# Enantioselective Heck Reactions Catalyzed by Chiral Phosphinooxazoline–Palladium Complexes

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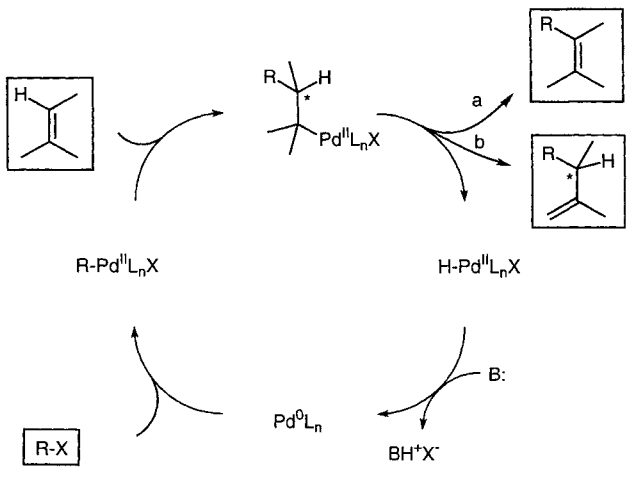
Dedicated to Professor Dieter Seebach on the occasion of his 60th birthday

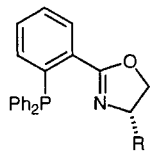
Palladium complexes with chiral phosphinooxazoline ligands are efficient catalysts for enantioselective Heck reactions with aryl or alkenyl triflates and cyclic alkenes. In the arylation and alkenylation of 1,2-dihydrofuran, cyclopentene, 2,3-dihydro-4*H*-pyran, 4,7-dihydro-1,3-dioxepin, and *N*-methoxycarbonyl-2,3-dihydropyrrole high yields and good to excellent enantioselectivities have been obtained. In contrast to analogous (BINAP)Pd-catalyzed reactions, isomerization of the products by C–C double bond migration was essentially not observed.

The Heck reaction is one of the most versatile catalytic methods for C–C bond formation.[1] In this process an aryl or alkenyl halide or triflate is coupled with an alkene (Scheme 1). The catalytic cycle starts with an oxidative addition of the organic halide or triflate to a Pd(0) complex followed by insertion of the alkene. The resulting Pd(II) alkyl complex then undergoes $\beta$-hydride elimination. Depending on the structure of the substrate, several isomeric products can be formed. If the C–C double bond is restored in the original position (path a), a stereogenic center is not created in the overall process. However, if $\beta$-hydride elimination takes a different direction (path b), the stereogenic C atom introduced in the insertion step is retained. In this case, the use of chiral palladium complexes makes it possible to carry out such reactions in an enantioselective manner. Shibasaki and Overman have reported remarkable examples of highly enantioselective intramolecular Heck reactions and have convincingly demonstrated the value of such transformations in the synthesis of complex natural products.[2] High enantioselectivities have also been obtained in certain intermolecular Heck reactions by Hayashi and co-workers.[3] In all these reactions, BINAP has been used as chiral ligand.[4] Although this versatile diphosphine ligand often allows effective enantiocontrol, there are also many cases where Pd–BINAP catalysts do not provide satisfactory results and, therefore, it would be highly desirable to have alternative ligands at hand.




**Scheme 1**

We have recently found that chiral phosphinooxazolines **1**[5,6] are very efficient ligands for enantioselective Heck reactions.[7] In several cases, these ligands gave higher enantiomeric excesses and different product distributions compared to analogous Pd(BINAP)-catalyzed reactions. Here, we discuss these studies in detail and report additional applications which illustrate the scope and limitations of Pd-phosphinooxazoline complexes as enantioselective catalysts in Heck reactions.

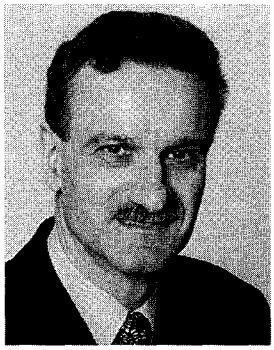



**1a** R = $CH_3$
**1b** R = $CH(CH_3)_2$
**1c** R = $C(CH_3)_3$
**1d** R = $C_6H_5$
**1e** R = $CH_2(C_6H_5)$
**1f** R = $CH_2CH(CH_3)_2$
**1g** R = $CH_2C(CH_3)_3$

The reaction between 2,3-dihydrofuran and 1-cyclohexenyl triflate was chosen to screen different ligands and catalyst precursors and to optimize the reaction conditions. Scheme 2 shows the results obtained by Ozawa, Hayashi and co-workers[3] in this reaction, using a Pd–BINAP catalyst. In the Pd-alkyl intermediate derived from dihydrofuran only C(4) has a hydrogen atom *cis* to the Pd–C bond. Therefore, $\beta$-hydride elimination takes place exclusively between C(3) and C(4), leaving the stereogenic center intact. Under the reaction conditions, the C–C double bond migrates by reinsertion into the Pd–H bond with reversed regioselectivity and subsequent $\beta$-hydride elimination to give the thermodynamically more stable 2,3-dihydrofuran derivative (see Scheme 2). In analogous reactions with aryl triflates, this double bond migration was found to involve kinetic resolution. This made it possible to obtain the corresponding 2-aryl-2,3-dihydrofuran derivatives with high ee, even though the insertion of dihydrofuran into the Pd–aryl bond proceeded with only moderate enantioselectivity.

The use of phosphinooxazolines as chiral ligands gave strikingly different results (Table 1). The best enantioselectivity and also the highest catalyst activity was observed with the *tert*-butyloxazoline ligand **1c**. Using 3 mol% of catalyst, prepared in situ from $[Pd_2(dba)_3 \cdot dba]$[8] and 5–6 mol% of ligand **1c**, the 2,5-dihydrofuran derivative **2** was formed in high yield and with excellent enantioselectivity. The corresponding 2,3-dihydrofuran derivative, the product of the Pd(BINAP)-catalyzed reaction, was not detected. With Pd(BINAP) catalysts, 1,8-bis(dimethylamino)naphthalene (proton sponge) was required as a base for optimum results, whereas in our case simpler bases such as triethylamine or *N,N*-diisopropylethylamine proved to be equally effective. Usually, 1.5–2 equivalents of ligand **1c** were used. With just 1 equivalent (3 mol% **1c**, 3 mol% $[Pd_2(dba)_3 \cdot dba]$) the ee's and yields were slightly lower (98 *vs.* 99% ee, 85 *vs.* 95% yield).

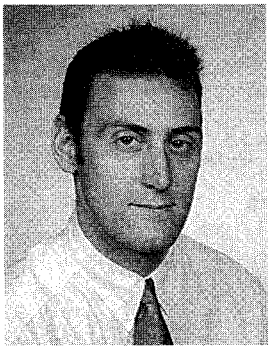
## Biographical Sketches



**Andreas Pfaltz** was born in 1948 in Basel, Switzerland. He studied chemistry at the ETH in Zürich where he received a diploma in natural sciences and a Ph.D. degree in 1978, working under the direction of Albert Eschenmoser. After postdoctoral studies with Gilbert Stork at Columbia University, he returned to the ETH. There he began his independent research and was appointed Privatdozent in 1987. In 1990 he joined the faculty at the University of Basel as Professor of Organic Chemistry. In 1995 he moved to the Max-Planck-Institut für Kohlenforschung in Mülheim an der Ruhr, Germany, where he is a director and head of the homogeneous catalysis section. He is working in the areas of synthetic organic and organometallic chemistry. He is also interested in biological processes involving transition metals. The main emphasis of his current research is on homogeneous and heterogeneous asymmetric catalysis.

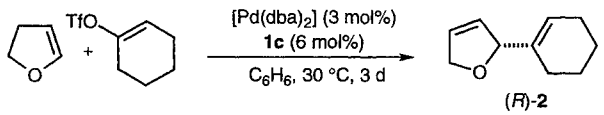
**Olivier Loiseleur** was born in Luzern, Switzerland, in 1968. He studied chemistry at the University Louis Pasteur in Strasbourg and at the Ecole Nationale Supérieure de Chimie in Mulhouse, France, where he received a 'Diplôme d'études approfondies' in organic chemistry in 1991. He then joined the research group of Andreas Pfaltz at the University of Basel and after moving to the Max-Planck-Institut für Kohlenforschung in Mülheim, Germany, he received his Ph.D. degree in 1996. He is currently a postdoctoral fellow in Prof. Dale Boger's group at Scripps.

**Masahiko Hayashi** was born in Nagoya in 1960. He received his bachelors', masters' and Ph.D. degree from Nagoya University. After completion of his Ph.D. thesis under the direction of Prof. Ryoji Noyori in 1988, he worked as a research associate in the Chemistry Department of Yamaguchi University. There he became Associate Professor in 1993. From November 1995 to March 1997 he was a visiting scientist at the Max-Planck-Institut für Kohlenforschung working in the research group of Andreas Pfaltz. His research interests are in the area of synthetic organic chemistry, including organometallic chemistry, asymmetric synthesis and the synthesis of natural and unnatural products.



**Norbert Schmees** was born in Meppen, Germany, in 1969. He studied chemistry at the Rupert Karls University in Heidelberg where he graduated in 1995. Since 1996 he has been working towards his Ph.D. degree under the direction of Andreas Pfaltz at the Max-Planck-Institut für Kohlenforschung in Mülheim.

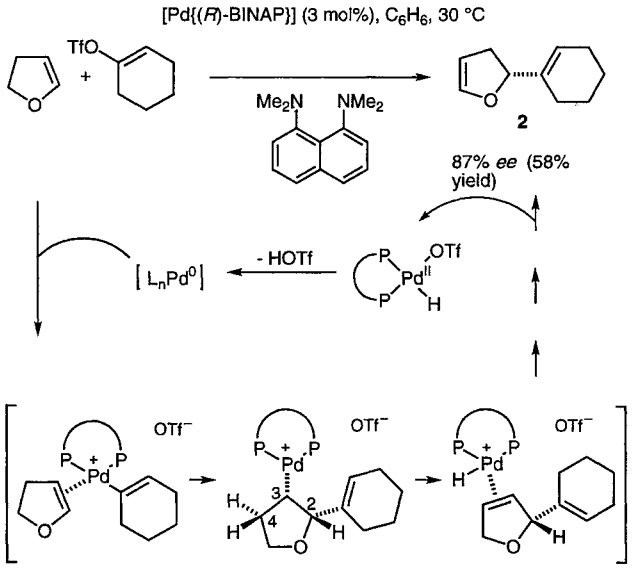
**Table 1.** Enantioselective Heck reaction of 2,3-dihydrofuran




| Base | Enantiomeric Excess | Yield[a] [%] |
|---|---|---|
| 1,8-bis(dimethylamino)naphthalene | 98% *ee* | 95 |
| 2,2, 6,6-tetramethylpiperidine | 99% *ee* | 95 |
| triethylamine | > 99% *ee* | 78 |
| *N,N*-diisopropylamine | > 99% *ee* | 92 |
| *N,N*-diisopropylethylamine | 99% *ee* | 98[b] |
| sodium carbonate | 98% *ee* | 34 |
| sodium acetate | 98% *ee* | 50 |

[a] Determined by GC with *n*-tridecane as internal standard

[b] Yield of purified product: 92%

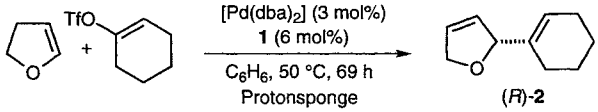



**Scheme 2**

Interestingly, with phosphinooxazolines containing less bulky groups at the stereogenic center, the reaction was much slower as reflected by the low conversion (Table 2). This finding was unexpected because steric hindrance near the metal center often slows down a metal-catalyzed process and no obvious explanation can be offered at this stage. The effect of the R substituent at the oxazoline ring on enantioselectivity was less pronounced.

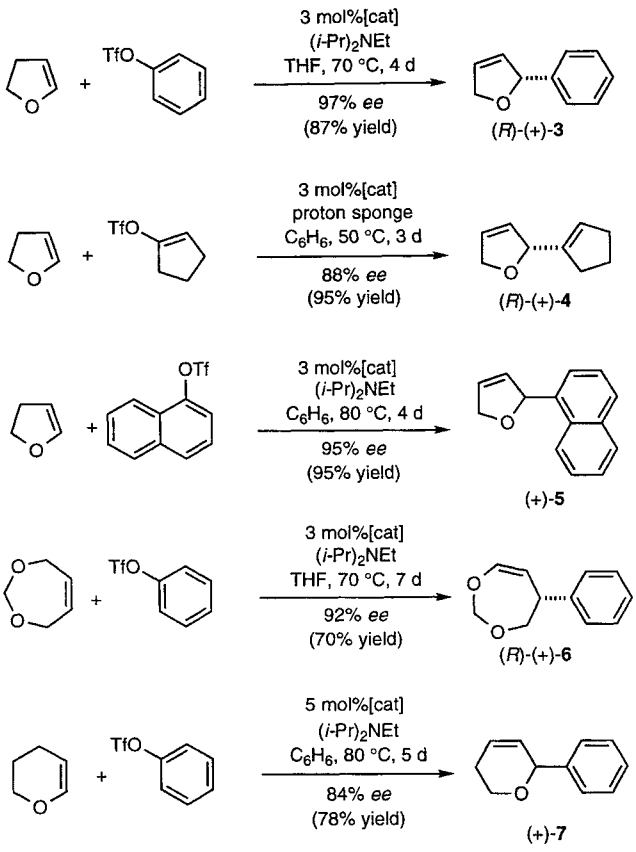
Similar results were obtained with phenyl, 1-naphthyl and 1-cyclopentenyl triflate (Scheme 3). Arylation of 4,7-dihydro-1,3-dioxepin, which leads to a masked hydroxy aldehyde, also proceeds with good enantioselectivity and satisfactory yield. The corresponding Pd(BINAP)-catalyzed process[9] was reported to give 72% ee and 84% yield in this reaction. The absolute configurations of **3**, **4**, **6** and **8** were determined by comparison of the optical rotation with the literature values.[16] Dihydropyran proved to be less reactive than dihydrofuran but at somewhat higher temperature also gave the desired product in good yield with 84% ee. With BINAP, a 3:2 mixture of 5,6- and 3,6-dihydro-2-phenyl-*2H*-pyran was formed with low enantioselectivity (< 20% ee for both isomers).

**Table 2.** Ligand Screening




| Ligand | Enantiomeric Excess | Conversion[a] |
|---|---|---|
| **1e** | 90% *ee* | 24% |
| **1f** | 95% *ee* | 18% |
| **1g** | 98% *ee* | 25% |
| **1c** | 98% *ee* | 95% |

[a] Determined by GC with *n*-tridecane as internal standard

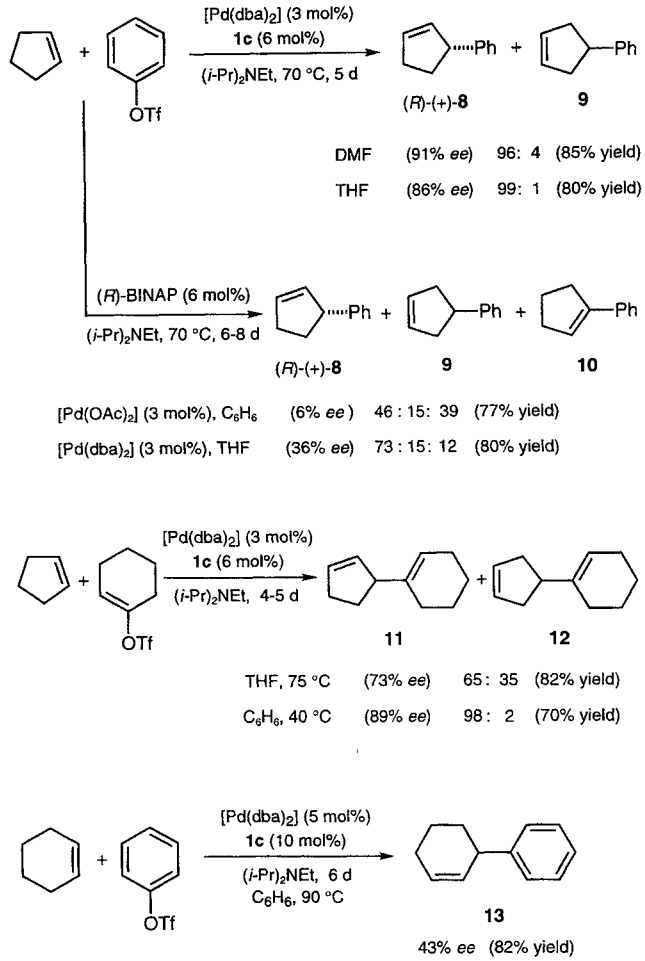



[cat] = $[Pd_2(dba)_3 \cdot dba]$ / **1c**

**Scheme 3**

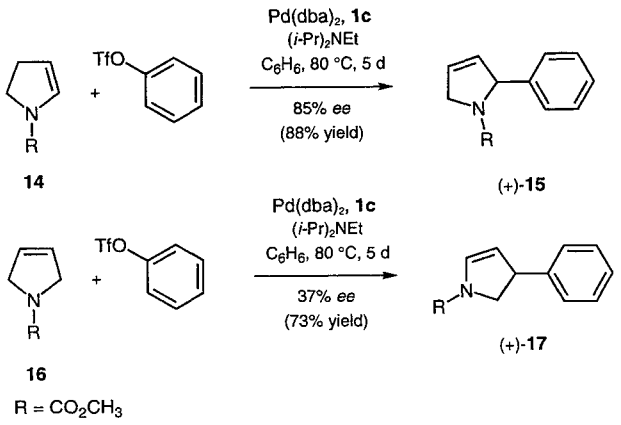
The reaction was found to be highly sensitive to traces of chloride ions and chloroform. No reaction was observed in the presence of $Et_4NCl$ or with a catalyst generated from [(**1c**)$PdCl_2$] and BuLi. [$Pd_2(dba)_3 \cdot CHCl_3$] as a catalyst precursor gave lower conversion than [$Pd_2(dba)_3 \cdot dba$], and large fluctuations in yields and enantiomeric excesses were observed.[10]

The low tendency of Pd(phosphinooxazoline) catalysts to promote C–C double bond migration makes it possible to use substrates such as cyclopentene which are converted to mixtures of isomers with Pd(BINAP) catalysts (Scheme 4). The observed product distributions are dependent on the solvent and the base. However, under optimized conditions, the desired chiral 3-substituted cyclopentene derivatives **8** and **11** are obtained in good yield and with high preference over the corresponding achiral isomers **9** and **12**. Other isomers are formed only in trace amounts under these conditions, in contrast to the corresponding Pd(BINAP)-catalyzed reactions which lead to complex mixtures of isomers and low ee's due to extensive double bond migration. Ligands **1a**, **1b** and **1d–g** all gave low conversion and lower ee's (62–68%) than the standard ligand **1c**. Cyclohexene is less reactive and requires prolonged heating at 90°C. Under these conditions the desired product **13** is formed in good yield but with low ee.



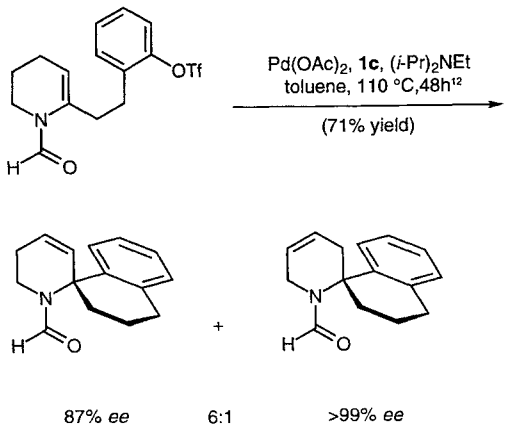

**Scheme 4**

The 2,3-dihydropyrrole derivative **14** also requires relatively high reaction temperatures. However, in this case, the arylation product **15** is obtained with an ee of 85%. The corresponding 2,3-dihydro isomer is not detected, whereas under similar conditions with a catalyst prepared from $Pd(OAc)_2$ and BINAP, the 2-phenyl-2,3-dihydropyrrole derivative is formed as the main product in 68% yield with 74% ee while the minor isomer **15** is isolated in 27% yield with 27% ee. The 2,5-dihydropyrrole derivative **16**[11] reacts with much lower enantioselectivity under the same conditions.




**Scheme 5**

So far we have not studied any intramolecular Heck reactions. However, Ripa and Hallberg[12] have recently reported a Pd-catalyzed cyclization leading to a spiro ring system with high enantioselectivity and good yield, using the phosphinooxazoline **1c** as chiral ligand (Scheme 6). BINAP proved to be ineffective in this case.




**Scheme 6**

A mechanistic rationalization of the observed selectivities seems premature at the present stage because experimental data on the structure, relative stability, and reactivity of the intermediates in the catalytic cycle are still lacking.[13] Unless we can distinguish between two possible pathways, one involving *cis* the other *trans* coordination of the alkene and the P atom, a meaningful mechanism of enantioselection cannot be proposed.

The remarkable selectivities obtained with phosphinooxazolines indicate a considerable scope for P,N-ligands of this type in enantioselective Heck reactions. Due to the low extent of C–C double bond migration, the product distribution can differ substantially from analogous Pd(BINAP)-catalyzed reactions. Particularly, where double bond migration leads to undesired mixtures of isomers or racemization, phosphinooxazolines are clearly superior to diphosphine ligands.

Phosphinooxazolines are attractive ligands because they are readily synthesized from simple precursors[5,6] and because their modular structure allows extensive and independent variation of the backbone, the oxazoline ring, and the phosphine group. This leaves room for further catalyst improvement by optimizing the steric and electronic properties of the ligand.

Benzene, *N,N*-diisopropylethylamine, *n*-tridecane: Fluka puriss. 2,8-Bis(dimethylamino)-naphthalene: Fluka puriss. dist. prior to use. Vinyl triflates, phenyl triflates, 4,7-dihydro-1,3-dioxepin and *N*-(methoxycarbonyl)-2-pyrroline were synthesized using literature procedures.[14] *N*-(Methoxycarbonyl)-3-pyrroline was used as a mixture in a 7:3 ratio with the corresponding *N*-(methoxycarbonyl)-3-pyrrolidine derivative.[11] $[Pd_2(dba)_3 \cdot dba]$ was synthesized according to Ukai et al.[15] Standard syringe techniques were used to transfer solvents and for addition of liquid reagents. Reactions were carried out under Ar using dried glassware. Flash column chromatography: silica gel 0.040–0.063 mm, Merck, TLC: silica gel 60 Macherey Nagel, 0.25 mm, F 254, staining with basic $KMnO_4$. Specific rotation: concentration in g/100 mL of solution, estimated error: ± 5%. IR: selected bands in $cm^{-1}$. $^1H$ NMR: 300 MHz, $^{13}C$ NMR: 75 MHz, $CDCl_3$ as solvent. MS: selected peaks; *m/z* (%; fragment).

**(+)-(*R*)-2-(Cyclohex-1′-en-1′-yl)-2,5-dihydrofuran (2): Typical Procedure:**

$[Pd_2(dba)_3 \cdot dba]$ (77.5 mg, 66.5 μmol, 0.135 mmol based on Pd) and (-)-(4*S*)-4-*tert*-butyl-4,5-dihydro-2-[2′-(diphenylphosphino)phenyl]-oxazole (**1c**) (104.6 mg, 0.270 mmol) were placed under Ar in an ampoule equipped with a magnetic stirring bar and a Young valve and treated with a solution of cyclohex-1-en-1-yl trifluoromethanesulfonate (1.048 g, 4.55 mmol) and *n*-tridecane (424 mg, 2.30 mmol) as internal GC standard in Ar saturated benzene (10 mL), followed by 2,3-dihydrofuran (1.35 mL, 17.9 mmol), *N,N*-diisopropylethylamine (1.57 mL, 9.17 mmol), and Ar saturated benzene (50 mL). The ampoule was sealed under Ar and the mixture stirred at 24 °C (red solution, precipitation of *N,N*-diisopropylethylammonium triflate) until the reaction was complete according to GC analysis [65 h; *MN Permabond OV 1701*; 50m, 90–210 °C, 0.7 °C $min^{-1}$, 120 kPa: $t_R$ = 21.7 min (*n*-tridecane), 22.3 min (**2**)]. The mixture was diluted with pentane (*ca.* 150 mL) and the resulting red suspension was filtered through a 2 cm layer of silica gel (∅ = 7 cm). Further elution with $Et_2O$ and concentration gave a red oil which was purified by flash chromatography (silica gel, 4 × 25 cm; *n*-pentane/$CH_2Cl_2$ 1:1) followed by Kugelrohr distillation (125 °C, 12 mbar) to afford (+)-(*R*)-**2** (629 mg, 92%) as a colorless oil.[16]

$[\alpha]_D$ = +201 (c = 1.06, $CHCl_3$, 24 °C, 99% ee by GC).

GC (*Chiraldex γ-CD-TFA*; 30m, 80–140 °C, 0.3 °C $min^{-1}$, 60 kPa): 29.3 min (*S*), 30.4 min (*R*).

IR ($CHCl_3$): *ν* = 2931s, 2858w, 1437m, 1351w, 1262m, 1058s, 922m, 893m, 839m $cm^{-1}$.

$^1H$ NMR: *δ* = –1.44–1.73 (m, 4H, $H_2C(4')$, $H_2C(5')$); 1.76–2.14 (m, 4H, $H_2C(3')$, $H_2C(6')$); 4.63 (dddd, 1H, *J* 12.6, 4.2, 2.7, 1.8 Hz), 4.69 (dddd, 1H, *J* 12.6, 5.7, 2.4, 1.5 Hz) ($H_2C(5)$); 5.08–5.17 (m, 1H, HC(2)); 5.63–5.78 (m, 2H, HC(2′), HC(3) or HC(4)); 5.94 (ddt, 1H, *J* 6.3, 2.4, 1.5 Hz, HC(3) or HC(4)).

$^{13}C$ NMR: *δ* = 22.5, 23.3, 25.0 ($H_2C(3')$, $H_2C(4')$, $H_2C(5')$, $H_2C(6')$); 75.6 ($H_2C(5)$); 90.6 (HC(2)); 124.2 (HC(2′)); 127.0 (HC(4)); 128.7 (HC(3)); 138.0 (C(1′)).

MS (EI): *m/z* (%) = 150 (90, $M^+$), 122 (11), 121 (75), 109 (27), 108 (18), 107 (40), 95 (45), 94 (24), 93 (35), 92 (12), 91 (54), 82 (50), 81 (84), 79 (100), 78 (20), 77 (60), 69 (63), 68 (57), 67 (47), 66 (19), 65 (28), 63 (13), 55 (24), 54 (17), 53 (46), 52 (17), 51 (29), 50 (14), 41 (98).

TLC: $R_f$ = 0.26 (pentane/$CH_2Cl_2$ 1:1).

**(+)-(*R*)-2-Phenyl-2,5-dihydrofuran (3):**

According to the typical procedure, a solution of $[Pd_2(dba)_3 \cdot dba]$ (17.8 mg, 15.0 μmol) and **1c** (18.9 mg, 49 μmol) in anhyd THF (5 mL) was stirred for 10 min. Phenyl triflate (223.2 mg, 0.99 mmol), 2,3-dihydrofuran (212 mg, 3.03 mmol), *N,N*-diisopropylethylamine (257.2 mg, 2.0 mmol) and *n*-tridecane (43.6 mg, 0.24 mmol) were added. The reaction was carried out at 70 °C. After 4 d, standard workup and flash chromatography (silica-gel, 3 × 15 cm, *n*-pentane/$CH_2Cl_2$ 1:1) afforded **3** (125.7 mg, 87%) as a colorless oil.

$[\alpha]_D$ = +280 (c = 1.06, $CHCl_3$, 24 °C, 97% ee by GC).

GC (*FS-595 tert-butyldimethylsilyl dimethyl β-CD/SE-54*;[17] 30m, 80–240 °C, 1.5 °C $min^{-1}$, 90 kPa): 26.6 min (*S*), 27.8 min (*R*).

IR ($CHCl_3$): *ν* = 3086w, 3066w, 3006s, 2956w, 2856s, 1950w, 1811w, 1602w, 1492m, 1454m, 1354m, 1324w, 1264m, 1080m, 1061s, 1028m, 1021m, 1010m, 898m, 841m, 687s $cm^{-1}$.

$^1H$ NMR: *δ* = 4.76 (dddd, 1H, *J* 12.6, 4.2, 2.4, 1.5 Hz), 4.87 (dddd, 1H, *J* 12.6, 6.0, 2.4, 1.5 Hz) ($H_2C(5)$); 5.76–5.82 (m, 1H, HC(2)); 5.88 (dtd, 1H, *J* 6.0, 2.4, 1.5 Hz), 6.03 (ddt, 1H, *J* 6.0, 2.4, 1.5 Hz) (HC(3), HC(4)); 7.23–7.39 (m, 5H, arom. H).

$^{13}C$ NMR: *δ* = 75.7 ($H_2C(5)$); 87.8 (HC(2)); 126.3, 126.5, 127.7, 128.4, 129.9 (HC(3), HC(4), arom. CH); 142.0 (arom. C).

MS (EI): *m/z* (%) = 146 (44, $M^+$), 145 (41), 127 (12), 117 (40), 116 (13), 115 (60), 105 (100), 91 (21), 77 (40), 69 (14), 63 (11), 51 (19).

TLC: $R_f$ = 0.21 (*n*-pentane/$CH_2Cl_2$ 1:1).

**(+)-(*R*)-2-(Cyclopent-1′-en-1′-yl)-2,5-dihydrofuran (4):**

According to the typical procedure, a solution of $[Pd_2(dba)_3 \cdot dba]$ (18.5 mg, 15.6 μmol) and **1c** (20.3 mg, 52.5 μmol) in anhyd benzene (5 mL) was stirred for 10 min. Cyclopent-1-en-1-yl triflate (224.3 mg, 1.04 mmol), 2,3-dihydrofuran (223.6 mg, 3.13 mmol), *N,N*-diisopropylethylamine (261.4 mg, 2.03 mmol) and *n*-tridecane (66.3 mg, 0.36 mmol) were added. The reaction was carried out at 50 °C. After 3 d, standard workup and flash chromatography (silica gel, 3 × 15 cm, *n*-pentane/$CH_2Cl_2$ 1:1) afforded **4** (134.4 mg, 95%) as a colorless oil.

$[\alpha]_D$ = +201 (c = 1.27, $CHCl_3$, 20 °C, 92% ee by GC).

GC (*FS-595 tert-butyldimethylsilyl dimethyl β-CD/SE-54*;[17] 30m, 80–320 °C, 1.5 °C $min^{-1}$, 90 kPa): 17.6 min (*S*), 18.3 min (*R*).

$^1H$ NMR: *δ* = 1.80–1.99 (m, 2H, $H_2C(4')$; 2.15–2.44 (m, 4H, $H_2C(3')$, $H_2C(5')$); 4.64 (dddd, 1H, *J* 12.6, 4.2, 2.4, 1.5 Hz), 4.71 (dddd, 1H, *J* 12.6, 5.7, 2.4, 1.5 Hz) ($H_2C(5)$); 5.36–5.45 (m, 1H, HC(2)); 5.60–5.66 (m, 1H, HC(2′)); 5.75 (dtd, 1H, *J* 6.3, 2.4, 1.5 Hz), 5.94 (ddt, 1H, *J* 6.3, 2.4, 1.5 Hz) (HC(3), HC(4)).

$^{13}C$ NMR: *δ* = 23.2 ($H_2C(4')$); 30.9, 32.3 ($H_2C(3')$, $H_2C(5')$); 75.2 ($H_2C(5)$); 84.7 (HC(2)); 126.5, 126.8 (HC(2′), HC(4)); 128.4 (HC(3)); 144.6 (C(1′)).

MS (EI): *m/z* (%) = 136 (92, $M^+$), 135 (27), 108 (70), 107 (54), 105 (11), 95 (67), 93 (23), 91 (41), 81 (13), 80 (35), 79 (100), 78 (18), 77 (43), 69 (31), 68 (79), 67 (68), 66 (21), 65 (34), 63 (12), 55 (12), 53 (17), 52 (13), 51 (25), 50 (14), 41 (75).

TLC: $R_f$ = 0.31 (*n*-pentane/$CH_2Cl_2$ 1:1).

**(+)-2-(1-Naphthyl)-2,5-dihydrofuran (5):**

According to the typical procedure, a solution of $[Pd_2(dba)_3 \cdot dba]$ (14.4 mg, 12.1 μmol) and **1c** (17.3 mg, 44 μmol) in anhyd benzene (5 mL) was stirred for 10 min. 1-Naphthyl triflate (222.2 mg, 0.81 mmol), 2,3-dihydrofuran (170.1 mg, 2.43 mmol), *N,N*-diisopropylethylamine (207.2 mg, 1.98 mmol) and *n*-tridecane (53.2 mg, 0.29 mmol) were added. The reaction was carried out at 80 °C. After 4 d, standard workup and flash chromatography (silica gel, 3 × 15 cm, *n*-pentane/$CH_2Cl_2$ 1:1) afforded **5** (150.8 mg, 95%) as a colorless oil.

$[\alpha]_D$ +201 (c = 1.13, $CHCl_3$, 19 °C, 95% ee by HPLC).

HPLC (*Chiralcel OD-H*; 0.46 × 25 cm, 0.5 mL $min^{-1}$, heptane/isopropanol 90:10, detection at 220 nm): 15.7 min (+), 17.9 min (−).

IR (KAP): $\nu$ = 3049m, 2950m, 2848s, 1943w, 1733w, 1687w, 1596m, 1510s, 1258m, 1084s, 1059s, 1014m, 798s, 782s $cm^{-1}$.

$^1$H NMR: $\delta$ = 4.82–4.99 (m, 2H, $CH_2O$); 6.03–6.15 (m, 2H, HC=CH); 6.53–6.57 (m, 1H, CHO); 7.40–7.57 (m, 4H, aromatic protons); 7.75–7.88 (m, 2H, aromatic protons); 8.09–8.14 (m, 1H, aromatic proton).

$^{13}$C NMR: $\delta$ = 75.3 ($H_2C(5)$); 84.4 (HC(2)); 122.9, 125.2, 125.8, 126.7, 127.8, 128.4, 128.9 (HC(3), HC(4), arom. CH), 130.5, 133.5, 137.2 (arom. C).

MS (EI): *m/z* (%) = 196 (100, $M^+$), 195 (54), 177 (10), 167 (46), 166 (16), 165 (56), 164 (12), 163 (13), 155 (35), 153 (12), 152 (30), 139 (11), 128 (72), 127 (47), 126 (11), 49 (11).

TLC: $R_f$ = 0.5 (hexane/EtOAc 4:1)

HRMS: *m/z* (%) = 196.08872 (calcd for $C_{14}H_{12}O$: 196.0888).

**(+)-(*R*)-4,5-Dihydro-5-phenyl-1,3-dioxepin (6):**

According to the typical procedure, a solution of [$Pd_2(dba)_3$ · dba] (19.8 mg, 16.7 μmol) and **1c** (23.3 mg, 60.1 μmol) in anhyd THF (5 mL) was stirred for 10 min. Phenyl triflate (246.2 mg, 1.09 mmol), 4,7-dihydro-1,3-dioxepin (344.3 mg, 3.44 mmol), *N,N*-diisopropylethylamine (285.3 mg, 2.21 mmol) and *n*-tridecane (59.2 mg, 0.32 mmol) were added. The reaction was carried out at 70 °C. After 7 d, standard workup and flash chromatography (silica gel, 3 × 15 cm, hexane/*tert*-butyl methyl ether 93:7) afforded **6** (134.3 mg, 70 %) as a colorless oil.

$[\alpha]_D$ = +35 (c = 0.99, $CHCl_3$, 24 °C, 92 % ee by HPLC).

HPLC (*Chiralcel OD-H*; 0.46 × 25 cm, 0.5 mL $min^{-1}$, hexane/isopropanol 99:1, detection at 220 nm): 16.9 min (*R*), 19.8 min (*S*).

IR ($CHCl_3$): $\nu$ = 3064w, 3006m, 2966w, 2940w, 2905w, 2873m, 2803w, 1650s, 1602w, 1492m, 1469w, 1453m, 1396w, 1368w, 1285m, 1174s, 1131m, 1119m, 1102m, 1046s, 1031m, 1019m, 1008m, 956m, 927m, 630m $cm^{-1}$.

$^1$H NMR: $\delta$ = 3.46 (dd, 1H, *J* 11.6, 8.6 Hz, $H_2C(4)$); 3.80 (dddd, 1H, *J* 8.6, 4.4, 3.7, 2.3 Hz, HC(5)); 3.97 (ddd, 1H, *J* 11.6, 4.4, ≅ 1 Hz, $H_2C(4)$); 4.85 (d, 2H, *J* 7.0 Hz, $H_2C(2)$); 4.94 (ddd, 1H, *J* 7.4, 3.7, 0.8 Hz, HC(6)); 5.19 (d, 1H, *J* 7.0 Hz, $H_2C(2)$); 6.46 (dd, 1H, *J* 7.4, 2.3 Hz, HC(7)); 7.17–7.40 (m, 5H, arom. H).

$^{13}$C NMR: $\delta$ = 48.4 (HC(5)); 76.8 ($H_2C(4)$); 98.1 ($H_2C(2)$); 112.0 (HC(6)); 126.9, 127.9, 128.6 (arom. CH); 140.9 (arom. C); 146.0 (HC(7)).

MS (EI): *m/z* (%) = 176 (20, $M^+$), 146 (66), 145 (71), 132 (12), 131 (41), 129 (13), 128 (18), 127 (13), 118 (67), 117 (81), 116 (30), 115 (100), 103 (16), 91 (46), 89 (15), 78 (24), 77 (19), 65 (15), 63 (14), 51 (16).

TLC: $R_f$ = 0.43 (hexane/*tert*-butyl methyl ether 93:7).

**(+)-5,6-Dihydro-2-phenyl-2*H*-pyran (7):**[18]

According to the typical procedure, a solution of [$Pd_2(dba)_3$ · dba] (28.2 mg, 23.8 μmol) and **1c** (36.8 mg, 95.0 μmol) in anhyd benzene (5 mL) was stirred for 10 min. Phenyl triflate (215.2 mg, 0.95 mmol), 3,4-dihydro-2*H*-pyran (245.2 mg, 2.92 mmol), *N,N*-diisopropylethylamine (248.1 mg, 1.92 mmol) and *n*-tridecane (102.4 mg, 0.56 mmol) were added. The reaction was carried out at 80 °C. After 5 d, standard workup and flash chromatography (silica gel, 3 × 15 cm, *n*-pentane/$CH_2Cl_2$ 1:1) afforded **7** (118.6 mg, 78 %) as a colorless oil.

$[\alpha]_D$ +109.6 (c = 0.6, $CHCl_3$, 20 °C, 84 % ee by GC).

GC (*Chiraldex* γ-CD-TFA; 25 m, 80–180 °C, 0.3 °C/min, 100 kPa); 29.8 min (+), 31.8 min (−).

IR (KAP): $\nu$ = 3062m, 3032m, 2962m, 2921m, 2854m, 1649w, 1603w, 1493m, 1452m, 1427m, 1365w, 1259m, 1180m, 1082s (C–O–C), 1062m, 907m, 755s, 700s, 675m $cm^{-1}$.

$^1$H NMR $\delta$ = 2.06 (dddd, *J* = 16.5, 3.7, 4.6, 0.9 Hz, 1H, $H_2C(5)$), 2.32 (dddd, *J* = 16.5, 0.7, 4.6, 3.0 Hz, 1H, $CH_2C(5)$), 3.80 (ddd, *J* = 4.2, 8.6, 11.3 Hz, 1H, $CH_2C(6)$), 4.00 (ddd, *J* = 11.3, 3.7, 5.4 Hz, 1H, $CH_2C(6)$), 5.14 (ddt, *J* = 2.9, 2.2, 2.3 Hz, HC(2)), 5.81 (ddd, *J* = 10.2, 3.8, 2.0 Hz, 1H), 6.00 (dddd, *J* = 10.2, 4.7, 0.6, 2.5 Hz, 1H, HC(3), HC(4)), 7.25–7.4 (m, 5H).

$^{13}$C NMR: $\delta$ = 24.8 (C(5)), 62.8 (C(6)), 75.7 (C(2)), 124.8, 127.1, 127.5, 128.1, 129.2, 141.0.

MS (EI): *m/z* = 160 (62, $M^+$), 159 (41), 131 (22), 129 (22), 128 (18), 115 (20), 105 (100), 104 (12), 91 (16), 78 (11), 77 (43), 55 (12), 51 (29), 39 (21).

TLC: $R_f$ = 0.48 (*n*-pentane/$CH_2Cl_2$ 1:1).

**(+)-(*R*)-3-Phenylcyclopentene (8):**

According to the typical procedure, a solution of [$Pd_2(dba)_3$ · dba] (19.9 mg, 16.7 μmol) and **1c** (20.7 mg, 53.4 μmol) in anhyd THF (5 mL) was stirred for 10 min. Phenyl triflate (253.3 mg, 1.12 mmol), cyclopentene (243.2 mg, 3.58 mmol), *N,N*-diisopropylethylamine (276.3 mg, 2.14 mmol) and *n*-tridecane (72.2 mg, 0.39 mmol) were added. The reaction was carried out at 70 °C. After 5 d, standard workup and flash chromatography (silica gel, 3 × 15 cm, *n*-pentane) afforded **8** (129.0 mg, 80 %) as a colorless oil.

$[\alpha]_D$ = +184 (c = 1.00, $CHCl_3$, 23 °C, 91 % ee by GC).

GC (*Chiraldex* γ-*CD-TFA;* 30m, 60–140 °C, 0.3 °C $min^{-1}$, 60 kPa): 46.7 min (*R*), 48.0 min (*S*).

IR ($CHCl_3$): $\nu$ = 3059s, 3006s, 2943s, 2852s, 1949w, 1885w, 1872w, 1809w, 1755w, 1655w, 1600s, 1491s, 1451s, 1355m, 1287w, 1146w, 1076m, 1029m, 1010m, 985w, 915s, 694s, 565m $cm^{-1}$.

$^1$H NMR: $\delta$ = 1.66–1.78 (m, 1H, $H_2C(4)$); 2.30–2.57 (m, 3H, $H_2C(4)$, $H_2C(5)$); 3.81–3.93 (m, 1H, HC(3)); 5.77 (dq, 1H, *J* 5.7, 2.1 Hz), 5.92 (dq, 1H, *J* 5.7, 2.1 Hz) (HC(1), HC(2)); 7.12–7.20 (m, 3H, arom. H); 7.22–7.31 (m, 2H, arom. H).

$^{13}$C NMR: $\delta$ = 32.5 ($H_2C(4)$); 33.8 ($H_2C(5)$); 51.3 (HC(3)); 126.0, 127.2, 128.3 (arom. CH), 131.9 (HC(1)); 134.3 (HC(2)); 146.5 (arom. C).

MS (EI): *m/z* (%) = 145 (11), 144 (94, $M^+$), 143 (76), 141 (10), 130 (11), 129 (100), 128 (68), 127 (17), 115 (40), 91 (14), 77 (13), 66 (20), 65 (15), 63 (12), 51 (15).

TLC: $R_f$ = 0.38 (*n*-pentane).

**(+)-3-(Cyclohex-1′-en-1′-yl)cyclopentene (11):**[19]

According to the typical procedure, a solution of [$Pd_2(dba)_3$ · dba] (23.5 mg, 19.8 μmol) and **1c** (27.6 mg, 71.3 μmol) in anhyd benzene (7.5 mL) was stirred for 10 min. Cyclohex-1-en-1-yl triflate (302.5 mg, 1.32 mmol), cyclopentene (307.8 mg, 4.53 mmol), *N,N*-diisopropylethylamine (342.6 mg, 2.66 mmol) and *n*-tridecane (46.2 mg, 0.25 mmol) were added. The reaction was carried out at 40 °C. After 5 d, standard workup and flash chromatography (silica gel, 3 × 17 cm, *n*-pentane) afforded **11** (136.7 mg, 70 %) as a colorless oil.

$[\alpha]_D$ = +158 (c = 0.67, $CHCl_3$, 18 °C, 89 % ee by GC).

GC (*FS-595, CHIRAL*; 30m, 60–120 °C, 0.5 °C $min^{-1}$, 90 kPa): 17.9 min (+); 18.9 min (−).

IR ($CHCl_3$): $\nu$ = 3051m, 2994w, 2927s, 2856s, 2836s, 2660w, 1664w, 1613w, 1458m, 1447m, 1438m, 1374w, 1350w, 1316w, 1288w, 1269w, 1134w, 1079w, 1046w, 1012w, 921m, 838w, 801w, 756w, 727m, 538w $cm^{-1}$.

$^1$H NMR: $\delta$ = 1.48–1.73 (m, 5H, $H_2C(4')$, $H_2C(5')$, $H_2C(4)$ or $H_2C(5)$); 1.86–2.13 (m, 5H, $H_2C(3')$, $H_2C(6')$, $H_2C(4)$ or $H_2C(5)$); 2.20–2.44 (m, 2H, $H_2C(4)$ or $H_2C(5)$); 3.97 (m, 1H, HC(3)); 5.38–5.45 (m, 1H, HC(2′)); 5.61 (dq, 1H, *J* 5.7, 2.2), 5.78 (dq, 1H, *J* 5.7, 2.3) (HC(1), HC(2)).

$^{13}$C NMR: $\delta$ = 22.9, 23.3, 25.4, 26.5, 29.4, 32.4 ($H_2C(3')$, $H_2C(4')$, $H_2C(5')$, $H_2C(6')$, $H_2C(4)$, $H_2C(5)$); 52.9 (HC(3)); 119.8 (HC(2′)); 131.2, 133.7 (HC(1), HC(2)); 141.0 (C(1′)).

MS (EI): *m/z* (%) = 148 (78, $M^+$), 133 (12), 119 (28), 107 (11), 106 (17), 105 (33), 93.0 (27), 92 (26), 91 (79), 81.0 (27), 80 (100), 79 (62), 78 (17), 77 (32), 67 (51), 66 (26), 65 (19), 53 (12), 51 (11), 41 (30).

TLC: $R_f$ = 0.61 (*n*-pentane).

**(+)-3-Phenylcyclohexene (13):**[20]

According to the typical procedure, a solution of [$Pd_2(dba)_3$ · dba] (32.3 mg, 27.2 μmol) and **1c** (39.5 mg, 102 μmol) in anhyd benzene

(5 mL) was stirred for 10 min. Phenyl triflate (243.2 mg, 1.08 mmol), cyclohexene (287.3 mg, 3.50 mmol), *N,N*-diisopropylethylamine (284.3 mg, 2.20 mmol) and *n*-tridecane (92.6 mg, 0.50 mmol) were added. The reaction was carried out at 90 °C. After 6 d, standard workup and flash chromatography (silica gel, 3 × 15 cm, pentane) afforded **13** (139.9 mg, 82 %) as a colorless oil.

$[\alpha]_D = +47$ (c = 0.85, $CDCl_3$, 21 °C, 43 % ee by GC).

GC (*Chiraldex γ-CD-TFA*; 30m, 60–140 °C, 0.3 °C $min^{-1}$, 60 kPa): 58.3 min (+), 59.5 min (−).

IR (KAP): $\nu$ = 3061m, 3023s, 2929s, 2856s, 2837m, 1649w, 1602w, 1491m, 1452m, 1433w, 880m, 755s, 723m, 700vs, 674m $cm^{-1}$.

$^1$H NMR: $\delta$ = 1.46–2.22 (2m, 6H, 3 × $CH_2$), 3.33–3.48 (m, 1H, ArCH), 5.67–5.78 (m, 1H, CHCH=CH), 5.84–5.97 (m, 1H, $CH_2$CH=CH), 7.13–7.42 (m, 5H, $CH_{Ar}$).

$^{13}$C NMR: $\delta$ = 21.5, 25.0, 32.6 (3t, 3 × $CH_2$), 41.9 (d, ArCH), 125.9, 127.7, 128.2, 128.3, 139.2 (5d, $CH_{Ar}$, CH=CH), 147 (q, $C_{Ar}$).

MS (EI): *m/z* (%) = 158 (98, $M^+$), 143 (52), 130 (72), 129 (100), 128 (44), 127 (13), 117 (17), 115 (72), 104 (21), 91 (37), 80 (15), 79 (13), 78 (12), 77 (22), 51 (29).

TLC: $R_f$ = 0.48 (pentane).

**(+)-1-(Methoxycarbonyl)-5-phenyl-3-pyrroline (15):**[3b]
According to the typical procedure, a solution of $[Pd_2(dba)_3 \cdot dba]$ (39.6 mg, 33.3 μmol) and **1c** (44.9 mg, 116 μmol) in anhyd benzene (5 mL) was stirred for 10 min. Phenyl triflate (253.2 mg, 1.12 mmol), *N*-methoxycarbonyl-2-pyrroline (721.6 mg, 5.68 mmol), *N,N*-diisopropylethylamine (296.9 mg, 2.30 mmol) and *n*-tridecane (77.1 mg, 0.42 mmol) were added. The reaction was carried out at 80 °C. After 5 d, EtOAc (10 mL) was added and the mixture was extracted with sat. $Na_2CO_3$ (2 × 10 mL) solution. The organic layer was dried ($Na_2SO_3$). After evaporation the resulting orange oil was purified by flash chromatography (silica gel, 3 × 15 cm, hexane/EtOAc 5:1) to afford **15** (200.1 mg, 88 %) as a yellow oil.

$[\alpha]_D = +297$ (c = 0.6, $CHCl_3$, 20 °C, 85 % ee by HPLC).

HPLC (*Chiralcel OD-H*; 0.46 × 25 cm, 0.5 mL $min^{-1}$, heptane/isopropanol 90:10, detection at 220 nm); 12.5 min (*S*)-(−), 14.2 min (*R*)-(+).

IR (KAP): $\nu$ = 3061w, 3029w, 2954w, 2863w, 1707vs, 1654m, 1622m, 1576w, 1494w, 1450vs, 1384vs, 1191s, 1121s, 767m, 696s $cm^{-1}$.

$^1$H NMR: $\delta$ = 3.56 and 3.67 (both s, 1.5H, each, $OCH_3$), 4.33 (br s 1H, $NCH_2$), 4.40 (br s 1H, $NCH_2$), 5.51 (br d, 1H, NCH), 5.72–5.80 (m, 1H, CH=CH), 5.88–5.92 (m, 1H, CH=CH), 7.2–7.4 (m, 5H, aromatic protons).

$^{13}$C NMR: $\delta$ = 52.0, 53.3, 53.9, 124.4, 126.1, 126.6, 127.0, 128.1, 130.8.

MS (EI): *m/z* (%) = 203 (71, $M^+$), 202 (18), 188 (67), 171 (27), 144 (48), 143 (35), 142 (12), 126 (100), 125 (12), 118 (12), 117 (18), 116 (15), 115 (47), 91 (20), 77 (23), 67 (37), 59 (31), 39 (28).

TLC: $R_f$ = 0.32 (hexane/EtOAc 5:1).

**(+)-1-(Methoxycarbonyl)-4-phenyl-2-pyrroline (17):**[11]
According to the typical procedure, a solution of $[Pd_2(dba)_3 \cdot dba]$ (22.0 mg, 18.5 μmol) and **1c** (24.2 mg, 62.5 μmol) in anhyd benzene (5 mL) was stirred for 10 min. Phenyl triflate (166.3 mg, 0.74 mmol), *N*-methoxycarbonyl-3-pyrroline (820.3 mg, 4.52 mmol), *N,N*-diisopropylethylamine (197.1 mg, 1.53 mmol) and *n*-tridecane (51.6 mg, 0.28 mmol) were added. The reaction was carried out at 80 °C. After 5 d, EtOAc (10 mL) was added and the mixture was extracted with sat. $Na_2CO_3$ (2 × 10 mL) solution. The organic layer was dried ($Na_2SO_3$). After evaporation the resulting orange oil was purified by flash chromatography (silica gel, 3 × 15 cm, hexane/EtOAc 4:1) to afford **17** (109.7 mg, 73 %) as a yellow oil.

$[\alpha]_D$ + 51 (c = 0.83, $CHCl_3$, 21 °C, 37 % ee by GC).

GC (*FS-595 tert-butyl-dimethylsilyl dimethyl β-CD/SE-54*;[17] 30m, 80–180 °C, 0.3 °C $min^{-1}$, 60 kPa): 73.4 min (−), 73.6 min (+).

IR (KAP): $\nu$ = 3062w, 3029w, 2956w, 1709vs, 1618w, 1496w, 1452s, 1393s, 1340m 1273m, 1194m, 1134m, 758m, 700m $cm^{-1}$.

$^1$H NMR $\delta$ = 3.78 (br s, 4H, $OCH_3$, ArCH), 4.19 (br s, 2H, $NCH_2$), (5.16 br s, 1H, NCH=C*H*), 6.70, 6.84 (2 br s, 1H, NCH, rotamers), 7.19–7.34 (m, 5H, ArH).

$^{13}$C NMR: $\delta$ = 47.2, 48.4 (2 bq, $CH_3$, rotamers), 52.7 (d, ArCH), 54.0 (t, $CH_2$), 112.3, 112.5 (2 d, *C*H=CH, rotamers), 127.0, 127.2, 128.8 (3 d, $C_{Ar}$), 129.6, 130.4 (2 d, CH=*C*H, rotamers), 143.8 (s, $C_{Ar}$).

MS (EI): *m/z* = 203 (100, $M^+$), 202 (40), 201 (20), 188 (50), 170 (8), 144 (29), 143 (17), 128 (11), 126 (23), 117 (9), 116 (11), 115 (39), 91 (9), 59 (9).

TLC: $R_f$ = 0.32 (hexane/ EtOAc 4:1).

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(1) Reviews: (a) Schmalz, H.G. *Nachr. Chem. Tech. Lab.* **1994**, *42*, 270.
(b) Larock, R.C. *Adv. Metal-Org. Chem.* **1994**, *3*, 97.
(c) de Meijere, A.; Meyer, F.E., *Angew. Chem.* **1994**, *106*, 2473; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2379.
(d) Cabri, W.; Candiani, I. *Acc. Chem. Res.* **1995**, *28*, 2.

(2) (a) Sato, Y.; Sodeoka, M.; Shibasaki, M. *J. Org. Chem.* **1989**, *54*, 4738.
Kondo, K.; Sodeoka, M.; Mori, M.; Shibasaki, M. *Synthesis* **1993**, 920.
Kondo, K.; Sodeoka, M.; Shibasaki, M. *J. Org. Chem.* **1995**, *60*, 4322.
(b) Ashimori, A.; Matsuura, T.; Overman, L.E.; Poon, D.J. *J. Org. Chem.* **1993**, *58*, 6949;
Overman, L.E. *Pure Appl. Chem.* **1994**, *66*, 1423.
(c) See also: Tietze, L.F.; Schimpf, R. *Angew. Chem.* **1994**, *106*, 1138; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1089.
(d) Overman, L.E.; Poon, D.J. *Angew. Chem.* **1997**, *109*, 536, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 518.

(3) (a) Ozawa, F.; Kubo, A.; Hayashi, T. *J. Am. Chem Soc.* **1991**, *113*, 1417.
(b) Ozawa, F.; Kobatake, Y.; Hayashi, T. *Tetrahedron Lett.* **1993**, *34*, 2505.
(c) Ozawa, F.; Kubo, A.; Matsumoto, Y.; Hayashi, T.; Nishioka, E.; Yanagi, K.; Moriguchi, K. *Organometallics* **1993**, *12*, 4188.
(d) Hayashi, T.; Kubo, A.; Ozawa, F. *Pure Appl. Chem.* **1992**, *64*, 421. See also ref. 9.

(4) BINAP = 2,2′-bis(diphenylphosphano)-1,1′-binaphthyl: Noyori, R.; Takaya, H., *Acc. Chem. Res.* **1990**, *23*, 345.

(5) (a) von Matt, P.; Pfaltz, A. *Angew. Chem.* **1993**, *105*, 614; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 566.
von Matt, P.; Loiseleur, O.; Koch, G.; Pfaltz, A.; Lefeber, C.; Feucht, T.; Helmchen, G. *Tetrahedron: Asymmetry* **1994**, *5*, 573.
(b) Koch, G.; Lloyd-Jones, G.C.; Loiseleur, O.; Pfaltz, A.; Prétét, R.; Schaffner, S.; Schnider, P.; von Matt, P. *Recl. Trav. Chim. Pays-Bas* **1995**, *114*, 206.

(6) (a) Sprinz, J.; Kiefer, M.; Helmchen, G.; Reggelin, M.; Huttner, G.; Walter, O.; Zsolnai, L. *Tetrahedron Lett.* **1994**, *35*, 1523.
Sennhenn, P.; Gabler, B.; Helmchen, G. *Tetrahedron Lett.* **1994**, *35*, 8595.
Peer, M.; de Jong, J.C.; Kiefer, M.; Langer, T.; Rieck, H.; Schell, H.; Sennhenn, P.; Sprinz, J.; Steinhagen, H.; Wiese, B.; Helmchen, G. *Tetrahedron* **1996**, *52*, 7547.
(b) Dawson, G.J.; Frost, C.G.; Williams, J.M.J.; Coote, S.J. *Tetrahedron Lett.* **1993**, *34*, 3149.
Dawson, G.J.; Williams, J.M.J. *Tetrahedron Lett.* **1995**, *36*, 461.
Baldwin, I.C.; Williams, J.M.J.; Beckett, R.P. *Tetrahedron: Asymmetry* **1995**, *6*, 679.

(7) Loiseleur, O.; Meier, P.; Pfaltz, A. *Angew. Chem.* **1996**, *108*, 218; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 200.
(8) [$Pd_2(dba)_3 \cdot dba$]: Takahashi, Y.; Ito, Ts.; Sakai, S.; Ishii, Y. *J. Chem. Soc., Chem. Commun.* **1970**, 1065.
Ukai, T.; Kawazura, H.; Ishii, Y.; Bonnet, J.J.; Ibers, J.A. *J. Organomet. Chem.* **1974**, *65*, 253.
(9) Koga, Y.; Sodeoka, M.; Shibasaki, M. *Tetrahedron Lett.* **1994**, *35*, 1227.
(10) For the effect of halide ions in Heck reactions, see e.g. refs. 1d and 2c. Facile oxidative addition of chloroform to [(diphosphane)(dba)Pd(0)] complexes has been reported: Herrmann, W.A.; Thiel, W.R.; Broßmer, C.; Öfele, K.; Priermeier, T.; Scherer, W. *J. Organomet. Chem.* **1993**, *461*, 51.
(11) Sonesson, C.; Larhed, M.; Nyqvist, C.; Hallberg, A. *J. Org. Chem.* **1996**, *61*, 4756.
(12) Ripa, L.; Hallberg, A. *J. Org. Chem.* **1997**, *62*, 595.
(13) For elegant mechanistic studies of Heck reactions, see: Brown, J.M.; Hii, K.K. (Mimi) *Angew. Chem.* **1996**, *108*, 679; *Angew. Chem. Int. Ed. Engl.* **1996**, 35, 657.
Brown, J.M.; Hii, K.K. (Mimi); Claridge, T.D.W. *Angew. Chem.* **1997**, *109*, 1033, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 984.
(14) Cyclohex-1-en-1-yl trifluoromethanesulfonate, cyclopent-1-en-1-yl trifluoromethanesulfonate, phenyl trifluoromethanesulfonate, and naphthyl trifluoromethanesulfonate: Stang, P.J.; Hanack, M.; Subramanian, L.R. *Synthesis* **1982**, 85.
*N*-(Methoxycarbonyl)-2-pyrroline: (a) Kraus, G.A.; Neuenschwander, K. *J. Org. Chem.* **1981**, *46*, 4791.
(b) Nomura, Y.; Ogawa, K.; Takeuchi, Y.; Tomoda, S. *Chem. Lett.* **1977**, 693.
4,7-Dihydro-1,3-dioxepin: (a) Gras, J.L.; Nouguier, R.; Mchich, M. *Tetrahedron Lett.* **1987**, *28*, 6601.
(b) Scharf, H.D.; Frauenrath, H. *Chem. Ber.* **1980**, *113*, 1472.
(15) Ukai, T.; Kawazura, H.; Ishii, Y.; Bonnet, J.J.; Ibers, J.A. *J. Organomet. Chem.* **1974**, *65*, 253.
(16) Configurational assignments: **2** and (*R*)-(-)-2-(1-cyclohexenyl)-2,3-dihydrofuran were converted to (*R*)-(+)-2-(1-cyclohexenyl) THF.[3b]
(*R*)-(+)-**3**: ref. [3a].
(*R*)-(+)-**4**: CD comparison with (*R*)-(+)-**2**. (*R*)-(+)-**6**: Koga, Y.; Sodeoka, M.; Shibasaki, M. *Tetrahedron Lett.* **1994**, *35*, 1227.
(*R*)-(+)-**8**: Hopps, H.B. *Diss. Abstr.* **1962**, *23*, 439.
(17) Kobor, F., Dissertation 1994; Universität Wuppertal, MPI für Kohlenforschung in Mülheim.
(18) Marko, I.E.; Bayston, D.J. *Tetrahedron* **1994**, *50*, 7141.
(19) Larock, R.C.; Gong, W.H. *J. Org. Chem.* **1989**, *54*, 2047.
(20) Cortese, N.A.; Ziegler, C.B.; Hrnjez, B.J.; Heck, R.F., *J. Org. Chem.* **1978**, *43*, 2952.