Synthesis of a Novel C_2-Symmetric Bis-oxazoline (= Bis[4,5-dihydrooxazole]) and Its Application as Chiral Ligand in Asymmetric Transition Metal Catalysis

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The new C_2-symmetric bis-oxazoline (= bis[4,5-dihydrooxazole]) **2** with a chiral *trans*-(2*R*,3*R*)-2,3-bis(3,5-diphenylphenyl)cyclopropylidene (= *trans*-(2*R*,3*R*)-2,3-bis([1,1′:3′,1″-terphenyl]-5′-yl)cyclopropylidene) backbone was efficiently synthesized (*Scheme*). All synthetic steps were easy to perform and led to the desired product in good overall yields. Compound **2** was tested and compared as ligand in several enantioselective catalytic reactions such as palladium(0)-catalyzed enantioselective allylic alkylations and copper(I)-catalyzed enantioselective cyclopropanations and aziridinations.

Introduction. – Bis-oxazoline (= bis[4,5-dihydrooxazole]; box) ligands have received the greatest share of attention in N-containing ligands, *e.g.* semicorrins [1], diimines [2], salen [3], 2,2′-bipyridines [4], amidines [5], sulfoximines [6], and, recently, imidates with an exocyclic coordinating N-atom [7]. They are known as cheap, easily accessible, and stable ligands [8]. As a result, the design, synthesis, and application of C_2-symmetric box ligands has received a lot of attention [9]. Since their initial report, a lot of research has been devoted towards the synthesis and application of these box ligands. During the last decade, numerous chiral box ligands with different backbones, such as aliphatic chains [10], aromatic rings [11], 4,5-dioxolane [12], dibenzo[*a*,*c*]cycloheptene [13], biphenyl and binaphthyl [14], and cyclic rings [15] have been reported.

Generally, the large majority of box ligands are derived from optically active β-amino alcohols to produce a 4,5-dihydrooxazole ring with a chiral center. As a consequence, the presence of a stereogenic center next to the coordinating N-atom of the dihydrooxazole ring directly influences the stereochemical outcome of the enantioselective reaction. Recently, we investigated the efficiency of backbone chirality of the bis[dihydrooxazole] containing no extra chiral center at the dihydrooxazole moiety. Therefore, C_2-symmetric bis[dihydrooxazole] ligand **1** (*Fig.*) with a *trans*-(2*R*,3*R*)-2,3-diphenylcyclopropylidene backbone was developed and evaluated in palladium(0)-catalyzed asymmetric allylic alkylations, copper(I)-catalyzed cyclopropanations, and copper(I)-catalyzed aziridinations by our group [16]. Our results established that ligand **1** showed poor enantioselectivities. The highest enantioselectivity in the catalysis of ligand **1** was obtained in asymmetric allylic alkylation of a cyclic

substrate **9** (67% ee; see *Table 1*, below). Increasing of the bulky groups at the cyclopropane moiety may be one of the options to obtain high enantioselectivities due to the steric-hindrance effect. Therefore, in the present article, we describe the synthesis of the new box ligand **2** (*Fig.*) with a more bulky cyclopropane backbone than in the earlier reported ligand **1**, *i.e.*, **2** contains a (*trans*-(2*R*,3*R*)-2,3-bis(3,5-diphenylphenyl)cyclopropylidene (=*trans*-(2*R*,3*R*)-2,3-bis([1,1′:3′,1″-terphenyl]-5′-yl)cyclopropylidene) moiety. This new box ligand **2** was tested in the same enantioselective catalytic reactions as **1**, such as palladium(0)-catalyzed asymmetric allylic alkylations, copper(I)-catalyzed cyclopropanations, and copper(I)-catalyzed aziridinations.

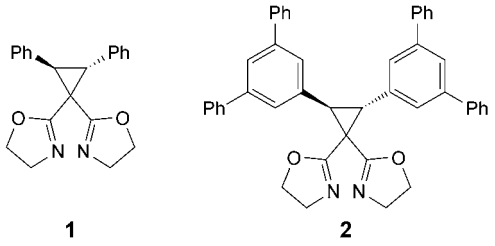
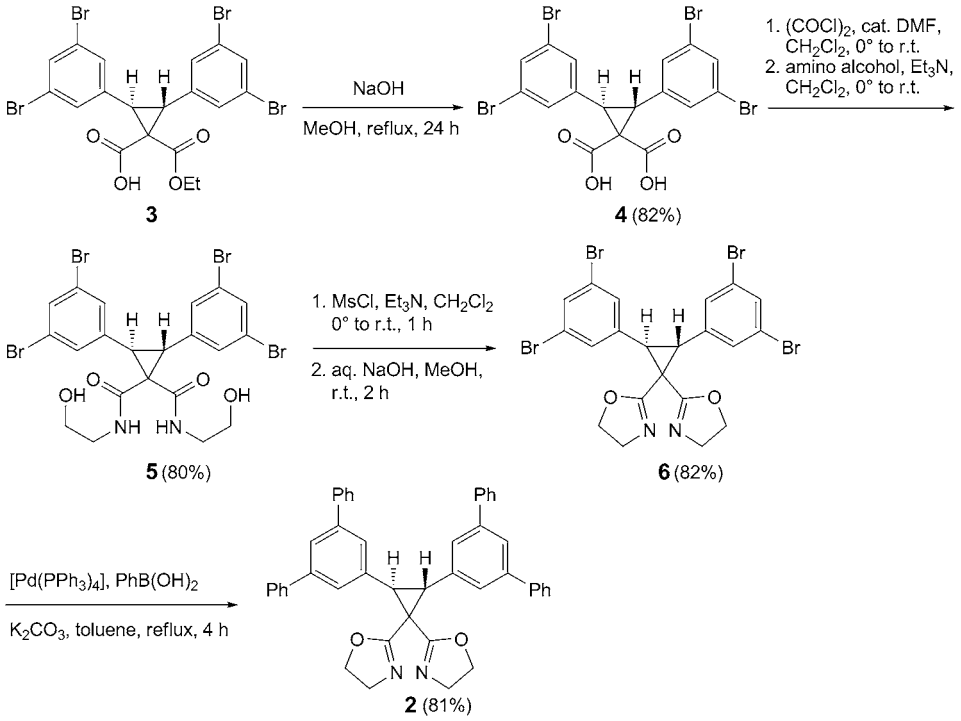


Figure. *Bis[dihydrooxazole] ligands*

Results and Discussion. – The synthetic route towards enantiomerically pure bis[dihydrooxazole] **2** started with acid ester **3** which was earlier described by our group (*Scheme*) [17]. The most widely used method to develop bis[dihydrooxazoles] is the reaction of diacid derivatives with chiral amino alcohols followed by a cyclization. According to this general procedure, acid ester **3** was first converted by saponification to the corresponding diacid **4** and then to the bis(acyl chloride) by treatment with oxalyl chloride. Without further purification, this bis(acyl chloride) was used in the next step. Within 1 h, with 2 equiv. of amino alcohol in the presence of triethylamine, the bis(acyl chloride) was converted smoothly into the corresponding bis(hydroxyamide) **5** [18]. The alcohol functions therein were further transformed into good leaving groups by treatment with mesyl chloride. Subsequent cyclization in an aqueous MeOH solution of sodium hydroxide gave the tetrabromo-substituted bis[dihydrooxazole] **6** in good yield (82%). The last step of our synthetic route was the introduction of four phenyl groups *via* a *Suzuki* cross-coupling reaction. Thus, **6** was treated with phenylboronic acid and K_2CO_3 in the presence of $[Pd(PPh_3)_4]$ in EtOH/H_2O/toluene 1:2:4 at reflux temperature, yielding tetraphenyl-substituted bis[dihydrooxazole] **2** in excellent yield (81%).

The palladium(0)-catalyzed asymmetric allylic alkylation is one of the most versatile methods for the formation of C–C bonds (for reviews about asymmetric allylic substitution, see [19]). We began with this catalytic test reaction to determine the efficiency of the new bis[dihydrooxazole] ligand **2**. The first substrate was 1,3-diphenylprop-2-en-1-yl acetate (**7**) in the reaction with dimethyl malonate (=dimethyl propanedioate), which is regarded as a standard test substrate for evaluating enantioselective catalysts (*Table 1*). The nucleophile was generated from dimethyl malonate (3 equiv.) in the presence of *N*,*O*-bis(trimethylsilyl)acetamide (BSA;

Scheme. *Synthesis of Bis[dihydrooxazole] Ligand* **2**

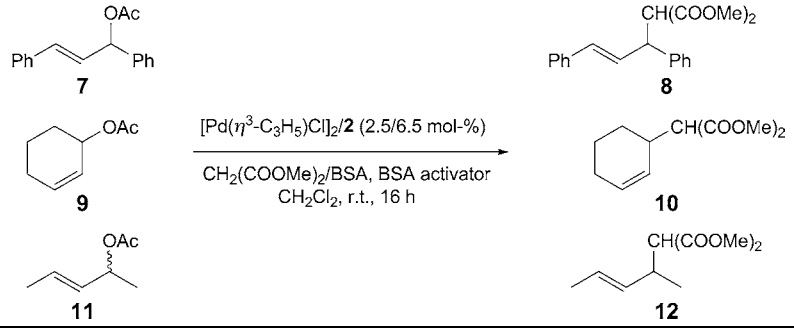


3 **4** (82%) **5** (80%) **6** (82%) **2** (81%)

3 equiv.) and BSA activator (0.1 mol-%). The catalytic system palladium(0)/bis[dihydrooxazole] **2** exhibited a high conversion but poor enantioselectivity (*Table 1*, *Entry 1*). When we used AcOLi as a BSA activator, a sharp decrease in conversion was obtained; however, the enantioselectivity was roughly the same (*Table 1*, *Entry 2*). Although highly selective catalysts have been developed for cyclic substrates, *e.g.*, *Trost*'s ligand, they generally exhibit low enantioselectivity in more hindered substrates, such as substrate **7**. Ligands with a broad substrate scope are very rare [20]. When we performed the reaction with our bis[dihydrooxazole] ligand **2**, we observed moderate enantioselectivity with low conversion (*Table 1*, *Entry 3*). To our disappointment, we observed no conversion when we used unhindered linear acetate **11** (*Table 1*, *Entry 4*).

The bis[dihydrooxazole] ligand **2** was further tested in Cu^{I}-catalyzed enantioselective reactions. The first reaction was enantioselective cyclopropanation of olefins. The enantioselective cyclopropanation of styrene (**13**) with ethyl diazoacetate is considered as another benchmark reaction to determine the efficiency of newly developed ligands [10a][21]. To prevent the formation of diethyl malonate, we added the solution of ethyl diazoacetate slowly over 5 h with a syringe pump to an excess of styrene (**13**). A moderate yield of **14** and **15** and poor enantioselectivity were observed (*Table 2*, *Entry 1*). Aziridines are very versatile building blocks in organic chemistry as they exhibit a similar reactivity pattern as epoxides [22]. An interesting methodology to obtain chiral aziridines is the Cu^{I}-catalyzed asymmetric aziridination of alkenes [23].

Table 1. *Pd^0-Catalyzed Asymmetric Allylic Alkylation of* **7**, **9**, *and* **11** *with Dimethyl Malonate in the Presence of Bis[dihydrooxazole] Ligand* **2**



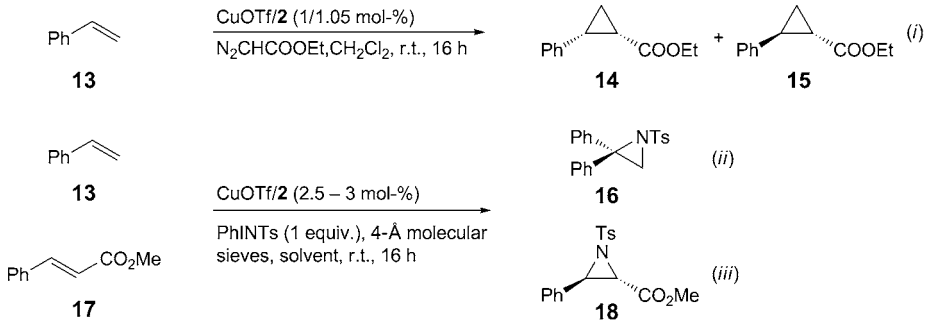
Entry	Substrate	BSA Activator	Yield[a]) [%]	ee[b])[c]) [%]
1	**7**	AcOK	89	22 (*S*)
2	**7**	AcOLi	19	18 (*S*)
3	**9**	AcOLi	2	52[d]) (*R*)
4	**11**	AcOLi	n.d.[e])	–

[a]) Isolated yield. [b]) Determined by HPLC analysis with a chiral stationary phase (*Chiralpak AD-H*). [c]) The absolute configuration was assigned by the sign of the optical rotation. [d]) Determined by GC analysis with a chiral stationary phase (*Supelco β-Dex*). [e]) n.d. = not determined.

Thus the catalytic asymmetric aziridination of styrene (**13**) and methyl cinnamate (**17**) was carried out with [(*p*-toluenesulfonyl)imino]phenyl-λ^3-iodane (=4-methyl-*N*-(phenyl-λ^3-iodanylidene)benzenesulfonamide = {[(4-methylphenyl)sulfonyl]imino}-phenyliodine; PhINTs) as a nitrene precursor at room temperature. In contrast with the asymmetric cyclopropanation reaction, the best yield was obtained in the Cu^I-catalyzed enantioselective aziridination of **13** (→**16**). Although the conversion was noteworthy, the enantioselectivity was very poor (*Table 2*, *Entry 2*). We obtained also poor results in the asymmetric aziridination of methyl cinnamate (**17**) in MeCN (→**18**; *Table 2*, *Entry 3*). Changing the solvent to benzene resulted in a slightly better result (*Table 2*, *Entry 4*).

In summary, our aim was to develop an efficient chiral bis[dihydrooxazole] ligand containing no stereogenic center at the dihydrooxazole moiety. Therefore, we focused on the backbone chirality by increasing the bulky groups at the chiral backbone group of a bis[dihydrooxazole] ligand to determine if the steric-hindrance effect played a role in asymmetric induction. For this purpose, we synthesized the new bis[dihydrooxazole] ligand **2** containing a chiral *trans*-(2*R*,3*R*)-2,3-bis-(3,5-diphenylphenyl)cyclopropylidene moiety as bulky backbone and evaluated this ligand in Pd^0-catalyzed asymmetric allylic alkylations, Cu^I-catalyzed cyclopropanations and Cu^I-catalyzed aziridinations. The best catalytic result with ligand **2** was obtained in the Pd^0-catalyzed asymmetric allylic alkylations (ee up to 52%). We demonstrated that the steric-hindrance effect of the bulky chiral backbone did not help to obtain acceptable enantioselectivities.

Table 2. *Cu^{I}-Catalyzed Enantioselective Reactions: Cyclopropanation and Aziridination of Styrene* (**13**) *and Aziridination of Methyl Cinnamate* (**17**) *in the Presence of Bis[dihydrooxazole] Ligand* **2**



Entry (*Eqn.*)	Solvent	Yield[a]) [%]	ee[b]) [%]	*cis*/*trans* ratio[c])	ee *cis*[c])[d]) [%]	ee *trans*[c])[d]) [%]
1 (*i*)	CH_2Cl_2	57		36 : 64	7 (1*S*,2*R*)	13 (1*S*,2*S*)
2 (*ii*)	C_6H_6	95	6 (2*R*)	–	–	–
3 (*iii*)	MeCN	11	*rac*	–	–	–
4 (*iii*)	C_6H_6	26	7 (2*R*,3*S*)	–	–	–

[a]) Isolated yield. [b]) Determined by HPLC analysis with a chiral stationary phase (*Chiralcel OD-H* or *Chiralpak AD-H*). The absolute configuration was assigned by the sign of the optical rotation. [c]) The *cis*/*trans* ratio and the enantioselectivity were determined by GC analysis with a chiral stationary phase (*Cyclosil-β*). [d]) The absolute configuration was assigned by the sign of the optical rotation.

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Experimental Part

General. All reactions were carried out under Ar in dry solvents under anh. conditions, unless stated otherwise. All reagents were purchased and used without purification, unless noted otherwise. Anal. TLC: *Macherey-Nagel-SIL-G-25-UV$_{254}$* plates. Flash chromatography (FC): *Rocc* silica gel (SiO_2; 0.040–0.063 mm). Anal. HPLC: *Agilent-1100* HPLC system with DAD detection; t_R in min. M.p.: *Kofler* melting-point apparatus. Optical rotations: *Perkin-Elmer-241* polarimeter. IR Spectra: *Perkin-Elmer Spectrum-1000* FT-IR spectrometer with a pike miracle horizontal attenuated total reflectance (HATR) module; in cm^{-1}. ^{1}H- and ^{13}C-NMR Spectra: *Bruker-Avance-300* or *Bruker-DRX-500* spectrometer as indicated; δ in ppm rel. to Me_4Si as internal standard, *J* in Hz; attached-proton test for ^{13}C-NMR. EI-MS: *Hewlett-Packard-5988A* mass spectrometer for EI-MS; *Agilent-1100* HPLC with quaternary pump, DAD and single-quadrupole MS detector type *VL* with an API-ES source, and *Phenomenex-Luna-C$_{18}$*(2) column (250 × 4.6 mm, particle size 5 μm) for LC/ESI-MS; quadrupole/orthogonal-acceleration time-of-flight (Q/oaTOF) tandem mass spectrometer (*qTof 2*, *Micromass*, Manchester, UK), equipped with a standard electrospray-ionization (ESI) interface for HR-ESI-MS; in *m*/*z*.

*(2*R*,3*R*)-2,3-Bis(3,5-dibromophenyl)cyclopropane-1,1-dicarboxylic Acid* (**4**). To a soln. of acid ester **3** [17] (0.83 g, 1.33 mmol) in MeOH (5 ml) was added 2N aq. NaOH (5 ml). The mixture was refluxed for 24 h, and subsequently, MeOH was evaporated. The residue was cooled to 0° and acidified with 6N aq. HCl. The acidified mixture was extracted with Et_2O (3 × 20 ml), and the org. phase dried (Na_2SO_4) and concentrated: **4** (0.65 g, 82%). Colorless oil-like foam. The crude **4** was used in the next step without

further purification. $[\alpha]_D^{20} = +18.2$ ($c = 1.0$, $CHCl_3$). IR (HATR): 2929, 1700, 1583, 1552, 1409, 1361, 1253, 1211, 1134, 1100, 1052, 853, 739, 674, 656. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.72 (*s*, 2 H); 7.35 (*s*, 4 H); 7.55 (*s*, 2 H). ^{13}C-NMR (75.4 MHz, $CDCl_3$): 35.53 (CH); 45.18 (C); 123.02 (C); 132.06 (CH); 133.34 (CH); 141.09 (C); 168.65 (C). ESI-MS: 598.7 ($[M+H]^+$), 615.8 ($[M+NH_4]^+$).

*(2*R,*3*R*)-2,3-Bis(3,5-dibromophenyl)*-N,N′*-bis(2-hydroxyethyl)cyclopropane-1,1-dicarboxamide* (**5**). Oxalyl chloride (0.388 g, 3.06 mmol) was added dropwise over 20 min to a soln. of **4** (0.63 g, 1.05 mmol) and DMF (30 µl) in CH_2Cl_2 (5 ml) at 0° under Ar. The mixture was allowed to warm to r.t. and stirred for another 5 h. The volatiles were evaporated, affording the crude acyl chloride. The acyl chloride was dissolved in CH_2Cl_2 (6 ml), and this soln. added dropwise over 40 min to a mixture of 2-aminoethanol (0.116 g, 1.09 mmol) and Et_3N (0.481 g, 4.75 mmol) in CH_2Cl_2 (12 ml). After 1 h, the resulting suspension was diluted with CH_2Cl_2 and washed with 1N HCl (15 ml), sat. $NaHCO_3$ soln. (15 ml), and brine (15 ml). The combined org. phase was dried (Na_2SO_4) and concentrated, and the crude product purified by FC (CH_2Cl_2/MeOH 94:6): 0.50 g (80%) of pure **5**. White solid. M.p. 120–122°. $[\alpha]_D^{20} = +43$ ($c = 1.0$, EtOH). IR (HATR): 3282, 3069, 2175, 1633, 1583, 1550, 1412, 1304, 1209, 1054, 854, 740, 679. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.85–2.95 (*m*, 2 H); 3.05–3.25 (*m*, 4 H); 3.3–3.4 (*m*, 2 H); 3.45 (*s*, 2 H); 7.1 (*t*, J = 5.5, 2 H); 7.25 (*d*, $J = 1.5$, 4 H); 7.35 (*t*, $J = 1.5$, 2 H). ^{13}C-NMR (75.4 MHz, $CDCl_3$): 32.41 (CH); 42.63 (CH_2); 48.93 (C); 61.38 (CH_2); 122.93 (C); 130.38 (CH); 133.21 (CH); 138.88 (C); 166.15 (C). HR-EI-MS: 684.8242 ($C_{21}H_{20}Br_4N_2O_4^+$; calc. 684.8231).

*2,2′-[(2*R,*3*R*)-2,3-Bis(3,5-dibromophenyl)cyclopropylidene]bis[4,5-dihydrooxazole]* (**6**). A mixture of **5** (0.45 g, 0.66 mmol) and Et_3N (0.748 g, 7.4 mmol) in CH_2Cl_2 (12 ml) was stirred at 0°. MsCl (0.151 g, 1.32 mmol) was added dropwise over 10 min. The mixture was allowed to warm to r.t. and stirred for an additional hour. The mixture was washed with H_2O, and the org. phase dried (Na_2SO_4) and concentrated to give the corresponding crude bis-mesylate as a yellow oil. The crude bis-mesylate was dissolved in MeOH (10 ml) and treated with 1N aq. NaOH (2 ml) at r.t. for 2 h. After evaporation of MeOH, CH_2Cl_2 was added, and the mixture washed with H_2O. The org. phase was dried (Na_2SO_4) and concentrated, and the crude product purified by FC (CH_2Cl_2/MeOH 95:5): 0.35 g (82%) of pure **6**. Colorless viscous oil-like foam. $[\alpha]_D^{20} = +43.49$ ($c = 1.0$, $CHCl_3$). IR (HATR): 2916, 2341, 2005, 1663, 1584, 1550, 1412, 1256, 1151, 1090, 990, 924, 854, 743, 677. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.36–3.46 (*m*, 2 H); 3.49 (*s*, 2 H); 3.58–3.7 (*m*, 2 H); 3.86–3.95 (*m*, 4 H); 7.25 (*d*, $J = 1.51$, 4 H); 7.38 (*t*, $J = 1.51$, 2 H). ^{13}C-NMR (75.4 MHz, $CDCl_3$): 33.71 (CH); 34.35 (C); 54.07 (CH_2); 68.38 (CH_2); 122.57 (C); 130.60 (CH); 133.11 (CH); 138.64 (C); 162.25 (C). ESI-MS: 648.7 ($[M+H]^+$). HR-ESI-MS: 648.8004 ($C_{21}H_{16}Br_4N_2O_2^+$; calc. 648.8020).

*2,2′-[(2*R,*3*R*)-2,3-Bis([1,1′:3′:1″-terphenyl]-5′-yl)cyclopropylidene]bis[4,5-dihydrooxazole]* (**2**). Phenylboronic acid (0.123 g, 0.99 mmol) in EtOH (2.8 ml) and 2M aq. K_2CO_3 (5 ml) was added to a soln. of **6** (0.108 g, 0.166 mmol) and $[Pd(PPh_3)_4]$ (0.024 g, 0.02 mmol) in toluene (11 ml) under Ar. The mixture was refluxed for 4 h. After addition of H_2O, the aq. layer was extracted with CH_2Cl_2 (3 × 50 ml), the combined org. phase washed with brine (10 ml), dried ($MgSO_4$), and concentrated, and the crude product purified by FC (toluene/AcOEt/Et_3N 1:1:0.01): 0.085 g (81%) of pure **2**. Light yellow viscous oil. $[\alpha]_D^{20} = +74.2$ ($c = 1.0$, $CHCl_3$). IR (HATR): 3038, 2972, 2360, 1661, 1595, 1576, 1497, 1457, 1356, 1258, 1196, 1146, 1077, 993, 930, 907, 759, 730, 700. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.4–3.55 (*m*, 2 H); 3.65–3.77 (*m*, 2 H); 3.85–3.94 (*m*, 4 H); 4.04 (*s*, 2 H); 7.25–7.42 (*m*, 12 H); 7.55–7.62 (*m*, 12 H); 7.66 (*t*, (app. *s*), 2 H). ^{13}C-NMR (75.4 MHz, $CDCl_3$): 34.41 (C); 34.70 (CH); 54.21 (CH_2); 68.02 (CH_2); 124.80 (CH); 126.72 (CH); 127.16 (CH); 127.50 (CH); 128.81 (CH); 136.25 (C); 140.81 (C); 141.45 (C); 163.41 (C). ESI-MS: 637 ($[M+H]^+$). HR-ESI-MS: 637.2876 ($C_{45}H_{36}N_2O_2^+$; calc. 637.2849).

Pd^0-Catalyzed Asymmetric Allylic Alkylation: General Procedure. Ligand **2** (0.05 mmol) and $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (0.02 mmol) were dissolved in degassed CH_2Cl_2 under Ar by using *Schlenk* techniques. The mixture was stirred for 1 h at 50° and then cooled to r.t. Racemic 1,3-diphenylprop-2-en-1-yl acetate (**7**; 1 mmol) in CH_2Cl_2 was added, and the mixture stirred at r.t. for 30 min. Finally, a soln. of BSA (3 mmol), AcOLi (0.1 mmol), and dimethyl malonate (3 mmol) were added, and the mixture was stirred for 16 h at r.t. Next, Et_2O was added, the org. phase washed with sat. NH_4Cl soln, dried ($MgSO_4$), and concentrated, and the crude product purified by FC (SiO_2, hexane/AcOEt 9:1) to afford the target compound. All adducts were fully characterized by comparison of their spectral data with those reported in the literature. The absolute configurations were assigned *via* correlation of their optical rotation with literature values [24].

*Dimethyl 2-[(2*E*)-1,3-Diphenylprop-2-en-1-yl]propanedioate* (**8**): The ee was determined by HPLC (*Chiralpak AD-H* (250 × 4.6 mm, particle size 10 μm), hexane/EtOH 7:3, flow rate 1 ml/min, T = 35°): t_R 9.7 ((−)-(*S*)-**8**), and 15.2 ((+)-(*R*)-**8**).

Dimethyl 2-(Cyclohex-2-en-1-yl)propanedioate (**10**): The ee was determined by GC (*Supelco β-Dex 120* (30m × 0.25 mm × 0.25 μm), 120° (isothermic)): t_R 36.7 ((−)-(*S*)-**10**) and 37.2 ((+)-(*R*)-**10**).

*Dimethyl 2-[(2*E*)-1-Methylbut-2-en-1-yl]propanedioate* (**12**): The ee was determined by ^{1}H-NMR (300 MHz, $CDCl_3$) with (+)-Eu(hfc)$_3$ as a resolving agent.

Asymmetric Cyclopropanation: General Procedure. A suspension of CuOTf · ½ C_6H_6 (0.01 mmol) and ligand **2** (0.012 mmol) in CH_2Cl_2 was stirred under Ar at r.t. After 1 h, styrene (**13**; 7.5 mmol) was added to the resulting green soln. Next, ethyl diazoacetate (1 mmol) was slowly added over 5 h *via* a syringe pump. The mixture was stirred at r.t. overnight. The excess **13** and CH_2Cl_2 were evaporated and the crude product was purified by FC (pentane/AcOEt 96:4) to afford the cyclopropane esters. All adducts were fully characterized by comparison of their spectral data with those reported in the literature. The absolute configurations were assigned *via* correlation of their optical rotation with literature values [10a].

Ethyl cis- *and* trans-*2-Phenylcyclopropanecarboxylate* (**14** and **15**): The ee was determined by GC (*Cyclosil B* (30 m × 0.25 mm × 0.25 μm); 50° for 3 min, then increasing to 240° (5°/min), and then 240° for 3 min): t_R 26.6 ((1*S*,2*R*)-**14**), 26.88 ((1*R*,2*S*)-**14**), 27.93 ((1*R*,2*R*)-**15**), and 29.99 ((1*S*,2*S*)-**15**).

Asymmetric Aziridination: General Procedure. Ligand **2** (0.150 mmol) and CuOTf · ½ C_6H_6 (0.125 mmol) were dissolved in MeCN or benzene (1 ml) and stirred for 1 h at r.t. To this soln. were added styrene (**13**; 25 mmol) or methyl cinnamate (**17**; 25 mmol) and activated 4-Å molecular sieves. Subsequently, PhI = NTs (5 mmol) was added, and the mixture was stirred at r.t. for 16 h. The crude product was purified by FC (SiO_2, hexane/AcOEt 9:1). The adducts **16** and **18** were fully characterized by comparison of their spectral data with those reported in the literature. The absolute configurations were assigned *via* correlation of their optical rotation with literature values [23a][25].

1-[(4-Methylphenyl)sulfonyl]-2-phenylaziridine (**16**): The ee was determined by HPLC (*Chiralpak AD-H*, hexane/EtOH 9:1, flow rate 1 ml/min, *T* 35°): t_R 14.6 ((*R*)-**16**) and 15.2 ((*S*)-**16**).

Methyl 1-[(4-Methylphenyl)sulfonyl]-3-phenylaziridine-2-carboxylate (**18**): The ee was determined by HPLC: *Chiralcel OD-H* (250 × 4.6 mm, particle size 10 μm), hexane/EtOH 9:1, flow rate 1 ml/min, *T* 35°): t_R 10.7 ((2*R*,3*S*)-**18**) and 16.4 ((2*S*,3*R*)-**18**).

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