Experimental

General Methods. All reactions were performed in oven or flame dried glassware under an inert atmosphere of N_2 or argon. Conjugate additions were carried out using standard Schlenk techniques. Toluene, THF and diethyl ether were distilled from sodium; hexane and CH_2Cl_2 from CaH_2. Dialkylzinc reagents: Me_2Zn (2M in toluene), Et_2Zn (1M in hexane) and *i*-Pr_2Zn (1M in toluene) were purchased from Aldrich, Bu_2Zn (1M in heptane) was purchased from Fluka. Me_3Al (1 M in heptane) was purchased from Aldrich. Thin-layer chromatography (TLC) was performed on Merck silica gel 60 TLC-plates F254 and visualized using UV irradiation or phosphomolybdic acid. Flash chromatography was carried out on silica gel (Aldrich, 230 – 400 mesh). ^{1}H NMR spectra were recorded at 300 or 400 MHz with $CDCl_3$ as solvent, ^{13}C NMR spectra were recorded at 50 or 100 MHz in $CDCl_3$ (Varian spectrometers). Chemical shifts were determined relative to the residual solvent peaks ($CHCl_3$, δ = 7.26 ppm for hydrogen atoms, δ = 77.0 for carbon atoms). Optical rotations were recorded using a Schmidt+Haench Polartronic MH8 instrument at 589 nm. Gas chromatography was performed using a Hewlett-Packard HP 6890 Series GC System with flame ionization detector on chiral columns and HPLC on Shimadzu LC-10AD VP instrument equipped with 6 parallel normal phase chiral columns, using a diode array detector. Mass spectra were recorded on an JEOL JMS·600H mass spectrometer.

1-*t*-Butoxycarbonyl-2,3-dehydro-4-piperidone (2).[1]

4-Methoxypyridine (0.50 mL, 5.0 mmol) was dissolved in *i*-PrOH (10 mL) and cooled to -15 °C (ice-methanol). K(*i*-PrO)$_3$BH[2] (10 mL, 10 mmol, 1M in THF) was added to this solution followed by Boc_2O (1.20 g, 5.5 mmol) in Et_2O (3 mL). The resulting mixture was stirred for 1 h at -15 °C and then 10% aq. citric acid (20 mL) was added and the stirring continued for 10 min at r.t. The solution was diluted with Et_2O, phases were separated and the aqueous phase extracted with Et_2O. The combined organic extracts were washed with brine, dried ($MgSO_4$) and concentrated. The crude product was purified by flash chromatography (heptane/AcOEt=2:1) to give 409 mg (41%) of **2** as a white solid. M.p. 53-54°C. δ_H(300 MHz, $CDCl_3$) = 7.80 (d, *J* = 5.9 Hz, 1H), 5.29 (d, *J* = 8.1 Hz, 1H), 3.96 (t, *J*=7.1 Hz, 2H), 2.53 (t, J=7.1 Hz, 2H), 1.53 (s, 9H). δ_C(50 MHz, $CDCl_3$) = 193.6, 144.0, 106.72, 83.5, 42.3, 41.2, 35.7, 28.0. Elem. anal. found C, 60.90; H, 7.72; N, 7.13% $C_{10}H_{15}NO_3$ requires C, 60.90; H, 7.67; N, 7.10%. *m/z* (EI) 197.1058 ($C_{10}H_{15}NO_3$ requires 197.1052).

***tert*-Butyl 2-methyl-4-oxopiperidine-1-carboxylate (3).**

$Cu(OTf)_2$ (180 mg, 0.5 mmol) and ligand (*S*,*R*)-**L1** (1 mmol) were dissolved in anhydrous toluene (40 mL) and stirred for 40 min at r.t. To this solution 1 mmol of dry Et_2O was added, followed by a solution of substrate (10 mmol) in toluene (60 mL) and the mixture cooled to -50°C. A solution of Me_3Al (20 mmol) was added dropwise and the reaction mixture was stirred overnight. The reaction was stopped after 16 h at 80% conversion. The reaction mixture was quenched with sat. aq. NH_4Cl and extracted with Et_2O (3x). The combined organic extracts were washed with brine, dried ($MgSO_4$) and concentrated. The crude product was purified by flash chromatography (SiO_2; EtOAc / pentane 25:75) affording compound **3** (1.55 g, 73%) as a white solid. Mp = 57.7 ºC. GC on CP Chiralsil Dex CB column, 25m × 0.25mm × 0.25 μm, He-flow: 1mL/min, oven temp.: 120 ºC, init., time: 10 min, rate: 1 ºC/min, final temp.: 150 ºC, t_R = 23.5 min (minor), t_R = 23.9 min (major). $[\alpha]_D$ -18.6 (c 2.01 in $CHCl_3$) for 96% ee. δ_H(300 MHz, $CDCl_3$) 4.67-4.65 (m, 1H), 4.21-4.15 (m, 1H), 3.31-3.21 (m, 1H), 2.62 (dd, *J* = 14.4 Hz, 6.7 Hz, 1H), 2.48-2.37 (m, 1H), 2.30-2.17 (m, 2H), 1.43 (s, 9H), 1.12 (d, *J* = 6.9 Hz, 3H) ppm. δ_C(50 MHz, $CDCl_3$) = 208.4, 154.4, 80.3, 47.9, 46.6, 4.06, 38.3, 28.4, 18.9 ppm. *m/z* (EI) 213.13836 ($C_{11}H_{19}NO_3$ requires 213.13647).

tert-Butyl 7-methyl-1,4-dioxa-8-azaspiro[4.5]decane-8-carboxylate (4).[3]

Compound **3** (620 mg; 2.9 mmol) was dissolved in toluene (6 mL). Ethylene glycol (0.48 mL; 8.7 mmol) and p-toluenesulfonic acid (270 mg; 1.45 mmol) were added and the reaction mixture was heated at reflux overnight in the presence of molecular sieves (3Å). After cooling down to rt, the molecular sieves were removed by filtration and the reaction mixture was poured in a saturated $NaHCO_3$ aqueous solution. The aqueous phase was extracted with Et_2O (2 × 10 mL), and the combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. Purification by column chromatography (SiO_2; EtOAc / pentane 10:90) afforded compound **4** (447 mg, 60%) as a colorless oil and the remaining starting material. $[\alpha]_D$ -28.5 (c 0.92 in $CHCl_3$), 96% ee. δ_H(400 MHz, $CDCl_3$) 4.44-4.39 (m, 1H), 3.97-3.84 (m, 2a), 3.05-2.98 (m, 1H), 1.81 (dd, J = 13.6 Hz, 6.6 Hz, 1H), 1.62-1.52 (m, 2a), 1.40 (s, 9H), 1.17 (d, J = 7.1 Hz, 3H) ppm. δ_C(50 MHz, $CDCl_3$) 154.6, 107.3, 79.4, 64.6, 63.7, 46.5, 38.3, 36.7, 34.5, 28.4, 17.4 ppm. *m/z* (EI) 257.16269 ($C_{13}H_{23}NO_4$ requires 257.16335.

General procedure A for the lithiation.[3]

TMEDA (0.090 mL; 0.6 mmol) was added to a solution of compound **4** (64.2 mg; 0.25 mmol) in Et_2O (4 mL). The resulting solution was cooled to -78 ºC and a solution of *s*-BuLi (1.3 M in cyclohexane, 0.46 mL; 0.6 mmol) was added. The reaction mixture was stirred at -78 ºC. After 3 h a solution of the electrophile (0.6 mmol) in Et_2O (1 mL) was added. The reaction mixture was allowed to slowly warm up to rt. After stirring overnight the mixture was poured in H_2O (5 mL). The water layer was extracted with Et_2O (2 × 10 mL) and the combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*.

General procedure B for the lithiation.[4]

TMEDA (0.18 mL; 1.2 mmol) was added to a solution of compound **4** (128.5 mg; 0.5 mmol) in Et_2O (9 mL). The resulting solution was cooled to -78 ºC and a solution of *s*-BuLi (1.3 M in cyclohexane, 0.92 mL; 1.2 mmol) was added. The reaction mixture was stirred at -78 ºC. After 3 h a solution in THF (3.5 mL) of the copper complex [CuCN·2LiCl], freshly prepared from CuCN (107 mg; 1.2 mmol) and LiCl (100 mg; 2.4 mmol), was added. The reaction mixture was warmed to -50 ºC and stirred at this temperature for 30 min. Then, the temperature was brought once again to -78 ºC and a solution of the electrophile (1.2 mmol) in Et_2O (1 mL) was added. The reaction mixture was allowed to slowly warm up rt. After stirring overnight the mixture was poured in H_2O (5 mL). The water layer was extracted with Et_2O (2 × 10 mL) and the combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*.

(7*R*,9*R*)-*tert*-Butyl 7,9-dimethyl-1,4-dioxa-8-azaspiro[4.5]decane-8-carboxylate (5).[3]

From procedure A. Purification by column chromatography (SiO_2; EtOAc / pentane 1:9) afforded compound **5** (48 mg, 71%) as a colorless oil. Rf = 0.3. $[\alpha]_D$ +4.6 (c 0.57 in $CHCl_3$), 96% ee and dr 95:5. δ_H(400 MHz, $CDCl_3$) 4.10-4.05 (m, 2H), 3.98-3.92 (m, 2H), 3.88-3.82 (m, 2H), 2.20 (dd, J = 14.7 Hz, 5.5 Hz, 2H), 1.82 (dd, J = 14.7 Hz, 3.0 Hz, 2H), 1.45 (s, 9H), 1.25 (d, J = 6.9 Hz, 6H) ppm. δ_C (50 MHz, $CDCl_3$) 154.8, 106.4, 79.1, 63.7, 46.0, 39.2, 28.5, 20.9 ppm. *m/z* (EI) 271.1780 ($C_{12}H_{25}NO_4$ requires 271.1784).

(7*R*,9*R*)-*tert*-Butyl 7-methyl-9-(trimethylsilyl)-1,4-dioxa-8-azaspiro[4.5]decane-8-carboxylate (6).

From procedure A. Purification by column chromatography (SiO_2; EtOAc / pentane 5:95) afforded compound **6** (61 mg, 74%) as a colorless oil. Rf = 0.7. $[\alpha]_D$ -13.2 (c 0.55 in $CHCl_3$), 96% ee and dr 96:4. δ_H(400 MHz, $CDCl_3$) 4.46-4.38 (m, 1H), 3.98-3.87 (m, 2a), 2.64 (dd, J = 12.6 Hz, 2.6 Hz, 1H), 1.80-1.75 (m, 1H), 1.64-1.52 (m, 3H), 1.41 (s, 9H), 1.24 (d, J = 7.1 Hz, 3H), 0.05 (s,

9H) ppm. δ_C(50 MHz, CDCl3) 155.0, 108.0, 79.1, 64.4, 63.7, 48.1, 39.6, 38.8, 35.8, 28.4, 18.1, -0.5 ppm. *m/z* (CI): 330 $(M+H)^+$. *m/z* (EI) 314.1778 (M-CH_3, $C_{15}H_{28}NO_4Si$ requires 314.1788).

(7*S*,9*R*)-*tert*-Butyl 7-formyl-9-methyl-1,4-dioxa-8-azaspiro[4.5]decane-8-carboxylate (7).

From procedure A. Purification by column chromatography (SiO_2; EtOAc / pentane 2:8) afforded compound **7** (40 mg, 56%) as a colorless oil. Rf = 0.5. $[\alpha]_D$ -19.6 (c 0.58 in $CHCl_3$), 96% ee and dr 1:1. δ_H(400 MHz, $CDCl_3$) mixture of the two diastereoisomers 9.61 (d, *J* = 1.0 Hz, 1H), 9.44 (d, *J* = 2.1 Hz, 1H), 4.65-4.62 (m, 1H), 4.51-4.47 (m, 1H), 4.40-4.36 (m, 1H), 3.97-3.97 (m, 8H), 2.44-2.40 (m, 1H), 1.98-1.91 (m, 2H), 1.80-1.74 (m, 2H), 1.67-1.56 (m, 2a), 1.46 (s, 9H), 1.43 (s, 9H), 1.29-12.7 (m, 6H) ppm. δ_C(50 MHz, $CDCl_3$) 202.3, 196.0, 155.1, 106.5, 106.1, 81.6, 80.6, 64.8, 64.3, 63.9, 63.8, 59.8, 58.7, 48.0, 47.4, 38.8, 37.6, 34.0, 32.3, 28.3, 28.2, 20.7, 18.7 ppm. *m/z* (CI) 286 $(M+H)^+$. *m/z* (EI) 256.1558 (M-CHO, $C_{13}H_{22}NO_4$ requires 256.1549).

(7*R*,9*R*)-*tert*-Butyl 7-allyl-9-methyl-1,4-dioxa-8-azaspiro[4.5]decane-8-carboxylate (8).

From procedure B. Purification by column chromatography (SiO_2; EtOAc / pentane 1:9) afforded compound **8** (95 mg, 64%) as a colorless oil. Rf = 0.6. $[\alpha]_D$ +27.4 (c 0.50 in $CHCl_3$), 96% ee and dr > 99:1. δ_H(400 MHz, $CDCl_3$) 5.78-5.68 (m, 1H), 5.09-5.00 (m, 2H), 4.05-4.02 (M, 1H), 3.95-3.77 (m, 5H), 2.45-2.39 (m, 1H), 2.35-2.28 (m, 1H), 2.14 (dd, *J* = 14.7 Hz, 5.4 Hz, 1H), 1.98 (d, *J* = 4.1 Hz, 2H), 1.81 (dd, *J* = 14.7 Hz, 3.3 Hz, 1H), 1.44 (s, 9H), 1.25 (d, *J* = 6.8 Hz, 3H) ppm. δ_C(50 MHz, $CDCl_3$) 154.7, 135.5, 117.2, 106.3, 79.2, 63.8, 63.5, 50.6, 46.1, 39.6, 38.6, 34.8, 28.5, 20.8 ppm. *m/z* (CI) 298 $(M+H)^+$.

(7*R*,9*R*)-*tert*-Butyl-7-(4-chlorobutyl)-9-methyl-1,4-dioxa-8-azaspiro[4.5]decane-8-carboxylate (9).

From procedure B. Purification by column chromatography (SiO_2; EtOAc / pentane 1:9) afforded compound **9** (107 mg, 62%) as a colorless oil. Rf = 0.5. $[\alpha]_D$ +8.2 (c 0.49 in $CHCl_3$), 96% ee and dr 99:1. δ_H(400 MHz, $CDCl_3$) 3.99-3.79 (m, 6H), 3.50 (t, *J* = 6.7 Hz, 2H), 2.10-1.98 (m, 2H), 1.93-1.89 (m, 1H), 1.79-1.71 (m, 3H), 1.70-1.52 (m, 2H), 1.47-1.31 (m, 2H), 1.42 (s, 9H), 1.24 (d, *J* = 6.9 Hz, 3H) ppm. δ_C(50 MHz, $CDCl_3$) 154.8, 106.5, 79.2, 63.8, 63.7, 50.5, 46.1, 44.9, 39.5, 35.7, 33.2, 32.3, 28.4, 23.9, 20.8 ppm. *m/z* (EI) 347.1847 ($C_{17}H_{30}NO_4{}^{35}Cl$ requires 347.1863).

(4*R*,9a*R*)-4-Methylhexahydro-1H-quinolizin-2(6H)-one. (+)-Myrtine. (1).[5]

Compound **9** (100 mg, 0.29 mmol) was refluxed in a mixture of acetone (3 mL) and H_2O (0.5 mL) to which conc. HCl (1 mL) had been added. After 16 h the reaction mixture was cooled to 0 ºC in a ice bath and the pH was increased by slowly adding $NaHCO_3$. The reaction mixture was stirred at rt for an additional 16 h and then poured in H_2O (10 mL). The aqueous layer was extracted with Et_2O (3 × 10 mL) and the combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. Purification by column chromatography (SiO_2; EtOAc / pentane 2:8) afforded compound **1** (23 mg, 50%) as a yellow oil. Rf = 0.7. $[\alpha]_D$ +10.2 (c 1.77 in $CHCl_3$), 96% ee and dr 97:3; lit.[5a] $[\alpha]^{28}_D$ +11.3 (c 2.7 in $CHCl_3$). Spectroscopic data correspond to the literature.[5b] δ_H(400 MHz, $CDCl_3$) 3.40-3.33 (m, 1H), 2.83 (dd, *J* = 13.4 Hz, 5.9 Hz, 1H), 2.80-2.75 (m, 1H), 2.67-2.60 (m, 1H), 2.46 (dt, *J* = 11.5 Hz, 2.8 Hz, 1H), 2.27-2.15 (m, 3H), 1.71-1.55 (m, 2a), 1.31-1.18 (m, 2H), 0.95 (t, *J* = 6.8 Hz, 3H) ppm. δ_C(50 MHz, $CDCl_3$) 209.5, 57.1, 53.5, 51.4, 48.6, 48.0, 34.2, 25.8, 23.4, 11.0 ppm. *m/z* (CI) 168 $(M+H)^+$.

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