Supporting Information

Enantioselective Palladium-Catalysed Conjugate Addition of Arylsiloxanes

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General: ^{1}H NMR spectra were recorded at 300 or 400 MHz with $CDCl_3$ as solvent. ^{13}C NMR spectra were obtained at 75.4 or 100.6 MHz in $CDCl_3$, (Varian VXR300 or AMX400 spectrometers). Chemical shifts were determined relative to the residual solvent peaks (δ = 7.26 ppm for hydrogen, δ = 77.0 for carbon). Data are reported as follows: chemical shifts, integration, multiplicity (s = singlet, d = doublet, t =triplet, q = quartet, br = broad, m = multiplet) and coupling constants (Hz). Mass spectra were recorded on a AEI-MS-902 mass spectrometer. Enantioselectivities were determined by capillary GC analysis (Chiraldex G-TA column (30 m x 0.25 mm) or Chiraldex α-TA column (30 m x 0.25 mm)) using a flame ionization detector and compared with the racemic 1,4-addition products. HPLC analysis was carried out on a Shimadzu LC-10AD*VP* HPLC equipped with a Shimadzu SPD-M10A*VP* diode array detector. Conversions were determined by GC with an HP1 or HP5 column (Agilent Technologies, Palo Alto, CA) using *n*-dodecane as internal standard. Thin-layer chromatography (TLC) was performed on silica gel 60, components were visualized by staining with $KMnO_4$ reagent. Flash chromatography was performed on silica gel 60 Å (SiliCycle). Optical rotations were measured ona Schmidt and Haensch Polartronic MH8. All reactions were carried out under nitrogen atmosphere using dried glassware. All solvents were dried and distilled before use according to standard procedures.

(*R,R*)-MeDUPHOS was purchased from Strem. All starting materials and products have been described in the literature.

Enone **1e** was synthesized according to a literature procedure.[1]

Lactam **1f** was synthesized according to a literature procedure.[2]

Arylsiloxanes **2a**, **2d**, **2e** and **2f** were purchased from Sigma Aldrich. Arylsiloxanes **2b** and **2c** were synthesized according to literature procedures.[3]

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[1] Brown, M. K.; Degrado, S. J.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2005**, *44*, 5306-5310.

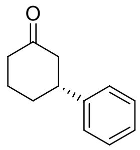
[2] Giovannini, A.; Savoia, D.; Umani-Ronchi, A. *J. Org. Chem.* **1989,** *54,* 228-234; Casamitjana, N.; López, v.; Jorge, A.; Bosch, J.; Molins, E.; Roig, A. *Tetrahedron* **2000**, *56*, 4027-4042.

[3] Manoso, A. S.; Ahn, C.; Soheili, A.; Handy, C. J.; Correia, R; Seganish, W. M.; DeShong, P. *J. Org. Chem.* **2004**, *69*, 8305-8314.

General procedure for the palladium catalysed asymmetric conjugate addition of arylsiloxanes.

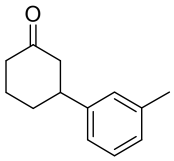
In a flame dried Schlenk tube equipped with a septum and stirring bar, $Pd(CH_3CN)_4(BF_4)_2$ (5 mol%, 0.025 mmol, 11.0 mg) and ligand $\mathbf{L_1}$ (5.5 mol%, 0.0275 mmol, 8.4 mg) were dissolved in dry dioxane (4 mL) and stirred under nitrogen atmosphere at room temperature for 30 min. The solution remained turbid and a dark yellow precipitate was observed on the bottom of the Schlenk tube. All compounds solubilize after the addition of H_2O. Arylsiloxane **2** (2 eq., 1.0 mmol) was added, followed by the addition of ZnF_2 (1 eq., 0.5 mmol, 51.5 mg), enone **1** (0.5 mmol) and *n*-dodecane (30 μL). The sample t^0 was taken from the mixture and filtered over a plug of silica gel and $MgSO_4$ before the injection in GC. After the addition of H_2O (1.0 mL) the mixture was degassed by alternating vacuum-nitrogen cycles and then heated to 50 °C. When the reaction was complete according to TLC or GC analysis, the mixture was cooled down to room temperature and diluted with *n*-pentane (~20 mL). The solution was then filtered over a plug of silica, dried on $MgSO_4$, concentrated and purified by flash chromatography (Et_2O/pentane) to yield the corresponding products **3**. The composition and the conversion in the crude mixture were determined by NMR, GC and GC-MS analysis.

(R)-3-Phenyl cyclohexanone (3a)



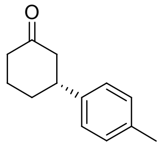
According to the general procedure ketone **3a** was obtained after purification by flash chromatography (eluent pentane/Et_2O 5:1) in 75% yield, 99% ee. Spectral data were in accordance with the literature.[4] Conversion was determined by GC analysis by injection on a HP1 column. E.e. was determined by HPLC analysis, Chiralpak AD column, Heptane/*i*-PrOH 99:1, detection at 209 nm, retention times: 11.8 min (minor) / 13.5 min (major).

(+)-3-(3-Methylphenyl)-cyclohexanone (3c)



According to the general procedure ketone **3c** was obtained without purification in 75% yield, 96% ee. Spectral data were in accordance with the literature.[5] Conversion was determined by GC analysis by injection on a HP1 column. E.e. was determined by chiral HPLC analysis, Chiralpak OD column, Heptane/*i*-PrOH 99:1, detection at 209 nm, retention times: 14.2 min (minor) / 16.6 min (major).

(+)-(R)-3-*p*-Tolyl-cyclohexanone (3d)



According to the general procedure ketone **3d** was obtained after purification by flash chromatography (eluent pentane/Et_2O 5:1) in 64% yield, 98% ee. Spectral data were in accordance with the literature.[4] Conversion was determined by GC analysis by injection on HP1 column. E.e. was determined by Chiralpak AD column, Heptane/*i*-PrOH 98:2, detection at 209 nm, retention times: 7.5 min (minor) / 7.86 min (major).

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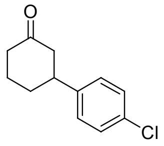
[4] Takaya, Y.; Ogasawara, M.; Hayashi, T.; Sakai, M.; Miyaura, M. *J. Am. Chem. Soc.* **1998**, *120*, 5579. For the absolute configuration determination of **3d** see: Takaya, Y.; Ogasawara, M.; Hayashi, T. *Tetrahedron Lett.* **1999**, *40*, 6957.

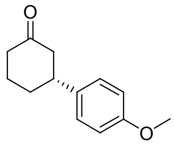
[5] Boiteau, J.; Imbos, R.; Minnaard, A. J.; Feringa, B. L. *Org. Lett.* **2003***, 5*, 681-684. For the absolute configuration determination of **3f** see: Takaya, Y.; Ogasawara, M.; Hayashi, T. *Tetrahedron Lett.* **1999**, *40*, 6957.

(+)-3-(4-Chlorophenyl)-cyclohexanone (3e)



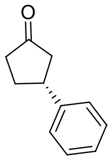
According to the general procedure ketone **3e** was obtained after purification by flash chromatography (eluent pentane/Et_2O 5:1) in 70% yield, 95% ee. Spectral data were in accordance with the literature.[6] Conversion was determined by GC analysis by injection on HP1 column. E.e. was determined by chiral HPLC analysis, Chiralcel AS column, Heptane/*i*-PrOH 97:3, detection at 210 nm, retention times: 11.5 min (major) / 13.6 min (minor).

(+)-(R)-3-(4-Methoxyphenyl)-cyclohexanone (3f)



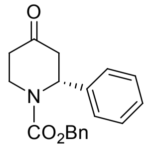
According to the general procedure at 50 °C ketone **3f** was obtained after purification by flash chromatography (eluent pentane/Et_2O 5:1) in 60% yield, 96% ee. Spectral data were in accordance with the literature.[5] Conversion was determined by GC analysis by injection on HP5 column. E.e. was determined by chiral HPLC analysis, Chiralcel OJ column, Heptane/*i*-PrOH 90:10, detection at 210 nm, retention times: 9.6 min (major) / 10.8 min (minor).

(+)-(R)-3-Phenyl-cyclopentanone (3g)



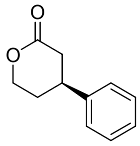
According to the general procedure ketone **3g** was obtained after purification by flash chromatography (eluent pentane/Et_2O 5:1) in 80% yield, 90% ee. Spectral data were in accordance with the literature.[4] Conversion was determined by GC analysis by injection on HP1 column. E.e. was determined by chiral GC, Chiraldex α-TA column (30 m x 0.25 mm) 140°C, retention times: 16.6 min (minor) / 17.5 min (major).

(+)-(R)-N-Carbobenzyloxy-2-Phenyl-4-piperidone (3h)



According to the general procedure piperidone **3h** was obtained after purification by flash chromatography (eluent pentane/Et_2O 1:1) in 84% yield, 99% ee. Spectral data were in accordance with the literature.[7] Conversion was determined following the reaction by TLC. E.e. was determined by Chiralcel OD-H column, Heptane/*i*-PrOH 90:10, detection at 210 nm, retention times: 26.6 min (minor, not visible) / 31.2 min (major).

(+)-(S)-4-Phenyl-tetrahydro-2H-pyran-2-one (3i)



According to the general procedure at 100°C pyranone **3i** was obtained after purification by flash chromatography (eluent pentane/Et_2O 3:2) in 20% yield, 88% ee. Spectral data were in accordance with the literature.[8] Conversion was determined by GC analysis by injection on HP1 column. E.e. was determined by chiral GC, Chiraldex G-TA column (30 m x 0.25 mm), 170 °C, retention times: 128.6 min (minor) / 131.4 min (major).

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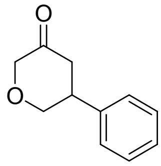
[6] Cho, C. S.; Motofusa, S.; Ohe, K.; Uemura, S. *J. Org. Chem.* **1995**, *60*, 883-888.

[7] Shintani, R.; Tokunaga, N.; Doi, H.; Hayashi, T. *J. Am. Chem. Soc.* **2004**, *126*, 6240-6241.

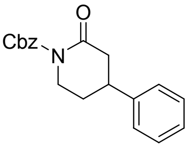
[8] Takaya, Y.; Senda, T.; Kurushima, H.; Ogasawara, M.; Hayashi, T. *Tetrahedron: Asym.* **1999**, *10*, 4047-4056.

(+)-5-Phenyl-dihydro-2*H*-pyran-3 (4*H*)-one (3j)



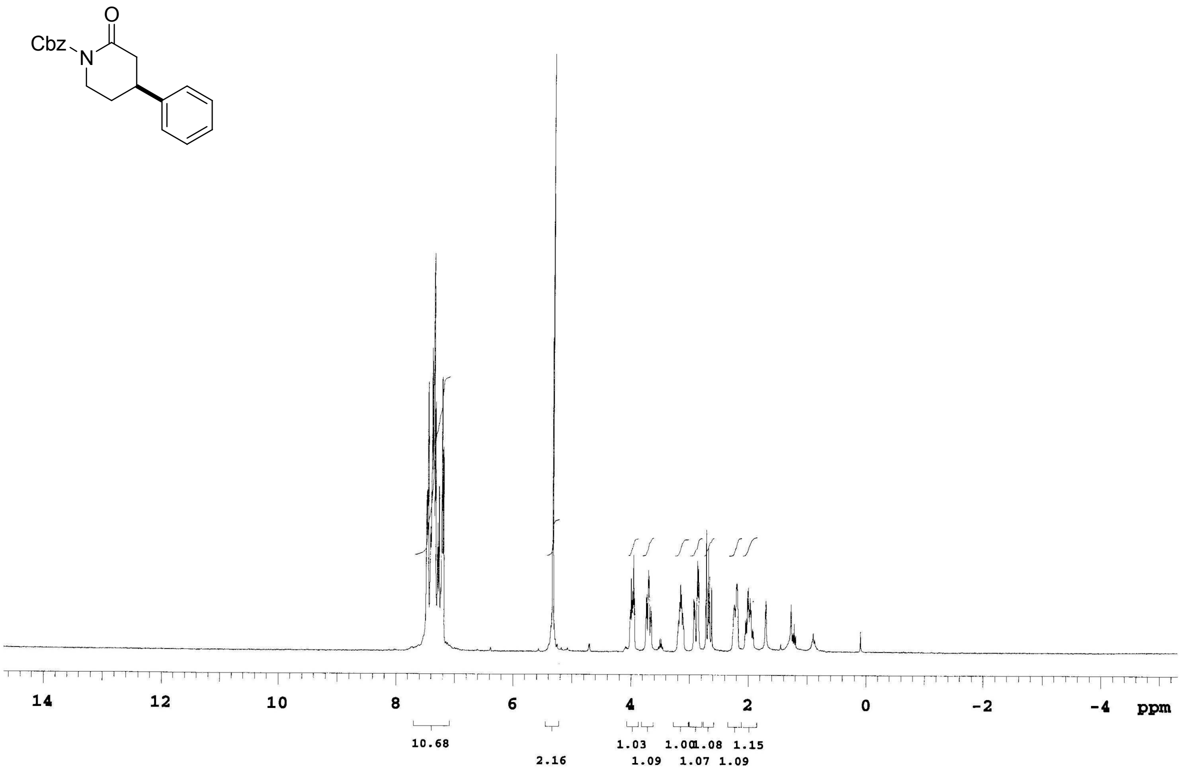
According to general procedure at 50 °C pyranone **3j** was obtained without further purification in 50% yield, 78% ee. Conversion was determined by GC analysis by injection on HP1 column. ^{1}H-NMR (400 MHz) δ 2.68-2.75 (1H, dd, J = 10.99 and 16.12 Hz), 2.82-2.87 (1H, dd, J = 5.33 and 16.13 Hz), 3.41-3.46 (1H, m), 3.69-3.77 (1H, m), 4.01-4.18 (3H, m), 7.21-7.37 (5H, m); ^{13}C-NMR δ 206.79, 139.91, 128.91, 127.39, 127.03, 74.39, 71.74, 44.50, 42.39. HRMS for $C_{11}H_{12}O_2$ calcd 176.0837, found 176.0843. MS, *m/z* (%): 176 (M+, 89.2), 131 (72.9), 104 (100). E.e. was determined by Chiralcel AS-H column, Heptane/*i*-PrOH 99:1, detection at 210 nm, retention times: 39.1 min (major) / 45.7 min (minor).

(+)-*N*-Benzyloxycarbonyl-4-phenyl-2-piperidinone (3k)

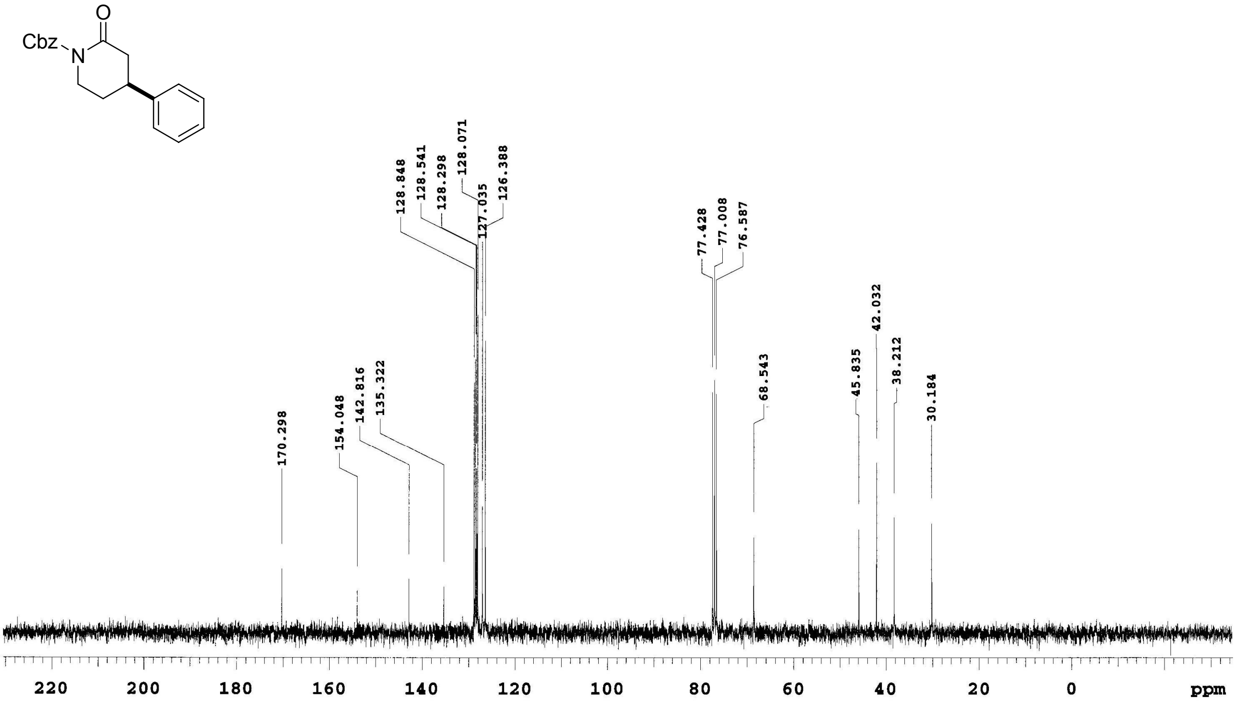


According to the general procedure piperidone **3k** was obtained without further purification in 60% yield, 94% ee. Conversion was determined following the reaction by TLC. ^{1}H-NMR (400 MHz) δ 1.91-2.01 (1H, m), 2.16-2.22 (1H, m), 2.62-2.69 (1H, dd, J = 11.0 and 17.23 Hz), 2.84-2.90 (1H, m), 3.09-3.15 (1H, m), 3.64-3.71 (1H, m), 3.93-3.99 (1H, m), 5.30 (2H, s), 7.18-7.46 (10H, m); ^{13}C-NMR δ 170.3, 154.05, 142.8, 135.3, 128.9, 128.5, 128.3, 128.07, 127.03, 126.4, 68.5, 45.8, 42.03, 38.2, 30.2. HRMS for $C_{18}H_{19}NO_3$ calcd 309.1380, found 309.1365. MS, *m/z* (%): 309 (M+, 25.6), 175 (39.2), 91 (100). E.e. was determined by Chiralcel AD column, Heptane/*i*-PrOH 98:2, detection at 210 nm, retention times: 56.8 min (major) / 61.2 min (minor).

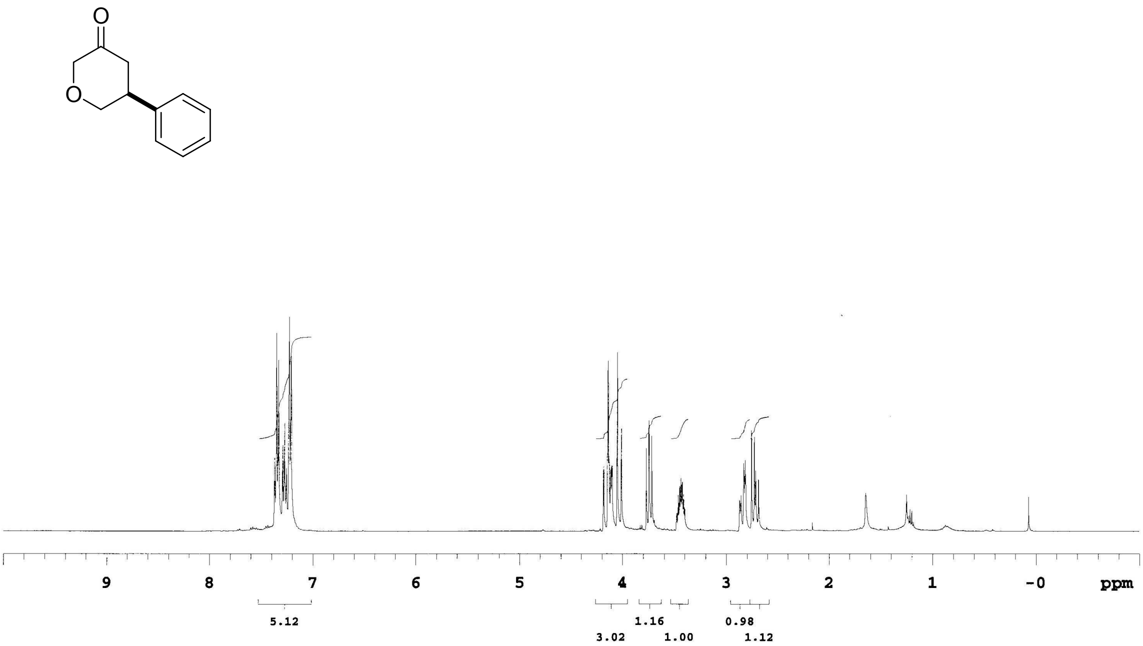
^{1}H-NMR of compound 3k



^{13}C-NMR of compound 3k



^{1}H-NMR of compound 3j



^{13}C-NMR of compound 3j