Chem 41c Final Exam

Stoltz, Spring 2009, June 8, 2009

The exam begins when you turn to page 2. You have 4 hours to complete the exam. This is a closed note and closed book exam with no collaboration. You may use the periodic table on the last page of this packet. You may not use any other materials. The exam has a total of 170 points and counts for 40% of your course grade. Good luck.

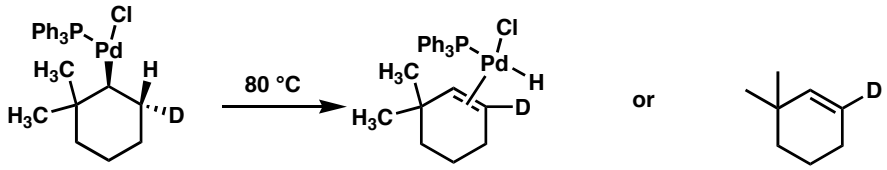
There are 16 pages in this exam packet.

The Exam is due by Friday June 12, 2009 by 5 PM.

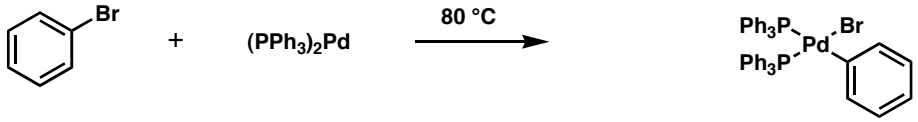
*Name:*_____

1. Predict the major non-volatile products (if any) of the following reactions or sequences. Clearly mark your answers by placing a **box** around the compound that you believe to be the major product. (5 points each).

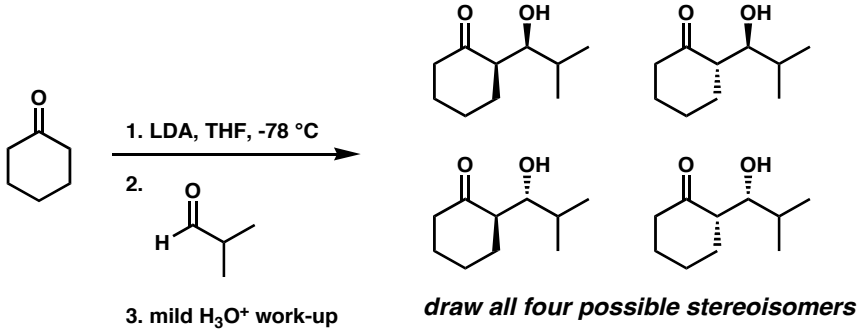
a.



b.

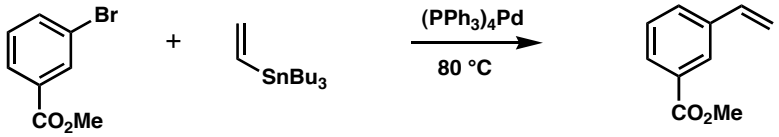


c.

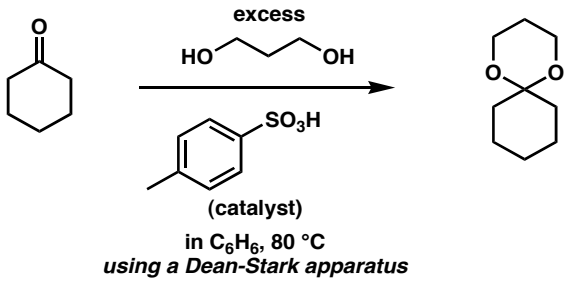


draw all four possible stereoisomers

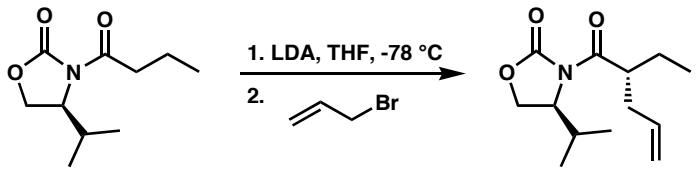
d.



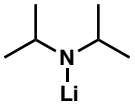
e.



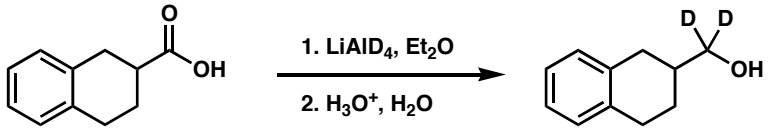
f.



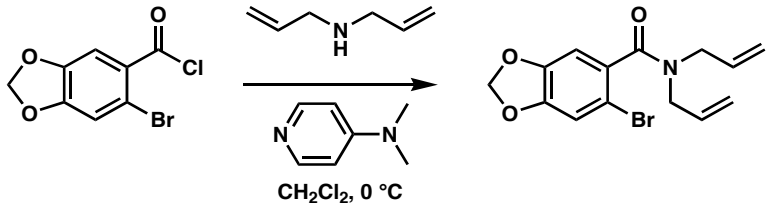
5 point bonus: what is the structure of LDA?



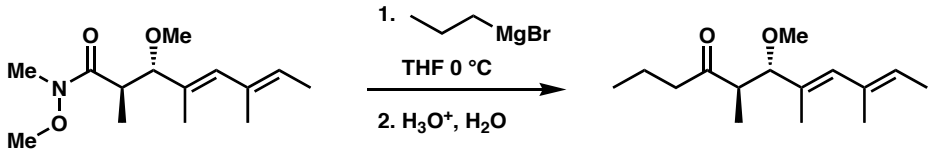
g.



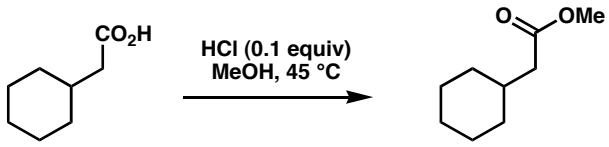
h.



i.

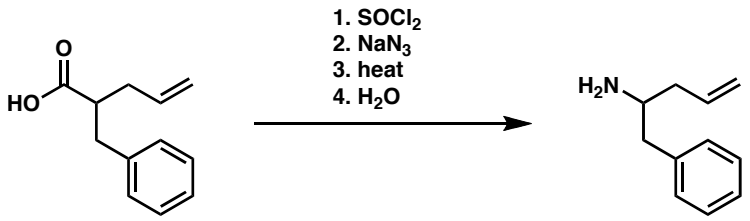

1.
MgBr
THF 0 °C
2. H_3O^+, H_2O
Me
N
O
Me
O
OMe
O
OMe

j.

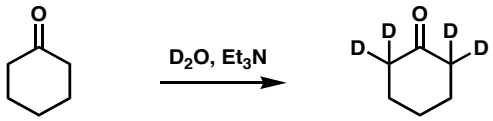

CO_2H
HCl (0.1 equiv)
MeOH, 45 °C
O
OMe

2. Provide reagents for the following transformations. They may be multistep processes, but should not be longer than 5 steps. (5 points each)

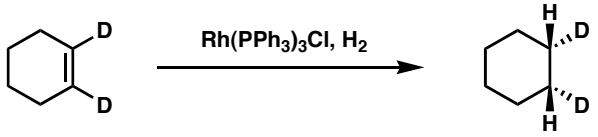
a.



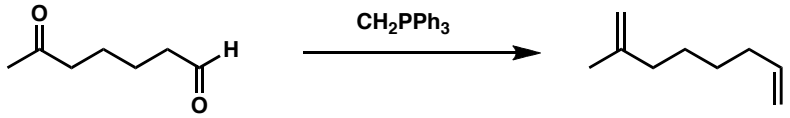
b.



c.

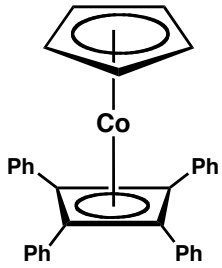


d.



3. In the following complexes, what is the formal oxidation state of the metal, the d^n description, and the electron count? Feel free to use the periodic table in the room (5 points each-no partial credit)

a.



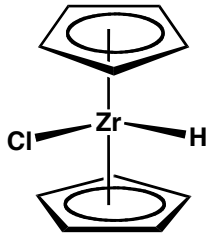
Co(I) or Co^{1+} **d^8** **18 electron complex**

b.

$(PPh_3)_3RhCl$

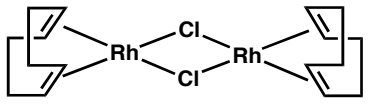
Rh(I) or Rh^{1+} **d^8** **16 electron complex**

c.



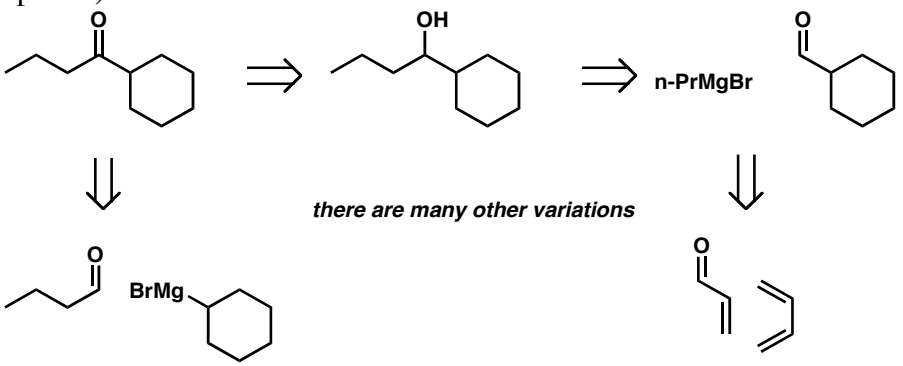
Zr(IV) or Zr^{4+} **d^0** **16 electron complex**

d.



Rh(I) or Rh^{+1} **d^8** **16 electron each Rh**

4. Draw two distinct retrosytheses for the following molecule going back to starting materials of 6 carbons or less (10 points).



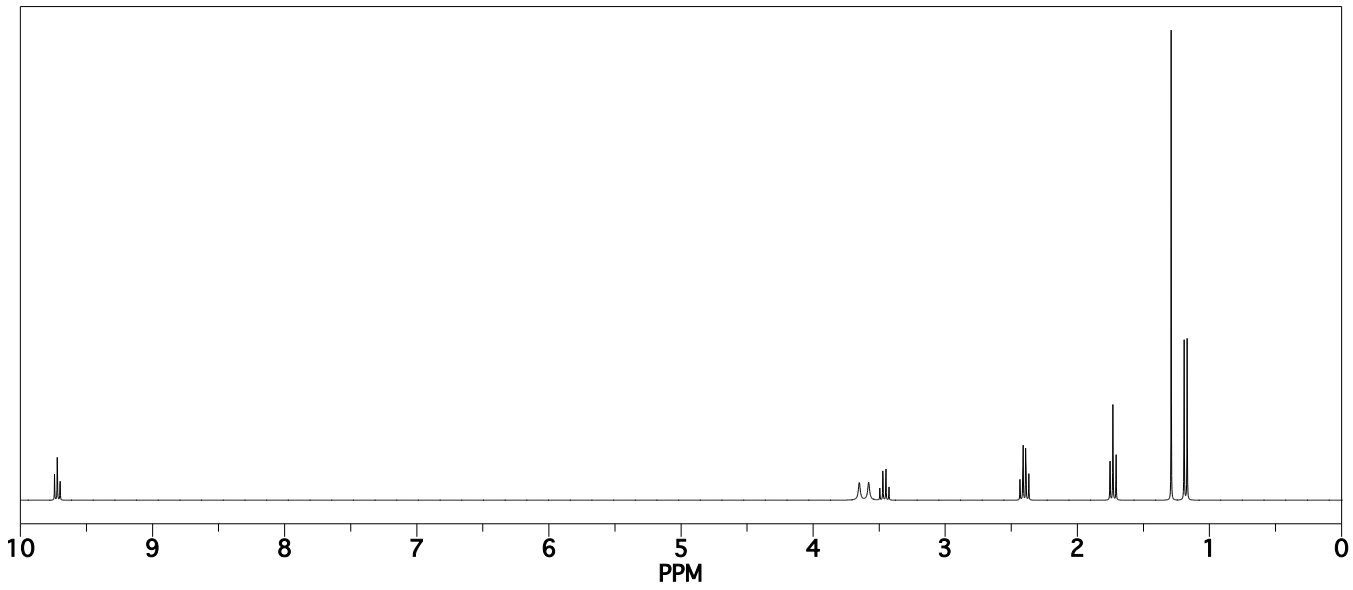
Show the forward reactions needed to accomplish one of your designed routes above (10 points).

5. Treatment of olefinic aldehyde **1** with OsO_4 produced an intermediate **A**. Upon treatment with a simple reagent set, **A** is converted to **B**. Selected ^{1}H NMR data for **A** is provided. Predict the structure of **A** (mindful of stereochemistry), and provide reagents with a plausible mechanism for the conversion of **A** to **B**. (10 points)

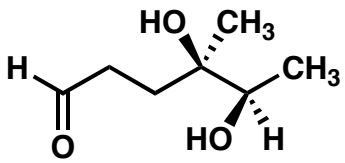
1 *B*

^{1}H NMR spectrum of A

a	δ 9.72 (t, 1H)	*d*	δ 1.73 (t, 2H)
b	δ 3.46 (q, 1H)	*e*	δ 1.29 (s, 3H)
c	δ 2.40 (dt, 2H)	*f*	δ 1.18 (d, 3H)



-structure of **A**:



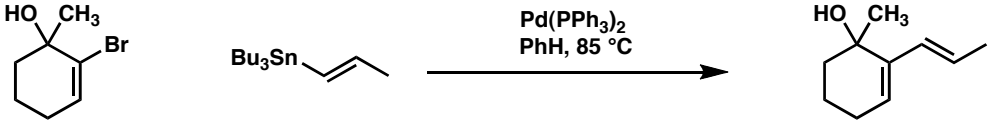
-Reagents to convert **A** to **B**:

H^+, H_2O

-Mechanism for the conversion of **A** to **B**:

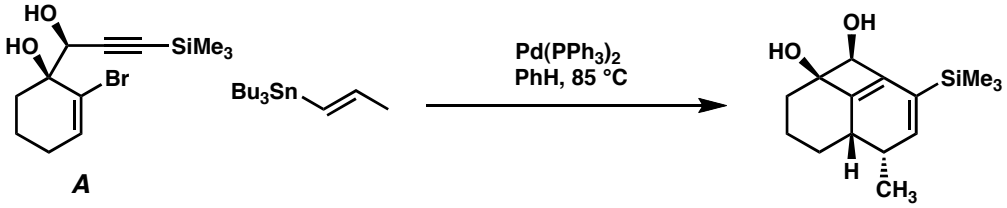
acetal formation mechanism

6. a) The following palladium-catalyzed reaction was reported in the literature. Draw a mechanism for the process and clearly label all elementary steps (i.e., reductive elimination, oxidative addition, insertion, etc.) (10 points).

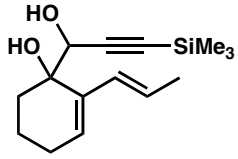


Answer: Oxidative addition, transmetallation, reductive elimination

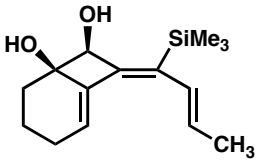
b) Interestingly, it was found that treatment of related bromide **A** produced none of the expected **B**, but compound **D** instead. This compound is believed to arise from intermediate **C**, although **C** was not observed directly either. Provide a mechanistic rationale for the formation of **C** and **D** (hint: the final step (**C**→**D**) does not involve palladium). (5 points)



A ***D***



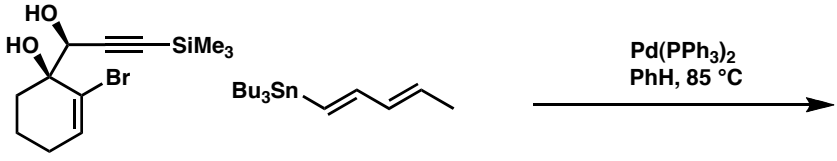
B
(not observed)



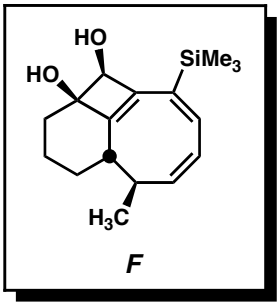
C
(not observed, but believed to be an intermediate)

Answer: Oxidative addition, olefin insertion, transmetallation, reductive elimination, 6π-electrocyclization (disrotatory)

c) Furthermore, when dienyl stananne **E** was used in the coupling, a product **F** was formed. Predict the structure of **F** and include stereochemistry. (5 points)

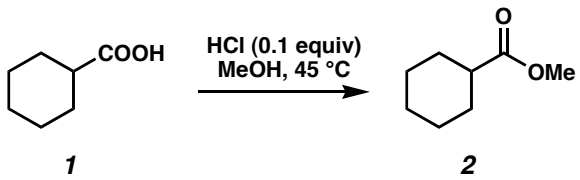


A ***E***



F

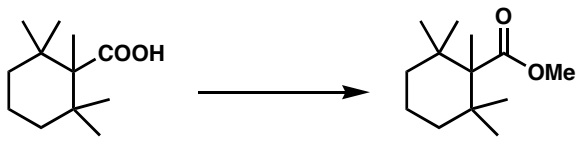
7. a) Provide a detailed curved arrow mechanism for the following reaction. What drives the equilibrium to the product side? (5 points)



1 *2*

Answer: Fischer esterification mechanism.

b) In contrast to part a of this problem, under the same conditions the following reaction (**3**→**4**) is extremely slow. Why do you think this is the case? Provide an alternative method for preparing the methyl ester **4** from carboxylic acid **3** that you believe would be fast and high yielding. Provide a detailed curved arrow mechanism for your new synthesis of **4** from **3** and explain why the new method should be better. (5 points)

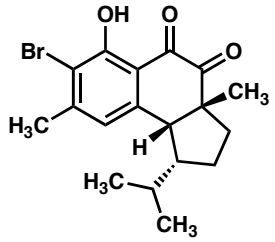


3 *4*

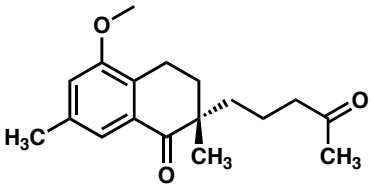
Answer: Diazomethane or base + MeI. Both use the carboxylate as a nucleophile and don't require attack at the carbonyl carbon.

8. Your friend Herschel is desperately trying to finish his research project before graduating (the synthesis of the natural product Hamigeran B (**1**)). He is nearly there, but a problematic and surprising outcome of an aldol addition reaction is causing problems.

a. Draw the possible outcomes of the intramolecular aldol reaction of diketone **2** (hint, there are 6 possible aldol addition products, and 2 aldol condensation products-draw all 8 of them). (10 points)

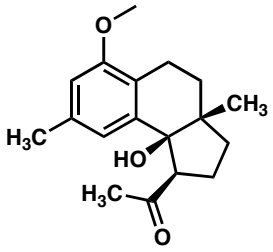


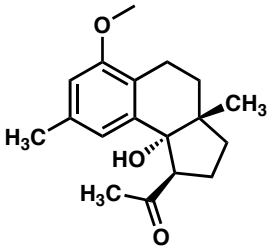
Hamigerin B (1)

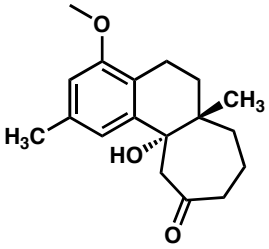


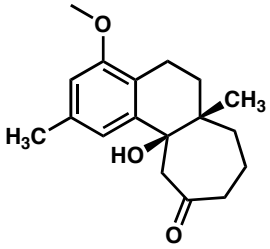
2

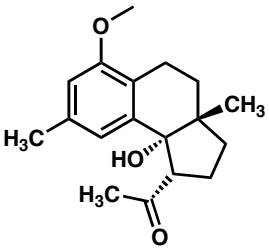
KOH, EtOH, 80 C

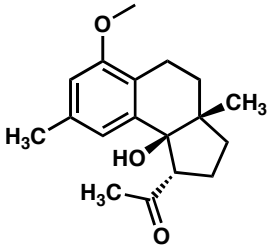


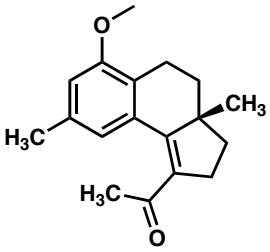


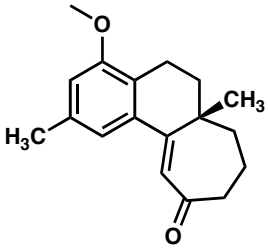




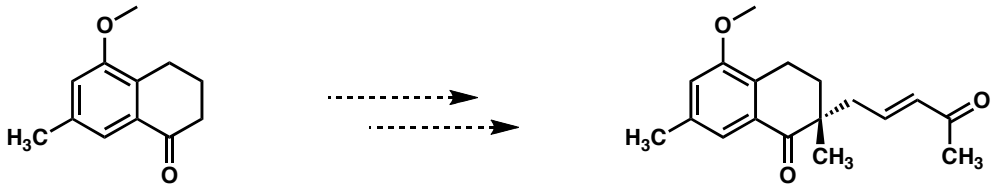






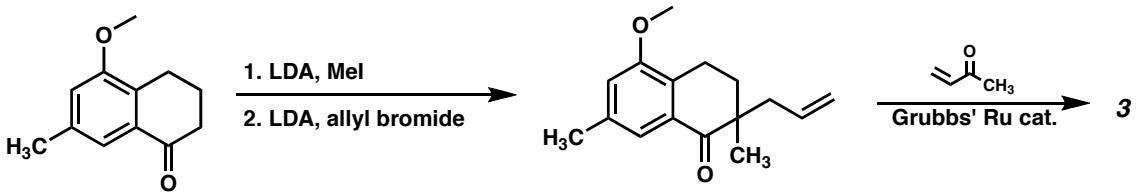


b. Unfortunately, Herschel keeps isolating the unwanted 7-membered ring products. He concludes that the problem is selective enolization and decides to treat the precursor to **2**, enone **3**, with a CuH reagent. This reagent saves the day and produces the desired product, albeit in low yield. Since he is running low on compound **3**, Herschel asks you to lend a hand by making more. Unfortunately, Herschel is away at Senior Week. He did leave the starting material, ketone **4**, but no instructions. Provide a detailed synthetic plan for producing more of enone **3** so that Herschel can finish his project before commencement on Friday! (10 points)



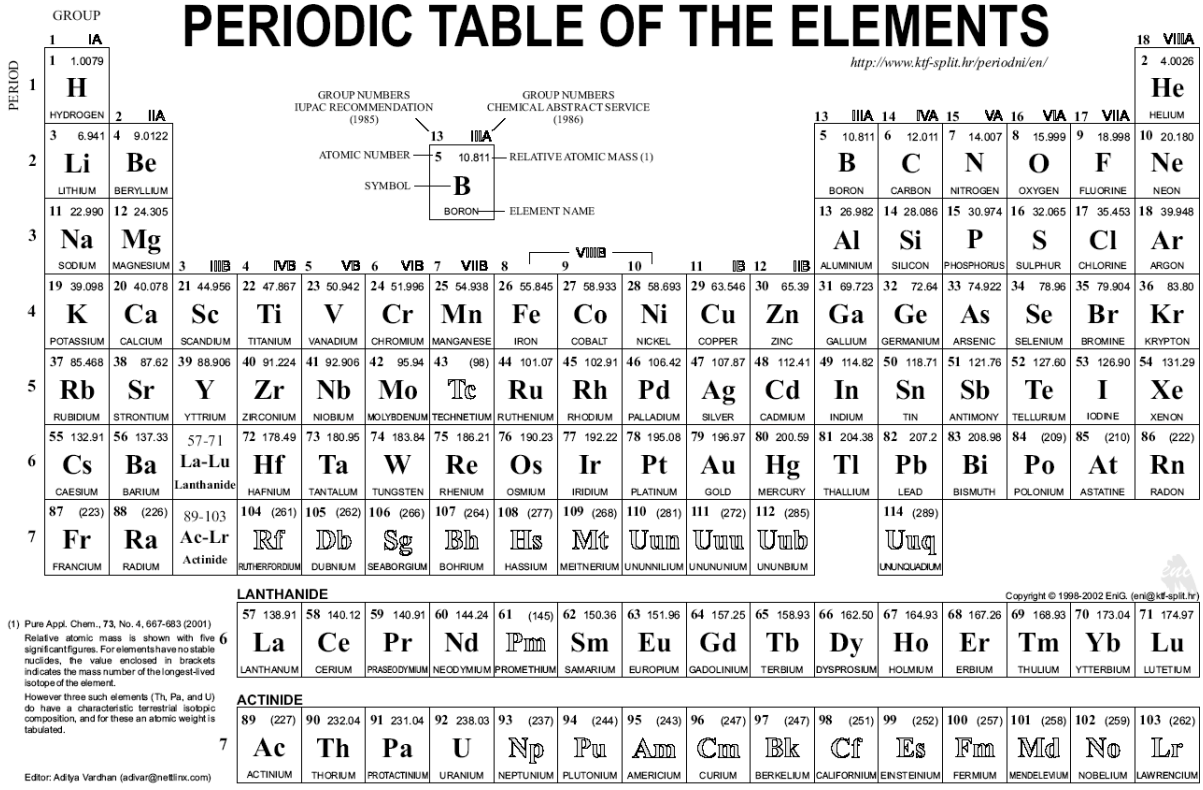
4 ***3***

One possibility:



4

Bonus: Provide a mechanistic rationale for how the CuH reagent produced the desired outcome (5 points).


PERIODIC TABLE OF THE ELEMENTS
http://www.ktf-split.hr/periodni/en/
GROUP
PERIOD
GROUP NUMBERS IUPAC RECOMMENDATION (1985)
GROUP NUMBERS CHEMICAL ABSTRACT SERVICE (1986)
ATOMIC NUMBER
SYMBOL
RELATIVE ATOMIC MASS (1)
ELEMENT NAME
1 IA
2 IIA
3 IIIB
4 IVB
5 VB
6 VIB
7 VIIB
8
9
10 VIIIB
11 IB
12 IIB
13 IIIA
14 IVA
15 VA
16 VIA
17 VIIA
18 VIIIA
1 1.0079 H HYDROGEN
2 4.0026 He HELIUM
3 6.941 Li LITHIUM
4 9.0122 Be BERYLLIUM
5 10.811 B BORON
6 12.011 C CARBON
7 14.007 N NITROGEN
8 15.999 O OXYGEN
9 18.998 F FLUORINE
10 20.180 Ne NEON
11 22.990 Na SODIUM
12 24.305 Mg MAGNESIUM
13 26.982 Al ALUMINIUM
14 28.086 Si SILICON
15 30.974 P PHOSPHORUS
16 32.065 S SULPHUR
17 35.453 Cl CHLORINE
18 39.948 Ar ARGON
19 39.098 K POTASSIUM
20 40.078 Ca CALCIUM
21 44.956 Sc SCANDIUM
22 47.867 Ti TITANIUM
23 50.942 V VANADIUM
24 51.996 Cr CHROMIUM
25 54.938 Mn MANGANESE
26 55.845 Fe IRON
27 58.933 Co COBALT
28 58.693 Ni NICKEL
29 63.546 Cu COPPER
30 65.39 Zn ZINC
31 69.723 Ga GALLIUM
32 72.64 Ge GERMANIUM
33 74.922 As ARSENIC
34 78.96 Se SELENIUM
35 79.904 Br BROMINE
36 83.80 Kr KRYPTON
37 85.468 Rb RUBIDIUM
38 87.62 Sr STRONTIUM
39 88.906 Y YTTRIUM
40 91.224 Zr ZIRCONIUM
41 92.906 Nb NIOBIUM
42 95.94 Mo MOLYBDENUM
43 (98) Tc TECHNETIUM
44 101.07 Ru RUTHENIUM
45 102.91 Rh RHODIUM
46 106.42 Pd PALLADIUM
47 107.87 Ag SILVER
48 112.41 Cd CADMIUM
49 114.82 In INDIUM
50 118.71 Sn TIN
51 121.76 Sb ANTIMONY
52 127.60 Te TELLURIUM
53 126.90 I IODINE
54 131.29 Xe XENON
55 132.91 Cs CAESIUM
56 137.33 Ba BARIUM
57-71 La-Lu Lanthanide
72 178.49 Hf HAFNIUM
73 180.95 Ta TANTALUM
74 183.84 W TUNGSTEN
75 186.21 Re RHENIUM
76 190.23 Os OSMIUM
77 192.22 Ir IRIDIUM
78 195.08 Pt PLATINUM
79 196.97 Au GOLD
80 200.59 Hg MERCURY
81 204.38 Tl THALLIUM
82 207.2 Pb LEAD
83 208.98 Bi BISMUTH
84 (209) Po POLONIUM
85 (210) At ASTATINE
86 (222) Rn RADON
87 (223) Fr FRANCIUM
88 (226) Ra RADIUM
89-103 Ac-Lr Actinide
104 (261) Rf RUTHERFORDIUM
105 (262) Db DUBNIUM
106 (266) Sg SEABORGIUM
107 (264) Bh BOHRIUM
108 (277) Hs HASSIUM
109 (268) Mt MEITNERIUM
110 (281) Uun UNUNNILIUM
111 (272) Uuu UNUNUNIUM
112 (285) Uub UNUNBIUM
114 (289) Uuq UNUNQUADIUM
LANTHANIDE
57 138.91 La LANTHANUM
58 140.12 Ce CERIUM
59 140.91 Pr PRASEODYMIUM
60 144.24 Nd NEODYMIUM
61 (145) Pm PROMETHIUM
62 150.36 Sm SAMARIUM
63 151.96 Eu EUROPIUM
64 157.25 Gd GADOLINIUM
65 158.93 Tb TERBIUM
66 162.50 Dy DYSPROSIUM
67 164.93 Ho HOLMIUM
68 167.26 Er ERBIUM
69 168.93 Tm THULIUM
70 173.04 Yb YTTERBIUM
71 174.97 Lu LUTETIUM
ACTINIDE
89 (227) Ac ACTINIUM
90 232.04 Th THORIUM
91 231.04 Pa PROTACTINIUM
92 238.03 U URANIUM
93 (237) Np NEPTUNIUM
94 (244) Pu PLUTONIUM
95 (243) Am AMERICIUM
96 (247) Cm CURIUM
97 (247) Bk BERKELIUM
98 (251) Cf CALIFORNIUM
99 (252) Es EINSTEINIUM
100 (257) Fm FERMIUM
101 (258) Md MENDELEVIUM
102 (259) No NOBELIUM
103 (262) Lr LAWRENCIUM
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(1) Pure Appl. Chem., 73, No. 4, 667-683 (2001)
Relative atomic mass is shown with five significant figures. For elements have no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotope of the element.
However three such elements (Th, Pa, and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.
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The End