General procedure for 1,4-addition of dialkylzinc reagents to cyclohexadienones **2-6** *and* **13-16***:*
Under Argon, a solution of $Cu(OTf)_2$ (9.0 mg, 0.024 mmol) and **L*-1** (26 mg , 0.048 mmol) in 5.0 ml of toluene was stirred for 1 h at rt. The colorless solution was cooled to -25°C and 1.0 mmol of dienone and 1.5 ml of R_2Zn (1.1M in toluene) were added. After 16 h, the reaction mixture was quenched with saturated aqueous NH_4Cl (5.0 ml) and then extracted with Et_2O (3x 20 ml). The combined organic layers were extracted with 2.0 N KOH (30 ml) and brine (30 ml) and dried on Na_2SO_4. Column chromatography (SiO_2 (hexane/EtOAc, 5/1)) yielded the pure 1,4-adduct. Yields and e.e.'s are given in Tables 1 and 2.

5-ethyl-4,4-dimethoxy-2-cyclohexenone (**7**)
^{1}H NMR ($CDCl_3$) δ 0.80 (t, 3H), 1.03 (m,1H), 1.49 (m, 1H), 2.11 (m, 1H), 2.38 (m 1H), 2.66 (m, 1H), 3.13 (s 3H), 3.16 (s, 3H), 5.88 (d, *J* = 10.3 Hz, 1H), 6.56 (dd, *J* = 10.3 and 1.5 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 9.34, 18.55, 35.82, 40.20, 45.23, 47.18, 96.54, 128.39, 144.55, 196.54. HRMS (M^+) found 184.108, calc. for $C_{10}H_{16}O_3$ 184.110
E.e. determination: GC CP-Cyclodex-B, 115 °C, rt (min) 18.1, 18.4.

5-ethyl-4,4-diethoxy-2-cyclohexenone (**8**)
^{1}H NMR ($CDCl_3$) δ 0.95 (t, 3H), 1.15 (t, 6H), 2.13 (m, 1H), 2.45 (m, 1H), 2.86 (m, 1H), 3.53 (m, 4H), 5.94 (d, *J* = 9.4 Hz, 1H), 6.71 (d, *J* = 9.4 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 11.62, 14.91, 15.22, 20.74, 38.29, 43.30, 66.19, 57.32, 98.59, 130.23, 148.00, 199.39. HRMS (M^+) found 212.142, calc. for $C_{12}H_{20}O_3$ 212.141.
E.e. determination: GC CP-Cyclodex-B column, 125°C, rt (min) 51.9, 52.8.

10-ethyl-1,4-dioxaspiro[4,5]dec-6-en-8-one (**9**)
^{1}H NMR ($CDCl_3$) δ 0.95 (t, 3H), 1.13 (m, 1H), 1.76 (m, 1H), 2.19 (m, 1H), 2.45 (m, 1H), 2.77 (m, 1H), 3.93 (m, 4H), 5.95 (d, *J* = 9.6 Hz, 1H), 6.59 (d, *J* = 9.6 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 11.11, 20.61, 39.64, 44.31, 65.42, 65.49, 105.87, 129.44, 146.60, 199.15. HRMS (M^+) found 182.096, calc. for $C_{10}H_{14}O_3$ 182.094.
E.e. determination: GC GTA column, 140°C, rt (min) 43.5, 46.1.

11-ethyl-1,5-dioxaspiro[5,5]undec-7-en-9-one (**10**)
^{1}H NMR ($CDCl_3$) δ 0.88 (t, 3H), 1.15 (m, 1H), 1.56 (m, 1H), 2.12 (m, 3H), 2.56 (m, 2H), 4.01 (m, 4H), 6.00 (d, *J* = 10 Hz, 1H), 7.35 (d, *J* = 10 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 11.48, 20.32, 25.07, 38.32, 45.60, 60.24, 60.47, 95.47, 129.75, 143.86, 199.38. HRMS (M^+) found 196.108, calc. for $C_{11}H_{16}O_3$ 196.110
E.e. determination: GC GTA column, 160°C, rt (min) 31.2, 32.9.

11-ethyl-3,3-dimethyl-1,5-dioxaspiro[5,5]undec-7-en-9-one (**11**)

^{1}H NMR ($CDCl_3$) δ 0.82 (s, 3H), 0.95 (t, 3H), 1.13 (s, 3H), 1.32 (m, 1H), 2.08 (m, 2H), 2.48 (m, 3H), 3.40-3.98 (m, 4H), 6.01 (d, *J* = 11 Hz, 1H), 7.26 (d, *J* = 11 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 11.36, 20.18, 21.96, 22.62, 29.84, 38.35, 45.69, 60.23, 70.75, 70.99, 95.27, 129.93, 143.52, 199.41. HRMS (M^+) found 224.137 calc. for $C_{13}H_{20}O_3$ 224.141.

E.e. determination: GC CP-cyclodex-B column, 140 °C, rt (min) 110, 112.

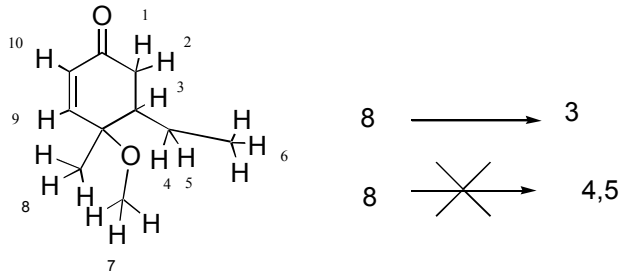
5-methyl-4,4-dimethoxy-2-cyclohexenone(**12**)

^{1}H NMR ($CDCl_3$) δ 0.95 (d, *J* = 7.1 Hz, 3H), 2.20 (d, *J* = 7 Hz, 1 H), 2.58, (m, 1 H), 2.88 (d, *J* = 7 Hz, 1H), 3.23 (d, *J* = 3 Hz, 6 H), 6.01 (d, *J* = 10.6 Hz, 1H), 6.65 (d, *J* = 10.6 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 14.64, 35.28, 42.01, 47.4, 49.59, 99.02, 130.48, 146.45, 198.93. HRMS (M^+) found 170.096, calc for $C_9H_{14}O_3$ 170.094.

E.e. determination: GC GTA column, 150°C, rt (min), 15.5, 16.3.

5-ethyl-4-methyl-4-methoxy-2-cyclohexenone (**17**)

^{1}H NMR ($CDCl_3$) δ 0.91 (t, *J* = 7 Hz , 3H), 1.28 (m, 1H), 1.42 (s, 3H), 1.76 (m, 1H), 1.90 (m, 1H), 2.50 (m, 2H), 3.26 (s, 3H), 5.99 (d, *J* = 10 Hz, 1H), 6.77 (d, J = 10 Hz, 1 H). ^{13}C NMR ($CDCl_3$) δ 11.64, 20.80, 22.26, 38.28, 45.69, 50.24, 73.09, 129.41, 152.87, 199.78. HRMS (M+1) 168.119, calc. for $C_{10}H_{16}O_2$ 168.115. No e.e. determination method could be developed for this compound. However, the e.e. of the hydrogenated product **17A** could be determined



NOESY interactions:

3-ethyl-4-methyl-4-methoxy-cyclohexanone (**17A**)

A spatula of Pd/C was added to a solution of 0.3 mmol of **17** was 10 ml of CH_2Cl_2 and the flask was connected to a balloon filled with H_2. After 16 h the reaction mixture was filtered over Celite and the solvent evaporated after which pure **17A** was obtained.

^{1}H NMR ($CDCl_3$) δ 0.85 (t, 3H), 1.23 (s, 3H), 1.58 (m, 4H), 2.30 (m, 5H), 3.23 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 11.52, 21.26, 21.85, 33.23, 36.95, 41.26, 48.77, 73.50.

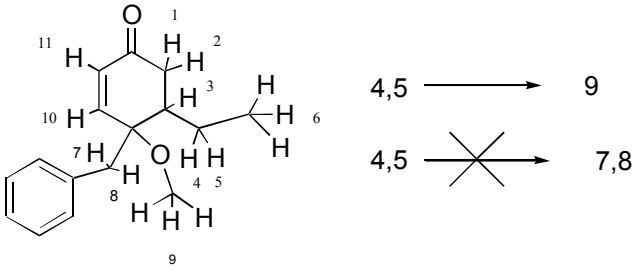
E.e. determination: GC Cp Cyclodex B column, T= 120 °C, rt (min.) 44.8, 45.3, 46.4, 48.3.

4-benzyl-5-ethyl-4-methoxy-2-cyclohexenone (**18**)

^{1}H NMR ($CDCl_3$) δ 0.93 (t, 3H), 1.35 (m, 1H), 1.92 (m, 2H), 2.49 (m, 2H), 3.02 (d, *J* = 14 Hz, 1H), 3.21 (d, *J* = 14 Hz, 1 H), 3.37 (s, 3H), 6.06 (d, *J* = 10 Hz, 1H), 6.80 (d, *J* = 10 Hz, 1H), 7.27 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 11.52, 21.26, 29.61, 38.53, 41,53, 42.26, 51.27, 126.67, 128.23 (2x), 130.09 (2x), 130.95, 136.16, 150.94, 194.65.

No e.e. determination method could be developed for this compound. However, the e.e. of the hydrogenated product **18A** could be determined.

NOESY interactions:



4-benzyl-3-ethyl-4-methoxy-cyclohexanone (**18A**)

A spatula of Pd/C was added to a solution of 0.3 mmol of **18** was 10 ml of CH_2Cl_2 and the flask was connected to a balloon filled with H_2. After 16 h the reaction mixture was filtered over Celite and the solvent evaporated after which pure **18A** was obtained.

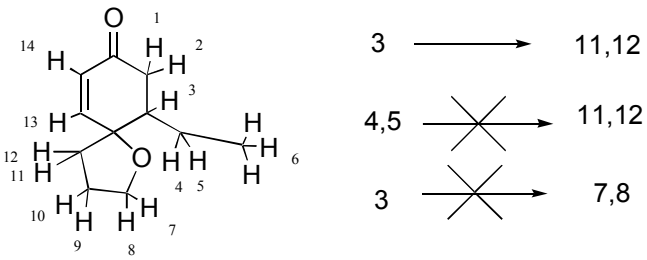
^{1}H NMR ($CDCl_3$) δ 0.89 (t, 3H), 1.39 (m, 1H), 1.60 (m, 2H), 2.02 (m, 1H), 2.19 (m, 2H), 2.35 (m, 2H), 2.45 (m, 1H), 3.03 (q, 2H), 3.39 (s, 3H), 7.23 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 11.15, 22.46, 29.99, 36.65, 38.70, 41.26, 44.08, 126.44, 128.17, 130.10, 189.14.

E.e. determination: HPLC AS column, flow rate 1.5 ml/min, hexane/ipa: 90/10, rt (min) 6.9, 8.1.

10-ethyl-1-oxaspiro[4,5]dec-6-en-8-one (**19**)

^{1}H NMR ($CDCl_3$) δ 0.86 (t, 3H), 1.23 (m, 1H), 1.69 (m, 1H), 1.85 (m, 2H), 1.98 (m, 2H), 2.13 (m, 1H), 2.48 (m, 2H), 3.91 (m, 2H), 5.82 (d, *J* = 10 Hz, 1H), 6.58 (d, *J* = 10 Hz, 1 H). ^{13}C NMR ($CDCl_3$) δ 11.87, 21.02, 26.06, 35.95, 39.64, 45.50, 68.33, 82.00, 127.40, 152.73, 199,14. HRMS (M^+) found 180.110, calc. for $C_{11}H_{16}O_2$ 180.115.

E.e. determination: HPLC AS column, flow rate 1.5 ml/min, hexane/ipa:95/5, rt (min) 6.2, 7.4, 9.9, 15.1.



NOESY interactions:

4-benzyloxy-5-ethyl-4-methoxy-2-cyclohexenone (**20**)

^{1}H NMR ($CDCl_3$) δ 0.87 (t, 3H), 1.1 (m, 1H), 1.72 (m, 1H), 2.1 (m, 1H), 2.52 (m, 1H), 2.81 (m, 1H), 3.27 (s , 3H), 4.50 (m, 2H), 5.98 (d, *J* = 10 Hz, 1H), 6.72 (d, *J* = 10 Hz, 1H), 7.25 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 11.63, 20.95, 38.23, 43.08, 49.84, 64.40, 127.34, 127.62, 128.36, 130.85, 147.08, 196.54. HRMS (M^+): found 180.112, calc. for $C_{11}H_{16}O_2$ 180.115.

E.e. determination: HPLC AS column, flowrate 2.0 ml/min, hexane/ipa: 80/20, rt (min) 11.3, 15.6.