Mechanistic Insights for Iodane Mediated Aromatic Halogenation Reactions

Zheng-Wang Qu, Hui Zhu, and Stefan Grimme

Stable iodanes such as PhI(OAc)\(_2\) (Ac = acetyl) may be readily activated by electrophiles and salts for useful functional group transfer reactions under mild conditions, but the underlying reaction mechanism remains controversial. In this work, a general mechanism of iodane-mediated aromatic halogenation is revealed by extensive DFT calculations using PhI(OAc)\(_2\) and anisole PhOMe as model iodane and aromatic substrate, respectively. It is shown that facile OAc/X (X = Cl, Br) ligand exchange with electrophiles can be induced by electrophilic attack at acetyl C=O groups of PhI(OAc)\(_2\) to form more reactive iodanes, especially the non-symmetric iodanes PhI(X)OAc that can be activated by electrophiles to reach reactive iodonium PhI\(^+\) for further electrophilic halonium X\(^+\) transfer to aromatic substrates. Direct anionic OAc\(^-\)/X\(^-\) exchange of iodane are 4~7 kcal/mol endergonic, suggesting the crucial role of electrophilic iodane activation. Hetero- and homolytic I–X bond cleavages of neutral iodanes are more than 28 kcal/mol endergonic and thus unlikely under ambient conditions without electrophilic activation.

Aryl halides are useful building blocks in organic synthesis, widely used as precursors of organometallic reagents as well as substrates of transition-metal-catalyzed coupling reactions. In particular, since chlorination of aryl groups can modulate the electronic, lipophilic, and steric properties of the attached frameworks and hence is important in many fields such as pharmaceutical and material science to introduce chloro functional and thus unlikely under ambient conditions without electrophilic activation.

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Scheme 1. Recently proposed (top) and our new DFT-based (bottom) mechanism for the iodane-mediated electrophilic aromatic halogenation. The DFT calculations highlight the sequential electrophilic activation of acetyl groups of stable iodanes for efficient ligand exchange as well as the formation of transient iodonium PhI\(^+\) for electrophilic halogenation.

(A) Recent proposal (Fosu et al., 2019; Granados et al., 2019)

(B) This mechanistic work:
1. Electrophilic activation at acetoxy for ligand exchange;
2. Reactive iodonium PhI\(^+\) for electrophilic halogenation.

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of iodane activation and subsequent aromatic substitution reactions still remains controversial. For example, either nucleophiles$^{[11a,12]}$ such as halide anions $X^-$ or electrophilic$^{[11a,b,12b]}$ TMSX ($X = \text{Cl}, \text{Br}$) seem to be directly involved in ligand exchange with stable iodanes such as PhI(OAc)$_2$ followed by direct $I^-\cdots X$ bond cleavage of either non-symmetric$^{[11c]}$ or symmetric$^{[11b,12b]}$ iodanes to induce radical$^{[11a,12b]}$ or electrophilic$^{[11b,12b]}$ aromatic substitution reactions. A clear and general mechanistic picture is thus highly desirable for such iodane-mediated aromatic substitution reactions.

In this work, state-of-the-art DFT calculated free energies at the PW6B95-D3 + COSMO-RS//TPSS-D3 + COSMO level in dichloromethane CH$_2$Cl$_2$ solution (see below for computational details) are used to explore the mechanism of the iodane-mediated electrophilic chlorination of anisole PhOMe, using HX, TMSX ($X = \text{Cl}, \text{Br}$) and AcCl as electrophilic activator (Scheme 1). In contrast to recent mechanistic proposals,$^{[11a,12]}$ our DFT calculations clearly show that electrophilic activation of acetoxy groups of stable iodanes is crucial for both efficient ligand exchange and generation of transient iodonium PhI$^+$ for further electrophilic aromatic halogenation, while simple ligand exchange with nucleophilic halide anions $X^-$ is 4–7 kcal/mol endergonic and thus thermodynamically inefficient. In particular, once protic acids of HCl and HOAc are added or formed from PhI$^+$ mediated electrophilic aromatic halogenation, they may catalyze the formal reaction of PhICl$_2$ and stable PhI(OAc)$_2$ to form more reactive and non-symmetric iodane PhI(Cl)OAc, thus providing a simple and efficient mechanistic picture.

As shown in Figure 1A, in CH$_2$Cl$_2$ solution, the C–O protonation of bench-stable iodane PhI(OAc)$_2$ with protic acid HCl is almost neutral in free energy to form the ion pair complex PhI(OAc)$_2$H$^+$·Cl$^-$, requiring only 8.5 kcal/mol to reach the separated ion pair of electrophilic iodonium PhI(OAc)$^+$ and CHCl$^-$ via the elimination of the loosely bound acetic acid (HOAc) ligand and HCl stabilization of chloride anion Cl$^-$. Such ion pair of iodonium PhI(OAc)$^+$ and chloride is likely responsible for the experimentally observed electrophilic $C\cdots H$ bond activation of mesitylene forming diaryl iodane.$^{[12b,13]}$ Alternatively, the formal OAc/Cl ligand exchange via ionic $I^-\cdots Cl$ recombination within PhI(OAc)$_2$H$^+$·Cl$^-$ is $\sim$15.5 kcal/mol exergonic over a low barrier of only 7.2 kcal/mol (via transition structure TS1) to form the non-symmetric iodane PhI(Cl)OAc (along with HOAc), which is kinetically 1.8 kcal/mol more favourable. Similar C–O protonation of PhI(OAc)Cl with HCl is 1.1 kcal/mol endergonic to form the ion pair complex PhI(Cl)OAc$^+$·Cl$^-$, which needs further 10.2 kcal/mol to reach the separated ion pair of electrophilic iodonium PhICl$_2$ and CHCl$^-$.

In CH$_2$Cl$_2$ solution, the free chloride anion Cl$^-$ is stabilized by both HCl and HOAc via H-bonding by 4.1 and 1.7 kcal/mol, respectively. Without additional nucleophile for efficient PhI$^+$ trapping, the formal OAc/Cl ligand exchange between PhI(Cl)OAc and HCl is $\sim$13.3 kcal/mol exergonic over a low barrier of only 7.4 kcal/mol (TS2) via again ionic $I^-\cdots Cl$ recombination.

Figure 1. Proposed DFT computed free energy paths in CH$_2$Cl$_2$ solution (in kcal/mol, at 298 K and 1 M concentration) for: (A) the electrophilic activation of PhI(OAc)$_2$ with protic acid HCl to form transient iodonium PhICl$_2$ and CHCl$^-$ ion pair; (B) iodonium-mediated electrophilic chlorination of anisole PhOMe as a typical aromatic substrate. Except for contact complexes connected by central dots, all dissociated species are computed separately. The crucial C, H, O, Cl and I atoms in ball-and-stick models are highlighted by grey, white, red, green and violet balls, while partially breaking bonds are indicated by dashed lines. Note that the formation of PhICl$_2$ is reversible and 2.4 kcal/mol less exergonic than the formation of PhI(Cl)OAc that is favoured at low HCl molar ratio.
within transient Ph(Cl)OAc₂⁻·Cl⁻ to form the symmetric iodane PhICl₂ (along with HOAc), which is kinetically 3.9 kcal/mol more favourable than the formation of PhClI⁺ + Cl⁻⁻ ion pair. The reverse conversion from PhICl₂ and HOAc encounters a moderate barrier of 20.7 kcal/mol (TS₂) and thus is still possible under ambient conditions. Since the formation of Ph(Cl)OAc from PhI(OAc)₂ is −2.4 kcal/mol more exergonic than the formation of PhICl₂ from Ph(Cl)OAc via formal OAc/Cl ligand exchange with HCl, Ph(Cl)OAc should be thermodynamically favoured and dominate at low HCl molar ratio, though PhICl₂ is eventually reached with excess HCl, fully consistent with experimental results mixing 0.5 and 2.0 equivalent of HCl with PhI(OAc)₂.¹¹

In CH₄Cl₂ solution, heterolytic I−Cl cleavage of Ph(Cl)OAc and PhICl₂ (forming chloride Cl⁻) are endergonic by 28.1 and 28.7 kcal/mol while heterolytic I−OAc cleavage of PhI and Ph(Cl)OAc (forming acetate anion AcO⁻) are endergonic by 32.2 and 35.3 kcal/mol, respectively, clearly indicating relatively weaker I−Cl than I−OAc bonding in these iodonanes. In contrast, homolytic I−Cl cleavage of Ph(Cl)OAc and PhICl₂ (forming Cl radical) are 25.1 and 17.4 kcal/mol more endergonic than the corresponding heterolytic I−Cl cleavage and thus are unlikely under ambient conditions. Our DFT calculations suggest that the iodonanes Ph(Cl)OAc and PhICl₂ show similar thermal stability in solution but are less stable than the known bench-stable Ph(OAc)₂.

Aided by excess HCl, heterolytic I−Cl cleavage of Ph(Cl)OAc and PhICl₂ becomes 4.1 kcal/mol more favourable due to additional stabilization of Cl⁻ with HCl (still endergonic by 24.0 and 24.7 kcal/mol, respectively), which should be possible under moderate heating in solution. On the other hand, due to strong electrophilic activation upon C−O protonation with HCl, heterolytic I−OAc cleavage in PhOAc₂ and Ph(Cl)OAc is now endergonic by only 8.8 and 11.3 kcal/mol, respectively, totally reversing the thermal stability of I−Cl and I−OAc bonds.

Excess HCl is often used as protic PhI(OAc)₂ activator in experiment for aromatic chlorination reactions. As seen in Figure 1B, once generated from HCl activation of Ph(Cl)OAc, the electrophilic iodonium PhClI⁺ may easily transfer Cl⁻⁻ to anisole PhOMe as aromatic substrate, which is −17.5 kcal/mol exergonic and almost barrierless to form the arenium Cl⁺·PhOMe and stable Ph. Further deprotonation of Cl⁺·PhOMe with CHCl₃ is highly exergonic by −30.6 kcal/mol and also barrierless to form the chlorinated product 4-chloroanisole p-C₆H₅ClOMe. According to the overall reaction of PhI(OAc)₂ + HCl + PhOMe → Ph + 2HOAc + p-C₆H₅ClOMe, equal molar HCl should be consumed in such iodane-mediated chlorination reaction, rate-limited by the protic activation of Ph(Cl)OAc using HCl over a lower barrier of 11.3 kcal/mol forming iodonium PhClI⁺. More facile electrophilic activation is possible with stronger protic acid HBr; in contrast, the weak acid HOAc is much less efficient as protic activator for iodonanes, reducing the free energies of heterolytic I−Cl and I−OAc cleavage by only 1.7 and 2.6 kcal/mol via H-bond stabilization of anions Cl⁻ and AcO⁻, respectively (see ESI).

Experimentally, other electrophiles such as TMSX (X = Cl and Br) have also been identified as efficient activator of stable iodonanes such as PhI(OAc)₂.¹¹ As shown in Figure 2A, nucelophilic replacement at the Si-center of TMSCl with a acetyl C−O group of PhI(OAc)₂ can easily release a chloride anion Cl⁻, which is only 10.1 kcal/mol endergonic to form the cation PhI(OAc)₂TMS⁺. Further release of TMSOAc from the evidently elongated (activated) I−O bond of PhI(OAc)₂TMS⁺ is only 6.8 kcal/mol endergonic to form the iodonium PhI(OAc)²⁺ with a highly electrophilic I−center that may be trapped by either electron-rich substrate or separated Cl⁻ in solution. The first formal OAc/Cl ligand exchange with TMSCl is thus −11.2 kcal/mol.

Figure 2. DFT computed free energy paths in CH₄Cl₂ solution (in kcal/mol, at 298 K and 1 M concentration) for the electrophilic activation of iodonane PhI(OAc)₂ using various electrophiles: (A) trimethylsilyl chloride = TMSCl (and bromide TMSBr in parentheses for comparison); (B) acetyl chloride = AcCl. Except for contact complexes connected by central dots, all dissociated species are computed separately. The crucial C, H, O, N, S and Cl atoms in ball-and-stick models are highlighted by grey, white, red, blue, yellow and green balls, while partially breaking bonds indicated by dashed lines. Note that reactive TMSBr may favour the formation of Br, instead of iodonane PhIBr₂, while AcCl may selectively lead to the non-symmetric Ph(Cl)OAc.
mol exergonic over a low barrier of 16.9 kcal/mol to form the non-symmetric iodane PhI(Cl)OAc. The relatively low reactivity of TMSCl as compared with protic HCl as activator is mainly due to weaker electrophilic activation by TMS 2 as “fatty proton” and partially to the lack of H-bonding stabilization of Cl -. Similar OAc/Br ligand exchange with more reactive electrophile TMSBr is ~16.6 kcal/mol exergonic over a low barrier of 9.4 kcal/mol to form the non-symmetric iodane PhI(Br)OAc.

Note that the heterolytic I–X cleavage of iodanes PhI(X)OAc (X = Cl and Br) is still 28.1 and 26.5 kcal/mol endergonic, respectively, thus should be slow under ambient conditions in solution. Further electrophilic activation of PhI(X)OAc with TMSX is still possible. Again, nucleophilic replacement at the Si-functional group of PhI(OAc) 2 may either transfer Cl - to electron-rich aromatic substrates or recombine with separated Cl +, which is 14.6 kcal/mol endergonic to form the cation PhICl + AcOTMS. Further TMSOAc elimination is 5.4 kcal/mol exergonic to reach the electrophilic iodonium PhICl + that may either transfer Cl - to electron-rich aromatic substrates or recombine with separated Cl + in solution. Alternatively, anion Cl - aided TMSOAc release from PhICl +. AcOTMS is kinetically 5.4 kcal/mol more favourable via TS3 to form PhICl 2. The second OAc/Cl ligand exchange between PhI(Cl)OAc and TMSCl is ~8.8 kcal/mol exergonic over a low barrier of 15.4 kcal/mol to form PhICl 2, and TMSOAc; the formation of Cl 2 and Ph (via Cl–Cl type recombination) is 2.9 kcal/mol endergonic thus thermodynamically disfavoured. In contrast, the reaction of PhI(Br)OAc and more electrophilic TMSBr is only 9.5 kcal/mol endergonic to reach the reactive iodonium PhIBr +, from which both I–Br and Br–Br types of recombination with Br - are now energetically possible to form PhBr 2 and Ph + Br 2, respectively, with the latter being ~4.7 kcal/mol more exergonic.

As shown in Figure 2B, nucleophilic attack of a acetyl C=O group of PhI(OAc) 2 at the electrophilic C-center of acetyl chloride AcCl is 13.0 kcal/mol endergonic over a moderate barrier of 21.3 kcal/mol (via TS4) to release Cl -, followed by a facile I–Cl type recombination to form PhI(Cl)OAc and released AcO that is ~25.4 kcal/mol exergonic. The first OAc/Cl ligand exchange with AcCl is thus ~12.4 kcal/mol exergonic and irreversible (due to high reverse barrier of 33.7 kcal/mol). Similar nucleophilic attack of PhI(Cl)OAc to AcCl is 14.6 kcal/mol endergonic over a 2.5 kcal/mol higher barrier (via TS5) to release Cl -, followed again by a facile I–Cl recombination that is ~24.6 kcal/mol exergonic to form PhICl 2 and released AcO. The second OAc/Cl ligand exchange with AcCl is thus ~10.0 kcal/mol exergonic and again irreversible (high reverse barrier of 33.8 kcal/mol). Consistent with experiment,[11a] our DFT calculations indicate that AcCl is less reactive than TMSCl and HCl as electrophilic iodane activator but is more selective for the formation of the desirable PhI(Cl)OAc for further electrophilic atom transfer reactions.

In practice, when non-protic AcCl is used as an activator of PhI(OAc) 2, in electrophilic aromatic chlorination reactions (anisole PhOMe as example), transient protic HCl should still be produced from the reactive iodonium PhICl + according to: PhICl + PhOMe + Cl –→ Ph + p-C 6 H 4 OMe + HCl. Since HCl is much more reactive than AcCl for electrophilic iodane activation, it should be rapidly consumed. In such case, the overall reaction is: PhI(OAc) 2 + AcCl + PhOMe → Ph + Ac 2 O + p-C 6 H 4 OMe + HCl, forming stoichiometric acetic acid HClOAc that could stabilize intermediate Cl – by 1.7 kcal/mol in CH 2 Cl 2 solution via H-bonding. In this way, after an initial induction period corresponding to relatively slow iodane activation with AcCl as well as electrophilic chlorination of the aromatic substrate, fast PhI(OAc) 2 formation can be expected due to HCl activation of stable PhI(OAc) 2 and further non-protic AcCl activation of PhI(Cl)OAc with additional stabilizing of released Cl – with HOAc. Moreover, our DFT calculations show that acetonitrile (CH 3 CN) as polar solvent may lead to 1–2 kcal/mol higher barriers for protic iodane activation mainly due to better HCl solubility than in CH 2 Cl 2; such solvent effect becomes smaller for bulky electrophiles such as TMSCl and AcCl (see ESI, Table S2).

It was recently proposed that nucleophilic Cl – may also react with stable iodane PhI(OAc) 2 via direct ionic AcO /Cl – exchange.[11a,b] Our DFT calculations clearly show that all direct AcO /X (X = Cl, Br) exchange reactions of PhI(OAc) 2 and PhI(X)OAc are thermodynamically disfavoured by about 4–7 kcal/mol (see ESI). However, the increasing Lewis basicity of anions Br – < Cl – < OAc – may also increase their relative affinities with Lewis acidic cations such as K + in the same order. Indeed, our DFT calculations show that AcO – may bind to K + cation 4.6 kcal/mol stronger than Cl – does in CH 2 Cl 2 solution, which nearly compensates the free energy required for the first AcO /Cl – exchange with PhI(OAc) 2. These results emphasize the role of electrophilic counter-ions of halide salts in activating iodanes[11a] and are consistent with the lower reactivity observed for nBu 4 NC1 (non-coordinating ammonium) than KCl.[12b]

In summary, extensive DFT calculations show that stable iodanes such as PhI(OAc) 2 can be activated by various electrophiles via formal OAc/X (X = Cl, Br) ligand exchange to form more reactive iodanes, especially the desirable non-symmetric PhI(X)OAc that can be further activated by electrophiles to obtain reactive iodonium PhIX + for efficient halonium X – transfer to electron-rich aromatic substrates. The acetyl chloride AcCl is less reactive than TMSCl and protic HCl as electrophilic iodane activator but more selective for the formation of desirable non-symmetric iodanes. Such mechanistic insights seem to be useful also for other iodane-mediated electrophilic functional group transfer reactions.

Computational Methods

All DFT calculations are performed with the TURBOMOLE 7.3 suite of programs.[14] The structures are fully optimized at the TPSS-D3/def2-TZVP + COSMO(CH 2 Cl 2) level, which combines the TPSS meta-GGA density functional[15] with the BJ-damped DFT-D3 dispersion correction[16] and the def2-TZVP basis set,[17] using the Conductor-like Screening Model (COSMO)[18] for CH 2 Cl 2 solvent (dielectric constant = 8.93 and diameter R m = 2.94 Å). The well-established density-fitting RI-J approach[19] is used, which speeds up semi-local DFT functional calculations by a factor of ~20 at practically no loss of accuracy. Chemically reasonable reaction paths are generated manually and tested in DFT calculations. Useful initial guesses of transition structures are obtained from interpolation between
optimized reactant/intermediate/ product structures and constrained optimizations with appropriate reaction coordinates. The optimized structures are characterized by frequency analysis (no imaginary frequency for true minima and only one imaginary frequency for transition states) to provide thermal free-energy corrections (at 298.15 K and 1 atm) according to the modified ideal gas-rigid rotor-harmonic oscillator model. The connection of the transition state with reactants and products is checked visually by careful examining the vibrational transition mode.

More accurate solution free energies in CHCl₃ are computed with the COSMO-RS model[21] (parameter file: BP_TZVP_C30_1601.ctd) using the COSMOtherm package[22] based on the TPSS-D3 optimized structures, corrected by +1.89 kcal/mol to account for the 1 mol/L reference concentration in solution. To check the effects of the chosen density functional on the reaction energies and barriers, single-point calculations at both TPSS-D3[23] and hybrid-meta-GGA PW6B95-D3[24] levels are performed using the large def2-QZVPP[25] basis set. Final reaction free energies (ΔG) are determined from the electronic single-point energies plus TPSS-D3 thermal corrections and COSMO-RS solution free energies. The reaction energies from both DFT functionals are in good mutual agreement with average deviations of 0.9±2.4 (average±standard deviation) kcal/mol (see ES1). In the discussion, the more reliable PW6B95-D3+COSMO-RS free energies (in kcal/mol, at 298.15 K and 1 mol/L standard state concentration) are used unless specified otherwise. The applied DFT methods in combination with the large AO basis sets provide usually accurate electronic energies with typical errors of 1–2 kcal/mol for chemical energies (including barriers), which has been tested thoroughly for the huge data base GMTKN55[24] that is the common standard in the field of DFT benchmarking.

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Conflict of Interest

The authors declare no conflict of interest.

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[1] a) L. G. Voskrenensky, N. E. Golantsov, A. M. Maharramov, Synthesis-Stuttgart 2016, 48, 615–643; b) I. Saikia, A. J. Borah, P. Phukan, Chem. Rev. 2016, 116, 6837–7042.
[2] a) J. Hassan, M. Sevignon, C. Gozzi, E. Schulz, M. Lemaire, Chem. Rev. 2002, 102, 1359–1469; b) K. C. Nicolau, P. G. Bulger, D. Sarlah, Angew. Chem. Int. Ed. 2005, 44, 4442–4489; Angew. Chem. 2005, 117, 4516–4563; c) I. J. S. Fairlamb, Chem. Soc. Rev. 2007, 36, 1036–1045.
[3] a) M. J. Adam, D. S. Wilbur, Chem. Soc. Rev. 2005, 34, 153–163; b) M. L. Tang, Z. Bao, Chem. Mater. 2011, 23, 446–455; c) S. L. Pimlott, A. Sutherland, Chem. Soc. Rev. 2011, 40, 149–162; d) T. Cernak, K. D. Dykstra, S. Tyagarajan, P. Vachal, S. W. Krasa, Chem. Soc. Rev. 2016, 45, 546–576.
[4] a) R. A. Rodriguez, C.-M. Pan, Y. Yabe, Y. Kawamata, M. D. Eastgate, P. S. Baran, J. Am. Chem. Soc. 2014, 136, 6908–6911.
[5] a) J. Li, Matsuoi, D. Iida, H. Yamanaka, T. Mukaiyama, Tetrahedron 2003, 59, 6739–6750; b) L. De Luca, G. Giacomelli, G. Nieddu, Synlett 2005, 2003, 223–226.
[6] W. Liu, S. D. Christenson, S. Standage, B. Shen, Science 2002, 297, 1170–1173.
[7] R. A. Rodriguez, C.-M. Pan, Y. Yabe, Y. Kawamata, M. D. Eastgate, P. S. Baran, J. Am. Chem. Soc. 2014, 136, 6908–6911.
[8] M. Z. Wang, Y. Y. Zhang, T. Wang, C. Wang, D. Xue, J. L. Xiao, Org. Lett. 2018, 16, 1976–1979.
[9] a) Y. Kita, H. Tohma, K. Hatanaoka, T. Takada, S. Fujita, S. Mitoh, H. Sakurai, S. Oka, J. Am. Chem. Soc. 1994, 116, 3684–3691; b) P. A. Evans, T. A. Brandt, J. Org. Chem. 1997, 62, 5321–5326; c) R. Akula, M. Galligian, H. Ibrahim, Chem. Commun. 2009, 6991–6993.
[10] S. Izquierdo, S. Essafi, I. del Rosal, P. Vidossich, R. Pleixats, A. Vallinbera, G. Ujaje, A. Lledós, A. Shafir, J. Am. Chem. Soc. 2016, 138, 12747–12750.
[11] a) S. C. Fousi, C. M. Hambira, A. D. Chen, J. R. Fuchs, D. A. Nagib, Chem. Commun. 2019, 5, 417–428; b) A. Granados, A. Shafir, A. Arrieta, F. P. Cossio, A. Vallinbera, J. Org. Chem. 2020, 85, 2142–2150; c) P. D. Nahide, V. Ramadoss, K. A. Juarez-Onelias, Y. Satkar, R. Ortiz-Alvarado, J. M. J. Cervera-Villanueva, A. J. Alonso-Castro, J. R. Zapata-Morales, M. A. Ramirez-Moreno, A. J. Ruiz-Padilla, M. A. Deveze-Alvarez, C. R. Solorio-Alvarado, Eur. J. Org. Chem. 2018, 2018, 485–493; d) A. Segura-Quezada, Y. Satkar, D. Patil, N. Mali, K. Wrobel, G. Gonzalez, R. Zarraga, R. Ortiz-Alvarado, C. R. Solorio-Alvarado, Tetrahedron 2019, 60, 1515–1535; e) Y. Satkar, L. F. Yera-Ledesma, N. Mali, D. Patil, P. Navarro-Santos, L. A. Segura-Quezada, P. I. Ramirez-Morales, C. R. Solorio-Alvarado, J. Org. Chem. 2019, 84, 4149–4164; f) Y. Satkar, V. Ramadoss, P. D. Nahide, E. Garcia-Medina, K. A. Juarez-Onelias, A. J. Alonso-Castro, R. Chavez-Rivera, J. C. Jimenez-Hallera, C. R. Solorio-Alvarado, J. Org. Chem. 2020, 85, 17806–17812.
[12] a) S. Kang, S. Lee, H. Kim, Asian J. Org. Chem. 2015, 4, 137–140; b) A. Granados, Y. Z. Jia, M. del Olmo, A. Vallinbera, Eur. J. Org. Chem. 2019, 2019, 2812–2818.
[13] a) J. Zhao, S. Li, J. Org. Chem. 2017, 82, 2984–2991.
[14] TURBOMOLE V7.3, 2018, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989–2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com.
[15] J. Tao, P. J. Perdew, V. N. Staroverov, G. E. Scuseria, Phys. Rev. Lett. 2003, 91, 146401.
[16] a) S. Grimm, J. Antony, S. Ehrlich, H. Krieg, J. Chem. Phys. 2010, 132, 154104–154119; b) S. Grimm, S. Ehrlich, L. Goerigk, J. Comput. Chem. 2011, 32, 1456–1465.
[17] F. Weigend, R. Ahlrichs, Phys. Chem. Chem. Phys. 2005, 7, 3297–3305.
[18] A. Klamt, G. Schüürmann, J. Chem. Soc. Perkin Trans. 2 1993, 799–805.
[19] F. Weigend, Phys. Chem. Chem. Phys. 2006, 8, 1057–1065.
[20] S. Grimm, Chem. Eur. J. 2012, 18, 9955–9964.
[21] F. Eckert, A. Klamt, ALCHE 2002, 48, 369–385.
[22] F. Eckert, A. Klamt, COSMOTherm, Version C3.0, Release 16.01; COSMO-Logic GmbH & Co. KG, Leverkusen, Germany 2015.
[23] Y. Zhao, D. G. Truhlar, J. Phys. Chem. A 2005, 109, 5656–5667.
[24] L. Goerigk, A. Hansen, C. Bauer, S. Ehrlich, A. Najibi, S. Grimm, Phys. Chem. Chem. Phys. 2017, 19, 32184–32125.