



This open access document is posted as a preprint in the Beilstein Archives at <https://doi.org/10.3762/bxiv.2021.83.v1> and is considered to be an early communication for feedback before peer review. Before citing this document, please check if a final, peer-reviewed version has been published.

This document is not formatted, has not undergone copyediting or typesetting, and may contain errors, unsubstantiated scientific claims or preliminary data.

Preprint Title Design and Synthesis of Planar Chiral Bisphosphine Ligands Based on Diphenyl [2.2]-Paracyclophane

Authors Shaoying Huang, Jiaping Jin and Xufeng Lin

Publication Date 30 Nov. 2021

Article Type Full Research Paper

Supporting Information File 1 PCBPs-SI.docx; 2.9 MB

ORCID® iDs Xufeng Lin - <https://orcid.org/0000-0003-4611-0507>

Design and Synthesis of Planar Chiral Bisphosphine Ligands Based on Diphenyl [2.2]-Paracyclophane

Shaoying Huang, Jiaping Jin, Xufeng Lin*

Department of Chemistry, Zhejiang University, Hangzhou 310027, China;

E-mail: lxfok@zju.edu.cn

Abstract

Planar chiral bisphosphine ligands based on diphenyl [2.2]paracyclophane (PhPhanePHOS) were successfully synthesized in a practical manner in four steps from commercially available 4,12-bisbromo-[2.2]paracyclophane as a new family of bisphosphine ligands. The novel PhPhanePHOS ligands provide high catalytic activity in Pd-catalyzed asymmetric allylalkylation reactions in preliminary experiments.

Key words

asymmetric catalysis, planar chiral ligand, bisphosphine ligand, paracyclophane, asymmetric reactions

Introduction

The development of chiral ligands plays a pivotal role in the development of highly efficient transition metal-catalyzed asymmetric reactions,^[1-5] in which chiral bisphosphine ligands are particularly important due to their widespread application in many aspects.^[6-8] The design of innovative frameworks was the basis for the development of chiral ligands. In the last few decades, various types of backbones for chiral bisphosphines (Figure 1), such as binaphthyl^[9-14], biphenyl^[15-17], heteroaryl^[18,19],

cyclophane²⁰, ferrocenyl^[21-23], and spiro^[24-26] backbones, have been developed and have proven to be effective and useful in the field of metal-catalyzed asymmetric reactions. Despite the impressive and extensive advances in this field, the development of chiral bisphosphines bearing novel scaffolds with excellent efficiency and readily accessible is still a major challenge and very valuable to meet the need for excellent enantioselective transformations with potential industrial application.

In recent years, planar chirality has been increasingly used in the preparation of catalysts.^[27-35] Some research groups, such as Pye and Rossen, Knoll and Zippel, Falk and Fröhlich, Schwartz and Holmes, Nguyen and Herkommer, Grasa and Zanotti-Gerosa, have successfully used planar chiral catalysts in a variety of organometallic enantioselective reactions, including hydrosilylation,^[36] hydrogenations,^[37-39] hydroxymethylations,^[40,41] hydroaminations,^[42] and coupling^[43] reactions. These new chiral catalysts, derived from [2.2]paracyclophane, exhibit special properties. Recently, our group has also developed a new type of planar chiral phosphoric acids (PPAs) based on [2.2]paracyclophane,^[44] which have been successfully used in asymmetric Aza-Friedel-Crafts reactions as strong Brønsted acid organocatalysts, as shown in Figure 2.

Inspired by these pioneering studies, here we have designed and synthesized eight planar chiral bisphosphine ligands based on diphenyl [2.2]paracyclophane (PhPhanePHOS, Figure 1), and reported some preliminary catalytic experiments. The main design principles are outlined in Figure 3. We hypothesise that the introduction of a phenyl substitution into the planar framework of PhPhanePHOS alters freely the dihedral angle of the conformationally

planar chiral bisphosphine, which may be compatible with different metals. Planar chiral bisphosphines formed by phenylsubstitution in different positions can show their different nature and in some cases may be improve the enantioselectivity of the catalytic reactions.

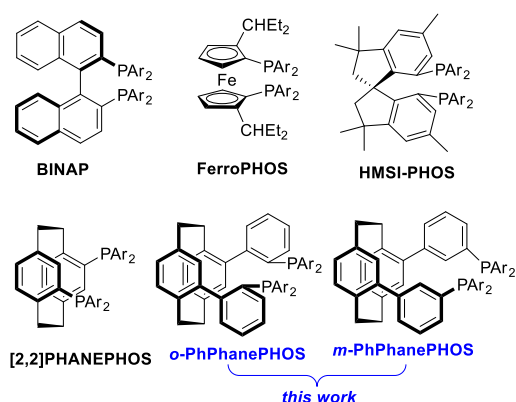


Figure 1: Chiral bisphosphine ligands

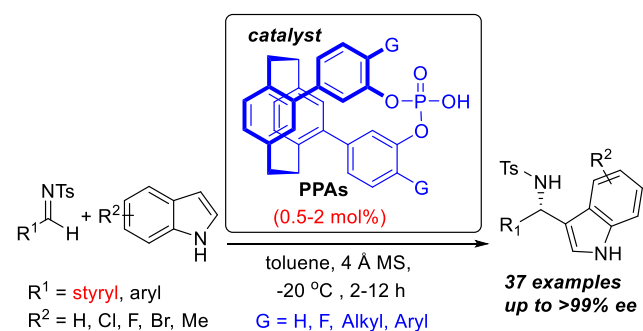


Figure 2: Planar chiral phosphoric acids

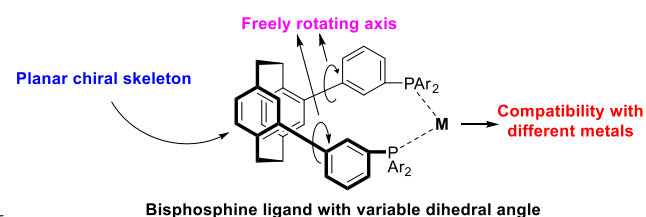


Figure 3: Ligand design principles

Results and Discussion

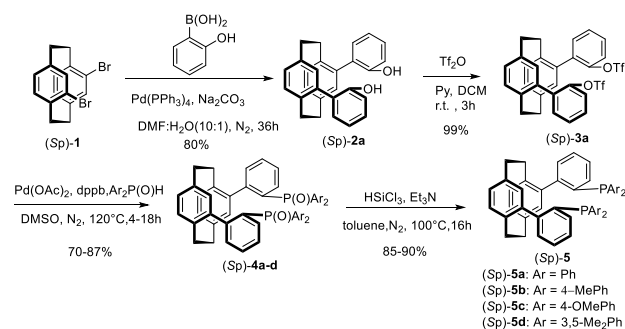
Four planar chiral bisphosphines **5a-d** (*o*-PhPhanePHOS) were first prepared according to Scheme 1. The synthesis

procedure for *o*-PhPhanePHOS begins with the Suzuki coupling reaction between commercially available reagent (*S_p*)-**1** ((*S_p*)-4,12-dibromo[2.2]paracyclophane) and appropriate 2-hydroxyphenylboronic acid.

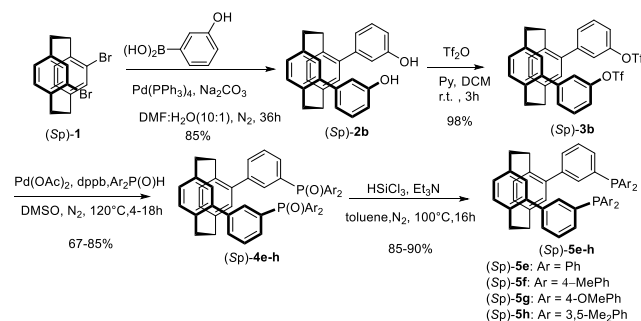
The desired compound (*S_p*)-**2a** was obtained in 80% yield. Compound (*S_p*)-**2a** was treated with trifluoromethanesulfonic anhydride (Tf₂O) in the presence of pyridine to afford the triflate derivative (*S_p*)-**3a** in 99% yield.

Subsequently, (*S_p*)-**3a** was reacted with Ar₂P(O)H using Pd(OAc)₂/dppb as the catalyst to give (*S_p*)-**4a-d** in 70-87% yield. Finally, *o*-PhPhanePHOS (*S_p*)-**5a-d** was obtained in 85-90% yield by reduction of phosphine oxide with HSiCl₃. Thus, *o*-PhPhanePHOS was prepared in 4 steps with overall yield of about 66%. Similarly, other four planar chiral bisphosphines **5e-h** (*m*-PhPhanePHOS) were also prepared with

good overall yields according to the above route, as shown in Scheme 2. We hypothesize that these ligands *o*-PhPhanePHOS and *m*-PhPhanePHOS may have an interesting effect on the metal-catalyzed asymmetric reactions.



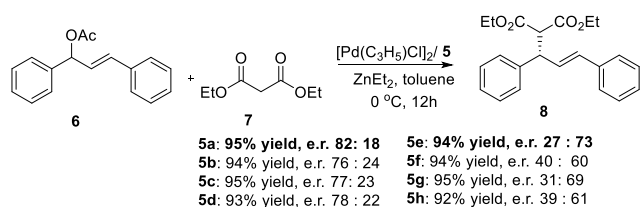
Scheme 1: Synthesis of *o*-PhPhanePHOS **5a-d**



Scheme 2: Synthesis of *m*-PhPhanePHOS **5e-h**

In addition, the efficiency of PhPhanePHOS in catalytic asymmetric allylic alkylation was tested.^[45-52] As shown in Scheme 3, 1,3-diphenylpropen-1-yl acetate was treated with diethyl malonate using 5 mol% [Pd(C₃H₅)Cl]₂ and 10 mol% of *o*-PhPhanePHOS **5a** in toluene, and the desired chiral product **8** was obtained in 95% yield with e.r. 82:18. The ligands *o*-PhPhanePHOS **5b-d** all gave the similar results. On the other hand, the product **8** with **5e-h** as the chiral ligand, was obtained in excellent yield with a little low e.r., and the position of the phosphine group in the PhPhanePHOS can greatly affect the

enantioselectivity of the product, which had a completely opposite conformation.



Scheme 3: Asymmetric allylic alkylation reactions.

In conclusion, we developed a simple and scalable route to new specie of planar chiral bisphosphine ligands based on diphenyl [2.2]paracyclophane (PhPhanePHOS) in four steps and with good overall yields. The PhPhanePHOS was tested in Pd-catalyzed asymmetric allylic alkylation reactions, with good yield and moderate enantioselectivity. Moreover, different positions of the phosphines, such as *o*-PhPhanePHOS and *m*-PhPhanePHOS showed a great influence on the enantioselectivity of the reaction. Further application of these new planar chiral ligands in asymmetric catalysis is currently in progress.

Experimental

All reagents and solvents were purchased from commercial sources. ¹HNMR and ¹³CNMR data were recorded on Bruker AVANCE III 400 spectrometer. The chemical shifts (δ) were quoted in parts per million (ppm) downfield relative to the

internal standard TMS (0.0 ppm) and referenced to the solvent peaks in the NMR solvent (CDCl₃ = δ 7.26 ppm; δ 77.16 ppm). Spin multiplicities were reported using the following abbreviations: s = singlet, d = doublet, t = triplet, dd = doublet of doublet, td = triplet of doublet, m = multiplet. Infrared spectra were recorded on Nicolet NEXUS 470 spectrometer. HRMS data were measured on a GC-TOF. Optical rotations were measured on a PerkinElmer Model 341 polarimeter at 20 °C. The enantiomeric excess (ee) was measured by chiral HPLC analysis.

The synthesis of (*S*_p)-2

A 100 mL three necked round-bottom flask was charged with (*S*)-4,12-dibromo[2.2]paracyclophane ((*S*_p)-1) (3 mmol, 1.0 equiv), 2-hydroxyphenylboronic acid or 3-hydroxyphenylboronic acid (24 mmol, 8 equiv), Pd(PPh₃)₄ (0.3 mmol, 0.1 equiv), Na₂CO₃ (30 mmol, 10.0 equiv) in the mixed solvent DMSO : H₂O (10 : 1) (30 mL) under a nitrogen atmosphere and then stirred the mixture at 100 °C for 36 hours. After cooling to room temperature, the resulting mixture was diluted with EtOAc (100 mL) and 1 M HCl (100 mL). The resulting mixture was then extracted three times with EtOAc (3x50 mL). The organic layer was washed with brine, dried over

anhydrous Na₂SO₄, and solvent was removed in vacuo. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 10/1) to give the product **2** as a white solid.

(S_p)-2,2'-(1,4(1,4)-dibenzenacyclohexane-1²,4³-diyl)diphenol (2a)

940 mg, 80% yield; white solid. M.p. 218-219 °C. [α]_D²⁰ = 88.2° (c 1.00, DCM); IR (film): γ = 3457, 3015, 2922, 2885, 2851, 1903, 1583, 1489, 1473, 1446, 1404, 1344, 1270, 1226, 1196, 1094, 1038, 1023, 952, 916, 811, 760, 736, 649, 510 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.63 (dd, *J* = 7.6, 1.4 Hz, 2H), 7.33 – 7.25 (m, 2H), 7.03 (m, 2H), 6.95 (d, *J* = 8.1 Hz, 2H), 6.83 (d, *J* = 7.4 Hz, 2H), 6.72 (m, 4H), 5.21 (s, 2H), 3.22 (m, 2H), 3.17 – 3.07 (m, 2H), 2.90 (m, 2H), 2.65 (m, 2H) ppm, ¹³C NMR (101 MHz, CDCl₃) δ 152.64, 141.20, 138.11, 136.14, 133.41, 132.96, 131.36, 129.27, 128.40, 126.95, 120.45, 115.49, 34.53, 34.32 ppm; HRMS (GC-TOF): calculated for C₂₈H₂₃O₂⁻([M-H]⁻): m/z 391.1698, found: 391.1703

(S_p)-3,3'-(1,4(1,4)-dibenzenacyclohexane-1²,4³-diyl)diphenol (2b)

998 mg, 85% yield; white solid. M.p. 214-215 °C. [α]_D²⁰ = 526.842° (c 1.00, DCM); IR (film): γ = 3306, 3206, 2923, 2852, 1655, 1579, 1468, 1405, 1340, 1300, 1210, 1160, 1047, 1024, 1004, 882, 789, 736, 722, 703

cm⁻¹; ¹H NMR (400 MHz, DMSO) δ 9.41 (s, 2H), 7.17 (t, *J* = 7.8 Hz, 2H), 6.79 – 6.70 (m, 6H), 6.70 – 6.58 (m, 4H), 6.52 (d, *J* = 1.2 Hz, 2H), 3.44 – 3.38 (m, 2H), 3.11 – 3.00 (m, 2H), 3.00 – 2.87 (m, 2H), 2.73 – 2.61 (m, 2H) ppm; ¹³C NMR (101 MHz, DMSO) δ 157.11, 142.02, 139.82, 139.06, 136.39, 135.42, 132.05, 129.43, 129.37, 119.19, 115.77, 113.67, 33.85, 33.73 ppm; HRMS (GC-TOF): calculated for C₂₈H₂₃O₂⁻([M-H]⁻): m/z 391.1698, found: 391.1705.

The synthesis of (S_p)-3

To a solution of (S_p)-**2** (1.3 g, 2.6 mmol), pyridine (0.4 mL, 5.5 mmol) in CH₂Cl₂ (25 mL), Tf₂O (0.4 mL, 5.5 mmol) was added at 0 °C. The resulting mixture was stirred under nitrogen atmosphere for 3 hours. After completion of the reaction, 1 M HCl (10 mL) was added to the mixture. The resulting mixture was then extracted three times with CH₂Cl₂ (3×25 mL). The organic phase was separated and washed with saturated NaHCO₃ and brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 30/1) to afford (S_p)-**3**.

**(S_p)-1,4(1,4)-dibenzenacyclohexaphane-
1²,4³-diylbis(2,1-phenylene)
bis(trifluoromethanesulfonate) (3a)**

1.68 g, 99% yield; white solid. M.p. 129-130
°C. [α]_D²⁰ = 18.049° (c 1.00, DCM); IR (film): ν
= 3010, 2933, 2858, 1589, 1475, 1422, 1245,
1209, 1145, 1090, 1045, 949, 916, 885, 856,
824, 779, 767, 741, 650, 627, 595, 572, 503
cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.78 –
7.67 (m, 2H), 7.52 – 7.41 (m, 4H), 7.39 –
7.28 (m, 2H), 6.80 (d, *J* = 7.7 Hz, 2H), 6.75
(dd, *J* = 7.8, 1.5 Hz, 2H), 6.62 (d, *J* = 1.0 Hz,
2H), 3.21 – 3.12 (m, 2H), 3.12 – 3.03 (m,
2H), 3.02 – 2.91 (m, 2H), 2.70 – 2.55 (m, 2H)
ppm; ¹³C NMR (101 MHz, CDCl₃) δ 147.24,
139.17, 138.57, 135.40,
134.93, 134.09, 131.40, 130.36 (d, *J* = 42.9
Hz), 128.60 (d, *J* = 78.1 Hz), 122.21, 119.78,
116.59, 34.51 33.94 ppm; HRMS (GC-TOF):
calculated for C₃₀H₂₂F₆NaO₆S₂⁺ ([M+Na]⁺):
m/z 679.0660, found: 679.0656.

**(S_p)-1,4(1,4)-dibenzenacyclohexaphane-
1²,4³-diylbis(3,1-phenylene)
bis(trifluoromethanesulfonate) (3b)**

1.67 g, 98% yield, colorless oil. [α]_D²⁰ =
266.667° (c 1.00, DCM).
IR (film): ν = 3007, 2934, 2860, 1890, 1609,
1573, 1476, 1424, 1245, 1212, 1140, 1044,
943, 893, 863, 847, 796, 759, 734, 696, 606,
573, 514 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ
7.57 (d, *J* = 7.6 Hz, 1H), 7.51 – 7.42 (m, 2H),
7.30 (dd, *J* = 17.9, 7.6 Hz, 3H), 7.23 (d, *J* =

0.9 Hz, 2H), 6.76 (d, *J* = 7.7 Hz, 2H), 6.70
(dd, *J* = 7.7, 1.5 Hz, 2H), 6.60 (d, *J* = 1.6 Hz,
2H), 3.62 – 3.36 (m, 2H), 3.22 – 3.08 (m,
2H), 3.00 (m, 2H), 2.75 (m, 2H) ppm; ¹³C
NMR (101 MHz, CDCl₃) δ 149.64, 143.47,
139.90, 138.28, 137.12, 135.99, 133.23,
130.30, 129.84, 129.01, 121.73, 119.41,
34.44, 34.00 ppm; HRMS (GC-TOF):
calculated for C₃₀H₂₂F₆NaO₆S₂⁺ ([M+Na]⁺):
m/z 679.0660, found: 679.0653.

The synthesis of (S_p)-4

A 25 mL three necked round-bottom flask
was charged with (S_p)-3 (1 mmol, 1.0 equiv),
Ar₂P(O)H (4 mmol, 2.0 equiv), palladium
acetate (0.1 mmol, 0.1 equiv), 1,4-
bis(diphenylphosphino)butane (dppb, 0.1
mmol, 0.1 equiv), and *N,N*-
diisopropylethylamine (0.7 mL, 4.0 equiv)
was stirred in degassed DMSO (10 mL) at
120 °C under a dry nitrogen atmosphere.
The progress of the reaction was monitored
by TLC until complete conversion. After
cooling to room temperature, the reaction
solution was diluted with water and the
aqueous phase was extracted three times
with EtOAc (3x20 mL). The organic layer
was washed sequentially with 5% aqueous
HCl, saturated NaHCO₃ and brine, dried
over anhydrous Na₂SO₄, and concentrated
under reduced pressure. The resulting
residue was purified by flash

chromatography (ethyl acetate/petroleum ether = 2/1) to give the target product.

(S_p)-(1,4(1,4)-dibenzenacyclohexaphane-1²,4³-diylbis(2,1-phenylene))bis(diphenylphosphine oxide) (4a)

660 mg, 87% yield; white solid. M.p. 164-165 °C. $[\alpha]_D^{20} = -353.994^\circ$ (c 1.00, DCM); IR (film): $\gamma = 3386, 3054, 2956, 2926, 2853, 1717, 1588, 1562, 1483, 1459, 1437, 1403, 1378, 1263, 1194, 1115, 1030, 896, 863, 733, 720, 706, 542 \text{ cm}^{-1}$; ¹H NMR (400 MHz, CDCl₃) δ 7.67 (dd, $J = 7.2, 4.2 \text{ Hz}$, 2H), 7.54 (t, $J = 6.4 \text{ Hz}$, 2H), 7.41 – 7.31 (m, 12H), 7.29 (d, $J = 3.6 \text{ Hz}$, 3H), 7.26 – 7.20 (m, 5H), 7.20 – 7.12 (m, 4H), 6.37 (s, 2H), 6.26 (d, $J = 7.6 \text{ Hz}$, 2H), 6.12 (d, $J = 7.7 \text{ Hz}$, 2H), 2.90 – 2.65 (m, 4H), 2.55 – 2.38 (m, 4H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 146.61 (d, $J = 8.5 \text{ Hz}$), 138.56, 137.51, 134.70 (d, $J = 4.1 \text{ Hz}$), 134.25 (t, $J = 6.2 \text{ Hz}$), 133.54 (d, $J = 7.4 \text{ Hz}$), 133.23, 132.46, 132.20, 131.45, 131.36, 131.27, 130.81, 129.55 (d, $J = 9.6 \text{ Hz}$), 127.89 (t, $J = 12.3 \text{ Hz}$), 126.29 (d, $J = 12.6 \text{ Hz}$), 34.23, 34.00 ppm; ³¹P NMR (162 MHz, CDCl₃) δ 26.78 (s) ppm; HRMS (GC-TOF): calculated for C₅₂H₄₂NaO₂P₂⁺([M+Na]⁺): m/z 783.2558, found: 783.2553.

(S_p)-(1,4(1,4)-dibenzenacyclohexaphane-1²,4³-diylbis(2,1-phenylene))bis(di-p-tolylphosphine oxide) (4b)

693 mg, 85% yield; white solid. M.p. 134-135 °C. $[\alpha]_D^{20} = -393.291^\circ$ (c 1.00, DCM); IR (film): $\gamma = 3366, 3021, 2955, 2925, 2854, 1916, 1716, 1602, 1563, 1500, 1459, 1434, 1400, 1378, 1264, 1215, 1184, 1114, 1031, 1021, 895, 863, 808, 769, 733, 660, 620, 538, 517 \text{ cm}^{-1}$ ppm; ¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, $J = 3.0 \text{ Hz}$, 2H), 7.51 (t, $J = 7.1 \text{ Hz}$, 2H), 7.37 – 7.28 (m, 3H), 7.25 – 7.16 (m, 9H), 7.03 (d, $J = 7.4 \text{ Hz}$, 4H), 6.97 (d, $J = 7.6 \text{ Hz}$, 4H), 6.35 (s, 2H), 6.28 (d, $J = 7.5 \text{ Hz}$, 2H), 6.12 (d, $J = 7.2 \text{ Hz}$, 2H), 2.82 (t, $J = 11.2 \text{ Hz}$, 2H), 2.71 (t, $J = 12.0 \text{ Hz}$, 2H), 2.50 – 2.39 (m, 4H), 2.31 (s, 6H), 2.25 (s, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 146.55 (d, $J = 8.4 \text{ Hz}$), 140.90, 138.44, 137.41, 134.80, 134.17 (d, $J = 11.5 \text{ Hz}$), 133.78, 133.47, 131.28 (dd, $J = 20.8, 11.2 \text{ Hz}$), 130.62, 129.55, 128.60 (t, $J = 11.9 \text{ Hz}$), 126.15 (d, $J = 12.7 \text{ Hz}$), 34.22, 34.05, 21.47, 21.39; ³¹P NMR (162 MHz, CDCl₃) δ 27.00 (s) ppm; HRMS (GC-TOF): calculated for C₅₆H₅₀NaO₂P₂⁺([M+Na]⁺): m/z 839.3184, found: 839.3185.

(S_p)-(1,4(1,4)-dibenzenacyclohexaphane-1²,4³-diylbis(2,1-phenylene))bis(bis(4-methoxyphenyl)phosphine oxide) (4c)

704 mg, 80% yield; white solid. M.p. 158-159 °C. $[\alpha]_D^{20} = -325.240^\circ$ (c 1.00, DCM); IR (film): $\gamma = 33783004, 2928, 2840, 1907, 1716, 1597, 1570, 1502, 1461, 1405, 1293, 1253, 1178, 1116, 1027, 863, 830, 801, 769,$

734, 683, 664, 622, 549 cm⁻¹ ppm; ¹H NMR (400 MHz, CDCl₃) δ 7.65 (s, 2H), 7.52 (t, *J* = 6.7 Hz, 2H), 7.39 – 7.27 (m, 6H), 7.23 (d, *J* = 9.5 Hz, 6H), 6.72 (dd, *J* = 21.9, 7.7 Hz, 8H), 6.36 (s, 2H), 6.30 (d, *J* = 7.2 Hz, 2H), 6.18 (d, *J* = 7.4 Hz, 2H), 3.78 (s, 6H), 3.73 (s, 6H), 2.83 (t, *J* = 11.1 Hz, 2H), 2.71 (t, *J* = 11.6 Hz, 2H), 2.55 – 2.38 (m, 4H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 161.60 (d, *J* = 11.0 Hz), 146.43 (d, *J* = 8.4 Hz), 138.44, 137.47, 134.86, 134.17, 133.84, 133.56, 133.07 (d, *J* = 10.5 Hz), 132.81, 131.23 (d, *J* = 20.6 Hz), 129.54 (d, *J* = 9.5 Hz), 126.23 (d, *J* = 12.2 Hz), 125.14 (d, *J* = 11.0 Hz), 124.04 (d, *J* = 10.7 Hz), 113.55 (dd, *J* = 13.0, 7.1 Hz), 55.28 (d, *J* = 3.4 Hz), 34.25, 34.04 ppm; ³¹P NMR (162 MHz, CDCl₃) δ 27.11 (s) ppm; HRMS (GC-TOF): calculated for C₅₆H₅₀NaO₆P₂⁺([M+Na]⁺): m/z 903.2980, found: 903.2981.

(S_p)-(1,4(1,4)-dibenzenacyclohexaphane-1²,4³-diylbis(2,1-phenylene))bis(bis(3,5-dimethylphenyl)phosphine oxide)(4d)

610 mg, 70% yield; yellow solid. M.p. 124-125 °C. [α]_D²⁰ = -305.8° (c 1.00, DCM); IR (film): γ = 3391, 2954, 2925, 2855, 1730, 1601, 1460, 1434, 1377, 1272, 1181, 1165, 1126, 1081, 1044, 870, 850, 769, 700, 577, 530, 477 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.64 (dd, *J* = 7.4, 4.2 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 2H), 7.39 – 7.28 (m, 6H), 7.00 (s, 2H), 6.97 (s, 2H), 6.94 (s, 4H), 6.87 (s, 2H), 6.39

(s, 2H), 6.27 (d, *J* = 7.6 Hz, 2H), 6.07 (d, *J* = 7.6 Hz, 2H), 2.90 – 2.80 (m, 2H), 2.79 – 2.68 (m, 2H), 2.54 – 2.41 (m, 4H), 2.17 (d, *J* = 11.6 Hz, 24H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 138.28, 137.48, 137.35, 137.29, 137.16, 133.99, 133.03, 132.45, 131.52, 131.03, 131.02, 129.37, 129.32, 129.28, 129.05, 128.96, 128.90, 128.81, 126.25, 119.28, 99.99, 34.32, 33.84; ³¹P NMR (162 MHz, CDCl₃) δ 26.82 (s) ppm; HRMS (GC-TOF): calculated for C₆₀H₅₈NaO₂P₂⁺([M+Na]⁺): m/z 895.3810, found: 895.3812.

(S_p)-(1,4(1,4)-dibenzenacyclohexaphane-1²,4³-diylbis(3,1-phenylene))bis(diphenylphosphine oxide)(4e)

645 mg, 85% yield; white solid. M.p. 95-96 °C. [α]_D²⁰ = -627.705° (c 1.00, DCM); IR (film): γ = 3390, 3054, 2929, 2858, 1967, 1899, 1717, 1589, 1466, 1437, 1384, 1265, 1194, 1119, 1029, 998, 871, 800, 749, 724, 701, 596, 542 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.75 – 7.64 (m, 12H), 7.58 – 7.49 (m, 5H), 7.48 – 7.39 (m, 10H), 7.24 (s, 1H), 6.64 (d, *J* = 7.7 Hz, 2H), 6.58 (d, *J* = 7.6 Hz, 2H), 6.35 (s, 2H), 3.30 – 3.14 (m, 2H), 3.06 – 2.92 (m, 2H), 2.89 – 2.73 (m, 2H), 2.45 – 2.31 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 141.11 (d, *J* = 12.1 Hz), 139.64, 139.06, 137.01, 135.70, 133.24, 132.98, 132.68 (t, *J* = 5.4 Hz), 132.40 (d, *J* = 2.2 Hz), 132.18, 132.15,

132.10 , 132.08 , 132.05, 130.46 (d, $J = 9.5$ Hz), 129.80 , 129.08 (d, $J = 12.6$ Hz), 128.64 (d, $J = 12.1$ Hz), 34.25, 34.06 ppm; ^{31}P NMR (162 MHz, CDCl_3) δ 29.74 (s) ppm; HRMS (GC-TOF): calculated for $\text{C}_{52}\text{H}_{42}\text{NaO}_2\text{P}_2^+([\text{M}+\text{Na}]^+)$: m/z 783.2558, found: 783.2549.

(S_p)-(1,4(1,4)-dibenzenacyclohexaphane-1²,4³-diylbis(3,1-phenylene))bis(di-p-tolylphosphine oxide) (4f)

677 mg, 83% yield; white solid. M.p. 85-86 °C. $[\alpha]_{\text{D}}^{20} = -491.071^\circ$ (c 1.00, DCM); IR (film): $\gamma = 3378, 3043, 2924, 2860, 1916, 1720, 1601, 1500, 1465, 1399, 1382, 1310, 1265, 1214, 1186, 1116, 1020, 871, 808, 763, 733, 712, 662, 621, 536, 518 \text{ cm}^{-1}$; ^1H NMR (400 MHz, CDCl_3) δ 7.73 – 7.52 (m, 12H), 7.39 (t, $J = 6.2$ Hz, 2H), 7.22 (d, $J = 7.8$ Hz, 10H), 6.64 (d, $J = 7.7$ Hz, 2H), 6.57 (dd, $J = 7.7, 1.4$ Hz, 2H), 6.33 (s, 2H), 3.28 – 3.18 (m, 2H), 3.04 – 2.92 (m, 2H), 2.88 – 2.76 (m, 2H), 2.40 (d, $J = 7.0$ Hz, 2H), 2.37 (s, 6H), 2.34 (s, 6H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 142.52, 142.50, 142.48 , 141.06, 140.94, 139.64, 139.18 , 137.02, 135.64 , 132.62 , 132.17 (d, $J = 2.9$ Hz), 132.07 (d, $J = 2.8$ Hz), 130.45 (d, $J = 9.5$ Hz), 129.81, 129.04 , 128.91, 34.18 , 34.06, 21.58 ppm; ^{31}P NMR (162 MHz, CDCl_3) δ 29.85 (s) ppm; HRMS (GC-TOF): calculated for $\text{C}_{56}\text{H}_{50}\text{NaO}_2\text{P}_2^+([\text{M}+\text{Na}]^+)$: m/z 839.3184, found: 839.3181.

(S_p)-(1,4(1,4)-dibenzenacyclohexaphane-1²,4³-diylbis(3,1-phenylene))bis(bis(4-methoxyphenyl)phosphine oxide) (4g)

660 mg, 75% yield; white solid. M.p. 84-85°C. $[\alpha]_{\text{D}}^{20} = -364.886^\circ$ (c 1.00, DCM); IR (film): $\gamma = 3367, 3005, 2927, 2841, 2553, 1908, 1717, 1597, 1569, 1504, 1463, 1406, 1382, 1294, 1256, 1179, 1119, 1026, 831, 801, 763, 733, 704, 667, 623, 547 \text{ cm}^{-1}$; ^1H NMR (400 MHz, CDCl_3) δ 7.73 – 7.57 (m, 12H), 7.46 – 7.39 (m, 2H), 7.22 (d, $J = 7.6$ Hz, 2H), 6.96 – 6.87 (m, 8H), 6.65 (d, $J = 7.7$ Hz, 2H), 6.58 (d, $J = 7.7$ Hz, 2H), 6.37 (s, 2H), 3.81 (s, 6H), 3.77 (s, 6H), 3.31 – 3.18 (m, 2H), 3.05 – 2.95 (m, 2H), 2.90 – 2.77 (m, 2H), 2.47 – 2.36 (m, 2H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 162.49 , 141.02 (d, $J = 12.1$ Hz), 139.64 , 139.19 , 137.02 , 135.67, 133.92 (dd, $J = 11.3, 3.0$ Hz), 132.64 , 132.14, 130.35 (d, $J = 9.9$ Hz), 129.83, 128.97 (d, $J = 12.6$ Hz), 124.44 (d, $J = 19.3$ Hz), 123.42, 114.17 (d, $J = 13.2$ Hz), 77.36, 77.05, 76.73, 55.36, 34.17 (d, $J = 14.0$ Hz) ppm; ^{31}P NMR (162 MHz, CDCl_3) δ 29.40 (s) ppm; HRMS (GC-TOF): calculated for $\text{C}_{56}\text{H}_{50}\text{NaO}_6\text{P}_2^+([\text{M}+\text{Na}]^+)$: m/z 903.2980, found: 903.2984.

(S_p)-(1,4(1,4)-dibenzenacyclohexaphane-1²,4³-diylbis(3,1-phenylene))bis(bis(3,5-dimethylphenyl)phosphine oxide) (4h)

584 mg, 67% yield; yellow solid. M.p. 127-128°C. $[\alpha]_D^{20} = -472.204^\circ$ (c 1.00, DCM); IR (film): $\nu = 3378, 2954, 2924, 2856, 1736, 1599, 1465, 1379, 1273, 1191, 1129, 1043, 873, 852, 800, 733, 693, 577, 524 \text{ cm}^{-1}$; ^1H NMR (400 MHz, CDCl_3) δ 7.80 – 7.71 (m, 2H), 7.66 (d, $J = 12.4 \text{ Hz}$, 2H), 7.32 (d, $J = 11.9 \text{ Hz}$, 9H), 7.11 (d, $J = 17.9 \text{ Hz}$, 7H), 6.64 (d, $J = 4.8 \text{ Hz}$, 2H), 6.57 (d, $J = 7.0 \text{ Hz}$, 2H), 6.23 (s, 2H), 3.27 (t, 2H), 3.07 – 2.94 (m, 2H), 2.90 – 2.79 (m, 2H), 2.46 – 2.36 (m, 2H), 2.26 (s, 12H), 2.22 (s, 12H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 140.93 (d, $J = 12.1 \text{ Hz}$), 139.63, 139.29, 138.30 (d, $J = 12.6 \text{ Hz}$), 137.03, 135.66, 133.82, 132.96, 132.75, 132.64, 132.14 (d, $J = 42.1 \text{ Hz}$), 131.60, 130.75, 130.51 (d, $J = 9.2 \text{ Hz}$), 129.87, 129.70 (d, $J = 9.7 \text{ Hz}$), 129.12 (d, $J = 12.5 \text{ Hz}$), 34.08 (d, $J = 19.8 \text{ Hz}$), 21.28 (d, $J = 4.5 \text{ Hz}$) ppm; ^{31}P NMR (162 MHz, CDCl_3) δ 30.18 (s) ppm; HRMS (GC-TOF): calculated for $\text{C}_{60}\text{H}_{58}\text{NaO}_2\text{P}_2^+([\text{M}+\text{Na}]^+)$: m/z 895.3810, found: 895.3805.

The synthesis of (Sp)-5

A 25 mL three necked round-bottom flask was charged with (Sp)-4 (0.5 mmol, 1.0 equiv), trichlorosilane (7.5 mmol, 15 equiv), and triethylamine (7.5 mmol, 15 equiv) in degassed toluene (5 mL) and stirred at 100 °C under a dry nitrogen atmosphere for 12h. After cooling to room temperature, the

reaction solution was diluted with water and the aqueous phase was extracted three times with EtOAc (3x10 mL). The organic layer was washed with brine, dried over anhydrous Na_2SO_4 , and concentrated under reduced pressure. The resulting residue was purified by flash chromatography (ethyl acetate/petroleum ether = 1/50) to give the target product 5.

(Sp)-1²,4³-bis(2-(diphenylphosphanyl)phenyl)-1,4(1,4)-dibenzencyclohexaphane (5a)

327 mg, 90% yield; white solid. M.p. 105-106°C. $[\alpha]_D^{20} = 677.202^\circ$ (c 1.00, DCM); IR (film): $\nu = 3050, 2959, 2926, 2853, 1958, 1738, 1583, 1456, 1434, 1378, 1263, 1091, 1026, 862, 801, 743, 696, 498 \text{ cm}^{-1}$; ^1H NMR (400 MHz, CDCl_3) δ 7.75 (dd, $J = 7.0, 3.7 \text{ Hz}$, 2H), 7.45 – 7.38 (m, 2H), 7.34 – 7.26 (m, 6H), 7.25 – 7.22 (m, 2H), 7.19 – 7.07 (m, 10H), 7.00 – 6.88 (m, 6H), 6.57 – 6.48 (m, 4H), 6.45 (d, $J = 1.3 \text{ Hz}$, 2H), 2.98 – 2.86 (m, 2H), 2.78 – 2.66 (m, 2H), 2.53 – 2.40 (m, 4H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 146.92 (d, $J = 27.1 \text{ Hz}$), 138.58 (d, $J = 3.4 \text{ Hz}$), 138.50 (d, $J = 6.4 \text{ Hz}$), 137.64 (d, $J = 12.3 \text{ Hz}$), 137.42 (d, $J = 6.5 \text{ Hz}$), 137.15 (d, $J = 12.9 \text{ Hz}$), 134.76, 134.41 (d, $J = 20.8 \text{ Hz}$), 133.53 (d, $J = 19.7 \text{ Hz}$), 133.33 (d, $J = 35.8 \text{ Hz}$), 130.77 (d, $J = 1.6 \text{ Hz}$), 128.43, 128.24 (d, $J = 3.3 \text{ Hz}$), 128.15, 128.10 (d, $J = 4.2 \text{ Hz}$), 127.96 (d, $J = 4.8 \text{ Hz}$), 127.87, 127.03,

34.43, 34.31 (d, $J = 4.0$ Hz) ppm; ^{31}P NMR (162 MHz, CDCl_3) δ -13.24 (s) ppm; HRMS (GC-TOF): calculated for $\text{C}_{52}\text{H}_{43}\text{P}_2^+([\text{M}+\text{H}]^+)$: m/z 729.2840, found: 729.2839.

(S_p)-1²,4³-bis(2-(di-p-tolylphosphanyl)phenyl)-1,4(1,4)-dibenzenacyclohexaphane (5b)

348 mg, 89% yield; white solid. M.p. 111-112°C. $[\alpha]_{\text{D}}^{20} = -489.118^\circ$ (c 1.00, DCM); IR (film): $\nu = 3012, 2954, 2924, 2853, 1907, 1743, 1582, 1496, 1457, 1398, 1307, 1263, 1185, 1155, 1091, 1020, 862, 805, 767, 746, 627, 511$ cm⁻¹; ^1H NMR (400 MHz, CDCl_3) δ 7.75 (dd, $J = 6.8, 4.2$ Hz, 2H), 7.39 (td, $J = 7.5, 1.3$ Hz, 2H), 7.26 (s, 1H), 7.23 (dd, $J = 7.5, 0.9$ Hz, 1H), 7.09 – 7.01 (m, 8H), 7.00 – 6.95 (m, 2H), 6.93 (d, $J = 7.5$ Hz, 4H), 6.82 (t, $J = 7.6$ Hz, 4H), 6.56 – 6.49 (m, 4H), 6.46 (d, $J = 1.2$ Hz, 2H), 2.98 – 2.86 (m, 2H), 2.76 – 2.65 (m, 2H), 2.50 – 2.39 (m, 4H), 2.33 (s, 6H), 2.23 (s, 6H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 146.88 (d, $J = 27.1$ Hz), 139.04 (d, $J = 12.7$ Hz), 138.79, 138.60, 137.95 (d, $J = 53.0$ Hz), 137.51 (d, $J = 6.5$ Hz), 134.72, 134.45 (d, $J = 4.9$ Hz), 134.29 (d, $J = 5.1$ Hz), 133.81 (d, $J = 11.5$ Hz), 133.56, 133.40 (d, $J = 5.8$ Hz), 133.09, 130.72, 128.97 (d, $J = 7.3$ Hz), 128.72 (d, $J = 6.8$ Hz), 128.06, 126.93, 34.43, 34.36 (d, $J = 4.0$ Hz), 21.29 (d, $J = 13.6$ Hz) ppm; ^{31}P NMR (162 MHz, CDCl_3) δ -15.33 (s) ppm; HRMS (GC-TOF): calculated

for $\text{C}_{56}\text{H}_{51}\text{P}_2^+([\text{M}+\text{H}]^+)$: m/z 785.3466, found: 785.3455.

(S_p)-1²,4³-bis(2-(bis(4-methoxyphenyl)phosphanyl)phenyl)-1,4(1,4)-dibenzenacyclohexaphane (5c)

373 mg, 88% yield; white solid. M.p. 233-234°C. $[\alpha]_{\text{D}}^{20} = -143.125^\circ$ (c 1.00, DCM); IR (film): $\nu = 3048, 3002, 2956, 2927, 2835, 2043, 1893, 1593, 1567, 1497, 1456, 1441, 1402, 1284, 1246, 1177, 1094, 1030, 862, 825, 797, 768, 737, 532$; ^1H NMR (400 MHz, CDCl_3) δ 7.78 – 7.68 (m, 2H), 7.38 (t, $J = 7.3$ Hz, 2H), 7.25 – 7.19 (m, 2H), 7.07 (t, $J = 7.6$ Hz, 4H), 6.97 – 6.90 (m, 2H), 6.86 (t, $J = 7.5$ Hz, 4H), 6.80 (d, $J = 8.1$ Hz, 4H), 6.66 (d, $J = 8.1$ Hz, 4H), 6.51 (q, $J = 7.7$ Hz, 4H), 6.43 (s, 2H), 3.79 (s, 6H), 3.70 (s, 6H), 2.98 – 2.84 (m, 2H), 2.79 – 2.64 (m, 2H), 2.53 – 2.38 (m, 4H); ^{13}C NMR (101 MHz, CDCl_3) δ 159.82 (d, $J = 37.2$ Hz), 139.62 (d, $J = 12.9$ Hz), 138.82, 138.54, 137.46 (d, $J = 6.1$ Hz), 135.88 (d, $J = 22.2$ Hz), 135.00 (d, $J = 21.1$ Hz), 134.73, 133.11, 130.74, 128.82 (d, $J = 9.2$ Hz), 128.35 (d, $J = 9.9$ Hz), 128.13, 127.46 (d, $J = 105.7$ Hz), 113.89 (d, $J = 7.9$ Hz), 113.67 (d, $J = 7.5$ Hz), 55.17 (d, $J = 8.9$ Hz), 34.51, 34.44 ppm; ^{31}P NMR (162 MHz, CDCl_3) δ -16.23 (s) ppm; HRMS (GC-TOF): calculated for $\text{C}_{56}\text{H}_{51}\text{O}_4\text{P}_2^+([\text{M}+\text{H}]^+)$: m/z 849.3263, found: 849.3249.

(S_p)-1²,4³-bis(2-(bis(3,5-dimethylphenyl)phosphanyl)phenyl)-1,4(1,4)-dibenzenacyclohexaphane (5d)

357 mg, 85% yield; white solid. M.p. 95-96°C. $[\alpha]_{\text{D}}^{20} = -388.235^{\circ}$ (c 1.00, DCM); IR (film): $\nu = 3022, 2923, 2855, 2729, 1930, 1780, 1738, 1598, 1581, 1456, 1434, 1376, 1264, 1124, 1100, 1038, 946, 894, 847, 802, 767, 737, 694, 654, 553, 523, 492 \text{ cm}^{-1}$; ¹H NMR (400 MHz, CDCl₃) δ 7.71 (dd, $J = 7.0, 4.2 \text{ Hz}$, 2H), 7.39 (t, $J = 7.1 \text{ Hz}$, 2H), 7.30 – 7.21 (m, 2H), 6.99 (dd, $J = 7.2, 3.1 \text{ Hz}$, 2H), 6.90 (s, 2H), 6.76 (d, $J = 8.8 \text{ Hz}$, 6H), 6.58 (d, $J = 7.7 \text{ Hz}$, 4H), 6.53 (d, $J = 7.5 \text{ Hz}$, 2H), 6.47 (d, $J = 9.9 \text{ Hz}$, 4H), 2.92 (m, 2H), 2.78 – 2.63 (m, 2H), 2.58 – 2.38 (m, 4H), 2.22 (s, 12H), 2.12 (s, 12H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 145.80 (d, $J = 26.8 \text{ Hz}$), 138.03 (d, $J = 13.4 \text{ Hz}$), 137.62, 137.45 (d, $J = 2.3 \text{ Hz}$), 136.35 (d, $J = 3.5 \text{ Hz}$), 136.30, 136.22, 136.01 (d, $J = 7.1 \text{ Hz}$), 135.74 (d, $J = 11.8 \text{ Hz}$), 133.62, 132.17 (d, $J = 48.7 \text{ Hz}$), 131.14 (d, $J = 21.0 \text{ Hz}$), 130.33 (d, $J = 20.0 \text{ Hz}$), 129.72, 128.88 (d, $J = 37.0 \text{ Hz}$), 126.92 (d, $J = 4.8 \text{ Hz}$), 125.83, 33.49, 33.26, 20.22 (d, $J = 8.3 \text{ Hz}$) ppm; ³¹P NMR (162 MHz, CDCl₃) δ -12.80 (t) ppm; HRMS (GC-TOF): calculated for C₆₀H₅₉P₂⁺([M+H]⁺): m/z 841.4092, found: 841.4092.

(S_p)-1²,4³-bis(3-(diphenylphosphanyl)phenyl)-1,4(1,4)-dibenzenacyclohexaphane (5e)

327 mg, 90% yield; white solid. M.p. 91-92°C. $[\alpha]_{\text{D}}^{20} = -107.509^{\circ}$ (c 1.00, DCM) ppm; IR (film): $\nu = 3051, 2927, 2856, 1954, 1888, 1815, 1731, 1661, 1584, 1477, 1464, 1434, 1405, 1381, 1307, 1264, 1200, 1156, 1091, 1027, 998, 949, 912, 893, 872, 850, 797, 742, 696, 657, 593, 508 \text{ cm}^{-1}$; ¹H NMR (400 MHz, CDCl₃) δ 7.49 – 7.21 (m, 26H), 6.98 (d, $J = 6.8 \text{ Hz}$, 2H), 6.58 (d, $J = 7.7 \text{ Hz}$, 2H), 6.52 (dd, $J = 7.7, 1.2 \text{ Hz}$, 2H), 6.29 (d, $J = 1.3 \text{ Hz}$, 2H), 3.28 – 3.15 (m, 2H), 3.01 – 2.85 (m, 2H), 2.81 – 2.68 (m, 2H), 2.38 – 2.21 (m, 2H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 141.16 (d, $J = 6.3 \text{ Hz}$), 139.82, 139.61, 137.38 (d, $J = 11.3 \text{ Hz}$), 137.17 (d, $J = 11.4 \text{ Hz}$), 136.94, 135.40, 134.11, 133.95 (d, $J = 2.7 \text{ Hz}$), 133.80 (d, $J = 6.3 \text{ Hz}$), 133.64, 132.20, 132.01 (d, $J = 21.1 \text{ Hz}$), 129.90 (d, $J = 22.5 \text{ Hz}$), 128.84, 128.73, 128.68, 128.62 (d, $J = 1.7 \text{ Hz}$), 128.56, 34.22, 34.08 ppm; ³¹P NMR (162 MHz, CDCl₃) δ -5.12 (s) ppm; HRMS (GC-TOF): calculated for C₅₂H₄₃P₂⁺([M+H]⁺): m/z 729.2840, found: 729.2832.

(S_p)-1²,4³-bis(3-(di-p-tolylphosphanyl)phenyl)-1,4(1,4)-dibenzenacyclohexaphane (5f)

352 mg, 90% yield; white solid. M.p. 75-76°C. $[\alpha]_{\text{D}}^{20} = 163.614^{\circ}$ (c 1.00, DCM); IR

(film): $\gamma = 3013, 2923, 2860, 1908, 1800, 1748, 1647, 1585, 1496, 1463, 1395, 1380, 1307, 1264, 1186, 1092, 1040, 1020, 948, 893, 872, 806, 767, 733, 710, 657, 641, 627, 612, 512 \text{ cm}^{-1}$; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.33 (d, $J = 7.5 \text{ Hz}$, 2H), 7.30 – 7.19 (m, 12H), 7.11 (dd, $J = 13.9, 7.6 \text{ Hz}$, 8H), 6.95 (d, $J = 6.9 \text{ Hz}$, 2H), 6.59 (d, $J = 7.7 \text{ Hz}$, 2H), 6.52 (d, $J = 7.6 \text{ Hz}$, 2H), 6.31 (s, 2H), 3.31 – 3.15 (m, 2H), 3.00 – 2.87 (m, 2H), 2.83 – 2.70 (m, 2H), 2.30 (d, $J = 15.2 \text{ Hz}$, 14H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 141.17 (d, $J = 6.1 \text{ Hz}$), 140.03, 139.74, 138.83 (d, $J = 12.3 \text{ Hz}$), 137.95 (d, $J = 11.4 \text{ Hz}$), 137.07, 135.48, 134.09, 133.97, 133.89, 133.78, 132.25, 131.89 (d, $J = 20.9 \text{ Hz}$), 130.13, 129.63, 129.59, 129.53 (d, $J = 2.8 \text{ Hz}$), 129.48, 128.80 (d, $J = 7.6 \text{ Hz}$), 34.23, 21.43 (d, $J = 3.0 \text{ Hz}$) ppm; $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ -6.80 (t) ppm; HRMS (GC-TOF): calculated for $\text{C}_{56}\text{H}_{51}\text{P}_2^+([\text{M}+\text{H}]^+)$: m/z 785.3466, found: 785.3456.

(S_p)-1²,4³-bis(3-(bis(4-methoxyphenyl)phosphanyl)phenyl)-1,4(1,4)-dibenzenacyclohexaphane (5g)

368 mg, 87% yield; white solid. M.p. 87–88°C. $[\alpha]_{\text{D}}^{20} = 188.396^\circ$ (c 1.00, DCM); IR (film): $\gamma = 3004, 2939, 2835, 2531, 2044, 1893, 1593, 1567, 1497, 1463, 1441, 1402, 1381, 1285, 1247, 1177, 1095, 1030, 950, 893, 872, 826, 796, 733, 706, 657, 530 \text{ cm}^{-1}$; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.35 – 7.19 (m,

14H), 6.96 (d, $J = 6.9 \text{ Hz}$, 2H), 6.85 (t, $J = 8.6 \text{ Hz}$, 8H), 6.59 (d, $J = 7.7 \text{ Hz}$, 2H), 6.53 (d, $J = 7.4 \text{ Hz}$, 2H), 6.32 (s, 2H), 3.76 (s, 6H), 3.73 (s, 6H), 3.30 – 3.17 (m, 2H), 3.00 – 2.87 (m, 2H), 2.84 – 2.71 (m, 2H), 2.41 – 2.27 (m, 2H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 160.27 (d, $J = 8.3 \text{ Hz}$), 141.07, 139.93, 139.59, 138.61 (d, $J = 11.0 \text{ Hz}$), 136.93, 135.50, 135.39 (d, $J = 3.2 \text{ Hz}$), 135.24 (d, $J = 9.1 \text{ Hz}$), 133.45 (d, $J = 18.2 \text{ Hz}$), 132.16, 131.32 (d, $J = 19.6 \text{ Hz}$), 129.67 (d, $J = 68.2 \text{ Hz}$), 128.63 (d, $J = 7.0 \text{ Hz}$), 128.48, 114.36 (d, $J = 4.6 \text{ Hz}$), 114.28 (d, $J = 4.7 \text{ Hz}$), 55.21 (d, $J = 2.4 \text{ Hz}$), 34.14 (d, $J = 6.7 \text{ Hz}$) ppm; $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ -8.28 (t). HRMS (GC-TOF): calculated for $\text{C}_{56}\text{H}_{51}\text{O}_4\text{P}_2^+([\text{M}+\text{H}]^+)$: m/z 849.3263, found: 849.3257.

(S_p)-1²,4³-bis(3-(bis(3,5-dimethylphenyl)phosphanyl)phenyl)-1,4(1,4)-dibenzenacyclohexaphane (5h)

357 mg, 85% yield; white solid. M.p. 69–70°C. $[\alpha]_{\text{D}}^{20} = 166.783^\circ$ (c 1.00, DCM); IR (film): $\gamma = 3024, 2921, 2857, 2730, 1889, 1784, 1742, 1598, 1582, 1464, 1415, 1379, 1264, 1168, 1125, 1105, 1040, 995, 893, 872, 847, 796, 733, 707, 693, 657, 579557, 503, 480 \text{ cm}^{-1}$; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.30 (dd, $J = 9.3, 7.5 \text{ Hz}$, 4H), 7.20 (dd, $J = 7.6, 1.6 \text{ Hz}$, 2H), 6.98 (dd, $J = 17.5, 8.1 \text{ Hz}$, 10H), 6.91 – 6.82 (m, 4H), 6.59 (d, $J = 7.7 \text{ Hz}$, 2H), 6.52 (dd, $J = 7.7, 1.5 \text{ Hz}$, 2H), 6.15

(d, $J = 1.6$ Hz, 2H), 3.33 – 3.18 (m, 2H), 3.02 – 2.88 (m, 2H), 2.82 – 2.70 (m, 2H), 2.42 – 2.33 (m, 2H), 2.21 (s, 12H), 2.15 (s, 12H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 140.94 (d, $J = 5.1$ Hz), 140.08, 139.56, 137.98 (d, $J = 5.8$ Hz), 137.91 (d, $J = 5.6$ Hz), 137.59 (d, $J = 11.5$ Hz), 137.21 (d, $J = 10.6$ Hz), 136.91, 136.76, 135.29, 133.82 (d, $J = 14.2$ Hz), 132.31, 131.89 (d, $J = 34.0$ Hz), 131.50 (d, $J = 4.0$ Hz), 131.29, 130.57 (d, $J = 13.6$ Hz), 129.81 (d, $J = 39.6$ Hz), 128.59 (d, $J = 8.6$ Hz), 34.03 (d, $J = 9.6$ Hz), 21.26 (d, $J = 5.2$ Hz) ppm; ^{31}P NMR (162 MHz, CDCl_3) δ -4.82 (dt, $J = 15.6, 7.8$ Hz) ppm; HRMS (GC-TOF): calculated for $\text{C}_{60}\text{H}_{59}\text{P}_2^+([\text{M}+\text{H}]^+)$: m/z 841.4092, found: 841.4088.

Diethyl (E)-2-(1,3-diphenylallyl)malonate (8)

Under a nitrogen atmosphere, the solution of ligand (*Sp*)-**5** (7.3 mg, 10 mol%), and $[\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2$ (1.7 mg, 5 mol%) in toluene (1 mL) was stirred at room temperature for 1 hour, and a solution of 1,3-diphenyl-2-propyl acetate (**6**) (0.1 mmol) in toluene (1.0 mL) was added. After 10 min, dialkyl malonate **7** (0.3 mmol) in toluene (1.0 mL) and Et_2Zn (0.3 mmol, 1 M in hexane) were added to the mixture and the resulting solution was stirred at 0°C for 12 h. The reaction mixture was diluted with ethyl acetate (10 mL), and washed with saturated aqueous ammonium chloride. The organic phase was separated

and dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography with petroleum ether/ethyl acetate = 20/1 to afford the corresponding product **8** as a colorless oil.

HPLC analysis: 64% ee (with (*Sp*)-**5a**), Chiralpak IA, *i*-PrOH/*n*-hexane = 85/15, 1.0 mL/min, 254 nm; $t_1 = 6.8$ min; $t_2 = 8.4$ min; IR (film): $\gamma = 3060, 2981, 1755, 1732, 1600, 1495, 1454, 1390, 1368, 1309, 1255, 1174, 1154, 1095, 1031, 966, 746, 698$ cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.30 (s, 7H), 7.22 (dd, $J = 16.4, 8.6$ Hz, 3H), 6.48 (d, $J = 15.8$ Hz, 1H), 6.34 (dd, $J = 15.7, 8.5$ Hz, 1H), 4.30 – 4.22 (m, 1H), 4.17 (q, $J = 7.1$ Hz, 2H), 3.95 (dt, $J = 24.0, 8.4$ Hz, 3H), 1.20 (t, $J = 7.1$ Hz, 3H), 1.01 (t, $J = 7.1$ Hz, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 167.87, 167.45, 140.32, 136.86, 131.69, 129.36, 128.67, 128.48, 128.01, 127.54, 127.12, 126.37, 61.61, 61.40, 57.80, 49.25, 14.16, 13.80. HRMS (GC-TOF): calculated for $\text{C}_{22}\text{H}_{24}\text{O}_4^+([\text{M}]^+)$: m/z 352.1675, found: 352.1674.

Supporting Information

Supporting information for this article is available.

Acknowledgments

Financial support from the National Natural Science Foundation of China (22071213), Leading Talents of Special Support Program of Zhejiang Province High-level Talents (2020R52008) and Center of Chemistry for Frontier Technologies of Zhejiang University is gratefully acknowledged.

References

1. Ojima, I. *Catalytic Asymmetric Synthesis*, Wiley-VCH: Weinheim, **2000**.
2. Jacobsen, E. N.; Pfaltz, A.; Yamamoto, H. *Comprehensive Asymmetric Catalysis*, Springer, Berlin, **2004**.
3. Berthod, M.; Mignani, G.; Woodward, G.; Lemaire, M. *Chem. Rev.* **2005**, *105*, 1801–1836.
4. Brunel, J. M. *Chem. Rev.* **2005**, *105*, 857–898.
5. Chakraborty, S.; Almasalma, A. A.; Vries J. G. D. *Catal. Sci. Technol.* **2021**, *11*, 5388–5411.
6. Hayashi, T. *Acc. Chem. Res.* **2000** *33*, 354–362.
7. Zhang, W.; Chi, Y.; Zhang X. *Acc. Chem. Res.* **2007**, *40*, 1278–1290.
8. Hems, W. P.; Groarke, M.; Zanotti-Gerosa, A.; Grasa, G. A. *Acc. Chem. Res.* **2007**, *40*, 1340–1347.
9. Miyashita, A.; Yasuda, A.; Takaya, H.; Toriumi, K.; Ito, T.; Souchi, T.; Noyori, R. *J. Am. Chem. Soc.* **1980**, *102*, 7932–7934.
10. Noyori, R.; Takaya, H. *Acc. Chem. Res.* **1990**, *23*, 345–350.
11. Akutagawa, S. *Appl. Catal. A: Gen.* **1995**, *128*, 171–207.
12. Kumobayashi, H. *Recl. Trav. Chim. Pays-Bas.* **1996**, *115*, 201–210.
13. Framery, E.; Andrioletti, B.; Lemaire, M. *Tetrahedron: Asymmetry* **2010**, *21*, 1110–1124.
14. Noyori, R. *Angew. Chem., Int. Ed.* **2002**, *41*, 2008–2022.
15. Schmid, R.; Broger, E. A.; Cereghetti, M.; Cramer, Y.; Foricher, J.; Lalonde, M.; Müller, R. K.; Scalone, M.; Schoettel, G.; Zutter, U. *Pure Appl. Chem.* **1996**, *68*, 131–138.
16. Chen, J.; Butt, N.; Zhang, W. *Res Chem Intermed.* **2019**, *45*, 5959–5974.
17. Saito, T., Yokozawa, T., Ishizaki, T., Moroi, T., Sayo, N., Miura, T. and Kumobayashi, H. *Adv. Synth. Catal.* **2001**, *343*, 264–267.
18. Botman, P. N.; M. Fraanje, J.; Goubitz, K.; Peschar, R.; Verhoeven, J. W.; Maarseveen, J. H.; Hiemstra, H. *Adv. Synth. Catal.* **2004**, *346*, 743–754.
19. Zhang, Z.; Qian, H.; Longmire J.; Zhang, X. *J. Org. Chem.* **2000**, *65*, 6223–6226.
20. Tan, B.; Candeias, N. R.; Barbas, C. F. *J. Am. Chem. Soc.* **2011**, *133*, 4672–4675.

21. Zhang, W.; Kida, T.; Nakatsuji, Y.; Ikeda, T. *Tetrahedron Lett.* **1996**, *37*, 7995–7998.
22. Burk, M. J.; Gross, M. F. *Tetrahedron Lett.* **1994**, *35*, 9363–9366.
23. Jäkel, C.; Paciello, R. *Chem. Rev.* **2006**, *106*, 2912–2942.
24. Chang, S.; Wang, L.; Lin, X. *Org. Biomol. Chem.* **2018**, *16*, 2239–2247.
25. Xie, J.; Zhou, Q. *Acc. Chem. Res.* **2008**, *41*, 581–593.
26. Xie, J.; Wang, L.; Fu, Y.; Zhu, S.; Fan, B.; Duan, H.; Zhou, Q. *J. Am. Chem. Soc.* **2003**, *125*, 4404–4405.
27. Pye, P. J.; Rossen, K.; Reamer, R. A.; Tsou, N. N.; Volante, R. P.; Reider, P. J. *J. Am. Chem. Soc.* **1997**, *119*, 6207–6208.
28. Schwartz, L.A.; Holmes, M.; Brito, G. A.; Gonçalves, T. P.; Richardson, J.; Ruble, J. C.; Huang, K.; Krische, M. J. *J. Am. Chem. Soc.* **2019**, *141*, 2087–2096.
29. Jiang, B.; Lei, Y.; Zhao, X. *J. Org. Chem.* **2008**, *73*, 7833–7836.
30. Sarcher, C.; Lühl, A.; Falk, F.C.; Lebedkin, S.; Kühn, M.; Wang, C.; Paradies, J.; Kappes, M.M.; Klopffer, W.; Roesky, P.W. *Eur. J. Inorg. Chem.* **2012**, *2012*, 5033–5042.
31. Falk, F. C.; Fröhlich, R.; Paradies, J. *Chem. Commun.* **2011**, *47*, 11095–11097.
32. Kitagaki, S.; Nakamura, K.; Kawabata, C.; Ishikawa, A.; Takenaga, N.; Yoshida, K. *Org. Biomol. Chem.* **2018**, *16*, 1770–1778.
33. Tiaouinine, S.; Gonzalez, J. F.; Lefeuvre, B.; Guizouarn, T.; Cordier, M.; Dorcet, V.; Kaboub, L.; Cador, O.; Pointillart, F. *Eur. J. Inorg. Chem.* **2021**, *2021*, 2374–2383.
34. Kitagaki, S.; Ohta, Y.; Tomonaga, S.; Takahashi, R.; Mukai, C. *Tetrahedron: Asymmetry* **2011**, *22*, 986–991.
35. Vaghi, L.; Cirilli, R.; Pierini, M.; Rizzo, S.; Terraneo, G.; Benincori, T. *Eur. J. Org. Chem.* **2021**, *2021*, 2367–2374.
36. Greb, L.; Oña-Burgos, P.; Kubas, A.; Falk, F. C.; Breher, F.; Fink, K.; Paradies, J. *Dalton Trans.* **2012**, *41*, 9056–9060.
37. Pye, P. J.; Rossen, K.; Reamer, R.A.; Volante, R. P.; Reider, P. J. *Tetrahedron Lett.* **1998**, *39*, 4441–4444.
38. Marques, C. S.; Dindaroğlu, M.; Schmalz, H.; Burke, A. J. *RSC Adv.* **2014**, *4*, 6035–6041.
39. Li, X.; Chen, W.; Hems, W.; King, W.; Xiao, J. *Org. Lett.* **2003**, *5*, 4559–4561.
40. Holmes, M.; Nguyen, K. D.; Schwartz, L. A.; Luong T.; Krische, M. J. *J. Am. Chem. Soc.* **2017**, *139*, 8114–8117.
41. Nguyen, K. D.; Herkommer, D.; Krische, M. J. *J. Am. Chem. Soc.* **2016**, *138*, 14210–14213.

42. Wang, Y.; Zhang, T.; Liu, L. *Chin. J. Chem.* **2012**, *30*, 2641–2646.
43. Fan, B.; Li, X.; Peng, F.; Zhang, H.; Chan, A. S. C.; Shao, Z. *Org. Lett.* **2019**, *12*, 304–306.
44. Xie, E.; Huang, S.; Lin, X.; *Org. Lett.* **2019**, *21*, 3682–3686.
45. Xie, J.; Duan, H.; Fan, B.; Cheng, X.; Wang, L.; Zhou, Q. *Adv. Synth. Catal.* **2004**, *346*, 625–632.
46. Trost, B. M. *Chem. Rev.* **1996**, *96*, 395–422.
47. Trost, B. M.; Crawley, M. L. *Chem. Rev.* **2003**, *103*, 2921–2944.
48. Lu Z.; Ma, S. *Angew. Chem. Int. Ed.* **2008**, *47*, 258–297.
49. Trost, B. M. *J. Org. Chem.* **2004**, *69*, 5813–5837.
50. Faller, J. W.; Wilt, J. C. *Org. Lett.* **2005**, *7*, 633–636.
51. Trost, B. M.; Thaisrivongs, D. A.; Hartwig, J. *J. Am. Chem. Soc.* **2011**, *133*, 12439–12441.
52. Wang, X. M.; Meng, F. Y.; Wang, Y.; Han, Z. B.; Chen, Y. J.; Liu, L.; Wang Z.; Ding, K. L. *Angew. Chem. Int. Ed.* **2012**, *51*, 9276–9282.