

Supporting Information

Quantitative Kinetic Investigation of Triazole-Gold(I) Complex (TA-Au) Catalyzed [3,3]-Rearrangement of Propargyl Ester

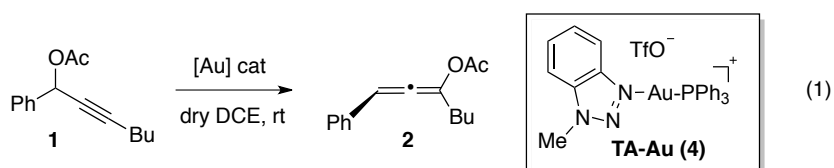
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I. General Methods and Materials

All of the reactions dealing with air and/or moisture-sensitive reactions were carried out under an atmosphere of nitrogen using oven/flame-dried glassware. Unless otherwise noted, all commercial reagents and solvents were obtained from the commercial provider and used without further purification. ^1H NMR, ^{13}C NMR, and ^{31}P NMR, spectra were recorded on Agilent 400 MHz spectrometer. Chemical shifts were reported relative to internal tetramethylsilane (δ 0.00 ppm) or CDCl_3 (δ 7.26 ppm) for ^1H and CDCl_3 (δ 77.0 ppm) for ^{13}C . For the reaction monitoring, the reaction spectra were recorded using a ReactIR 15 from Mettler-Toledo AutoChem.

General procedure for the monitoring of [3,3]-rearrangement of propargyl ester¹



The reaction was carried out as follows: a three-necked reaction vessel was fitted with a magnetic stirring bar. The IR probe was inserted through an adapter into the middle neck; the other two necks were capped by septa. The reaction vessel was charged with substrate **1** (29 mg, 0.125 mmol) in dry DCE (1.2 mL) followed by immediate initiation of data collection. TA-Au (**4**) was then added and *in situ* IR spectra ($2800\text{-}650\text{cm}^{-1}$) were recorded over the course of the reaction. The collected spectra were analyzed by iC IR 4.3 software and Origin 8.0. Peaks 1211 cm^{-1} and 1757 cm^{-1} were used to calculate the concentration.

The substrate was synthesized according to Nolan's and our previous communications.²

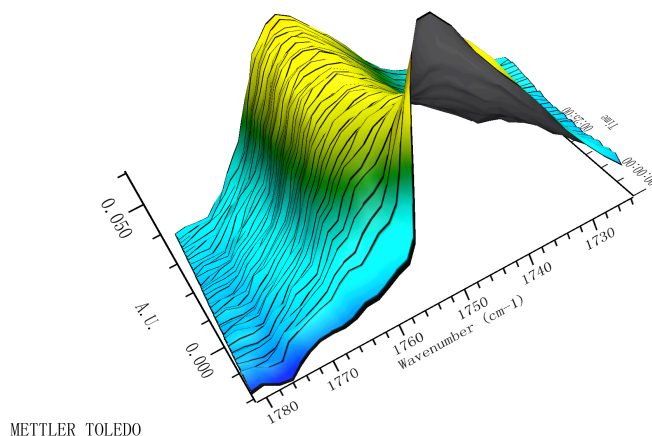


Figure S1. Kinetic profile of [3,3]-rearrangement of propargyl ester catalyzed by TA-Au (**4**).

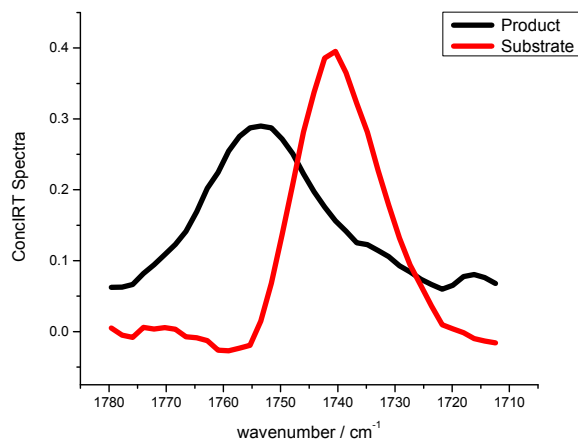


Figure S2. ConcIRT spectra of **1** (red) and **2** (black).

II. Kinetic Profiles

1. Determination of kinetic order of [4]

The reactions were monitored according to general procedure. Reaction conditions are: **1** (0.10 M in DCE, 1.2 mL), **4** (0.002, 0.004, 0.006, 0.008 M in DCE), 30°C.

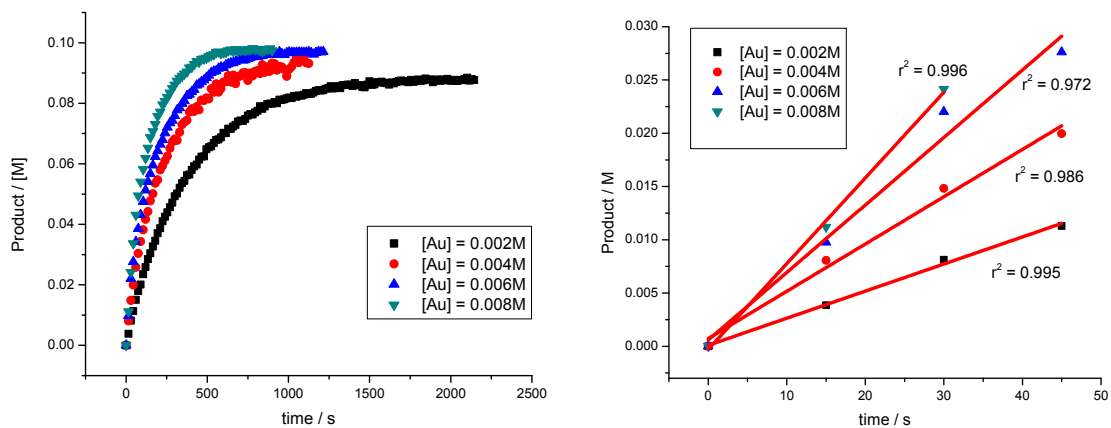


Figure S3. Determination of kinetic order of [4].

2. Determination of kinetic order of [1]

The reactions were monitored according to general procedure. Reaction conditions are: **1** (0.10, 0.14, 0.17, 0.20 M in DCE, 1.2 mL), **4** (0.003 M in DCE), 30°C.

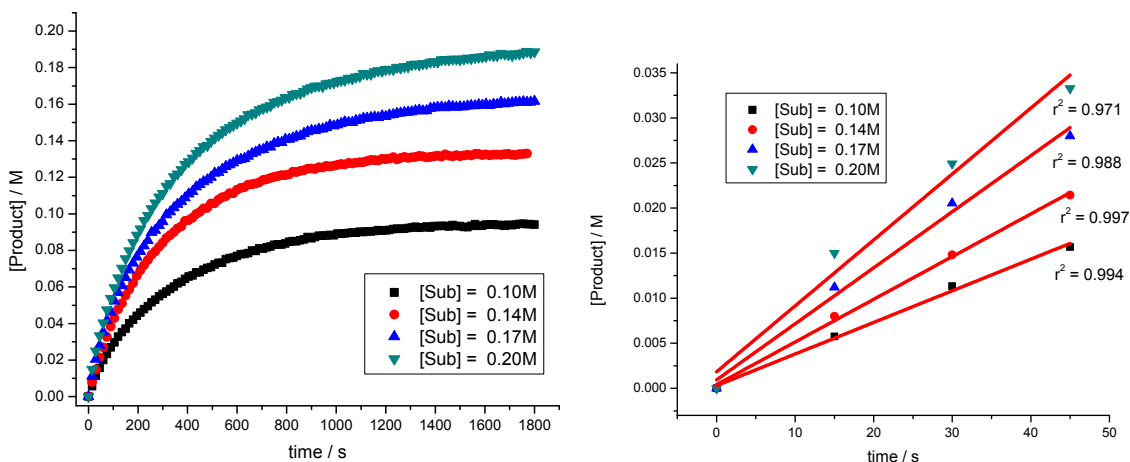


Figure S4. Determination of kinetic order of [1].

3. Variable temperature experiment

The reactions were monitored according to general procedure. Reaction conditions are: **1** (0.10 M in DCE, 1.2 mL), **4** (0.003 M in DCE), at 22, 32, 38, and 46°C.

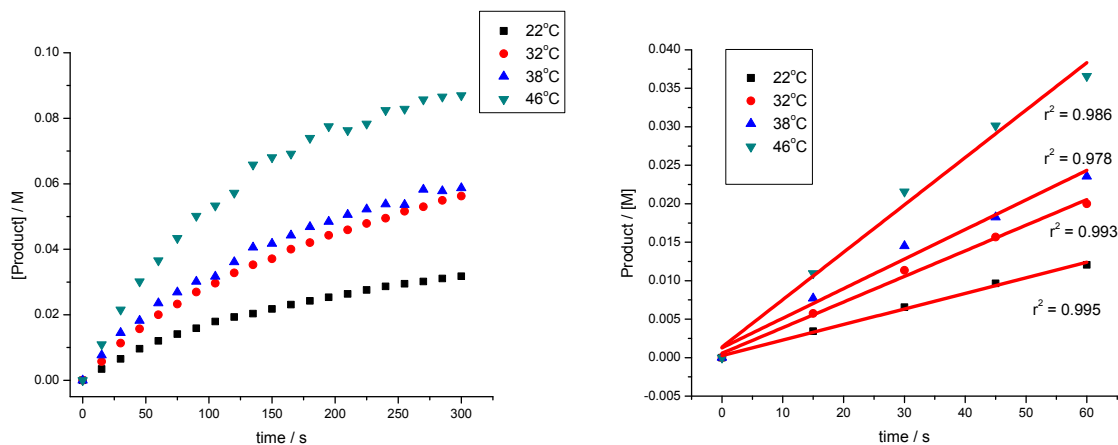


Figure S5. Kinetics profile at different temperatures.

4. Hammett plot with various modified TA-Au catalysts

The reactions were monitored according to general procedure. Reaction conditions are: **1** (0.10 M in DCE, 1.2 mL), TA-Au (0.003 M in DCE), 26°C.

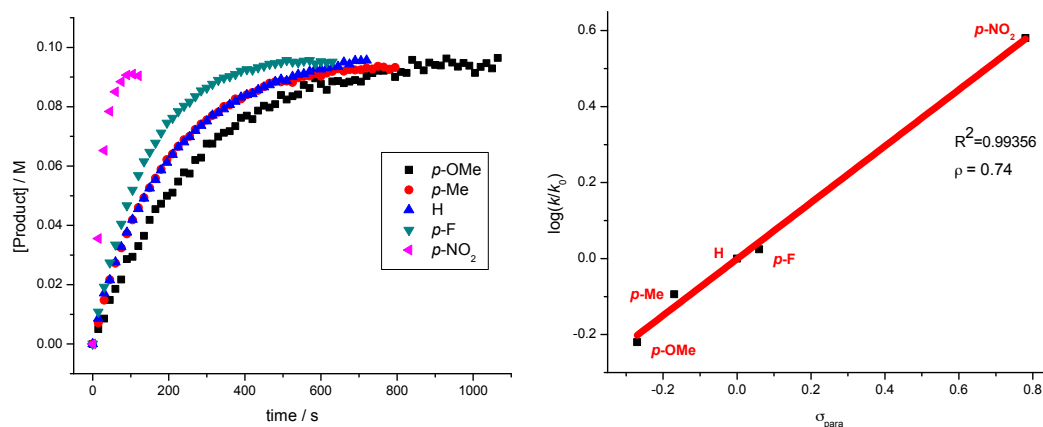


Figure S6. Kinetics profile using various TA-Au catalysts.

III. ³¹P NMR Experiments

Variable temperature experiment with catalyst 4

A NMR tube containing catalyst 4 (0.025 M) in CD₂Cl₂ (0.7 mL) was inserted in NMR machine. ³¹P NMR spectrum was recorded at 25°C, 0°C, and -40°C.

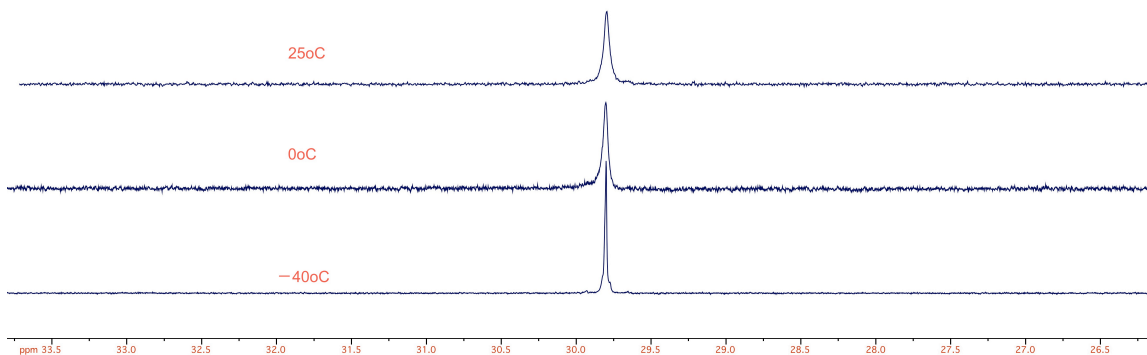


Figure S7. Variable temperature experiment with catalyst 4

³¹P NMR monitoring of the reaction progress

A NMR tube was charged with catalyst 4 (2 mol %, 0.002 M) and 1 (1 equiv.) in CD₂Cl₂ (0.6 mL). The tube was shaken periodically and NMR spectrum was taken at 0 min, 5 min, 15 min, and 60 min.

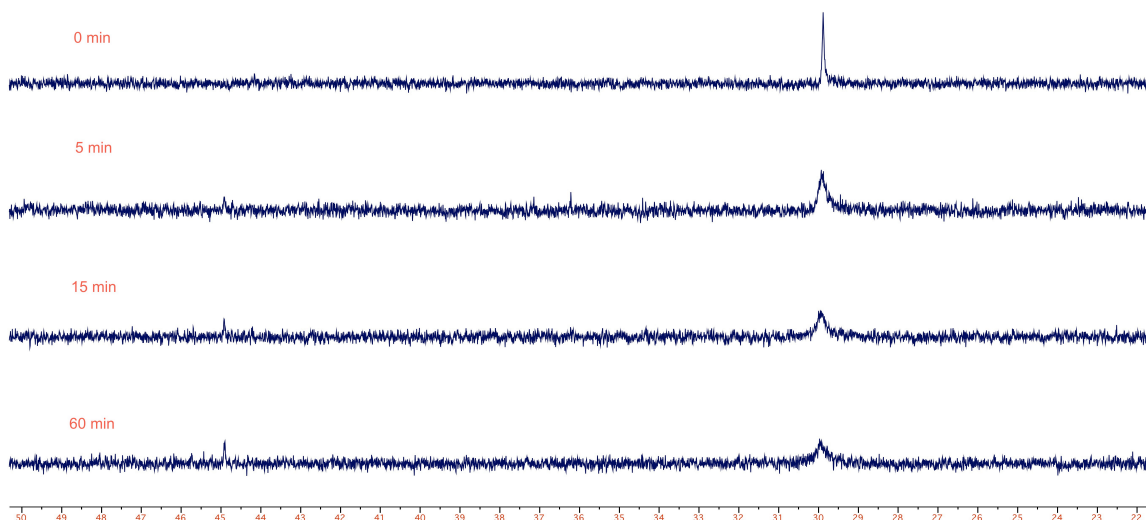
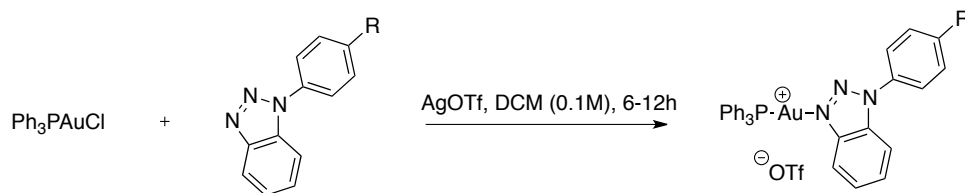


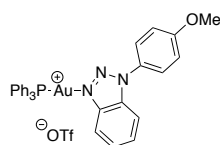
Figure S8. ^{31}P NMR monitoring of the reaction progress.

IV. Catalyst Characterization

General procedure for TA-Au synthesis³



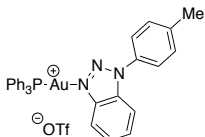
A 20 mL screw-cap vial was charged with Ph_3PAuCl (1 equiv.) and benzotriazole derivative (1 equiv.) in dry DCM (0.1 M), followed by the addition of AgOTf (1 equiv.). The vial was allowed to stir at ambient temperature for 6-12h, and concentrated *in vacuo* to give the product in >90% yield. Pure gold catalyst was obtained through diffusion of hexanes into DCM solution.



^1H -NMR (400 MHz, CDCl_3) δ 8.25-8.22 (m, 1H), 7.95-7.93 (m, 1H), 7.84-7.80 (m, 2H), 7.76-7.74 (m, 2H), 7.68-7.51 (m, 15H), 7.22-7.20 (m, 2H), 3.93 (s, 3H).

^{13}C -NMR (100 MHz, CDCl_3) δ 161.3, 143.4, 134.1, 133.9, 132.9, 129.8, 129.7, 129.0, 126.7, 126.1, 126.1, 125.2, 117.1, 115.5, 112.2, 55.8.

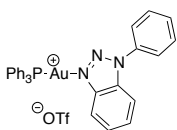
^{31}P -NMR (162 MHz, CDCl_3) δ 31.9.



$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 8.28-8.26 (m, 1H), 7.98-7.95 (m, 1H), 7.87-7.81 (m, 2H), 7.73-7.71 (m, 2H), 7.68-7.58 (m, 15H), 7.53-7.51 (m, 2H), 2.51 (s, 3H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 143.5, 141.6, 134.1, 134.0, 132.9, 131.1, 131.0, 129.9, 129.7, 129.2, 126.8, 126.1, 123.5, 119.2, 112.2, 21.3.

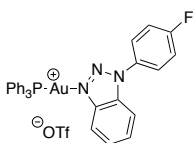
$^{31}\text{P-NMR}$ (162 MHz, CDCl_3) δ 30.7.



$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 8.30-8.28 (m, 1H), 7.98-7.95 (m, 1H), 7.86-7.80 (m, 4H), 7.75-7.71 (m, 2H), 7.69-7.58 (m, 15H), 7.54-7.49 (m, 1H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 135.1, 134.2, 134.1, 132.9, 131.1, 130.9, 130.5, 129.9, 129.8, 128.9, 126.8, 126.2, 123.7, 117.8, 112.0.

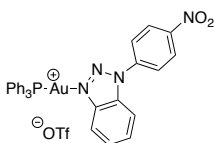
$^{31}\text{P-NMR}$ (162 MHz, CDCl_3) δ 30.4.



$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 8.26-8.22 (m, 1H), 7.98-7.95 (m, 1H), 7.92-7.87 (m, 2H), 7.83-7.79 (m, 2H), 7.66-7.57 (m, 15H), 7.44-7.38 (m, 2H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 143.8, 134.2, 134.1, 132.9, 131.2, 129.9, 129.9, 129.8, 128.9, 126.9, 126.2, 126.1, 126.0, 117.8, 112.1.

$^{31}\text{P-NMR}$ (162 MHz, CDCl_3) δ 30.3.



$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 8.53 (d, $J = 8.8$ Hz, 2H), 8.25 (d, $J = 8.4$ Hz, 3H), 8.18 (d, $J = 8.0$ Hz, 1H), 7.90-7.81 (m, 2H), 7.66-7.53 (m, 15H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 148.3, 143.7, 139.7, 134.1, 134.0, 132.8, 132.0, 129.8, 129.7, 126.8, 126.1, 125.8, 124.6, 117.3, 112.5.

$^{31}\text{P-NMR}$ (162 MHz, CDCl_3) δ 30.2.

V. DFT Calculation

To examine the structural and energy aspects of this reaction, density function theory (DFT) theoretical calculations were carried out with the Gaussian 03 program. In brief, the geometrical optimizations and single point energy calculations were performed using Becke's three-parameter exchange functional and the nonlocal correlation functional of Lee, Yang and Parr (B3LYP) with the 6-311G basis set.

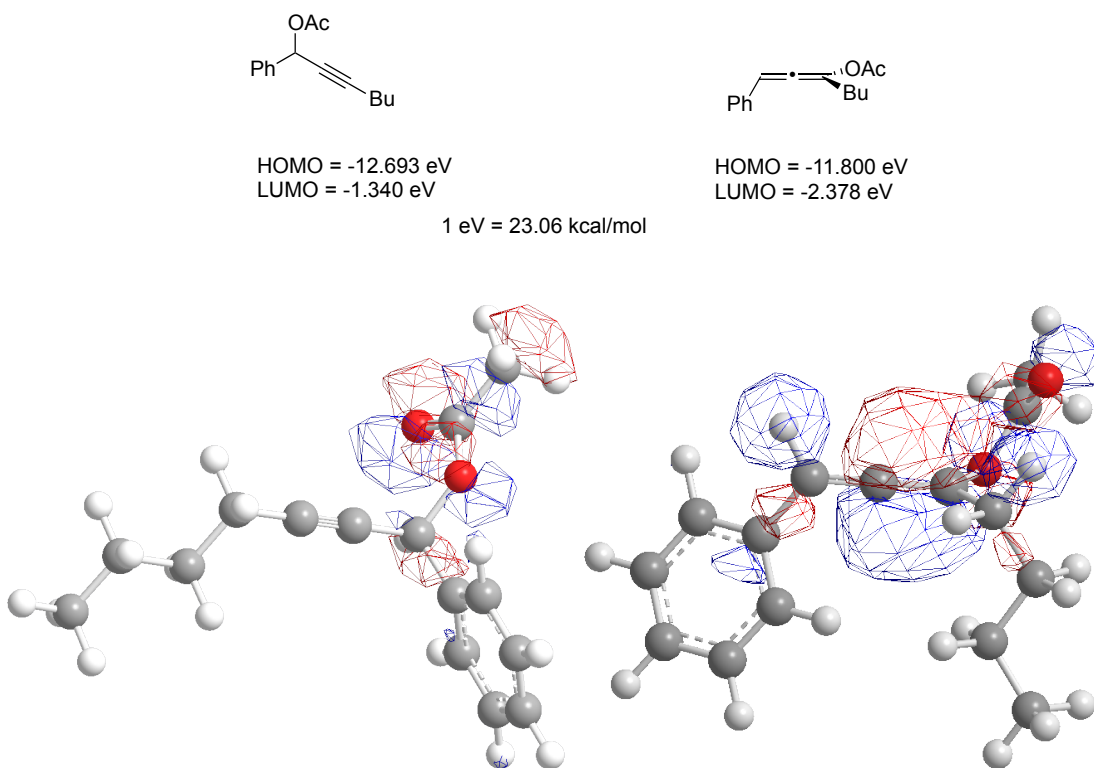
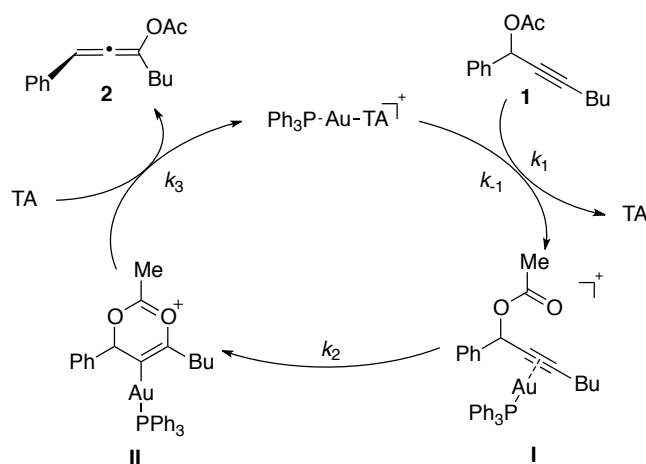


Figure S9. DFT calculation result.

VI. Derivation of Rate Law



Overall rate equation:

$$r = k_3[\text{II}][\text{TA}]$$

Since the resting-state is Ph_3PAuTA , we can use steady-state approximation for I and II.

Steady-state for [I]:

$$k_1[\text{Ph}_3\text{PAuTA}][\text{I}] = k_{-1}[\text{I}][\text{TA}] + k_2[\text{I}]$$

Steady-state for [II]:

$$k_3[\text{II}][\text{TA}] = k_2[\text{I}]$$

Overall rate equation:

$$r = k_3[\text{II}][\text{TA}] = \frac{k_1 k_2}{k_{-1}[\text{TA}] + k_2} [\text{Ph}_3\text{PAuTA}][\text{I}]$$

VII. Reference

1. C. He, J. Ke, H. Xu and A. Lei, *Angew. Chem. Int. Ed.*, 2013, **52**, 1527
2. D. Wang, L. N. S. Gautam, C. Bollinger, A. Harris, M. Li and X. Shi, *Org. Lett.*, 2011, **13**, 2618; N. Marion, S. Díez-Gonzalez, P. Fremont, A. R. Noble and S. P. Nolan, *Angew. Chem. Int. Ed.*, 2006, **45**, 3647.
3. K. Wang, M. Chen, Q. Wang, X. Shi and J. K. Lee, *J. Org. Chem.*, 2013, **78**, 7249.