Supporting Information

Chiral self-sorting behaviour of [2.2]paracyclophane-based bis(pyridine) ligands

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General experimental information

All reactions with air and moisture sensitive compounds were performed under argon atmosphere using standard Schlenk techniques, oven-dried glassware and dry solvents.

The following chemicals were obtained commercially from *Alfa Aesar*, *Sigma-Aldrich*, *Carbolution*, *Fluorochem* or abcr and used as received: 4-(trimethylsilyl)phenylboronic acid, caesium fluoride, tetrakis(triphenylphosphine)palladium(0), iodine monochloride, 4-pyridylboronic acid, tricyclohexylphosphine, potassium phosphate, 3-pyridinylboronic acid, tetrakis(acetonitrile)palladium(II) tetrafluoroborate.

The following chemicals were synthesized according to known literature synthesis procedures: 4,15-diiodo[2.2]paracyclophane (rac)-1, tris(dibenzylideneacetone)dipalladium(0)-chloroform, [1,3-bis(diphenylphosphino)propane]palladium(II) triflate.

All solvents were obtained from commercial sources. Dry solvents were obtained from the solvent purification system MS-SPS 800 from *MBraun*. Other reaction solvents and solvents for specific rotation value, UV-Vis or CD measurements were solvents of *p.a.* grade. For flash column chromatography freshly distilled solvents of technical grade and for high performance liquid chromatography solvents of HPLC grade were used.

Thin-layer chromatography was performed on silica gel-coated aluminium plates with fluorescent indicator F254 from *Merck*. Detection was done by UV-light (254 and 366 nm).

Products were purified by flash column chromatography on silica gel 60 (particle size 0.040-0.063 mm) from *Merck* or on reversed phase silica gel (C18-RP, 17% C, 0.048-0.065 mm) from *Acros Organics*.

1H, 13C, 19F, 31P, H,H-COSY, HSQC, HMBC and 1H-2D-DOSY NMR experiments were performed on a *Bruker Avance I 400* spectrometer, a *Bruker Avance I 500* spectrometer, a *Bruker Avance III HD 500* spectrometer with a *Prodigy cryo* probe or a *Bruker Avance III HD 700* spectrometer with a cryo probe. 1H NMR chemical shifts are reported relative to residual non-deuterated solvent as internal standard. 13C NMR chemical shifts are reported relative to deuterated solvent as internal standard. 19F and 31P chemical shifts are reported relative to a mixture of trifluoracetic acid-d1 (19F: δ = -76.6 ppm) and phosphoric acid-d3 (31P: δ = 0.0 ppm) in D2O as external standard using a *Wilmad®* coaxial insert from *Sigma Aldrich*. All shifts are reported on the δ scale in ppm and NMR multiplicities are abbreviated as s (singlet), d (doublet), t (triplet), dd (doublet of doublets), ddd (doublet of doublet of doublets) or m (multiplet). Coupling constants *J* are reported in Hertz. All spectra were processed using the *MestReNova 8.0.1* program from *Mestrelab*. 1H-2D-DOSY NMR spectra were evaluated using the software *Topsin 3.5* from *Bruker* and the *Stokes-Einstein equation*, normally used for spherical particles, with a correction factor for ellipsoids *(equation 1)*.5

\[
D = \frac{k_B T}{6 \pi \eta f R_b}
\]


(High-resolution) electrospray ionization mass spectra in positive mode (ESI(+)-MS) were measured on an *Orbitrap XL* mass spectrometer from *Thermo Fischer Scientific* or a *micrOTOF-Q* time-of-flight mass spectrometer from *Bruker Daltonics*. Electron ionization mass spectra (EI-MS) were measured on a *MAT 95 XL* or a *MAT 90* sector field mass spectrometer from *Thermo Finnigan*.

Elementary analyses were performed on a *Vario EL* elemental analyzer from *Heraeus*.

Melting points were determined with a *DigiMelt MPA 161* instrument from *Stanford Research Systems*.

UV-Vis spectra were measured on a *Specord 200* instrument from *Analytik Jena* and analysed using the software *WinASPECT 1.7.2.0*. Quartz glass cuvettes from *Hellma Analytics* with a layer thickness of 10 mm (solutions of ligand precursors/ligands) and 0.01 mm (complex solutions) were used.
Circular dichroism spectra were measured on a J-810 spectrometer from Jasco. Quartz glass cuvettes from Hellma Analytics with a layer thickness of 1 mm (solutions of ligand precursors/ligands) and 0.01 mm (complex solutions) were used.

Specific rotation values were measured on an Anton Paar Model MCP 150 polarimeter with a standard wavelength of 589 nm using a cuvette with a layer thickness of 100 mm.

High performance liquid chromatography on analytical scale was performed on a PLATINblue HPLC system from Knauer, equipped with two pumps, an online degasser and a photodiode array detector PDA-1 with a deuterium and tungsten-halogen lamp (190-1000 nm). For analytical HPLC resolution a CHIRALPAK® IA column (4.6 mm Ø, 250 mm) by Daicel or a CHIRALPAK® IB column (4.6 mm Ø, 250 mm) by Daicel was used. High performance liquid chromatography on semi-preparative scale was performed on an Azura HPLC system from Knauer, equipped with a binary HPG pump P 6.1L, an online degasser, a multi wavelength detector MWL 2.1L with deuterium lamp (190-700 nm) and a fraction collector. For semi-preparative HPLC resolution a CHIRALPAK® IA column (20 mm Ø, 250 mm) by Daicel or a CHIRALPAK® IB column (20 mm Ø, 250 mm) by Daicel was used.

Synthesis route

\[
\begin{align*}
\text{1} & \rightarrow \text{TMS} \rightarrow \text{2} \\
\text{2} & \rightarrow \text{ICI, CH}_2\text{Cl}_2 \rightarrow \text{3} \\
\text{3} & \rightarrow \text{4} \\
\text{4} & \rightarrow \text{5}
\end{align*}
\]

Scheme S1: Synthesis route to ligand 4 and 5.

Synthesis and characterization of ligand precursors

4,15-Bis-(4-(trimethylsilylphenyl)(2.2)paracyclophane 2

Under an atmosphere of argon, \((rac)-\text{1}^{1}\) (900 mg, 1.96 mmol, 1.00 eq.), 4-(trimethylsilyl)phenylboronic acid (875 mg, 4.51 mmol, 2.30 eq.), caesium fluoride (1.79 mg, 11.8 mmol, 6.00 eq.), tetrakis(triphenylphosphine)palladium(0) (226 mg, 0.196 mmol, 10.0 mol%) were dissolved in dry tetrahydrofuran (75 mL). The reaction mixture was degassed at room temperature and then, heated to reflux for 48 h. After cooling to room temperature the solution was quenched by the addition of saturated aqueous ethylenediaminetetraacetic acid disodium salt solution and dichloromethane. The mixture was extracted with dichloromethane. The combined organic layers were washed with brine, dried with anhydrous magnesium sulphate and the solvent was removed under reduced pressure. The crude product was subjected to flash
column chromatography on silica gel (cyclohexane/dichloromethane 10:1) to give (rac)-2 (733 mg, 1.45 mmol, 74%) as a white solid.

**Chemical formula:** C$_{34}$H$_{40}$Si$_2$

**Exact mass:** 504.2669 u

**Molecular weight:** 504.86 g/mol

$^1$H NMR (500.1 MHz, CDCl$_3$, 298 K): $\delta$ [ppm] = 7.63-7.60 (m, 4H, H-19), 7.49-7.46 (m, 4H, H-18), 6.72 (d, 2H, H-5, H-16, $^3$J$_{5,7}$ = $^3$J$_{16,12}$ = 1.9 Hz), 6.68 (d, 2H, H-8, H-13, $^3$J$_{8,7}$ = $^3$J$_{13,12}$ = 7.8 Hz), 6.56 (dd, 2H, H-7, H-12, $^3$J$_{7,8}$ = $^3$J$_{12,13}$ = 7.8 Hz, $^3$J$_{7,5}$ = $^3$J$_{12,16}$ = 1.9 Hz), 3.26-3.07 (m, 6H, H-1, H$_2$, H-9, H$_{-10}$), 2.64-2.55 (m, 2H, H-1, H$_{-2}$), 0.33 (s, 18H, H$_{-21}$).

$^{13}$C NMR (125.8 MHz, CDCl$_3$, 298 K): $\delta$ [ppm] = 142.7 (C-4, C-15), 141.7 (C-17), 139.6 (C-6, C-11), 138.8 (C-20), 137.6 (C-3, C-14), 133.7 (C-19), 132.5 (C-8, C-13), 132.0 (C-5, C-16), 131.5 (C-7, C-12), 129.1 (C-18), 133.7 (C-9, C-10), 35.3 (C-1, C-2), -0.84 (C-21).

MS (EI) m/z (intens. %): 504.3 (73) [2$^+$], 489.3 (11) [2-CH$_3$]$^+$, 416.2 (33) [2-C$_4$H$_{12}$Si]$^+$, 356.3 (7) [2-C$_9$H$_{12}$Si]$^+$, 237.2 (58) [2-C$_{18}$H$_{33}$Si]$^+$, 73.1 (100) [C$_3$H$_9$Si]$^+$; HR-MS (EI) m/z: calculated for C$_{34}$H$_{40}$Si$_2$ [2$^+$]: 504.2669, found: 504.2672.

Elementary analysis: calculated for C$_{34}$H$_{40}$Si$_2$: C: 80.89, H: 7.99, found: C: 80.70, H: 7.98.

Melting point: 111 °C

R$_t$ (cyclohexane/dichloromethane 5:1): 0.48

UV-Vis (CH$_3$CN, c = 1.98 µM): $\lambda$ [nm] = 233, 285.

HPLC analytical (CHIRALPAK® IB, methanol/ethanol (90:10 v/v), 1 mL/min): (R$_p$)-2 $t_R$ = 4.55 min, (S$_p$)-2 $t_R$ = 4.98 min.

HPLC semi-preparative recycling mode (CHIRALPAK® IB, methanol/ethanol (90:10 v/v), 18 mL/min): (R$_p$)-2 99% ee, (S$_p$)-2 97% ee.

Specific rotation: (−)-(R$_p$)-2: $[\alpha]_{D}^{23}$ = −442° (c = 2.00 mg/mL = 3.96 mm, CH$_2$Cl$_2$), (+)-(S$_p$)-2: $[\alpha]_{D}^{23}$ = +420° (c = 2.00 mg/mL = 3.96 mm, CH$_2$Cl$_2$).

CD (CH$_3$CN, c = 198 µM): $\lambda$ [nm] (A$_{mc}$ [L/(mol cm)]) = (R$_p$)-2: 214 (−76), 228 (+36), 292 (−88), 237 (+11), 251 (−91); (S$_p$)-2: 214 (+84), 228 (−36), 237 (+13), 251 (−100), 292 (+98).
Figure S1: $^1$H NMR spectrum (500.1 MHz, CDCl$_3$, 298 K) of 2.
Figure S2: $^{13}$C NMR spectrum (125.8 MHz, CDCl$_3$, 298 K) of 2.

Figure S3: $^1$H, $^{13}$C-HSQC NMR spectrum (500.1 MHz, 125.8 MHz, CDCl$_3$, 298 K) of 2.
Figure S4: $^1$H, $^{13}$C-HMBC NMR spectrum (500.1 MHz, 125.8 MHz, CDCl$_3$, 298 K) of 2.

Figure S5: EI mass spectrum of 2.
**Figure S6**: High resolution accurate mass determinations for 2.

**Figure S7**: Non-normalized UV-Vis spectrum of 2 (c = 1.98 µM, CH₃CN).
Figure S8: Chromatogram of chiral resolution of 2 via analytical HPLC (chiral stationary phase: CHIRALPAK® IB column, eluent: methanol/ethanol (90:10 v/v), flow rate: 1 mL/min). When upscaling to semi-preparative mode, the flow rate was increased to 18 mL/min.

Figure S9: CD spectra of 2 (c = 198 µM, CH₃CN).
4,15-Bis-(4-iodophenyl)[2.2]paracyclophane 3

Under an atmosphere of argon, (rac)-/(R₆)-/(S₆)-2 (350 mg, 0.693 mmol, 1.00 eq.) was dissolved in dry dichloromethane (5 mL) and cooled to 0 °C. At 0 °C iodine monochloride solution (1.40 mL, 1 M in dichloromethane, 1.40 mmol, 2.00 eq.) was added slowly over 45 min and the red reaction mixture was stirred at 0 °C for further 45 min. Then, it was warmed up to room temperature and stirred for another hour. Subsequently, saturated aqueous sodium sulphite solution was added and the mixture was stirred until discoloration. The phases were separated and the aqueous phase was extracted with dichloromethane. The combined organic layers were washed with brine, dried with anhydrous magnesium sulphate and the solvent was removed under reduced pressure. The crude product was subjected to flash column chromatography on silica gel (cyclohexane/dichloromethane 20:1) to give (rac)-/(R₆)-/(S₆)-3 (260 mg, 0.425 mmol, 61%) as a white solid.

![Chemical structure of 3](image)

Chemical formula: C₂₈H₂₂I₂

Exact mass: 611.9811

Molecular weight: 612.29 g/mol

³H NMR (500.1 MHz, CDCl₃, 298 K): δ [ppm] = 7.82-7.78 (m, 4H, H-19), 7.24-7.21 (m, 4H, H-18), 6.65 (d, 2H, H-5, H-16), 4.90 (d, 2H, H-8, H-13), 3.79 (m, 4H, H-12), 3.25-3.18 (m, 2H, H-9, H-10), 3.16-3.05 (m, 4H, H-1, H-2, H-9, H-10), 2.56-2.48 (m, 2H, H-1, H-2).

¹³C NMR (125.8 MHz, CDCl₃, 298 K): δ [ppm] = 141.5 (C-4, C-15), 140.7 (C-17), 140.0 (C-6, C-11), 137.9 (C-19), 137.3 (C-3, C-14), 132.4 (C-8, C-13), 131.8 (C-5, C-16), 131.6 (C-7, C-12), 131.6 (C-18), 93.0 (C-20), 35.2 (C-9, C-10), 33.5 (C-1, C-2).

MS (EI) m/z (intens. %): 611.8 (47) [3]⁺, 485.0 (58) [3-Δ]⁺, 304.9 (45) [3-C₁₆H₁₂I]⁺, 179.0 (100) [3-C₁₆H₁₂I]⁺; HR-MS (EI) m/z: calculated for C₂₈H₂₂I₂ [3]⁺: 611.9811, found: 611.9816.

Elementary analysis: calculated for C₂₈H₂₂I₂: C: 56.45, H: 3.79, found: C: 56.37, H: 4.18.

Melting point: 229 °C

R₆ (cyclohexane/dichloromethane 5:1): 0.47

UV-Vis (CH₃CN, c = 16.3 μM): λ [nm] = 245, 288.

Specific rotation: (−)-(R₆)-3: [α]₀°D = −354° (c = 2.00 mg/mL = 4.90 mm, CH₂Cl₂), (+)-(S₆)-3: [α]₀°D = +370° (c = 2.00 mg/mL = 4.90 mm, CH₂Cl₂).

CD (CH₃CN, c = 163 μM): λ [nm] (Δε [L/(mol cm)]) = (R₆)-3: 217 (−78), 231 (+36), 242 (−40), 255 (+80), 297 (−97); (S₆)-3: 217 (+61), 231 (−28), 242 (+32), 255 (−61), 296 (+77).
Figure S10: $^1$H NMR spectrum (500.1 MHz, CDCl$_3$, 298 K) of 3.

Figure S11: $^{13}$C NMR spectrum (125.8 MHz, CDCl$_3$, 298 K) of 3.

Figure S12: $^1$H, $^{13}$C-HMQC NMR spectrum (500.1 MHz, 125.8 MHz, CDCl$_3$, 298 K) of 3.
Figure S13: $^1$H, $^{13}$C-HMBC NMR spectrum (500.1 MHz, 125.8 MHz, CDCl$_3$, 298 K) of 3.

Figure S14: EI mass spectrum of 3.
Figure S15: High resolution accurate mass determinations for 3.

Figure S16: Non-normalized UV-Vis spectrum of 3 (c = 16.3 µM, CH3CN).

Figure S17: CD spectra of 3 (c = 163 µM, CH3CN).
Synthesis and characterization of ligands

4,15-Bis-(4-(pyridin-4-yl)phenyl)[2.2]paracyclophane 4

Under an atmosphere of argon, (rac)-3 (200 mg, 0.327 mmol, 1.00 eq.), 4-pyridinylboronic acid (92.4 mg, 0.752 mmol, 2.30 eq.), tris(dibenzylideneacetone)dipalladium(0)-chloroform (33.8 mg, 0.0327 mmol, 10.0 mol%), tricyclohexylphosphine (22.9 mg, 0.0818 mmol, 25.0 mol%) und potassium phosphate (208 mg, 1.96 mmol, 6.00 eq.) were dissolved in 1,4-dioxane (7.2 mL) and water (2.1 mL). The reaction mixture was degassed at room temperature and then, heated to reflux for 48 h. After cooling to room temperature the solution was quenched by the addition of saturated aqueous ethylenediaminetetraacetic acid disodium salt solution and dichloromethane. The mixture was extracted with dichloromethane. The combined organic layers were washed with brine, dried with anhydrous magnesium sulphate and the solvent was removed under reduced pressure. The crude product was subjected to flash column chromatography on silica gel (cyclohexane/ethyl acetate 1:1 + 0.5% triethylamine) and reversed-phase silica gel (chloroform/methanol 1:1) to give (rac)-4 (82.9 mg, 0.161 mmol, 49%) as a white solid.

Chemical formula: C_{38}H_{33}N_{2}

Exact mass: 514.2409 u

Molecular weight: 514.67 g/mol

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{^1}H \text{ NMR (500.1 MHz, CD}_{2}Cl_{2}, 298 K):} \delta [ppm] = 8.70-8.66 (m, 4H, H-23), 7.82-7.80 (m, 4H, H-19), 7.66-7.64 (m, 4H, H-18) 7.63-7.61 (m, 4H, H-22), 6.79 (d, 2H, H-5, H-16), J_{6,7} = J_{16,12} = 1.9 Hz), 6.75 (d, 2H, H-8, H-13), J_{8,7} = J_{13,12} = 7.8 Hz), 6.66 (dd, 2H, H-7, H-12), J_{7,8} = J_{12,13} = 7.8 Hz, J_{12,5} = J_{13,16} = 1.9 Hz), 3.31-3.20 (m, 4H, H-1, H-2, H-9, H-10), 3.18-3.10 (m, 2H, H-9, H-10), 2.61-2.53 (m, 2H, H-1, H-2).

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{^{13}}C \text{ NMR (125.8 MHz, CD}_{2}Cl_{2}, 298 K):} \delta [ppm] = 150.9 (C-23), 148.3 (C-21), 142.6 (C-17), 142.2 (C-4, C-15), 140.6 (C-6, C-11), 138.1 (C-3, C-14), 137.1 (C-20), 133.0 (C-8, C-13), 132.4 (C-5, C-16), 132.1 (C-7, C-12), 130.9 (C-18), 127.7 (C-19), 122.0 (C-22), 35.6 (C-9, C-10), 34.0 (C-1, C-2).

\[
{^1}H \text{ NMR (700.4 MHz, CD}_{2}Cl_{2}:CD}_{3}CN 1:1, 298 K):} \delta [ppm] = 8.62-8.59 (m, 4H, H-23), 7.79-7.77 (m, 4H, H-19), 7.62-7.58 (m, 8H, H-18, H-22), 6.74 (d, 2H, H-5, H-16), J_{6,7} = J_{16,12} = 1.8 Hz), 6.68 (d, 2H, H-8, H-13), J_{8,7} = J_{13,12} = 7.8 Hz), 6.63 (dd, 2H, H-7, H-12), J_{7,8} = J_{12,13} = 7.8 Hz, J_{12,5} = J_{13,16} = 1.8 Hz), 3.23-3.15 (m, 4H, H-1, H-2, H-9, H-10), 3.11-3.05 (m, 2H, H-9, H-10), 2.51-2.45 (m, 2H, H-1, H-2).

\[
{^{13}}C \text{ NMR (176.1 MHz, CD}_{2}Cl_{2}:CD}_{3}CN 1:1, 298 K):} \delta [ppm] = 150.6 (C-23), 147.7 (C-21), 142.2 (C-17), 141.8 (C-4, C-15), 140.3 (C-6, C-11), 137.6 (C-3, C-14), 136.6 (C-20), 132.6 (C-8, C-13), 132.0 (C-5, C-16), 131.8 (C-7, C-12), 130.6 (C-18), 127.4 (C-19), 121.5 (C-22), 35.0 (C-9, C-10), 33.6 (C-1, C-2).

\[
{^1}H \text{ NMR (700.4 MHz, CD}_{2}CN, 298 K):} \delta [ppm] = 8.68-8.66 (m, 4H, H-23), 7.90-7.87 (m, 4H, H-19), 7.73-7.71 (m, 4H, H-22), 7.70-7.68 (m, 4H, H-18), 6.84 (d, 2H, H-5, H-16), J_{6,7} = J_{16,12} = 1.7 Hz), 6.75 (dd, 2H, H-7, H-12), J_{7,8} = J_{12,13} = 7.8 Hz, J_{7,5} = J_{12,16} = 1.7 Hz), 6.73 (d, 2H, H-8, H-13), J_{8,7} = J_{13,12} = 7.8 Hz), 3.29-3.20 (m, 4H, H-1, H-2, H-9, H-10), 3.16-3.11 (m, 2H, H-9, H-10), 2.53-2.47 (m, 2H, H-1, H-2).

\[
{^{13}}C \text{ NMR (176.1 MHz, CD}_{2}CN, 298 K):} \delta [ppm] = 151.3 (C-23), 148.3 (C-21), 143.0 (C-17), 142.5 (C-4, C-15), 141.3 (C-6, C-11), 138.2 (C-3, C-14), 137.2 (C-20), 133.4 (C-8, C-13), 132.8 (C-5, C-16), 132.7 (C-7, C-12), 131.4 (C-18), 128.2 (C-19), 122.3 (C-22), 35.5 (C-9, C-10), 34.3 (C-1, C-2).

MS (ESI+) m/z: 515.2475 [4+H]^+; 258.1273 [4+2H]^2; HR-MS (ESI+) m/z: calculated for C_{38}H_{33}N_{2} [4+H]^+: 515.2482, found: 515.2475.
Elementary analysis: calculated for $\text{C}_{38}\text{H}_{30}\text{N}_2 \cdot \frac{1}{6} \text{CH}_2\text{Cl}_2$: C: 86.69, H: 5.78, N: 5.30, found: C: 86.83, H: 6.00, N: 5.21.

Melting point: 240 °C (decomposition)

$R_f$ (cyclohexane/ethyl acetate 1:1 + 0.5% triethylamine): 0.12

UV-Vis (CH$_3$CN, c = 19.4 µM): $\lambda$ [nm] = 261, 302.

HPLC analytical (CHIRALPAK® IA, dichloromethane/ethanol (95:5 v/v), 1 mL/min): ($S_p$)-4 $t_R$ = 3.69 min, ($R_p$)-4 $t_R$ = 5.65 min.

HPLC semi-preparative (CHIRALPAK® IA, dichloromethane/ethanol (95:5 v/v), 15 mL/min): ($S_p$)-4 > 99% ee, ($R_p$)-4 98% ee.

Specific rotation: (-)-($S_p$)-4: $[\alpha]_{D}^{20} = -656^\circ$ (c = 2.00 mg/mL = 3.89 mm, CH$_2$Cl$_2$), (+)-($R_p$)-4: $[\alpha]_{D}^{20} = +619^\circ$ (c = 2.00 mg/mL = 3.89 mm, CH$_2$Cl$_2$).

CD (CH$_3$CN, c = 194 µM): $\lambda$ [nm] ($\Delta\varepsilon$ [L/(mol cm)]) = ($R_p$)-4: 212 (−9), 236 (+31), 247 (+11), 266 (+38), 313 (−87); ($S_p$)-4: 211 (+5), 236 (−27), 247 (−9), 266 (−34), 313 (+83).

Figure S18: $^1$H NMR spectrum (500.1 MHz, CD$_2$Cl$_2$, 298 K) of 4.

Figure S19: $^{13}$C NMR spectrum (125.8 MHz, CD$_2$Cl$_2$, 298 K) of 4.
Figure S20: $^1$H, $^{13}$C-HSQC NMR spectrum (500.1 MHz, 125.8 MHz, CD$_2$Cl$_2$, 298 K) of 4.

Figure S21: $^1$H, $^{13}$C-HMBC NMR spectrum (500.1 MHz, 125.8 MHz, CD$_2$Cl$_2$, 298 K) of 4.
Figure S22: $^1$H NMR spectrum (700.4 MHz, CD$_2$Cl$_2$:CH$_3$CN 1:1, 298 K) of 4.

Figure S23: $^{13}$C NMR spectrum (176.1 MHz, CD$_2$Cl$_2$:CD$_3$CN 1:1, 298 K) of 4.

Figure S24: $^1$H, $^{13}$C-HSQC NMR spectrum (700.4 MHz, 176.1, CD$_2$Cl$_2$:CH$_3$CN 1:1, 298 K) of 4.
Figure S25: $^1$H, $^{13}$C-HMBC NMR spectrum (700.4, 176.1 MHz, CD$_2$Cl$_2$:CH$_3$CN 1:1, 298 K) of 4.

Figure S26: $^1$H NMR spectrum (700.4 MHz, CH$_3$CN, 298 K) of 4.

Figure S27: $^{13}$C NMR spectrum (176.1 MHz, CD$_2$CN, 298 K) of 4.
Figure S28: $^1$H, $^{13}$C-HSQC NMR spectrum (700.4 MHz, 176.1 MHz, CH$_3$CN, 298 K) of 4.

Figure S29: $^1$H, $^{13}$C-HMBC NMR spectrum (700.4 MHz, 176.1 MHz, CH$_3$CN, 298 K) of 4.
Figure S30: ESI positive mass spectrum of 4.

Figure S31: Non-normalized UV-Vis spectrum of 4 (c = 19.4 μM, CH₃CN).
**Figure S32**: Chromatogram of chiral resolution of 4 via analytical HPLC (chiral stationary phase: CHIRALPAK® IA column, eluent: dichloromethane/ethanol (95:5 v/v), flow rate: 1 mL/min). When upscaling to semi-preparative mode, the flow rate was increased to 15 mL/min.

**Figure S33**: CD spectra of 4 (c = 194 µM, CH₂CN).
4,15-Bis-(4-pyridin-3-ylphenyl)[2.2]paracyclophane 5

Under an atmosphere of argon, (rac)-/(R)-/(/S)-3 (150 mg, 0.245 mmol, 1.00 eq.), 3-pyridinylboronic acid (69.3 mg, 0.564 mmol, 2.30 eq.), tris(dibenzylideneacetone)dipalladium(0)-chloroform (25.4 mg, 0.0245 mmol, 10.0 mol%), tricyclohexylphosphine (17.2 mg, 0.0613 mmol, 25.0 mol%) und potassium phosphate (156 mg, 1.47 mmol, 6.00 eq.) were dissolved in 1,4-dioxane (7.2 mL) and water (2.1 mL). The reaction mixture was degassed at room temperature and then, heated to reflux for 48 h. After cooling to room temperature the solution was quenched by the addition of saturated aqueous ethylenediaminetetraacetic acid disodium salt solution and dichloromethane. The mixture was extracted with dichloromethane. The combined organic layers were washed with brine, dried with anhydrous magnesium sulphate and the solvent was removed under reduced pressure. The crude product was subjected to flash column chromatography on silica gel (cyclohexane/ethyl acetate 1:1 + 0.5% triethylamine) to give (rac)-/(R)-/(/S)-5 (98.9 mg, 0.192 mmol, 78%) as a white solid.

Chemical formula: C_{38}H_{36}N_{2}

Exact mass: 514.2409 u

Molecular weight: 514.67 g/mol
$^{13}$C NMR (125.8 MHz, DMSO-$d_6$, 298 K): $\delta$ [ppm] = 148.5 (C-24), 147.6 (C-25), 141.3 (C-4, C-15), 140.5 (C-17), 139.7 (C-6, C-11), 136.6 (C-3, C-14), 135.5 (C-20), 135.2 (C-21), 134.0 (C-22), 132.1 (C-8, C-13), 131.7 (C-5, C-16, C-7, C-12), 130.1 (C-18), 127.1 (C-19), 123.9 (C-23), 34.4 (C-9, C-10), 33.1 (C-1, C-2).

MS (ESI+) $m/z$: 515.2480 [5+H]$^+$, 258.1277 [5+2H]$^{2+}$; HR-MS (ESI+) $m/z$: calculated for C$_{38}$H$_{31}$N$_2$ [5+H]$^+$: 515.2482, found: 515.2480.

Elementary analysis: calculated for C$_{38}$H$_{30}$N$_2$: C: 86.69, H: 5.78, N: 5.30, found: C: 86.83, H: 5.60, N: 5.21.

Melting point: 255 °C (decomposition)

R$_f$ (cyclohexane/ethyl acetate 1:1 + 0.5% triethylamine): 0.18

UV-Vis (CH$_3$CN, c = 19.4 µM): $\lambda$ [nm] = 256, 298.

Specific rotation: (−)-(R$_p$)-5: $[\alpha]^{23}_D = -570^\circ$ (c = 2.00 mg/mL = 5.83 mM, CH$_2$Cl$_2$), (+)-(S$_p$)-5: $[\alpha]^{23}_D = +556^\circ$ (c = 2.00 mg/mL = 5.83 mM, CH$_2$Cl$_2$).

CD (CH$_3$CN, c = 194 µM): $\lambda$ [nm] ($\Delta$ε [L/(mol cm)]) = (R$_p$)-5: 217 (−41), 234 (+64), 248 (+11), 263 (+49), 310 (−118); (S$_p$)-5: 217 (+43), 231 (−68), 247 (−11), 263 (−51), 311 (+125).

Figure S34: $^1$H NMR spectrum (500.1 MHz, CD$_2$Cl$_2$, 298 K) of 5.

Figure S35: $^{13}$C NMR spectrum (125.8 MHz, CD$_2$Cl$_2$, 298 K) of 5.
**Figure S36:** $^1$H, $^{13}$C-HSQC NMR spectrum (500.1 MHz, 125.8 MHz, CD$_2$Cl$_2$, 298 K) of 5.

**Figure S37:** $^1$H, $^{13}$C-HMBC-NMR spectrum (500.1 MHz, 125.8 MHz, CD$_2$Cl$_2$, 298 K) of 5.
Figure S38: $^1$H NMR spectrum (500.1 MHz, CD$_3$CN, 298 K) of 5:

![Figure S38: $^1$H NMR spectrum (500.1 MHz, CD$_3$CN, 298 K) of 5.](image)

Figure S39: $^{13}$C NMR spectrum (125.8 MHz, CD$_3$CN, 298 K) of 5.

![Figure S39: $^{13}$C NMR spectrum (125.8 MHz, CD$_3$CN, 298 K) of 5.](image)

Figure S40: $^1$H, $^{13}$C-HSQC NMR spectrum (500.1 MHz, 125.8 MHz, CD$_3$CN, 298 K) of 5.

![Figure S40: $^1$H, $^{13}$C-HSQC NMR spectrum (500.1 MHz, 125.8 MHz, CD$_3$CN, 298 K) of 5.](image)
Figure S41: $^1$H, $^{13}$C-HMBC NMR spectrum (500.1 MHz, 125.8 MHz, CD$_3$CN, 298 K) of 5.

Figure S42: $^1$H NMR spectrum (500.1 MHz, DMSO-d$_6$, 298 K) of 5:

Figure S43: $^{13}$C NMR spectrum (125.8 MHz, DMSO-d$_6$, 298 K) of 5.
Figure S44: $^1$H, $^{13}$C-HSQC NMR spectrum (500.1 MHz, 125.8 MHz, DMSO-d$_6$, 298 K) of 5.

Figure S45: $^1$H, $^{13}$C-HMBC NMR spectrum (500.1 MHz, 125.8 MHz, DMSO-d$_6$, 298 K) of 5.
Figure S46: ESI positive mass spectrum of 5.

Figure S47: Non-normalized UV-Vis spectrum of 5 (c = 19.4 µM, CH$_3$CN).
Figure S48: CD spectra of 5 (c = 194 µM, CH$_3$CN).
Self-assembly and characterization of palladium(II) complexes

\[ \text{[Pd}_2(\text{dppp})_4(\text{OTf})_4 \text{] in dichloromethane:acetonitrile 1:1} \]

\((\text{rac})-, (R)_-\text{-}4\) (2.88 mg, 5.60 \(\mu\)mol, 1.00 eq.) was dissolved in deuterated dichloromethane (0.3 mL) and a solution of \([\text{Pd(dppp)}]_2(\text{OTf})_2\) (4.61 mg, 5.64 \(\mu\)mol, 1.01 eq.) in deuterated acetonitrile (0.3 mL) was added. The mixture was filtrated.

\[ \begin{align*}
\text{[Pd}_2(\text{dppp})_2\{((S)_-4)\}_2\text{]}(\text{OTf})_4
\end{align*} \]

\(\text{^1H NMR (700.4 MHz, CD}_3\text{CN:CD}_2\text{Cl}_2\ 1:1, 298 K): } \delta [ppm] = 8.69-8.64 \text{ (m, 8H, H-23), 7.72-7.50 \text{ (m, 40H, H-18, H-19, dppp-Ph}_{ortho}, dppp-Ph}_{para}), 7.44-7.34 \text{ (m, 24H, H-22, dppp-Ph}_{meta}), 6.72-6.65 \text{ (m, 12H, H-5, H-7, H-8, H-12, H-13, H-16), 3.32-2.90 \text{ (m, 24H, H-1, H-2, H-9, H-10, dppp-CH}_2\text{PPh}_{2}), 2.33-2.21 \text{ (m, 4H, dppp-CH}_2\text{)}}.\]

\(\text{^13C NMR (176.1 MHz, CD}_3\text{CN:CD}_2\text{Cl}_2\ 1:1, 298 K): } \delta [ppm] = 150.5 \text{ (C-23), 143.8*, 141.4*, 141.0*, 137.8*, 133.8*, 133.1*, 133.0*, 132.5*, 132.0*, 131.0*, 130.2*, 128.0*, 122.7*, 120.9*, 35.2*, 33.9*}.\)

*Signals could not be unambiguously assigned.

\(\text{^31P-NMR (202.1 MHz, CD}_3\text{CN:CD}_2\text{Cl}_2\ 1:1, 298 K): } \delta [ppm] = 8.37 \text{ (s, dppp-P).}\)

\(\text{H-DOSY-NMR (700.4 MHz, CD}_3\text{CN:CD}_2\text{Cl}_2\ 1:1, 298 K): } D = 5.88 \cdot 10^{-10} \text{ m}^2\text{s}^{-1}, R_H = 11.7 \text{ Å.}\)

\(\text{MS (ESI+)} m/z: 516.6 \text{ [Pd}_2(\text{dppp})_2\{((S)_-4)\}_2\text{]}^{2+}, 536.6 \text{ [Pd(dppp)]_2((S)_-4)(CH}_3\text{CN})^{2+}, 553.0 \text{ [(Pd(dppp)]_2((S)_-4)]Cl}^{+}, 666.9 \text{ [Pd(dppp)]_2(\text{OTf})}^{+}, 738.4 \text{ [(Pd}_2(\text{dppp})_2\{((S)_-4)\}_2\text{]}\text{OTf}^{3+}, 773.2 \text{ [Pd(dppp)]_2((S)_-4)]_2^{2+}, 1183.2 \text{ [(Pd}_2(\text{dppp})_2\{((S)_-4)\}_2\text{]}(\text{OTf})_2^{2+} \text{ and [(Pd(dppp)]_2((S)_-4)]OTf}^{+}.\)

**Figure S49:** \(^1\text{H NMR spectrum (700.4 MHz, CD}_3\text{CN:CD}_2\text{Cl}_2\ 1:1, 298 K) of [Pd}_2(\text{dppp})_2\{((S)_-4)\}_2\text{]}(\text{OTf})_4.\)**
**Figure S50:** $^{13}$C NMR spectrum (176.1 MHz, CD$_3$CN:CD$_2$Cl$_2$ 1:1, 298 K) of [Pd$_2$(dppp)$_2$][(S$_p$)$_4$]$_2$(OTf)$_4$.

**Figure S51:** $^{31}$P NMR spectrum (202.1 MHz, CD$_3$CN:CD$_2$Cl$_2$ 1:1, 298 K) of [Pd$_2$(dppp)$_2$][(S$_p$)$_4$]$_2$(OTf)$_4$. 

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Figure S52: $^1$H, $^1$H-COSY NMR spectrum (700.4 MHz, CD$_3$CN:CD$_2$Cl$_2$ 1:1, 298 K) of [Pd$_2$(dppp)$_2$(S$_p$)$_4$]$_2$(OTf)$_4$.

Figure S53: $^1$H, $^{13}$C-HSQC NMR spectrum (700.4 MHz, 176.1 MHz, CD$_3$CN:CD$_2$Cl$_2$ 1:1, 298 K) of [Pd$_2$(dppp)$_2$(S$_p$)$_4$]$_2$(OTf)$_4$. 

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**Figure S54**: $^1$H-DOSY NMR spectrum (700.4 MHz, CD$_3$CN:CD$_2$Cl$_2$ 1:1, 298 K) of [Pd$_2$(dppp)$_2$((S$_4$)-4)$_2$](OTf)$_4$.

**Figure S55**: ESI positive mass spectrum of 1:1 mixture of (S$_4$)-4 and [Pd(dppp)](OTf)$_2$ in CD$_3$CN:CD$_2$Cl$_2$ 1:1 measured on a micrOTOF-Q time-of-flight mass spectrometer.
Figure S56: Experimental and calculated high resolution ESI positive mass spectra of $[\text{Pd}_2(\text{dppp})_2(S_p-4)_2]^{4+}$ (left) measured on a *micrOTOF-Q* time-of-flight mass spectrometer and $[\text{Pd}(\text{dppp})_2(S_p-4)_2][\text{OTf}]^{3+}$ (right) in CD$_3$CN:CD$_2$Cl$_2$ 1:1 measured on an *Orbitrab XL* mass spectrometer.

$[\text{Pd}_2(\text{dppp})_2]\{\text{(rac)-4}\}_2][\text{OTf}]_4$

$^1$H NMR (700.4 MHz, CD$_3$CN:CD$_2$Cl$_2$ 1:1, 298 K): $\delta$ [ppm] = 8.69-8.64 (m, 8H, H-23), 7.72-7.50 (m, 40H, H-18, H-19, dppp-Ph$_{ortho}$, dppp-Ph$_{para}$), 7.44-7.34 (m, 24H, dppp-Ph$_{meta}$, H-7, H-8, H-12, H-13, H-16), 3.32-2.90 (m, 24H, dppp-CH$_2$-PPh$_2$).

$^{13}$C NMR (176.1 MHz, CD$_3$CN:CD$_2$Cl$_2$ 1:1, 298 K): $\delta$ [ppm] = 150.5 (C-23), 143.8*, 141.4*, 141.1*, 137.8*, 133.8*, 133.1*, 133.0*, 132.5*, 132.1*, 131.0*, 128.0*, 122.7*, 120.9*, 35.2*, 34.0*.

*Signals could not be unambiguously assigned.

$^{31}$P NMR (202.1 MHz, CD$_3$CN:CD$_2$Cl$_2$ 1:1, 298 K): $\delta$ [ppm] = 8.39 (s, dppp-P).

$^1$H-DOSY NMR (499.1 MHz, CD$_3$CN:CD$_2$Cl$_2$ 1:1, 298 K): $D = 4.51 \cdot 10^{-10}$ m$^2$s$^{-1}$; $R_u = 13.7$ Å.

MS (ESI+) $m/z$: 516.1530 [$\text{Pd}_2(\text{dppp})_2][\text{(rac)-4}]^{3+}$ and $[\text{Pd}(\text{dppp})][\text{(rac)-4}]^{3+}$, 536.6661 [$\text{Pd}(\text{dppp})][\text{(rac)-4}]^{3+}$ (CH$_3$CN)], 595.1025 [$\text{Pd}(\text{dppp})(\text{CH}_3\text{CN})][\text{Cl}]^{3+}$, 667.0122 [$[\text{Pd}(\text{dppp})][\text{OTf}]^{3+}$, 738.5217 [$[\text{Pd}_2(\text{dppp})]_2][\text{(rac)-4}]_2][\text{OTf}]^{3+}$, 773.2753 [Pd(dppp)][(rac)-4]$_2]^{3+}$, 1182.2599 [$[\text{Pd}_2(\text{dppp})][\text{(rac)-4}]_2][\text{OTf}]_2]^{2+}$ and $[\text{Pd}(\text{dppp})][\text{(rac)-4}]_2][\text{OTf}]^{3+}$. 

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**Figure S57**: $^1$H NMR spectrum (700.4 MHz, CD$_3$CN:CD$_2$Cl$_2$ 1:1, 298 K) of [Pd$_2$(dppp)$_2$((rac)-4)$_2$](OTf)$_4$.

**Figure S58**: $^{13}$C NMR spectrum (176.1 MHz, CD$_3$CN:CD$_2$Cl$_2$ 1:1, 298 K) of [Pd$_2$(dppp)$_2$((rac)-4)$_2$](OTf)$_4$.

**Figure S59**: $^{31}$P NMR spectrum (202.1 MHz, CD$_3$CN:CD$_2$Cl$_2$ 1:1, 298 K) of [Pd$_2$(dppp)$_2$((rac)-4)$_2$](OTf)$_4$.
Figure S60: $^1$H,$^1$H-COSY NMR spectrum (700.4 MHz, CD$_3$CN:CD$_2$Cl$_2$ 1:1, 298 K) of [Pd$_2$(dppp)$_2$((rac)-4)$_2$](OTf)$_4$.

Figure S61: $^1$H, $^{13}$C-HSQC NMR spectrum (700.4 MHz, 176.1 MHz, CD$_3$CN:CD$_2$Cl$_2$ 1:1, 298 K) of [Pd$_2$(dppp)$_2$((rac)-4)$_2$](OTf)$_4$. 
Figure S62: $^1$H-DOSY NMR spectrum (499.1 MHz, CD$_3$CN:CD$_2$Cl$_2$ 1:1, 298 K) of [Pd$_2$(dppp)$_2$((rac)-4)$_2$](OTf)$_4$. 
Figure S63: ESI positive mass spectrum of 1:1 mixture of (rac)-4 and [Pd(dppp)][OTf]$_2$ in CD$_3$CN:CD$_2$Cl$_2$ 1:1 measured on a micrOTOF-Q time-of-flight mass spectrometer.

Figure S64: Experimental and calculated high resolution ESI positive mass spectra of [Pd$_2$(dppp)$_2$]([rac]-4)$_2$$_{4+}$ in CD$_3$CN:CD$_2$Cl$_2$ 1:1 measured on an Orbitrap XL mass spectrometer.
Figure S65: Experimental and calculated high resolution ESI positive mass spectra of \([\text{Pd}_2(dppp)_2(rac-4)_2]\{\text{OTf}\}\) in CD$_3$CN:CD$_2$Cl$_2$ 1:1 measured on an Orbitrap XL mass spectrometer.
[Pd_{2}(dpdp)_{2}]_{4}(OTf)_{4} in acetonitrile

(rac)-, (R_{p})- or (S_{p})-4 (2.05 mg, 3.98 µmol, 1.00 eq.) was dissolved in deuterated acetonitrile (0.5 mL) and a solution of [Pd(dpdp)](OTf)_{2} (3.27 mg, 4.00 µmol, 1.01 eq.) in deuterated acetonitrile (0.1 mL) was added. The mixture was filtrated.

\[ \text{[Pd}_{2}(\text{dpdp})_{2}\{(\text{R}_{p})\text{-}4\}^{2}\}(\text{OTf})_{4}\]

\[ {^1}H \text{ NMR (499.1 MHz, CD}_{3}CN, 298 K): } \delta [\text{ppm}] = \text{8.59-8.53 (m, 8H, H-23), 7.72-7.52 (m, 40H, H-18, H-11, H-16), 6.69-6.64 (m, 4H, H-8, H-13), 3.32-2.94 (m, 24H, H-1, H-2, H-9, H-10, dpdp-CH}_{2}-\text{PPh}_{2}).}\]

\[ {^{13}}C \text{ NMR (125.5 MHz, CD}_{3}CN, 298 K): } \delta [\text{ppm}] = 150.8 (C-23), 144.2*, 141.5*, 138.1*, 134.1*, 133.6*, 133.3*, 132.5*, 131.4*, 130.4*, 128.4*, 126.0*, 124.5*, 123.5*, 120.9*, 35.4*, 34.2*}.\]

*Signals could not be unambiguously assigned.

\[ {^{31}}P \text{ NMR (202.1 MHz, CD}_{3}CN, 298 K): } \delta [\text{ppm}] = 8.65 (s, dpdp-P).\]

\[ {^{1}}H-\text{DOSY NMR (499.1 MHz, CD}_{3}CN, 298 K): } D = 5.15 \cdot 10^{-10} \text{ m}^2 \text{s}^{-1}, R_{H} = 13.2 \text{ Å}.\]

MS (ESI+) m/z: 516.1511 [Pd_{2}(dpdp)_{2}\{(R_{p})\text{-}4\}^{2}\}(OTf)_{4}]^{2+}, 536.6639 [Pd(dpdp)](R_{p})-4](CH}_{3}CN)_{2}]^{2+}, 667.0102 [Pd(dpdp)](OTf)_{2}]^{2+}, 738.5190 [Pd(dpdp)](R_{p})-4]_{2}(OTf)_{2}]^{3+}, 773.2728 [Pd(dpdp)](R_{p})-4]_{2}]^{3+}, 1181.2550 [Pd_{2}(dpdp)_{2}\{(S_{p})\text{-}4\}^{2}\}(OTf)_{2}]^{2+}, [Pd(dpdp)](R_{p})-4)]^{2+}.\]

UV-Vis (CH}_{3}CN, c = 3.32 mm): \lambda [\text{nm}] = 275, 324.

CD (CH}_{3}CN, c = 3.32 mm): \lambda [\text{nm}] (\Delta [L/(\text{mol cm})]) = [Pd_{2}(dpdp)_{2}\{(R_{p})\text{-}4\}^{2}\}(OTf)_{2}]^{2+}: 214 (25), 237 (+120), 257 (3), 273 (+53), 291 (1), 305 (+18), 338 (236); [Pd_{2}(dpdp)_{2}(S_{p})-4)]^{2}\}(OTf)_{2}]^{2+}: 214 (+33), 237 (20), 258 (+4), 272 (52), 291 (2), 304 (9), 337 (247).

**Figure S66:** \text{^1}H \text{ NMR spectrum (499.1 MHz, CD}_{3}CN, 298 K) of [Pd_{2}(dpdp)_{2}\{(R_{p})\text{-}4\}^{2}\}(OTf)_{2].}
Figure S67: $^{13}$C NMR spectrum (125.5 MHz, CD$_3$CN, 298 K) of [Pd$_2$(dppp)$_2$((R$_p$)-4)$_2$][OTf]$_4$. 

Figure S68: $^{31}$P NMR spectrum (202.1 MHz, CD$_3$CN, 298 K) of [Pd$_2$(dppp)$_2$((R$_p$)-4)$_2$][OTf]$_4$. 

Figure S69: $^1$H,$^1$H-COSY NMR spectrum (499.1 MHz, CD$_3$CN, 298 K) of [Pd$_2$(dppp)$_2$((R$_p$)-4)$_2$][OTf]$_4$. 

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Figure S70: $^1$H, $^{13}$C-HSQC NMR spectrum (499.1 MHz, 125.5 MHz, CD$_3$CN, 298 K) of [Pd$_2$(dppp)$_2$](R$_p$)$_2$][OTf]$_4$.

Figure S71: $^1$H-DOSY NMR spectrum (499.1 MHz, CD$_3$CN, 298 K) of [Pd$_2$(dppp)$_2$](R$_p$)$_2$][OTf]$_4$. 

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**Figure S72:** ESI positive mass spectrum of 1:1 mixture of \((R_4^-)\cdot 4\) and \([\text{Pd(dppp)}][\text{OTf}]_2\) in CD$_3$CN measured on an Orbitrap XL mass spectrometer.

**Figure S73:** Experimental and calculated high resolution ESI positive mass spectra of \([\text{Pd}_2(\text{dppp})_2([R_4^-]_4)_2]^{4+}\) in CD$_3$CN measured on an Orbitrap XL mass spectrometer.
Figure S74: Experimental and calculated high resolution ESI positive mass spectra of $\left[\text{Pd}_2(\text{dppp})_2(\text{R}_p^-)_2\right]\text{OTf}^{3+}$ in CD$_3$CN measured on an Orbitrap XL mass spectrometer.

Figure S75: Experimental and calculated high resolution ESI positive mass spectra of $\left[\text{Pd}_2(\text{dppp})_2(\text{R}_p^-)_2\right]\text{OTf}^{2+}$ in CD$_3$CN measured on an Orbitrap XL mass spectrometer.
Figure S76: Non-normalized UV-Vis spectrum of [Pd₂(dppp)₂][OTf]₄ (c = 3.32 mM in CH₃CN).

Figure S77: CD spectra of [Pd₂(dppp)₂][OTf]₄ (c = 3.32 mM, CH₃CN).
$[\text{Pd}_2(\text{dppp})_2\{(\text{rac}-4)\}_2](\text{OTf})_4$.  

$^1$H NMR (499.1 MHz, CD$_3$CN, 298 K): $\delta$ [ppm] = 8.59-8.53 (m, 8H, H-23), 7.72-7.52 (m, 40H, H-18, H-19, dppp-Ph$_{ortho}$, dppp-Ph$_{meta}$), 6.78-6.70 (m, 8H, H-5, H-7, H-12, H-16), 6.69-6.64 (m, 4H, H-8, H-13), 3.32-2.94 (m, 24H, H-1, H-2, H-9, H-10, dppp-CH$_2$-PPh$_2$), 2.33-2.17 (m, 4H, dppp-CH$_2$).  

$^{13}$C NMR (125.5 MHz, CD$_3$CN, 298 K): $\delta$ [ppm] = 150.7 (C-23), 144.1*, 141.5*, 138.1*, 134.0*, 133.3*, 132.9*, 131.4*, 130.5*, 128.4*, 126.0*, 124.6*, 123.5*, 120.9*, 35.4*, 34.2*.  

*Signals could not be unambiguously assigned.  

$^{31}$P NMR (202.1 MHz, CD$_3$CN, 298 K): $\delta$ [ppm] = 8.65 (s, dppp-P).  

$^1$H-DOSY NMR (499.1 MHz, CD$_3$CN, 298 K): D = 4.89 · 10$^{-10}$ m$^2$ s$^{-1}$, R$_H$ = 13.9 Å.  

MS (ESI+) m/z: 516.1529 [Pd$_2$(dppp)$_2${(rac)-4}$]^{1+}$ and [Pd(dppp){(rac)-4}]$^{2+}$, 536.1661 [Pd(dppp){(rac)-4} (CH$_3$CN)]$^{2+}$, 595.1030 [{[Pd(dppp)(CH$_3$CN)]Cl}]$^+$, 667.0126 [{[Pd(dppp)OTf}]$^+$, 738.51220 [{Pd$_2$(dppp)$_2${(rac)-4}$]OTf}]$^{2+}$, 773.2757 [Pd(dppp){(rac)-4}]$^{2+}$, 1181.2600 [{Pd$_2$(dppp)$_2${(rac)-4}$]OTf$_2}]^{2+}$ and [{Pd(dppp){(rac)-4}OTf}]$^+$.  

Figure S78: $^1$H NMR spectrum (499.1 MHz, CD$_3$CN, 298 K) of [Pd$_2$(dppp)$_2${(rac)-4}$]_{4}$(OTf)$_4$.  

Figure S79: $^{13}$C NMR spectrum (125.5 MHz, CD$_3$CN, 298 K) of [Pd$_2$(dppp)$_2${(rac)-4}$]_{4}$(OTf)$_4$.  

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Figure S80: $^{31}$P NMR spectrum (202.1 MHz, CD$_3$CN, 298 K) of [Pd$_2$(dppp)$_2$]$_2$[(rac)-4]$_2$][OTf]$_4$.

Figure S81: $^1$H, $^1$H-COSY NMR spectrum (499.1 MHz, CD$_3$CN, 298 K) of [Pd$_2$(dppp)$_2$][(rac)-4]$_2$][OTf]$_4$. 
Figure S82: $^1$H, $^{13}$C-HSQC NMR spectrum (499.1 MHz, 125.5 MHz, CD$_3$CN, 298 K) of [Pd$_2$(dppp)$_2$(rac-4)$_2$](OTf)$_4$.

Figure S83: $^1$H-DOSY NMR spectrum (499.1 MHz, CD$_3$CN, 298 K) of [Pd$_2$(dppp)$_2$(rac-4)$_2$](OTf)$_4$. 
Figure S84: ESI positive mass spectrum of 1:1 mixture of (rac)-4 and [Pd(dppp)](OTf)$_2$ in CD$_3$CN measured on an Orbitrap XL mass spectrometer.

Figure S85: Experimental and calculated high resolution ESI positive mass spectra of [Pd$_2$(dppp)$_2$((rac)-4)$_2$]$^{4+}$ in CD$_3$CN measured on an Orbitrap XL mass spectrometer.
Figure S86: Experimental and calculated high resolution ESI positive mass spectra of [(Pd₂(dppp)₂[(rac)-4]₁)OTf]⁺ in CD₃CN measured on an Orbitrap XL mass spectrometer.
[Pd₅S₄]{(BF₄)₄} in acetonitrile

(rac)-, (R)ₙ- or (S)ₙ-5 (4.00 mg, 7.77 µmol, 1.00 eq.) was dissolved in deuterated acetonitrile (1 mL) and a solution of [Pd(CH₃CN)₂]{(BF₄)₂} (1.76 mg, 3.96 µmol, 0.51 eq.) in deuterated acetonitrile (0.5 mL) was added. The mixture was stirred at 70 °C for 15 h and then filtrated.

![Diagram of [Pd₅S₄]{(BF₄)₄}]

[Figure S87: ¹H NMR spectrum (499.1 MHz, CD₃CN, 298 K) of [Pd₅{(R)ₙ-5}]{(BF₄)₄}.]
Figure S88: $^{13}$C NMR spectrum (125.5 MHz, CD$_3$CN, 298 K) of [Pd$_2$(R$_p$-5)$_4$](BF$_4$)$_4$.

Figure S89: $^{19}$F NMR spectrum (469.6 MHz, CD$_3$CN, 298 K) of [Pd$_2$(R$_p$-5)$_4$](BF$_4$)$_4$.

Figure S90: $^1$H, $^{13}$C-HSQC NMR spectrum (499.1 MHz, 125.5 MHz, CD$_3$CN, 298 K) of [[Pd$_2$(R$_p$-5)$_4$](BF$_4$)$_4$].
Figure S91: $^1$H, $^{13}$C-HMBC NMR spectrum (499.1 MHz, 125.5 MHz, CD$_3$CN, 298 K) of [Pd$_2$((R$_p$)-5)$_4$][BF$_4$]$_4$.

Figure S92: $^1$H-DOSY NMR spectrum (499.1 MHz, CD$_3$CN, 298 K) of [Pd$_2$((R$_p$)-5)$_4$][BF$_4$]$_4$. 
Figure S93: ESI positive mass spectrum of 2:1 mixture of (R₉)-S and [Pd(CH₃CN)_4][BF₄]₂ in CD₃CN measured on a microTOF-Q time-of-flight spectrometer.

Figure S94: Experimental and calculated high resolution ESI positive mass spectra of [Pd₃((R₉)-S)₄]^{4+} (left) and [{Pd₂[(rac)-S]₄][BF₄]}^{3+} (right) in CD₃CN measured on an Orbitrap XL mass spectrometer.
Figure S95: Non-normalized UV-Vis spectrum of [Pd$_2$S$_5$]$_4$(BF$_4$)$_4$ (c = 3.24 mM in CH$_3$CN).

Figure S96: CD spectra of [Pd$_2$S$_5$]$_4$(BF$_4$)$_4$ (c = 3.24 mM, CH$_3$CN).
$[\text{Pd}_2(\text{rac}-5)_4]\text{[BF}_4\text]_4$

$^{19}\text{F NMR (469.6 MHz, CD}_3\text{CN, 298 K): } \delta \text{ [ppm]} = -151.60 \text{ (s, BF}_4\text), -151.65 \text{ (s, BF}_4\text).$

$^1\text{H-DOSY NMR (700.4 MHz, CD}_3\text{CN, 298 K): } D = 6.52 \cdot 10^{-10} \text{ m}^2\text{s}^{-1}, R_H = 10.4 \text{ Å}.$

$\text{MS (ESI+)} m/z: 567.8 \text{ [Pd}_2(\text{rac}-5)_4\text]^{4+}, 786.0 \text{ ([Pd}_2(\text{rac}-5)_4\text][\text{BF}_4\text])^{3+}, 1222.5 \text{ ([Pd}_2(\text{rac}-5)_4\text][\text{BF}_4\text])^{2+}.$

Figure S97: $^1\text{H NMR spectrum (700.4 MHz, CD}_3\text{CN, 298 K) of [Pd}_2(\text{rac}-5)_4\text][\text{BF}_4\text].$

Figure S98: $^{19}\text{F NMR spectrum (469.6 MHz, CD}_3\text{CN, 298 K) of [Pd}_2(\text{rac}-5)_4\text][\text{BF}_4\text].$
Figure S99: $^1$H-DOSY NMR spectrum (499.1 MHz, CD$_3$CN, 298 K) of [Pd$_2$((rac)-5)$_4$(BF$_4$)$_4$].

Figure S100: ESI positive mass spectrum of 2:1 mixture of (rac)-5 and [Pd(CH$_3$CN)$_4$(BF$_4$)$_2$] in CD$_3$CN measured on a micrOTOF-Q time-of-flight spectrometer.
Figure S101: Experimental and calculated high resolution ESI positive mass spectra of \([\text{Pd}_2(\text{rac}-5)_4]^{4+}\) (left) and \([\text{Pd}_2(\text{rac}-5)_4\text{BF}_4]^{3+}\) (right) in CD$_3$CN measured on an Orbitrap XL mass spectrometer.
[Pd_2S_5]_2(BF_4)_4 in dimethyl sulfoxide

(rac)-, (R)_5- or (S)_5- (4.00 mg, 7.77 µmol, 1.00 eq.) was dissolved in deuterated dimethyl sulfoxide (1 mL) and a solution of [Pd(CH_3CN)_4](BF_4)_2 (1.76 mg, 3.96 µmol, 0.51 eq.) in deuterated dimethyl sulfoxide (0.5 mL) was added. The mixture was stirred at 70 °C for 15 h and then filtrated.

\[ \text{[Pd}_2\text{S}_5\text{]}_2\text{(BF}_4\text{)}_4 \]

\[ \text{1H NMR (700.4 MHz, DMSO-}d_6\text{, 298 K)}: \delta [\text{ppm}] = 9.67 (d, 8H, H-25, J_{25,22} = 2.4 \text{ Hz}), 9.35 (dd, 8H, H-24, J_{24,23} = 5.7 \text{ Hz}, J_{24,22} = 1.4 \text{ Hz}), 8.45-8.42 (m, 8H, H-22), 7.90 (dd, 8H, H-23, J_{23,22} = 7.8 \text{ Hz}, J_{23,24} = 5.7 \text{ Hz}), 7.71-7.68 (m, 16H, H-19), 7.65-7.62 (m, 16H, H-18), 6.7 (d, 8H, H-5, H-16, J_{5,16} = 2.2 \text{ Hz}), 6.67-6.64 (m, 8H, H-7, H-12), 6.51 (d, 8H, H-8, H-13, J_{8,7} = J_{13,12} = 7.8 \text{ Hz}), 3.36-3.30* (m, 8H, H-1, H-2, H-9, H-10), 3.18-3.12* (m, 8H, H-1, H-2, H-9, H-10), 2.98-2.92* (m, 8H, H-1, H-2, H-9, H-10), 2.31-2.25* (m, 8H, H-1, H-2, H-9, H-10).

* Signals could not be unambiguously assigned.

\[ \text{13C NMR (176.1 MHz, DMSO-}d_6\text{, 298 K)}: \delta [\text{ppm}] = 150.2 (C-24), 148.8 (C-25), 141.5 (C-17), 140.2 (C-4, C-15), 139.2 (C-22), 138.4 (C-21), 135.4 (C-3, C-14), 133.4 (C-20), 132.3 (C-8, C-13), 132.1 (C-5, C-16), 131.3 (C-7, C-12), 130.2 (C-18), 127.5 (C-19), 127.4 (C-23), 118.1 (C-6, C-11), 34.1 (C-1, C-2, C-9, C-10).

\[ \text{19F NMR (469.6 MHz, DMSO-}d_6\text{, 298 K): } \delta [\text{ppm}] = -148.8 (s, BF}_4\text{), -167.6 (s, BF}_4\text{).}

\[ \text{1H-DOSY NMR (700.4 MHz, DMSO-}d_6\text{, 298 K): } D = 1.04 \cdot 10^{-10} \text{ m}^2\text{s}^{-1}, R_H = 10.6 \text{ Å}.

\[ \text{MS (ESI+)} m/z: 567.6956 \text{ [Pd}_2\text{(R}_5\text{-S}_5\text{)]}_4^{4+}, 785.9290 \text{ [Pd}_2\text{(R}_5\text{-S}_5\text{)]}_4\text{(BF}_4\text{)}_4^{3+}, 1221.3960 \text{ [Pd}_2\text{(R}_5\text{-S}_5\text{)]}_4\text{(BF}_4\text{)}_2^{2+}.

Figure S102: \text{1H NMR spectrum (700.4 MHz, DMSO-}d_6\text{, 298 K) of [Pd}_2\text{(R}_5\text{-S}_5\text{)]}_4\text{(BF}_4\text{)}_4.}
Figure S103: $^{13}$C NMR spectrum (176.1 MHz, DMSO-$d_6$, 298 K) of $[\text{Pd}_2((R)_p-5)_2]_4(\text{BF}_4)_4$.

Figure S104: $^{19}$F NMR spectrum (469.6 MHz, DMSO-$d_6$, 298 K) of $[\text{Pd}_2((R)_p-5)_2]_4(\text{BF}_4)_4$.

Figure S105: $^1$H, $^{13}$C-HSQC NMR spectrum (700.4 MHz, 176.1 MHz, DMSO-$d_6$, 298 K) of $[\text{Pd}_2((R)_p-5)_2]_4(\text{BF}_4)_4$. 
Figure S106: $^1$H, $^{13}$C-HMBC NMR spectrum (700.4 MHz, 176.1 MHz, DMSO-$d_6$, 298 K) of $\{[\text{Pd}_2((R)_p-5)_4]\}([\text{BF}_4]_4$.

Figure S107: $^1$H-DOSY NMR spectrum (499.1 MHz, DMSO-$d_6$, 298 K) of $[\text{Pd}_2((R)_p-5)_4][\text{BF}_4]_4$. 
Figure S108: ESI positive mass spectrum of 2:1 mixture of (R)-5 and [Pd(CH₂CN)₄](BF₄)₂ in DMSO-d₆ measured on an Orbitrap XL mass spectrometer.

Figure S109: Experimental and calculated high resolution ESI positive mass spectra of [[Pd₂[(R)-5]₂(BF₄)]³⁺ in DMSO-d₆ measured on an Orbitrap XL mass spectrometer.
$[^{19}\text{F}]\text{NMR (469.6 MHz, DMSO-$d_6$, 298 K)}$: $\delta$ [ppm] = $-148.74$ (s, BF$_4$), $-148.79$ (m, BF$_4$).

$[^1\text{H}]\text{DOSY NMR (700.4 MHz, DMSO-$d_6$, 298 K)}$: $D = 1.06 \cdot 10^{-10}$ m$^2$/s, $R_H = 10.4$ Å.

MS (ESI+) $m/z$: 567.6967 $[^{1}\text{Pd}_2\{[^{\text{rac}}-5\}_4\}[^{\text{BF}_4}]_{4}^{4+}$, 785.9302 $[^{3}\text{Pd}_2\{[^{\text{rac}}-5\}_4\}[^{\text{BF}_4}]_{3}^{3+}$, 1222.8984 $[^{2}\text{Pd}_2\{[^{\text{rac}}-5\}_4\}[^{\text{BF}_4}]_{2}^{2+}$.

Figure S110: $[^1\text{H}]\text{NMR spectrum (700.4 MHz, DMSO-$d_6$, 298 K)}$ of $[^{1}\text{Pd}_2\{[^{\text{rac}}-5\}_4\}[^{\text{BF}_4}]_{4}$.

Figure S111: $[^{19}\text{F}]\text{NMR spectrum (469.6 MHz, DMSO-$d_6$, 298 K)}$ of $[^{1}\text{Pd}_2\{[^{\text{rac}}-5\}_4\}[^{\text{BF}_4}]_{4}$.
Figure S112: $^1$H-DOSY NMR spectrum (499.1 MHz, DMSO-$d_6$, 298 K) of \([\text{Pd}_2\{(\text{rac})-5\}]_4\)(BF$_4$)$_4$.

Figure S113: ESI positive mass spectrum of 2:1 mixture of (rac)-5 and \([\text{Pd(CH}_3\text{CN})_4]_2\)(BF$_4$)$_2$ in DMSO-$d_6$ measured on an Orbitrap XL mass spectrometer.
Figure S114: Experimental and calculated high resolution ESI positive mass spectra of $\left[\text{Pd}_2(\text{rac-5})_4\right]^{3+}$ in DMSO-$d_6$ measured on an Orbitrap XL mass spectrometer.
NMR experiments concerning the kinetics of structural rearrangements upon mixing of preassembled enantiomerically pure complexes \([\text{Pd}_2\{([R]_p)-\text{S}_5\}_4]\text{[BF}_4\}_4\) and \([\text{Pd}_2\{([S]_p)-\text{S}_5\}_4]\text{[BF}_4\}_4\)

\((R)_p\)- and \((S)_p\)-5 (4.00 mg, 7.77 µmol, 1.00 eq.) were each dissolved in deuterated acetonitrile or deuterated dimethyl sulfoxide (1 mL) and a solution of \([\text{Pd}\{(\text{CH}_3\text{CN})_4]\text{[BF}_4\}_2\) (1.76 mg, 3.96 µmol, 0.51 eq.) in deuterated acetonitrile or dimethyl sulfoxide (0.5 mL) were added to each ligand solution. Both mixtures were stirred at 70 °C for 15 h. The enantiomerically pure complex solutions were mixed and analysed by NMR spectroscopy.

\[\text{H}^1\] NMR spectra (400.1 MHz, ACN-\(d_3\), 298 K) of a) \([\text{Pd}_2\{([R]_p)-\text{S}_5\}_4]\text{[BF}_4\}_4\), b) mixture of \([\text{Pd}_2\{([R]_p)-\text{S}_5\}_4]\text{[BF}_4\}_4\) and \([\text{Pd}_2\{([S]_p)-\text{S}_5\}_4]\text{[BF}_4\}_4\) immediately after mixing, c) mixture of \([\text{Pd}_2\{([R]_p)-\text{S}_5\}_4]\text{[BF}_4\}_4\) and \([\text{Pd}_2\{([S]_p)-\text{S}_5\}_4]\text{[BF}_4\}_4\) after 12 h at room temperature, d) mixture of \([\text{Pd}_2\{([R]_p)-\text{S}_5\}_4]\text{[BF}_4\}_4\) and \([\text{Pd}_2\{([S]_p)-\text{S}_5\}_4]\text{[BF}_4\}_4\) after another 15 h at 70 °C, e) mixture of \([\text{Pd}_2\{([R]_p)-\text{S}_5\}_4]\text{[BF}_4\}_4\) and \([\text{Pd}_2\{([S]_p)-\text{S}_5\}_4]\text{[BF}_4\}_4\) again after another 15 h and f) \([\text{Pd}_2\{(\text{rac})-\text{S}_5\}_4]\text{[BF}_4\}_4\).

**Figure S115:** \[\text{H}^1\] NMR spectra (400.1 MHz, ACN-\(d_3\), 298 K) of a) \([\text{Pd}_2\{([R]_p)-\text{S}_5\}_4]\text{[BF}_4\}_4\), b) mixture of \([\text{Pd}_2\{([R]_p)-\text{S}_5\}_4]\text{[BF}_4\}_4\) and \([\text{Pd}_2\{([S]_p)-\text{S}_5\}_4]\text{[BF}_4\}_4\) immediately after mixing, c) mixture of \([\text{Pd}_2\{([R]_p)-\text{S}_5\}_4]\text{[BF}_4\}_4\) and \([\text{Pd}_2\{([S]_p)-\text{S}_5\}_4]\text{[BF}_4\}_4\) after 12 h at room temperature, d) mixture of \([\text{Pd}_2\{([R]_p)-\text{S}_5\}_4]\text{[BF}_4\}_4\) and \([\text{Pd}_2\{([S]_p)-\text{S}_5\}_4]\text{[BF}_4\}_4\) after another 15 h at 70 °C, e) mixture of \([\text{Pd}_2\{([R]_p)-\text{S}_5\}_4]\text{[BF}_4\}_4\) and \([\text{Pd}_2\{([S]_p)-\text{S}_5\}_4]\text{[BF}_4\}_4\) again after another 15 h and f) \([\text{Pd}_2\{(\text{rac})-\text{S}_5\}_4]\text{[BF}_4\}_4\).
Figure S116: $^1$H NMR spectra (400.1 MHz, DMSO-$d_6$, 298 K) of a) [Pd$_2$((R)-5)$_4$](BF$_4$)$_4$, b) mixture of [Pd$_2$((R)-5)$_4$](BF$_4$)$_4$ and [Pd$_2$((S)-5)$_4$](BF$_4$)$_4$ immediately after mixing, c) mixture of [Pd$_2$((R)-5)$_4$](BF$_4$)$_4$ and [Pd$_2$((S)-5)$_4$](BF$_4$)$_4$ after 12 h at room temperature, d) mixture of [Pd$_2$((R)-5)$_4$](BF$_4$)$_4$ and [Pd$_2$((S)-5)$_4$](BF$_4$)$_4$ after another 15 h at 70 °C, e) [Pd$_2$((rac)-5)$_4$](BF$_4$)$_4$. 
X-ray crystallography

X-Ray experimental details for (Rp)-4, the racemic mixture of [Pd2(dppp)2((Rp)-4)2](OTf)4 & [Pd2(dppp)2((Sr)-4)2](OTf)4 and [Pd2((R)-5)4](BF4)2 are below. The single-crystal X-ray data for (Rp)-4 were measured on a Rigaku SuperNova diffractometer equipped with an Eos CCD detector using monochromated Mo-Kα (λ = 0.71073 Å) radiation. Data for the racemic mixture of [Pd2(dppp)2((Rp)-4)2](OTf)4 & [Pd2(dppp)2((Sr)-4)2](OTf)4 and [Pd2((R)-5)4](BF4)2 were measured using a dual-source Rigaku SuperNova diffractometer equipped with an Atlas detector using mirror-monochromated Cu-Kα (λ = 1.54184 Å) radiation. The data collection and reduction were performed using the CrysAlisPro software which utilizes the SHELX software which utilizes the SHELXL-2015 module. In [Pd2((R)-5)4](BF4)2 one tetrafluoroborate anion anion could not be found using electron fourier difference map. This is due to weakly diffracting power of the crystals and disordered solvent molecules. Therefore, one tetrafluoroborate anion anion is modelled and thermal movement of fluorine atoms on both tetrafluoroborate anion anions were physically restrained to give roughly tetrahedral geometry.

Crystal data for (Rp)-4: CCDC-1893943, C60H34d11N8, M = 937.40, light orange plate, 0.174 x 0.075 x 0.068 mm³, tetragonal, space group P 41212, a = 13.41045(10) Å, b = 13.41045(10) Å, c = 40.0935(5) Å, α = 90°, β = 90°, γ = 90°, V = 7210.41(14) Å³, Z = 8, Dc = 1.727 g/cm³, F000 = 3632, µ= 2.633 mm⁻¹, T = 120.00(16) K, θmax = 29.06°, 99301 total reflections, 8071 with Io > 2σ(Io), Rint = 0.0525, 9148 data, 416 parameters, 0 restraints, GooF = 1.106, R = 0.0448 and wR= 0.1136 [lo > 2σ(lo)], R = 0.0551 and wR= 0.1188 (all reflections), 1.120 <d∆ρ < -0.876 e/Å³, Flack = -0.004(8).

Crystal data for [Pd2((R)-5)4](BF4)2: CCDC-1893944, C152H120B4F16N8Pd4, M = 2618.59, colourless plate, 0.176 x 0.079 x 0.048 mm³, tetragonal, space group P41212, a = 32.9899(5) Å, b = 32.9899(5) Å, c = 14.3593(4) Å, α = 90°, β = 90°, γ = 90°, V = 15627.7(6) Å³, Z = 4, Dc = 1.113 g/cm³, F000 = 5376, µ= 2.397 mm⁻¹, T = 120.01(10) K, θmax = 66.748°, 48137 total reflections, 10932 with Io > 2σ(lo), Rint = 0.0493, 13861 data, 806 parameters, 31 restraints, GooF = 1.031, R = 0.0861 and wR= 0.2445 [lo > 2σ(lo)], R = 0.0997 and wR= 0.2598 (all reflections), 1.233 <d∆ρ < -1.572 e/Å³, Flack = 0.049(6).

Crystal data for [the racemic mixture of [Pd2(dppp)2((Rp)-4)2](OTf)4 & [Pd2(dppp)2((Sr)-4)2](OTf)4]: CCDC-1893945, C598H248F8N10O8Pd2S2, M = 5542.69, colourless plate, 0.256 x 0.226 x 0.079 mm³, monoclinic, space group C2/c, a = 46.6905(8) Å, b = 26.3232(3) Å, c = 31.9982(5) Å, α = 90°, β = 97.750(2°), γ = 90°, V = 38968.0(10) Å³, Z = 4, Dc = 0.945 g/cm³, F000 = 11392, µ= 2.653 mm⁻¹, T = 120.01(10) K, θmax = 66.749°, 109627 total reflections, 25716 with Io > 2σ(lo), Rint = 0.0411, 34510 data, 1732 parameters, 97 restraints, GooF = 1.033, R = 0.0815 and wR= 0.2423 [lo > 2σ(lo)], R = 0.0992 and wR= 0.2681 (all reflections), 4.275 <d∆ρ < -1.553 e/Å³.
Figure S117. X-Ray crystal structure of \((R)_2\)-4 in ball & stick model (acetonitrile solvent is omitted for viewing clarity; colour code: grey – carbon, white – hydrogen, blue – nitrogen, purple – iodine)

References