Fukuyama Group - Group Meeting Problems
07/01/2009

1) (+)-(Ipc)₂BCl, Et₂N, Et₂O, 0 °C; A, -78 °C; H₂O₂, pH 7 buffer, MeOH, rt
2) Me₂NHB(OAc)₃, MeCN, AcOH, -35 °C
3) PhSeCH₂CH(OEt)₂, PPTS, DME, 85 °C, 67%
4) NaIO₄, EtOAc-MeOH-H₂O, rt
5) OTBS, DBU, m-xylene

A. B. Holmes et al., Synlett, 972 (1999)

2) Me—Cl
n-BuLi
THF
-78 to -40 °C


3) Pd(OAc)₂ (3.0 mol%), n-Bu₄NCl (2.0 equiv), 4-penten-1-ol (1.1 equiv), LiCl (1.0 equiv), LiOAc (3.0 equiv), DMF, rt, 63%
1) Br₂, CHCl₃, rt
2) Aq. NaOH


4) BuLi, THF, 0 °C, 30 min;
(OC)₃Cr, OTMS, Ph, 78 °C to rt;
THF, 90 °C, 3 h; air, sunlight, hexane, 2 h; filtration;
conc. HCl, acetone, rt, 15 min

Fukuyama Group - Group Meeting Problems
07/07/2009

1

\[
\text{asymmetric bicyclic compound}
\]


2


3

F. L. Bideau et al., Synlett., 800 (2007)

4

T. Aoyama et al., Tetrahedron, 64, 1753 (2008)
Fukuyama Group - Group Meeting Problems
07/15/2009

1

\[
\begin{align*}
\text{Me-SO}_3^N \quad + \quad \text{DEAD} \\
\text{1,4-dioxane} \\
10^\circ \text{C to rt, 5 h} \\
\end{align*}
\]

\[
\begin{align*}
\text{Me-SO}_3^N \quad \rightarrow \\
\text{Me-SO}_3^N \\
\end{align*}
\]

76%


2

\[
\begin{align*}
\text{BnO} \quad \text{Me} \\
\text{N} \quad \text{S} \quad \text{O} \\
\text{Boc} \quad \text{iPr} \\
\end{align*}
\]

1) Zn/CuCl
\[
\begin{align*}
\text{Cl}_3\text{CCOCl (excess)} \\
\text{THF,} -5^\circ \text{C} \\
54-55\% \\
\end{align*}
\]

2) \text{n-Bu}_3\text{SnH, AIBN}
\text{toluene, reflux} \\
80-85%


3

\[
\begin{align*}
\text{OMe} \\
\text{Me} \\
\text{Cl} \\
\text{PMBO} \quad \text{OTBS} \\
\end{align*}
\]

1) \text{Cp}_2\text{Zr, BF}_3\text{OEt}_2 \\
\text{toluene} \\
85%

\[
\begin{align*}
\text{OMe} \\
\text{Me} \\
\text{Cl} \\
\text{PMBO} \quad \text{OTBS} \\
\end{align*}
\]

1) \text{DMP, NaHCO}_3, \\
\text{CH}_2\text{Cl}_2, \text{rt, 3 h} \\
2) \text{BrMg-SiMe}_3 \\
\text{THF,} 0^\circ \text{C, 3 h, 65\% (2 steps)} \\
3) 1\% \text{HCl, MeOH, rt, 4 h, 68\%} \\
4) \text{C}_6\text{H}_6, \text{reflux, 4 h, 100\%}


4

\[
\begin{align*}
\text{MeO} \\
\text{MeO}_2\text{C} \quad \text{Cl} \\
\end{align*}
\]

1) m\text{CPBA} \\
\text{CH}_2\text{Cl}_2, \text{rt, 82\%} \\
2) \text{NaOH} \\
\text{MeOH, rt, 71\%} \\
3) \text{TFA} \\
\text{CH}_2\text{Cl}_2, \text{rt, 52\%}

Fukuyama Group - Group Meeting Problems

07/22/2009

1

\[
\text{F}_3\text{C}-\text{I}-\text{CH}_2-\text{NH-Ph} \quad \text{F}_3\text{C}-\text{CH}_2-\text{NH-Ph}
\]

1) DAST, \(\text{CH}_2\text{Cl}_2\), -78 °C, 86%
2) SeO\(_2\), dioxane microwave, 110 °C, 62%
3) \(\text{H}_2\) (1 atm), Pd\(_2\)O
   \(\text{CH}_2\text{Cl}_2\), 67%
   dr 19:1

Pigza et al., J. Org. Chem., DOI: 10.1021/jo900654y

2

\[
\text{O-Me, CO}_2\text{Me} \quad \text{CO}_2\text{Me}
\]

1) CAN(2.2 eq)
   MeCN-H\(_2\)O, rt 99%
2) \(\text{Et}_3\text{N}, \text{CH}_2\text{Cl}_2\)
   0 °C to rt 94%
3) CAN(2.1 eq)
   H\(_2\)O-MeCN(1:1), 0 °C, 99%
4) K\(_2\)CO\(_3\)(5 eq)
   DMF, 100 °C 70%


3

\[
\text{O} \quad \text{COOMe}
\]

1) \(\text{Et}_3\text{N}, \text{TMSCl}, \text{DMF}\)
2) \(\text{n-BuLi}, 1,1\)-dichloroethane anhydrous ether, -30 °C to rt
3) toluene, \(\Delta\)
4) TIPSOTf, diisopropylethylamine
   \(\text{CH}_2\text{Cl}_2\), -78 °C to rt, 90%
5) methyl propiolate, Et\(_2\)Cl
   \(\text{CH}_2\text{Cl}_2\), -40°C to rt, 92%

MeOOCCO


4

\[
\text{OH} \quad \text{O}_3
\]

1) Pd(OAc)\(_2\) (2.5 mol%)
   dppe (2.5 mol%)
   CF\(_3\)CO\(_2\)H-AcOH
   reflux, 65%
2) \(\text{O} \quad \text{O}_3\)
   (1.2 eq)
   toluene, reflux, 86%
3) LAH (3 eq)
   THF
   0 °C to 60 °C
   78%
4) Tricyclic compound
   methylcyclohexane chloroform pyridine (cat.)
   -60 °C
   30%

M. Santelli et al., Tetrahedron, 63, 9100 (2007)