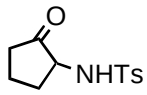
Supplementary Information for *Chem. Commun.*

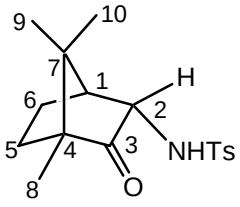
Amidation of Silyl Enol Ethers and Cholesteryl Acetates with Chiral Ruthenium(II) Schiff-Base Catalysts: Catalytic and Enantioselective Studies

Jiang-Lin Liang, Xiao-Qi Yu and Chi-Ming Che*

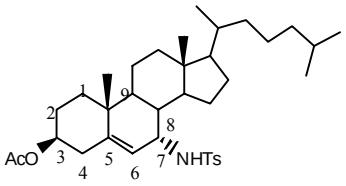
Department of Chemistry and Open Laboratory of Chemical Biology of the Institute of Molecular Technology for Drug Discovery and Synthesis, The University of Hong Kong, Pokfulam Road, Hong Kong, and Shanghai-Hong Kong Joint Laboratory on Chemical Synthesis, Shanghai Institute of Organic Chemsitry, Shanghai, China. Email: cmche@hku.hk

1. 

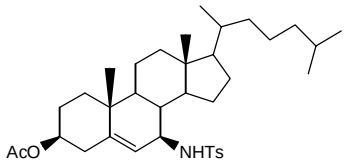
EI MS *m/z* 253 (M^+); HRMS *m/z* (M^+) calcd. for $C_{12}H_{15}NO_3S$ 253.0773, found 253.0778; ^{1}H NMR ($CDCl_3$) δ 7.75 (d, 2H, *J* = 8.3 Hz Ar-H), 7.30 (d, 2H, *J* = 8.1 Hz Ar-H), 3.64 (t, 1H, CH-N), 2.55 (m, 2H, CH_2), 2.42 (m, 2H, CH_2), 2.36 (m, 2H, CH_2).

2. 

mp 111-112 °C (literature 1: 110°C); HRMS *m/z* ($[M-CH_3]^+$) calcd. for $C_{16}H_{20}NO_3S$ 306.1164, found 306.1238; ^{1}H NMR ($CDCl_3$) δ 7.89 (d, 2H, *J* = 8.3 Hz Ar-H), 7.36 (d, 2H, *J* = 8.0 Hz Ar-H), 3.94 (1H, m, C_2-H), 2.66 (1H, t, C_1-H), 2.49 (1H, m, C_6-H), 2.45 (3H, s, Ts-CH_3), 1.94 (2H, m, C_6-H), 1.80 (2H, m, C_5-H), 1.03 (3H, s, C_9-H), 0.92 (3H, s, C_8-H), 0.79 (3H, s, C_{10}-H). ^{13}C NMR ($CDCl_3$) δ 207.1, 144.8, 138.2, 129.7, 128.7, 72.8, 59.5, 46.7, 45.7, 29.7, 21.7, 21.6, 19.5, 18.3, 9.6. There is no NOESY signal between C_2-H and C_5-H, or C_6-H, so the configuration of product is *endo*.



3.. MS *m/z* 597 ($[M]^+$); HRMS *m/z* ($[M\text{-}AcO]^+$) calcd. for $C_{34}H_{51}NO_2S$ 537.3641, found 537.3632; ^1H NMR ($CDCl_3$) δ 7.75 (d, 2H, *J* = 8.3 Hz, Ar-H), 7.31 (d, 2H, *J* = 8.0 Hz, Ar-H), 4.98 (d, *J*=4 Hz, 1H, H_6), 4.47 (m, 1H, H_3), 4.10 (d, 1H, *J* = 9.8 Hz, NH), 3.60 (m, 1H, H_7), 2.37 (s, 3H, Ts-CH_3), 2.02 (s, 3H, CH_3CO_2), 2.20~0.63 (m, 41H, steroid envelope). There is no NOESY signal between H_7 and H_3. So the configuration of NHTs group is α. The ^1H NMR data are also same as reported in literature 2.



5. MS m/z 597 ($[M]^+$); HRMS m/z ($[M\text{-}AcO]^+$) calcd. for $C_{34}H_{51}NO_2S$ 537.3641, found 537.3647; ^1H NMR ($CDCl_3$) δ 7.73 (d, 2H, *J* = 8.2 Hz, Ar-H), 7.30 (d, 2H, *J* = 8.2 Hz, Ar-H), 4.76 (s, 1H, H_6), 4.51 (m, 1H, H_3), 4.04 (d, 1H, *J* = 9.2 Hz, NH), 3.65 (t, 1H, H_7), 2.44 (s, 3H, Ts-CH_3), 2.00 (s, 3H, CH_3CO_2), 2.20~0.85 (m, 40H, steroid envelope). There is NOESY signal between H_7 and H_3. So the configuration of NHTs group is β.

Preparation of ruthenium(II) salen complexes. A solution of H_2salen (200 mg) in ethanol was purged with argon for 20 min. $[Ru^{II}(PPh_3)_3Cl_2]$[3] (400 mg) and triethylamine (1 ml) was subsequently added. The solution mixture was refluxed for 12 h under argon atmosphere. A deep-colored solid gradually formed. The solution was cooled to room temperature and the solid was collected. The complex was recrystallized by diffusion of diethyl ether into dichloromethane solution. Yield: ~ 80%.

Reference:

1. R. A. Chittenden and G. H. Copper, *J. Chem. Soc., C*, 1970, 49.

2. D. H. R. Barton, R. S. Hay-Motherwell and W. B. Motherwell, *J. Chem. Soc., Perkin Trans. 1*, 1983, 445.
3. *T. A. Stephenson and G. Wilkinson, J. Inorg. Nucl. Chem.,* 1966, **28**, 945.