Mechanism, reactivity, and regioselectivity in rhodium-catalyzed asymmetric ring-opening reactions of oxabicyclic alkenes: a DFT Investigation

Zheng-Hang Qi, Yi Zhang, Yun Gao, Ye Zhang, Xing-Wang Wang & Yong Wang

The origin of the enantio- and regioselectivity of ring-opening reaction of oxabicyclic alkenes catalyzed by rhodium/Josiphos has been examined using M06-2X density functional theory (DFT). DFT calculations predict a 98% ee for the enantioselectivity and only the 1,2-trans product as one regio- and diastereomer, in excellent agreement with experimental results. The solvent tetrahydrofuran (THF) plays a key role in assisting nucleophilic attack. Orbital composition analysis of the LUMO and the NPA atomic charge calculations were conducted to probe the origins of the regioselectivity. The orbital composition analysis reveals two potential electrophilic sites of the Rh–π-allyl intermediate M3 and the NPA atomic charges demonstrate that Cα carries more positive charges than Cγ, which suggests that Cα is the electrophilic site.

Ligands promoted organometallic catalysis has consistently attracted considerable interest for both academia and industry, due to its broad applications in synthetic transformations. Among enormous transition metal catalysts used in organic synthesis, catalytic active rhodium has been of great significance in this regard. Since the discovery of the Wilkinson complex [RhCl(PPh₃)₃] which was proved to be the harbinger of the development of modern organorhodium chemistry, the new field of homogeneous catalysis was opened. Particularly in the preparation of enantiomERICALLY enriched compounds, numerous rhodium-catalyzed reactions have been developed, such as asymmetric hydrogenation, isomerization of olefins, hydroacylation, cycloaddition and C–H insertion, etc. Over the past decade, several metal-catalyzed asymmetric ring closing reactions have been developed that generate ring-opened products in high yield and enantiomeric excess. Generally, some transition metals, such as rhodium, copper as well as palladium, have been commonly employed for this type nucleophilic ring opening reactions. Lautens reported in 2000 that rhodium/Josiphos catalyzed the asymmetric ring-opening (ARO) reaction of oxabicyclic alkenes involving heteroatom nucleophiles. In this reaction, very high regio- and diastereoselectivity, and excellent enantioselectivity were observed (Fig. 1). This pioneering work has been regarded as a landmark in rapid access to chiral building blocks, as the resulting allylic compounds are important structural motifs in medicinal chemistry. Since then, various nucleophiles were applied to this catalytic system including oxygen nucleophiles, nitrogen nucleophiles, sulfur nucleophiles and halogen atoms.

As depicted in Fig. 2, the commonly accepted mechanism for the ARO reaction of oxabicyclic alkenes is given by Lautens et al. Dimeric metal salt [Rh(cod)Cl], is cleaved by solvation, substrate binding, or reaction with the nucleophile to give monomeric complex I. Then, the π-allyl or enyl rhodium alkoxide complex II or III was generated by oxidative insertion with retention into a bridgehead C–O bond, which is regarded as the enantiodiscriminating step in the catalytic cycle. Subsequently, II or III could be protonated by the alcohol prenucleophile. After II or III, cationic rhodium complex IV and an alkoxide or phenoxide was proposed. Finally, the product was liberated and the rhodium catalyst was regenerated from nucleophilic attack with inversion. Inspired by Lautens’s pioneering efforts, we are interested in examining the mechanisms of rhodium-catalyzed ARO reactions. In this context, in view of the high importance of this methodology, in-depth mechanistic understandings.
of this reaction are in great demand. Through calculations, the structural information on the key transition states and intermediates as well as the energy profile could be investigated clearly. Herein, we report the full account of this study.

**Computational Details**
Computations were performed using Gaussian 09 suite of quantum chemical program. The M06-2X functional was used for the gas-phase geometry optimization of all species, which was demonstrated to be suitable for studying transition metal catalysis. The LANL2DZ basis set was employed for Rh and Fe, and the 6–31 G(d) basis set was used for other atoms (GEN1). Frequency analysis at the same level was performed to ensure the stationary point as minimum or transition state. The intrinsic reaction coordinate (IRC) calculations were applied for each transition state to confirm that it connects the right reactant and product. For the solvent effect, the single-point calculations on the gas-phase optimized geometry with SMD solvation model.
positive charge, and (ii) the nucleophile is rendered to be more nucleophilic by deprotonation. Unfortunately, proton transfer has two effects: (i) the organorhodium species is made more electrophilic as a result of the obtained cationic rhodium complex and an alkoxide or phenoxide as proposed by Lautens. In the case of an alkoxide, the rhodium alkoxide complex could be protonated by the alcohol prenucleophile to generate a ketene intermediate. However, no potential transition state or intermediate concerning with proton transfer was obtained.

We first turn our attention to the coordination of OA to Rh/Josiphos (Figure S1). There are four possible isomeric intermediates concerning different orientations of OA to Josiphos and Cl atom, which adopts a square-pyramidal geometry. The Rh(I) center of the formed intermediates is saturated coordinatively and electronically (i.e., an 18e Rh(I) complex). In M1-a and M1-b, the bridged oxygen of OA is positioned cis to the two tertiary butyl of the ligand, while in M1-c and M1-d, the alkyl group of OA is positioned cis to the two tertiary butyl of the ligand. Our calculations show that two relatively lower energy structures M1-a and M1-b are about 4 and 10 kcal/mol more stable than M1-c and M1-d. This is due to the alkyl group being positioned cis to the bulky tert-butyl group of the ligand in M1-c and M1-d, causing steric repulsion, while the small oxygen atom would not cause such larger steric effects.

Once OA is coordinated to Rh (M1-a, M1-b, M1-c, M1-d), the ring-opening may occur in two directions through corresponding transition states, which is assumed as the enantio-determining step. As a result, there are eight possible transition states in total from the four intermediates as depicted in Fig. 4. The top four transition states can lead to the products experimentally obtained, while the bottom four transition states can result in the constitutional enantiomers. The lowest transition state is TS1-22A. Taking all the eight transition states into consideration, the formation of (R,R)-products is most favored, and the calculated ee value is 98% by applying the Boltzmann distribution, which is in excellent agreement with the results obtained experimentally.

To gain further insights into the origins of enantioselectivity of Rh/Josiphos-catalyzed ARO reactions of OA, we analyzed the activation barriers using the distortion/interaction model (or activation strain model), as listed in Table S2. In this model, the energy differences between the distorted transition states and optimized ground-state structures are the distortion energies of the catalyst (E_{dist-cat}) and OA (E_{dist-OA}), respectively. The interaction energy (E_{int}) is the difference between the activation energy (E_{act}) and total distortion energy (E_{act} = E_{dist-cat} + E_{dist-OA}). It is obvious that although the distortion energy (E_{dist-OA} = 61.50 kcal/mol; Table S2, entry 3) is quite high in TS1-22A with a longest breaking C–O bond of 2.20 Å (Figure S2), the lowest distortion energy of the catalyst (E_{dist-cat} = 31.90 kcal/mol; Table S2, entry 3) causes TS1-22A to be the lowest one in energy.

After the ARO of OA, M2-2A is formed via TS1-22A. M2-2A is a π-allylrhodium(III) intermediate though the alkyl part of OA coordinates to Rh weakly (2.36 Å, 2.91 Å, Fig. 5). To be coordinatively and electronically saturated, the OA moiety of M2-2A rotates around the Rh center and arrives at the π-allylrhodium(III) intermediate M3. M3 is an octahedral intermediate and 14.24 kcal/mol more stable than M2-2A thermodynamically. Once M3 has been formed, the rhodium alkoxide complex could be protonated by the alcohol prenucleophile to generate cationic rhodium complex and an alkoxide or phenoxide as proposed by Lautens et al. It was thought that the proton transfer has two effects: (i) the organorhodium species is made more electrophilic as a result of the obtained positive charge, and (ii) the nucleophile is rendered to be more nucleophilic by deprotonation. Unfortunately, all of our efforts on locating such a transition state or intermediate concerning with proton transfer were failed. Starting from the two separated substrates M3 and MeOH, we conducted a relaxed potential energy surface scan at M06-2X/6–31 G(d)–LANL2DZ level of theory (Figures S3–S6) and found no discernible peaks that would indicate a potential transition state and intermediate structure.

Such repeated attempts suggest us that the methanol itself may act as a nucleophile in the assistance of some Lewis bases (i.e., the solvent THF). Fortunately, we have located such transitions states successfully (Fig. 6). The THF forms a hydrogen bond with the methanol (1.67 Å) to enhance the nucleophilicity of the nucleophile. In other words, the THF acts as a co-catalyst in the system. The successful application of aprotic silyl ketene acetics

Results and Discussion

In this study, the ARO reactions between oxabicyclic alkene (OA) and methanol (MeOH) catalyzed by [Rh(cod)Cl]2/(R,S)PPF–P2B2 (Rh/Josiphos) were chosen as the benchmark model (Fig. 3). For the computational systems, the ligands are fully considered and optimized without any simplification.

Figure 3. Computational model.
and enol ethers, acting as the nucleophiles, also supported such a process. Though it was found that the reaction of an alkoxide or phenoxide does not give ring-opened products, our calculations showed that the alkoxide can poison the catalyst by coordinating to the central Rh metal (Figure S9). As expected, the forming rhodium alkoxide complexes are quite stable thermodynamically, thus the substrates are inhibited from coordinating to the rhodium.

In general, the nucleophilic attack can take place either at $\alpha$ or $\gamma$ carbon to the position of the alkoxy group. Thus, a detailed sampling of the conformers arising due to different orientations of methyl moiety of the methanol is carried out to identify energetically the regioselectivity (Figures S7 and S8). The results in these two figures clearly indicate that the nucleophilic attack at $\text{C}_{\alpha}$ is favored by more than 15 kcal/mol relative to $\text{C}_{\gamma}$, which

Figure 4. Eight possible transition states of ARO of OA (distances in Å, free energies in kcal/mol).

Figure 5. Optimized geometries of intermediates M2-2A and M3. Selected distances (in Å) and Gibbs free energies are shown.
indicates that Cα position is the only electrophilic site of M3. Unfortunately, we failed to locate TS3-4b5 and TS3-4b6 due to the steric repulsion between the methyl group of the methanol and the phenyl ring of OA.

In order to probe the origins of the regioselectivity among the potential electrophilic sites of M3, we conducted orbital composition analysis of the lowest unoccupied molecular orbital (LUMO) and calculated the natural population analysis (NPA) charges (Fig. 7). The LUMO distribution shows that there are two potential electrophilic sites in the allyl moiety of M3 (10.9% for Cα; 14.2% for Cγ). Though the LUMO distribution of Cα is a bit lower than Cγ, conventional chemical wisdom would anticipate that the information of the atomic charge distribution in a molecule should suffice in quantifying the property. As shown in Fig. 7, Cα carries more...
positive charge than C_7 indicating that C_α should be the electrophilic site. In addition, it is worth noting that nucleophilic attack at C_7 would destroy the π−π conjugation between the allyl group and the phenyl ring of OA. Comparatively, the same regioselectivity is also observed when phenol, N-methylaniline and mercaptan act as the nucleophilic reagents respectively (Figures S10–S12).

We concurrently studied the possible side reaction of the formation of the syn-1,2 diastereomers of the product. As shown in Figure S13, one methanol is pressed into M3 to coordinate with Rh, which is endergonic by 8.38 kcal/mol and forms a π-allylrhodium(III) intermediate M3-syn. Subsequently, the proton of the methanol transfers to the oxygen of the opening OA, crossing a barrier of 15.38 kcal/mol (TS3-4syn relative to M3). After that, M4-syn undergoes C−O reductive elimination at the Rh(III) center via TS4-5syn, leading to the syn-1,2 diastereomers of the product. The C−O reductive elimination bears an insurmountable barrier of about 50 kcal/mol (TS4-5syn relative to M3), which indicates that it is impossible to generate the syn-1,2 diastereomers of the product under the experimental conditions. The results are in quantitative agreement with the diastereoselectivity observed experimentally.

Through our calculations, the computed Gibbs free energy surface for the most favored path of the ARO reaction of oxabicyclic alkene with methanol catalyzed by Rh/Josiphos is summarized in Fig. 8. [Rh(cod)Cl]_2 first undergoes cleavage to coordinate with the ligand Josiphos and the substrate OA to form a relatively stable intermediate M1-b by releasing 1.97 kcal/mol of energy, which is a coordinatively and electronically saturated square-pyramidal structure. The ring-opening step via TS1-22A has an activation energy of 32.74 kcal/mol, which is the rate- and enantio-determining step in the whole catalytic cycle and produces the π-allylrhodium(III) complex M2-2A. We next considered the π-allylrhodium(III) complex M3, which is 14.24 kcal/mol more stable than M2-2A. M3 then undergoes nucleophilic attack of one methanol in the assistance of THF via TS3-4a1, which is a late transition state, to form a new carbon−oxygen bond. The barrier for the nucleophilic attack is 31.02 kcal/mol, which is competitive with the ring-opening step. Finally, the proton transfer is completed by the solvent, which is about 32 kcal/mol exergonic and another molecule of the substrate OA replace the formed product to start the next catalytic cycle.

**Conclusions**

In summary, the mechanism, stereo- and regioselectivity of the Rh/Josiphos-catalyzed ARO reactions of oxabicyclic alkenes with methanol have been studied by DFT calculations. Based on the model advanced by Lautens et al., we performed the M06-2X calculations to explore the detailed mechanism carefully. Through calculations, we have found that the ring-opening step via TS1-22A is the rate- and enantio-determining step in the whole catalytic cycle with a lowest activation energy of 32.74 kcal/mol. The lower distortion energy of the catalyst in the ring-opening transition state makes the breaking C−O activation more favorable. In the nucleophilic attack step, the solvent THF forms a hydrogen bond with the nucleophile, and assists the attack at the allyl group of the π-allylrhodium(III) intermediate M3. In terms of regioselectivity, the formed π-allylrhodium(III) M3 is attacked by nucleophiles at the C_α site which bears more positive charge. Also, the formation of the syn-1,2 diastereomers of the product is inhibited by the high barrier of the C−O reductive elimination at the Rh(III) center. In the study of transition-metal-catalyzed reactions, most attention is paid on the metal center, experimentally and theoretically. In a reaction system, the most species is the solvent usually but it is often regarded as the reaction medium.
only. Though the solvent effects appear in many transition-metal-catalyzed reactions, less attention is paid on the association with reaction process. Here we present an example that how the solvent would play a role in the reaction mechanism explicitly. In combination with those experimental findings, the mechanistic studies presented herein are likely to induce a paradigm shift in the development of more active catalysts and may be helpful in the search for more selective catalysts.

References

1. Evans, P. A. (Ed.) Modern Rhodium Catalyzed Organic Reactions (Wiley-VCH, Weinheim, Germany, 2005).
2. Spenger, T., Sanhueza, I. A., Kalvet, I. & Schoenebeck F. Computational Studies of Synthetically Relevant Homogeneous Organometallic Catalysis Involving Ni, Pd, Ir, and Rh: An overview of commonly employed DFT methods and mechanistic insights. *Chem. Rev.* **115**, 9532–9586 (2015).
3. Jacobsen, E. N., Pfärr, A. & Yamamoto, H. (Ed.) Comprehensive Asymmetric Catalysis (Springer, Berlin, 1999).
4. Tanaka, K., Qiao, S., Tobisu, M., Lo, M. M.-C. & Fu, G. C. Enantioselective isomerization of allylic alcohols catalyzed by a rhodium/phosphine complex. *J. Am. Chem. Soc.* **122**, 9870–9871 (2000).
5. Tanaka, K. & Fu, G. C. A versatile new method for the synthesis of cyclopentenones via an unusual rhodium-catalyzed intramolecular trans hydroacylation of an alkene. *J. Am. Chem. Soc.* **123**, 11492–11493 (2001).
6. Wang, Y. & Yu, Z.-X. Rhodium-catalyzed [5 + 2 + 1] cyclodaddition of ene-vinylcyclopropanes and CO: reaction design, development, application in natural product synthesis, and inspiration for developing new reactions for synthesis of eight-membered carbocycles. *Acc. Chem. Res.* **48**, 2288–2296 (2015).
7. Archambeau, A., Miege, F., Meyer, C. & Cossy, J. Intramolecular cyclopropanation and C–H insertion reactions with metal carboanions generated from cyclopropanes. *Acc. Chem. Res.* **48**, 1021–1031 (2015).
8. Lautens, M., Fagnou, K. & Rovis, T. Rhodium-catalyzed asymmetric alcoholsysis and aminolysis of oxabenonorbornadiene: a new enantioselective carbon-heteroatom bond forming process. *J. Am. Chem. Soc.* **122**, 5650–5651 (2000).
9. Lautens, M., Renaud, J.-L. & Hieber, S. Palladium-catalyzed enantioselective allylic ring opening. *J. Am. Chem. Soc.* **122**, 1804–1805 (2000).
10. Zhang, T.-K., Mo, D.-L., Dai, L.-X. & Hou, X.-L. Palladacycle-catalyzed highly efficient kinetic resolution of 1-hydroxy-2-aryl-1,2-dihydropyridines via dehydrogenation reaction. *Org. Lett.* **10**, 5337–5340 (2008).
11. Bos, P. H., Rudolph, A., Pérez, M., Fañansa-Masral, M., Harutyunyan, S. R. & Feringa, B. L. Copper-catalyzed asymmetric ring opening of oxacyclic alkenes with organolithium reagents. *Chem. Commun.* **48**, 1748–1750 (2012).
12. Lautens, M., Fagnou, K. & Hieber, S. Transition metal-catalyzed enantioselective ring-opening reactions of oxacyclic alkenes. *Acc. Chem. Res.* **36**, 48–58 (2003).
13. Lautens, M., Fagnou, K. & Taylor, M. Rhodium-catalyzed asymmetric ring opening of oxacyclic alkenes with phenols. *Org. Lett.* **2**, 1677–1679 (2000).
14. Lautens, M., Fagnou, K., Taylor, M. & Rovis, T. Rhodium-catalyzed asymmetric ring opening of oxacyclic alkenes with heteroatom nucleophiles. *J. Organomet. Chem.* **624**, 259–270 (2001).
15. Leong, F. & Lautens, M. Rhodium-catalyzed asymmetric ring opening of oxacyclic alkenes with sulfur nucleophiles. *J. Org. Chem.* **69**, 2194–2196 (2004).
16. Zhang, L., Le, C. M. & Lautens, M. The use of silyl ketene acetics and enol ethers in the catalytic enantioselective allylic ring opening of axa/aza bicyclic alkenes. *Angew. Chem. Int. Ed.* **53**, 5951–5954 (2014).
17. Zhu, J., Tsui, G. C. & Lautens, M. Rhodium-catalyzed enantioselective nucleophilic fluorination: ring opening of oxacyclic alkenes. *Angew. Chem. Int. Ed.* **51**, 12353–12356 (2012).
18. Lautens, M. & Fagnou, K. Rhodium-catalyzed asymmetric ring opening reactions of oxacyclic alkenes: catalyst and substrate studies leading to a mechanistic working model. *Proc. Natl. Acad. Sci. USA* **101**, 5455–5460 (2004).
19. Frisch, M. J. et al. Gaussian 09, Revision C.01. (Gaussian, Inc., Wallingford, CT, 2010).
20. Zhao, Y. & Truhlar, D. G. The Mo6 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 Mo6-class functionals and 12 other functionals. *Theor. Chem. Acc.* **120**, 215–241 (2008).
21. Zhao, Y. & Truhlar, D. G. Density functionals with broad applicability in chemistry. *Acc. Chem. Res.* **41**, 157–167 (2008).
22. Schäfer, A., Jurca, T., Turner, J., Vance, J. R., Lee, K., Du, V. A., Haddow, M. F., Whittell, G. R. & Manners, I. Iron-catalyzed dehydrogenolysis: a convenient route to poly(phosphinoboranes) with molecular-weight control. *Angew. Chem. Int. Ed.* **54**, 4836–4841 (2015).
23. Zheng, C., Zhuo, C.-X. & You, S.-L. Mechanistic insights into the Pd-catalyzed intermolecular asymmetric allylic dearylmethylation of multisubstituted pyridines: understanding the remarkable regio- and enantioselectivity. *J. Am. Chem. Soc.* **136**, 16251–16259 (2014).
24. Hay, P. J. & Wadt, W. R. Ab initio effective core potentials for molecular calculations. Potentials for K to Au including the outermost core orbitals. *J. Chem. Phys.* **82**, 299–310 (1985).
25. Marenich, A. V., Cramer, C. J. & Truhlar, D. G. Universal solvation model based on solute electron density and a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions. *J. Phys. Chem. B* **113**, 6378–6396 (2009).
26. Lan, Y., Liu, P., Newman, S. G., Lautens, M. & Houk, K. N. Theoretical study of Pd(0)-catalyzed carbohalogenation of alkenes: mechanism of origins of reactivities and selectivities in alkyl halide reductive elimination from Pd(II) species. *Chem. Sci.* **3**, 1987–1995 (2012).
27. Lu, E. & Chen, F. Multiflux: a multifunctional wavefunction analyzer. *J. Comput. Chem.* **33**, 580–592 (2012).
28. Legault, C. Y. CYLview, 1.0b. (Université de Sherbrooke, http://www.cylview.org, 2009).
29. Ess, D. H. & Houk, K. N. Distortion/interaction energy control of 1,3-dipolar cycloaddition reactivity. *J. Am. Chem. Soc.* **129**, 10646–10647 (2007).
30. Legault, C. Y., Garcia, Y., Merlic, G. A. & Houk, K. N. Origin of regioselectivity in palladium-catalyzed cross-coupling reactions of polyhalogenated heterocycles. *J. Am. Chem. Soc.* **129**, 12664–12665 (2007).
31. Ess, D. H. & Houk, K. N. Theory of 1,3-dipolar cycloadditions: distortion/interaction and frontier molecular orbital models. *J. Am. Chem. Soc.* **130**, 10187–10198 (2008).
32. Wang, Y., Wang, Y., Zhang, W., Zhu, Y., Wei, D. & Tang, M. Mechanisms and stereoselectivities of the Rh(I)-catalyzed carbene carbon insertion reaction of benzocyclobutenol with diazoester. *Org. Biomol. Chem.* **13**, 6575–6579 (2015).
33. Wang, Y., Guo, X., Wu, B., Wei, D. & Tang, M. Mechanistic and stereochemical study for the reaction of trifluoroacetamides with arylnitrenes catalyzed by a cationic Lewis acid rhodium complex. *RSC Adv.* **5**, 100147–100158 (2015).
34. van Zest, W.-J. & Bickelhaupt, F. M. The activation strain model of chemical reactivity. *Org. Biomol. Chem.* **8**, 3118–3127 (2010).
35. Fernández, I. & Bickelhaupt, F. M. The activation strain model and molecular orbital theory: understanding and designing chemical reactions. *Chem. Soc. Rev.* **43**, 4953–4967 (2014).
36. Wolters, L. P. & Bickelhaupt, F. M. The activation strain model and molecular orbital theory. *WIREs Comput. Mol. Sci.* **5**, 324–343 (2015).
37. Liu, S. B. Where does the electron go? The nature of ortho/para and meta group directing in electrophilic aromatic substitution. *J. Chem. Phys.* **140**, 194109–197115 (2014).


Acknowledgements
We are grateful for the financial support from the National Natural Science Foundation of China (21272166, 21572150), the Major Basic Research Project of the Natural Science Foundation of the Jiangsu Higher Education Institutions (13KJA150004), the Program for New Century Excellent Talents in University (NCET-12-0743), a Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

Author Contributions
Z.-H.Q. performed DFT calculations, analyzed data and wrote the paper under the direction of Y.W. and X.-W.W. Y.Z., Y.Z., Y.G, Y.W. and X.-W.W. revised the paper. All the authors contributed to discussions.

Additional Information
Supplementary information accompanies this paper at http://www.nature.com/srep

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Qi, Z.-H. et al. Mechanism, reactivity, and regioselectivity in rhodium-catalyzed asymmetric ring-opening reactions of oxabicyclic alkenes: a DFT Investigation. Sci. Rep. 7, 40491; doi: 10.1038/srep40491 (2017).

Publisher’s note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

This work is licensed under a Creative Commons Attribution 4.0 International License. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder to reproduce the material. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/

© The Author(s) 2017