

## Supporting information

# Potassium Tris(triflyl)methide (KCTf<sub>3</sub>): A Broadly Applicable Promoter for Cationic Metal Catalysis

Junbin Han,<sup>a</sup> Zhichao Lu,<sup>a</sup> Weibo Wang,<sup>a</sup> Gerald B. Hammond,<sup>a,\*</sup>  
Bo Xu<sup>b,\*</sup>

<sup>a</sup> Department of Chemistry, University of Louisville, Louisville, Kentucky 40292, United States; <sup>b</sup> College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, 2999 North Renmin Lu, Shanghai 201620, China

### Section 1. General

<sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectra were recorded at 400, 100 and 162 MHz respectively, using CDCl<sub>3</sub> as a solvent. The chemical shifts are reported in δ (ppm) values relative to CHCl<sub>3</sub> (δ 7.26 ppm for <sup>1</sup>H NMR and δ 77.0 ppm for <sup>13</sup>C NMR) and CFC<sub>3</sub> (δ 0 ppm for <sup>19</sup>F NMR), multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), h (hextet), m (multiplet) and br (broad). Coupling constants, *J*, are reported in Hertz. All air and/or moisture sensitive reactions were carried out under argon atmosphere. Solvents (tetrahydrofuran, ether, dichloromethane and DMF) were chemically dried using a commercial solvent purification system. All other reagents and solvents were employed without further purification. The products were purified using a CombiFlash system or a regular glass column. TLC was developed on Merck silica gel 60 F254 aluminum sheets. KCTf<sub>3</sub> was purchased from Synquest Labs or can be prepared using a literature report.<sup>[1]</sup> All other chemicals like metal catalysts and ligands were purchased from Aldrich, Alfa Aesar or Strem. *All the products formed in these reactions have been reported in the literature (references are found in the manuscript), hence we only use NMR or MS to confirm their identity by comparison with the published spectra.*

### Section 2. General procedure for kinetic measurements

#### 2.1 Monitoring of reactions using *in situ* NMR spectroscopy

When <sup>1</sup>H NMR was used to monitor the progress of a reaction, a solution of tetramethylsilane in CDCl<sub>3</sub> (sealed in a capillary tube) was used as external standard for NMR integration. In some cases, 1,3,5-tri-*tert*-butylbenzene

(internal standard) was used. The reactions were monitored with  $^1\text{H}$  NMR (single pulse or 1 scan for fast reactions, 8 scans for slow reactions). Some NMR measurements were conducted using NMR experiment array (a series of spectra measured at predetermined time intervals over a period of time by adjusting the pre-acquisition delay). NMR experiment array gives better precision for both concentration (*via* integrations) and reaction time, because each measurement is conducted at almost identical shimming and temperature conditions. The concentrations of substrate and product were determined by relative integration to the *t*-butyl peak in the standard (tetramethylsilane or 1,3,5-tri-*tert*-butylbenzene).

## **2.2 Monitoring of reactions using GC-MS.**

The model reaction was conducted in the presence of internal standard (hexadecane or acetophenone). For analysis, 1-5  $\mu\text{L}$  of sample was taken from the reaction mixture and was diluted with a suitable solvent (e.g. hexane or ethyl acetate). The diluted solution was injected into a GC-MS using an autosampler. Each GC reading is the average of three runs. Typically three reactions under the same conditions were conducted in parallel.

## **Section 3. Synthesis of starting materials**

**Synthesis of gold complexes (L-AuCl).** All gold complexes (L-AuCl) were synthesized using a slightly modified version of a literature method.<sup>[2]</sup> These complexes were prepared via the following general procedure:

Sodium tetrachloroaurate(III) dihydrate (1 mmol) was dissolved in water, and the orange solution was cooled in ice. To this solution, 2,2'-thiodiethanol (3 mmol) was slowly added (ca. 45 min) with stirring. A solution of the phosphine ligand (1 mmol) in EtOH (if the ligand could not be dissolved, more EtOH was used) was added dropwise to yield a white solid. The solid was filtered off, washed with water followed by EtOH, and ultimately dried in vacuum.

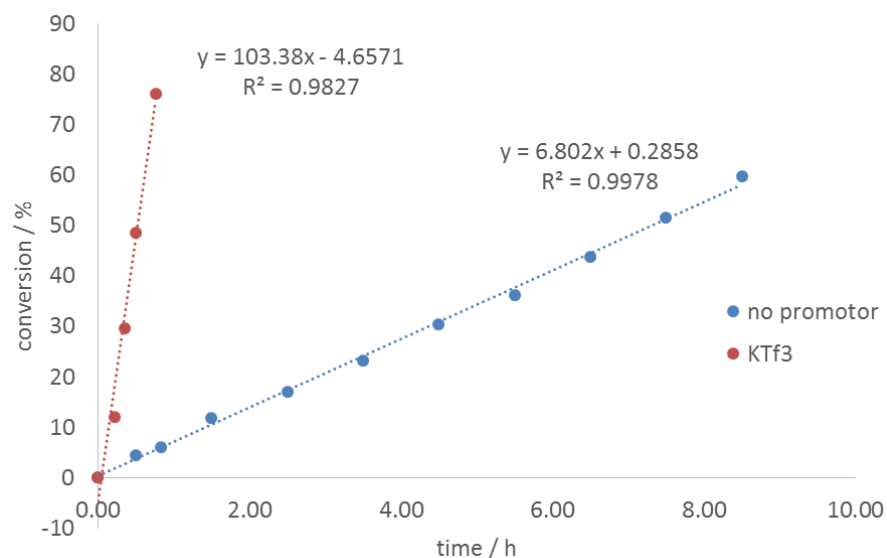
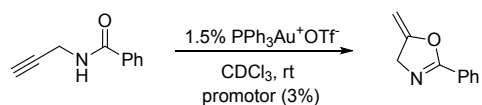
**Preparation of cationic gold (L-Au<sup>+</sup>OTf) stock solution.** Standard stock solutions of cationic gold catalyst were made by weighing the L-Au(I)Cl complex into a vial and adding corresponding deuterated solvent, then 1.2 equiv of AgOTf was added, the vial was sonicated for 3-5 min at 5-10 °C, then the vial was centrifuged and the clear solution was transferred to a clean glass vial with a screw cap. The solution was kept in freezer (-20°C) until it was used.

## **Section 6. Effects of promoter in various ionic reactions.**

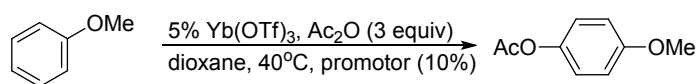
All the following reactions were monitored using the general procedure for kinetic measurement.

## Gold catalyzed cyclization of propargyl amide

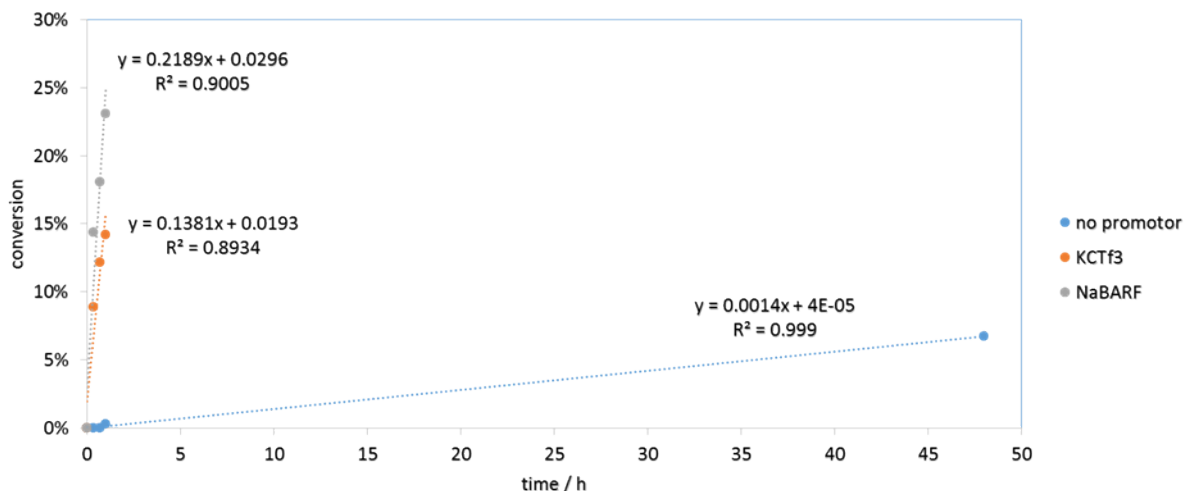
Following the general procedure for kinetic experiments using *in situ* NMR spectroscopy, 0.15 mL of a standard cationic gold solution in CDCl<sub>3</sub> (0.01 M) and 0.35 mL CDCl<sub>3</sub> were introduced into a NMR tube, and then propargyl amide (16 mg, 0.1 mmol) and the internal standard were introduced in its solid state. The reaction was kept at room temperature and was monitored by single pulse <sup>1</sup>H NMR. <sup>1</sup>H NMR of product:



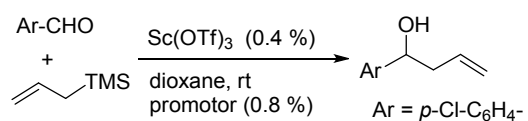
## Friedel-Crafts acylation



A standard solution of starting material was prepared by dissolving anisole (1.4 mmol), Yb(OTf)<sub>3</sub> (5 mol%) and n-hexadecane (internal standard) in 3.5 mL dioxane. Different promoters (10 mmol%) and acetic anhydride (0.6 mmol) were added into the corresponding reactors containing 0.5 mL standard solution. All reactions were stirred and carried out at 40°C. The progress of reaction was monitored by GC/MS.

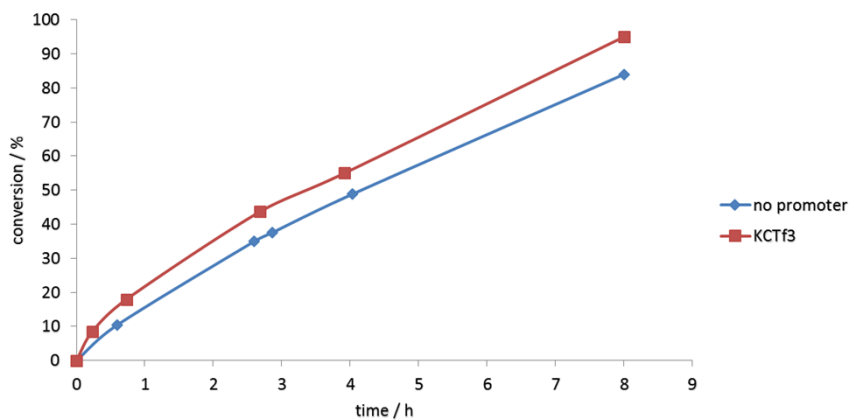
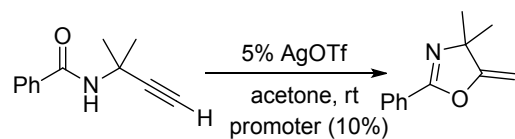


### Hosomi-Sakurai reaction

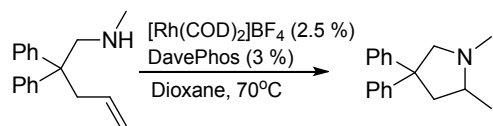


A standard solution of starting material was prepared by dissolving 4-chlorobenzaldehyde (0.4 mmol), allyltrimethylsilane (0.8 mmol) and n-hexadecane (internal standard) in dioxane. Different promoters and Sc(OTf)<sub>3</sub> (0.4 mol%) were added to the corresponding reactors containing 1 mL standard solution. All reactions were conducted at room temperature. The progress of reaction was monitored by GC/MS.

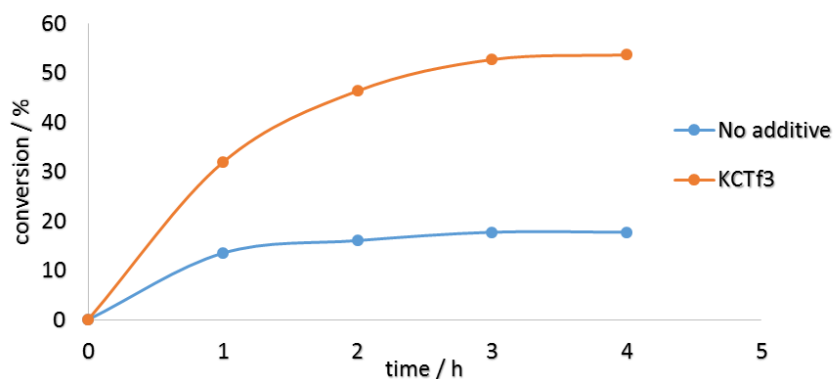
### Silver catalyzed cyclization of propargyl amide



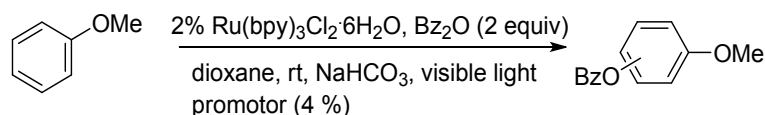
## Rhodium catalyzed hydroamination of alkene



A standard solution of starting material was prepared by dissolving aminoalkene (0.5 mmol) and n-hexadecane (internal standard for GC) in dioxane (2.5 mL).  $[\text{Rh}(\text{COD})_2]\text{BF}_4$  (2.5 mol%), DavePhos (3 mol%) and different promoters were added into the corresponding reactors containing 0.5 mL standard solution. All reactions were stirred and heated to 70°C.

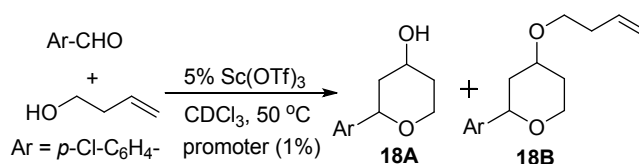


## Visible-Light photocatalysis



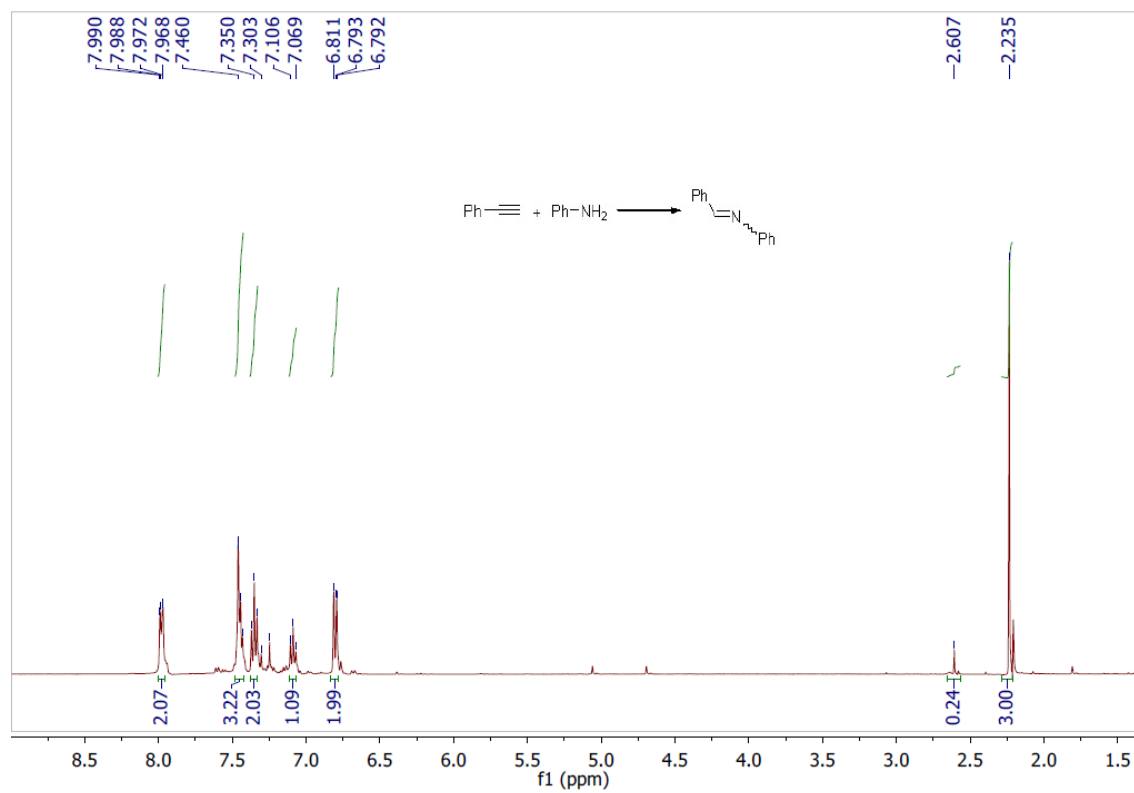
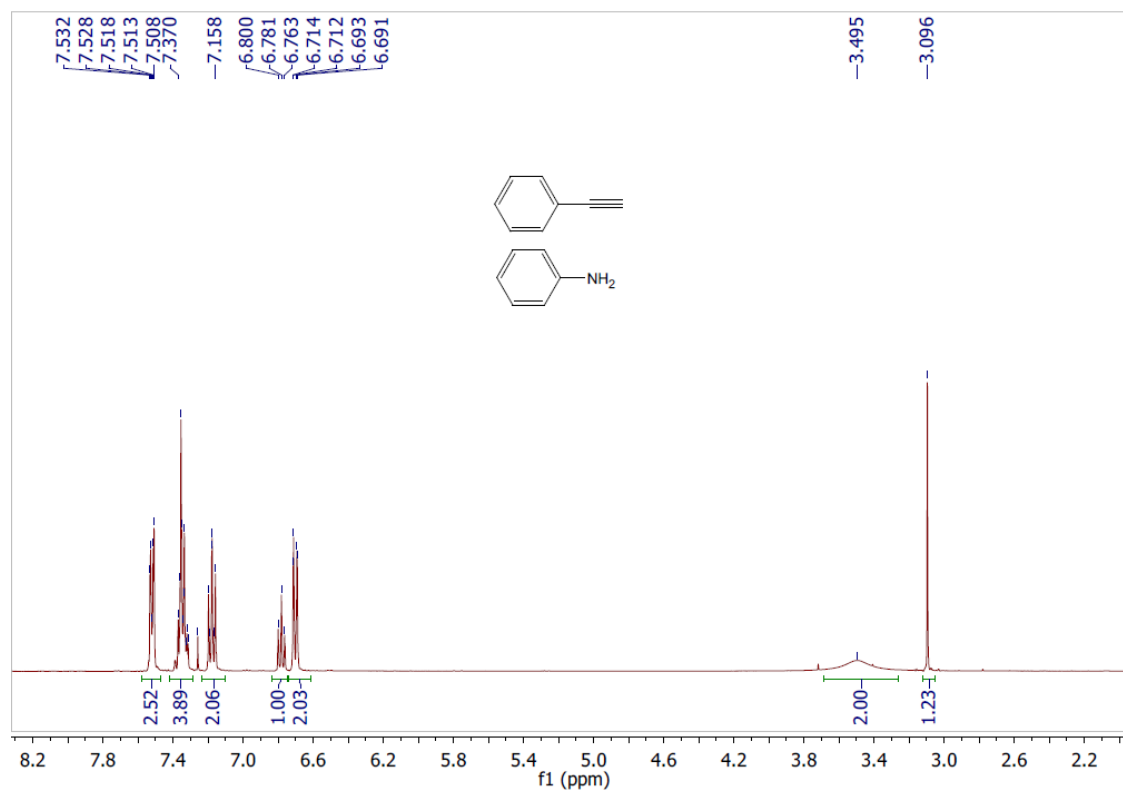
A standard solution was prepared by dissolving benzoyl peroxide (2 mmol) and anisole (1 mmol) in 4 mL dioxane. Photoredox catalyst  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  (2 mmol%), sodium bicarbonate (0.75 mmol), and different promoters (4 mmol%) were added into the corresponding reactor containing 1 mL standard solution. The reactions were stirred at room temperature and were illuminated with a 26-W household bulb. The reaction was monitored by GC/MS.

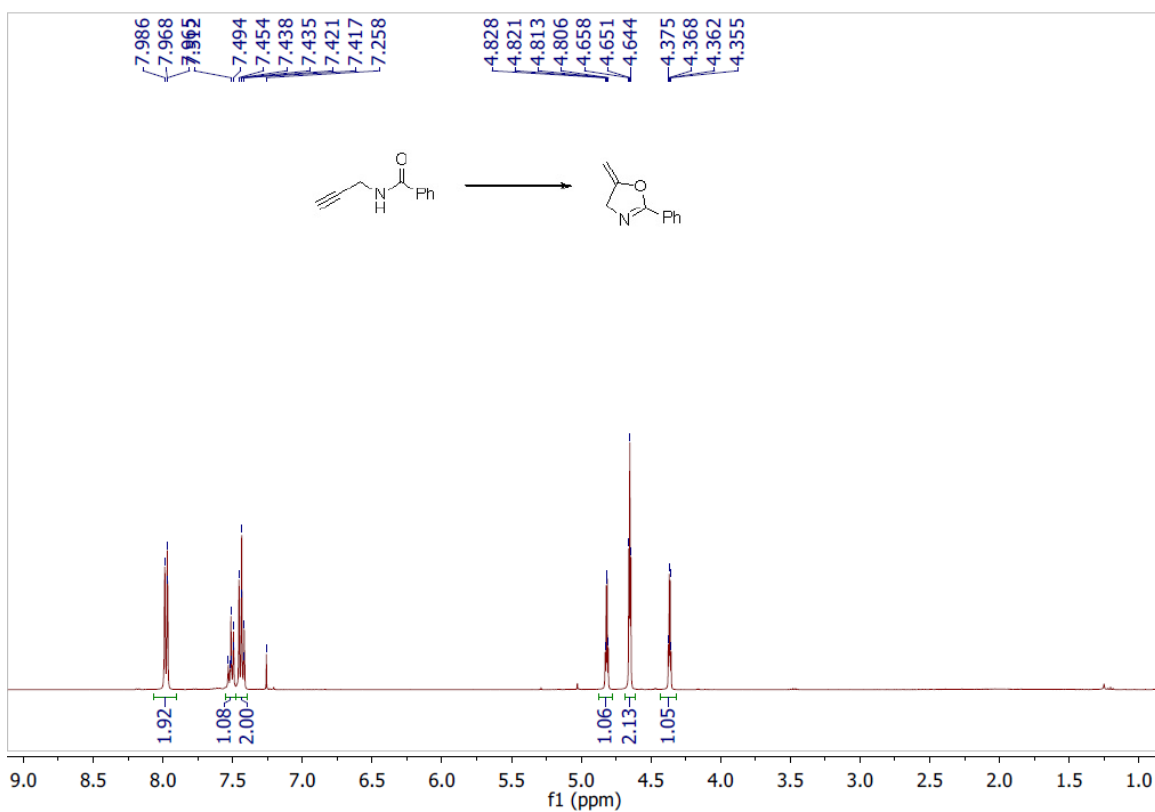
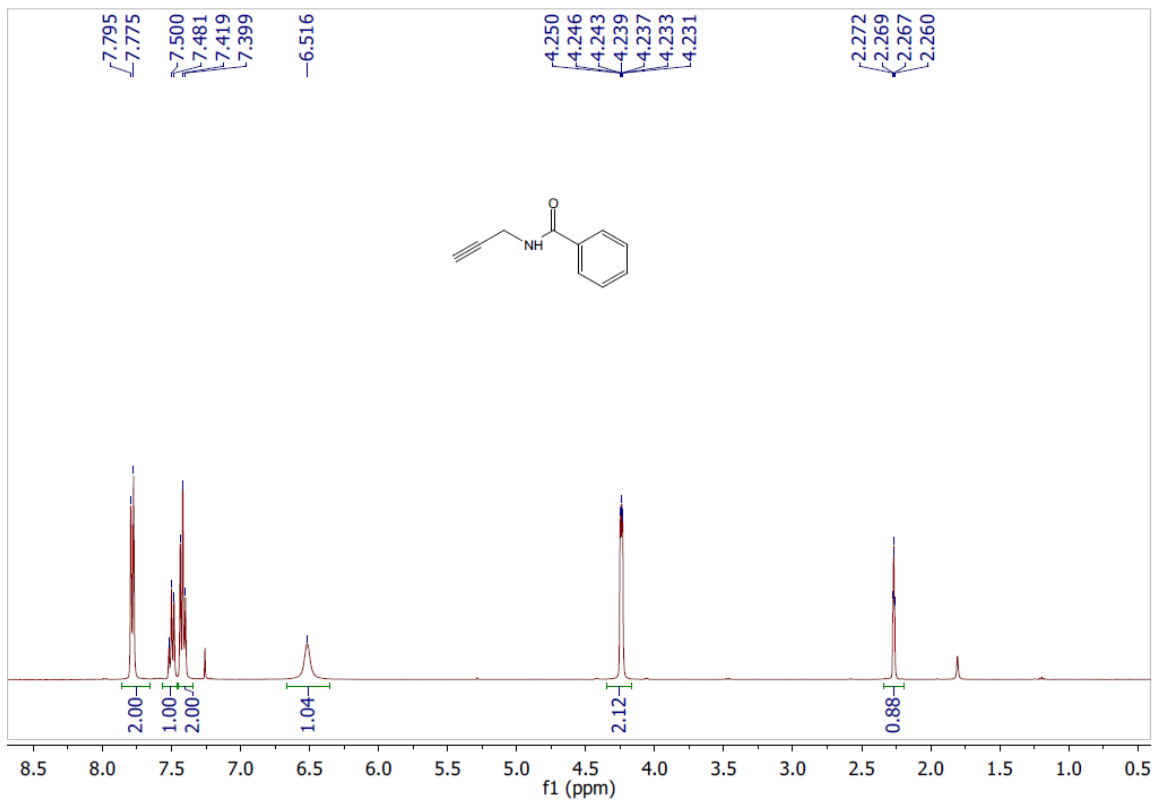
## Prins-type cyclization:



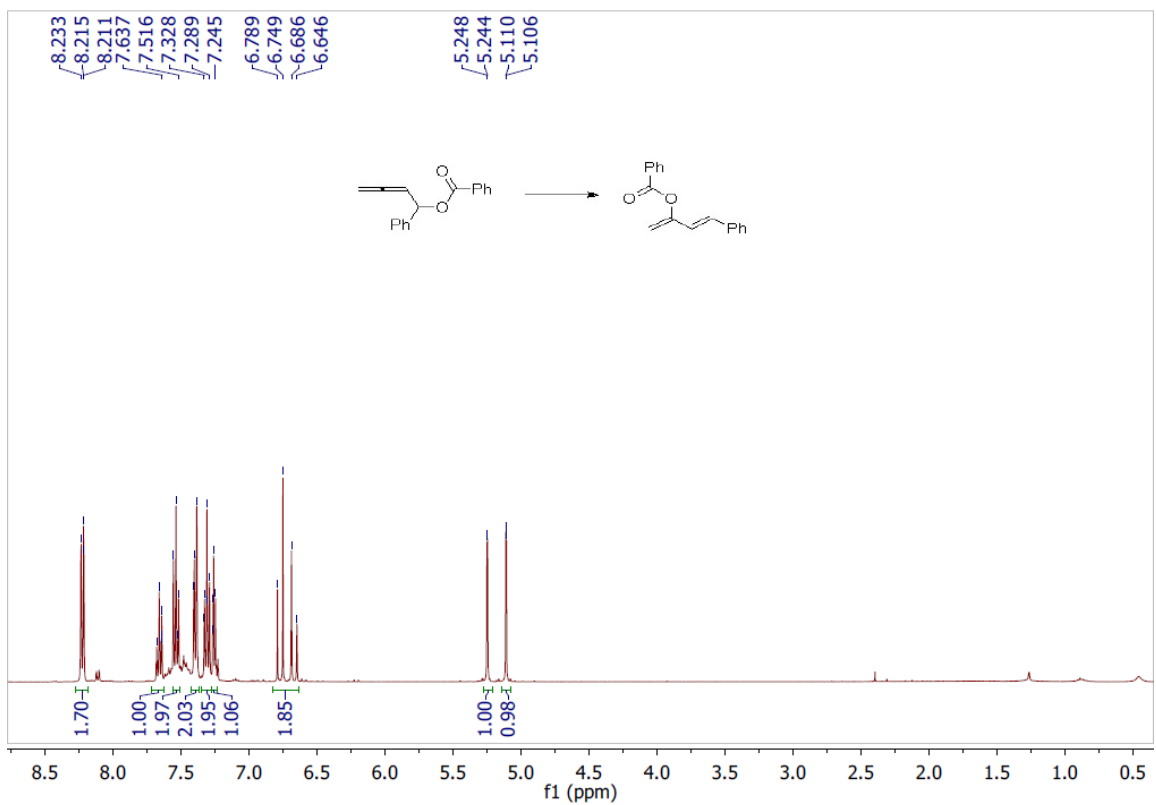
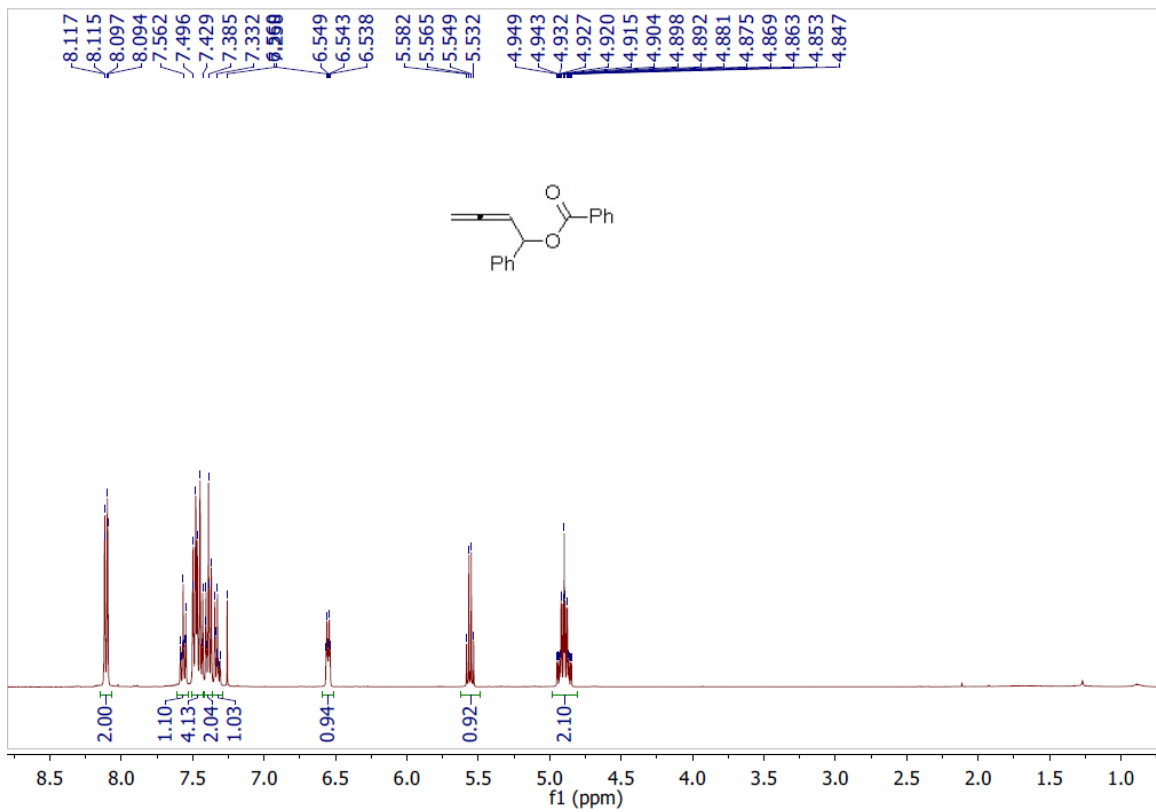
A mixture of 4-chlorobenzaldehyde (64 mg, 0.4 mmol), 3-buten-1-ol (58 mg, 0.8mmol) and scandium triflate (10 mg, 0.02 mmol, 5 mol% relative to the aldehyde) in chloroform (1 mL) was stirred at 50 °C under nitrogen. The reaction was monitored by H-NMR (20 min, 3h, 16h). 50 mL of the reaction solution will be used for each time of H-NMR.

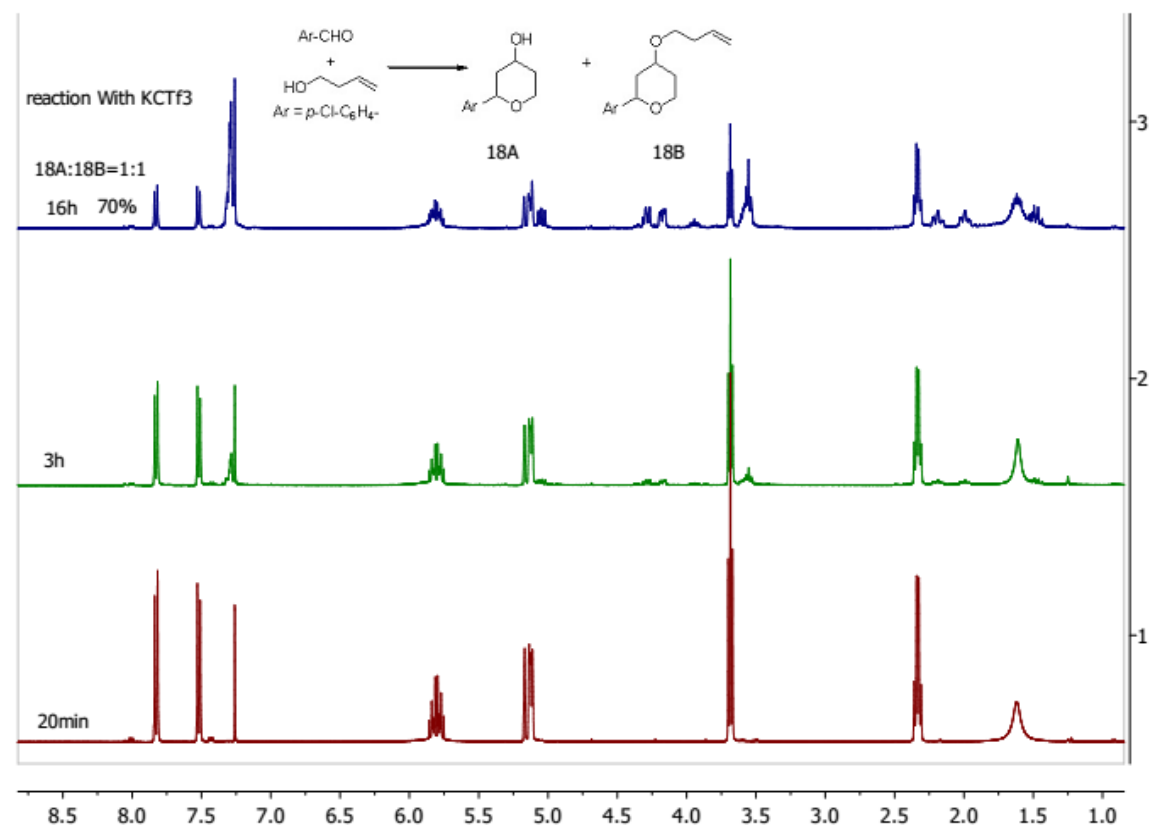
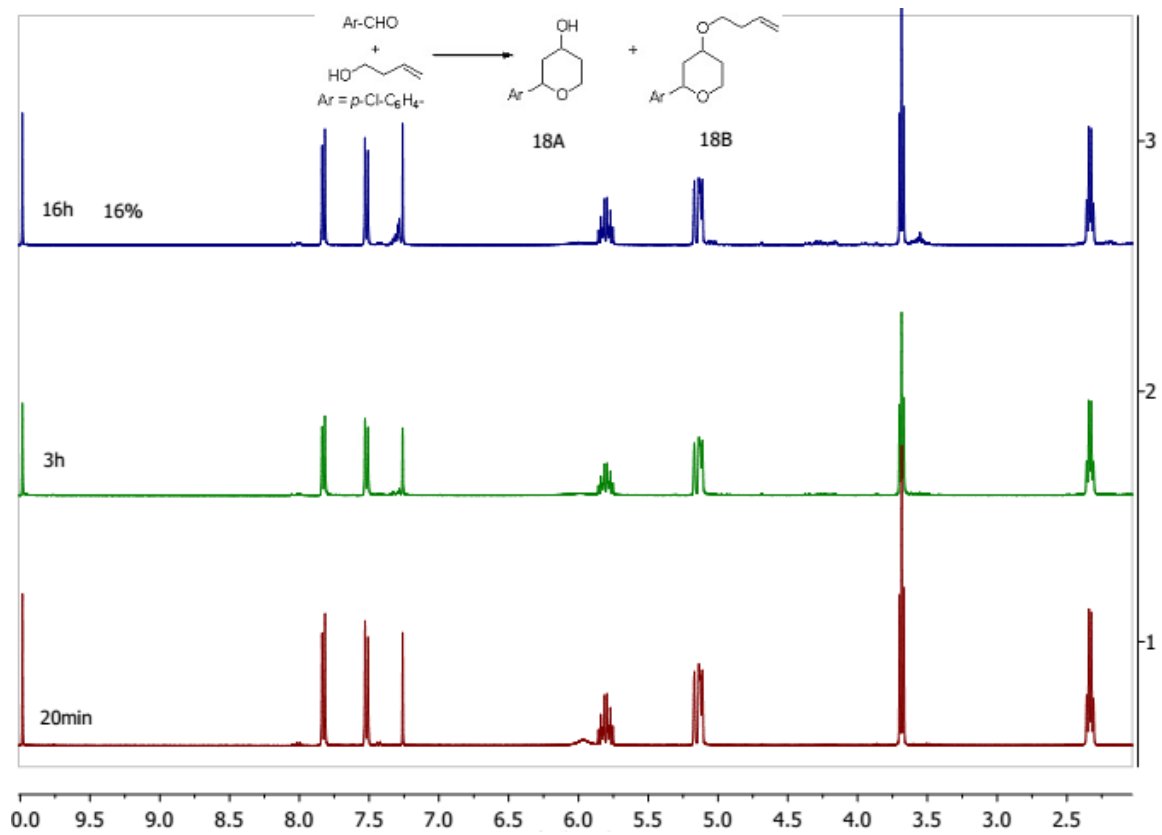
## Section 7. Copies of related NMR spectrums











## Section 8. References

- [1] T. Nanmyo, S. Sasaki, T. Kume, **US 8,304,580**.
- [2] C. Nieto-Oberhuber, S. López, A. M. Echavarren, *J. Am. Chem. Soc.* **2005**, *127*, 6178-6179.