m-and p-monosubstituted benzaldehyde as calculated using wB97XD method. All values are in Hartree.

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Species | | 6-31+G(d,p) | | 6-311++G(2df,2p) | |  | 6-31+G(d,p) | | 6-311++G(2df,2p) | |
| ZPE | E (Hartree) | ZPE | E (Hartree) |  | ZPE | E (Hartree) | ZPE | E (Hartree) |
|  | **H** | | | | |  | **3F** | | | |
| Neutral | | 0.11090 | -345.47275 | 0.11052 | -345.56068 |  | 0.10250 | -444.68581 | 0.10220 | -444.80653 |
| Anion | | 0.10711 | -345.48394 | 0.10682 | -345.57251 | 0.09896 | -444.70679 | 0.09868 | -444.82743 |
|  | | **3-CH3** | | | |  | **4-F** | | | |
| Neutral | | 0.13860 | -384.78253 | 0.13824 | -384.87925 |  | 0.10265 | -444.68736 | 0.10239 | -444.80824 |
| Anion | | 0.13476 | -384.79292 | 0.13442 | -384.89043 | 0.09870 | -444.70115 | 0.09845 | -444.82153 |
|  | | **4-CH3** | | | |  | **3-CN** | | | |
| Neutral | | 0.13863 | -384.78328 | 0.13795 | -384.87999 |  | 0.10942 | -437.67905 | 0.10912 | -437.79341 |
| Anion | | 0.13439 | -384.79107 | 0.13391 | -384.88821 | 0.10577 | -437.71590 | 0.10559 | -437.83102 |
|  | | **3-OCH3** | | | |  | **4-CN** | | | |
| Neutral | | 0.14383 | -459.96674 | 0.14333 | -460.08888 |  | 0.10938 | -437.67877 | 0.10910 | -437.79312 |
| Anion | | 0.13967 | -459.97639 | 0.13943 | -460.09876 | 0.10668 | -437.72573 | 0.10656 | -437.84065 |
|  | | **3-Cl** | | | |  | **3-NO2** | | | |
| Neutral | | 0.10127 | -805.05112 | 0.10102 | -805.17156 |  | 0.11366 | -549.91417 | 0.11330 | -550.06755 |
| Anion | | 0.09768 | -805.07515 | 0.09747 | -805.19595 | 0.11063 | -549.97013 | 0.11030 | -550.12169 |
|  | | **4-Cl** | | | |  | **4-NO2** | | | |
| Neutral | | 0.10126 | -805.05190 | 0.10107 | -805.17239 |  | 0.11352 | -549.91321 | 0.11325 | -550.06659 |
| Anion | | 0.09773 | -805.07393 | 0.09756 | -805.19477 | 0.11130 | -549.98028 | 0.11113 | -550.13206 |

Table S5. Single point energies of the 12 *m-* and *p-*monosubstituted benzaldehyde as calculated using 15 DFT methods based on B3LYP/6-31+G(d,p) geometries. All values are in Hartree.

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | neutral | anion | neutral | anion | neutral | anion | neutral | anion | neutral | anion | neutral | anion |
|  | H | | 3-CH3 | | 4-CH3 | | OCH3 | | 3-Cl | | 4-Cl | |
| B3LYP | -345.69038 | -345.70706 | -385.02066 | -385.03693 | -385.02151 | -385.03495 | -460.24918 | -460.26902 | -805.31590 | -805.34523 | -805.31691 | -805.34387 |
| B3PW91 | -345.54647 | -345.56346 | -384.86240 | -384.87886 | -384.86325 | -384.87697 | -460.05981 | -460.07985 | -805.11978 | -805.14920 | -805.12085 | -805.14789 |
| CAM-B3LYP | -345.50410 | -345.51873 | -384.80922 | -384.82332 | -384.81006 | -384.82108 | -460.01843 | -460.03639 | -805.13313 | -805.16033 | -805.13403 | -805.15910 |
| B97D | -345.43680 | -345.45314 | -384.73865 | -384.75460 | -384.73946 | -384.75296 | -459.92459 | -459.94414 | -805.07492 | -805.10360 | -805.07600 | -805.10224 |
| TPSSTPSS | -345.74369 | -345.75932 | -385.07945 | -385.09482 | -385.08027 | -385.09327 | -460.31761 | -460.33664 | -805.37756 | -805.40591 | -805.37868 | -805.40455 |
| BMK | -345.45619 | -345.46640 | -384.75499 | -384.76472 | -384.75574 | -384.76236 | -459.95241 | -459.96591 | -804.94927 | -804.97290 | -804.95017 | -804.97133 |
| M11 | -345.48531 | -345.50031 | -384.78747 | -384.80194 | -384.78814 | -384.79971 | -459.99617 | -460.01488 | -805.09158 | -805.11929 | -805.09245 | -805.11811 |
| wB97 | -345.60890 | -345.62067 | -384.93161 | -384.94290 | -384.93245 | -384.94062 | -460.14990 | -460.16531 | -805.22370 | -805.24774 | -805.22456 | -805.24660 |
| wB97x | -345.58461 | -345.59634 | -384.90429 | -384.91548 | -384.90509 | -384.91341 | -460.11421 | -460.12948 | -805.19663 | -805.22093 | -805.19748 | -805.21980 |
| wB97XD | -345.55961 | -345.57158 | -384.87799 | -384.88935 | -384.87878 | -384.88715 | -460.08236 | -460.09742 | -805.17027 | -805.19475 | -805.17113 | -805.19358 |
| M05-2x | -345.64445 | -345.65878 | -384.96768 | -384.98168 | -384.96848 | -384.97914 | -460.18952 | -460.20740 | -805.25340 | -805.28068 | -805.25436 | -805.27909 |
| M06 | -345.43076 | -345.44634 | -384.72774 | -384.74322 | -384.72852 | -384.74123 | -459.92557 | -459.94497 | -805.02800 | -805.05592 | -805.02901 | -805.05456 |
| M06-2X | -345.53681 | -345.55025 | -384.84610 | -384.85935 | -384.84685 | -384.85688 | -460.05184 | -460.06886 | -805.14063 | -805.16682 | -805.14151 | -805.16530 |
| M06-L | -345.63396 | -345.64656 | -384.95812 | -384.97012 | -384.95905 | -384.96848 | -460.17458 | -460.19065 | -805.24124 | -805.26622 | -805.24246 | -805.26484 |
| N12-SX | -345.52107 | -345.53329 | -384.83014 | -384.84188 | -384.83104 | -384.84012 | -460.02366 | -460.03906 | -805.07573 | -805.10065 | -805.07682 | -805.09961 |
|  | 3-F | | 4-F | | 3-CN | | 4-CN | | 3-NO2 | | 4-NO2 | |
| B3LYP | -444.96249 | -444.98835 | -444.96416 | -444.98278 | -437.95903 | -438.00242 | -437.95894 | -438.01179 | -550.26317 | -550.32519 | -550.26232 | -550.33602 |
| B3PW91 | -444.78136 | -444.80711 | -444.78313 | -444.80149 | -437.77285 | -437.81693 | -437.77275 | -437.82634 | -550.04021 | -550.10099 | -550.03938 | -550.11207 |
| CAM-B3LYP | -444.75975 | -444.78392 | -444.76146 | -444.77808 | -437.73209 | -437.77241 | -437.73182 | -437.78197 | -550.01489 | -550.07353 | -550.01398 | -550.08380 |
| B97D | -444.66211 | -444.68682 | -444.66380 | -444.68170 | -437.64082 | -437.68466 | -437.64085 | -437.69359 | -549.90186 | -549.96262 | -549.90111 | -549.97307 |
| TPSSTPSS | -445.02350 | -445.04788 | -445.02524 | -445.04264 | -438.02873 | -438.07188 | -438.02878 | -438.08099 | -550.35520 | -550.41599 | -550.35449 | -550.42659 |
| BMK | -444.69764 | -444.71712 | -444.69940 | -444.71086 | -437.67574 | -437.71280 | -437.67556 | -437.72261 | -549.93220 | -549.98980 | -549.93130 | -550.00070 |
| M11 | -444.74342 | -444.76843 | -444.74509 | -444.76249 | -437.71270 | -437.75307 | -437.71232 | -437.76284 | -549.99736 | -550.05447 | -549.99653 | -550.06460 |
| wB97 | -444.87126 | -444.89276 | -444.87300 | -444.88672 | -437.86218 | -437.89878 | -437.86180 | -437.90861 | -550.15976 | -550.21263 | -550.15887 | -550.22232 |
| wB97x | -444.83724 | -444.85852 | -444.83897 | -444.85256 | -437.82734 | -437.86429 | -437.82700 | -437.87410 | -550.11023 | -550.16370 | -550.10936 | -550.17368 |
| wB97XD | -444.80514 | -444.82618 | -444.80685 | -444.82032 | -437.79174 | -437.82939 | -437.79142 | -437.83908 | -550.06542 | -550.11975 | -550.06452 | -550.13021 |
| M05-2x | -444.91116 | -444.93541 | -444.91295 | -444.92913 | -437.90727 | -437.94785 | -437.90698 | -437.95792 | -550.19082 | -550.24957 | -550.18990 | -550.26047 |
| M06 | -444.67578 | -444.70023 | -444.67762 | -444.69446 | -437.64220 | -437.68484 | -437.64193 | -437.69397 | -549.90951 | -549.96993 | -549.90850 | -549.98037 |
| M06-2X | -444.78221 | -444.80489 | -444.78385 | -444.79851 | -437.77850 | -437.81738 | -437.77827 | -437.82759 | -550.03755 | -550.09363 | -550.03677 | -550.10481 |
| M06-L | -444.89426 | -444.91511 | -444.89614 | -444.90918 | -437.89494 | -437.93558 | -437.89497 | -437.94510 | -550.19166 | -550.24924 | -550.19095 | -550.26026 |
| N12-SX | -444.76817 | -444.78981 | -444.76996 | -444.78430 | -437.74269 | -437.78248 | -437.74254 | -437.79208 | -549.99596 | -550.05485 | -549.99503 | -550.06569 |

Table S6. Single point electronic energies as calculated using three DFT methods (wB97, wB97X and wB97XD) and Zero-point energies at B3LYP/6-31+G(d,p) level of theory of the 17 *m-* and *p-*monosubstituted benzaldehyde as calculated. All values are in Hartree.

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | neutral | |  | anion | |  | neutral | |  | anion | |
|  | E | ZPE |  | E | ZPE |  | E | ZPE |  | E | ZPE |
|  | wB97 | | | | |  | wB97X | | | | |
| 3-CHO | -458.95428 | 0.11894 |  | -458.98465 | 0.11527 |  | -458.91773 | 0.11894 |  | -458.94885 | 0.11527 |
| 3-OH | -420.85190 | 0.11372 |  | -420.86587 | 0.10923 |  | -420.81917 | 0.11372 |  | -420.83296 | 0.10923 |
| 3-COOH | -534.23192 | 0.12470 |  | -534.25895 | 0.12088 |  | -534.18738 | 0.12470 |  | -534.21486 | 0.12088 |
| 3-COOCH3 | -573.53457 | 0.15251 |  | -573.55527 | 0.14806 |  | -573.48698 | 0.15251 |  | -573.50800 | 0.14806 |
| 3-NH2 | -400.98138 | 0.12621 |  | -400.99091 | 0.12249 |  | -400.95081 | 0.12621 |  | -400.96015 | 0.12249 |
| 3-N(CH3)2 | -479.60689 | 0.17832 |  | -479.59901 | 0.18256 |  | -479.56984 | 0.17832 |  | -479.56216 | 0.18256 |
| 3-ph | -576.68093 | 0.19069 |  | -576.69915 | 0.18636 |  | -576.63987 | 0.19069 |  | -576.65855 | 0.18636 |
| 3-OCOCH3 | -573.52724 | 0.15082 |  | -573.55824 | 0.14740 |  | -573.47967 | 0.15082 |  | -573.51052 | 0.14740 |
| 4-CHO | -458.95333 | 0.11890 |  | -459.00157 | 0.11645 |  | -458.91683 | 0.11890 |  | -458.96563 | 0.11645 |
| 4-OH | -458.95428 | 0.11894 |  | -458.98465 | 0.11527 |  | -458.91773 | 0.11894 |  | -420.83296 | 0.10923 |
| 4-COOH | -534.23077 | 0.12463 |  | -534.27286 | 0.12167 |  | -534.18626 | 0.12463 |  | -534.22859 | 0.12167 |
| 4-COOCH3 | -573.53478 | 0.15252 |  | -573.57307 | 0.14939 |  | -573.48724 | 0.15252 |  | -573.52585 | 0.14939 |
| 4-NH2 | -400.98522 | 0.12626 |  | -400.98430 | 0.12188 |  | -400.95467 | 0.12626 |  | -400.95357 | 0.12188 |
| 4-N(CH3)2 | -479.60236 | 0.18268 |  | -479.60402 | 0.17789 |  | -479.60236 | 0.18268 |  | -479.56697 | 0.17789 |
| 4-ph | -576.68134 | 0.19059 |  | -576.70959 | 0.18693 |  | -576.64035 | 0.19059 |  | -576.66880 | 0.18693 |
| 4-OCH3 | -460.15781 | 0.14230 |  | -460.16171 | 0.13745 |  | -460.12200 | 0.14230 |  | -460.12597 | 0.13745 |
| 4- OCOCH3 | -573.52829 | 0.15082 |  | -573.55512 | 0.14736 |  | -573.48069 | 0.15082 |  | -573.50748 | 0.14736 |
|  | wB97XD | | | | |  |  |  |  |  |  |
| 3-CHO | -458.91773 | 0.11894 |  | -458.94885 | 0.11527 |  |  |  |  |  |  |
| 3-OH | -420.81917 | 0.11372 |  | -420.83296 | 0.10923 |  |  |  |  |  |  |
| 3-COOH | -534.18738 | 0.12470 |  | -534.21486 | 0.12088 |  |  |  |  |  |  |
| 3-COOCH3 | -573.48698 | 0.15251 |  | -573.50800 | 0.14806 |  |  |  |  |  |  |
| 3-NH2 | -400.95081 | 0.12621 |  | -400.96015 | 0.12249 |  |  |  |  |  |  |
| 3-N(CH3)2 | -479.56984 | 0.17832 |  | -479.56216 | 0.18256 |  |  |  |  |  |  |
| 3-ph | -576.63987 | 0.19069 |  | -576.65855 | 0.18636 |  |  |  |  |  |  |
| 3-OCOCH3 | -573.47967 | 0.15082 |  | -573.51052 | 0.14740 |  |  |  |  |  |  |
| 4-CHO | -458.91683 | 0.11890 |  | -458.96563 | 0.11645 |  |  |  |  |  |  |
| 4-OH | -458.91773 | 0.11894 |  | -420.83296 | 0.10923 |  |  |  |  |  |  |
| 4-COOH | -534.18626 | 0.12463 |  | -534.22859 | 0.12167 |  |  |  |  |  |  |
| 4-COOCH3 | -573.48724 | 0.15252 |  | -573.52585 | 0.14939 |  |  |  |  |  |  |
| 4-NH2 | -400.95467 | 0.12626 |  | -400.95357 | 0.12188 |  |  |  |  |  |  |
| 4-N(CH3)2 | -479.60236 | 0.18268 |  | -479.56697 | 0.17789 |  |  |  |  |  |  |
| 4-ph | -576.64035 | 0.19059 |  | -576.66880 | 0.18693 |  |  |  |  |  |  |
| 4-OCH3 | -460.12200 | 0.14230 |  | -460.12597 | 0.13745 |  |  |  |  |  |  |
| 4- OCOCH3 | -573.48069 | 0.15082 |  | -573.50748 | 0.14736 |  |  |  |  |  |  |

Figure S1. Correlation of (a) calculated AEA of G3B3 vs CBS-QB3, (b) calculated AEA of G3B3 vs CAM-B3LYP/6-311++G(2df,2p), (c) calculate AEA of G3B3 *vs* wb97XD/6-311++G(2df,2p) and (d) average AEA of C3B3 and CBS-QB3 *vs* average AEA of CAM-B3LYP and wB97XD in combination with 6-311++G(2df,2p)//6-31+G(d,p) methods.



Figure S2. Correlations of experimental AEA values with the theoretical AEA a calculated by (a) G3B3, (b) CBS-QB3, (c) wb97XD/6-311++G(2df,2p) and (d) wB97/6-311++G(2df,2p)//6-31+G(d,p) methods.



Figure S3. Graphical representation of the root means square error (RMSE) of the high-level composite ab initio and the hybrid DFT methods. All values are in kcal/mol.

S1: corresponds to Strategy 1 (Composite high level ab initio methods)

S2, BS1: Corresponds to Strategy 2 (hybrid DFT methods using 6-31+G(d,p) basis set)

S2, BS2: Corresponds to Strategy 2 (hybrid DFT methods using 6-311++G(2df,2p) basis set)

S3: correspond to strategy 3 (using single DFT with 6-311++G(2df,2p) basis set at the B3LYP/6-31+G(d,p) geometry.

