Concise asymmetric synthesis of (−)-bilobalide

M. A. Baker, R. M. Demoret, M. Ohtawa, R. A. Shenvi

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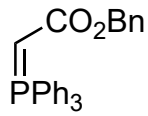
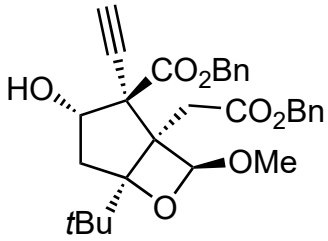


1-9



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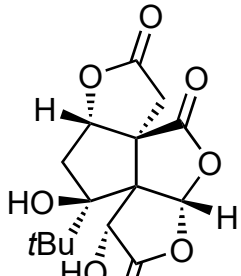
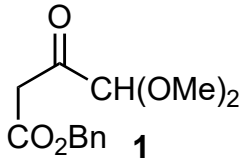
10-12

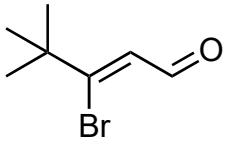


(–)-bilobalide

1) Br_2
2) **1**
3) **2**, **3**, Et_2Zn
4) Bu_3SnH, AIBN
5) $Mn(dmp)_3$, $Ph(iPrO)SiH_2$, C_7H_{14}, O_2
6) **4**
7) IBX
8) **5**, *then* TBAF
9) SmI_2



1



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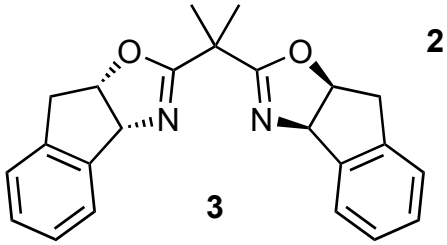

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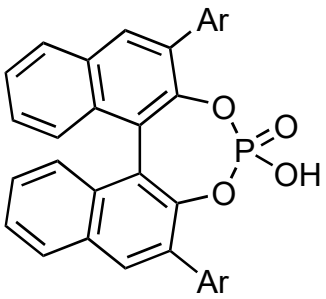
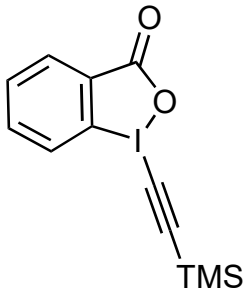


Ar = 9-phenanthryl

4

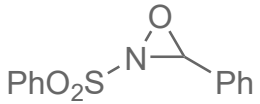


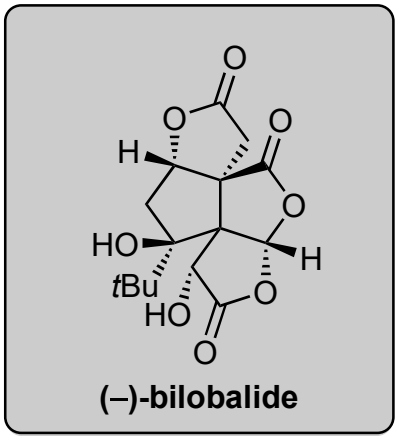
5

10) LiHMDS, $B(OMe)_3$, *then* *m*CPBA
11) H_2, Pd/C, *then* 3 M HCl, 80 °C
12) Bz_2O, DMAP, *then* KHMDS, Davis reagent, *then* 3 M HCl

2) Name the reaction
2) How can you prepare **1**?
Wittig olefination
3) Name the reaction
3) How can you prepare **2**?
Reformatsky
4) Name the Reaction
4) Explain the observed diastereoselectivity
Giese
5) Name the reaction
Mukaiyama Hydration

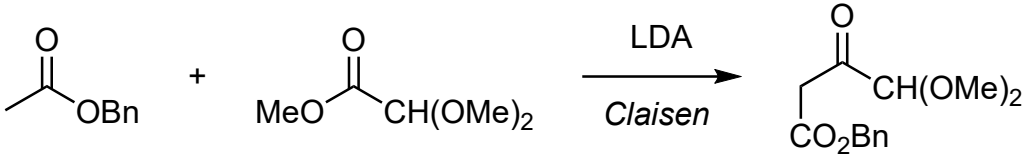
10) Provide a possible mechanism for alkyne oxidation
12) Show the structure of both intermediates
12) Structure of Davis reagent?



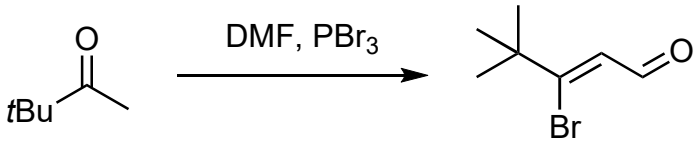


(–)-bilobalide

Preparation of 1:

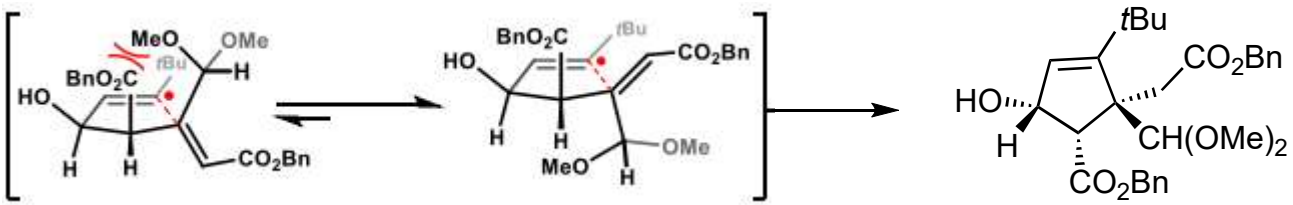


Preparation of 2:

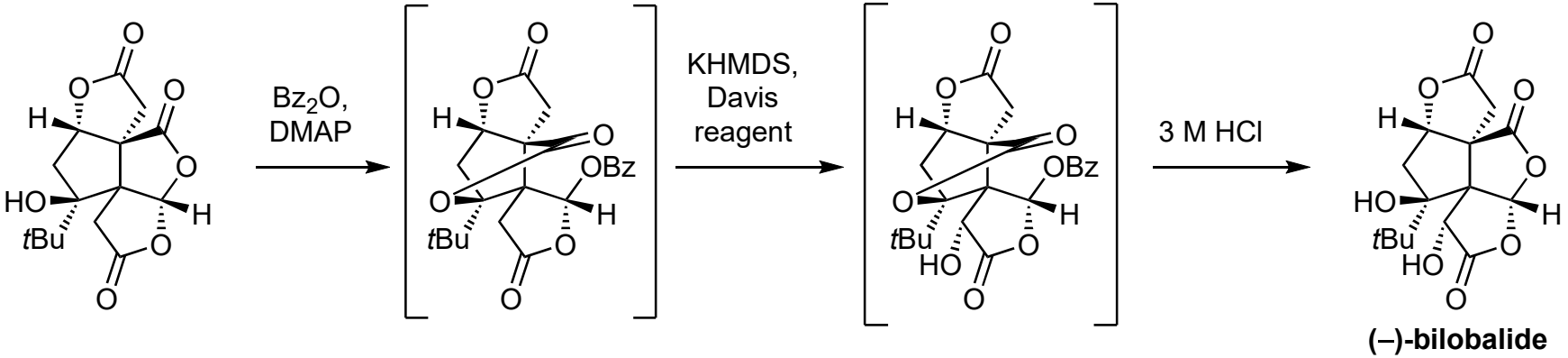


pinacolone

Diastereoselectivity model for step 4:



Step 12:



A possible reaction mechanism for alkyne oxidation for step 10:

Org. Lett. **2021**, *23*, 7, 2831-2835.