*Supporting Information*

# A Reaction Mechanism for Gold-Catalyzed Hydroamination/Cyclization of o-Phenylendiamine and Propargylic Alcohols. A DFT Study

Yueyue Wang, Baoping Ling, Peng Liu*, Siwei Bi*

School of Chemistry and Chemical Engineering, Qufu Normal University, Qufu 273165, People's Republic of China

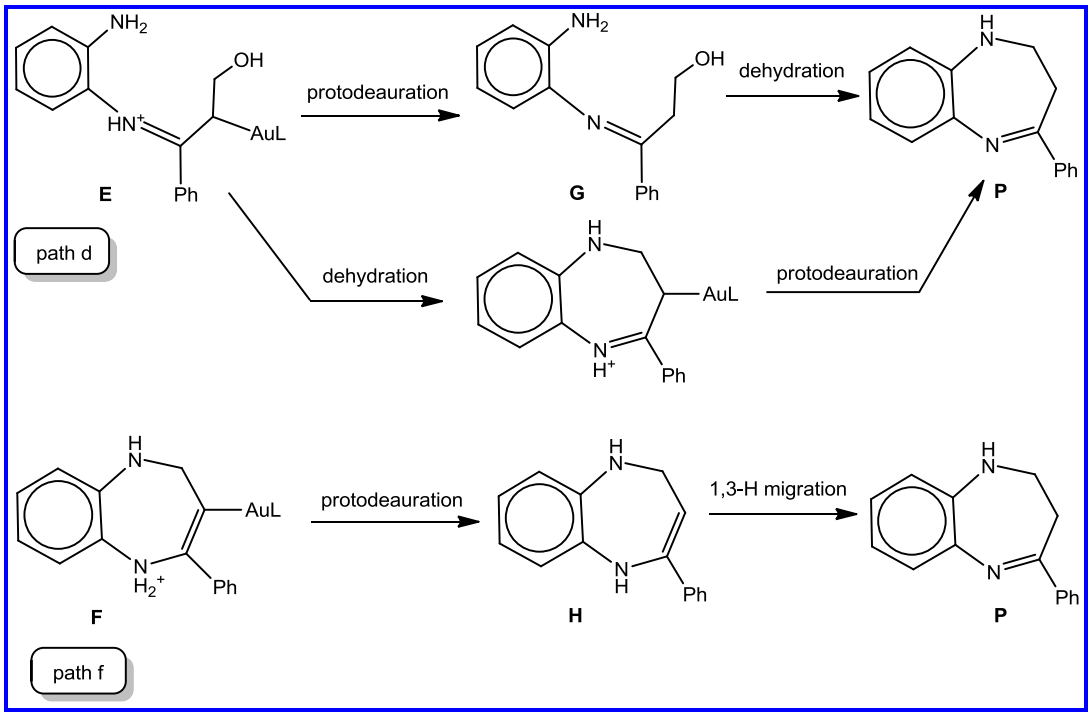
# Table of Contents

Brief Pathways for E and F Accessing into the Product P ..... S3

A Scan of R(C···N) *vs* ΔE ..... S4

Calculated energies of all intermediates and transition states in DCM ..... S5

**Scheme 1S. Brief Pathways for E and F Accessing into the Product P**



**Scheme 2S. A Scan of R(C···N) *vs* ΔE. The Energies in Parentheses are given in kcal/mol**

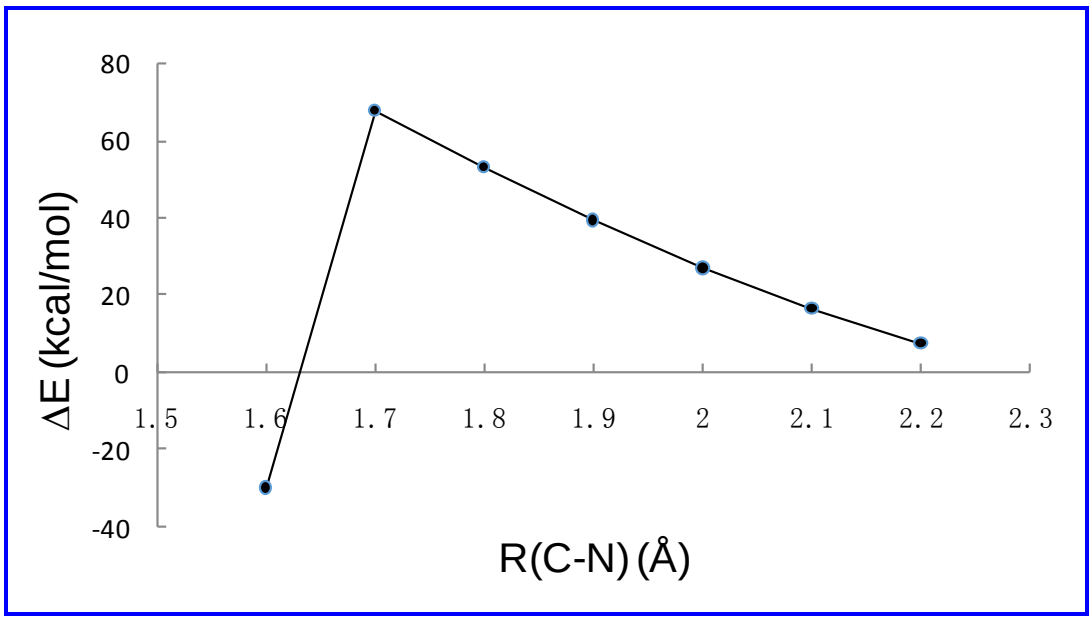


**Table 1S. Calculated thermodynamic corrections, solution-phase single-point energies in DCM and solution-phase Gibbs free energies in DCM of all the intermediates and transition states for o-Phenylendiamine with Propargylic Alcohols (in Hartree).**

| | Gas-Phase Gibbs Free Energies Corrections | Solution-Phase Single-Point Energy | Solution-Phase Gibbs free energies | | Gas-Phase Gibbs Free Energies Corrections | Solution-Phase Single Point Energy | Solution-Phase Gibbs free energies |
|---|---|---|---|---|---|---|---|
| **S1** | 0.105433 | -422.7424282 | -422.6369952 | **TS6-7** | 0.626425 | -2020.575856 | -2019.949431 |
| **Au-S1** | 0.494441 | -1677.73292 | -1677.238479 | **7** | 0.628808 | -2020.594694 | -2019.965886 |
| **S2** | 0.103339 | -342.8170493 | -342.7137103 | **8** | 0.757134 | -2443.352152 | -2442.595018 |
| **1** | 0.626487 | -2020.575288 | -2019.948801 | **TS8-9** | 0.752787 | -2443.3196 | -2442.566813 |
| **TS1-E** | 0.621037 | -2020.480563 | -2019.859526 | **9** | 0.758233 | -2443.367105 | -2442.608872 |
| **E** | 0.622775 | -2020.607299 | -2019.984524 | **10** | 0.757747 | -2443.372174 | -2442.614427 |
| **G** | 0.756319 | -2443.330405 | -2442.574086 | **TS8-9'** | 0.624817 | -2020.538023 | -2019.913206 |
| **TSG-H** | 0.754389 | -2443.242431 | -2442.488042 | **TS8-9''** | 0.648742 | -2096.998681 | -2096.349939 |
| **H** | 0.759699 | -2443.368034 | -2442.608335 | **P** | 0.214379 | -689.1878624 | -688.9734834 |
| **I** | 0.757782 | -2443.332431 | -2442.574649 | $H_2O$ | 0.004047 | -76.42609454 | -76.42204754 |
| **J** | 0.610398 | -2020.120601 | -2019.510203 | $ROH_2^+$ | 0.111859 | -423.1278731 | -423.0160141 |
| **L** | 0.757026 | -2443.336353 | -2442.579327 | **TS2-11** | 0.622941 | -2020.560978 | -2019.938037 |
| **TSL-M** | 0.757379 | -2443.277179 | -2442.5198 | **11** | 0.628713 | -2020.582634 | -2019.953921 |
| **M** | 0.757469 | -2443.320063 | -2442.562594 | **12** | 0.628447 | -2020.593869 | -2019.965422 |
| **TS1-2** | 0.62575 | -2020.533915 | -2019.908165 | **TS12-13** | 0.622306 | -2020.561593 | -2019.939287 |
| **2** | 0.62085 | -2020.583271 | -2019.962421 | **13** | 0.628238 | -2020.622027 | -2019.993789 |
| **TS2-3** | 0.622413 | -2020.561756 | -2019.939343 | **14** | 0.627531 | -2020.613207 | -2019.985676 |
| **3** | 0.618161 | -2020.567942 | -2019.949781 | **TS14-15** | 0.626648 | -2020.603306 | -2019.976658 |
| **TS3-4** | 0.615696 | -2020.550016 | -2019.93432 | **15** | 0.625598 | -2020.60441 | -2019.978812 |
| **4** | 0.626237 | -2020.587018 | -2019.960781 | **TS15-16** | 0.619676 | -2020.582187 | -2019.962511 |
| **TS4-5** | 0.618943 | -2020.57107 | -2019.952127 | **16** | 0.624832 | -2020.601002 | -2019.97617 |
| **5** | 0.618346 | -2020.572365 | -2019.954019 | **17** | 0.624005 | -2020.611526 | -2019.987521 |
| **6** | 0.622376 | -2020.584718 | -2019.962342 | **18** | 0.626705 | -2020.618481 | -2019.991776 |
| **6'** | 0.622652 | -2020.594641 | -2019.971989 | | | | |