Supplementary Material for:

$TiCl_4$ Mediated Reduction of 1,3-Diketones with BH_3-pyridine Complex: a Highly Diastereoselective Method for the Synthesis of *syn*-1,3-Diols.

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General Considerations: Flash chromatography was performed on Merck silica gel (0.040-0.063 nm). All reactions were carried out in oven dried glassware under dry argon atmosphere. ^{1}H-NMR, J-resolved and decoupling experiments were recorded at 300 MHz with a Varian Gemini instrument. ^{13}C-NMR and DEPT experiments were acquired at 75 MHz with a Varian Gemini instrument. Chemical shifts are given in p.p.m. from Me_4Si. Coupling constants are given in Hertz.

Benzoyl acetone (1a), 6-methyl-2,4-heptanedione (1b), 2,2,5,5-tetramethyl-3,5-heptanedione (1e) and **dibenzoylmethane (1g)** are commercially available. **6-Phenyl-2,4-hexanedione (1c), 5-methyl-1-phenyl-2, 4-hexanedione (1d)** and **1-*p*-Cl-phenyl-1, 3-hexanedione (1f)** were obtained by hydrolysis (HCl, MeOH, H_2O, overnight) from the corresponding enaminoketones.[1]

Compound **6-phenyl-2, 4-hexanedione (1c)**[2] was recognized by comparison with literature data. Selected spectroscopic data for unknown products follow.

5-methyl-1-phenyl-2, 4-hexanedione (1d): ^{1}H NMR: 1.11 (d, 6H, $2CH_3$, J_{HH}=6.9), 1.7 (bs, 1H, OH), 2.35-2.50 (m, 1H, $CHMe_2$), 3.60 (s, 2H, CH_2), 5.46 (s, 1H, CH), 7.20-7.40 (m, 5H, Ph); $C_{13}H_{16}O_2$: calcd. C 76.43, H 7.90; found C 76.56, H 7.74.

1-*p*-Cl-phenyl-1, 3-hexanedione (1f): ^{1}H NMR: 1.24 (t, 3H, CH_3, J_{HH}=7.3), 1.85-2.10 (m, 2H, CH_2), 2.60-2.75 (m, 2H, CH_2), 2.9 (bs, 1H, OH), 6.29 (s, 1H, CH), 7.50-7.90 (m, 4H, Ph); ^{13}C NMR: 13.6 (CH_3), 19.0 (CH_2), 40.6 (CH_2), 101.1 (CH), 195.5 (C); $C_{12}H_{13}ClO_2$: calcd. C 64.27, H

General procedure for the reduction of 1,3-diketones 1a-g: To a CH_2Cl_2 solution of 1,3-diketone **1** (0.2 g, 1eq) 1.1 eq of $TiCl_4$ (solution 1M in CH_2Cl_2) and 0.1 eq of pyridine are added at –30°C. After 30 min the mixture is cooled to –78°C and an excess of BH_3-py (3-4 eq, solution 8M in pyridine) is added. After 2h the reaction is quenched with aqueous HCl (1 M). Then the reaction mixture is treated following Method A or Method B procedure:

Method A: The organic layer is separated, dried over $MgSO_4$ and the solvent is removed on a rotary evaporator. The crude product, a mixture of *syn*-**2** and of a boron cyclic derivative *syn*-**3**, is submitted to treatment with H_2O_2 in basic medium (EtOH, NaOH).[3] After 3 days, the mixture is diluted with H_2O and extracted with Et_2O. The organic layer, separated and dried over $MgSO_4$, is concentrated under reduced pressure to give *syn*-**2**, which is purified by column chromatography on silica gel (petroleum ether/Et_2O= 70/30).

Method B: After quenching the reaction with aqueous HCl (1 M) the mixture is left to stir overnight. The organic layer, separated and dried over $MgSO_4$, is concentrated under reduced pressure to give *syn*-**2**, which is purified by column chromatography on silica gel (petroleum ether/Et_2O= 70/30).

Compounds **(1R*, 3R*)-1-phenyl-1,3-propanediol (*syn*-2a)[4], (3R*, 5S*)-2,2,5,5-tetramethyl-3,5-heptanediol (2e)**[5], **(1R*, 3S*)-1,3-diphenyl-1,3-propanediol (2g)[6]** were recognized by comparison with literature data. Selected spectroscopic data for unknown products follow.

(4R*, 6R*)-4-methyl-6-phenyl-1,3,2-dioxaborinan-2-ol (*syn*-3a): ^{1}H NMR: 1.30 (d, 3H, CH_3, J_{HH}=6.2), 1.55-1.70 (m, 1H, CH_2), 2.05-2.20 (m, 1H, CH_2), 4.25-4.40 (m, 1H, CHMe), 5.10 (dd, 1H, CH, J_{HH}=2.8, J_{HH}=11.5), 7.25-7.40 (m, 5H, Ph).

(2R*, 4S*)-6-methyl-2, 4-heptanediol (2b): ^{1}H NMR: 0.94 (d, 6H, $2CH_3$, J_{HH}=6.5), 1.22 (d, 3H, CH_3, J_{HH}=6.2), 1.15-1.35 (m, 2H, CH_2), 1.40-1.60 (m, 2H, CH_2), 1.70-1.85 (m, 1H, $CHMe_2$), 2.8 (bs, 2H, OH), 3.90-4.00 (m, 1H, CH, J_{HH}=2.5, J_{HH}=8.3), 4.05-4.15 (m, 1H, CH, J_{HH}=2.7, J_{HH}=8.5); ^{13}C NMR: 22.1 (CH_3), 23.2 (CH_3), 23.9 (CH_3), 24.2 (CH), 45.0 (CH_2), 47.3 (CH_2), 68.9 (CH), 70.9 (CH); $C_7H_{18}O_2$: calcd. C 62.63, H 13.52; found C 62.80, H 13.44.

(2R*, 4S*)-6-phenyl-2, 4-hexanediol (2c): ^{1}H NMR: 1.21 (d, 3H, CH_3, J_{HH}=6.1), 1.55-1.65 (m, 2H, CH_2), 1.70-1.85 (m, 2H, $C\underline{H_2}CH_2Ph$), 2.60-2.80 (m, 2H, CH_2Ph), 3.5 (bs, 2H, OH), 3.85-3.95

J_{HH}=6.1), 7.15-7.35 (m, 5H, Ph); ^{13}C NMR: 24.1 (CH_3), 31.6 (CH_2), 39.6 (CH_2), 44.4 (CH_2), 69.3 (CH), 72.4 (CH); $C_{12}H_{18}O_2$: calcd. C 74.18, H 9.34; found C 3.97, H 9.42.

(2R*, 4R*)-5-methyl-1-phenyl-2, 4-hexanediol (2d): ^{1}H NMR: 0.80 (d, 3H, CH_3, J_{HH}=6.8), 0.81 (d, 3H, CH_3, J_{HH}=6.8), 1.35-1.60 (m, 3H, CH and CH_2), 2.67 (d, 2H, CH_2Ph, J_{HH}=6.5), 3.3 (bs, 2H, OH), 3.45-3.55 (m, 1H, CH, J_{HH}=3.6, J_{HH}=9.5, J_{HH}=6.8), 3.90-4.00 (m, 1H, CH, J_{HH}=2.2, J_{HH}=9.6, J_{HH}=6.5), 7.10-7.30 (m, 5H, Ph); ^{13}C NMR: 17.3 (CH_3), 18.2 (CH_3), 34.0 (CH), 38.7 (CH_2), 44.6 (CH_2), 74.0 (CH), 77.4 (CH); $C_{13}H_{20}O_2$: calcd. C 74.95, H 9.68; found C 75.16, H 9.84.

(1R*, 3R*)-1-*p*-Cl-phenyl-1, 3-hexanediol (2f): ^{1}H NMR: 0.84 (t, 3H, CH_3, J_{HH}=7.1), 1.20-1.45 (m, 4H, 2CH_2), 1.52 (dt, 1H, CH_2, J_{HH}=10.1, J_{HH}=14.9), 1.83 (dt, 1H, CH_2, J_{HH}=2.2, J_{HH}=14.9), 3.3 (bs, 1H, OH), 3.90-4.00 (m, 1H, CH, J_{HH}=10.1, J_{HH}<1), 4.1 (bs, 1H, OH), 5.22 (dd, 1H, CH, J_{HH}=10.1, J_{HH}=2.2), 7.10-7.60 (m, 4H, Ph); ^{13}C NMR: 14.0 (CH_3), 18.4 (CH_2), 40.1 (CH_2), 43.4 (CH_2), 71.7 (CH), 72.9 (CH); $C_{13}H_{17}ClO_2$: calcd. C 63.13, H 7.51; found C 63.27, H 7.74.

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