

Supplementary References

- 1 Green, M. R. & Sambrook, J. Molecular Cloning: A Laboratory Manual (Fourth Edition). (Cold Spring Harbor Laboratory Press, 2012).
- 2 Kagiyama, I. *et al.* Taichunamides: Prenylated Indole Alkaloids from Aspergillus taichungensis (IBT 19404). *Angew. Chem. Int. Ed. Engl.* **55**, 1128-1132 (2016).
- 3 Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr. C Struct. Chem.* **71**, 3-8 (2015).
- 4 Xu, X., Zhang, X., Nong, X., Wang, J. & Qi, S. Brevianamides and mycophenolic acid derivatives from the deep-sea-derived fungus *Penicillium brevicompactum* DFFSCS025. *Mar. Drugs* **15** (2017).
- 5 Li, S. *et al.* Biochemical characterization of NotB as an FAD-dependent oxidase in the biosynthesis of notoamide indole alkaloids. *J. Am. Chem. Soc.* **134**, 788-791 (2012).
- 6 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.* **120**, 215-241 (2008).
- 7 Rassolov, V. A., Ratner, M. A., Pople, J. A., Redfern, P. C. & Curtiss, L. A. 6-31G* basis set for third-row atoms. *J. Comput. Chem.* **22**, 976-984 (2001).
- 8 Franch, M. M. *et al.* Self-consistent molecular-orbital methods. 23. A polarization-type basis set for second-row elements. *J. Chem. Phys.* **77**, 3654-3665 (1982).
- 9 Hariharan, P. & Pople, J. A. Influence of polarization functions on molecular-orbital hydrogenation energies. *Theor. Chim. Acta* **28**, 213-222 (1973).
- 10 Hehre, W. J., Ditchfield, R. & Pople, J. A. Self-consistent molecular-orbital methods. 12. Further extensions of Gaussian-type basis sets for use in molecular-orbital studies of organic-molecules. *J. Chem. Phys.* **56**, 2257-2261 (1972).
- 11 Clark, T., Chandrasekhar, J., Spitznagel, G. W. & Schleyer, P. V. Efficient diffuse function-augmented basis sets for anion calculations. III. The 3-21+G basis set for first-row elements, Li-F. *J. Comput. Chem.* **4**, 294-301 (1983).
- 12 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.* **132** (2010).
- 13 Goerigk, L. *et al.* A look at the density functional theory zoo with the advanced GMTKN55 database for general main group thermochemistry, kinetics and noncovalent interactions. *Phys. Chem. Chem. Phys.* **19**, 32184-32215 (2017).
- 14 Ripplinger, C., Pinski, P., Becker, U., Valeev, E. F. & Neese, F. Sparse maps-A systematic infrastructure for reduced-scaling electronic structure methods. II. Linear scaling domain based pair natural orbital coupled cluster theory. *J. Chem. Phys.* **144** (2016).
- 15 Ripplinger, C., Sandhoefer, B., Hansen, A. & Neese, F. Natural triple excitations in local coupled cluster calculations with pair natural orbitals. *J. Chem. Phys.* **139** (2013).
- 16 Ripplinger, C. & Neese, F. An efficient and near linear scaling pair natural orbital based local coupled cluster method. *J. Chem. Phys.* **138**, 034106 (2013).
- 17 Pople, J. A., Headgordon, M. & Raghavachari, K. Quadratic configuration interaction. A general technique for determining electron correlation energies. *J. Chem. Phys.* **87**, 5968-5975 (1987).

- 18 Purvis, G. D. & Bartlett, R. J. A full coupled-cluster singles and doubles model: The inclusion of disconnected triples. *J. Chem. Phys.* **76**, 1910-1918 (1982).
- 19 Dunning, T. H. Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. *J. Chem. Phys.* **90**, 1007-1023 (1989).
- 20 Davidson, E. R. Comment on Dunning's correlation-consistent basis sets - Comment. *Chem. Phys. Lett.* **260**, 514-518 (1996).
- 21 Woon, D. E. & Dunning, T. H. Gaussian basis sets for use in correlated molecular calculations. 3. The atoms aluminum through argon. *J. Chem. Phys.* **98**, 1358-1371 (1993).
- 2 Cances, E., Mennucci, B. & Tomasi, J. A new integral equation formalism for the polarizable continuum model: Theoretical background and applications to isotropic and anisotropic dielectrics. *J. Chem. Phys.* **107**, 3032-3041 (1997).
- 23 Mennucci, B., Cances, E. & Tomasi, J. Evaluation of solvent effects in isotropic and anisotropic dielectrics and in ionic solutions with a unified integral equation method: Theoretical bases, computational implementation, and numerical applications. *J. Phys. Chem. B* **101**, 10506-10517 (1997).
- 24 Scalmani, G. & Frisch, M. J. Continuous surface charge polarizable continuum models of solvation. I. General formalism. *J. Chem. Phys.* **132** (2010).
- 25 Tomasi, J., Mennucci, B. & Cances, E. The IEF version of the PCM solvation method: an overview of a new method addressed to study molecular solutes at the QM ab initio level. *J. Mol. Struc. (THEOCHEM)* **464**, 211-226 (1999).
- 26 Mennucci, B. & Tomasi, J. Continuum solvation models: A new approach to the problem of solute's charge distribution and cavity boundaries. *J. Chem. Phys.* **106**, 5151-5158 (1997).
- 27 Marenich, A. V., Cramer, C. J. & Truhlar, D. G. Universal solvation model based on solute electron density and on a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions. *J. Phys. Chem. B* **113**, 6378-6396 (2009).
- 28 Neese, F. The ORCA program system. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2**, 73-78 (2012).
- 29 Neese, F. Software update: the ORCA program system, version 4.0. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **8** (2018).
- 30 Liakos, D. G., Sparta, M., Kesharwani, M. K., Martin, J. M. L. & Neese, F. Exploring the accuracy limits of local pair natural orbital coupled-cluster theory. *J. Chem. Theory Comput.* **11**, 1525-1539 (2015).
- 31 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.* **9**, 2151-2155 (2013).
- 32 Truhlar, D. G. Basis-set extrapolation. *Chem. Phys. Lett.* **294**, 45-48 (1998).
- 33 Fukui, K. The path of chemical reactions - the IRC approach. *Acc. Chem. Res.* **14**, 363-368 (1981).
- 34 Grimme, S. Supramolecular binding thermodynamics by dispersion-corrected density functional theory. *Chem. Eur. J.* **18**, 9955-9964 (2012).
- 35 Funes-Ardoiz, I. & Paton, R. S. GoodVibes: version 2.0.3. (Zenodo, 2018).
- 36 Alecu, I. M., Zheng, J., Zhao, Y. & Truhlar, D. G. Computational thermochemistry: scale factor databases and scale factors for vibrational frequencies obtained from electronic model chemistries. *J. Chem. Theory Comput.* **6**, 2872-2887 (2010).

- 37 Frisch, M. J. *et al.* Gaussian 16, Revision B.01. (2016).
- 38 Glendening, E. D., Landis, C. R. & Weinhold, F. NBO 6.0: Natural bond orbital analysis program. *J. Comput. Chem.* **34**, 1429-1437 (2013).
- 39 Sure, R. & Grimme, S. Comprehensive Benchmark of Association (Free) Energies of Realistic Host-Guest Complexes. *J. Chem. Theory Comput.* **11**, 3785-3801 (2015).
- 40 Williams, R. M., Sanz-Cervera, J. F., Sancenon, F., Marco, J. A. & Halligan, K. M. Biomimetic Diels-Alder cyclizations for the construction of the brevianamide, paraherquamide, sclerotamide, asperparaline and VM55599 ring systems. *Bioorg. Med. Chem.* **6**, 1233-1241 (1998).