Axially Chiral Amidinium Ions as Inducers of Enantioselectivity in Diels-Alder Reactions

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Supporting Information: Chemical correlation of compound 5a with (+)-estrone[1]

The tetraphenyl borate salt of amidine **8** (380 mg, 0.49 mmol) and diketone **2a** (54 mg, 0.49 mmol) were dissolved in 15 ml dry CH_2Cl_2 and cooled to -25 °C. A solution of diene **1** (135 mg, 0.73 mmol) in 1 ml CH_2Cl_2 was added and the mixture kept at -25 °C for 14 d. Purification of the cycloadducts by flash chromatography on 25g silica gel (ethyl acetate / hexane, 1 : 4) without separation of the isomers yielded 128 mg of **5** + *ent*-**5** + **6** + *ent*-**6** (0.43 mmol, 88 %). The mixture was treated at 20 °C for 15 h with 1.3 eq. TBDPS chloride and 2.6 eq. imidazole in 5 ml DMF. After filtration over 25 g silica (ethyl acetate / hexane 1 : 10), a ratio of (**10** + *ent*-**10**) / (**11** + *ent*-**11**) = 2.5 : 1 was determined by analytical HPLC (Macherey Nagel 50-10; (methyl acetate / hexane, 1 : 33) + 25 % CH_2Cl_2). Preparative HPLC using the same solvent and silica type produced 139 mg of (**10** + *ent*-**10**) (0.26 mmol) and 49 mg of (**11** + *ent*-**11**) (0.09 mmol), each as a colorless solid.

The mixture of **10** and *ent*-**10** was treated with 4 eq of TBAF in 5 ml dry THF. After complete deprotection, washing of the solution with aqueous NH_4Cl, reextraction with ethyl ether and drying ($MgSO_4$) yielded **5** + *ent*-**5**. This mixture was dissolved in 5 ml CH_2Cl_2 together with 7 drops of concentrated aqueous HCl and stirred vigorously for 30 min at 20 °C. The dried ($MgSO_4$) and evaporated residue of **12** + *ent*-**12** was then silylated with TBDPS chloride as described before. A second preparative HPLC purification finally afforded a mixture of **13** + *ent*-**13** (conditions: see above).

Specific optical rotation at 20 °C: $[\alpha]_{589}$ = -30.2° (c = 0.981 in $CHCl_3$). Compound **13** ($[\alpha]_{589}$ = +201.5°; >97.6 % ee) has been already transformed into natural (+)-estrone.[2] Comparison of the optical rotations shows that amidine **8** has induced 15 % ee in favor of *ent*-**13** (unnatural configuration). The spectroscopic data of compounds **10** to **13** are already published.[2]

(1) M. Bauch, Ph. D. thesis, University of Frankfurt am Main 1993

(2) Quinkert, G.; Del Grosso, M.; Döring, A.; Döring, W.; Schenkel, R. I.; Bauch, M.; Dambacher, G. T.; Bats, J. W.; Zimmermann, G.; Dürner, G. *Helv. Chim. Acta* **1995**, *78*, 1345.