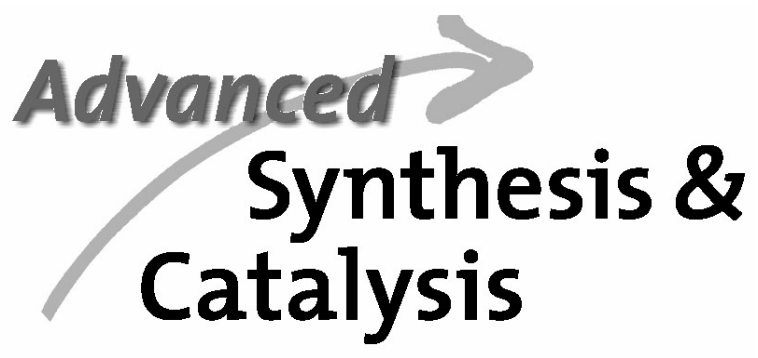

Supporting Information

Highly efficient threonine-derived organocatalysts for the direct asymmetric aldol reactions in water

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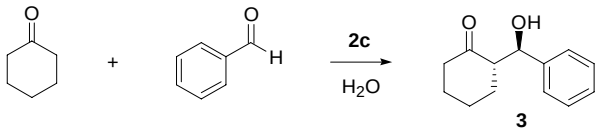
General methods

Chemicals and solvents were purchased from commercial suppliers and used as received. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ACF300 (300MHz) or AMX500 (500MHz) spectrometer. Chemical shifts are reported in parts per million (ppm), and the residual solvent peak was used as an internal reference. Low resolution mass spectra were obtained on a VG Micromass 7035 spectrometer in EI mode, a Finnigan/MAT LCQ spectrometer in ESI mode, and a Finnigan/MAT 95XL-T mass spectrometer in FAB mode. All high resolution mass spectra were obtained on a Finnigan/MAT 95XL-T spectrometer. For thin-layer chromatography (TLC), Merck pre-coated TLC plates (Merck 60 F_{254}) was used, and compounds were visualized with a UV light at 254 nm. Further visualization was achieved by staining with 5% ninhydrin in ethanol, ceric molybdate or $KMnO_4$ solution followed by heating on a hot plate. Flash chromatography separations were performed on Merck 60 (0.040 - 0.063mm) mesh silica gel. All the aldol reactions were performed under an atmosphere of argon in a closed system at ambient temperature. The assignments of *syn* and *anti* isomers and the diastereomeric ratios of the aldol products were determined by ^{1}H NMR analysis of the crude products. The enantiomeric excesses were determined by chiral-phase HPLC analysis.

All the substrates are commercially available and used as received: cyclohexanone (108-94-1), benzaldehyde (100-52-7), 4-nitrobenzaldehyde (555-16-8), 3-nitrobenzaldehyde (99-61-6), 2-nitrobenzaldehyde (552-89-6), 4-cyanobenzaldehyde (105-07-7), 4-bromobenzaldehyde (1122-91-4), 2-naphthaldehyde (66-99-9), 1-naphthaldehyde (66-77-3), 4-methoxybenzaldehyde (123-11-5), 3-methoxybenzaldehyde (591-31-1).

The representative procedure for the aldol reactions in water



3

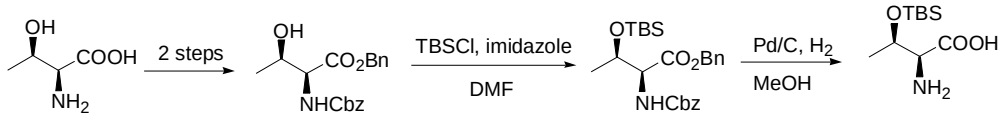
To a mixture of catalyst **2c** (4.6 mg, 0.02 mmol) and cyclohexanone (0.2 ml, 2 mmol) were added benzaldehyde (102 μL, 1 mmol) and water (18 μL, 1 mmol). The resulting mixture was stirred at room temperature under an atmosphere of argon for 45 hours. The reaction mixture was diluted with ethyl acetate and filtered through silica gel (1 g) to remove the catalyst. The solvent was removed *in vacuo* to afford the crude product as a

pale yellow oil, which was purified by column chromatography (ethyl acetate:hexane = 1:10 to 1:5) to afford **3** as a colorless oil (117 mg, 58%).
Anti:*syn* = 8:1. *ee* of the *anti* isomer 96% (by chiral HPLC analysis using a chiralcel AS-H column, λ = 210 nm, *i*-PrOH:hexane = 5:95, 0.5 mL/min, t_R = 33.45 min (major), t_R = 35.58 min (minor)). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.25-1.30 (m, 1H), 1.59-1.90 (m, 4H), 2.05-2.20 (m, 1H), 2.35-2.75 (m, 3H), 4.80-4.85 (d, *J* = 8.4 Hz, 1H), 7.30-7.45 (m, 5H).

The recycling of the catalyst 2c

To a mixture of catalyst **2c** (46 mg, 0.2 mmol) and cyclohexanone (1.6 mL, 16 mmol) were added benzaldehyde (408 μL, 4 mmol) and water (72 μL, 4 mmol). The mixture was stirred at room temperature under an atmosphere of argon for a period of time as specified in Table 3. The reaction mixture was then diluted with ethyl acetate (10 mL) and washed with water (5 mL). The organic layer was diluted with hexane (40 mL) and filtered through silica gel (4 g). The silica gel was washed with methanol (10 mL). The layers of methanol and water were combined and concentrated *in vacuo* to recover **2c**, which was used directly in the next run. The solution of ethyl acetate and hexane was concentrated to afford a pale yellow oil, which was purified by flash column chromatography (ethyl acetate:hexane = 1:10 to 1:5) to afford **3** as a colorless oil.
The above procedure was repeated for the 2nd and 3rd runs.

The synthesis of the catalysts



2c

N-Benzyloxycarbonyl-L-threonine benzyl ester: This compound was prepared according to the literature procedure.[1]
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19-1.28 (d, *J* = 6.4 Hz, 3H), 1.80-2.20 (br, 1H), 4.20-4.45 (m, 2H), 5.05-5.30 (m, 4H), 5.60 (br, 1H), 7.30-7.40 (m, 10H); $[\alpha]_D^{20}$ = -11 (c = 8.1, $CHCl_3$).

N-Benzyloxycarbonyl-O-(*tert*-Butyldimethylsiloxy)-L-threonine benzyl ester:
N-Benzyloxycarbonyl-L-threonine benzyl ester (1.372 g, 4 mmol) was dissolve in minimum amount of anhydrous DMF. To this solution was added TBSCl (0.752 g, 5 mmol) and imidazole (0.544 g, 8 mmol), respectively. After stirring at room temperature for 30 hours, the reaction mixture was diluted with ether and washed with water. The organic layer was dried, filtered and concentrated. The crude product was dissolved in a minimum amount of ethyl acetate, silica gel (10 g) was added under vigorous stirring, followed by a mixture of ethyl acetate and hexanes (50 mL, EtOAc/Hex = 1/10). The above mixture filtered, and the silica gel was further washed with ethyl acetate and hexane (50 mL x 2). The organic solvents were combined and removed *in vacuo* to afford the product as a colorless oil (1.60 g, 87% yield), which was pure enough and used directly in next reaction.

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.016 (s, 6H), 0.82 (s, 9H), 1.19 (d, *J* = 6.0 Hz, 3H), 4.29-4.35 (dd, *J* = 1.8 Hz and 10.2 Hz, 1H), 4.42-4.50 (dq, *J* = 1.8 Hz and 6.3 Hz, 1H), 5.05-5.22 (m, 4H), 5.10-5.15 (d, *J* = 10.2 Hz, 1H), 7.30-7.40 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ –5.33, -4.44, 17.76, 20.81, 25.57, 60.00, 67.05, 68.71, 128.09, 128.28, 128.35, 128.48, 128.53, 135.12, 136.23, 156.73, 170.67; HRMS (ESI) m/z calcd for ($C_{25}H_{35}NO_5Si$ +Na) 480.2177, found 480.2190.

O-(*tert*-Butyldimethylsiloxy)-L-threonine (2c):
To N-benzyloxycarbonyl-O-(*tert*-Butyldimethylsilyloxy)-L- threonine benzyl ester (1.4 g, 6 mmol) in methanol (8 mL) was added Pd/C (140 mg, 10 wt%) at room temperature, and the resulting mixture was stirred for 12 hours under an atmosphere of H_2. The mixture was filtered through celite and the filtrate was concentrated to afford the crude product. The crude was dissolved in a minimum amount of methanol, ether was added while the methanol solution was vigorously stirred. The pure **2c** precipitated out as white powder, which was collected and dried (0.58 g, 82% yield).
^{1}H NMR (300 MHz, DMSO) δ 0.009 (s, 3H), 0.032 (s, 3H), 0.83 (s, 9H), 1.16-1.18 (d, *J* = 6.6 Hz, 3H), 2.95-3.05 (d, *J* = 2.7 Hz, 1H), 4.29-4.40 (dq, *J* = 2.7 Hz and 6.6 Hz, 1H). ^{13}C NMR (75 MHz, DMSO) δ –4.45, 18.10, 20.81, 22.03, 26.05, 60.08, 67.05, 171.07. HRMS (ESI) m/z calcd for ($C_{10}H_{24}NO_3Si$) 234.1520, found 234.1528. $[\alpha]_D^{20}$ = -31.4 (c = 0.65, MeOH).

O-(triisopropylsiloxy)-L-threonine (2a):
^{1}H NMR (300 MHz, DMSO) δ 1.00 - 1.15 (m, 21H), 1.21-1.24 (d, *J* = 6.6 Hz, 3H), 3.00-3.03 (d, *J* = 1.95 Hz, 1H), 4.50-4.60 (dq, *J* = 1.95 Hz, 6.6 Hz, 1H). ^{13}C NMR (75 MHz, DMSO) δ 12.37, 18.34, 22.19, 26.05, 59.93, 67.88, 171.11. HRMS (ESI) m/z calcd for ($C_{13}H_{30}NO_3Si$) 276.1989, found 276.1999. $[\alpha]_D^{20}$ = -20.1 (c = 0.48, MeOH).

O-(*tert*-Butyldiphenylsiloxy)-L-threonine (2b):
^{1}H NMR (300 MHz, $CDCl_3$) δ 0.95 (m, 12H), 3.50 (m, 1H), 4.39 (m, 1H), 7.20-7.30 (m, 6H), 7.60-7.70 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.88, 21.94, 61.44, 69.86, 128.10, 128.28, 130.19, 130.48, 133.20, 134.55, 136.40, 136.54, 171.67. HRMS (ESI) m/z calcd for ($C_{20}H_{27}NO_3Si$+Na) 380.1652, found 380.1658. $[\alpha]_D^{20}$ = -28.9 (c = 0.53, MeOH).

O-(triisopropylsiloxy)-L-serine (1a):
^{1}H NMR (300 MHz, CD_3OD) δ 1.10 - 1.20 (m, 21H), 0.95 (s, 9H), 3.61-3.68 (dd, *J* = 6.4 Hz and 3.8 Hz, 1H), 4.05-4.25 (m, 2H). ^{13}C NMR (75 MHz, CD_3OD) δ 11.61, 16.88, 56.64, 62.39, 170.14. HRMS (ESI) m/z calcd for ($C_{12}H_{28}NO_3Si$) 262.1833, found 262.1836. $[\alpha]_D^{20}$ = -12.5 (c = 0.61, MeOH).

O-(*tert*-Butyldiphenylsiloxy)-L-serine (1b):
^{1}H NMR (300 MHz, $CDCl_3$) δ 0.80 - 1.10 (m, 9H), 3.70-4.10 (m, 3H), 4.05-4.25 (m, 2H), 7.05-7.40 (m, 6H), 7.50-7.70 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.68, 27.30, 57.64,

63.39, 172.84. HRMS (ESI) m/z calcd for ($C_{19}H_{26}NO_3Si$) 344.1676, found 344.1678 $[\alpha]_D^{20}$= -32.8 (c = 0.61, MeOH).

O-(*tert*-Butyldimethylsiloxy)-L-serine (1c):
^{1}H NMR (300 MHz, CD_3OD) δ 0.143 (s, 6H), 0.95 (s, 9H), 3.60-3.65 (dd, *J* = 6.3 Hz and 4.3 Hz, 1H), 3.95-4.1 (m, 2H). ^{13}C NMR (75 MHz, CD_3OD) δ –6.90, 17.76, 24.85, 56.50, 62.07, 170.27. HRMS (ESI) m/z calcd for ($C_9H_{22}NO_3Si$) 220.1363, found 220.1369. $[\alpha]_D^{20}$ = -29.3 (c = 0.174, MeOH).

The Aldol product characterizations

Compound **4**: *Anti*:*syn* = 10:1; *ee* of the *anti* isomer: 98% (by HPLC with a chiralcel AD-H column, λ = 254 nm, *i*-PrOH:Hexane = 20:80, 0.5 mL/min, t_R = 26.00 min (minor), t_R = 33.72 min(major)). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.30-1.90 (m, 5H), 2.05-2.20 (m, 1H), 2.25-2.60 (m, 3H), 4.85-4.95 (d, *J* = 8.4Hz, 1H), 7.50-7.65 (d, *J* = 9.0 Hz, 1H), 8.20-8.25 (d, *J* = 9.0 Hz, 1H).

Compound **5**: *Anti*:*syn* = 19:1; *ee* of the *anti* isomer: >99% (by HPLC with a chiralcel AD-H column, λ = 254 nm, *i*-PrOH:Hexane = 10:90, 0.5mL/min, t_R = 42.37 min (major), t_R = 45.18 min (minor)). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.60-2.00 (m, 5H), 2.00-2.20 (m, 1H), 2.30-2.55 (m, 2H), 2.75-2.90 (m, 1H), 5.45-5.50 (d, *J* = 7.1 Hz, 1H), 7.40- 7.50 (t, *J* = 7.5 Hz, 1H), 7.60-7.75 (t, *J* = 7.5 Hz, 1H), 7.78-7.85 (d, *J* = 7.5 Hz, 1H), 7.90-7.95 (d, *J* = 7.5Hz, 1H).

Compound **6**: *Anti*:*syn* = 11:1; *ee* of the *anti* isomer: >99% (by HPLC with a chiralcel AS-H column, λ = 254 nm, *i*-PrOH:Hexane = 3:97, 0.5 mL/min, t_R = 110.3 min (major), t_R = 115.6 min (minor)). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.35-2.00 (m, 5H), 2.10-2.25 (m, 1H), 2.35-2.70 (m, 3H), 4.90-4.95 (d, *J* = 8.4 Hz, 1H), 7.50-7.65 (t, *J* = 7.8 Hz, 1H), 7.65-7.70 (d, *J* = 7.8 Hz, 1H), 8.15-8.20 (d, *J* = 7.8 Hz, 1H), 8.24 (s, 1H).

Compound **7**: *Anti*:*syn* = 5:1; *ee* of the *anti* isomer: 96% (by HPLC with a chiralcel AD-H column, λ = 220 nm, *i*-PrOH:Hexane = 20:80, 0.8 mL/min, t_R = 14.62 min (minor), t_R = 18.00 min (major)). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.30-1.90 (m, 5H), 2.05-2.20 (m, 1H), 2.20-2.60 (m, 3H), 4.85-4.95 (d, *J* = 8.3Hz, 1H), 7.45-7.55 (d, *J* = 8.7Hz, 2H), 7.70-7.95 (d, *J* = 8.7 Hz, 2H).

Compound **8**: *Anti*:*syn* = 5:1; *ee* of the *anti* isomer: 98% (by HPLC with a chiralcel AD-H column, λ = 220 nm, *i*-PrOH:Hexane = 10:90, 0.8 mL/min, t_R = 19.43 min (minor), t_R = 22.85 min (major)). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.20-1.40 (m, 1H), 1.50-1.85 (m, 5H), 2.00-2.20 (m, 1H), 2.30-2.60 (m, 3H), 4.75-4.85 (d, *J* = 8.7 Hz, 1H), 7.15-7.20 (d, *J* = 8.4 Hz, 2H), 7.45-7.55 (d, *J* = 8.4 Hz, 2H).

Compound **9**: *Anti*:*syn* = 9:1; *ee* of the *anti* isomer: 96% (by HPLC with a chiralcel AS-H column, λ = 254 nm, *i*-PrOH:Hexane = 80:20, 0.5 mL/min, t_R = 27.94 min (major), t_R = 31.95 min (minor)). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.20-1.80 (m, 5H), 2.00-2.20 (m, 1H),

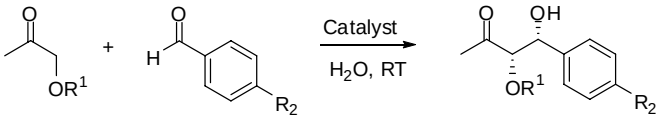
2.30-2.60 (m, 2H), 2.65-2.75 (m, 1H), 4.90-5.05 (d, *J* = 8.7 Hz, 1H), 7.40-7.55 (m, 2H), 7.70-7.90 (m, 4H).

Compound **10**: *Anti*:*syn* = 4:1; *ee* of the *anti* isomer: 97% (by HPLC with a chiralcel OD-H column, λ = 220 nm, *i*-PrOH:Hexane = 10:90, 0.5 mL/min, t_R = 78.22 min (minor), t_R = 85.55 min (major)). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.30-1.80 (m, 5H), 2.05-2.20 (m, 1H), 2.40-2.60 (m, 2H), 2.95-3.10 (m, 1H), 5.55-5.60 (d, *J* = 8.7 Hz, 1H), 7.45-7.65 (m, 4H), 7.70-7.95 (m, 2H), 8.25-8.35 (m, 1H).

Compound **11**: *Anti*:*syn* = 5:1; *ee* of the *anti* isomer: 93% (by HPLC with a chiralcel AD-H column, λ = 220 nm, *i*-PrOH:Hexane = 5:95, 0.5 mL/min, t_R = 74.19 min (minor), t_R = 76.82 min (major)). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.20-1.40 (m, 1H), 1.55-1.85 (m, 4H), 2.00-2.15 (m, 1H), 2.30-2.70 (m, 3H), 3.84 (s, 3H), 4.75-4.80 (d, *J* = 9.0 Hz, 1H), 6.85-6.90 (d, *J* = 8.7 Hz, 3H), 7.20-7.35 (d, *J* = 8.7 Hz, 3H).

Compound **12**: *Anti*:*syn* = 5:1; *ee* of the *anti* isomer: 91% (by HPLC with a chiralcel AD-H column, λ = 220 nm, *i*-PrOH:Hexane = 10:90, 0.5 mL/min, t_R = 39.73 min (minor), t_R = 43.24 min (major)). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.20-1.40 (m, 1H), 1.55-1.90 (m, 4H), 2.00-2.15 (m, 1H), 2.30-2.75 (m, 3H), 3.85 (s, 3H), 4.75-4.85 (d, *J* = 8.7 Hz, 1H), 6.80-7.00 (m, 3H), 7.28-7.33 (m, 1H).

The representative procedure for the aldol reactions between *O*-TBS-hydroxyacetone and various aldehydes in water



To a solution of the *para*-nitrobenzaldehyde (0.0378 g, 0.25 mmol) and catalyst **2b** (1.8 mg, 0.025 mmol) in distilled water (0.0675 mL, 3.75 mmol) was added *O*-TBDMS-hydroxypropanone (0.0942 g, 0.5 mmol). The resulting reaction mixture was stirred at room temperature for 6 h. The reaction mixture was diluted with ethyl acetate and filtered through silica gel to remove the catalyst. The solution was dried and concentrated *in vacuo* to afford the crude product as a yellow solid, which was purified by column chromatography (ethyl acetate : hexane = 1 : 10 to 1 : 5) to afford **14** as a white solid (0.0780 g, 92%).

Compound **14**: *Anti*:*syn* = 1:8. The *ee* of the *syn* isomer: 98% (by HPLC analysis using a chiralcel OD-H column, λ = 254 nm, *i*-PrOH : hexane = 10 : 90, 0.5 mL/min, t_R = 15.89 min (minor), t_R = 17.46 min (major)). ^{1}H NMR (300 MHz, $CDCl_3$) δ: -0.34 (s, 3H, CH_3), -0.02 (s, 3H, CH_3), 0.87 (s, 9H, $3CH_3$), 2.21 (s, 3H, CH_3), 4.10-4.18 (2 d's, *J* = 6.2 Hz and 2.8 Hz, 1H, CH), 4.90-5.02 (2 d's, *J* = 6.1 Hz and 2.6 Hz, 1H, CH), 7.52-7.55 (d, *J* = 8.9 Hz, 2H, ArH), 8.22-8.25 (d, *J* = 8.9 Hz, 2H, ArH); ^{13}C NMR (300 MHz, $CDCl_3$) δ: 210.8, 148.2, 147.5, 127.0, 123.4, 81.8, 74.6, 27.3, 25.6, 18.0, -5.1, -5.6; MS (ESI) calcd for ($C_{16}H_{25}NO_5Si$-H) M: 338.2; found *m/z* 338.0.

Compound **15**: *Anti*:*syn* = 1:7. The *ee* of the *syn* isomer: 96% (by HPLC analysis using a chiralcel OD-H column, λ = 254 nm, *i*-PrOH : hexane = 5 : 95, 0.5 mL/min, t_R = 24.32 min (minor), t_R = 30.01 min (major)). ^{1}H NMR (300 MHz, $CDCl_3$): δ : -0.37 (s, 3H, CH_3), -0.04 (s, 3H, CH_3), 0.85 (s, 9H, $3CH_3$), 2.21 (s, 3H, CH_3), 4.05-4.14 (d, *J* = 5.4 Hz, 1H, CH), 4.83-4.97 (d, *J* = 7.4 Hz, 1H, CH), 7.46-7.48 (d, *J* = 6.7 Hz, 2H, ArH), 7.65-7.67 (d, *J* = 6.9 Hz, 2H, ArH); ^{13}C NMR (300 MHz, $CDCl_3$) δ : 210.1, 146.2, 132.0, 126.9, 118.6, 111.7, 81.9, 74.7, 27.3, 25.6, 18.0, -5.1, -5.7; MS (ESI) calcd for ($C_{17}H_{25}NO_3Si$-H) M: 318.2; found *m/z* 318.0.

Compound **16**: *Anti*:*syn* = 1:3. The *ee* of the *syn* isomer: 91% (by HPLC analysis using a chiralcel OD-H column, λ = 254 nm, *i*-PrOH : hexane = 5 : 95, 0.5 mL/min, t_R = 13.68 min (minor), t_R = 14.85 min (major)). ^{1}H NMR (300 MHz, $CDCl_3$) δ : -0.37 (s, 3H, CH_3), -0.09 (s, 3H, CH_3), 0.86 (s, 9H, $3CH_3$), 2.18 (s, 3H, CH_3), 4.08-4.14 (2 d's, *J* = 6.6 Hz and 3.0 Hz, 1H, CH), 4.74-4.92 (2 d's, *J* = 6.4 Hz and 2.9 Hz, 1H, CH), 7.33-7.34 (m, 5H, ArH); ^{13}C NMR (300 MHz, $CDCl_3$) δ : 211.1, 140.5, 128.2, 126.0, 82.6, 75.2, 27.3, 25.6, 18.0, -5.6, -5.9; MS (ESI) calcd for ($C_{16}H_{26}O_3Si$-H) M: 293.2; found *m/z* 293.0.

Compound **17**: *Anti*:*syn* = 1:4. The *ee* of the *syn* isomer: 92% (by HPLC analysis using a chiralcel OD-H column, λ = 254 nm, *i*-PrOH : hexane = 5 : 95, 0.5 mL/min, t_R = 18.52 min (minor), t_R = 11.49 min (major)). ^{1}H NMR (300 MHz, $CDCl_3$): δ : -0.31 (s, 3H, CH_3), -0.05 (s, 3H, CH_3), 0.87 (s, 9H, $3CH_3$), 2.18 (s, 3H, CH_3), 4.05-4.11 (2 d's, *J* = 6.4 Hz and 3.1 Hz, 1H, CH), 4.74-4.88 (d, *J* = 6.4 Hz, 1H, CH), 7.28-7.31 (m, 4H, ArH); ^{13}C NMR (300 MHz, $CDCl_3$) δ : 211.1, 139.1, 133.6, 128.5, 128.4, 127.5, 82.3, 74.7, 27.3, 25.7, 18.0, -5.2, -5.7; MS (ESI) calcd for ($C_{16}H_{25}NClO_3Si$-H) M: 327.1 *m/z* 3; found 327.0.

Representative procedure for the desilylation

A 1M solution of TBAF in THF (0.2 mL, 0.2 mmol) was injected into a 10 mL of round-bound flask containing compound **14** (0.0679 g, 0.2 mmol, 95% *ee*) in an ice water bath, and the resulting mixture was stirred for 2 minntes. The reaction mixture was then diluted with ether (3 mL) and concentrated under reduced pressure to afford the crude product as a yellowish solid, which was purified by silica gel chromatography (ethyl acetate : hexane = 1 : 2) to afford 3,4-dihydroxy-4-(4-nitrophenyl)butan-2-one as a yellow solid (0.0388 g, 86%, 93% *ee*).

References

(1) S. Petursson and J. E. Baldwin *Tetrahedron,* **1998**, *54*, 6001.