# Supporting Information—Computational Details

BH9, a New Comprehensive Benchmark Dataset for Barrier Heights and Reaction Energies: Assessment of Density Functional Approximations and Basis Set Incompleteness Potentials

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#### Location of the transition states

In all cases, we used the Gaussian  $09/16^{1,2}$  software package. Our calculations employed a default SCF convergence criterion of  $10^{-8}$  Hartree, "ultrafine" integration grid (pruned  $99 \times 590$  grid), and tight optimization convergence criteria (maximum force =  $1.5 \times 10^{-5}$  Hartree/Bohr, RMS force =  $1 \times 10^{-5}$  Hartree/Bohr, maximum displacement =  $6 \times 10^{-5}$  Bohr, RMS displacement =  $4 \times 10^{-5}$  Bohr). The CalcFC and NoEigenTest options were used to specify the computation of force constants in the first step of the optimization and to suppress the curvature test during optimization, respectively. All calculations were carried out in the gas phase.

In the first step, preliminary TSs were located by geometry optimization followed by a frequency calculation. Finding the TS is often difficult because a good initial guess for the TS geometry is required for the optimization to succeed. In difficult cases, we ran series of constrained geometry minimizations where we fixed a few geometric parameters, then used the resulting structure as the initial guess for the TS search. The preliminary TS optimizations used the B3LYP hybrid density functional, <sup>3,4</sup> except in a few cases where the range-separated density functional CAM-B3LYP<sup>5</sup> was used. (The change in functional was prompted by the instability of B3LYP in the calculation of zwitterionic systems.) The D3 dispersion correction<sup>6</sup> with Becke-Johnson damping<sup>7,8</sup> was used in all cases. Due to the different sizes of the reactant molecules, depending on the reaction type, various Pople basis sets<sup>9-11</sup> (6-31G\*, 6-31+G\*, 6-31+G\*\*) were used together with their associated basis set incompleteness potentials<sup>12</sup> (BSIPs) to mitigate the effect of basis set incompleteness error (BSIE). 6-31G\*-BSIP was used to model radical addition and pericyclic reactions. 6-31+G\*-BSIP was used to model halogen atom transfer, nucleophilic substitution, nucleophilic addition, and the B- and Si-containing reactions. 6-31+G\*\*-BSIP was used to model hydrogen atom transfer, hydride transfer, and proton transfer reactions. Each preliminary TS was checked for the presence of a single imaginary frequency and visually inspected to confirm the imaginary-frequency eigenvector was oriented along the reaction coordinate.

The preliminary TSs were then subjected to a constrained conformer search using the commercial Schrödinger's MacroModel Suite<sup>13,14</sup> implemented in the Maestro<sup>15</sup> software package. This search is similar to the one used in previous works.<sup>16–18</sup> Bonds undergoing breaking and formation in the TS had their bond distances constrained to their values in the preliminary TS. The conformational search was performed using the mixed torsional/large-scale low-mode sampling option in Maestro, followed by a constrained post-optimization with the OPLS all-atom force field.<sup>19</sup> From this sampling, a maximum of 100 structures (fewer if the molecule was not sufficiently flexible) were then subjected to a single-point calculation using the same calculation level as in the preliminary TS optimization. A maximum of 9 lowest-energy conformers were chosen to undergo further refinement.

For each reaction, the nine TS conformers obtained in this manner plus the TS from the preliminary optimization were subjected to unconstrained optimization using the same method as above. We discarded all the structures whose optimization failed to locate a new TS or whose eigenvectors did not point in the direction of reactants and products. The lowest-energy conformer was then subjected to a final TS optimization and frequency calculation at a higher level of theory  $(CAM-B3LYP-D3(BJ)/6-311++G**^{20,21})$ . After verification of the imaginary frequencies and the direction of the imaginary-frequency eigenvector, this last structure was adopted as the TS for the reaction.

#### Reactant and product structures

The initial reactant and product structures were constructed from the optimized TS and subjected to geometry optimizations using CAM-B3LYP-D3(BJ) with the same combination of Pople basis sets and BSIPs as above (6-31G\*, 6-31+G\*, or 6-31+G\*\* depending on reaction type). All geometry optimizations employed a default SCF convergence

criterion of  $10^{-8}$  Hartree, "ultrafine" integration grid, and the default optimization convergence criteria (maximum force =  $4.5 \times 10^{-4}$  Hartrees/Bohr, RMS force =  $3 \times 10^{-4}$  Hartrees/Bohr, maximum displacement =  $1.8 \times 10^{-3}$  Bohr, RMS displacement =  $1.2 \times 10^{-3}$  Bohr).

After this initial relaxation, a 100-step Monte-Carlo multiple minimum<sup>22</sup> (MCMM) conformational search was carried out using the FullMonte<sup>23,24</sup> software package. The conformers generated in this way were optimized with the semi-empirical PM6-DH2<sup>25</sup> method using the MOPAC2016<sup>26</sup> software package. All conformers were then subjected to a single point calculation at the same level of theory used for their initial optimization. The ten lowest-energy conformers were selected for further optimization at the same level. The resulting lowest energy conformer was subjected to a final optimization and frequency calculation at a higher level of theory (CAM-B3LYP-D3(BJ)/6-311++G\*\*).

## Reference energy calculations

For the calculation of the reference energies, we used the ORCA program, version 4.2.1.<sup>27,28</sup> The aug-cc-pVNZ basis sets (in the following, aNZ for short; no tight d-functions were used) of Dunning and co-workers<sup>29–31</sup> were used for the complete-basis-set extrapolation, as well as the resolution of the identity MP2 method<sup>32–34</sup> (RI-MP2) with the aug-cc-pVNZ/C auxiliary basis sets.<sup>35</sup> The TightPNO and TightSCF threshold settings were used in the DLPNO-CCSD(T) calculation. The use of TightPNO was shown to be very important in the calculation of REs and BHs, particularly those of Diels-Alder reactions.<sup>36</sup> The frozen core approximation was used in all calculations. It has been shown to have a relatively minor impact on the accuracy of calculated thermochemical properties.<sup>37</sup>

The reference data was calculated using a focal-point approach, <sup>38,39</sup> which has been shown to be an effective way of approaching the CBS limit in similar calculations. <sup>37,40,41</sup> The BH9 reference energies are calculated as:

$$E = E_{\rm HF}^{\rm a\{T,Q\}Z} + \Delta E_{\rm MP2}^{\rm a\{T,Q\}Z} + \Delta E_{\rm DLPNO\text{-}CCSD(T)}^{\rm aTZ}$$
(1)

where  $E_{\rm HF}^{\rm a\{T,Q\}Z}$  is the HF energy calculated from the aTZ and aQZ energies using the CBS extrapolation formula:

$$E_{\rm HF}^{\rm L} = E_{\rm HF}^{\rm CBS} + A \exp(-\alpha \sqrt{L}) \tag{2}$$

where L is the cardinal number of the basis set (3 for aTZ, 4 for aQZ, etc.). From this formula, a two-point extrapolation approach can be easily derived:

$$E_{\rm HF}^{\rm CBS} = \frac{E_{\rm HF}^{\rm X} \times e^{-\alpha\sqrt{Y}} - E_{\rm HF}^{\rm Y} \times e^{-\alpha\sqrt{X}}}{e^{-\alpha\sqrt{Y}} - e^{-\alpha\sqrt{X}}}$$
(3)

where X and Y are the cardinal numbers of the basis set pair. Following the recommendations of Neese and Valeev, we used the optimized  $\alpha = 5.79$  value for the aTZ/aQZ pair.<sup>42</sup>

The MP2 correlation energy ( $\Delta E_{\text{MP2}}$ ) is calculated using the known inverse cube dependence of the correlation energy with the basis set cardinal number:<sup>43,44</sup>

$$\Delta E_{\rm MP2}^{\rm L} = \Delta E_{\rm MP2}^{\rm CBS} + AL^{-\beta} \tag{4}$$

with  $\beta = 3$  in the large-L limit. This yields the two-point extrapolation formula:

$$\Delta E_{\text{MP2}}^{\text{CBS}} = \frac{E_{\text{MP2}}^{X} \times X^{\beta} - E_{\text{MP2}}^{Y} \times Y^{\beta}}{X^{\beta} - Y^{\beta}}$$
(5)

In practice, optimized  $\beta$  parameters have been proposed for some basis set pairs, and it has been shown that  $\beta < 3$  improves the CBS estimate for low cardinal numbers.<sup>45</sup> The  $\beta = 3.05$  value proposed by Neese and Valeev for the aTZ/aQZ pair is used here.<sup>42</sup> Finally, the last component in our reference energy is:

$$\Delta E_{\text{DLPNO-CCSD(T)}}^{\text{aTZ}} = E_{\text{DLPNO-CCSD(T)}}^{\text{aTZ}} - E_{\text{MP2}}^{\text{aTZ}}$$
(6)

which is calculated using the aTZ basis set. The CCSD(T)/MP2 energy difference is routinely calculated at the aTZ level in the "gold standard" focal-point approach for non-covalent interactions, <sup>46–48</sup> and it is justified by the observation that high-order contributions to the correlation energy converge relatively quickly with the basis set size. <sup>49</sup> In fact, our method for the calculation of reference data is very similar to the "gold standard" method for intermolecular interactions, except for the use of DLPNO for the CCSD(T) calculation.

### DFT calculation details

We used Gaussian 16² to calculate the BH9 reactions using B3LYP, <sup>3,4</sup> LC-ωPBE, <sup>50,51</sup> M05-2X, <sup>52</sup> M06-2X, <sup>53</sup> MN15, <sup>54</sup> MN15-L, <sup>55</sup> revTPSS, <sup>56</sup> and ωB97XD. <sup>57,58</sup> Ultrafine grids were used for all calculations. The BLYP, <sup>4,59</sup> PBE, <sup>60</sup> TPSS, <sup>61</sup> BH&HLYP, <sup>4,62</sup> PBE0, <sup>63</sup> CAM-B3LYP, <sup>5</sup> B97M-V, <sup>64</sup> ωB97M-V, <sup>65</sup> and ωB97X-V<sup>66</sup> functionals were evaluated using ORCA, version 4.2.1. <sup>27,28</sup> The tight SCF convergence criteria and the "grid4" integration grid were used. Second-order SCF was deactivated. The resolution of the identity (RI) method was used in all cases. For the hybrid functionals (BH&HLYP and PBE0), RI was applied to both the Coulomb and exchange integrals (RI-JK keyword). For the range-separated hybrid functional (CAM-B3LYP), the chain-of-spheres approximation <sup>67</sup> was used to calculate the exchange energy. In all cases, the Def2-QZVPP basis set was used, <sup>68</sup> with the corresponding auxiliary basis sets (Def2/JK and Def2/J) used where appropriate. <sup>69</sup> Contrary to previous reports, <sup>70</sup> we did not observe any SCF convergence problems using the Minnesota functionals.

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- [1] Frisch, M. J. et al. Gaussian 09 Revision A.1. Gaussian Inc. Wallingford CT 2009.
- [2] Frisch, M. J. et al. Gaussian 16 Revision A.03. 2016; Gaussian Inc. Wallingford CT.
- [3] Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. J. Chem. Phys. 1993, 98, 5648-5652.
- [4] Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* **1988**, *37*, 785.
- [5] Yanai, T.; Tew, D. P.; Handy, N. C. A new hybrid exchange-correlation functional using the Coulomb-attenuating method (CAM-B3LYP). Chem. Phys. Lett. 2004, 393, 51–57.
- [6] Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. J. Chem. Phys. 2010, 132, 154104.
- [7] Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the damping function in dispersion corrected density functional theory. *J. Comput. Chem.* **2011**, *32*, 1456–1465.
- [8] Johnson, E. R.; Becke, A. D. A post-Hartree-Fock model of intermolecular interactions: Inclusion of higher-order corrections. J. Chem. Phys. 2006, 124, 174104.
- [9] Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. Self-consistent molecular orbital methods. XXIII. A polarization-type basis set for second-row elements. J. Chem. Phys. 1982, 77, 3654–3665.
- [10] Hariharan, P. C.; Pople, J. A. The influence of polarization functions on molecular orbital hydrogenation energies. *Theor. Chim. Acta* 1973, 28, 213–222.
- [11] Hehre, W. J.; Ditchfield, R.; Pople, J. A. Self-consistent molecular orbital methods. XII. Further extensions of Gaussian—type basis sets for use in molecular orbital studies of organic molecules. J. Chem. Phys. 1972, 56, 2257–2261.
- [12] Otero-de-la-Roza, A.; DiLabio, G. A. Improved basis-set incompleteness potentials for accurate dft calculations in large systems. J. Chem. Theory Comput. 2020, 16, 4176–4191.
- [13] Mohamadi, F.; Richards, N. G.; Guida, W. C.; Liskamp, R.; Lipton, M.; Caufield, C.; Chang, G.; Hendrickson, T.; Still, W. C. Macromodel—an integrated software system for modeling organic and bioorganic molecules using molecular mechanics. J. Comput. Chem. 1990, 11, 440–467.
- [14] Schrödinger Release 2020-3: MacroModel, Schrödinger, LLC. 2020; New York, NY.
- [15] Schrödinger Release 2020-3: Maestro, Schrödinger, LLC. 2020; New York, NY.
- [16] Medvedev, M. G.; Zeifman, A. A.; Novikov, F. N.; Bushmarinov, I. S.; Stroganov, O. V.; Titov, I. Y.; Chilov, G. G.; Svitanko, I. V. Quantifying possible routes for SpnF-catalyzed formal Diels-Alder cycloaddition. J. Am. Chem. Soc. 2017, 139, 3942–3945.
- [17] Medvedev, M. G.; Panova, M. V.; Chilov, G. G.; Bushmarinov, I. S.; Novikov, F. N.; Stroganov, O. V.; Zeifman, A. A.; Svitanko, I. V. Exhaustive conformational search for transition states: the case of catechol O-methyltransferase active site. *Mendeleev Commun.* 2017, 27, 224–227.
- [18] Fukaya, K.; Saito, A.; Nakajima, N.; Urabe, D. A computational study on the stereo-and regioselective formation of the C4α-C6' bond of tethered catechin moieties by an exhaustive search of the transition States. J. Org. Chem. 2019, 84, 2840-2849.
- [19] Jorgensen, W. L.; Maxwell, D. S.; Tirado-Rives, J. Development and testing of the OPLS all-atom force field on conformational energetics and properties of organic liquids. J. Am. Chem. Soc. 1996, 118, 11225–11236.
- [20] Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. Self-consistent molecular orbital methods. XX. A basis set for correlated wave functions. J. Chem. Phys. 1980, 72, 650–654.

- [21] McLean, A.; Chandler, G. Contracted Gaussian basis sets for molecular calculations. I. Second row atoms, Z= 11–18. *J. Chem. Phys.* **1980**, *72*, 5639–5648.
- [22] Chang, G.; Guida, W. C.; Still, W. C. An internal-coordinate Monte Carlo method for searching conformational space. J. Am. Chem. Soc. 1989, 111, 4379–4386.
- [23] https://github.com/bobbypaton/FullMonte.
- [24] Kim, S.; Chmely, S. C.; Nimlos, M. R.; Bomble, Y. J.; Foust, T. D.; Paton, R. S.; Beckham, G. T. Computational study of bond dissociation enthalpies for a large range of native and modified lignins. J. Phys. Chem. Lett. 2011, 2, 2846–2852.
- [25] Korth, M.; Pitonak, M.; Rezac, J.; Hobza, P. A transferable H-bonding correction for semiempirical quantum-chemical methods. J. Chem. Theory Comput. 2010, 6, 344–352.
- [26] Stewart, J. J. P. MOPAC2016 (http://OpenMOPAC.Net). 2016; Colorado Springs, CO, USA.
- [27] Neese, F. The ORCA program system. Wiley Interdiscip. Rev.: Comput. Mol. Sci. 2012, 2, 73–78.
- [28] Neese, F. Software update: the ORCA program system, version 4.0. Wiley Interdiscip. Rev.: Comput. Mol. Sci. 2018, 8, e1327.
- [29] Dunning Jr, T. H. Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. J. Chem. Phys. 1989, 90, 1007–1023.
- [30] Kendall, R. A.; Dunning Jr, T. H.; Harrison, R. J. Electron affinities of the first-row atoms revisited. Systematic basis sets and wave functions. J. Chem. Phys. 1992, 96, 6796–6806.
- [31] Woon, D. E.; Dunning Jr, T. H. Gaussian basis sets for use in correlated molecular calculations. III. The atoms aluminum through argon. J. Chem. Phys. 1993, 98, 1358–1371.
- [32] Feyereisen, M.; Fitzgerald, G.; Komornicki, A. Use of approximate integrals in ab initio theory. An application in MP2 energy calculations. *Chem. Phys. Lett.* **1993**, *208*, 359–363.
- [33] Bernholdt, D. E.; Harrison, R. J. Large-scale correlated electronic structure calculations: the RI-MP2 method on parallel computers. Chem. Phys. Lett. 1996, 250, 477–484.
- [34] Weigend, F.; Häser, M. RI-MP2: first derivatives and global consistency. Theor. Chem. Acc. 1997, 97, 331–340.
- [35] Weigend, F.; Köhn, A.; Hättig, C. Efficient use of the correlation consistent basis sets in resolution of the identity MP2 calculations. J. Chem. Phys. 2002, 116, 3175–3183.
- [36] Sandler, I.; Chen, J.; Taylor, M.; Sharma, S.; Ho, J. Accuracy of DLPNO-CCSD (T): Effect of Basis Set and System Size. J. Phys. Chem. A 2021, 125, 1553–1563.
- [37] Peterson, K. A.; Feller, D.; Dixon, D. A. Chemical accuracy in ab initio thermochemistry and spectroscopy: current strategies and future challenges. *Theor. Chem. Acc.* **2012**, *131*, 1–20.
- [38] East, A. L.; Allen, W. D. The heat of formation of NCO. J. Chem. Phys. 1993, 99, 4638–4650.
- [39] East, A. L.; Johnson, C. S.; Allen, W. D. Characterization of the  $\tilde{X}^1A'$  state of isocyanic acid. J. Chem. Phys. 1993, 98, 1299–1328.
- [40] Papajak, E.; Truhlar, D. G. What are the most efficient basis set strategies for correlated wave function calculations of reaction energies and barrier heights? *J. Chem. Phys.* **2012**, *137*, 064110.
- [41] Warden, C. E.; Smith, D. G.; Burns, L. A.; Bozkaya, U.; Sherrill, C. D. Efficient and automated computation of accurate molecular geometries using focal-point approximations to large-basis coupled-cluster theory. J. Chem. Phys. 2020, 152, 124109.
- [42] Neese, F.; Valeev, E. F. Revisiting the atomic natural orbital approach for basis sets: Robust systematic basis sets for explicitly correlated and conventional correlated ab initio methods? J. Chem. Theory Comput. 2011, 7, 33–43.
- [43] Helgaker, T.; Klopper, W.; Koch, H.; Noga, J. Basis-set convergence of correlated calculations on water. J. Chem. Phys. 1997, 106, 9639–9646.
- [44] Halkier, A.; Helgaker, T.; Jørgensen, P.; Klopper, W.; Koch, H.; Olsen, J.; Wilson, A. K. Basis-set convergence in correlated calculations on Ne, N2, and H2O. Chem. Phys. Lett. 1998, 286, 243–252.
- [45] Truhlar, D. G. Basis-set extrapolation. Chem. Phys. Lett. 1998, 294, 45–48.
- [46] Burns, L. A.; Marshall, M. S.; Sherrill, C. D. Appointing silver and bronze standards for noncovalent interactions: A comparison of spin-component-scaled (SCS), explicitly correlated (F12), and specialized wavefunction approaches. J. Chem. Phys. 2014, 141, 234111.
- [47] Jurečka, P.; Šponer, J.; Černý, J.; Hobza, P. Benchmark database of accurate (MP2 and CCSD (T) complete basis set limit) interaction energies of small model complexes, DNA base pairs, and amino acid pairs. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1985–1993.
- [48] Rezac, J.; Hobza, P. Describing noncovalent interactions beyond the common approximations: How accurate is the "gold standard," CCSD (T) at the complete basis set limit? J. Chem. Theory Comput. 2013, 9, 2151–2155.
- [49] Karton, A. Highly accurate CCSDT(Q)/CBS reaction barrier heights for a diverse set of transition structures: basis set convergence and cost-effective approaches for estimating post-CCSD(T) contributions. J. Phys. Chem. A 2019, 123, 6720–6732.
- [50] Vydrov, O. A.; Scuseria, G. E. Assessment of a long-range corrected hybrid functional. J. Chem. Phys. 2006, 125, 234109.
- [51] Vydrov, O. A.; Heyd, J.; Krukau, A. V.; Scuseria, G. E. Importance of short-range versus long-range Hartree-Fock exchange for the performance of hybrid density functionals. J. Chem. Phys. 2006, 125, 074106.
- [52] Zhao, Y.; Schultz, N. E.; Truhlar, D. G. Design of density functionals by combining the method of constraint satisfaction with parametrization for thermochemistry, thermochemical kinetics, and noncovalent interactions. *J. Chem. Theory Comput.* **2006**, *2*, 364–382.

- [53] Zhao, Y.; Truhlar, D. G. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.* 2008, 120, 215–241.
- [54] Haoyu, S. Y.; He, X.; Li, S. L.; Truhlar, D. G. MN15: A Kohn–Sham global-hybrid exchange–correlation density functional with broad accuracy for multi-reference and single-reference systems and noncovalent interactions. *Chem. Sci.* **2016**, *7*, 5032–5051.
- [55] Yu, H. S.; He, X.; Truhlar, D. G. MN15-L: A new local exchange-correlation functional for Kohn-Sham density functional theory with broad accuracy for atoms, molecules, and solids. *J. Chem. Theory Comput.* **2016**, *12*, 1280–1293.
- [56] Perdew, J. P.; Ruzsinszky, A.; Csonka, G. I.; Constantin, L. A.; Sun, J. Workhorse semilocal density functional for condensed matter physics and quantum chemistry. Phys. Rev. Lett. 2009, 103, 026403.
- [57] Chai, J.-D.; Head-Gordon, M. Systematic optimization of long-range corrected hybrid density functionals. J. Chem. Phys. 2008, 128, 084106.
- [58] Chai, J.-D.; Head-Gordon, M. Long-range corrected hybrid density functionals with damped atom-atom dispersion corrections. Phys. Chem. Chem. Phys. 2008, 10, 6615-6620.
- [59] Becke, A. D. Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys. Rev. A* 1988, 38, 3098
- [60] Perdew, J.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. Phys. Rev. Lett. 1996, 77, 3865–3868.
- [61] Tao, J.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E. Climbing the density functional ladder: Nonempirical meta—generalized gradient approximation designed for molecules and solids. *Phys. Rev. Lett.* 2003, 91, 146401.
- [62] Becke, A. D. A new mixing of Hartree–Fock and local density-functional theories. J. Chem. Phys. 1993, 98, 1372.
- [63] Adamo, C.; Barone, V. Toward reliable density functional methods without adjustable parameters: The PBE0 model. J. Chem. Phys. 1999, 110, 6158–6170.
- [64] Mardirossian, N.; Head-Gordon, M. Mapping the genome of meta-generalized gradient approximation density functionals: The search for B97M-V. J. Chem. Phys. 2015, 142, 074111.
- [65] Mardirossian, N.; Head-Gordon, M.  $\omega$  B97M-V: A combinatorially optimized, range-separated hybrid, meta-GGA density functional with VV10 nonlocal correlation. J. Chem. Phys. **2016**, 144, 214110.
- [66] Mardirossian, N.; Head-Gordon, M.  $\omega$ B97X-V: A 10-parameter, range-separated hybrid, generalized gradient approximation density functional with nonlocal correlation, designed by a survival-of-the-fittest strategy. *Phys. Chem. Chem. Phys.* **2014**, *16*, 9904–9924.
- [67] Neese, F.; Wennmohs, F.; Hansen, A.; Becker, U. Efficient, approximate and parallel Hartree–Fock and hybrid DFT calculations. A 'chain-of-spheres' algorithm for the Hartree–Fock exchange. Chem. Phys. 2009, 356, 98–109.
- [68] Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.
- [69] Weigend, F. Accurate Coulomb-fitting basis sets for H to Rn. Phys. Chem. Chem. Phys. 2006, 8, 1057–1065.
- [70] Goerigk, L.; Grimme, S. A thorough benchmark of density functional methods for general main group thermochemistry, kinetics, and noncovalent interactions. Phys. Chem. Chem. Phys. 2011, 13, 6670-6688.