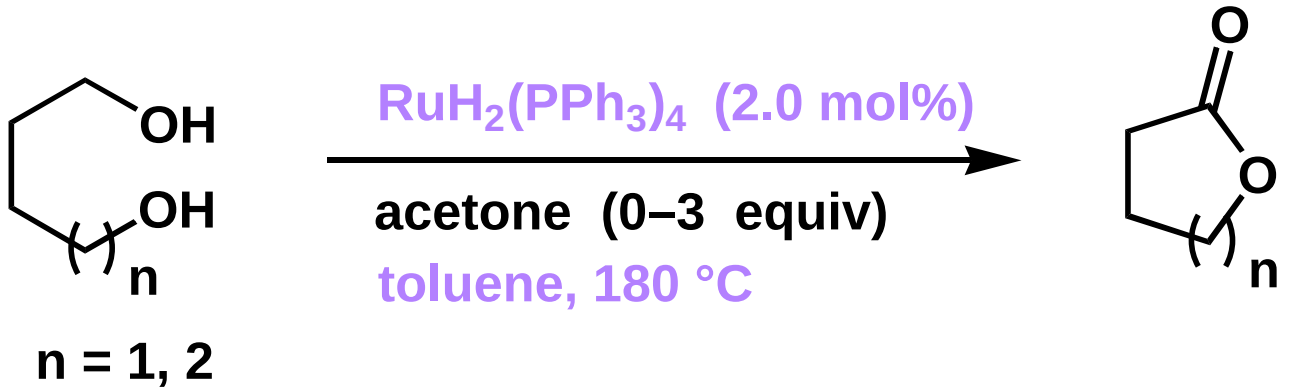
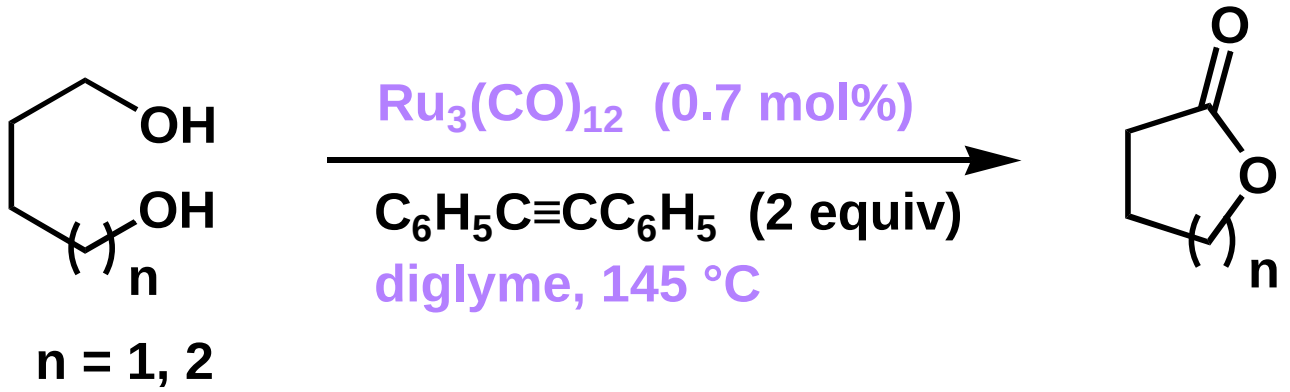
EARLY EXAMPLES FOR Ru–CATALYZED LACTONIZATION

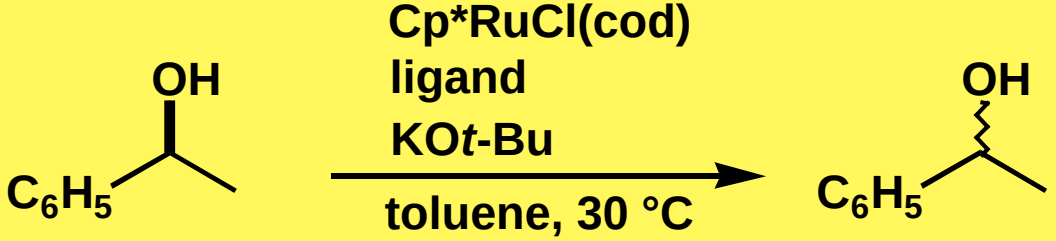


Murahashi, Ito, Naota, Maeda, *Tetrahedron Lett.*, **1981**, *22*, 5327.

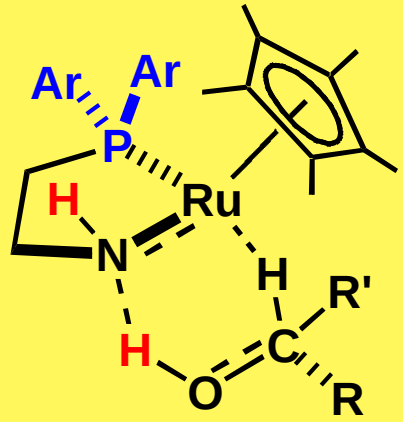


Shvo, Blum, Reshef, Menzin, *J. Organomet. Chem.*, **1982**, *226*, C21.

NEW CATALYSTS FOR DEHYDROGENATIVE OXIDATION OF *sec*-ALCOHOL

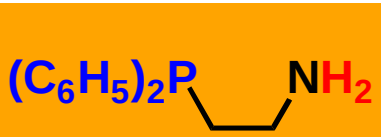


alcohol:Ru:ligand:KO*t*-Bu = 100:1:1:1

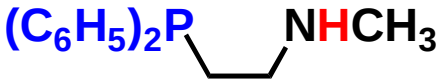


possible transition state

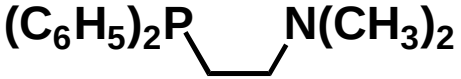
ligand:



476 TOF/h^{-1}



188



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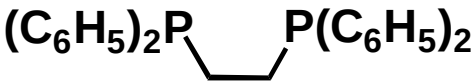

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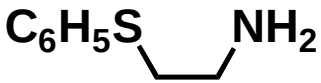
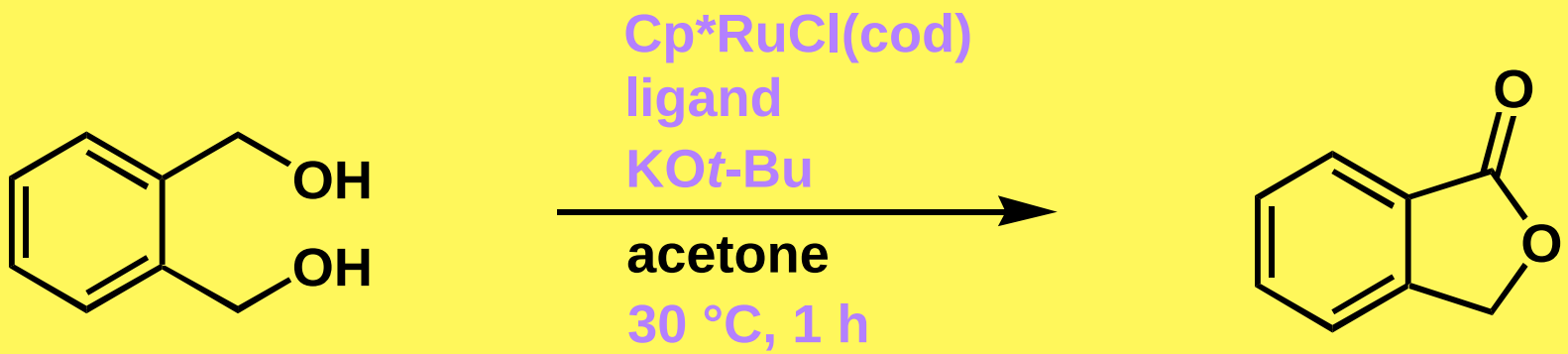


14

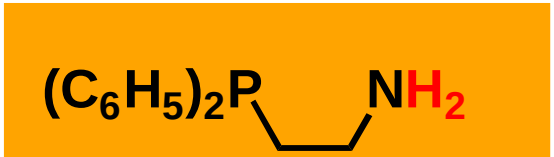
<1

LIGAND ACCELERATION IN LACTONIZATION OF DIOL

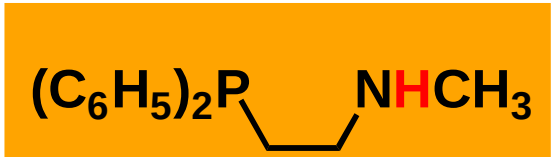


diol:Ru:ligand:KO*t*-Bu = 100:1:1:1, [diol] = 0.5 M

ligand:



>99% conv



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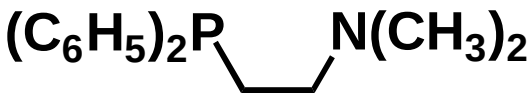
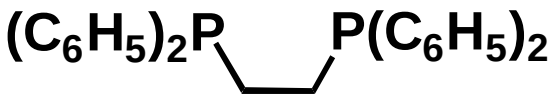


5%



0%

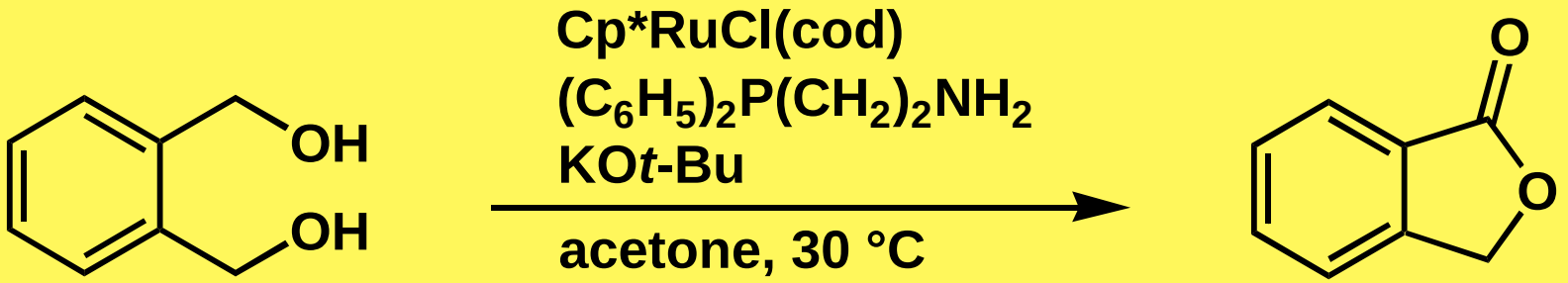
$RuH_2[P(C_6H_5)_4]$

17%

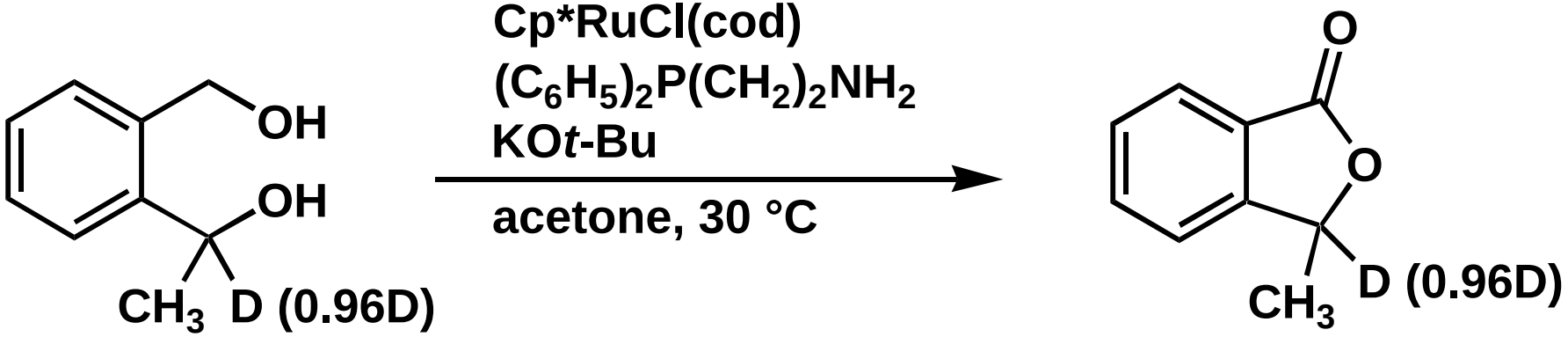
$Ru_3(CO)_{12}$

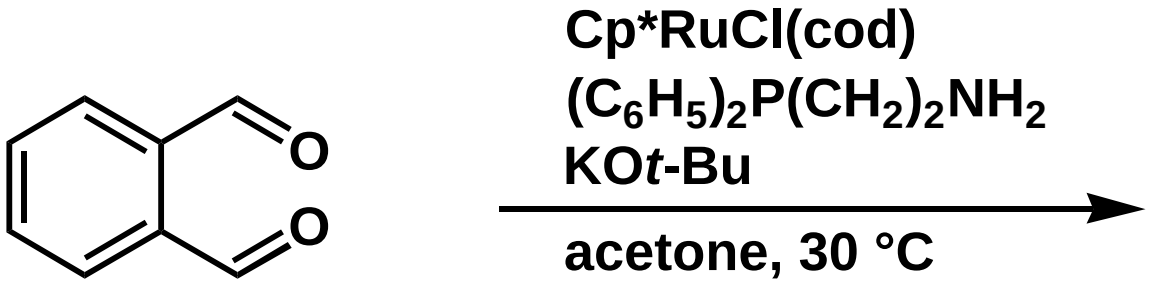
0%

A RAPID LACTONIZATION OF 1,2-BENZENEDIMETHANOL

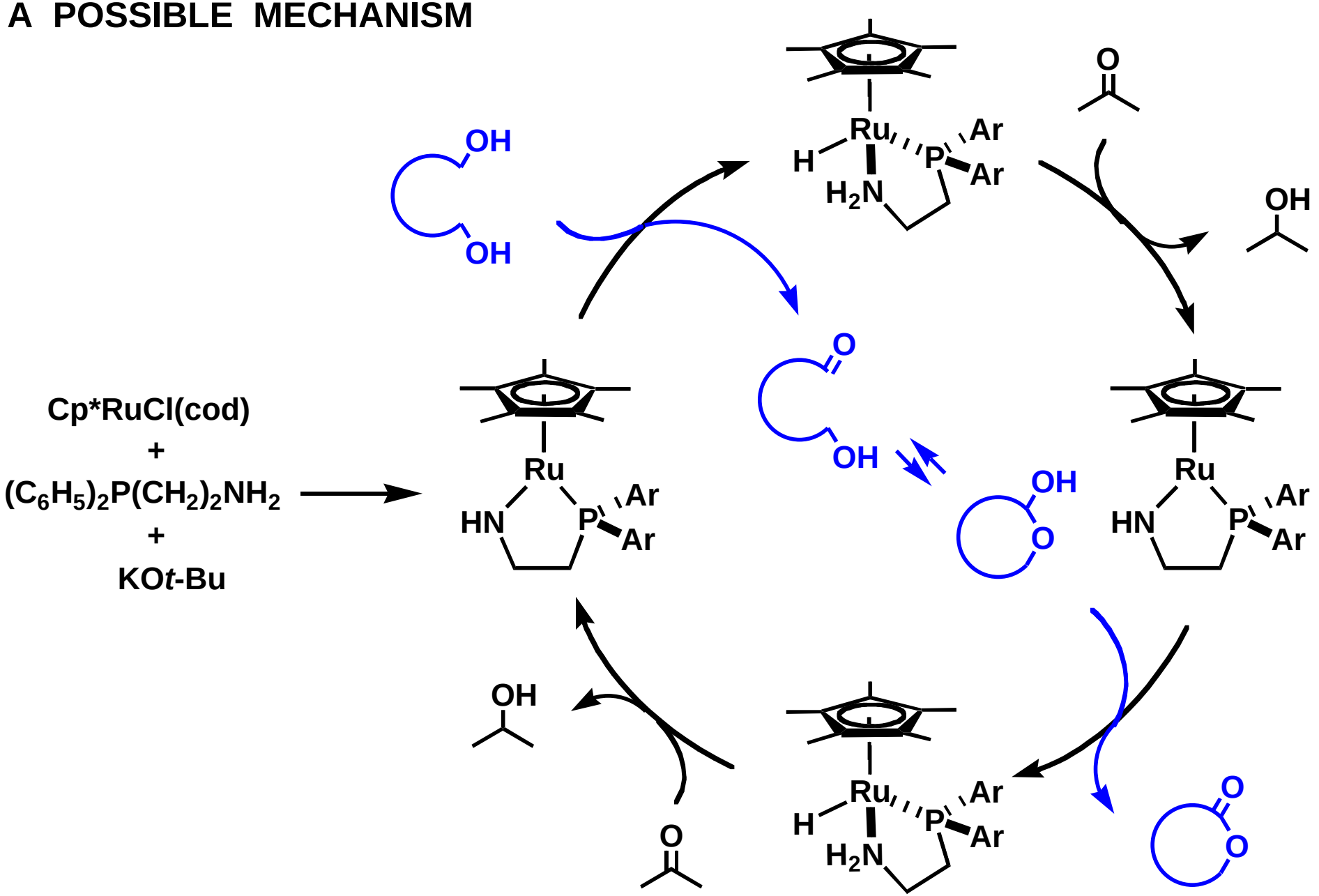


diol:Ru:ligand:KO*t*-Bu = 500:1:1:1, [diol] = 0.5 M 575 TOF/h^{-1}

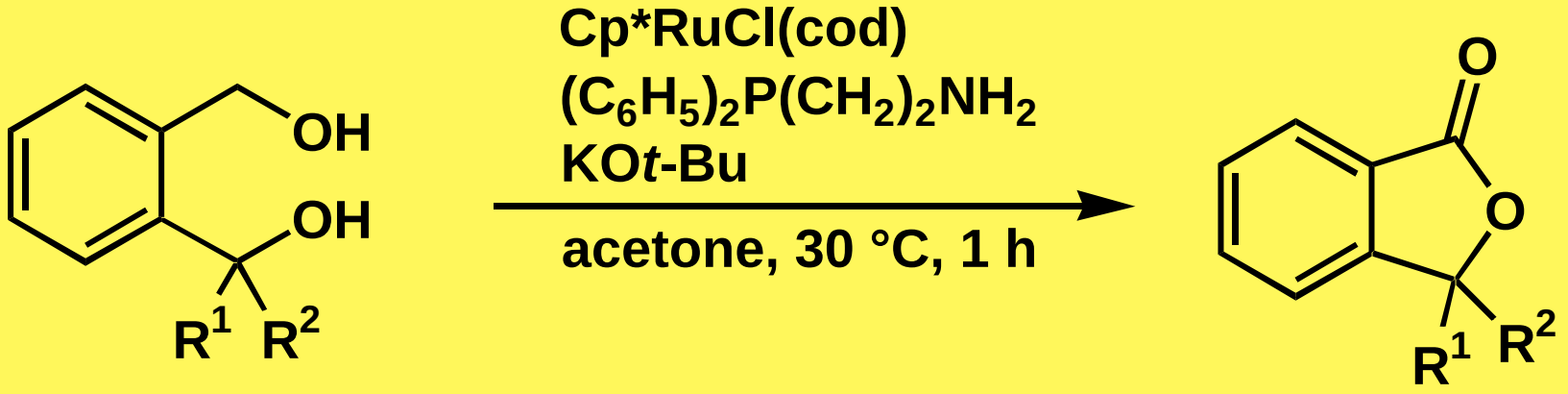




A POSSIBLE MECHANISM



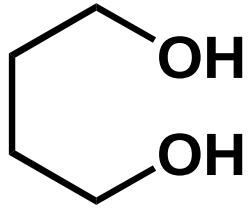
LACTONIZATION OF UNSYMMETRICAL DIOLs



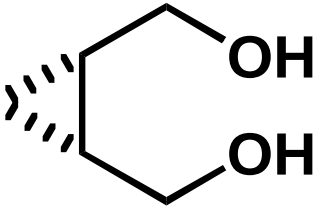
diol:Ru:ligand:KO*t*-Bu = 100:1:1:1, [diol] = 0.5 M

R^1	R^2	yield, %
CH_3	H	>99
CH_3	D (96%)	>99 (96% atom D)
CH_3	CH_3	>99

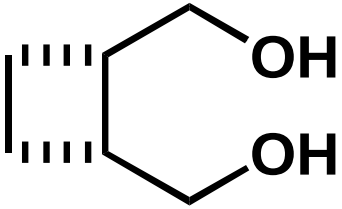
EXAMPLES OF VARIOUS 1,4–DIOLs



>99% yield



>99%



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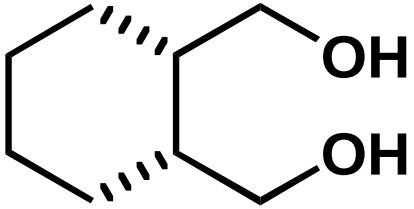

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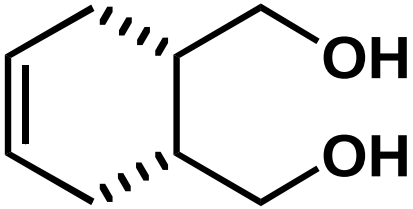

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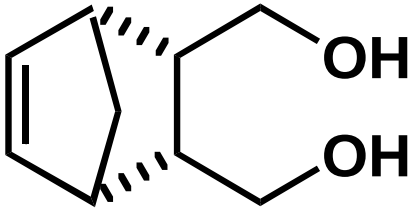

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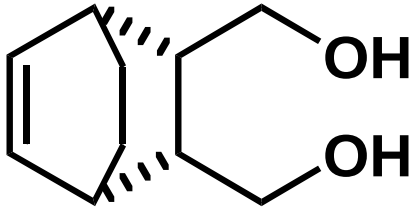
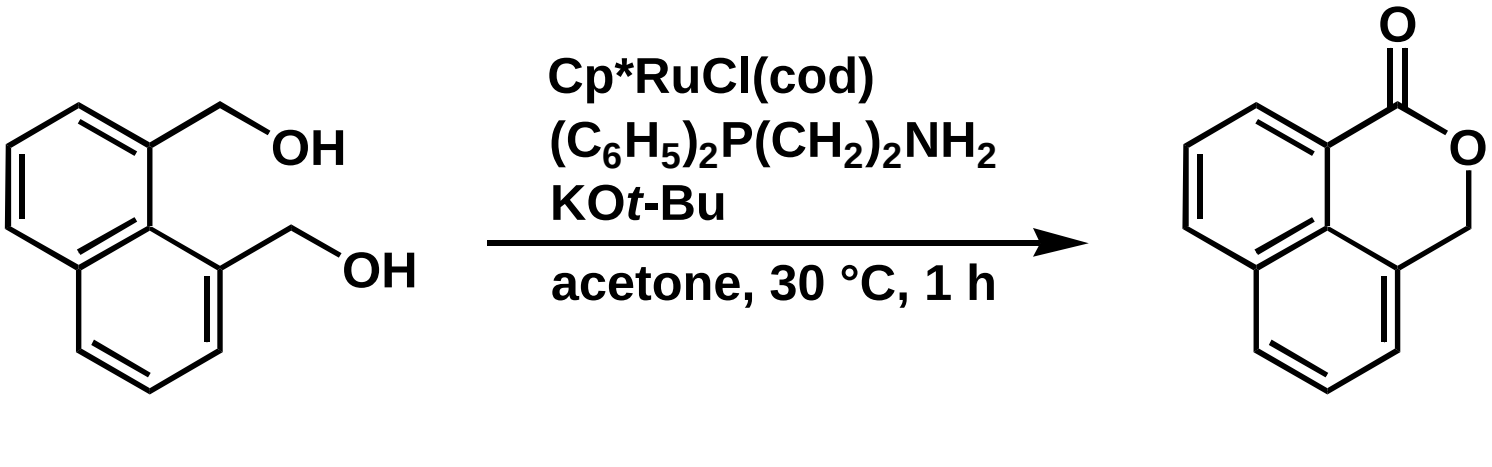


>99%

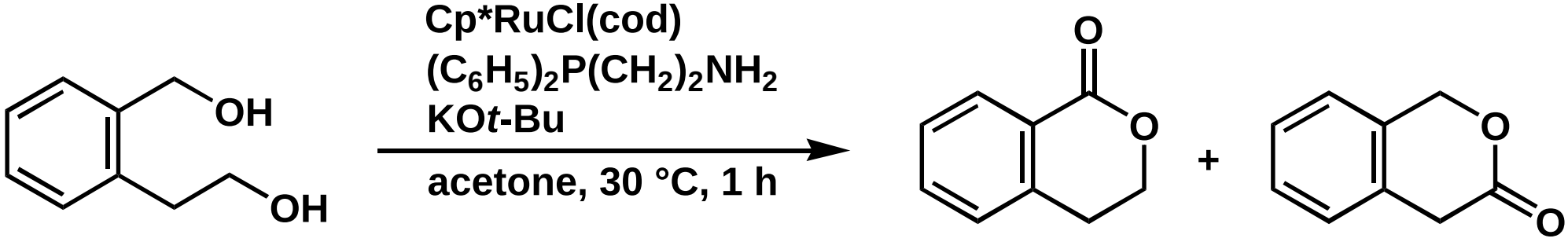
Conditions; diol:Cp*RuCl(cod):$(C_6H_5)_2P(CH_2)_2NH_2$:KO*t*-Bu = 100:1:1:1

[diol] = 0.5 M in acetone, 30 °C, 1 h

EXAMPLES OF 1,5–DIOLs



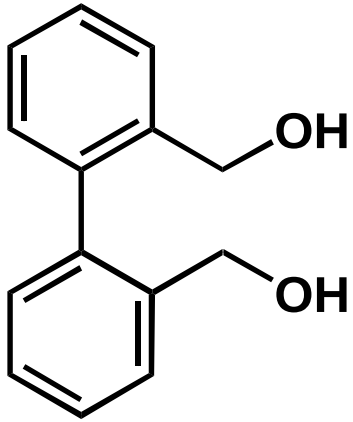
>99% yield



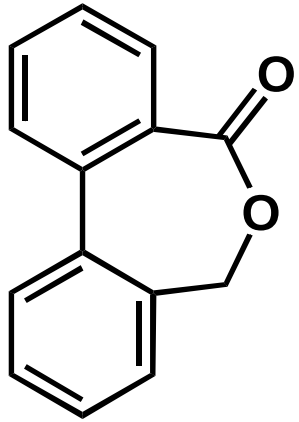
74 : 26
>99% yield

diol:Ru:ligand:KO*t*-Bu = 100:1:1:1, [diol] = 0.5 M

EXAMPLES OF 1,6–DIOLs

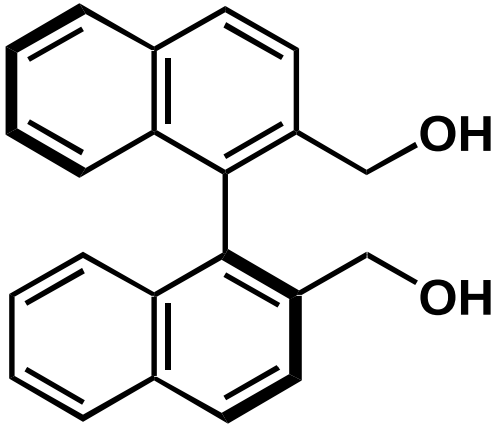


Cp*RuCl(cod)
$(C_6H_5)_2P(CH_2)_2NH_2$
KO*t*-Bu
acetone, 30 °C, 2 h



diol:Ru:ligand:KO*t*-Bu = 100:1:1:1, [diol] = 0.5 M

97% yield

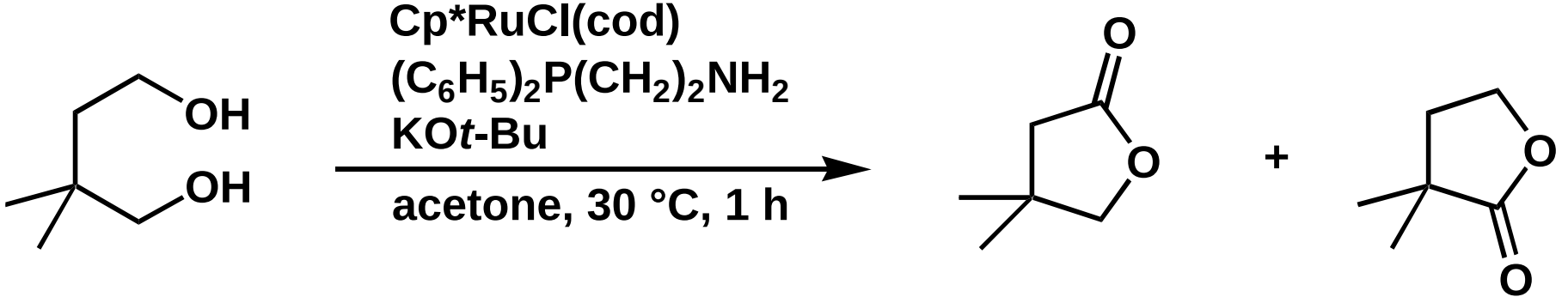


Cp*RuCl(cod)
$(C_6H_5)_2P(CH_2)_2NH_2$
KO*t*-Bu
acetone, 30 °C, 1 h

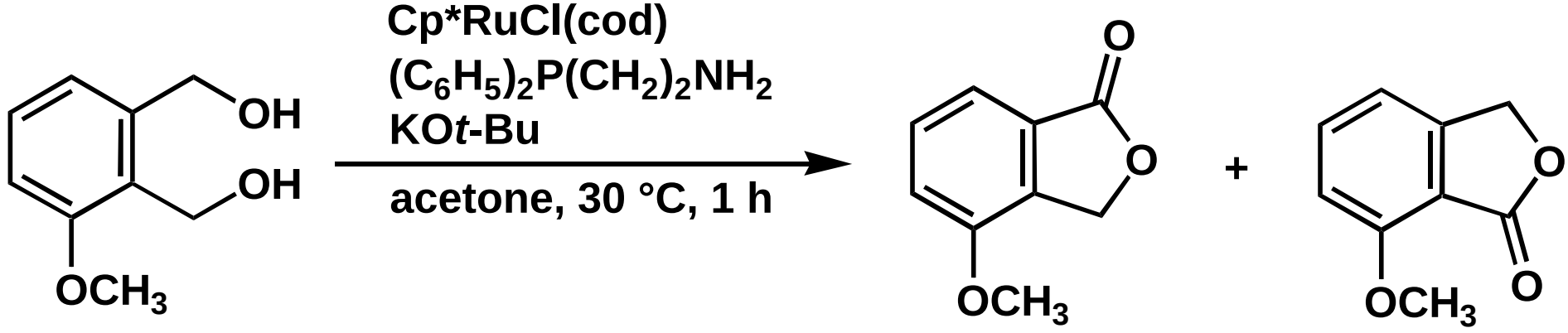
N. R.

diol:Ru:ligand:KO*t*-Bu = 50:1:1.3:1.7, [diol] = 0.25 M

REGIOSELECTIVITY OF LACTONIZATION



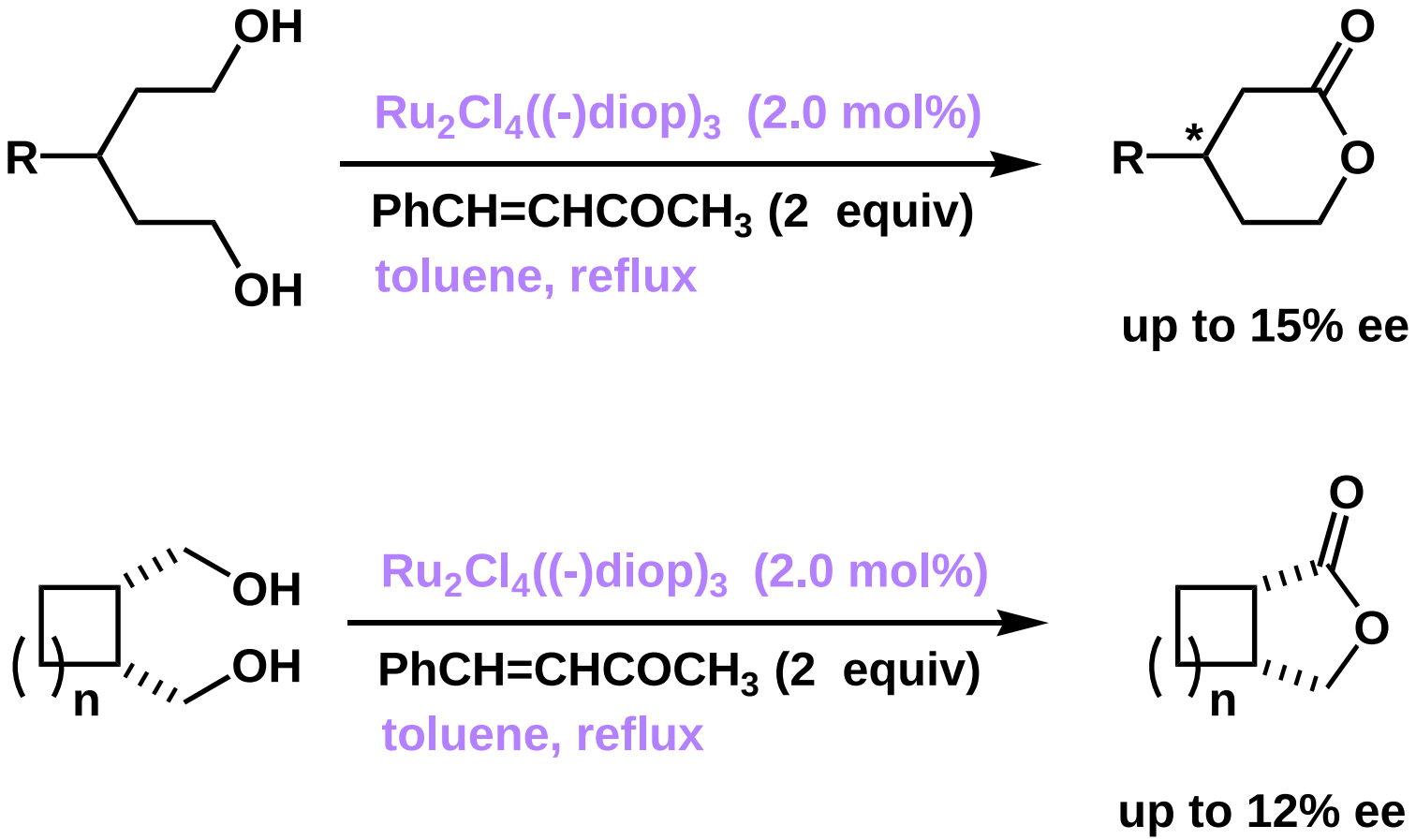
95 : 5
>99% yield



26 : 74
>99% yield

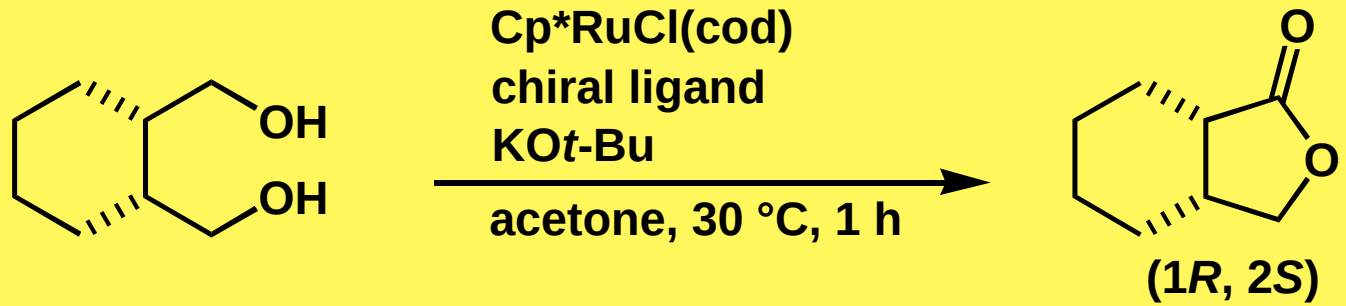
diol:Ru:ligand:KO*t*-Bu = 100:1:1:1, [diol] = 0.5 M

FIRST REPORT ON Ru–CATALYZED ASYMMETRIC LACTONIZATION



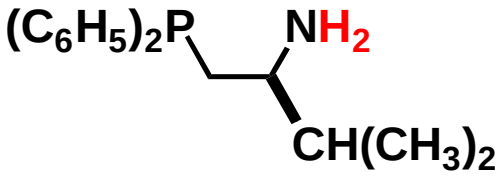
Ishii, Osakada, Ikariya, Saburi, Yoshikawa, *Chem Lett.*, **1982**, 1179.

ENANTIOSELECTIVE LACTONIZATION OF *meso*-DIOL

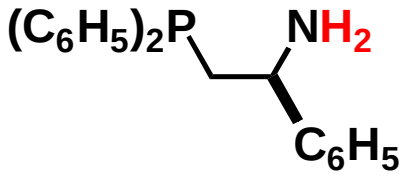


diol:Ru:ligand:KO*t*-Bu = 100:1:1:1, [diol] = 0.5 M >99% yield

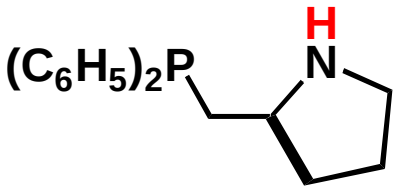
chiral ligand:



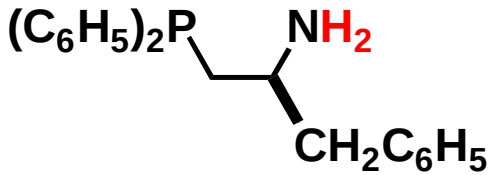
23% ee



18% ee



7% ee



32% ee
44% ee (0°C, 8 h)