Supporting Information for

Selectivity Control of Pd(PMe₃)₄-Catalyzed Hydrogenation of

Internal Alkynes to E-alkenes by Reaction Time and Water

Content in Formic Acid

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Table of content

1.	Computation investigation of stage 1	S2
2.	Computation investigation of stage 2	S36
3.	Experimental Studies on the Reaction Mechanism	S67
4.	Supplementary References	S86

- **1.** Computation investigation of stage 1
- **1.1** Gibbs free energy profile of oxidation addition step in the Pd(PMe₃)₄- catalyzed hydrogenation of R with HCOOH.



Figure S1. Gibbs free energy profile of oxidation addition step in the $Pd(PMe_3)_4$ catalyzed hydrogenation of R with HCOOH to (*Z*)-alkene. Selected distances were shown in Å.

1.2 The conformations of intermediates and transition states of oxidation addition step in the $Pd(PMe_3)_4$ -catalyzed hydrogenation of R with HCOOH to (*Z*)-alkene.



∆G = -7.6 kcal/mol

M1_{Ph}-f ∆G = 5.6 kcal/mol

TS1_{Ph}-f ∆G = 21.9 kcal/mol



Figure S2. The conformations of intermediates and transition states of oxidation addition step in the $Pd(PMe_3)_4$ -catalyzed hydrogenation of R with HCOOH to (*Z*)-alkene. Selected distances were shown in Å.

1.3 The isomers of intermediates and transition states of oxidation addition step in the Pd(PMe₃)₄-catalyzed hydrogenation of R with H₂O.



with H₂O (Me/Ph)

Figure S3. The isomers of intermediates and transition states of oxidation addition step in the $Pd(PMe_3)_4$ -catalyzed hydrogenation of R with H₂O. Selected distances were shown in Å.

1.4 The isomers of intermediates and transition states of oxidation addition step in the Pd(PMe₃)₄-catalyzed hydrogenation of R with HCOOH and water. with HCOOH and water (Ph)





Figure S4. The isomers of intermediates and transition states of oxidation addition step in the Pd(PMe₃)₄-catalyzed hydrogenation of R with HCOOH and water to (*Z*)-alkene. Selected distances were shown in Å.

To understand why using aqueous HCOOH as hydrogen donor is more favorable to lower energy barrier, the distortion/interaction analyses¹ were performed on the transition state structures of rate-determining steps. In Figure S5, the activation energies (ΔE^{\neq}) was decomposed into several parts, activation (ΔE_{act}^{\pm}), distortion (ΔE_{dist}^{\pm}), and interaction (ΔE_{int}^{\pm}) energies, according to the distortion/interaction model¹ (or activation strain model²). Taking the oxidation addition transition states (*Z*)-TS1_{Ph}w-c (with the presence of water) and (*Z*)-TS1_{Ph}-f (without water) as examples, due to the intermolecular HBs between HCOOH and water in aqueous solution with an O···H bond distance of 1.81 Å, the distortion energies and interaction contributions are higher than those in TS1_{Ph}-f without the presence of water, hence lowering the contribution to the activation energy barrier in the presence of intermolecular HBs in water.

1.5 The transition state structures of the rate-determining step in the first stage.

S8



Figure S5. (a) The transition state structures of the rate-determining step and the relationships between activation (ΔE_{act}^{\neq}), distortion (ΔE_{dist}^{\neq}), and interaction (ΔE_{int}^{\neq}) energies. (b) Distortion/Interaction energy analysis of the oxidative addition of **M0** with HCOOH (aqueous HCOOH) are represented by arrows of different color. Blue: distortion energy of **M0**, purple: distortion energy of HCOOH (aqueous HCOOH), red: interaction energy, black: activation energy, and the units are in kcal/mol.



hydrogenation R with HCOOH to (*E*)-alkene.

Figure S6. Gibbs free energy profile of oxidation addition step in the $Pd(PMe_3)_4$ catalyzed hydrogenation of R with HCOOH and water to (*E*)-alkene. Selected distances were shown in Å.

1.7 The isomers of transition states and intermediates of oxidation addition step in

the $Pd(PMe_3)_4$ -catalyzed hydrogenation of R with HCOOH to (*E*)-alkene.





Figure S7. The isomers of transition states and intermediates of oxidation addition step in the Pd(PMe₃)₄-catalyzed hydrogenation of R with HCOOH to (*E*)-alkene. Selected distances were shown in Å.

1.8 The isomers of transition states and intermediates of oxidation addition step in

the $Pd(PMe_3)_4$ -catalyzed hydrogenation of R with HCOOH and water to (E)-

alkene.



 ΔG = -12.9 kcal/mol

 ΔG = -22.6 kcal/mol

∆G = -17.6 kcal/mol



Figure S8. The isomers of transition states and intermediates of oxidation addition step in the Pd(PMe₃)₄-catalyzed hydrogenation of R with HCOOH and water to (*E*)-alkene. Selected distances were shown in Å.

1.9 Gibbs free energy profile of the decarboxylation step of the decarboxylation step in the $Pd(PMe_3)_4$ -catalyzed hydrogenation of R with HCOOH to (*Z*)-alkene.



Figure S9. Gibbs free energy profile of the decarboxylation step in the $Pd(PMe_3)_4$ catalyzed hydrogenation of R with HCOOH to (*Z*)-alkene. The relative Gibbs free energies were given in kcal/mol.



1.10 The isomers of intermediates and transition states of decarboxylation step in the Pd(PMe₃)₄-catalyzed hydrogenation of R with HCOOH.

Figure S10. The isomers of intermediates and transition states of decarboxylation step in the Pd(PMe₃)₄-catalyzed hydrogenation of R with HCOOH to (*Z*)-alkene. Selected distances were shown in Å.

1.11 Gibbs free energy profile of the decarboxylation step of $Pd(PMe_3)_4$ -catalyzed hydrogenation of R with HCOOH to (*E*)-alkene.



Figure S11. Gibbs free energy profile of decarboxylation step in the $Pd(PMe_3)_4$ catalyzed hydrogenation of R with HCOOH to (*E*)-alkene. Selected distances were shown in Å. The relative Gibbs free energies were given in kcal/mol.

1.12 The isomers of intermediates and transition states of the decarboxylation step in the $Pd(PMe_3)_4$ -catalyzed hydrogenation of R with HCOOH to (*E*)-alkene.



Figure S12. The isomers of intermediates and transition states of the decarboxylation step in the $Pd(PMe_3)_4$ -catalyzed hydrogenation of R with HCOOH to (*E*)-alkene. Selected distances were shown in Å.

1.13 Gibbs free energy profile of reductive elimination step in the Pd(PMe₃)₄- catalyzed hydrogenation of R with HCOOH.



Figure S13. Gibbs free energy profile of reductive elimination step in the $Pd(PMe_3)_4$ catalyzed hydrogenation of R with HCOOH to (*Z*)-alkene. The relative Gibbs free energies were given in kcal/mol. **1.14** The isomers of intermediates and transition states of reductive elimination step in the Pd(PMe₃)₄-catalyzed hydrogenation of R with HCOOH.



Reductive elimination

Figure S14. The isomers of intermediate and transition states of reductive elimination step in the path of $Pd(PMe_3)_4$ -catalyzed hydrogenation of R with HCOOH to (*Z*)-alkene. Selected distances were shown in Å.

1.15 Gibbs free energy profile of reductive elimination step of Pd(PMe₃)₄-catalyzed hydrogenation of R with HCOOH to (*E*)-alkene.



Figure S15. The isomers of intermediates and transition states of the reductive elimination step in the $Pd(PMe_3)_4$ -catalyzed hydrogenation of R with HCOOH to (*E*)-alkene. The relative Gibbs free energies were given in kcal/mol.

1.16 The isomers of intermediates and transition states of the reductive elimination step in the $Pd(PMe_3)_4$ -catalyzed hydrogenation of R with HCOOH to (*E*)-alkene.



Figure S16. The isomers of intermediate and transition states of the reductive elimination step in the Pd(PMe₃)₄-catalyzed hydrogenation of R with HCOOH to (*E*)-alkene. Selected distances were shown in Å.



1.17 Gibbs energy profile of the $Pd(PMe_3)_4$ -catalyzed hydrogenation of **R** with HCOOH (HCOOH and water) to (*Z*)-alkene.

Figure S17. Gibbs energy profile of the $Pd(PMe_3)_4$ -catalyzed hydrogenation of **R** with HCOOH (HCOOH and water) to (*Z*)-alkene **M5Ph**. Selected distances were shown in Å.



1.18 Gibbs energy profile of the $Pd(PMe_3)_4$ -catalyzed hydrogenation of **R** with HCOOH (HCOOH and water) to (*E*)-alkene.

Figure S18. Gibbs energy profile of the Pd(PMe₃)₄-catalyzed hydrogenation of **R** with HCOOH (HCOOH and water) to (*E*)-alkene $M5_{Me}$ '. Selected distances were shown in Å.

- with AcOH (Ph) M1_{Ph}-Ac-a M1_{Ph}-Ac-c M1_{Ph}-Ac-e M1_{Ph}-Ac-b M1_{Ph}-Ac-d ∆G = 3.8 kcal/mol ∆G = 3.7 kcal/mol ∆G = 2.6 kcal/mol ∆G = 3.5 kcal/mol ∆G = 8.0 kcal/mol TS1_{Ph}-Ac-a TS1_{Ph}-Ac-b TS1_{Ph}-Ac-c TS1_{Ph}-Ac-d TS1_{Ph}-Ac-e ∆G = 22.0 kcal/mol ∆G = 23.7 kcal/mol ∆G = 24.1 kcal/mol ∆G = 23.0 kcal/mol ∆G = 27.8 kcal/mol M2_{Ph}-Ac-b M2_{Ph}-Ac-c M2_{Ph}-Ac-e M2_{Ph}-Ac-d M2_{Ph}-Ac-a ∆G = -5.5 kcal/mol ∆G = -5.5 kcal/mol ∆G = -12.1 kcal/mol ∆G = -13.4 kcal/mol ∆G = -6.4 kcal/mol with AcOH (CH3) M1_{Me}-Ac-a M1_{Me}-Ac-b M1_{Me}-Ac-d M1_{Me}-Ac-c ∆G = 2.9 kcal/mol ∆G = 7.7 kcal/mol ∆G = 8.4 kcal/mol ∆G = 2.6 kcal/mol 28.0 TS1_{Me}-Ac-a TS1_{Me}-Ac-b TS1_{Me}-Ac-c TS1_{Me}-Ac-c ∆G = 25.5 kcal/mol ∆G = 23.7 kcal/mol ∆G = 26.3 kcal/mol ∆G = 26.0 kcal/mol M2_{Me}-Ac-a M2_{Me}-Ac-b M2_{Me}-Ac-c M2_{Me}-Ac-d ∆G = -3.2 kcal/mol ∆G = -2.7 kcal/mol $\Delta G = -12.5 \text{ kcal/mol}$ $\Delta G = -4.0 \text{ kcal/mol}$
- **1.19** The isomers of intermediates and transition states of oxidation addition step in the Pd(PMe₃)₄-catalyzed hydrogenation of R with AcOH to alkenylpalladium containing *Z* manner.

Figure S19. The isomers of intermediates and transition states of oxidation addition step in the $Pd(PMe_3)_4$ -catalyzed hydrogenation of R with AcOH to alkenylpalladium intermediate containing Z manner. Selected distances were shown in Å.

1.20 The isomers of intermediates and transition states of oxidation addition step in the $Pd(PMe_3)_4$ -catalyzed hydrogenation of R with AcOH to alkenylpalladium containing *E* manner.



Figure S20. The isomers of intermediates and transition states of the oxidation addition step in the $Pd(PMe_3)_4$ -catalyzed hydrogenation of R with AcOH to alkenylpalladium containing *E* manner. Selected distances were shown in Å.

with AcOH and water (Ph) M1_{Ph}w-Ac-a M1_{Ph}w-Ac-b M1_{Ph}w-Ac-c M1_{Ph}w-Ac-d ∆**G = 5.8** ∆**G = 6.3** ∆G = 3.4 ∆**G = 0.3** 08.4° TS1_{Ph}w-Ac-a TS1_{Ph}w-Ac-d TS1_{Ph}w-Ac-b TS1_{Ph}w-Ac-c ∆G = 21.5 ∆**G = 24.7** ∆G = 18.9 ∆G = 21.5 136.3° M2_{Ph}w-Ac-b) M2_{Ph}w-Ac-c M2_{Ph}w-Ac-d M2_{Ph}w-Ac-a ∆**G = -6.9** ∆G = -6.6 ∆**G = -12.5** ∆G = -11.3 M1_{Ph}w-Ac-g M1_{Ph}w-Åc-f M1_{Ph}w-Ac-e M1_{Ph}w-Ac-h ∆G = 2.9 ∆**G = 0.8** ∆**G** = 1.8 ∆**G = 2.5** 1.78 .79 115.1 157.5 TS1_{Ph}w-Ac-e TS1_{Ph}w-Ac-f TS1_{Ph}w-Ac-g TS1_{Ph}w-Ac-h ∆G = 19.9 ∆G = 23.4 ∆G = 16.9 ∆**G = 26.1** 1.78 136.4° 35.0° 132.9° 🕻 Ì.80 M2_{Ph}w-Ac-e M2_{Ph}w-Ac-f M2_{Ph}w-Ac-g M2_{Ph}w-Ac-h ∆**G** = -18.5 ∆G = -14.2 ∆G = -12.2

∆G = -10.6

1.21 The isomers of intermediates and transition states of the oxidation addition step of Pd(PMe₃)₄-catalyzed hydrogenation R with AcOH and water to alkenylpalladium containing Z manner.



Figure S21. The configurations of intermediates and transition states of oxidation addition step in the Pd(PMe₃)₄-catalyzed hydrogenation of R with AcOH and water to alkenylpalladium containing Z manner. The relative Gibbs free energies were given in kcal/mol and the selected distances were shown in Å.

1.22 The configurations of intermediates and transition states of oxidation addition

step in the $Pd(PMe_3)_4$ -catalyzed hydrogenation of R with AcOH and water to alkenylpalladium containing *E* manner.





Figure S22. The isomers of intermediates and transition states of oxidation addition step in the Pd(PMe₃)₄-catalyzed hydrogenation of R with AcOH and water to alkenylpalladium containing *E* manner. The relative Gibbs free energies were given in kcal/mol and the selected distances were shown in Å.



1.23 The relaxed potential energy surface scans for the CH₃ of AcOH coordinating to Pd center in (a) M2_{Ph}-Ac-c, (b) M2_{Ph}'-Ac-c, (c) M2_{Ph}w-Ac-e, (d) M2_{Ph}'w-Ac-f.

Figure S23. The relaxed potential energy surface scans for the CH₃ of AcOH coordinating to Pd center in (a) $M2_{Ph}$ -Ac-c, (b) $M2_{Ph}$ '-Ac-c, (c) $M2_{Ph}$ w-Ac-e, (d) $M2_{Ph}$ 'w-Ac-f. Selected distances were shown in Å.

1.24 The isomers of intermediate and transition states of reductive elimination step in the Pd(PMe₃)₄-catalyzed hydrogenation of **R** with AcOH and water to (Z)-alkene.



Figure S24. The isomers of intermediate and transition states of reductive elimination step in the Pd(PMe₃)₄-catalyzed hydrogenation of **R** with AcOH to (*Z*)-alkene. Selected distances were shown in Å.



1.25 The isomers of intermediates and transition states of reductive elimination step in the $Pd(PMe_3)_4$ -catalyzed hydrogenation of **R** with AcOH to (*E*)-alkene.

Figure S25. The isomers of intermediates and transition states of reductive elimination step in the Pd(PMe₃)₄-catalyzed hydrogenation of **R** with AcOH to (*E*)-alkene. Selected distances were shown in Å.

1.26 Gibbs energy profile of the $Pd(PMe_3)_4$ -catalyzed hydrogenation of **R** with AcOH (AcOH and water) to (*E*)-alkene.



Figure S26. Gibbs free energy of the $Pd(PMe_3)_4$ -catalyzed hydrogenation of **R** with AcOH (AcOH and water) to (*E*)-alkene. Selected distances were shown in Å.

1.27 Gibbs energy profile of the $Pd(PMe_3)_4$ -catalyzed hydrogenation of **R** with AcOH (AcOH and water) to (*E*)-alkene.



Figure S27. The isomers of intermediates and transition states of the $Pd(PMe_3)_4$ catalyzed hydrogenation of **R** with AcOH (AcOH and water) to (*E*)-alkene **M5Me'-Ac**. Selected distances were shown in Å.





Figure S28. The electrostatic potential of HCOOH, AcOH and alkenenypalladium intermediates. Selected mulliken charges are given in black numbers.

- **2** Computation investigation of stage 2.
- **2.1** Gibbs free energy profile of the oxidative addition step in the $Pd(PMe_3)_{4-}$ catalyzed hydrogenation of (*Z*)-alkene with HCOOH.



Figure S29. Gibbs free energy of the oxidative addition step of $Pd(PMe_3)_4$ -catalyzed hydrogenation of (*Z*)-alkene with HCOOH to (*E*)-alkene. Selected distances were shown in Å.
2.2 The configurations of the intermediates and transition states of oxidation addition in the $Pd(PMe_3)_4$ -catalyzed hydrogenation of (*Z*)-alkene with HCOOH to alkyl-palladium intermediate with *Z* manner.



Oxidation addition (Ph)

Oxidation addition (Me)



Figure S30. The isomers of intermediates and transition states of oxidative addition step in the $Pd(PMe_3)_4$ -catalyzed hydrogenation of (*Z*)-alkene with HCOOH to alkylpalladium intermediate with *Z* manner. Selected distances were shown in Å.

2.3 The isomers of intermediates and transition states of the oxidative addition step of $Pd(PMe_3)_4$ -catalyzed hydrogenation of (*Z*)-alkenes with H₂O to alkyl-palladium intermediates with *Z* manner.



Figure S31. The isomers of intermediates and transition states of oxidative addition step in the Pd(PMe₃)₄-catalyzed hydrogenation of (*Z*)-alkene with H₂O to alkyl-palladium intermediate with *Z* manner. Selected distances were shown in Å.

2.4 Gibbs free energy of the oxidative addition step in the $Pd(PMe_3)_4$ -catalyzed hydrogenation of (*Z*)-alkene with HCOOH and water.



Figure S32. Gibbs free energy of the oxidative addition step in the $Pd(PMe_3)_4$ -catalyzed hydrogenation of (*Z*)-alkene **M5**_{Ph} with HCOOH and water to alkyl-palladium intermediate with *Z* manner. Selected distances were shown in Å.

2.5 The configurations of intermediates and transition states of oxidative addition

step in the $Pd(PMe_3)_4$ -catalyzed hydrogenation of (*Z*)-alkene with HCOOH and water to alkyl-palladium intermediate with *Z* manner.





Figure S33. The isomers of intermediates and transition states of oxidative addition step in the $Pd(PMe_3)_4$ -catalyzed hydrogenation of (*Z*)-alkene with HCOOH and water to alkyl-palladium intermediate with Z manner. Selected distances were shown in Å.

2.6 Three-dimensional illustration of intermediates and transition states of the oxidative addition steps.



Figure S34. Three-dimensional illustration of intermediates and transition states of the oxidative addition steps in the two stages.

2.7 Gibbs free energy of the isomerization step in the $Pd(PMe_3)_4$ -catalyzed hydrogenation of (*Z*)-alkene **M5**_{Ph} with HCOOH.



Figure S35. Gibbs free energy of the isomerization step of $Pd(PMe_3)_4$ -catalyzed hydrogenation of (*Z*)-alkene **M5**_{Ph} with HCOOH to *E*-alkene. Selected distances were shown in Å and the relative Gibbs free energies are given in kcal/mol.

2.8 The isomers of intermediates and transition states of the isomerization step in the Pd(PMe₃)₄-catalyzed hydrogenation of (*Z*)-alkene **M5**_{Ph} with HCOOH to *E*-alkene.





Figure S36. The isomers of intermediates and transition states of the isomerization step in the Pd(PMe₃)₄-catalyzed hydrogenation of (*Z*)-alkene **M5**_{Ph} with HCOOH. Selected distances were shown in Å.

2.9 Gibbs free energy of the isomerization step in the $Pd(PMe_3)_4$ -catalyzed hydrogenation of (*Z*)-alkene **M5**_{Ph} with HCOOH and water.



Figure S37. Gibbs free energy of the isomerization step in the $Pd(PMe_3)_4$ -catalyzed hydrogenation of (*Z*)-alkene **M5**_{Ph} with HCOOH and water. Selected distances were shown in Å and the relative Gibbs free energies are given in kcal/mol.

2.10 The isomers of intermediates and transition states of the isomerization step in the Pd(PMe₃)₄-catalyzed hydrogenation of (*Z*)-alkene **M5**_{Ph} with HCOOH and water.





Figure S38. The isomers of intermediates and transition states of the isomerization step in the Pd(PMe₃)₄-catalyzed hydrogenation of (*Z*)-alkene **M5**_{Ph} with HCOOH to (*E*)-alkene. Selected distances were shown in Å.

2.11 Gibbs free energy of the β -H elimination or decarboxylation step in the Pd(PMe₃)₄-catalyzed hydrogenation of (*Z*)-alkene with HCOOH.



Figure S39. Gibbs free energy of the β -H elimination or decarboxylation step in the Pd(PMe₃)₄-catalyzed hydrogenation of (*Z*)-alkene with HCOOH to (*E*)-alkene or alkane. The relative Gibbs free energies are given in kcal/mol.

2.12 Gibbs free energy of the β -H elimination or decarboxylation step in the Pd(PMe₃)₄-catalyzed hydrogenation of (*Z*)-alkene with HCOOH.



β-H elimination or decarboxylation

Figure S40. Gibbs free energy of the β -H elimination or decarboxylation step in the Pd(PMe₃)₄-catalyzed hydrogenation of (Z)-alkene with HCOOH to (E)-alkene or alkane. DFT-D3 calculations, at the same level, were performed on the optimized molecular structures. The relative Gibbs free energies are given in kcal/mol.

2.13 The isomers of the intermediates and transition states of β -H elimination step in the Pd(PMe₃)₄-catalyzed hydrogenation of (*Z*)-alkene with HCOOH to (*E*)-alkene.



Figure S41. The isomers of intermediates and transition states of β -H elimination step in the Pd(PMe₃)₄-catalyzed hydrogenation of (*Z*)-alkene with HCOOH to (*E*)-alkene. DFT-D3 calculations, at the same level, were also shown in brackets. Selected distances were shown in Å and Gibbs free energies were given in kcal/mol.



2.14 The isomers of intermediates and transition states of the decarboxylation step in the $Pd(PMe_3)_4$ -catalyzed hydrogenation of (*Z*)-alkene with HCOOH to alkane.

Figure S42. The isomers of intermediates and transition states of the decarboxylation step in the $Pd(PMe_3)_4$ -catalyzed hydrogenation of (*Z*)-alkene with HCOOH to alkane. DFT-D3 calculations, at the same level, were also shown in brackets. Selected distances were shown in Å and Gibbs free energies were given in kcal/mol.

2.15 Gibbs free energy of the β -H elimination or decarboxylation step in the Pd(PMe₃)₄-catalyzed hydrogenation of (*Z*)-alkene with HCOOH and water.



Figure S43. Gibbs free energy of the β -H elimination or decarboxylation step in the Pd(PMe₃)₄-catalyzed hydrogenation of (*Z*)-alkene with HCOOH and water to (*E*)-alkene or alkane. Selected distances were shown in Å and Gibbs free energies were given in kcal/mol.

2.16 Gibbs free energy of the β -H elimination or decarboxylation step in the Pd(PMe₃)₄-catalyzed hydrogenation of (*Z*)-alkene with HCOOH and water.



Figure S44. Gibbs free energy of the β -H elimination or decarboxylation step in the Pd(PMe₃)₄-catalyzed hydrogenation of (*Z*)-alkene with HCOOH and water to (*E*)-alkene or alkane. DFT-D3 calculations, at the same level, were performed on the optimized molecular structures. Selected distances were shown in Å and Gibbs free energies were given in kcal/mol.



2.17 The isomers of intermediates and transition states of the β -H elimination step in the Pd(PMe₃)₄-catalyzed hydrogenation of (*Z*)-alkene with HCOOH and water.



Figure S45. The isomers of intermediates and transition states of the β -H elimination step in the Pd(PMe₃)₄-catalyzed hydrogenation of (*Z*)-alkene with HCOOH and water to (*E*)-alkene. DFT-D3 calculations, at the same level, were also shown in brackets. Selected distances were shown in Å and Gibbs free energies were given in kcal/mol.



2.18 The isomers of intermediates and transition states of the decarboxylation step in the $Pd(PMe_3)_4$ -catalyzed hydrogenation of (*Z*)-alkene with HCOOH and water.

Figure S46. The isomers of intermediate and transition states of the decarboxylation step in the $Pd(PMe_3)_4$ -catalyzed hydrogenation of (*Z*)-alkene with HCOOH and water to alkane. DFT-D3 calculations, at the same level, were also shown in brackets. Selected distances were shown in Å and the Gibbs free energies were given in kcal/mol.

2.19 Gibbs free energy of the reductive elimination step in the $Pd(PMe_3)_4$ -catalyzed hydrogenation of (*Z*)-alkene to alkane.



Figure S47. Gibbs free energy of the reductive elimination step in the $Pd(PMe_3)_4$ catalyzed hydrogenation of (*Z*)-alkene to alkane. The relative Gibbs free energies were given in kcal/mol.

2.20 The isomers of intermediates and transition states of the reductive elimination step in the $Pd(PMe_3)_4$ -catalyzed hydrogenation of (*Z*)-alkene.



Figure S48. The isomers of intermediates and transition states of the reductive elimination step in the $Pd(PMe_3)_4$ -catalyzed hydrogenation of (*Z*)-alkene to alkane. DFT-D3 calculations, at the same level, were also shown in brackets. Selected distances were shown in Å and the Gibbs free energies were given in kcal/mol..

2.21 Gibbs free energy of the Pd(PMe₃)₄-catalyzed hydrogenation of (*E*)-alkene with HCOOH to Alkane.



Figure S49. Gibbs free energy of the $Pd(PMe_3)_4$ -catalyzed hydrogenation of (*E*)-alkene with HCOOH to Alkane. DFT-D3 calculations were executed on the optimized molecular structures.



2.22 Gibbs free energy of the Pd(PMe₃)₄-catalyzed hydrogenation of (*E*)-alkene with HCOOH and water to Alkane.

Figure S50. Gibbs free energy of the Pd(PMe₃)₄-catalyzed hydrogenation of (*E*)-alkene with HCOOH and water to Alkane. DFT-D3 calculations were executed on the optimized molecular structures. Selected distances were shown in Å..

2.23 The isomers of intermediates and transition states of the direct *E*-selectivity step in the $Pd(PMe_3)_4$ -catalyzed hydrogenation of (*Z*)-alkene with HCOOH.



Figure S51. The isomers intermediates and transition states of the direct *E*-selectivity step in the $Pd(PMe_3)_4$ -catalyzed hydrogenation of (*Z*)-alkene with HCOOH to (*E*)-alkene. DFT-D3 calculations, at the same level, were also displayed in brackets. The relative Gibbs free energies were given in kcal/mol and the selected distances were shown in Å.

2.24 The isomers of intermediates and transition states of the direct *E*-selectivity step in the $Pd(PMe_3)_4$ -catalyzed hydrogenation of (*Z*)-alkene with HCOOH and water.



Figure S52. The isomers of intermediates and transition states of the direct *E*-selectivity step in the Pd(PMe₃)₄-catalyzed hydrogenation of (*Z*)-alkene with HCOOH and water alkyl-intermediates with *Z* manners with water. DFT-D3 calculations, at the same level, were also displayed in brackets. The relative Gibbs free energies were given in kcal/mol and the selected distances were shown in Å.

2.25 Gibbs energy profile of the Pd(PMe₃)₄-catalyzed hydrogenation of (*Z*)-alkene with HCOOH to (*E*)-alkenes.



Figure S53. Gibbs energy profile of the $Pd(PMe_3)_4$ -catalyzed hydrogenation of (*Z*)-alkene with HCOOH to (*E*)-alkenes. Selected distances were shown in Å.

2.26 Gibbs energy profile of the $Pd(PMe_3)_4$ -catalyzed hydrogenation of (*Z*)-alkene with HCOOH and water to (*E*)-alkenes.



Figure S54. Gibbs energy profile of the isomerization step in the $Pd(PMe_3)_4$ -catalyzed hydrogenation of (*Z*)-alkene with HCOOH and water to (*E*)-alkenes. Selected distances were shown in Å.

3 Experimental Studies on the Reaction Mechanism.

3.1 General information

The Pd(PMe₃)₄-catalyzed hydrogenation reactions of alkynes to alkenes were conducted in a glove box ($O_2 < 0.1$ ppm, $H_2O < 0.1$ ppm). All the reactions were carried out in oven-dried Schlenk tubes under Ar atmosphere. Dry solvents were obtained by purification according to standard methods. Column chromatography was performed using Silica Gel 60 (particle size 40-50 µm), which was purchased from Kanto Chemical Co., Inc. The 1H NMR and ¹³C NMR data were acquired on a Bruker AVANCE III-400 spectrometer (400 MHz for ¹H, and 100 MHz for ¹³C spectroscopy) in deuterated solvents as indicated. Chemical shifts for 1H NMR are referred to internal Me₄Si (0 ppm) and reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. Data for ¹³C NMR were reported in ppm relative to the center line of a triplet at 77.0 ppm for chloroform-d. GC-MS analysis was performed on Shimadzu GCMS-QP2010 Plus Gas Chromatograph/Mass Spectrometer.

3.2 The control experiments[a]

When the substrate **R** (0.2 mmol) and HCOOH (0.4 mmol) were heated in 1,4-dioxane (0.4 mL) at 80°C for 10 h in the presence of 1 mol% $Pd_2(dba)_3$, 8 mol% of PMe₃ and 4 Å molecular sieve (10 mg), (*Z*)-1phenylpropene was obtained with a *Z/E*/alkane ratio of 86/8/5 as confirmed by GC-MS analysis (eq 1 and Fig. S56). When the HCOOH content was S67 increased from 0.4 to 1.2 mmol, the yield of (Z)-1-phenylpropene decreases from 86% to 57% (eq 2). Without using the 4 Å molecular sieve, the (*Z*)-1-phenylpropene was obtained with a *Z*/*E*/alkane ratio of 77/14/9 (eq 3 and Fig. S57). Except for the condition similar to equation 3, the selectivity became low (Z/E/alkane: 55/22/23) (eq 4 and Fig. S58) with the

addition of additional water.



[a] Yields were determined by GC-MS analysis of the crude mixture.

Figure S55. The effect of the amount of (a) formic acid; (b) water in the hydrogenation of 1-phenyl-1-propyne to (Z)-1-phenylpropene by using HCOOH as hydrogen source

3.2.1 Selective hydrogenation of alkyne with HCOOH and characterization of alkenes and alkane.



Figure S56. GC-MS analysis of the crude reaction mixture of **a** (0.2 mmol), Pd₂(dba)₃ (1 mol%), Me₃P (8 mol%), HCOOH (0.4mmol) and 4A MS (10 mg) in 1,4-dioxane (0.4 mL), 80 °C, 10 h, under Ar.

3.2.2 Selective hydrogenation of alkyne with HCOOH and characterization of alkenes and alkane.



S70



Figure S57. GC-MS analysis of the crude reaction mixture of **a** (0.2 mmol), $Pd_2(dba)_3$ (1 mol%), Me₃P (8 mol%) and HCOOH (0.4 mmol) in 1,4-dioxane (0.4 mL), 80 °C, 10 h, under Ar.



3.2.3 Synthesis and characterization of alkenes and alkane with aqueous HCOOH.

Figure S58. GC-MS analysis of the crude reaction mixture of **a** (0.2 mmol), $Pd_2(dba)_3$ (1 mol%), Me₃P (8 mol%) and 25% aq. HCOOH (0.4 mmol) in 1,4-dioxane (0.4 mL), 80 °C, 10 h, under Ar.
More surprisingly, when **R** (0.2 mmol) and AcOH (0.4 mmol) mixed in 1,4-dioxane (0.4 mL) were heated at 80°C for 10 h in the presence of palladium catalyst (Pd₂(dba)₃ and 8 mol% of PMe₃), neither (*Z*)- nor (*E*)- alkenes was produced (Fig. S59).

3.2.4 Selective hydrogenation and characterization of alkyne with AcOH.



Figure S59. GC-MS analysis of the crude reaction mixture of **1** (0.2 mmol), $Pd_2(dba)_3$ (1 mol%), Me₃P (8 mol%) and AcOH (0.4 mmol) in 1,4-dioxane (0.4 mL), 80 °C, 10 h, under Ar.



3.2.5 ¹H and ¹³C NMR spectrum of (Z)-1-phenylpropenes.

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 f1 (ppm)

Figure S60. Z: Colorless oil. ¹**H NMR** (400 MHz, CDCl₃) δ 7.43-7.34 (m, 4H), 7.32-7.25 (m, 1H), 6.50 (d, *J* = 11.6 Hz, 1H), 5.90-5.82 (m, 1H), 1.98-1.95 (m, 3H). ¹³**C NMR** (100 MHz, CDCl₃) δ 137.6, 129.9, 128.9, 128.1, 126.8, 126.4, 14.7.



3.2.6 1 H and 13 C NMR spectrum of *E*-alkene.

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 f1 (ppm)

Figure S61. *E*: Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.38-7.29 (m, 4H), 7.25-7.16 (m, 1H), 6.43 (dd, *J* = 15.8, 1.7 Hz, 1H), 6.27 (dq, *J* = 15.8, 6.5 Hz, 1H), 1.1 (dd, *J* = 6.5, 1.6 Hz, 3H).
¹³C NMR (100 MHz, CDCl₃) δ 137.9, 131.1, 128.5, 126.8, 125.8, 125.7, 18.5.

Me	Pd ₂ (dba) ₂ 1mol%, PMe ₃ 8mol% HCOOH 1.2 mmol, 4Å MS dioxane 0.4mL, 80 °C, <i>T</i> .	- CH ₃ +	CH ₃	+	Me
0.2mmol	10min	1 30.7%	2 2.6%	3 0.5%	4 66.2%
	20min	1 33.7%	2 2.9%	3 0.5%	4 62.9%
	40min	2 35.2%	2 3.2%	3 0.5%	4 61.1%
	60min	2 37.5%	2 3.4%	3 0.5%	4 58.6%
	90min	2 40.9%	2 3.8%	3 0.6%	4 54.8%
	120min	1 44.8%	2 4.3%	3 0.6%	4 50.3%
	150min	1 50.9%	2 4.8%	3 0.6%	4 43.6%
	180min	1 56.5%	2 5.5%	3 0.6%	4 37.4%
	210min	1 62.7%	2 6.5%	3 0.6%	4 30.2%
	240min	1 68.7%	2 8.0%	3 0.7%	4 22.6%
	270min	1 77.1%	2 9.5%	3 1.0%	4 12.4%
	300min	1 86.1%	2 9.6%	3 1.1%	4 3.15%
	330min	1 81.8%	2 15.7%	3 2.5%	4 0.0%
	360min	1 75.7%	2 19.7%	3 4.6%	4 0.0%
	600min	1 57.4%	2 30.5%	3 12.1%	4 0.0%
	960min	1 53.9%	2 31.8%	3 14.3%	4 0.0%

3.2.7 Selective hydrogenation of alkyne at different times.

Figure S62. Experiments for the hydrogenation of **R** to (Z)-1-phenylpropenes by using the molecular sieves (MS) at different times.



3.2.8 Experiments for the isomerization of (*Z*)-1-phenylpropenes to (*E*)-1-phenylpropenes.

[a] Yields were determined by GC-MS analysis of the crude mixture.

Figure S63. Experiments for the isomerization of (*Z*)-1-phenylpropenes to (*E*)-1-phenylpropenes with different content of water or without water (with 4 Å MS).

Z	Pd-(dba)- 1mol% PMe- 8mc	Z	E	Alkane
CH ₃	HCOOH 1.2 mmol dioxane 0.4mL, 80 °C, <i>T</i> .	≁ CH ₃ +	+ CH3	*
	5min	1 78%	2 21%	3 1%
	10min	1 68%	2 30%	3 2%
	20min	2 47%	2 49%	3 4%
	30min	2 33%	2 60%	3 7%
	40min	2 21%	2 71%	3 8%
	50min	1 17%	2 72%	3 11%
	60min	1 14%	2 74%	3 12%
	2h	1 7%	2 80%	3 13%
	4h	1 4%	2 78%	3 18%
	12h	1 5%	2 68%	3 27%
	16h	1 5%	2 66%	3 29%

3.2.9 Conversions of (*Z*)-1-phenylpropenes to (*E*)-1-phenylpropenes without water at different times.

Figure S64. Experiments for the isomerization of (Z)-1-phenylpropenes to (E)-1-phenylpropenes without water at different times.



3.2.10 Characterization of alkenes and alkane by GC-MS analysis with 4Å MS.

Figure S65. GC-MS analysis of the crude reaction mixture of **1** (0.2 mmol), Pd₂(dba)₃ (1 mol%), Me₃P (8 mol%), HCOOH (1.2 mmol), 4 Å-MS (10 mg) in 1,4-dioxane (0.4 mL), 80 °C, 12 h, under Ar.



3.2.11 Characterization of alkenes and alkane by GC-MS analysis without water.

Figure S66. GC-MS analysis of the crude reaction mixture of **1** (0.2 mmol), Pd₂(dba)₃ (1 mol%), Me₃P (8 mol%) and HCOOH (1.2 mmol) in 1,4-dioxane (0.4 mL), 80 °C, 12 h, under Ar.





Figure S67. GC-MS analysis of the crude reaction mixture of 1 (0.2 mmol), $Pd_2(dba)_3$ (1 mol%), Me₃P (8 mol%), HCOOH (1.2 mmol) and H₂O (5%) in 1,4-dioxane (0.4 mL), 80 °C, 12 h, under Ar.



Figure S68. GC-MS analysis of the crude reaction mixture of **1** (0.2 mmol), $Pd_2(dba)_3$ (1 mol%), Me₃P (8 mol%), HCOOH (1.2 mmol) and H₂O (10%) in 1,4-dioxane (0.4 mL), 80 °C, 12 h, under Ar.



Figure S69. GC-MS analysis of the crude reaction mixture of **1** (0.2 mmol), $Pd_2(dba)_3$ (1 mol%), Me₃P (8 mol%), HCOOH (1.2 mmol) and H₂O (30%) in 1,4-dioxane (0.4 mL), 80 °C, 12 h, under Ar.



Figure S70. GC-MS analysis of the crude reaction mixture of **1** (0.2 mmol), $Pd_2(dba)_3$ (1 mol%), Me_3P (8 mol%), HCOOH (1.2 mmol) and H_2O (32 µL, 50%) in 1,4-dioxane (0.4 mL), 80 °C, 12 h, under Ar.



Figure S71. GC-MS analysis of the crude reaction mixture of 1-phenyl-1-propyne (R, 0.2 mmol) using the molecular sieves (MS) with an available pore size of 4Å in the presence of $Pd_2(dba)_3$ (1.0 mol%), PMe₃ (8.0 mol%) and DCOOD (1.2 mmol) in 1,4-dioxane (0.4 mL), 80 °C, under Ar.

When the substrate R (0.2 mmol) and HCOOH (1.2 mmol) were heated in 1,4-dioxane (0.4 mL) at 80°C for 10 h in the presence of 1 mol% $Pd_2(dba)_3$, 8 mol% of PMe₃ and 4 Å molecular sieve (10 mg), the (Z)-1phenylpropene was obtained with a Z/E/alkane ratio of 57/31/12 as confirmed by GC-MS analysis (Fig. S72).

3.2.13 Selective hydrogenation and characterization of alkyne with HCOOH.



Figure S72. GC-MS analysis of the crude reaction mixture of **a** (0.2 mmol), Pd₂(dba)₃ (1 mol%), Me₃P (8 mol%) and HCOOH (1.2 mmol) in 1,4-dioxane (0.4 mL), 80 °C, 10 h, under Ar.

4 Supplementary References

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