Towards Asymmetric Catalysis in the Major Groove of 1,1′-Binaphthalenes

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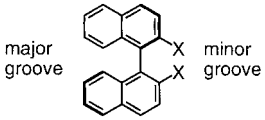
Four new diphosphane ligands, (*R*)-**4**, (*R*)-**5**, (*S*)-**6**, and (*R*)-**7** (*Schemes 3, 4, 6,* and *7*), featuring metal-coordination sites located in the major groove of chiral 1,1′-binaphthalene clefts, were prepared in enantiomerically pure form. The performance of this new class of ligands was tested in enantioselective, Pd-catalyzed allylic alkylation reactions with acyclic and cyclic methyl carbonates **28**–**30** as substrates under various reaction conditions (*Schemes 8* and *9*). Using sodium phenyl sulfinate as a nucleophile, the reactivity of the catalysts formed with the new ligands and suitable palladium precursors was found satisfactory (> 90%); however, the ee values were in all cases poor (< 4%). Slightly better results were obtained using anions of dimethyl malonate as nucleophiles, but, also in these cases, the ee values never exceeded 17% (*Table*). ^{31}P-NMR-Spectroscopic investigations revealed the formation of multiple-catalyst species in solution (*Fig. 2*), and molecular modeling suggested a lack of embedding of the coordinated substrate in a 'chiral pocket' (*Fig. 3*), which probably accounts for the observed low level of enantioselectvity.

1. Introduction. – Asymmetric transformations have seen tremendous application in the total synthesis of natural products and pharmaceuticals over the past decades [1]. A great variety of chiral transition-metal complexes, tunable by synthesis, have been developed for asymmetric catalysis [2][3], leading to an economic use of matter and energy [4]. Many of these complexes are formed by non-racemic C_2-symmetrical ligands derived from 1,1′-binaphthalene such as **1a**–**e**; they include BINOL (=1,1′-binaphthalene-2,2′-diol; **1a**) and BINAP (2,2′-bis(diphenylphosphanyl)-1,1′-binaphthalene; **1b**) as the most prominent representatives [5]. In nearly all catalysts that contain 1,1′-binaphthalene ligands the transition metal is complexed in the minor groove of the chiral cleft. Only recently, a few 1,1′-binaphthalene systems bearing the catalytic sites in the major groove have been reported for successful applications in catalysis [6].



1a X = OH
1b X = PPh_2
1c X = $OPPh_2$
1d X = $P(O)Ph_2$
1e X = NH_2

Molecular-recognition studies with conformationally preorganized, cleft-type molecular receptors featuring binding sites in the 6,6′-positions of 1,1′-binaphthalene moieties recently revealed a high potential of the major groove for chiral selection events [7]. High enantioselectivities $\Delta(\Delta G^0)$ (difference in binding free enthalpy between diastereoisomeric complexes) up to 6.9 kJ mol^{-1} were measured for the complexation of the enantiomers of *N*-(benzyloxycarbonyl)-protected aspartic and

glutamic acid by receptor (*R*)-**2** ($CDCl_3$, $T = 300$ K; *Fig. 1*). These results encouraged us to explore the use of the major groove of 1,1′-binaphthalenes as chiral metal-binding site for asymmetric catalysis. Molecular modeling indicated that (*R*)-**3**, with two PPh_2 residues (as in BINAP (**1b**)) attached *via m*-phenylene spacers to the 7,7′-positions in the major groove would provide a suitable asymmetric coordination site for catalytically active transition-metal centers.

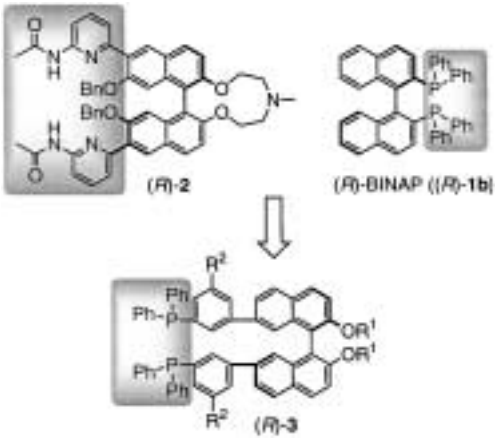
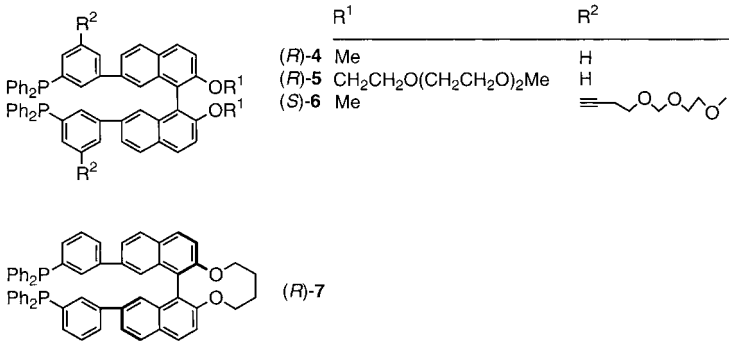


Fig. 1. *From molecular recognition in the major groove of 1,1′-binaphthalenes to new ligands for asymmetric catalysis*

The Pd-catalyzed allylic substitution reaction was chosen as a test reaction for assessing the performance of the new class of ligands (for an overview on Pd-catalyzed allylation reactions, see [8–14]). In addition to the parent structure (*R*)-**4**, a series of modified ligands was included in this exploratory study. *Hayashi* [15a], *Ito* and coworkers [15b,c], and *Trost et al.* [8j–k] had described that cation-binding residues attached to the chiral ligand favorably influenced both the reaction rate and selectivity. Therefore, two ligands with oligoether-derived cation-complexation sites, (*R*)-**5** and (*S*)-**6**, were included in this investigation. Our molecular-recognition studies had demonstrated the importance of ligand preorganization for chiral discrimination in the major groove. Therefore, we also prepared ligand (*R*)-**7**, in which rotation about the chirality axis passing through C(1) and C(1′) of the 1,1′-binaphthalene moiety is restricted by bridging the 2,2′-positions in the minor groove.

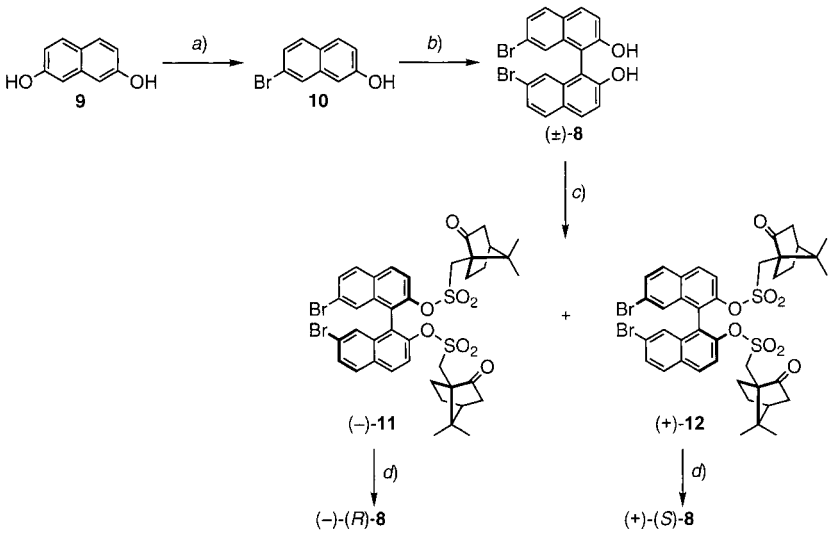
Here, we report the syntheses of the new ligands (*R*)-**4**, (*R*)-**5**, (*S*)-**6**, and (*R*)-**7**, and their use in enantioselective Pd-catalyzed allylic alkylations of dimethyl-malonate anions.

2. Results and Discussion. – 2.1. *Synthesis.* The optically active 1,1′-binaphthalene precursors for all new ligands, (*R*)- and (*S*)-**8**, were prepared starting from naphthalene-2,7-diol (**9**) [16], which was transformed with $PPh_3 \cdot Br_2$ into 7-bromonaphthalen-2-ol (**10**; 49% yield; *Scheme 1*) [17]. Oxidative coupling of **10** with catalytic amounts (1–2 mol-%) of freshly prepared [CuCl(OH)(TMEDA)] [18] (TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) in CH_2Cl_2 afforded (±)-**8** in 96%. The optical



resolution of (±)-**8** was achieved by flash chromatography (SiO_2; CH_2Cl_2/AcOEt 99:1) of the diastereoisomeric camphorsulfonates (−)-**11** and (+)-**12** [19] obtained in quantitative yield by treatment of (±)-**8** with (−)-camphor-10-sulfonyl chloride [7]. For both esters, the diastereoisomeric excess was determined as de >99.5% by HPLC (SiO_2; CH_2Cl_2/AcOEt 97:3). Saponification subsequently afforded (*R*)- and (*S*)-**8** in excellent yield (99%).

Scheme 1. *Synthesis of* (R)-**8** *and* (S)-**8**

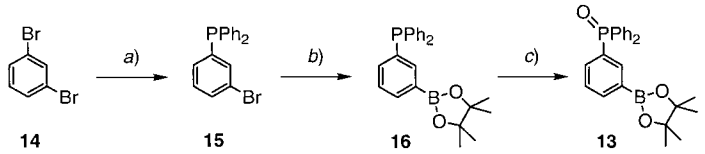


a) $Ph_3P \cdot Br_2$, 300°, 1.5 h; 49%. *b*) [CuCl(OH)(TMEDA)], air, CH_2Cl_2, 20°, 12 h; 96%. *c*) (−)-Camphor-10-sulfonyl chloride, Et_3N, CH_2Cl_2, 0°, 3 h; quant. yield. *d*) 1M NaOH, THF/MeOH, 60°, 8 h; 99%.

To introduce the metal-coordinating phosphane sites at the major groove, the *P*-protected building block **13** was prepared (*Scheme 2*). Mono-lithiation of 1,3-dibromobenzene (**14**) and quenching with chloro(diphenyl)phosphane afforded **15** (90%) [20]. A second lithiation, followed by quenching of the metallated species with trimethyl borate and subsequent acid-promoted transesterification with pinacol gave

boronate **16** (43%). To prevent the inhibition of the catalytic cycle of the planned *Suzuki* cross-coupling reaction [12], **16** was protected as the corresponding phosphane oxide **13** according to the method reported by *Ondrejovic* and co-workers [22], with an important modification. The transformation was achieved cleanly within 15 min by bubbling O_2 through a solution of **16** in MeCN at reflux in the presence of catalytic amounts (1–2 mol-%) of $Fe(SCN)_3$ and, importantly, a trace of I_2 to provide quantitatively **13** after washing with 5% aq. Na_2SO_3 solution.

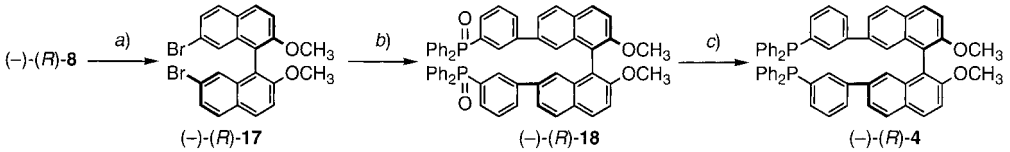
Scheme 2. *Synthesis of Boronate* **13**



a) BuLi, THF, −90°, 45 min, then Ph_2PCl, −90° → 20°; 90%. *b*) BuLi, THF, −90°, 1 h, then $(MeO)_3B$, −90° → 20°, then pinacol, NH_4Cl, PhMe, Δ, 2 h; 43%. *c*) $Fe(SCN)_3$, O_2, trace of I_2, MeCN, Δ, 15 min; quant. yield.

The synthesis of ligand (*R*)-**4** was completed by dimethylation of (*R*)-**8** with MeI to give (*R*)-**17** (80%), followed by *Suzuki* cross-coupling with boronate **13** (*Scheme 3*). The resulting intermediate bis(phosphane oxide) (*R*)-**18** was reduced with $LiAlH_4$ in the presence of finely ground, dry $CeCl_3$ to bis-phosphane (*R*)-**4** (91% over two steps) [23].

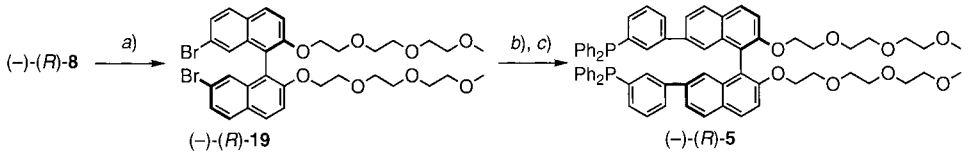
Scheme 3. *Synthesis of Ligand* (R)-**4**



a) MeI, K_2CO_3, MeCN, 80°, 8 h; 80%. *b*) **13**, $[PdCl_2(dppf)\cdot CH_2Cl_2]$ (dppf = 1,1′-bis(diphenylphosphanyl)ferrocene), Na_2CO_3, PhH/EtOH/H_2O, 80°, 3 h. *c*) $CeCl_3$, $LiAlH_4$, THF, 40°, 1.5 h; 91% (from (*R*)-**17**).

Ligand (*R*)-**5** was prepared in a similar way (*Scheme 4*). Dialkylation of (*R*)-**8** with the methanesulfonate of triethyleneglycol monomethyl ether [24] and Cs_2CO_3 in DMF afforded (*R*)-**19** (81%). *Suzuki* cross-coupling reaction with **13**, followed by reduction, gave (*R*)-**5** (48%).

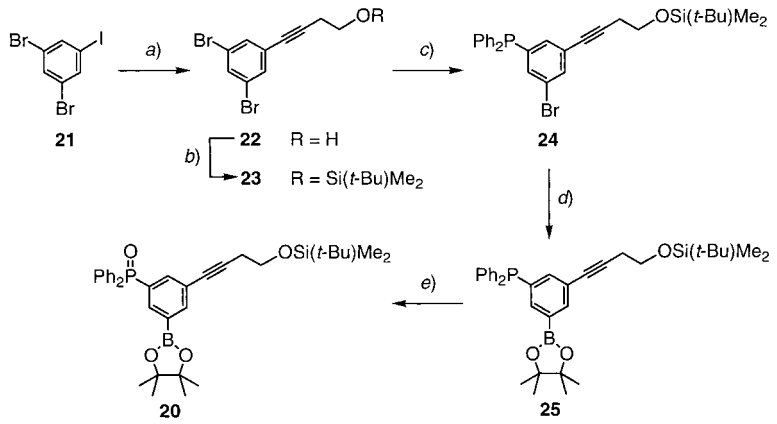
Scheme 4. *Synthesis of Ligand* (R)-**5**



a) $MeSO_2O(CH_2CH_2O)_3Me$, Cs_2CO_3, DMF, 100°, 4 h; 81%. *b*) **13**, $[PdCl_2(dppf)\cdot CH_2Cl_2]$, Na_2CO_3, PhH/EtOH/H_2O, 80°, 3 h. *c*) $CeCl_3$, $LiAlH_4$, THF, 40°, 1.5 h; 48% (2 steps).

For the synthesis of ligand (*S*)-**6**, boronate **20** was prepared starting from 1,3-dibromo-5-iodobenzene (**21**; *Scheme 5*). *Sonogashira* cross-coupling reaction [25] of **21** with but-3-ynol in Et_3N selectively afforded alcohol **22** (90%), which was quantitatively converted into silyl ether **23** with (*t*-Bu)Me_2SiCl and imidazole in DMF (*Scheme 5*). Mono-lithiation and quenching with chloro(diphenyl)phosphane gave **24** (78%), which was transformed into boronate **25** (44%) *via* lithiation, reaction with $(MeO)_3B$, and subsequent acid-promoted transesterification with pinacol. Oxidation as described above provided **20** in moderate yield (47%).

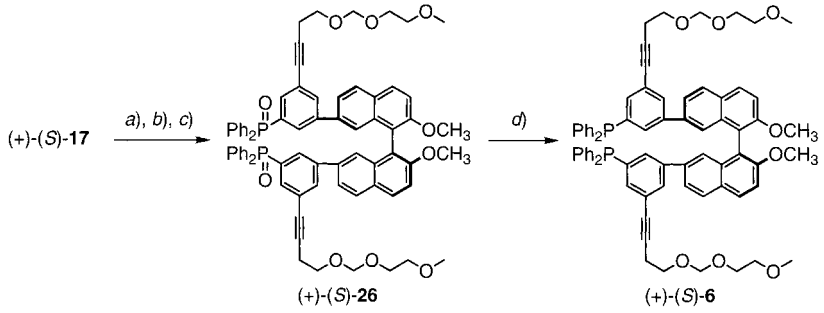
Scheme 5. *Synthesis of Boronate* **20**



a) But-3-ynol, [$PdCl_2(PPh_3)_2$], CuI, Et_3N, 20°, 1.5 h; 90%. *b*) (*t*-Bu)Me_2SiCl, imidazole, DMF, 20°, 16 h; 99%. *c*) BuLi, THF, −90°, 30 min, then Ph_2PCl, −90° → 20°; 78%. *d*) BuLi, THF, −90°, 30 min, then $(MeO)_3B$, −90° → 20°, then pinacol, NH_4Cl, PhMe, Δ, 2 h; 44%. *e*) $Fe(SCN)_3$, O_2, trace of I_2, MeCN, Δ, 45 min; 47%.

Suzuki cross-coupling of (*S*)-**17** with boronate **20**, followed by silyl-ether deprotection with Bu_4NF and attachment of (2-methoxyethoxy)methyl (MEM) residues with MEM-Cl and *Hünig*'s base (EtN(i-Pr)$_2$) in CH_2Cl_2 afforded (*S*)-**26** in 49% yield (over three steps; *Scheme 6*). Reduction of (*S*)-**26** was best achieved with $HSiCl_3$ and Bu_3N in dry xylenes at 140°, providing ligand (*S*)-**6** in high yield (83%) [26].

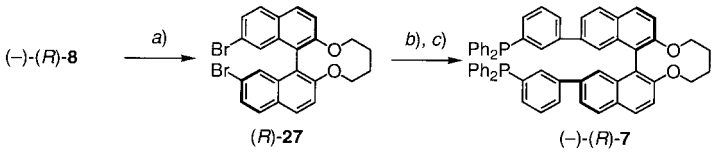
Scheme 6. *Synthesis of Ligand* (S)-**6**



a) **20**, [$PdCl_2$(dppf)], Na_2CO_3, PhH/EtOH/H_2O, 80°, 3 h. *b*) Bu_4NF, THF, 0°, 1.5 h. *c*) MEM-Cl, EtN(i-Pr)$_2$, CH_2Cl_2, 0° → 20°, 16 h; 49% (from (*S*)-**17**). *d*) $HSiCl_3$, Bu_3N, xylenes, 140°, 3 h; 83%.

Preparation of the conformationally enforced ligand (*R*)-**7** was achieved by macrocyclization of (*R*)-**8** with 1,4-dichlorobutane under high dilution and *Finkelstein* conditions to afford (*R*)-**27** as an intermediate (*Scheme 7*). *Suzuki* cross-coupling with **13**, followed by reduction with $HSiCl_3$, gave (*R*)-**7** (82% over two steps).

Scheme 7. *Synthesis of Ligand* (R)-**7**

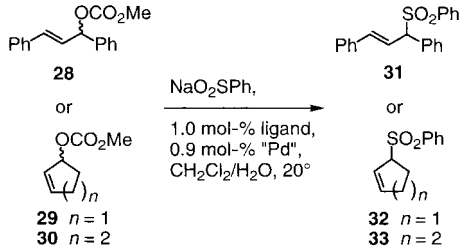


a) 1,4-Dichlorobutane, Cs_2CO_3, NaI, MeCN, Δ, 16 h; *ca.* 64%. *b*) **13**, [$PdCl_2$(dppf)], Na_2CO_3, PhH/EtOH/H_2O, 80°, 3 h. *c*) $HSiCl_3$, Bu_3N, xylenes, 140°, 3 h; 82% (2 steps).

2.2. *Catalysis Studies.* Catalysis studies were undertaken to investigate the performance of the new ligands in the Pd-catalyzed allylic substitution reactions with various nucleophiles and substrates (*cf. Schemes 8* and *9*). The active Pd-ligand species was prepared *in situ* by mixing a Pd-complex precursor ([Pd_2(dba)$_3$] (dba = dibenzylideneacetone) or [{(η^3-C_3H_5)PdCl}$_2$]) with ligands (*R*)-**4** to (*R*)-**7**, followed by equilibration of the catalyst solution for 20 min at the reaction temperature under an inert atmosphere. The substrate and nucleophile were then added, and the mixtures were stirred for the indicated amount of time and then submitted to extractive workup and column chromatography to afford the products (isolated yields).

In a series of test reactions, the Pd-catalyzed allylic alkylation of sodium benzenesulfinate (NaO_2SPh) with the allylic methyl carbonates **28**–**30** was investigated in the biphasic solvent mixture CH_2Cl_2/H_2O at 20° (*Scheme 8*) [8j]. All substrates were converted in good yields (> 90%) to the corresponding allylic phenyl sulfones **31**–**33**, respectively, within 12 to 24 h, with less than 1 mol-% of catalyst prepared from ligands (*R*)-**4** to (*R*)-**7** and [Pd_2(dba)$_3$]. When ligands (*R*)-**4** and (*R*)-**7** were used, tetrahexylammonium bromide (THAB) was added, since, in the absence of the phase-transfer catalyst (PTC), the allylations did not proceed under otherwise identical conditions. No PTC was needed when catalysts prepared from ligands (*R*)-**5** or (*S*)-**6** were used. Although the reactivities and stabilities of the catalysts formed with the new ligands (*R*)-**4** to (*R*)-**7** were satisfactory, they exhibited an almost complete

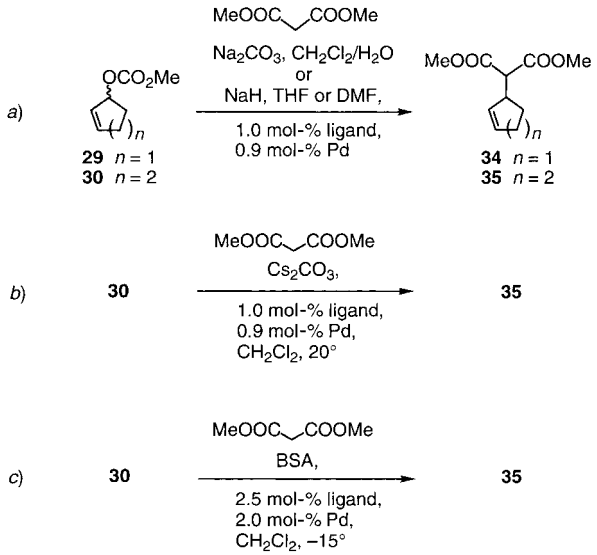
Scheme 8. *Formation of Sulfones* **31**–**33** *by Pd-Catalyzed Allylic Alkylation of Sodium Sulfinate with Acyclic and Cyclic Methyl Carbonates* **28**–**30**, *Respectively.* Catalysts were prepared from ligands (*R*)-**4** to (*R*)-**7** and [Pd_2(dba)$_3$]. In the reactions with (*R*)-**4** and (*R*)-**7**, tetrahexylammonium bromide (THAB) was added as PTC.



lack of enantioselectivity. A maximum ee value of *ca.* 4% was observed in the allylations with the cyclic substrate **30** and the ligands (*S*)-**6** or (*R*)-**7** and $[Pd_2(dba)_3]$. In all other cases, the ee values were even lower (0–2%) (for the determination of the ee values see *Exper. Part*).

Since phenyl sulfinate is a rather small nucleophile, we decided to investigate other, bulkier nucleophiles, in particular, salts of dialkyl malonate, expecting higher selectivities in the allylic alkylation reactions. A variety of reaction conditions (changes in solvent, base for malonate-anion formation, temperature, additives) have been reported in recent years for the Pd-catalyzed asymmetric allylation of dialkyl-malonate anions [27]. The results of the catalysis studies with the new ligands and sodium dimethyl malonate and the cyclic substrates **29** and **30** under different reaction conditions are summarized in *Scheme 9*,*a*, and in the *Table*.

Scheme 9. *Synthesis of Malonate Derivatives* **34** *and* **35** *by Pd-Catalyzed Allylic Alkylation of Sodium Dimethyl Malonate with Cyclic Methyl Carbonates* **29** *and* **30**, *Respectively.* For detailed conditions, see *Table.*



When the reactions were carried out with a catalyst (0.9 mol-%) prepared from (*R*)-**4** and $[\{(\eta^3\text{-}C_3H_5)PdCl\}_2]$ and Na_2CO_3 as the base in combination with THAB in CH_2Cl_2/H_2O, only hydrolysis of the starting materials was observed (*Table*, *Entry 1*). Ligand (*R*)-**5**, featuring additional polyether cation-binding residues in the 2,2′-positions of the minor groove, gave slightly better results to provide the desired product **35** in 11% yield after 15 h (*Table*, *Entry 2*).

The use of sodium malonate, generated with NaH, together with a catalyst prepared from (*R*)-**7** proved significantly more efficient. In either THF or DMF, yields of up to *ca.* 90% of malonate **35** were obtained after 16 h (*Table*, *Entries 4* and *6*). The product from the reaction in THF showed an ee value of 6% ((*S*)-isomer; *Table*, *Entry 6*); however, when the reaction was stopped early (2.5 h, 27% yield), an ee value of 17% was observed (*Table*, *Entry 5*).

Table. *Pd-Catalyzed Allylic Alkylations of* a) *Sodium Dimethyl Malonate*[a]), b) *Cesium Dimethyl Malonate*[a]), *and* c) *Dimethyl Malonate with* N,O-*Bis(trimethylsilyl)acetamide as Base*[b])

Entry	Type	Ligand	Substrate	Solvent	Time, Temp.	Yield[c]) (ee)[d])
1	*a*	(*R*)-**4**	**29**	CH_2Cl_2/H_2O + THAB[e])	48 h, 20°	hydrolysis only
2	*a*	(*R*)-**5**	**30**	CH_2Cl_2/H_2O	15 h, 20°	11% (0.5% (*S*))
3	*a*	(*R*)-**7**	**30**	DMF	2.5 h, 0°	<5% (n.d)
4	*a*	(*R*)-**7**	**30**	DMF	16 h, 0°	87% (9% (*S*))
5	*a*	(*R*)-**7**	**30**	THF	2.5 h, 20°	27% (17% (*S*))
6	*a*	(*R*)-**7**	**30**	THF	16 h, 20°	88% (6% (*S*))
7	*a*	(*S*)-**6**	**30**	CH_2Cl_2/H_2O	16 h, 20°	79% (13% (*R*))
8	*a*	(*S*)-**6**	**29**	CH_2Cl_2/H_2O	16 h, 20°	89% (8% (*R*))
9[f])	*a*	(*S*)-**6** (1 mol-%)	**30**	CH_2Cl_2/H_2O	20 h, 0°	95% (13% (*R*))
10[f])	*a*	(*S*)-**6** (3 mol-%)	**30**	CH_2Cl_2/H_2O	20 h, 0°	94% (14% (*R*))
11[f])	*a*	(*S*)-**6** (5 mol-%)	**30**	CH_2Cl_2/H_2O	20 h, 0°	53% (15% (*R*))
12	*b*	(*S*)-**6**	**30**	CH_2Cl_2	24 h, 20°	79% (15% (*R*))
13	*b*	(*R*)-**7**	**30**	CH_2Cl_2	18 h, 20°	64% (17% (*S*))
14	*c*	(*S*)-**6**	**30**	CH_2Cl_2	20 h, −15°	98% (8% (*R*))
15	*c*	(*R*)-**7**	**30**	CH_2Cl_2	20 h, −15°	99% (2% (*S*))

[a]) The catalyst is formed *in situ* with 1.0 mol-% ligand and 0.45 mol-% $[\{(\eta^3\text{-}C_3H_5)PdCl\}_2]$. [b]) The catalyst is formed *in situ* with 2.5 mol-% ligand and 1.0 mol-% $[\{(\eta^3\text{-}C_3H_5)PdCl\}_2]$. [c]) Isolated yields are given. [d]) Enantiomeric excesses (ee) of **34** and **35** were determined by ^{1}H-NMR spectroscopy in the presence of $[Eu(hfc)_3]$ (20–40 mol-%) in $CDCl_3$ at ambient temperature. The assignment of the absolute configuration was accomplished by comparison of the sign of the specific rotations of the isolated compounds in $CHCl_3$ with literature values reported by *Kudis* and *Helmchen* [9f]. [e]) THAB = Tetrahexylammonium bromide. [f]) *Entries 9–11* represent a study of the influence of the catalyst concentration on the ee value and, therefore, 1, 3, and 5 mol-% of catalyst were used.

Ligand (*S*)-**6**, in combination with $[\{(\eta^3\text{-}C_3H_5)PdCl\}_2]$, formed an efficient catalyst that allowed allylations of dimethyl malonate in up to 95% yield in the biphasic solvent system CH_2Cl_2/H_2O in the absence of THAB (*Table*, *Entries 7–12*). A dependence of the enantioselectivity on catalyst concentration was not observed; the ee values ranged between 13–15% in the presence of 1, 3, or 5 mol-% of catalyst (*Table*, *Entries 9–11*); however, rather surprisingly, the yield of **35** in the reaction with 5 mol-% of catalyst dropped to a low 53% (*Table*, *Entry 11*).

The finding that the counterion of the attacking nucleophile can strongly influence the reaction rate and selectivity (*cf.* [8j–k][15]) encouraged us to screen different bases such as Cs_2CO_3 and *N*,*O*-bis(trimethylsilyl)acetamide (BSA) for the formation of the malonate anion. In contrast to the previously described runs, the Pd-catalyzed allylations of Cs salts of the dimethyl-malonate anion in a suspension of Cs_2CO_3 in CH_2Cl_2 at 20° occur under heterogeneous conditions (*Scheme 9*,*b*) [8i]. Nevertheless, reaction rates were similar to those seen in the conversions of the Na salt under fully homogeneous conditions. Both catalysts prepared from ligands (*S*)-**6** or (*R*)-**7** and $[\{(\eta^3\text{-}C_3H_5)PdCl\}_2]$ afforded the desired product **35** in reasonable yields (79 and 64%) and with ee values of 15 and 17%, respectively (*Table*, *Entries 12* and *13*). These are the

best result obtained in enantioselective allylic alkylations with this first generation of 1,1′-binaphthalene major-groove ligands.

A last set of reaction conditions for allylic alkylations of dimethyl malonate **30** included the use of *N*,*O*-bis(trimethylsilyl)acetamide (BSA) as a base in CH_2Cl_2 at $-15°$ (*Scheme 9*,*c*) [28]. The reaction conditions, which included the use of a higher catalyst concentration (2.0 mol-%), proved very efficient and clean, and led to the isolation of product **35** in excellent yields (98% with (*S*)-**6** and 99% with (*R*)-**7**) after 20 h. The ee values however, were again lower than with the Cs salt (*Table*, *Entries 14* and *15*).

2.3. *Structural Investigations of the Major-Groove Catalysts.* To rationalize the low enantioselectivities in the allylations with Pd catalysts derived from ligands (*R*)-**4**, (*R*)-**5**, (*S*)-**6**, or (*R*)-**7**, and to guide future ligand design, investigations towards the structural elucidation of the complexes formed in the 1,1′-binaphthalene major groove were undertaken.

Monitoring complex formation in solution by ^{31}P-NMR spectroscopy confirmed the presence of several Pd complexes. A single resonance at -4.54 ppm was found in the ^{31}P-NMR spectrum for the free ligand (*R*)-**7** in $CDCl_3$ (*Fig. 2*,*a*); upon addition of 0.5 equiv. of $[\{(\eta^3\text{-}C_3H_5)PdCl\}_2]$, multiple species were observed (*Fig. 2*,*b*). Even upon heating a 1:1 ligand-metal mixture of (*R*)-**7** and $[\{(\eta^3\text{-}C_3H_5)PdCl\}_2]$ (0.5 equiv.) to 50° or 60° in $CDCl_2CDCl_2$, the resonances failed to coalesce. The presence of different, potentially catalytically active species, possibly featuring different stereoselectivities, is clearly detrimental to a high enantioselectivity.

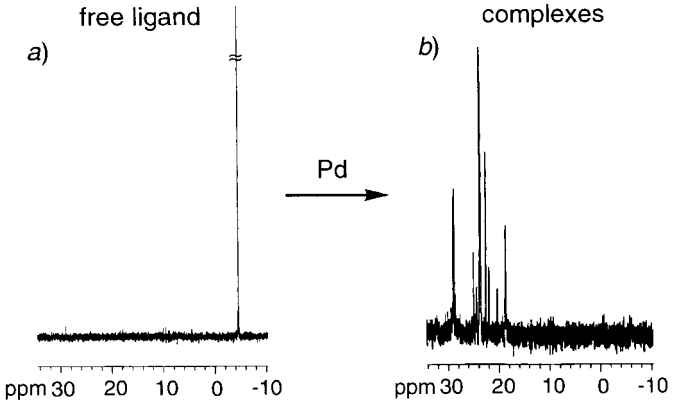


Fig. 2. *^{31}P-NMR Spectra* (121.5 MHz, $CDCl_3$, 296 K) *of* a) *free ligand (*R*)-***7*** and* b) *a 1:1 mixture of (*R*)-***7*** and 'Pd'* (added as $[\{(\eta^3\text{-}C_3H_5)PdCl\}_2]$)

All attempts to grow single crystals suitable for X-ray analysis of Pd complexes formed by the new ligands (*R*)-**4** and (*R*)-**7**, and $[Pd_2(dba)_3]$, $[\{(\eta^3\text{-}C_3H_5)PdCl\}_2]$, or $[PdCl_2(PhCN)_2]$ were unsuccessful. Variation of the counterion of the cationic complexes by ion exchange with $AgBF_4$ or AgOTf in solution also proved ineffective, and only films or powders were obtained.

With the results from the catalysis experiments in hand, a molecular-modeling study with molecular-mechanics minimizations (*Tripos 5.2* force field [29]) implemented in

the *SPARTAN 5.0.3* [30] software was undertaken to gain additional insight into the origin of the rather low enantioselectivities obtained in the allylation reactions. The computational studies were performed on the η^3-cyclohexenyl-palladium complex (*R*)-**36**, since the bridge in the minor groove of ligand (*R*)-**7** reduces the available conformational space. *Fig. 3* shows the two low-energy structures calculated for (*R*)-**36**; for clarity, the 1,1′-binaphthalene cores are omitted with the exception of the C(7)- and C(7′)-atoms. Structure (*R*)-**36b** is by *ca.* 1.6 kJ mol^{-1} higher in energy than (*R*)-**36a**. The main geometrical difference between the two consists of a *ca.* 180° rotation of the η^3-cyclohexenyl unit in the active site; for better visibility of this site, structure (*R*)-**36b** is shown from the opposite direction compared to (*R*)-**36a**. In both geometries, the active site bearing the cyclic substrate adopts a very 'open' conformation. Formation of the observed major product enantiomer ((*S*)-**35**) occurs through nucleophilic attack of the dimethyl-malonate anion at the indicated (→ ; *Fig. 3*) C-terminus of the complexed π-allyl residue. The modeling clearly shows that both C-termini of the coordinated π-allylic residue in complex (*R*)-**36** are rather openly exposed for nucleophilic attack. No

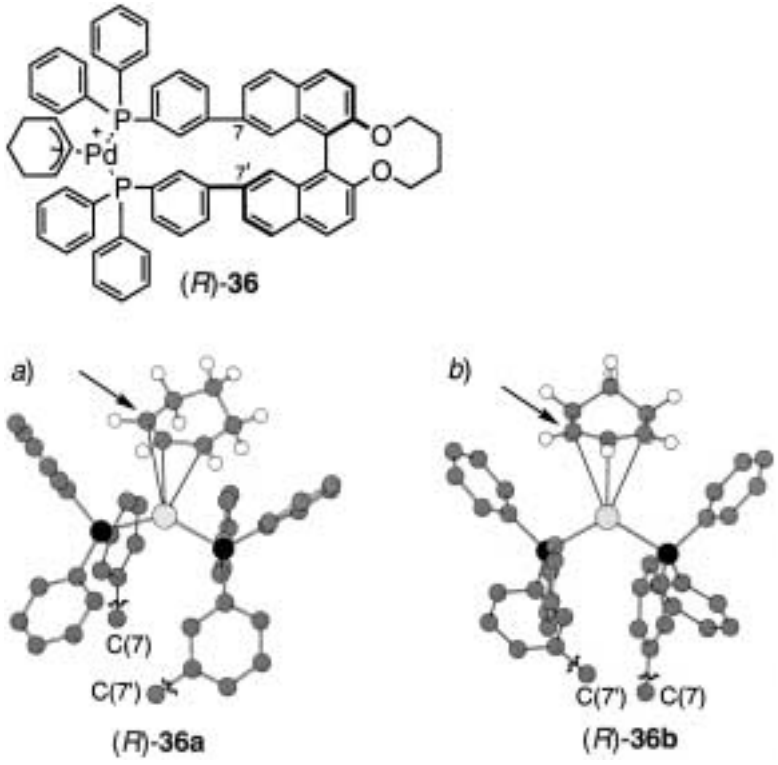


Fig. 3. *Computer-generated low-energy structures (*R*)-***36a*** and (*R*)-***36b*** of the active site of the η^3-cyclohexenylpalladium complex (*R*)-***36*** formed from ligand (*R*)-***7*** showing the 'open' conformation at the catalytically active Pd center.* The 1,1′-binaphthalene core is omitted for clarity, with the exception of C(7) and C(7′). The arrows indicate the positions attacked by the nucleophile to form the observed major product enantiomer (*S*)-**35**.

obvious steric discrimination for attack at one of the two C-termini, which would lead to the targeted selectivity, can be identified. Besides the formation of several metal-ligand species, the lack of a 'chiral pocket' [8j–k][27][31] for embedding the allyl residue in the active site probably accounts for the modest stereoselectivity observed in the bond-formation event between the allyl complex and the nucleophile.

3. Conclusions. – This work describes the investigation of a new class of 1,1′-binaphthalene-bis(phosphane) ligands for transition-metal-mediated enantioselective catalysis. In a logical continuation of molecular-recognition studies with 1,1′-binaphthalene major-groove receptors such as (*R*)-**2**, during which a dramatic increase of the enantioselectivity in the recognition process was observed upon suitable receptor preorganization, we decided to direct our work towards the use of similar structural elements for the construction of catalysts (*R*)-**3** for asymmetric synthesis.

Ligands (*R*)-**4**, (*R*)-**5**, (*S*)-**6**, and (*R*)-**7** were obtained by a modular strategy, providing rapid access to all four compounds. Their preparation starts from a single chiral core, (*R*)-**8** or (*S*)-**8**, and the synthetic route ends with a remarkably high-yielding sequence of a *Suzuki* cross-coupling reaction, followed by phosphane-oxide reduction.

Catalysis studies using Pd-mediated, enantioselective allylic alkylations of anions of benzenesulfinate or dimethyl malonate as test reactions generally revealed a high level of reactivity for the catalysts formed *in situ* by the new ligands and different Pd species. Enantiomeric excesses (ee) in allylic alkylations of dimethyl malonate, however, never exceeded 17% and were almost completely absent in the allylations of sodium benzenesulfinate. A number of reasons may account for the observed lack of enantioselectivity of the new catalysts. ^{31}P-NMR-Spectroscopic studies ($CDCl_3$, 296 K) revealed the formation of several Pd-ligand complexes, which potentially exhibit catalytic activity with differing stereoselectivity. Furthermore, molecular-mechanics minimizations indicated a very 'open' conformation of the active site in the catalyst-substrate complex (*R*)-**36**, with no obvious steric preference for nucleophilic attack at one of the two C-termini of the coordinated π-allylic residue.

Despite the current low level of enantioselectivity (up to 17% ee), the new class of 1,1′-binaphthalene ligands with metal-coordination sites located in the major groove is considered promising, since they introduce novel structural elements for asymmetric catalysis. Future work needs to be focused on the reduction of the conformational flexibility of the ligands – particularly in the vicinity of the coordination sites – and on providing a more extended 'chiral pocket' for a more precise embedding of the allylic substrates.

Experimental Part

General. All reactions were carried out under Ar. Solvents and reagents were reagent-grade commercials and were used without further purification unless otherwise stated. THF and Et_2O were freshly distilled from sodium benzophenone ketyl. MeCN was stored over molecular sieves (3 Å). Evaporation *in vacuo* was conducted at H_2O-aspirator pressure. Column chromatography (CC): SiO_2 *60* (230–400 mesh, 0.040–0.063 mm) from *Fluka* and *N-Alox* (neutral Al_2O_3, Act. 1) from *Woelm*. M.p.: *Büchi SMP-20*; uncorrected. IR Spectra (cm^{-1}): *Perkin-Elmer 1600-FT-IR*. NMR Spectra: *Varian Gemini-300* or *-200* at 296 or 300 K, with solvent peak as reference. The presence of P nuclei leads to highly complex ^{13}C-NMR spectra due to ^1J, ^2J, ^3J, and $^4J(^{13}C,^{31}P)$ coupling. Furthermore, overlap of resonances is caused by diastereoisotopic Ph moieties at the phosphane or phosphane oxide sites. In all cases, where a full interpretation of the ^{13}C-NMR spectra was

possible, multiplicities and coupling constants are indicated. For spectra with strongly overlapping resonances, only the observed resonances are given. MS (*m*/*z* (%)): FAB: *VG ZAB2-SEQ* spectrometer with 3-nitrobenzyl alcohol (NOBA) as matrix. HR-ESI-MS: *Finnigan New Star FT/MS* with 7 T magnet. Elemental analyses were performed by the Mikrolabor at the Laboratorium für Organische Chemie, ETH-Zürich.

Catalysis Experiments. Allylic Alkylations with Sodium Phenylsulfinate. A soln. of ligand (8.99 μmol, 1.0 mol-%), $[Pd_2(dba)_3 \cdot CHCl_3]$ (4.19 mg, 4.05 μmol, 0.45 mol-%), and sodium benzenesulfinate (221.5 mg, 1.34 mmol) in CH_2Cl_2/H_2O (5 ml/2 ml) was stirred at 20° under Ar for 20 min. Substrate **30** (140 mg, 0.899 mmol) was added, and the mixture was stirred for 12–24 h. The mixture was diluted with CH_2Cl_2 (40 ml), extracted with sat. aq. $NaHCO_3$ soln. and sat. aq. NaCl soln., dried ($MgSO_4$), and evaporated *in vacuo*. CC (SiO_2; hexane/Et_2O 19:1 → 2:1) afforded **33** as a colorless oil. ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.60–2.46 (*m*, 4 H); 3.50–3.75 (*m*, 2 H); 5.65–5.80 (*m*, 1 H); 7.55–7.90 (*m*, 7 H). Enantiomeric excesses (ee) of **33** were determined by GC (*Macherey-Nagel*, *LIPODEX E*, H_2, temp. gradient: 120° → 205° (1.5°/min)) (*cf.* [12a]). Similarly, ee values of **32** (obtained from **29** under the same conditions) were determined by chiral GC (*Macherey-Nagel*, *LIPODEX E*, H_2, temp. gradient: 120° → 200° (1.5°/min)). ee Values of **31** (obtained from **28** under the same conditions) were determined by chiral HPLC (*Regis*, *SS-Whelk-O1*; hexane/i-PrOH 4:1, detected at 254 nm, flow rate = 1.0 ml min^{-1}) (*cf.* [13h]).

Allylic Alkylations with Anions of Dimethyl Malonate. i) *Anhydrous Conditions.* A soln. of ligand (9.32 μmol, 1.0 mol-%) and $[\{(\eta^3\text{-}C_3H_5)PdCl\}_2]$ (1.53 mg, 4.19 μmol, 0.45 mol-%) in the indicated solvent (5 ml; *cf. Table*) was stirred at the indicated temp. under Ar for 20 min, then **30** (145 mg, 0.932 mmol) was added, and the mixture was stirred for another 10 min. A soln. of dimethyl malonate (159 μl, 1.40 mmol) and NaH (31.30 mg, 1.30 mmol) in the same solvent (2 ml) was added, and the mixture was stirred for the indicated amount of time (*cf. Table*). H_2O was added, and the mixture was extracted with CH_2Cl_2 (2 × 30 ml). The combined org. layers were washed with sat. aq. NaCl soln., dried ($MgSO_4$), and evaporated *in vacuo*. CC (SiO_2; hexane/Et_2O 20:1 → 11:1) afforded **35** as a colorless oil. ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.25–1.42 (*m*, 1 H); 1.46–1.82 (*m*, 3 H); 1.90–2.05 (*m*, 2 H); 2.85–2.98 (*m*, 1 H); 3.28 (*d*, *J* = 9.4, 1 H); 3.73 (*s*, 6 H); 5.49–5.54 (*m*, 1 H); 5.74–5.80 (*m*, 1 H). The ee values of **35** were determined by ^{1}H-NMR spectroscopy (300 MHz) in the presence of $[Eu(hfc)_3]$ (*ca.* 20–40 mol-%; hfc = 3-[(heptafluoropropyl)(hydroxy)methylene]-(+)-camphorate) in $CDCl_3$ at 20° by integration and comparison of the COO*Me* resonances. The assignment of the absolute configuration was achieved by comparison of the sign of the specific rotations of the isolated compounds in $CHCl_3$ with literature values reported by *Kudis* and *Helmchen* [9f].

ii) *Biphasic Conditions.* A soln. of ligand (9.32 μmol, 1.0 mol-%), $[\{(\eta^3\text{-}C_3H_5)PdCl\}_2]$ (1.53 mg, 4.19 μmol, 0.45 mol-%), and Na_2CO_3 (135 mg, 1.05 mmol) in CH_2Cl_2/H_2O (4 ml/2 ml) was stirred at 20° under Ar for 20 min. Substrate **30** (145 mg, 0.932 mmol) was added, and the mixture was stirred for another 10 min. Dimethyl malonate (122 μl, 1.21 mmol) was added, and the mixture was stirred for the indicated amount of time (*cf. Table*). H_2O was added, and the mixture was extracted with CH_2Cl_2 (2 × 30 ml). The combined org. layers were washed with sat. aq. NaCl soln., dried ($MgSO_4$), and evaporated *in vacuo*. CC (SiO_2; hexane/Et_2O 20:1 → 11:1) afforded **35** as a colorless oil.

*(*R,S*)-7,7′-Dibromo-1,1′-binaphthalene-2,2′-diol* ((±)-**8**). To **10** (10.5 g, 47.07 mmol) in CH_2Cl_2 (350 ml) in an open *Schlenk* flask (500 ml), fresh [CuCl(OH)(TMEDA)] (109.3 mg, 470.7 μmol) [18] was added. The mixture was sonicated for 10 min and subsequently vigorously stirred with exposure to air for 12 h. Evaporation *in vacuo*, plug filtration (SiO_2; CH_2Cl_2), and recrystallization (toluene/hexane) afforded (±)-**8** (10.04 g, 96%). Cream-colored needles. M.p. 197–198°. IR (KBr): 3469*s*, 3056*w*, 1610*s*, 1584*m*, 1498*s*, 1445*w*, 1418*m*, 1378*m*, 1351*m*, 1306*w*, 1250*w*, 1171*s*. ^{1}H-NMR ($CHCl_3$, 200 MHz): 5.02 (*s*, 2 H); 7.24 (*d*, *J* = 2.1, 2 H); 7.40 (*d*, *J* = 8.7, 2 H); 7.49 (*dd*, *J* = 8.7, 2.1, 2 H); 7.78 (*d*, *J* = 8.7, 2 H); 7.97 (*d*, *J* = 8.7, 2 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 109.53; 118.36; 122.52; 126.04; 127.85; 128.04; 130.26; 131.85; 134.71; 153.75. FAB-MS: 443.9 (100, *M*H$^+$), 284.1 (27). Anal. calc. for $C_{20}H_{12}Br_2O_2$ (444.12): C 54.09, H 2.72; found: C 54.05, H 2.63.

*Optical Resolution of (±)-***8** via *Diastereoisomeric Camphorsulfonates (−)-***11** *and (+)-***12**. To (±)-**8** (4.00 g, 9.00 mmol) and Et_3N (3.13 ml, 22.51 mmol) in dry CH_2Cl_2 (180 ml) at 0° under Ar, (−)-(1*R*,4*S*)-camphor-10-sulfonyl chloride (5.081 g, 20.26 mmol) was added. The soln. was stirred at 0° for 3 h and then quenched with H_2O (180 ml). Extraction with CH_2Cl_2 (3 × 100 ml), washing of the combined org. layers with sat. aq. NaCl soln., drying ($MgSO_4$), and evaporation *in vacuo* gave quantitatively the mixture of diastereoisomers. CC (SiO_2; CH_2Cl_2/AcOEt 99:1) afforded (−)-**11** (3.74 g, 48%) and (+)-**12** (3.81 g, 48%).

*(*R*)-(−)-7,7′-Dibromo-2,2′-bis{[((1*R*,4*S*)-7,7-dimethyl-2-oxobicyclo[2.2.1]hept-1-yl)methyl]sulfonyloxy}-1,1′-binaphthalene* ((−)-**11**). White foam. M.p. 99–112°. $[\alpha]_D^{23} = -32.4$ (*c* = 0.5, $CHCl_3$). de >99.5% (HPLC: SiO_2; CH_2Cl_2/AcOEt 97:3, detected at 254 nm, flow rate = 0.8 ml min^{-1}). IR (KBr): 2959*m*, 1748*s*, 1613*m*, 1583*w*, 1493*m*, 1367*s*, 1166*s*, 1080*m*, 981*m*, 815*s*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.66 (*s*, 6 H); 0.86 (*s*, 6 H);

1.15–1.45 (*m*, 4 H); 1.76–2.18 (*m*, 8 H); 2.19–2.38 (*m*, 2 H); 2.60 (*d*, J_{AB} = 14.9, 2 H); 3.02 (*d*, J_{AB} = 14.9, 2 H); 7.45 (*d*, *J* = 2.1, 2 H); 7.66 (*dd*, *J* = 8.9, 2.1, 2 H); 7.82–7.91 (*m*, 4 H); 8.09 (*d*, *J* = 8.9, 2 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 19.23; 19.33; 24.71; 26.61; 42.14; 42.67; 47.54; 49.04; 57.65; 121.59; 121.89; 122.56; 128.23; 129.98; 130.27; 130.99; 134.40; 146.61; 213.46 (19 of 20 resonances). FAB-MS: 873.6 (100, *M*H$^+$, $C_{40}H_{40}{}^{79}Br^{81}BrO_2S_2$), 871.6 (47, *M*H$^+$, $C_{40}H_{40}{}^{79}Br_2O_2S_2$). Anal. calc. for $C_{40}H_{40}Br_2O_2S_2 \cdot 0.2\ CH_2Cl_2$ (872.69): C 54.27, H 4.58, O 14.39; found: C 54.51, H 4.72, O 14.49.

*(+)-(*R*)-7,7′-Dibromo-2,2′-bis{[((1*R*,4*S*)-7,7-dimethyl-2-oxobicyclo[2.2.1]hept-1-yl)methyl]sulfonyloxy}-1,1′-binaphthalene* ((+)-**12**). White foam. M.p. 105–116°. $[\alpha]_D^{23} = +32.2$ (*c* = 0.5, $CHCl_3$). de > 99.5% (HPLC: *vide supra*); IR (KBr): 2959*m*, 1748*s*, 1614*m*, 1583*w*, 1493*m*, 1455*w*, 1364*s*, 1166*s*, 1080*m*, 982*m*, 816*s*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 0.54 (*s*, 6 H); 0.69 (*s*, 6 H); 1.18–1.42 (*m*, 4 H); 1.71–1.96 (*m*, 8 H); 2.17–2.30 (*m*, 2 H); 2.39 (*d*, J_{AB} = 14.9, 2 H); 3.38 (*d*, J_{AB} = 14.9, 2 H); 7.36 (*d*, *J* = 1.9, 2 H); 7.60 (*dd*, *J* = 8.9, 1.9, 2 H); 7.82–7.86 (*m*, 4 H); 8.04 (*d*, *J* = 8.9, 2 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 19.10; 19.15; 24.50; 26.61; 42.12; 42.56; 47.51; 49.09; 57.60; 121.59; 121.75; 122.48; 128.17; 130.03; 130.19; 130.29; 130.99; 134.46; 146.61; 213.48. FAB-MS: 873.4 (100, *M*H$^+$, $C_{40}H_{40}{}^{79}Br^{81}BrO_2S_2$), 871.5 (59, *M*H$^+$, $C_{40}H_{40}{}^{79}Br_2O_2S_2$). Anal. calc. for $C_{40}H_{40}Br_2O_2S_2$ (872.69): C 54.99, H 4.73; found: C 55.02, H 4.75.

Compounds (−)-**12** and (+)-**11** were synthesized in a similar manner from (±)-**8** and (+)-(1*S*,4*R*)-camphor-10-sulfonyl chloride. (−)-**12**: M.p. 98–110°. (+)-**11**: M.p. 102–112°.

*(*R*)-7,7′-Dibromo-1,1′-binaphthalene-2,2′-diol* ((*R*)-**8**). To (−)-**11** (1.60 g, 1.83 mmol) in THF (30 ml) and MeOH (30 ml) under Ar, 1M NaOH (24 ml, 24.63 mmol) was added, and the mixture was heated to 60° for 8 h, then stirred for another 12 h at 20°. The mixture was acidified with 2M HCl, neutralized with sat. aq. $NaHCO_3$ soln., concentrated *in vacuo*, and extracted with CH_2Cl_2 (3 × 120 ml). The combined org. layers were washed with sat. aq. NaCl soln., dried ($MgSO_4$), and evaporated *in vacuo*. Plug filtration (SiO_2; CH_2Cl_2) yielded (*R*)-**8** (806 mg, 99%). White foam. M.p. 109–111°. $[\alpha]_D^{23} = -95.2$ (*c* = 0.5, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 200 MHz): 5.02 (*s*, 2 H); 7.24 (*d*, *J* = 2.1, 2 H); 7.40 (*d*, *J* = 8.7, 2 H); 7.49 (*dd*, *J* = 8.7, 2.1, 2 H); 7.78 (*d*, *J* = 8.7, 2 H); 7.97 (*d*, *J* = 8.7, 2 H). FAB-MS: 443.9 (100, *M*H$^+$), 248.1 (27).

Compound (*R*)-**8** was obtained in a similar manner from (+)-**11**, and (*S*)-**8** from (+)-**12** or (−)-**12**. (*S*)-**8**: M.p. 110–112°. $[\alpha]_D^{23} = +96.1$ (*c* = 0.5, $CHCl_3$).

(3-Bromophenyl)diphenylphosphane (**15**) [20]. To 1,3-dibromobenzene (4.2 ml, 34.75 mmol) in dry THF (40 ml) at −90° under Ar, BuLi (1.6M in hexane, 22.8 ml, 36.49 mmol) was added dropwise, and the soln. was stirred for 45 min. Chloro(diphenyl)phosphane (6.23 ml, 7.667 g) was added dropwise, and the mixture was allowed to warm to 20°. Filtration through a pad of *Celite*, evaporation *in vacuo*, and plug filtration (SiO_2; hexane) afforded **15** (10.7 g, 90%). Colorless, viscous oil. ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.20–7.55 (*m*, 14 H). ^{31}P-NMR ($CDCl_3$, 121.5 MHz): −4.38 (*s*).

2-[3-(Diphenylphosphanyl)phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxoborolane (**16**). To **15** (10.7 g, 31.36 mmol) in dry THF (60 ml) at −90° under Ar, BuLi (1.6M in hexane, 13.17 ml, 32.92 mmol) was added, and the soln. was stirred for 1 h at −90°. $(MeO)_3B$ (7.12 ml, 62.72 mmol) was added rapidly, the mixture was allowed to warm to 20°, and the solvent was evaporated *in vacuo*. The residue was suspended in toluene (60 ml), and pinacol (3.891 g, 32.92 mmol) was added. The mixture was heated to reflux, and solid NH_4Cl (3.36 g, 62.72 mmol) was added in portions. After heating to reflux for 2 h, the solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2. The org. phase was washed with sat. aq. $NaHCO_3$ soln. and sat. aq. NaCl soln., dried ($MgSO_4$), and evaporated *in vacuo*. CC (SiO_2; hexane → hexane/CH_2Cl_2 4:1 → 3:2) gave **16** (5.22 g, 43%). Colorless, viscous oil, which eventually solidified upon standing. M.p. 124–125°. IR (KBr): 3049*m*, 2979*s*, 2920*m*, 1582*s*, 1476*s*, 1433*s*, 1387*s*, 1348*s*, 1320*s*, 1265*m*, 1208*w*, 1142*s*, 1072*s*, 1026*w*, 995*w*, 964*m*, 863*m*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.33 (*s*, 12 H); 7.22–7.39 (*m*, 12 H); 7.80 (*d*, *J* = 7.2, 1 H); 8.00 (*d*, *J* = 9.7, 1 H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): 24.74 (*s*); 83.86 (*s*); 128.10 (*d*, *J* = 3.7); 128.48 (*s*); 128.61 (*d*, *J* = 6.1); 133.78 (*d*, *J* = 19.5); 135.34 (*s*); 136.25 (*d*, *J* = 8.5); 136.48 (*d*, *J* = 10.6); 137.46 (*d*, *J* = 11.0); 141.14 (*d*, *J* = 30.5). ^{31}P-NMR ($CDCl_3$, 121.5 MHz): −5.41 (*s*). FAB-MS: 388.3 (100, *M*H$^+$).

Diphenyl[3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]phosphane Oxide (**13**). A soln. of **16** (5.12 g, 13.18 mmol), $FeCl_3 \cdot 6\ H_2O$ (101.8 mg, 263.7 μmol), and KSCN (76.88 mg, 791.2 μmol) was heated to 80° with vigorous bubbling of O_2, and I_2 (cat. amount) was subsequently added. After 15 min, the soln. was cooled to 20°, the solvent evaporated *in vacuo*, and the residue was dissolved in $CHCl_3$ (200 ml). The org. phase was washed with 5% aq. Na_2SO_3 soln. (40 ml) and H_2O (2 × 200 ml), dried ($MgSO_4$), and decolorized with active charcoal to give, after evaporation *in vacuo*, **13** (5.33 g, quant. yield). Cream-colored needles (AcOEt/hexane). M.p. 148–189°. IR ($CHCl_3$): 2984*m*, 1594*w*, 1436*w*, 1358*s*, 1318*m*, 1174*m*, 1126*s*, 963*w*, 840*w*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.33 (*s*, 12 H); 7.40–7.59 (*m*, 7 H); 7.60–7.75 (*m*, 5 H); 7.97 (*dd*, *J* = 7.5, 1.4, 1 H); 8.28 (*d*, *J* = 11.8, 1 H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): 24.73 (*s*); 83.07 (*s*); 127.66 (*d*, *J* = 11.0); 128.54 (*d*, *J* = 12.2);

131.87 (*d*, *J* = 102.7); 133.56; 131.92 (*d*, *J* = 3.7); 132.21 (*d*, *J* = 9.8); 134.67 (*d*, *J* = 11.0); 138.27 (*d*, *J* = 3.6); 138.40 (*d*, *J* = 8.5). ^{31}P-NMR ($CDCl_3$, 121.5 MHz): 29.30 (*s*). FAB-MS: 405.1 (100, MH^+). Anal. calc. for $C_{24}H_{26}BO_3P$ (404.25): C 71.31, H 6.48; found: C 71.42, H 6.54.

*(*R*)-7,7′-Dibromo-2,2′-dimethoxy-1,1′-binaphthalene* ((*R*)-**17**). To a suspension of (*R*)-**8** (700 mg, 1.58 mmol) and K_2CO_3 (1.742 g, 12.6 mmol) in dry MeCN (40 ml) at 80° under Ar, MeI (392 µl, 6.30 mmol) was added, and the mixture was heated to reflux for 8 h. After cooling to 20°, filtration through a pad of *Celite*, evaporation *in vacuo*, and plug filtration (SiO_2; CH_2Cl_2/hexane 1:1) gave (*R*)-**17** (599 mg, 80%). White solid. M.p. > 225° (dec.). $[\alpha]_D^{23} = -29.8$ (*c* = 0.5, $CHCl_3$). IR (KBr): 3005*w*, 2920*m*, 2818*m*, 1615*s*, 1582*m*, 1497*s*, 1462*s*, 1345*s*, 1321*m*, 1257*s*, 1170*m*, 1152*m*, 1100*s*, 1072*s*, 923*s*, 869*m*, 824*s*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 3.80 (*s*, 6 H); 7.20–7.29 (*m*, 2 H); 7.35–7.55 (*m*, 4 H); 7.76 (*d*, *J* = 8.7, 2 H); 7.97 (*d*, *J* = 9.1, 2 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 56.59; 117.95; 121.22; 126.96; 127.09; 127.63; 129.82; 135.21; 155.69 (10 of 11 resonances). FAB-MS: 472.0 (100, MH^+), 425.9 (18). Anal. calc. for $C_{22}H_{16}Br_2O_2$ (472.18): C 55.96, H 3.42; found: C 55.77, H 3.67.

Compound *(*S*)*-**17** (M.p. > 223° (dec.); $[\alpha]_D^{23} = +30.1$ (*c* = 0.5, $CHCl_3$)) was obtained in a similar manner from (*S*)-**8**.

*(*R*)-7,7′-Bis[3-(diphenylphosphanyl)phenyl]-2,2′-dimethoxy-1,1′-binaphthalene* ((*R*)-**4**). To (*R*)-**17** (499 mg, 1.06 mmol) and **13** (875.7 mg, 2.17 mmol) in PhH/EtOH 11:3 (50 ml), Na_2CO_3 (448 mg, 4.23 mmol) in H_2O (30 ml) was added. The mixture was heated with vigorous stirring under Ar to 80°, followed by addition of $[PdCl_2(dppf)\cdot CH_2Cl_2]$ (31 mg, 42.27 µmol). The mixture was heated for 3 h to 80°, cooled to 20°, concentrated *in vacuo*, and the residue was extracted with CH_2Cl_2 (3 × 50 ml). The combined org. layers were washed with sat. aq. $NaHCO_3$ soln. and sat. aq. NaCl soln., dried ($MgSO_4$), and evaporated *in vacuo* to yield crude (*R*)-**18** in quantitative yield. Dark foam. Finely ground $CeCl_3\cdot 7\,H_2O$ (1.181 g, 3.17 mmol) was dried in a *Schlenk* tube for 2 h at 140°/10^{-2} Torr. After cooling to 20°, dry THF (20 ml) was added under Ar, and the suspension was sonicated for 10 min, followed by addition of crude (*R*)-**18** in THF (20 ml). To this soln. at 40°, $LiAlH_4$ (1M in THF; 5.28 ml, 5.284 mmol) was added dropwise, and the mixture was stirred for 1.5 h. Excess $LiAlH_4$ was quenched by slow addition of EtOH, and the precipitate was dissolved with 6M HCl. The mixture was extracted with CH_2Cl_2 (3 × 80 ml), and the combined org. layers were washed with sat. aq. $NaHCO_3$ soln. and sat. aq. NaCl soln., dried ($MgSO_4$), and evaporated *in vacuo*. CC (SiO_2; CH_2Cl_2/hexane 2:3 → 3:2) afforded (*R*)-**4** (753 mg, 91%). White foam. M.p. > 98° (dec.). $[\alpha]_D^{23} = -97.7$ (*c* = 0.5, $CHCl_3$). IR (KBr): 3050*w*, 2933*w*, 2833*w*, 1622*m*, 1594*m*, 1506*s*, 1478*s*, 1456*s*, 1428*s*, 1350*m*, 1244*s*, 1172*m*, 1094*m*, 1068*s*, 833*s*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 3.72 (*s*, 6 H); 7.20–7.39 (*m*, 28 H); 7.40–7.55 (*m*, 6 H); 7.90 (*d*, *J* = 8.7, 2 H); 7.97 (*d*, *J* = 9.0, 2 H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): 56.70; 114.26; 119.63; 123.45; 128.02; 128.48; 128.51; 128.59; 128.70; 128.74; 128.78; 129.35; 132.33; 132.56; 132.60; 132.81; 133.59; 133.69; 133.85; 133.95; 134.17; 137.04; 137.12; 137.17; 137.26; 137.68; 137.84; 138.73; 141.81; 141.89; 155.41 (theor. 25 resonances). ^{31}P-NMR ($CDCl_3$, 121.5 MHz): −4.38 (*s*). FAB-MS: 867.0 (64, $[MH + O_2]^+$), 851.0 (100, $[MH + O]^+$), 835.0 (92, MH^+). Anal. calc. for $C_{58}H_{44}O_2P_2\cdot 0.5\ CH_2Cl_2\cdot H_2O$ (834.93): C 78.47, H 5.29; found: C 78.58, H 5.36.

*(*R*)-7,7′-Dibromo-2,2′-bis[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]-1,1′-binaphthalene* ((*R*)-**19**). To a suspension of (*R*)-**8** (400 mg, 901 µmol) and Cs_2CO_3 (1.6 g, 2.70 mmol) in DMF (30 ml) under Ar, triethyleneglycol monomethyl ether methane sulfonate (670.9 mg, 2.70 mmol) [24] was added, and the mixture was stirred for 4 h at 100°. After cooling to 20°, the solvent was evaporated *in vacuo*, and the residue was dried at 10^{-2} Torr. CC (SiO_2; hexane/AcOEt 1:1 → 1:2 → 1:4 → AcOEt → AcOEt/MeOH 99:1 → 98:2) gave (*R*)-**19** (534 mg, 81%). Colorless oil. $[\alpha]_D^{23} = -1.73$ (*c* = 0.5, $CHCl_3$). IR (neat): 2875*s*, 1613*s*, 1583*w*, 1497*s*, 1451*m*, 1342*m*, 1320*m*, 1256*s*, 1132*s*, 1099*s*, 941*w*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 3.10–3.28 (*m*, 8 H); 3.34 (*s*, 6 H); 3.45–3.55 (*m*, 12 H); 4.05–4.20 (*m*, 4 H); 7.26 (*s*, 2 H); 7.35–7.45 (*m*, 4 H); 7.72 (*d*, *J* = 8.7, 2 H); 7.90 (*d*, *J* = 9.0, 2 H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): 58.93; 69.46; 70.30; 70.42; 70.54; 71.82; 115.57; 118.74; 121.08; 127.20; 127.75; 129.66; 129.72; 135.29; 155.07 (theor. 17 resonances). FAB-MS: 739.0 (31, MH^+, $C_{34}H_{41}{}^{81}Br_2O_8$), 738.0 (60, M^+, $C_{34}H_{40}{}^{81}Br_2O_8$). Anal. calc. for $C_{34}H_{40}Br_2O_8$ (736.49): C 55.45, H 5.47, O 17.38; found: C 55.43, H 5.30, O 17.28.

*(*R*)-7,7′-Bis[3-(diphenylphosphanyl)phenyl]-2,2′-bis{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}-1,1′-binaphthalene* ((*R*)-**5**). To (*R*)-**19** (650 mg, 882.5 µmol) and **13** (731.3 mg, 1.809 mmol) in PhH/EtOH 11:3 (50 ml), Na_2CO_3 (249.8 mg, 2.36 mmol) in H_2O (30 ml) was added, and the mixture was heated with vigorous stirring to 80°. After addition of $[PdCl_2(dppf)\cdot CH_2Cl_2]$ (25.83 mg, 35.3 µmol), the mixture was stirred at 80° for 3 h, subsequently cooled to 20°, and evaporated *in vacuo*. The residue was extracted with CH_2Cl_2 (3 × 50 ml), the combined org. layers were washed with sat. aq. $NaHCO_3$ soln. and sat. aq. NaCl soln., dried ($MgSO_4$), and evaporated *in vacuo*. CC (SiO_2; AcOEt/NEt_3 99:1 → AcOEt/NEt_3/MeOH 97:1:2 → 95:1:4) gave the crude coupling product. Finely ground $CeCl_3\cdot 7\,H_2O$ (1.644 g, 4.412 mmol) was dried in a *Schlenk* tube for 2 h at 140°/10^{-2} Torr. After cooling to 20°, dry THF (30 ml) was added under Ar, and the suspension was sonicated for 10 min, followed by addition of the crude coupling product in THF (20 ml). To this soln. at 40°, $LiAlH_4$ (1M in

THF; 6.17 ml, 6.17 mmol) was added, and the resulting mixture was stirred for 1.5 h. Excess $LiAlH_4$ was quenched by slow addition of EtOH (5 ml), and the precipitate was dissolved with 6M HCl. The mixture was extracted with CH_2Cl_2 (3×80 ml), and the combined org. layers were washed with sat. aq. $NaHCO_3$ soln. and sat. aq. NaCl soln., dried ($MgSO_4$), and evaporated *in vacuo*. CC (SiO_2; AcOEt/NEt_3 99:1) afforded (*R*)-**5** (463 mg, 48%). Colorless glue. $[\alpha]_D^{23} = -40.5$ ($c = 0.5$, $CHCl_3$). IR ($CHCl_3$): 3056*w*, 3007*m*, 2926*m*, 2878*m*, 1622*m*, 1598*m*, 1508*m*, 1477*m*, 1434*m*, 1353*w*, 1306*w*, 1244*m*, 1137*s*, 1103*s*, 888*w*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 3.02–3.22 (*m*, 8 H); 3.33 (*s*, 6 H); 3.35–3.45 (*m*, 12 H); 3.95–4.13 (*m*, 4 H); 7.15–7.45 (*m*, 32 H); 7.49 (*dd*, $J =$ 8.6, 1.7, 2 H); 7.89 (*d*, $J = 8.4$, 2 H); 7.93 (*d*, $J = 9.0$, 2 H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): 58.86; 69.44; 69.72; 70.17; 70.32; 70.40; 71.77; 115.65; 120.50; 123.49; 123.64; 127.96; 128.46; 128.53; 128.67; 128.74; 128.82; 129.16; 132.31; 132.44; 132.57; 132.72; 133.56; 133.62; 133.82; 133.88; 134.29; 136.99; 137.13; 137.73; 137.89; 138.57; 141.61; 141.69; 154.77 (theor. 31 resonances). ^{31}P-NMR ($CDCl_3$, 121.5 MHz): −4.47 (*s*). FAB-MS: 1131.3 (38, $[M + O_2]^+$), 1115.3 (76, $[M + O]^+$), 1099.3 (100, MH^+). HR-FAB-MS: 1099.4450 (85, MH^+, $C_{70}H_{69}O_8P_2$; calc. 1099.4467).

1,3-Dibromo-5-iodobenzene (**21**) [32]. To 1,3,5-tribromobenzene (10.00 g, 31.76 mmol) in dry Et_2O (300 ml) at −90°, BuLi (1.6M in hexane; 20.25 ml, 32.4 mmol) was added *via* syringe pump over 30 min, and the obtained soln. was stirred for 30 min (*cf.* lithiation [33]). After fast addition of I_2 (8.46 g, 33.35 mmol) in dry THF (20 ml), the mixture was slowly warmed to 20°. The org. phase was extracted with 5% aq. Na_2SO_3 soln. (40 ml) and sat. aq. NaCl soln., dried ($MgSO_4$), and evaporated *in vacuo*. Recrystallization from hexane (−20°) afforded **21** (6.436 g, 56%). Yellow-orange needles. ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.64 (*d*, $J = 1.6$, 2 H); 7.90 (*t*, $J = 1.6$, 1 H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): 94.46; 123.45; 133.74; 138.61.

4-(3,5-Dibromophenyl)but-3-yn-1-ol (**22**). A suspension of **21** (2.42 g, 6.69 mmol), $[PdCl_2(PPh_3)_2]$ (38 mg, 53.5 μmol), and CuI (13 mg, 66.9 μmol) in dry Et_3N (40 ml) was degassed with pump-and-freeze cycles (3×). But-3-yn-1-ol (557 μl, 7.36 mmol) was added at 20°, and the mixture was stirred for 1.5 h under Ar. Filtration through a pad of *Celite* and evaporation *in vacuo* gave a residue to which CH_2Cl_2 (200 ml) was added. The org. phase was washed with sat. aq. NH_4Cl soln. and sat. aq. NaCl soln., dried ($MgSO_4$), and purified by CC (SiO_2; hexane → hexane/AcOEt 95:5 → 90:10 → 85:15) to afford **22** (1.83 g, 90%). IR (KBr): 3253*s*, 2933*m*, 2911*m*, 2227*w*, 1582*s*, 1535*s*, 1477*m*, 1428*m*, 1401*s*, 1346*m*, 1272*w*, 1246*m*, 1101*m*, 1046*s*, 850*s*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.85 (*t*, $J = 6.2$, 1 H); 2.70 (*t*, $J = 6.2$, 2 H); 3.83 (*m*, 2 H); 7.51 (*d*, $J = 2.0$, 2 H); 7.61 (*t*, $J = 2.0$, 1 H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): 23.58; 60.87; 79.59; 89.60; 122.57; 126.83; 133.25; 133.75. EI-MS: 303.8 (89, M^+), 273.8 (100), 192.9 (90). HR-EI-MS: 301.8941 (15, M^+, $C_{10}H_8{}^{79}Br_2O$; calc. 301.8943).

*1,3-Dibromo-5-{4-[(*tert*-butyl)dimethylsilyloxy]but-1-ynyl}benzene* (**23**). A mixture of **22** (1.83 g, 6.02 mmol), (*t*-Bu)Me_2SiCl (1.09 g, 7.24 mmol), and imidazole (1.024 g, 15.0 mmol) in dry DMF (12 ml) was stirred at 20° under Ar for 16 h. The mixture was diluted with pentane (100 ml), and the org. phase washed with H_2O (3×50 ml), dried ($MgSO_4$), and evaporated *in vacuo* to give **23** (2.492 g, 99%). Colorless oil. IR (neat): 2928*s*, 2855*s*, 2231*w*, 1581*s*, 1541*s*, 1471*m*, 1429*m*, 1401*s*, 1360*w*, 1255*s*, 1107*s*, 1058*w*, 916*w*, 837*s*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.12 (*s*, 9 H); 0.94 (*s*, 6 H); 2.63 (*t*, $J = 6.8$, 2 H); 3.82 (*t*, $J = 6.8$, 2 H); 7.48 (*d*, $J = 1.8$, 2 H); 7.60 (*t*, $J = 1.8$, 1 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): −5.28; 18.30; 23.76; 25.86; 61.57; 78.90; 90.46; 122.46; 127.22; 133.09; 133.41. HR-EI-MS: 400.9566 (2, $[M - Me]^+$, $C_{15}H_{19}{}^{79}Br^{81}BrOSi$; calc. 400.9572).

*1-Bromo-3-{4-[(*tert*-butyl)dimethylsilyloxy]but-1-ynyl}-5-(diphenylphosphanyl)benzene* (**24**). To **23** (1.48 g, 3.54 mmol) in dry THF (150 ml) at −90° under Ar, BuLi (1.6M in hexane; 2.32 ml, 3.72 mmol) was added dropwise, and the soln. was stirred for 30 min. Chloro(diphenyl)phosphane (699 μl, 3.89 mmol) was slowly added, and the mixture was allowed to warm to 20° and stirred for 2 h. Evaporation *in vacuo* and CC (SiO_2; hexane → hexane/CH_2Cl_2 90:10 → 85:15) yielded **24** (1.445 g, 78%). Colorless oil. IR (neat): 3054*m*, 2927*s*, 2845*s*, 2231*w*, 1577*s*, 1542*s*, 1471*s*, 1435*s*, 1385*s*, 1252*s*, 1109*m*, 1058*w*, 1027*w*, 911*m*, 1068*s*, 837*s*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 0.07 (*s*, 9 H); 0.89 (*s*, 6 H); 2.58 (*t*, $J = 7.0$, 2 H); 3.77 (*t*, $J = 7.0$, 2 H); 7.24–7.38 (*m*, 12 H); 7.50 (*t*, $J = 1.5$, 1 H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): −5.43 (*s*); 18.19 (*s*); 23.69 (*s*); 25.75 (*s*); 61.62 (*s*); 79.96 (*s*); 89.51 (*s*); 122.57 (*d*, $J = 7.3$); 126.02 (*d*, $J = 7.3$); 128.82 (*d*, $J = 7.3$); 129.25 (*s*); 133.92 (*d*, $J = 20.7$); 134.55 (*s*); 135.03 (*d*, $J = 19.5$); 135.23 (*d*, $J = 20.7$); 136.01 (*d*, $J = 11.0$); 140.66 (*d*, $J = 17.1$). ^{31}P-NMR ($CDCl_3$, 121.5 MHz): −4.13 (*s*). EI-MS: 525.1 (100, MH^+), 467.1 (57). HR-EI-MS: 522.1139 (15, M^+, $C_{28}H_{32}{}^{79}BrOPSi$; calc. 522.1143).

*2-(3-{4-[(*tert*-Butyl)dimethylsilyloxy]but-1-ynyl}-5-(diphenylphosphanyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxoborolane* (**25**). To **24** (21 g, 40.1 mmol) in dry THF (200 ml) at −90° under Ar, BuLi (1.6M in hexane, 27.6 ml, 44.1 mmol) was added *via* syringe pump over 30 min, and the soln. obtained was stirred for another 30 min. $(MeO)_3B$ (9.11 ml, 80.2 mmol) was added rapidly, the mixture was warmed to 20°, sonicated for 30 min, and evaporated *in vacuo*. Pinacol (5.69 g, 48.1 mmol) and toluene (150 ml) were added, and the mixture was heated to reflux for 2 h. The org. phase was washed with sat. aq. $NaHCO_3$ soln. and sat. aq. NaCl soln., dried (Na_2SO_4), and evaporated *in vacuo*. CC (SiO_2; hexane/CH_2Cl_2 1:5 → 2:3) provided **25** (10.2 g, 44%). White

gluey foam. IR ($CHCl_3$): 2970*m*, 2930*m*, 2852*w*, 1583*w*, 1471*w*, 1435*m*, 1408*m*, 1360*s*, 1238*m*, 1143*s*, 1115*s*, 964*w*, 843*m*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 0.06 (*s*, 6 H); 0.89 (*s*, 9 H); 1.31 (*s*, 12 H); 2.56 (*t*, J = 7.1, 2 H); 3.76 (*t*, J = 7.1, 2 H); 7.25 – 7.36 (*m*, 11 H); 7.84 – 7.88 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): – 5.46 (*s*); 18.14 (*s*); 23.64 (*s*); 24.70 (*s*); 25.75 (*s*); 61.79 (*s*); 81.32 (*s*); 83.92 (*s*); 87.69 (*s*); 123.81 (*d*, J = 3.7); 128.55 (*d*, J = 6.1), 128.74 (*s*); 133.75 (*d*, J = 19.5); 136.82 (*d*, J = 13.4); 136.93 (*d*, J = 11.0); 138.56 (*d*, J = 8.6); 138.75 (*s*); 140.00 (*d*, J = 30.5). ^{31}P-NMR ($CDCl_3$, 121.5 MHz): – 5.33 (*s*). EI-MS: 570.2 (62, M^+), 513.1 (100).

*(3-{4-[(*tert*-Butyl)dimethylsilyloxy]but-1-ynyl}-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl(diphenyl)phosphane Oxide* (**20**). A soln. of **25** (10.2 g, 17.9 mmol), $FeCl \cdot 6H_2O$ (276 mg, 715 μmol), and KSCN (208 mg, 2.14 mmol) in MeCN (50 ml) was heated to 80° with vigorous bubbling of O_2, and subsequently I_2 (cat. amount) was added. After 45 min, the mixture was cooled to 20° and the solvent evaporated *in vacuo*. The residue was dissolved in CH_2Cl_2 (200 ml), and the org. phase was washed with 5% aq. Na_2SO_3 soln. (50 ml) and H_2O (2 × 100 ml), and dried (Na_2SO_4). CC (SiO_2; $CH_2Cl_2 \rightarrow CH_2Cl_2$/MeOH 99 : 1 → 98 : 2) afforded **20** (4.94 = g, 47%). Colorless glass. IR ($CHCl_3$): 2984*m*, 2928*m*, 2857*w*, 1590*w*, 1471*w*, 1437*m*, 1411*m*, 1363*s*, 1324*w*, 1245*m*, 1123*s*, 964*w*, 846*w*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 0.00 (*s*, 6 H); 0.83 (*s*, 9 H); 1.23 (*s*, 12 H); 2.62 (*t*, J = 7.0, 2 H); 3.69 (*t*, J = 7.0, 2 H); 7.34 – 7.52 (*m*, 6 H); 7.53 – 7.66 (*m*, 5 H); 7.97 (*d*, J = 1.2, 1 H); 8.16 (*d*, J = 11.5, 1 H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): – 5.59 (*s*); 18.01 (*s*); 23.47 (*s*); 24.58 (*s*); 25.60 (*s*); 61.55 (*s*); 80.49 (*s*); 84.04 (*s*); 88.65 (*s*); 123.55 (*d*, J = 13.4); 128.48 (*d*, J = 12.2); 131.94 (*s*); 131.97 (*d*, J = 102.5); 132.07 (*s*); 132.13 (*d*, J = 105.0); 136.90 (*d*, J = 18.3); 136.94 (*s*); 141.33 (*d*, J = 3.7) (theor. 19 resonances). ^{31}P-NMR ($CDCl_3$, 121.5 MHz): 28.94 (*s*). EI-MS: 586.2 (6, M^+), 529.1 (100). HR-EI-MS: 586.2846 (7, M^+, $C_{34}H_{44}BO_4PSi$; calc. 586.2839).

(S)-1,1′-(2,2′-Dimethoxy-1,1′-binaphthalene-7,7′-diyl)bis(5-{4-[(2-methoxyethoxy)methoxy]but-1-ynyl}(1,3-phenylene))bis(diphenylphosphane Oxide) ((*S*)-**26**). To (*S*)-**17** (900 mg, 1.91 mmol) and **20** (2.46 g, 4.193 mmol) in PhH/EtOH 11 : 3 (50 ml), Na_2CO_3 (808 mg, 7.62 mmol) in H_2O (30 ml) was added, and the mixture was heated to 80° under Ar, followed by addition of [$PdCl_2$(dppf)] (53 mg, 76.2 μmol). The mixture was heated for 3 h to 80°, cooled to 20°, concentrated *in vacuo*, and extracted with CH_2Cl_2 (3 × 50 ml). The combined org. layers were washed with sat. aq. $NaHCO_3$ soln. and sat. aq. NaCl soln., dried ($MgSO_4$), and evaporated *in vacuo*. CC (SiO_2; $CH_2Cl_2 \rightarrow CH_2Cl_2$/MeOH 99 : 1 → 98 : 2) yielded crude coupling product (1.428 g, 61%). To a soln. of this intermediate in dry THF (50 ml) at 0° under Ar, Bu_4NF (1M in THF, 4.2 ml, 4.19 mmol) was added, and the mixture was stirred for 1.5 h. The solvent was evaporated *in vacuo*, and the residue was dissolved in CH_2Cl_2 (50 ml) and washed with sat. aq. NaCl soln. (2 × 30 ml). The org. layer was dried ($MgSO_4$) and evaporated *in vacuo*. CC (SiO_2; CH_2Cl_2/Et_3N 99 : 1 → CH_2Cl_2/Et_3N/MeOH 98 : 1 : 1 → 96 : 1 : 4) afforded the bis(butynol) as an intermediate. To a soln. of this intermediate in dry CH_2Cl_2 (40 ml) at 0° under Ar, EtN(i-Pr)$_2$ (6.64 ml, 38.12 mmol) and MEM-Cl (2.61 ml, 22.87 mmol) were added, and the mixture was allowed to warm to 20° over 16 h. The soln. was concentrated *in vacuo* and dried at 10^{-2} Torr. The residue was dissolved in CH_2Cl_2 (200 ml), and the org. layer was extracted with sat. aq. $NaHCO_3$ soln. and sat. aq. NaCl soln., dried (Na_2SO_4), and evaporated *in vacuo*. CC (SiO_2; AcOEt/Et_3N/MeOH 98 : 1 : 1) yielded (*S*)-**26** (1.11 g, 49%). White foam. M.p. 68 – 78°. $[\alpha]_D^{23} = +80.5$ (c = 0.5, $CHCl_3$). IR (KBr): 3052*w*, 2922*m*, 2877*m*, 1620*m*, 1595*m*, 1508*s*, 1460*m*, 1436*s*, 1357*w*, 1314*w*, 1258*s*, 1194*s*, 1119*s*, 1070*s*, 880*w*, 836*m*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 2.66 (*t*, J = 6.9, 4 H); 3.35 (*s*, 6 H); 3.48 – 3.54 (*m*, 4 H); 3.64 – 3.74 (*m*, 14 H); 4.74 (*s*, 4 H); 7.21 (*d*, J = 1.6, 2 H); 7.28 – 7.66 (*m*, 30 H); 7.91 (*d*, J = 8.4, 2 H); 7.98 (*d*, J = 9.0, 2 H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): 20.77; 56.57; 58.93; 65.84; 66.86; 71.68; 80.49; 88.55; 95.49; 114.44; 119.29; 123.09; 123.56; 124.53; 124.72; 128.49; 128.66; 128.93; 129.53; 129.90; 130.03; 131.36; 131.44; 131.94; 132.07; 132.75; 132.80; 132.83; 133.62; 133.77; 133.85; 133.96; 134.14; 137.31; 141.99; 142.15; 155.46 (theor. 32 resonances). ^{31}P-NMR ($CDCl_3$, 121.5 MHz): 28.54 (*s*). FAB-MS: 1180.3 (100, MH$^+$). HR-SIMS-MS: 1179.4318 (85, MH$^+$, $C_{74}H_{69}O_{10}P_2$; calc. 1179.4366).

(S)-7,7′-Bis(3-(diphenylphosphanyl)-5-{4-[(2-methoxyethoxy)methoxy]but-1-ynyl}phenyl)-2,2′-dimethoxy-1,1′-binaphthalene ((*S*)-**6**). To a thoroughly degassed soln. of (*S*)-**26** (950 mg, 805.5 μmol) and Bu_3N (1.4 ml, 5.904 mmol) in dry xylenes (30 ml) under Ar, $HSiCl_3$ (385 μl, 3.815 mmol) was added *via* syringe. The soln. was heated to reflux for 3 h and subsequently cooled to 0°. Thoroughly degassed 30% aq. NaOH soln. (10 ml) was added under Ar, and the mixture was vigorously stirred for 1 h at 0° and then for 16 h at 20°. The layers were separated, the aq. layer was extracted with Et_2O (2 × 50 ml), and the combined org. layers were washed neutral with sat. aq. NaCl soln., dried (Na_2SO_4), and evaporated *in vacuo*. CC (SiO_2; hexane/AcOEt 7 : 5 → 5 : 7 → 1 : 2) yielded (*S*)-**6** (765 mg, 83%). White foam. M.p. 65 – 77°. $[\alpha]_D^{23} = +87.2$ (c = 0.5, $CHCl_3$). IR (KBr): 2922*m*, 2878*m*, 2833*w*, 1620*m*, 1596*w*, 1507*s*, 1459*m*, 1434*s*, 1356*w*, 1257*s*, 1099*s*, 1070*s*, 866*w*, 834*m*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 2.65 (*t*, J = 6.7, 4 H); 3.35 (*s*, 6 H); 3.46 – 3.56 (*m*, 4 H); 3.62 – 3.78 (*m*, 14 H); 4.74 (*s*, 4 H); 7.16 – 7.32 (*m*, 26 H); 7.34 – 7.58 (*m*, 6 H); 7.90 (*d*, J = 8.4, 2 H); 7.96 (*d*, J = 9.0, 2 H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): 20.81; 56.62; 58.93; 65.95; 66.82; 71.69; 81.19; 87.39; 95.49; 114.31; 119.45; 123.35; 123.41; 124.08; 124.19; 128.53; 128.56; 128.61; 128.66; 128.72; 128.85; 128.90; 131.94; 132.20; 133.57; 133.70; 133.83; 133.96; 134.04; 135.14;

135.43; 136.55; 136.65; 136.70; 136.79; 138.07; 138.25; 141.87; 141.97; 155.35 (theor. 32 resonances). ^{31}P-NMR ($CDCl_3$, 121.5 MHz): −4.34 (*s*). FAB-MS: 1147.4 (100, MH^+). HR-FAB-MS: 1145.4309 (38, $[M-H]^+$, $C_{74}H_{67}O_8P_2$; calc. 1145.4311). Anal. calc. for $C_{74}H_{68}O_8P_2$ (1147.29): C 77.47, H 5.97, O 11.16; found: C 77.36, H 6.26, O 11.01.

*(*R*)-2,6-Bis[3-(diphenylphosphanyl)phenyl]-12,13,14,15-tetrahydrodinaphtho[2.1-*b*:1,2-*d*][1,6]dioxecine* ((*R*)-**7**). To a suspension of Cs_2CO_3 (3.609 g, 11.1 mmol) and NaI (1.107 g, 7.38 mmol) in dry MeCN (40 ml) at 80° under Ar, (*R*)-**8** (410 mg, 0.923 mmol) in MeCN (5 ml) and 1,4-dichlorobutane (101 µl, 923 µmol) in MeCN (5 ml) were simultaneously added *via* syringe pump over 16 h. The mixture was evaporated *in vacuo*, and the residue was suspended in CH_2Cl_2. The org. layer was extracted with sat. aq. NaCl soln., dried ($MgSO_4$), and evaporated *in vacuo*. CC (SiO_2; hexane/CH_2Cl_2 4:1 → 3:1 → 2:1) provided (*R*)-**27** (*ca.* 295 mg, 64%) in the mixture with another alkylation product. To crude (*R*)-**27** (290 mg, 582 µmol) and **13** (717.6 mg, 1.77 mmol) in PhH/EtOH 11:3 (50 ml), Na_2CO_3 (247 mg, 2.328 mmol) in H_2O (30 ml) was added, and the mixture was vigorously stirred for 15 min at 80° under Ar. After addition of [$PdCl_2$(dppf)] (17 mg, 23.3 µmol), the mixture was heated to 80° for 3 h and then evaporated *in vacuo*. The residue was extracted with CH_2Cl_2 (3 × 50 ml), and the combined org. layers were washed with sat. aq. $NaHCO_3$ soln. and sat. aq. NaCl soln., dried ($MgSO_4$), and evaporated *in vacuo* to give the crude coupling product as a dark foam. To a thoroughly degassed soln. of the crude coupling product and Bu_3N (1.1 ml, 863.1 mg, 4.66 mmol) in dry xylenes (30 ml), $HSiCl_3$ (294 µl, 2.91 mmol) was added under Ar *via* syringe, and the soln. was heated to reflux for 3 h, then cooled to 0°. Thoroughly degassed 30% aq. NaOH soln. (10 ml) was added under Ar, and the mixture was vigorously stirred for 1 h at 0°, then for 16 h at 20°. The layers were separated, the aq. layer was extracted with Et_2O (2 × 50 ml), and the combined org. layers were washed neutral with sat. aq. NaCl soln., dried (Na_2SO_4), and evaporated *in vacuo*. CC (SiO_2; CH_2Cl_2/hexane 1:3 → 1:2 → 1:1) yielded (*R*)-**7** (409 mg, 82%). White foam. M.p. > 96° (dec). $[\alpha]_D^{23} = -177.9$ (*c* = 0.5, $CHCl_3$). IR (KBr): 3050*m*, 2935*w*, 2833*w*, 1619*s*, 1596*s*, 1507*s*, 1476*s*, 1433*s*, 1364*w*, 1317*s*, 1229*s*, 1093*s*, 1020*m*, 933*w*, 836*m*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.65–1.90 (*m*, 4 H); 4.10–4.17 (*m*, 2 H); 4.50–4.54 (*m*, 2 H); 7.05–7.45 (*m*, 32 H); 7.47 (*d*, *J* = 9.0, 2 H); 7.86 (*d*, *J* = 8.4, 2 H); 7.93 (*d*, *J* = 9.0, 2 H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): 25.21; 70.24; 117.49; 122.36; 123.82; 124.00; 128.00; 128.43; 128.51; 128.64; 128.70; 128.80; 129.08; 129.32; 132.18; 132.43; 132.65; 132.94; 133.46; 133.56; 133.72; 133.82; 134.29; 137.03; 137.10; 137.18; 137.25; 137.55; 137.70; 138.75 (*s*); 141.61; 141.71; 153.97 (theor. 26 resonances). ^{31}P-NMR ($CDCl_3$, 121.5 MHz): −4.43 (*s*). FAB-MS: 861.3 (100, MH^+). Anal. calc. for $C_{60}H_{46}O_2P_2 \cdot CH_2Cl_2$ (860.97): C 77.46, H 5.11; found: C 77.59, H 5.31.

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