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Citation:

Total Synthesis of (+)-Xestoquinone Using an Asymmetric Palladium-Catalyzed Polyene Cyclization
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Abstract:

The first total asymmetric synthesis of (+)-xestoquinone (1) has been accomplished in 68% ee by a palladium(0)-catalyzed polyene cyclization of naphthyl triflate 44 using (S)-(+)-BINAP as the chiral ligand. Attempts at an asymmetric polyene cyclization using the corresponding naphthyl bromide 41 gave poor enantioselectivities even in the presence of silver salts, thus exemplifying the effect of the coordination state of palladium on the enantioselectivity. A new method for the preparation of 6,7-dihydroisobenzofurans is also described using a [1,2]-Wittig rearrangement on a seven-membered cyclic ether precursor.

Schemes:
Scheme 2

Scheme 3

a Reagents: (a) 2.2 equiv of n-BuLi, DME, 0 °C, 1 h; then add (MeO)B, 0 °C, 1 h; then add (1-MeO)B, 10% Na2CO3, 80 °C, 4 h; and (i) 2,3-iodo-2-butenone (88%), or (ii) 2,3-iodo-2-butenone (86%); or (iii) 2,3-iodo-2-butenone (86%); (b) acetonitrile, 0 °C (50-60%); (c) THF, 20 °C (86%); (d) THF, 0 °C (94%); (e) ether, -78 °C, 5 min, then 0 °C 1 h (92%, 17).

a Reagents: (a) imidazole, DMF (69%); (b) TMEDA, THF, -78 °C, 1 h; then 2-bromobenzaldehyde (73%); (c) Pd(PPh3)4, Ag2CO3, toluene, 110 °C; (d) AIBN, benzene, reflux.
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