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A novel C_2-symmetric bisphosphane ligand with a chiral cyclopropane backbone: synthesis and application in the Rh(I)-catalyzed asymmetric 1,4-addition of arylboronic acids

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ABSTRACT

The synthesis of a novel C_2-symmetric bisphosphane ligand was accomplished starting from *trans*-(2*R*,3*R*)-bis(3′,5′-diphenylphenyl)cyclopropane-1,1-dimethanol as a key intermediate. This ligand was tested in the asymmetric rhodium(I)-catalyzed 1,4-addition to cyclic enones. We also compared the new ligand with a similar phosphane ligand with a less bulky cyclopropane backbone. Good yields (up to 99%) and enantioselectivities (up to 89% ee) were observed. We demonstrated that the presence of a more bulky cyclopropane backbone resulted in a less effective ligand.

1. Introduction

Carbon–carbon bond-forming reactions are one of the most interesting transformations for constructing an organic molecule.[1] As a result, the use of transition metal-catalyzed reactions to form new C–C bonds in an enantioselective way is a topic of great interest. The asymmetric Rh(I)-catalyzed 1,4-addition to α,β-unsaturated enones has recently received much attention[2] and, thus a wide variety of ligands have been developed, for example, bisphosphanes,[3] amidomonophosphane,[4] bisphosphonites,[5] phosporamidites,[6] *N*-heterocyclic carbenes (NHC),[7] chiral dienes,[8,9] and hybrid phosphane-olefins.[10]

The choice of an appropriate ligand is crucial for the success of an asymmetric transition metal-catalyzed reaction. Given the complexity of most catalytic processes, the rational design of a chiral ligand is seldom straightforward. Therefore, we designed a C_2-symmetric ligand structure, shown in Figure 1, in order to address this problem. Variation of the bulkiness of the R substituents on the cycloalkane ring allows us to determine the optimal transfer of chirality from the backbone to the reaction center. The electronic and steric properties of the chelating atoms can also be tuned,[11] as well as their bite angle[12] by changing the ring size of the backbone ($n = 0, 1, 2$). Recently, we reported on a first set of diphenyl-substituted cyclopropane-based ligands (R = Ph, $n = 0$) with P or N as donor atoms.[13] Bisphosphane **1** (Fig. 2) showed some promising results in asymmetric Pd(0)-catalyzed allylic alkylation reactions and asymmetric Rh(I)-catalyzed hydrogenations.

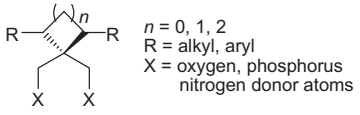

Figure 1. A C_2-symmetric modular ligand structure.

Herein we report the synthesis of the novel bisphosphane ligand **2** (Fig. 2) with an increased steric bulk of the backbone ($n = 0$, R = 3,5-diphenylphenyl). This new bisphosphane ligand **2**, together with bisphosphane ligand **1** ($n = 0$, R = phenyl)[13] was tested and compared in the asymmetric Rh(I)-catalyzed 1,4-addition of several arylboronic acids to cyclic enones.

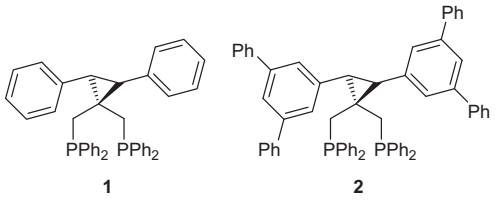

Figure 2. C_2-Symmetric bisphosphane ligands **1** and **2**.

2. Results and discussion

The synthesis of ligand **2** is analogous to our previously described synthesis of ligand **1**.[13] However, tetra-bromo-substituted (*E*)-stilbene **5** is not commercially available and needs to be synthesized. This product can be accessed via two different routes

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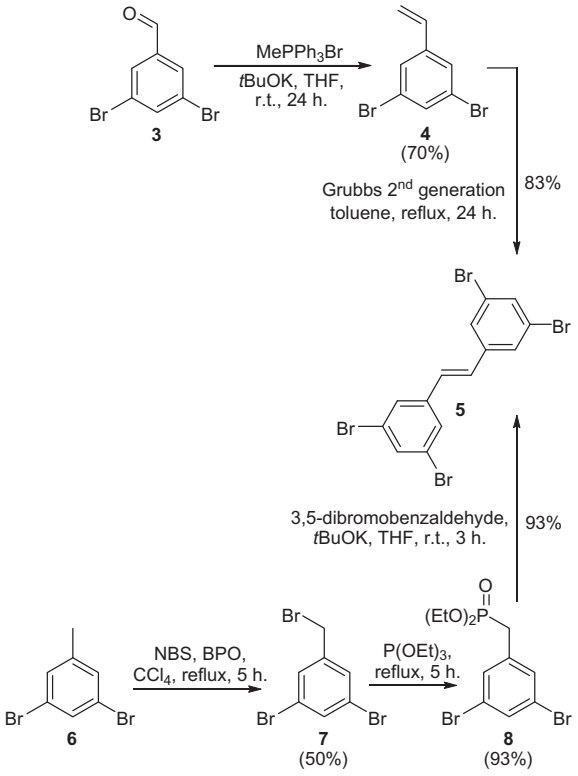
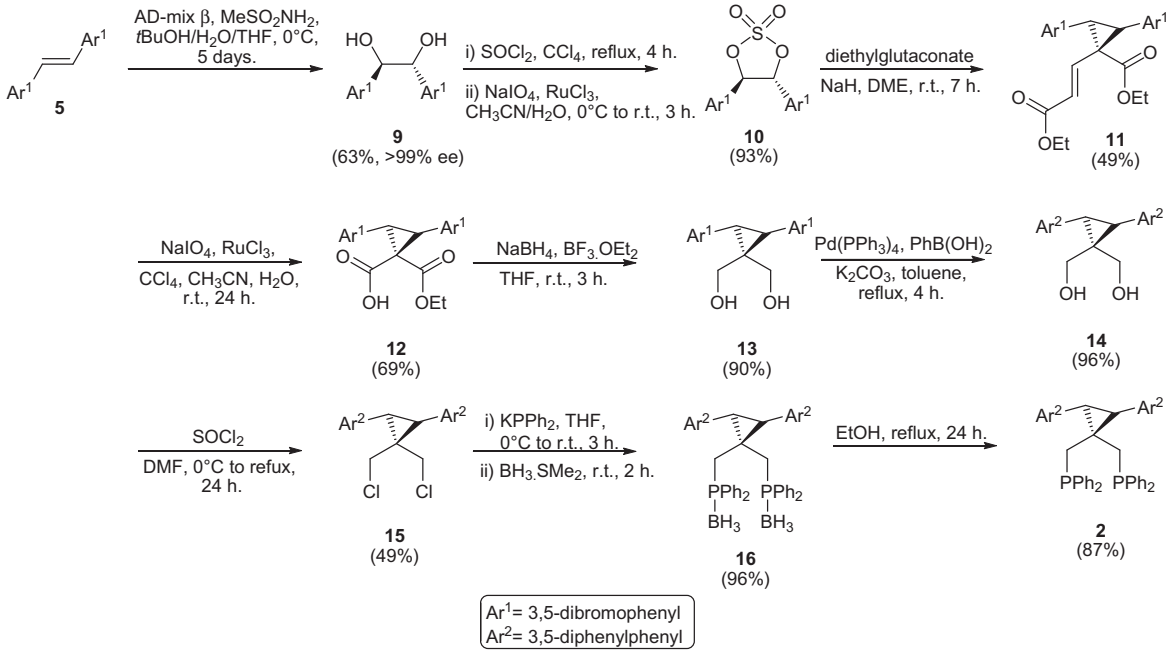


Scheme 1. Synthesis of bromo-substituted (*E*)-stilbene **5**.

(Scheme 1). The first route started with a Wittig reaction in order to obtain 3,5-dibromostyrene **4**. Next, **5** was obtained in good yield via a self-cross metathesis reaction. Although the overall yield was quite good, this route was not pursued because of the requirement of a rather large amount of the very expensive second generation Grubbs catalyst (20 mol %). Therefore, a second route was devised (Scheme 1). Hereby, 3,5-dibromotoluene **6** was monobrominated in a Wohl–Ziegler reaction with NBS.[14] Next, phosphonate **8** was obtained via an Arbuzov reaction and further used in a Wittig-type reaction in order to afford the substituted (*E*)-stilbene **5** in good overall yield. The latter route could be easily scaled up.

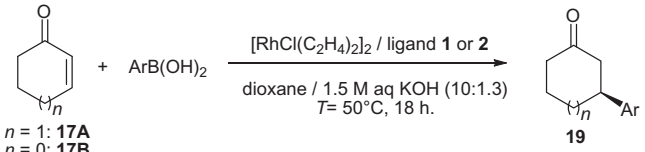
Next, tetrabromo-substituted (*E*)-stilbene **5** was used in the synthesis of bisphosphane ligand **2** (Scheme 2). Diol **9** was prepared via a Sharpless asymmetric dihydroxylation (>99% ee). Next, THF was added as a co-solvent in order to increase the solubility of **5**. This diol **9** was further converted into cyclic sulfate **10** in two high yielding steps. The cyclopropane moiety in **11** was obtained via a stereocontrolled double substitution of the cyclic sulfate **10** with the anion of diethyl glutaconate. Subsequent oxidative cleavage of **11** afforded monoester **12**, which was finally reduced to pivotal diol **13** with $NaBH_4$ in the presence of $BF_3{\cdot}OEt_2$. From a Suzuki cross coupling, four phenyl groups could be simultaneously introduced to afford **14** in excellent yield. Next, diol **14** was converted into dichloride **15**. A nucleophilic substitution with potassium diphenylphosphide in THF and subsequent in situ protection with $BH_3{\cdot}SMe_2$ afforded the protected phosphane ligand **16** in high yield. Normally, cleavage of the BH_3-protecting group can be achieved by treatment with strong acids[15] or an excess of amines.[16] However, we recently discovered that phosphane deprotection can be conveniently carried out under very mild neutral conditions by simply refluxing in ethanol for 16 h, to afford bisphosphane ligand **2** in 87% yield.[17] It is noteworthy that free bisphosphane ligand **2** appeared to be stable enough to be handled in air.

The efficiency of bisphosphane ligands **1** and **2** was evaluated in the rhodium(I)-catalyzed asymmetric 1,4-addition of boronic acids to cyclic enones (Table 1). In accordance with our earlier findings, the best results were obtained when the catalyst was generated in situ from $[Rh(C_2H_4)_2Cl]_2$ and bisphosphane **1** or **2** in the presence of KOH.[3a,9i,9n] In the 1,4-addition of $PhB(OH)_2$ **18a** to cyclohexenone **17A** in the presence of ligand **1**, a good conversion and enantioselectivity were obtained (Table 1, entry 1). When the more bulky bisphosphane ligand **2** was used, a comparable enantioselectivity but a higher yield was observed (Table 1, entry 2) in only 3 h reaction time. Next, other substituted arylboronic acids were used in this transformation. We observed the highest enantioselectivity (up to 89% ee) and yield with the electron-poor 4-trifluoromethyl-phenylboronic



Scheme 2. Synthesis of bisphosphane **2**.

Table 1
Rh(I)-catalyzed asymmetric 1,4-addition of boronic acids **18a–f** to cyclic enones **17A–C** using bisphosphane ligands **1** and **2**



n = 1: **17A**
n = 0: **17B**
n = 2: **17C**

18a Ar = Ph
18b Ar = 4-CF_3Ph
18c Ar = 4-MeOPh
18d Ar = 1-naphthyl
18e Ar = 2-CH_3Ph
18f Ar = 2,6-$(CH_3)_2$-Ph

Entry	Ligand	Cyclic enone	Arylboronic acid	Yield[a] (%)	ee[b,c] (%)
1	**1**	**17A**	**18a**	71	83 (*S*)
2[d]	**2**	**17A**	**18a**	84	81 (*S*)
3	**1**	**17A**	**18b**	99	89 (*S*)
4	**2**	**17A**	**18b**	70	76 (*S*)
5	**1**	**17A**	**18c**	64	71 (*S*)
6	**2**	**17A**	**18c**	16	45 (*S*)
7	**1**	**17A**	**18d**	46	83 (*S*)
8	**2**	**17A**	**18d**	16	<5 (nd)
9[e]	**1**	**17A**	**18e**	58	63 (*S*)
10[e]	**2**	**17A**	**18e**	78	59 (*S*)
11	**1**	**17A**	**18f**	nc	—
12	**2**	**17A**	**18f**	nc	—
13	**1**	**17B**	**18a**	68	<5 (nd)
14	**2**	**17B**	**18a**	25	<5 (nd)
15	**1**	**17C**	**18a**	9	67 (*S*)
16	**2**	**17C**	**18a**	36	53 (*S*)

[a] Isolated yield.
[b] Determined by HPLC analysis with a chiral stationary phase column (Chiracel OD-H, Chiralpak AS-H or Chiralpak AD-H).
[c] The absolute configuration was assigned by the sign of the specific rotation.
[d] Reaction time = 3 h.
[e] Determined by GC analysis with a chiral stationary phase column (Cyclosil B).

acid **18b** and ligand **1** (Table 1, entry 3). With the more bulky ligand **2**, a significantly lower enantioselectivity and conversion were obtained (Table 1, entry 4). The same trend was also observed for **18c** (Table 1, entries 5 and 6). With the bulky 1-naphthylboronic acid **18d**, a good enantioselectivity was observed with ligand **1**, however, the reaction was much slower due to the steric bulk of the reagent (Table 1, entry 7). With the more bulky ligand **2**, almost no conversion was observed with **18d**, and the selectivity was very low (Table 1, entry 8). The hindered *o*-tolylboronic acid **18e** gave a lower selectivity and yield (especially for ligand **1** (Table 1, entries 9 and 10), whereas no reaction was observed for the bulky 2,6-dimethylphenylboronic acid **18f** (Table 1, entries 11 and 12). Except for **18a** and **18e**, an increase in the steric bulk of the chiral ligand backbone leads in general to lower yields and to a less effective transfer of chirality from the backbone to the reaction center.

The rhodium(I)/bisphosphane catalyst system was also applied to 2-cyclopentenone **17B** and 2-cycloheptenone **17C** as acceptors (Table 1, entries 13–16). With 2-cyclopentenone **17B**, which can be considered as a more difficult substrate, rather poor conversions (especially with ligand **2**) and very low enantioselectivities were obtained (Table 1, entries 13 and 14). Similarly, poor results were observed with 2-cycloheptenone **17C** as a substrate (Table 1, entries 15 and 16).

3. Conclusion

In conclusion, we have synthesized a new bisphosphane ligand **2** with a more bulky cyclopropane backbone than our previously reported bisphosphane ligand **1**. We compared the efficiency of **1** and **2** in the Rh(I)-catalyzed asymmetric 1,4-addition to cyclic enones. In almost all cases, we observed that the less bulky bisphosphane ligand **1** was the most effective (up to 99% yield and up to 89% ee). An increase in the steric bulk of the chiral backbone generally led to a less efficient transfer of chirality from the backbone to the reaction center and to lower yields.

4. Experimental

4.1. General

All reactions were carried out under an argon atmosphere in dry solvents under anhydrous conditions, unless otherwise stated. Phosphane ligand **1** was synthesized according to our earlier described method.[13] All reagents were purchased and used without purification, unless otherwise noted. Analytical TLC was performed using Macherey-Nagel SIL G-25 UV_{254} plates. Flash chromatography was carried out with Rocc silica gel (0.040–0.063 mm). ^1H NMR, ^{13}C NMR and ^{31}P NMR were recorded on a Bruker Avance 300 or a Bruker DRX 500 spectrometer as indicated, with chemical shifts reported in ppm relative to TMS (for ^1H and ^{13}C), and relative to 85% aqueous phosphoric acid (for ^{31}P), using the residual solvent signal as a standard. ^{13}C NMR spectra were recorded using the attached proton test. IR-spectra were recorded on a Perkin–Elmer SPECTRUM-1000 FT-IR spectrometer with a Pike Miracle Horizontal Attenuated Total Reflectance (HATR) module. EI Mass spectra were recorded with a Hewlett–Packard 5988A mass spectrometer. LC–MS analysis was performed on an Agilent 1100 series HPLC with quaternary pump, DAD, and single quadrupole MS detector type VL with an API-ES source, using a Phenomenex Luna C18(2) column (250 × 4.6 mm, particle size 5 μm). Analytical chiral HPLC separations were performed on an Agilent 1100 series HPLC system with DAD detection. Exact molecular masses were measured on a quadrupole/orthogonal—acceleration time-of-flight (Q/oaTOF) tandem mass spectrometer (qTof 2, Micromass, Manchester, UK) equipped with a standard electrospray ionization (ESI) interface. HRMS-EI masses were measured on a Kratos MS50TC mass spectrometer. Optical rotations were measured with a Perkin–Elmer 241 polarimeter. Melting points were measured with a Kofler melting point apparatus.

4.2. 5-Bromomethyl-1,3-dibromobenzene 7

3,5-Dibromotoluene **6** (9.5 g, 36.8 mmol), NBS (6.6 g, 36.8 mmol) and a catalytic amount of benzoyl peroxide (266 mg, 1.1 mmol) were refluxed in CCl_4 (300 mL) for 5 h. The insoluble succinimide was removed via filtration and was washed with CCl_4. The filtrate was concentrated in vacuo and purified by flash chromatography over silica gel (Hexane/EtOAc, 99:1) resulting in 6.7 g of a mixture of 5-bromomethyl-1,3-dibromobenzene and 5-dibromomethyl-1,3-dibromobenzene. Recrystallization from ethanol gave 5.9 g (50%) of **7** as a pure white solid. ^1H NMR (300 MHz, $CDCl_3$): δ 4.40 (s, 2H), 7.52 (d, J = 1.6 Hz, 2H), 7.64 (t, J = 1.6 Hz, 1H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 30.8 (CH_2), 123.1 (C), 130.8 (CH), 134.1 (CH), 141.3 (C) ppm. IR (HATR): 3061, 1772, 1745, 1580, 1552, 1421, 1370, 1223, 1207, 1097, 861, 741, 685, 627 cm^{-1}. EI-MS m/z (rel. intensity%): 328 (M^+, 25), 249 (89), 168 (39), 89 (100). Mp: 91–93 °C. HRMS (EI): calcd for $C_7H_5{}^{79}Br_3$: 325.7941; found: 325.7935.

4.3. 1,3-Dibromo-5-(diethylphosphonyl)methyl-benzene 8

A mixture of 5-bromomethyl-1,3-dibromobenzene **7** (5.0 g, 15 mmol) and triethyl phosphite (5.325 g, 30 mmol) was refluxed at 140 °C for 5 h. The excess reagent was removed in vacuo. The crude product was purified by flash chromatography over silica gel (Pentane/EtOAc, 30:70) resulting in 5.40 g (93%) of pure **8** as a yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ 1.15 (t, J = 7.1 Hz, 6H),

2.94 (d, J = 21.8 Hz, 2H), 3.87–3.97 (m, 4H), 7.24–7.28 (m, 2H), 7.41–7.45 (m, 1H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 16.3 (d, J_{C-P} = 7.0 Hz, 2 × CH_3), 33.2 (d, J_{C-P} = 35.0 Hz, CH_2), 62.4 (d, J_{C-P} = 7.1 Hz, 2 × CH_2), 122.8 (d, J_{C-P} = 3.3 Hz, C), 131.5 (d, J_{C-P} = 6.6 Hz, CH), 132.6 (d, J_{C-P} = 3.3 Hz, CH), 135.7 (d, J_{C-P} = 8.8 Hz, C) ppm. ^{31}P NMR (121.4 MHz, $CDCl_3$): δ +24.4 ppm. IR (HATR): 2919, 1583, 1554, 1427, 1212, 1102, 859, 841, 742, 692, 666 cm^{-1}. ES-MS: 386.9 $[M+H]^+$.

4.4. 3,5-Dibromostyrene 4

3,5-Dibromobenzaldehyde **3** (2.0 g, 7.57 mmol) was added to a mixture of *t*-BuOK (0.927 g, 8.26 mmol) and methyltriphenylphosphonium bromide (3.01 g, 8.26 mmol) in dry THF (35 mL). The reaction mixture was stirred at room temperature for 4 h. A saturated aqueous NH_4Cl solution (10 mL) was added and the resulting mixture was concentrated in vacuo. The aqueous layer was extracted with CH_2Cl_2 (2 × 100 mL). The combined organic phases were washed with water (10 mL) and dried over $MgSO_4$, filtered off, and concentrated in vacuo. The crude product was purified by flash chromatography over silica gel (Pentane/EtOAc, 98:2) resulting in 1.390 g (70%) pure **4** as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.15 (d, J = 10.9 Hz, 1H), 5.55 (d, J = 17.6 Hz, 1H), 6.30–6.42 (dd, J = 10.9 Hz and J = 17.6 Hz, 1H), 7.25 (d, J = 1.7 Hz 2H), 7.33 (t, J = 1.7 Hz, 1H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 116.9 (CH_2), 123.1 (C), 128.0 (CH), 133.0 (CH), 134.3 (CH), 141.1 (C) ppm. IR (HATR): 3066, 2981, 1841, 1583, 1543, 1431, 1391, 1201, 1099, 988, 913, 847, 741, 635 cm^{-1}. EI-MS m/z (rel. intensity%): 262 (M^+, 53), 183 (30), 102 (100). HRMS (EI): calcd for $C_8H_6{}^{79}Br_2$: 259.8836; found: 259.8846.

4.5. (*E*)-3,3′,5,5′-Tetrabromostilbene 5

4.5.1. Method 1 (methathesis reaction)

Grubbs catalyst (2nd generation) (0.194 g, 0.229 mmol) dissolved in dry toluene (40 mL) was added in three portions to a solution of 3,5-dibromostyrene **8** (1.2 g, 4.58 mmol) in dry toluene (10 mL) under an argon atmosphere. The mixture was refluxed for 24 h. Subsequently, the reaction mixture was concentrated and the crude product was purified by flash chromatography over silica gel (Pentane/CH_2Cl_2/EtOH, 98:1.9:0.1) resulting in 1.0 g (83%) of pure (*E*)-**5** as a white solid.

4.5.2. Method 2 (Wittig reaction)

1,3-Dibromo-5-(diethylphosphonyl)methyl-benzene **8** (5.0 g, 13.0 mmol) dissolved in dry THF (100 mL) was added to a solution of 3,5-dibromobenzaldehyde (6.85 g, 26.0 mmol) in dry THF (380 mL) under an argon atmosphere at room temperature. Next, *t*-BuOK (2.184 g, 19.5 mmol) was added to the reaction mixture. The resulting reaction mixture was stirred at room temperature for an additional 3 h. After hydrolysis with water, the mixture was stirred for a further 30 min and the precipitated solid was filtered off, resulting in 6 g (93%) of **5** as a pure white solid. ^{1}H NMR (300 MHz, C_6D_6): δ 5.70 (s, 2H), 6.83 (d, J = 1.7 Hz, 4H), 7.08 (t, J = 1.7 Hz, 2H) ppm. ^{13}C NMR (75.4 MHz, C_6D_6): δ 123.4 (C), 128.1 (CH), 128.5 (CH), 133.3 (CH), 140.0 (C) ppm. IR (HATR): 3062, 2917, 2852, 1705, 1580, 1548, 1419, 1241, 1216, 1101, 961, 906, 846, 745, 675 cm^{-1}. EI-MS m/z (rel. intensity%): 496 (M^+, 100), 336 (91), 176 (95). Mp: 218–220 °C. HRMS (EI): calcd for $C_{14}H_8{}^{79}Br_4$: 491.7359; found: 491.7371.

4.6. (1*R*,2*R*)-1,2-Bis(3,5-dibromophenyl)-ethane-1,2-diol 9

At first, AD-mix-β (125 g) was dissolved in a mixture of *tert*-butyl alcohol (300 mL), THF (300 mL), and water (300 mL). Next, methanesulfonamide (5.8 g, 61.0 mmol) was added and the reaction mixture was cooled to 0 °C, whereupon the inorganic salts were partially precipitated. (*E*)-3,3′,5,5′-Tetrabromostilbene **5** (23.5 g, 47.0 mmol) was added in one portion and the heterogeneous slurry was stirred vigorously at 0 °C for 5 days. The mixture was allowed to warm to room temperature and Na_2SO_3 (80 g, 639.0 mmol) was added. The reaction mixture was stirred at room temperature for another 24 h. Next, EtOAc (300 mL) was added and the organic phase was separated, whereupon the aqueous phase was further extracted with EtOAc (2 × 300 mL). The combined organic phases were washed with 2 M KOH and dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography over silica gel (Toluene/EtOH, 97:3) resulting in 15.6 g (>99% ee, 63% yield) pure diol **9** as a white solid. ^{1}H NMR (300 MHz, C_6D_6): δ 1.65 (br s, 2H), 3.72 (s, 2H), 6.95 (d, J = 1.7 Hz, 4H), 7.35 (t, J = 1.7 Hz, 2H) ppm. ^{13}C NMR (75.4 MHz, C_6D_6): δ 75.2 (CH), 121.6 (C), 127.5 (CH), 132.3 (CH), 143.0 (C) ppm. IR (HATR): 3457, 3289, 3085, 2914, 1737, 1585, 1557, 1419, 1371, 1241, 1192, 1105, 1038, 856, 760, 745, 673 cm^{-1}. EI-MS (m/z, rel. intensity%): 530 (M^+, 2), 513 (5), 156 (40), 266 (60). $[\alpha]_D^{20} = -119.0$ (c 1.0, EtOH). Mp: 54–56 °C. HRMS (EI): calcd for $C_{17}H_{14}O_2{}^{79}Br_4$: 565.7727; found: 565.7708. Conditions for HPLC: Chiralpak AD-H column, solvent: *n*-hexane/EtOH (95:5), flow rate = 1 mL/min, T = 35 °C, retention times: 13.2 min for (1*R*,2*R*)-**9**, 15.3 min for (1*S*,2*S*)-**9**.

4.7. (4*R*,5*R*)-4,5-Bis(3′,5′-dibromophenyl)-(1,3,2)-dioxathiolane-(2,2)-dioxide 10

A dried 1 L three-neck flask was equipped with a reflux condenser carrying a drying tube with an HCl trap. (1*R*,2*R*)-1,2-bis(3,5-dibromophenyl)-ethane-1,2-diol **9** (15.5 g, 29 mmol) and CCl_4 (100 mL) were added under an argon atmosphere. Thionyl chloride (2.58 mL, 35 mmol) was added dropwise over 40 min. The resulting reaction mixture was refluxed for 4 h. The solution was cooled in an ice-water bath and then diluted with acetonitrile (100 mL). $NaIO_4$ (9.3 g, 43.5 mmol), $RuCl_3{\cdot}xH_2O$ (0.031 g, 0.116 mmol), and water (140 mL) were added. The resulting biphasic mixture was rapidly stirred at room temperature for 3 h. The mixture was diluted with diethyl ether (500 mL) and the two phases were separated. The organic phase was washed with H_2O (50 mL), saturated aqueous $NaHCO_3$ (2 × 50 mL), and brine (50 mL). After drying over Na_2SO_4, the organic phase was filtered through a small pad of silica to remove the dark color and concentrated to give 16.0 g (93%) of **10** as a colorless oil. This product decomposes at room temperature but is stable under an argon atmosphere at −20 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.50 (s, 2H), 7.40 (d, J = 1.7 Hz, 4H), 7.80 (t, J = 1.7 Hz, 2H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 87.0 (CH), 124.2 (C), 128.7 (CH), 134.0 (C), 136.9 (CH) ppm. IR (HATR): 3302, 3074, 1736, 1586, 1559, 1426, 1396, 1201, 1105, 957, 858, 804, 742, 677, 649 cm^{-1}. EI-MS m/z (rel. intensity%): 592 (M^+, 5), 496 (2) 336 (7). $[\alpha]_D^{20} = +79.1$ (c 1.0, $CHCl_3$). HRMS (EI): calcd for $C_{14}H_8O_4S^{79}Br_4$: 587.6877; found: 587.6899.

4.8. (2*R*,3*R*)-1-(Ethoxycarbonyl)-1-(2′-ethoxycarbonyl-vinyl)-2,3-bis(3″,5″-dibromophenyl)-cyclopropane 11

At first, NaH (95% powder, 700.0 mg, 15.67 mmol) was suspended in dry DME (25 mL) in a dried 250 mL two-neck flask fitted with a reflux condenser under argon. Next, diethyl glutaconate (1.3 mL, 6.48 mmol) was added dropwise over 40 min. Compound **10** (3.2 g, 5.4 mmol) was dissolved in dry DME (50 mL) and added dropwise to the anion mixture. The resulting orange solution was stirred at room temperature for 7 h. The reaction mixture was quenched by adding saturated aqueous NH_4Cl (60 mL) and the water phase was extracted with EtOAc (2 × 250 mL). The

combined organic phases were dried over Na_2SO_4, filtered off, and concentrated in vacuo. The crude product was purified by flash chromatography over silica gel (pentane/EtOAc, 92:8), resulting in 1.75 g (49%) of pure product **11** as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.10 (t, J = 7.1 Hz, 3H), 1.30 (t, J = 7.1 Hz, 3H), 3.20 (d, J = 8.1 Hz, 1H), 3.85 (d, J = 8.1 Hz, 1H), 4.10 (dq, J = 12.8, 7.1 Hz, 1H), 4.15 (dq, J = 12.8, 7.1 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 5.97 (d, J = 15.9 Hz, 1H), 6.70 (d, J = 15.9 Hz, 1H), 7.37 (dd, J = 1.7, 0.7 Hz, 2H), 7.41 (dd, J = 1.7, 0.7 Hz, 2H), 7.63 (app. t, J = 1.7 Hz, 1H), 7.64 (app. t, J = 1.7 Hz, 1H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 14.0 (CH_3), 14.2 (CH_3), 35.8 (CH), 37.1 (CH), 40.9 (C), 60.7 (CH_2), 62.0 (CH_2), 122.9 (C), 123.2 (C), 123.5 (CH), 130.8 (CH), 131.0 (CH), 133.4 (CH), 133.6 (CH), 138.2 (C), 138.4 (C), 141.5 (CH), 165.6 (C), 167.5 (C) ppm. IR (HATR): 2978, 1711, 1644, 1583, 1551, 1411, 1366, 1266, 1179, 1031, 977, 853, 741, 680, 675 cm^{-1}. ES-MS: 681 $[M+H]^+$. $[\alpha]_D^{20} = +75.3$ (c 1.0, $CHCl_3$). HRMS (EI): calcd for $C_{21}H_{15}O_3Br_4$ [M – EtO]: 634.7714; found: 634.7700.

4.9. (2*R*,3*R*)-1-(Ethoxycarbonyl)-2,3-bis(3′,5′-dibromophenyl)-cyclopropane-1-carboxylic acid 12

Compound **11** (1.40 g, 2.06 mmol) and $NaIO_4$ (3.55 g, 16.47 mmol) were dissolved in a mixture of CH_3CN (12 mL), CCl_4 (12 mL), and H_2O (18 mL). Next, $RuCl_3{\cdot}xH_2O$ (0.032 g, 0.164 mmol) was added to the reaction mixture, which was stirred at room temperature for 24 h. The solids were filtered over Celite and washed with water and CH_2Cl_2. The aqueous phase was extracted with CH_2Cl_2 (2 × 200 mL). The combined organic phases were dried over Na_2SO_4, filtered off, and concentrated in vacuo. The crude product was purified by flash chromatography over silica gel (CH_2Cl_2/MeOH/AcOH, 98.9:1:0.1) resulting in 0.893 g (69%) of pure **12** as a colorless oil. ^{1}H NMR (500 MHz, acetone-d_6): δ 1.02 (t, J = 7.1 Hz, 3H), 3.86 (d, J = 8.2 Hz, 1H), 3.89 (d, J = 8.2 Hz, 1H), 4.00 (dq, J = 10.8, 7.1 Hz, 1H), 4.08 (dq, J = 10.8, 7.1 Hz, 1H), 7.59 (d, J = 1.6 Hz, 2H), 7.62 (d, J = 1.6 Hz, 2H), 7.67 (t, J = 1.6 Hz, 1H), 7.69 (t, J = 1.6 Hz, 1H) ppm. ^{13}C NMR (125.7 MHz, acetone-d_6): δ 13.4 (CH_3), 33.1 (CH), 33.3 (CH), 46.0 (C), 61.4 (CH_2), 122.3 (C), 122.3 (C), 131.0 (CH), 131.1 (CH), 132.7 (CH), 139.6 (C), 165.9 (C), 166.2 (C) ppm. IR (HATR): 1706, 1584, 1552, 1412, 1369, 1263, 1218, 1178, 1134, 1100, 1029, 856, 734, 703, 678 cm^{-1}. ES-MS: 626.7 $[M+H]^+$. $[\alpha]_D^{20} = +27.3$ (c 1.0, $CHCl_3$). HRMS (EI): calcd for $C_{19}H_{14}O_4{}^{79}Br_4$: 621.7626; found: 621.7624.

4.10. (2*R*,3*R*)-2,3-Bis(3′,5′-dibromophenyl)-cyclopropane-1,1-dimethanol (13)

Compound **12** (1.0 g, 1.60 mmol) in THF (50 mL) was placed in an oven-dried 100 mL two-neck flask under an argon atmosphere and cooled to 0 °C. Next, $NaBH_4$ (575.0 mg, 14.38 mmol) was added to the solution and the resulting suspension was stirred for 20 min. Subsequently, $BF_3{\cdot}OEt_2$ (2.50 g, 17.58 mmol) was added dropwise to the resulting mixture at 0 °C. The reaction mixture was stirred at room temperature for another 3 h. The reaction was neutralized with aq 2 M NaOH (5 mL) until the pH of the mixture was around 8–9. Next, THF was evaporated in vacuo and the residue was extracted with Et_2O (3 × 150 mL). The combined organic phases were washed with H_2O (10 mL), dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by flash chromatography over silica gel (CH_2Cl_2/EtOAc, 9:1), resulting in 0.821 g (90%) of pure **13** as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.05 (br s, 2H), 2.60 (s, 2H), 3.52 (d, J = 10.8 Hz, 2H), 3.58 (d, J = 10.8 Hz, 2H), 7.35 (s, 4H), 7.50 (s, 2H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 30.8 (CH), 37.4 (C), 65.5 (CH_2), 123.1 (C), 130.9 (CH), 132.8 (CH), 140.6 (C) ppm. IR (HATR): 3349, 2933, 2884, 2356, 2012, 1581, 1549, 1429, 1405, 1288, 1170, 1071, 1021, 1013, 933, 859, 851, 743, 738, 700, 686 cm^{-1}. ES-MS: 587.8 $[M+NH_4]^+$, 552.7 $[M-H_2O+H]^+$, 534.7 $[M-2\times H_2O+H]^+$. $[\alpha]_D^{20} = -81.1$ (c 1.0, $CHCl_3$). Mp: 148–150 °C.

4.11. (*R*,*R*)-2,3-Bis(3′,5′-diphenylphenyl)-cyclopropane-1,1-dimethanol 14

To a solution of **13** (0.2 g, 0.351 mmol) and $Pd(PPh_3)_4$ (0.1 g, 0.084 mmol) in toluene (22 mL) were added phenylboronic acid (524.0 g, 4.21 mmol), EtOH (5.5 mL), and aq K_2CO_3 (2 M, 11 mL). The resulting reaction mixture was refluxed for 4 h. To the reaction mixture was added water (100 mL). The aqueous layer was further extracted with CH_2Cl_2 (3 × 100 mL) and the combined organic phases were washed with brine (20 mL), dried over $MgSO_4$, and concentrated in vacuo. The crude product was passed through a short pad of silica gel to remove the dark color and concentrated in vacuo to give 0.188 g (96%) of pure **14** as a gray-white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.10 (s, 2H), 4.05 (d, J = 11.5 Hz, 2H), 4.15 (d, J = 11.5 Hz, 2H), 7.35–7.50 (m, 12H), 7.55–7.85 (m, 14H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 31.8 (CH), 32.1 (C), 66.7 (CH_2), 124.9 (CH), 126.9 (CH), 127.3 (CH), 127.6 (CH), 128.8 (CH), 137.4 (C), 140.8 (C), 142.2 (C) ppm. IR (HATR): 3272, 3059, 2940, 2162, 1633, 1586, 1551, 1413, 1309, 1292, 1253, 1128, 1066, 854, 756, 738, 693, 640 cm^{-1}. ES-MS: 576 $[M+NH_4]^+$, 523 $[M-2\times H_2O+H]^+$, 541 $[M-H_2O+H]^+$. $[\alpha]_D^{20} = -76.8$ (c 1.0, $CHCl_3$). Mp: 240–242 °C. HRMS (EI): calcd for $C_{41}H_{30}$ $[M-2\times H_2O]$: 522.2347; found: 522.2334.

4.12. (2*R*,3*R*)-1,1-Bis(chloromethyl)-2,3-bis(3′,5′-diphenylphenyl)-cyclopropane 15

Diol **14** (390.0 mg, 0.698 mmol) was dissolved in dry DMF (4 mL) in an oven-dried 10 mL flask. The solution was cooled to 0 °C. Next, $SOCl_2$ (0.249 g, 2.09 mmol) was added dropwise to the solution and the resulting mixture was refluxed for 24 h. Water (10 mL) was added to the reaction mixture, which was extracted with CH_2Cl_2 (3 × 50 mL), dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by flash chromatography over silica gel (hexane/CH_2Cl_2, 70:30) resulting in 205.0 mg pure **15** as a pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.15 (s, 2H), 3.20 (d, J = 11.5 Hz, 2H), 3.90 (d, J = 11.5 Hz, 2H), 7.40–7.50 (m, 12H), 7.50–7.60 (m, 14H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 36.6 (CH), 36.8 (C), 47.7 (CH_2), 125.3 (CH), 126.9 (CH), 127.3 (CH), 127.7 (CH), 128.9 (CH), 136.7 (C), 140.7 (C), 142.3 (C) ppm. IR (HATR): 3043, 1594, 1576, 1496, 1426, 1333, 1264, 1178, 1075, 1029, 1005, 909, 876, 755, 694 cm^{-1}. ES-MS: 523.2 $[M-2Cl+H]^+$, 559.2 $[M-Cl+H]^+$. $[\alpha]_D^{20} = -88.6$ (c 1.0, $CHCl_3$). HRMS (EI): calcd for $C_{41}H_{32}{}^{35}Cl_2$: 594.1881; found: 594.1884.

4.13. (2*R*,3*R*)-1,1-Bis[(boratodiphenylphosphanyl) methyl]-2,3-bis(3′,5′-diphenylphenyl)-cyclopropane 16

At first, $KPPh_2$ in THF (0.5 M, 2.20 mL, 1.18 mmol) was placed in an oven-dried Schlenk tube under an argon atmosphere at 0 °C. Next, **15** (0.15 g, 0.252 mmol) in dry THF (2.40 mL) was added dropwise to the solution. The resulting mixture was stirred at room temperature for 3 h. Subsequently, $BH_3{\cdot}SMe_2$ (0.109 g, 1.429 mmol) was added dropwise to the reaction mixture at room temperature, followed by stirring for 2 h. After the addition of aq NH_4Cl, the reaction mixture was diluted with CH_2Cl_2 (20 mL) and the water phase was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash chromatography over silica gel (hexane/EtOAc, 90:10) resulting in 224 mg (96%) of pure product **16** as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.40–1.55 (br s, 6H, BH_3), 2.00 (dd (app. t), J = 15.7 Hz, 2H), 2.32 (s, 2H), 3.50 (dd, J = 6.2, 15.7 Hz, 2H), 7.05–7.75 (m, 46H) ppm.

^{13}C NMR (75.4 MHz, $CDCl_3$): δ 28.3 (C), 28.8 (CH_2), 30.8 (dd, J_{C-P} = 4.9, 10.4 Hz, CH), 124.7 (CH), 127.3 (CH), 127.4 (CH), 128.6 (CH), 128.2 (C), 128.7 (d, J_{C-P} = 9.0 Hz, CH), 128.9 (CH), 129.1 (d, J_{C-P} = 9.0 Hz, CH), 130.7 (d, J_{C-P} = 2.2 Hz, CH), 130.9 (C), 131.6 (d, J_{C-P} = 9.0 Hz, CH), 132.1 (d, J_{C-P} = 2.2 Hz, CH), 133.7 (d, J_{C-P} = 9.0 Hz, CH), 137.4 (C), 140.8 (C), 141.8 (C) ppm. ^{31}P NMR (121.4 MHz, $CDCl_3$): δ +14.1 ppm. IR (HATR): 3049, 2392, 1595, 1576, 1496, 1435, 1105, 1059, 878, 853, 757, 694 cm^{-1}. ES-MS: 940.3 $[M+NH_4]^+$. $[\alpha]_D^{20} = +82.4$ (*c* 1.0, $CHCl_3$). HRMS (EI): calcd for $C_{65}H_{58}B_2P_2$: 922.4200; found: 922.4198.

4.14. (2*R*,3*R*)-1,1-Bis[(diphenylphosphanyl)methyl]-2,3-bis(3′,5′-diphenylphenyl)-cyclopropane 2

Compound **16** (180.0 mg, 0.195 mmol) was dissolved in degassed EtOH (6 mL) in an oven-dried Schlenk tube under argon atmosphere. The solution was refluxed for 24 h, subsequently diluted with degassed CH_2Cl_2 (15 mL), and concentrated in vacuo. The crude product was purified by flash chromatography over silica gel with degassed solvents (hexane/EtOAc, 95:5) resulting in 152 mg of pure **2** as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ 2.05 (dd, *J* = 2.8, 14.4 Hz, 2H), 2.6 (s, 2H), 2.8 (dd (app. d), *J* = 14.4 Hz, 2H), 7.15–7.70 (m, 46H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 32.5 (t, J_{C-P} = 17.4 Hz, C), 33.1 (dd, J_{C-P} = 10.1, 13.7 Hz, CH_2), 33.6 (t, J_{C-P} = 7.3 Hz, CH), 124.2 (CH), 127.0 (CH), 127.4 (CH), 127.5 (CH) 127.9 (CH), 128.3 (d, J_{C-P} = 6.4 Hz, CH), 128.7 (CH), 128.8 (d, J_{C-P} = 8.2 Hz, CH), 129.7 (CH), 132.0 (d, J_{C-P} = 17.4 Hz, CH), 134.6 (d, J_{C-P} = 22.0 Hz, CH), 137.8 (d, J_{C-P} = 14.7 Hz, C), 139.0 (C), 139.8 (d, J_{C-P} = 13.8 Hz, C), 141.1 (C), 141.7 (C) ppm. ^{31}P NMR (121.4 MHz, $CDCl_3$): δ −20.5 ppm. IR (HATR): 3054, 2165, 1593, 1496, 1432, 1070, 1028, 909, 881, 760, 738, 695 cm^{-1}. ES-MS: 895.3 $[M+H]^+$. $[\alpha]_D^{20} = +95.3$ (*c* 1.0, $CHCl_3$). HRMS (ES): calcd for $C_{65}H_{52}P_2$: 895.3616; found: 895.3611.

4.15. General procedure for the rhodium-catalyzed asymmetric 1,4-addition of arylboronic acids to cyclic enones

Chiral ligand **1** or **2**, (8.58 μmol) and $[RhCl(C_2H_4)_2]_2$ (7.67 μmol) were dissolved in dry and degassed dioxane (1 mL) and stirred for 20 min at room temperature under an argon atmosphere. Next, KOH (1.5 M, 0.19 mmol) in degassed H_2O was added and the resulting solution was stirred for another 20 min. Subsequently, arylboronic acid (0.77 mmol) and cyclic enone (0.385 mmol) were added and stirred at 50 °C for 3 h. The reaction mixture was passed through a short pad of silica gel and was eluted with EtOAc. The crude product was purified by flash chromatography over silica gel (hexane/Et_2O, 85:15), resulting in pure **19**.

All adducts were fully characterized by comparison of their spectroscopic data with those reported in the literature.[3a,9i] The absolute configurations were assigned via correlation of their specific rotation with the literature values.

For 3-phenylcyclohexanone **19Aa**: The enantiomeric excess was determined by chiral HPLC analysis: Chiralpak AS-H column (250 × 4.6 mm, particle size 10 μm), solvent: *n*-hexane/*i*PrOH (98:2), flow rate = 1 mL/min, *T* = 35 °C, retention times: 18.3 min for *S* and 21.4 min for *R*.

For 3-(4-trifluoromethylphenyl)cyclohexanone **19Ab**: The enantiomeric excess was determined by chiral HPLC analysis: Chiralpak AD-H column (250 × 4.6 mm, particle size 10 μm), solvent: *n*-hexane/*i*PrOH (99:1), flow rate = 1 mL/min, *T* = 35 °C, retention times: 14.0 min for (+) and 15.1 min for (−).

For 3-(4-methoxyphenyl)cyclohexanone **19Ac**: The enantiomeric excess was determined by chiral HPLC analysis: Chiralcel OD-H column (250 × 4.6 mm, particle size 10 μm), solvent: *n*-hexane/*i*PrOH (98:2), flow rate = 1 mL/min, *T* = 35 °C, retention times: 13.0 min for (+) and 13.6 min for (−).

For 3-(1-naphthyl)cyclohexanone **19Ad**: The enantiomeric excess was determined by chiral HPLC analysis: Chiralcel AD-H column (250 × 4.6 mm, particle size 10 μm), solvent: *n*-hexane/*i*PrOH (98:2), flow rate = 1 mL/min, *T* = 35 °C, retention times: 12.1 min for (−) and 13.5 min for (+).

For 3-(*o*-tolyl)cyclohexanone **19Ae**: The enantiomeric excess was determined by chiral GC analysis: Cyclosil B 120 (30 m × 0.25 mm × 0.25 μm); carrier gas: H_2; temperature program: 50 °C for 3 min; increase to 200 °C (20 °C/min); 200 °C for 3 min; increase to 240 °C (20 °C/min); 240 °C for 5 min; retention times: 14.86 min for *R* and 14.93 min for *S*.

For 3-phenylcycloheptanone **19Ca**: The enantiomeric excess was determined by chiral HPLC analysis: Chiralcel OD-H column (250 × 4.6 mm, particle size 10 μm), solvent: *n*-hexane/*i*PrOH (98:2), flow rate = 1 mL/min, *T* = 35 °C, retention times: 11.7 min for (−) and 13.3 min for (+).

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