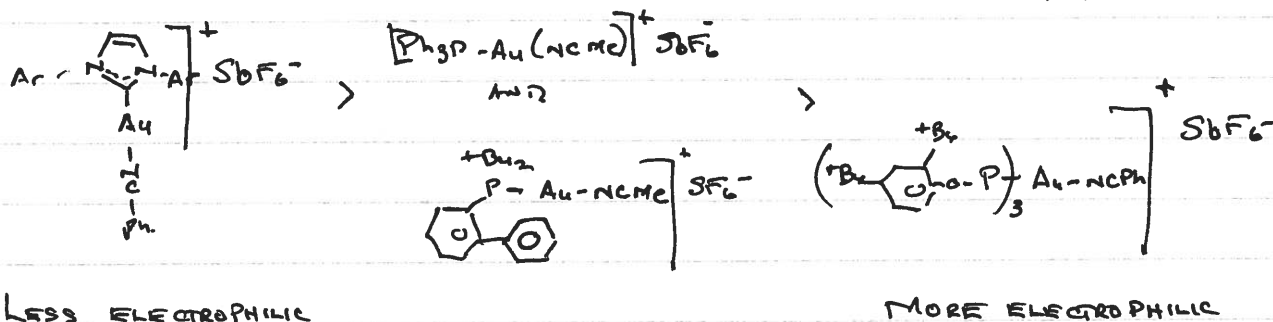


Au^I CATALYZED ADDNS TO ALKYNES

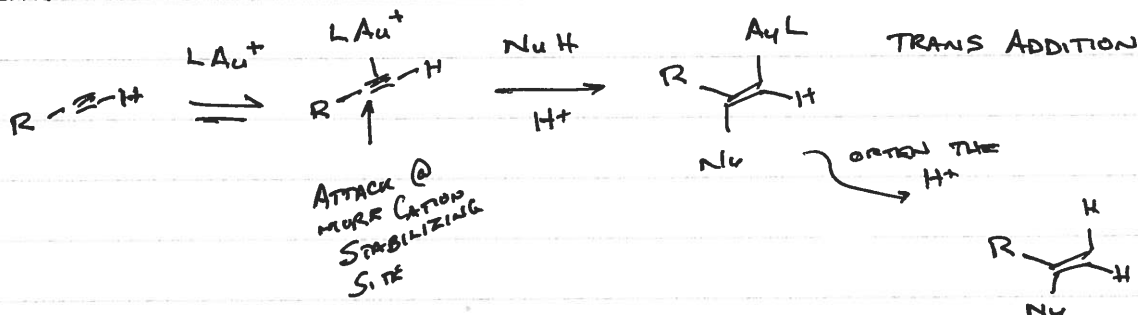
- IN SIMPLEST FORM, MANY METAL CATIONS ACTIVATE ALKYNES TO NUCLEOPHILIC ATTACK. - VAGUELY SIMILAR TO HECK TYPE RXNS OF Pd(II)
- INCLUDE Pt(II), Ag(I), AND Au(III)
- BUT ESPECIALLY Au(I).

- PREFER COMPLEXATION ALKYNES > ALKENES > CARBONYLS
 BUT ALKYNE COMPLEX IS MORE REACTIVE

- VERY TUNABLE
- OFTEN A Ag(I) ADDED TO TAKE L AuX TO [Au]⁺ - ASSUMED RATHER THAN PRESEN



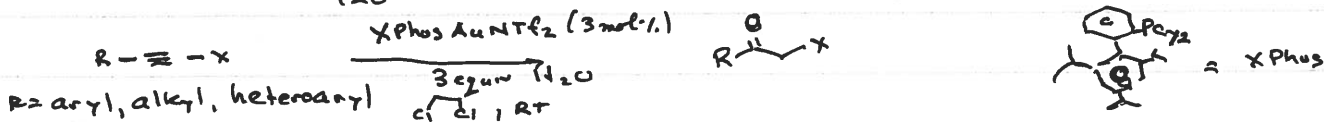
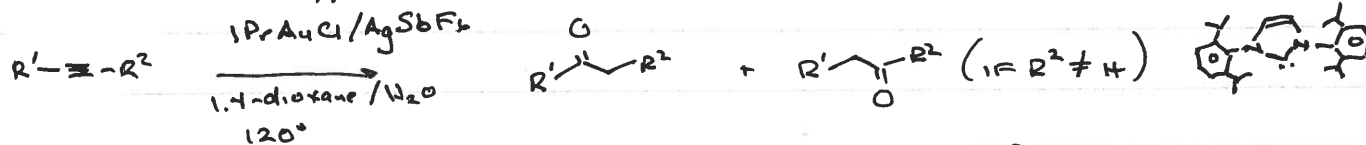
GENERAL RXN SCHEME

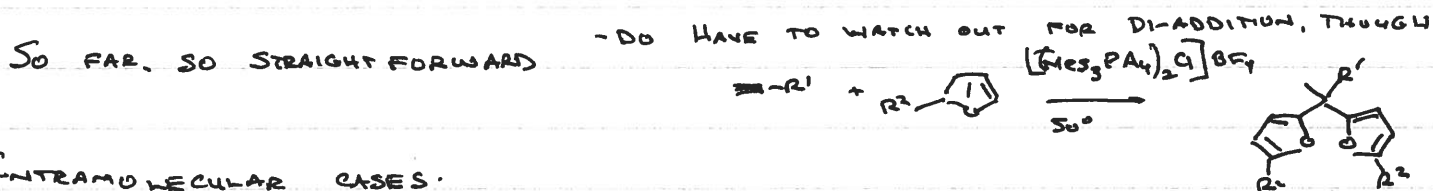
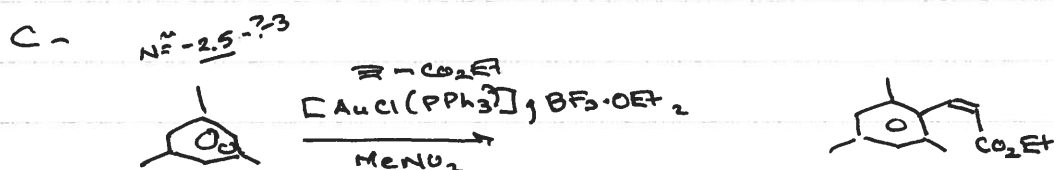
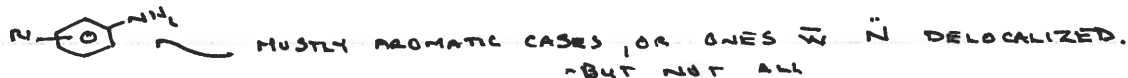
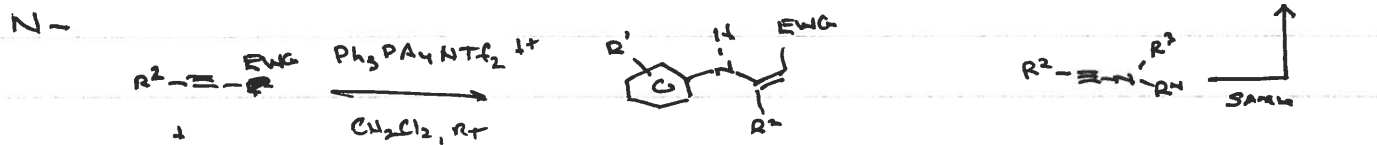
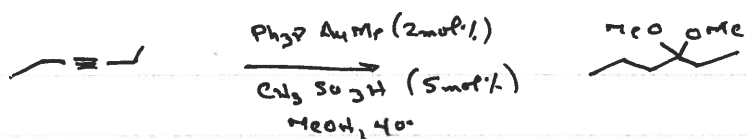


INTERMOLECULAR ATTACK OF NUCLEOPHILES

- MANY EXAMPLES OF O, N, AND SOME C NUCLEOPHILES

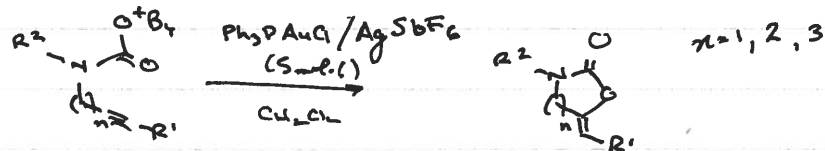
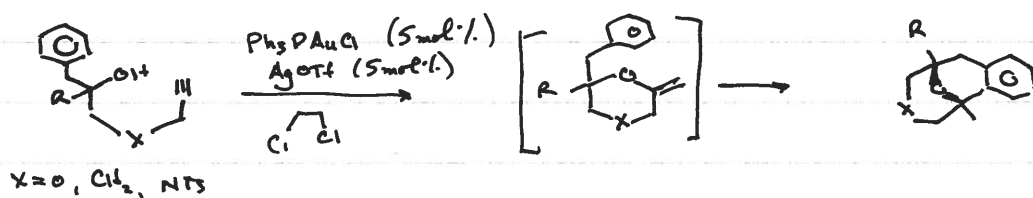
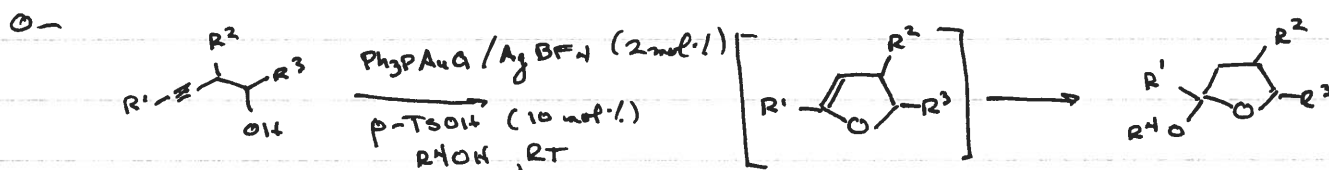
WITH H₂O, CAN BE REPLACED Hg²⁺ IN ADDN TO ALKYNES



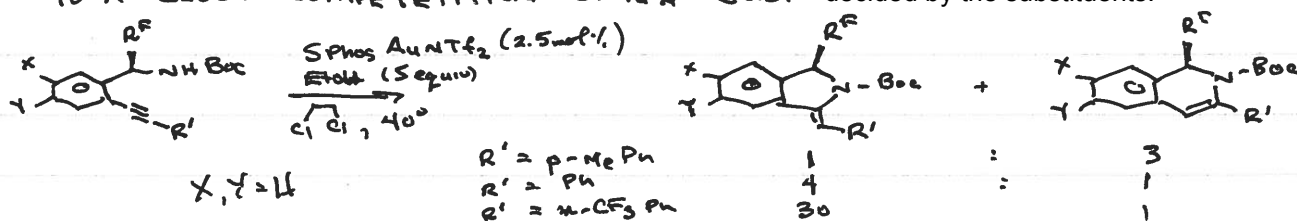


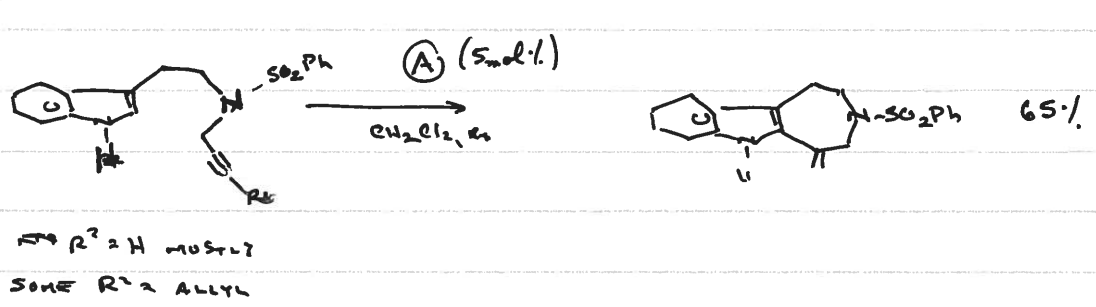
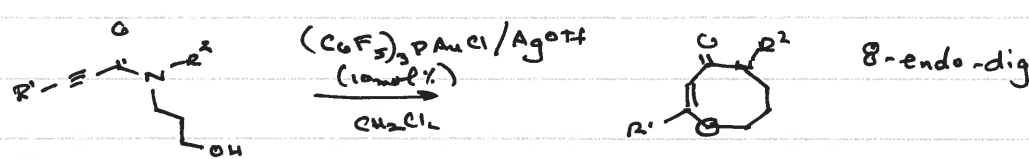
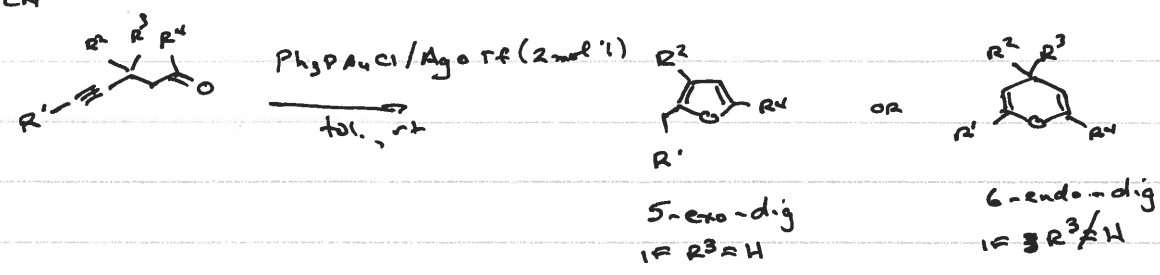
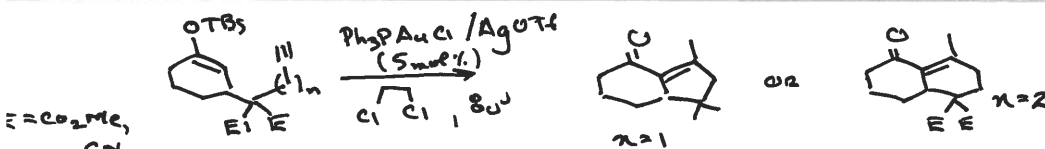
INTRAMOLECULAR CASES.

- THERE ARE MANY CASES WHERE REACTIVITY IS QUITE STRAIGHT FORWARD



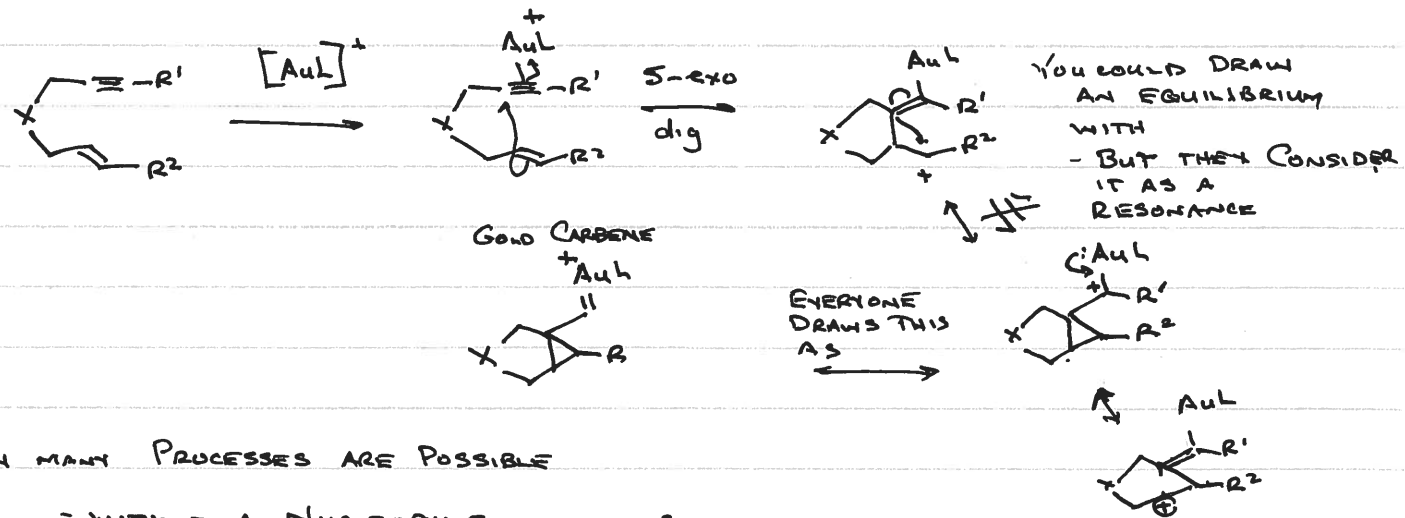
N-
 NOTE: IN YOUR EXPERIENCE, S-EXO ALWAYS WINS OVER G-ENDO - BUT WE'RE NOW IN TRIPLE BOND TERRITORY; I.E. S-EXO-DIG VS G-ENDO-DIG, AND THIS IS A CLOSE COMPETITION OFTEN JUST DECIDED BY THE SUBSTITUENTS.





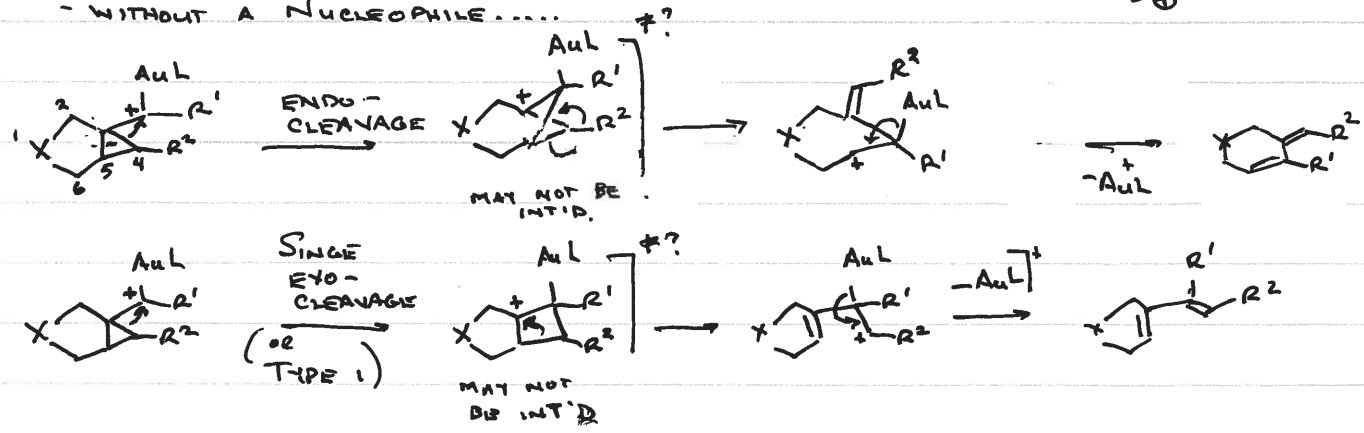
GOLD - CATALYZED 1,5- ENYNE CYCLIZATIONS

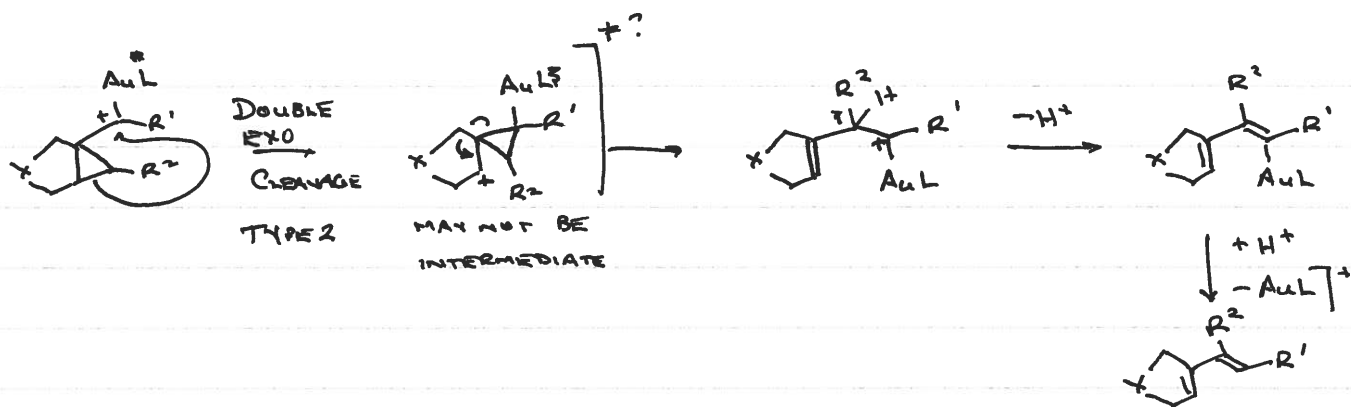
- WHEN THE GOING GETS WEIRD. MANY REARRANGEMENT PRODUCTS
- WHAT YOU WOULD EXPECT IS THE FOLLOWING, SINCE AuL^+ HAS 1 OPEN SITE ONLY.



THEN MANY PROCESSES ARE POSSIBLE

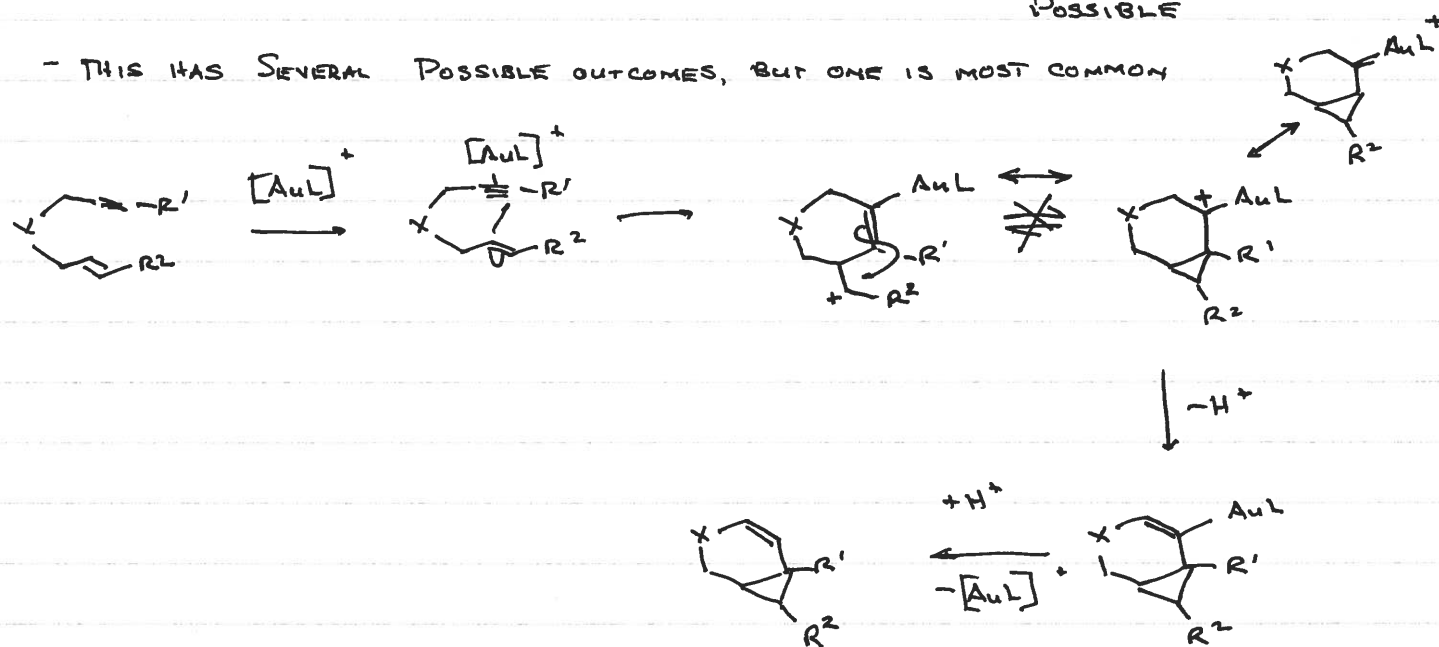
- WITHOUT A NUCLEOPHILE.....



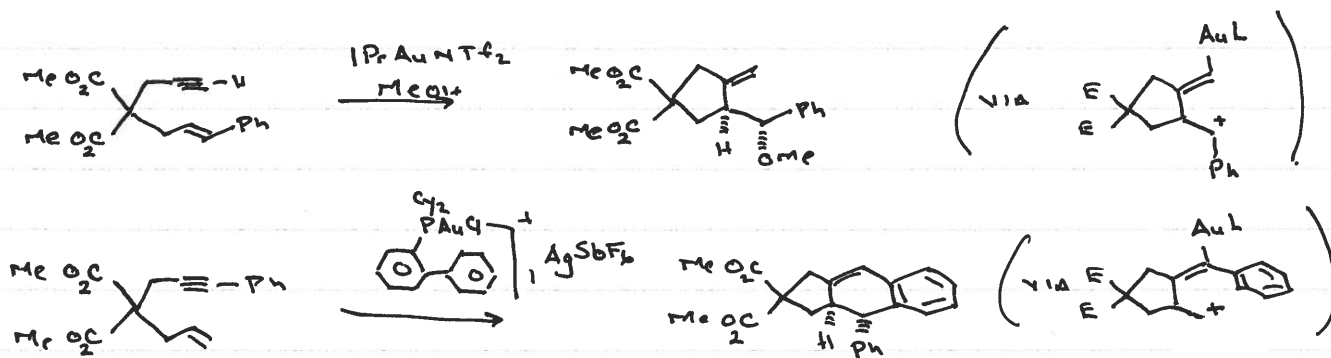


BUT RECALL ALSO, THE 6-ENDO-DIG CYCLIZATION HAS ALSO BECOME POSSIBLE

- THIS HAS SEVERAL POSSIBLE OUTCOMES, BUT ONE IS MOST COMMON

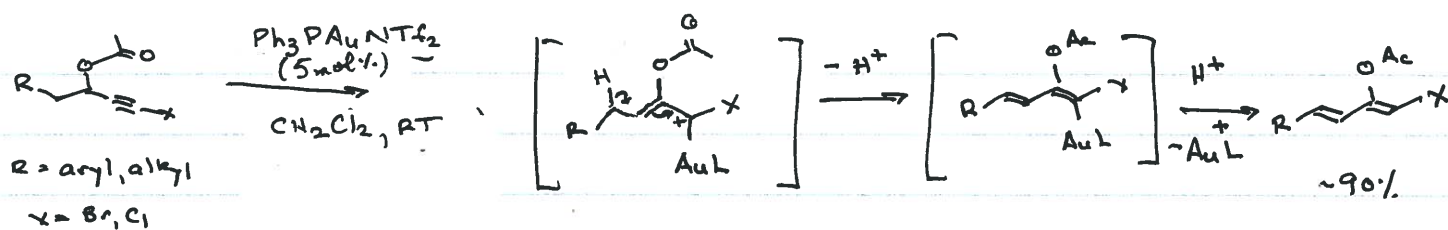


OF COURSE, IF A NUCLEOPHILE IS PRESENT, IT MAY INTERCEPT THE CATIONIC SPECIES AND LOOK CONVENTIONAL

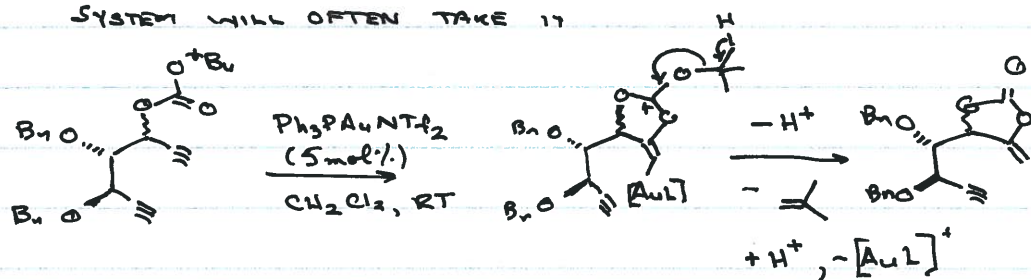


THERE ARE RXN MANIFOLDS SIMILARLY COMPLEX FOR 1,5-ENYNES AND 1,7-ENYNES, BUT WE'LL CALL THESE BEYOND THE COURSE'S SCOPE...

(IF NO NUCLEOPHILE)

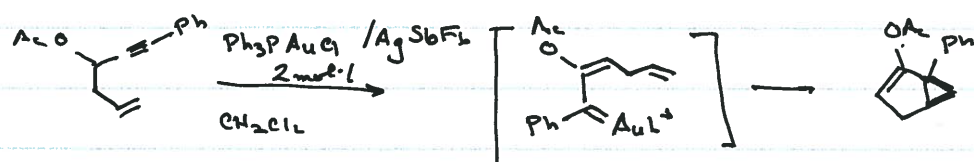
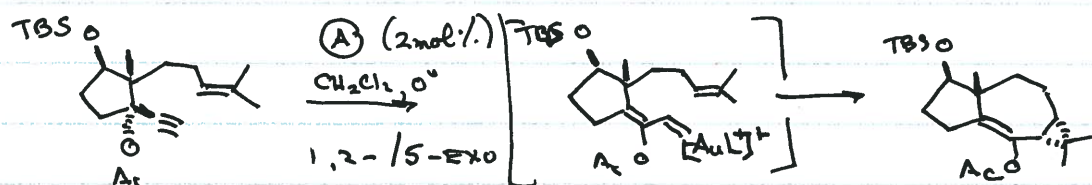


OR IF THERE'S A WAY OUT OF THE CATION WITHIN THE CARBOXYLATE, THE SYSTEM WILL OFTEN TAKE IT

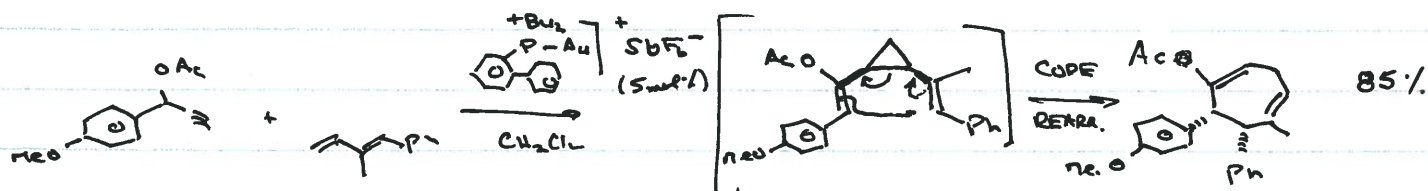



MOURIES-MAN SUY, V.;
 FENSTERBANK, L.
 ISR. J. CHEM 2018,
 58, 586.

- IF YOU ADD AN ALKENE, THE GOLD CARBENE OFTEN ACTS LIKE A REAL CARBENOID, CYCLOPROPANATING THE ALKENE



- YES, I DID FIND AN INTRAMOLECULAR CASE, BUT IT REARRANGES AFTERWARD,



-  ALLENES - 2ND MOST REACTIVE FUNCTIONAL GROUP FOR Au(I) (OR Au(III)) ACTIVATION - NO TIME, BUT SELF

YANG, W. ; HASMI, A.S.K. CHEM. SOC. REV 2014, 43, 2941.