A Modular Approach to Structurally Diverse Bidentate Chelate Ligands for Transition Metal Catalysis

Remo Kranich,[a] Knut Eis,[a] Oliver Geis,[a] Stefan Mühle,[+b] Jan W. Bats,[+c] and Hans-Günther Schmalz*[a, d]

Abstract: A modular approach to a new class of structurally diverse bidentate P/N, P/P, P/S, and P/Se chelate ligands has been developed. Starting from hydroquinone, various ligands were synthesized in a divergent manner via orthogonally bis-protected bromohydroquinones as the central building block. The first donor functionality (L^1) is introduced to the aromatic (hydroquinone) ligand backbone either by Pd-catalyzed cross-coupling (Suzuki coupling) with hetero-aryl bromides, by Pd-catalyzed amination, or by lithiation and subsequent treatment with electrophiles (e.g., chlorophosphanes, disulfides, diselenides, or carbamoyl chlorides). After selective deprotection, the second ligand tooth (L^2) is attached by reaction of the phenolic OH functionality with a chlorophosphane, a chlorophosphite, or a related reagent. Some of the resulting chelate ligands were converted into the respective PdX_2 complexes (X = Cl, I), two of which were characterized by X-ray crystallography. The methodology developed opens an access to a broad variety of new chiral and achiral transition metal complexes and is generally suited for the solid-phase synthesis of combinatorial libraries, as will be reported separately.

Keywords: hydroquinones · P ligands · palladium · synthesis design

Introduction

Transition metal catalyzed transformations play an extremely important role in the synthesis of complex organic molecules as well as in the industrial production of bulk, speciality, and fine chemicals.[1] In particular, homogeneous catalysts based on bidentate chelating ligands (e.g., P/P or P/N ligands) have found widespread application and clearly dominate the field of (non-oxidative) enantioselective transition metal catalysis.[2] Despite the fact that a number of highly active and selective catalysts have already been developed for certain transformations, the search for new, efficient transition metal catalysts still remains one of the most challenging tasks of chemical research.

It is an established fact that the efficiency (activity and selectivity) of a homogeneous metal catalyst depends on a variety of parameters, but crucially on a subtle electronic, geometric, and steric interplay between the ligand(s) and the metal center. Due to the complexity of the situation, the development of new metal catalysts only by rational design is usually impossible—in particular in enantioselective catalysis. Thus, new powerful catalysts are generally discovered by "variation and selection",[3] that is, by variation of the organic ligand attached to a catalytic metal center and subsequent testing (screening) of the resulting complexes. As a consequence, many homo- and heterobidentate ligands have been prepared and tested in the past, and an intense research activity can currently be observed in this field. In most cases, new (more or less rationally conceived) ligand structures are individually synthesized in a rather time-consuming manner, even though most of them will never lead to an efficient catalyst.

In order to speed up the process of catalyst development, *modular ligand architectures* are highly desirable,[4] because they facilitate the systematic variation and optimization of the ligand structure. Important classes of chiral catalysts based on

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[+] Crystallographic investigation.

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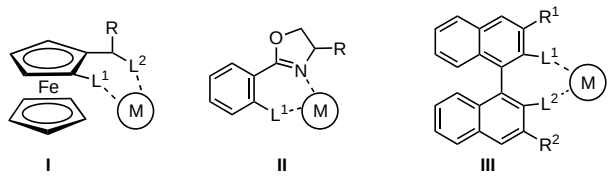
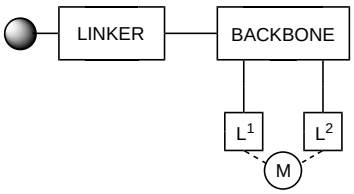
modular ligands are, for instance, ferrocenyl systems of type **I**,[5] chiral oxazolines of type **II**,[6] and binaphthyl derived complexes of type **III**.[7]



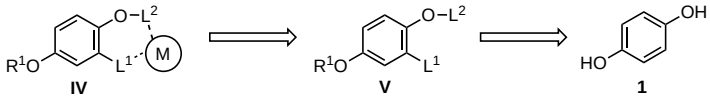
In recent years, the advent of combinatorial chemistry[8] has brought about new concepts and powerful tools for the synthesis of whole libraries of organic compounds. In particular, the development of new techniques for the solid-phase synthesis of small organic molecules has opened new opportunities for parallelization and automatization: this greatly reduces the amount of time needed for the synthesis and the screening of compound libraries.

It is, of course, an evident thought to exploit the techniques of "combinatorial chemistry" also to the search for new homogeneous (single site) metal complex catalysts.[9–11] In order to tackle this goal, methods are needed that allow for the solid-phase synthesis of libraries of organic ligands and their respective metal complexes by using "combinatorial" methods. While solid-phase *peptide* chemistry has been used by a number of groups to synthesize libraries of (linear) modular ligands,[9c–g, k, o, q, r] the solid-phase synthesis of modular *non-peptidic* ligand systems suited for the complexation of low-valent transition metals (e.g., branched architectures of type **A**) still remains a major challenge.[9m,n, 11]



In the course of our own program aiming at the search for new metal catalysts we are interested in modular complexes of type **IV**. These complexes derive from ligand architechtures (**V**) that have an achiral arene backbone and two variable ligand teeth (L^1 and L^2). The attachment to a polymeric support could be achieved by means of the additional functionality (R^1O). In a retrosynthetic sense, such compounds can be easily traced back to hydroquinone (**1**) as a readily available starting material (Scheme 1).

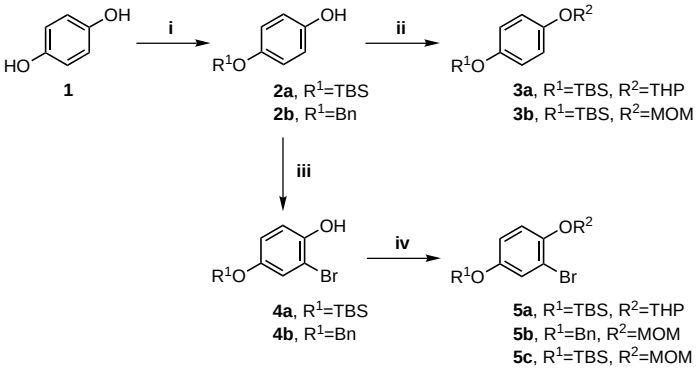
As a first step towards the realization of the above sketched concept and as a prerequisite for the projected synthesis of complex libraries by using solid-phase techniques, we here disclose the results of a study carried out in order to develop the underlying chemistry in the homogeneous series. We report the synthesis and characterization of a variety of ligands of type **V** and some of their complexes **IV**. At this stage of the project it was, of course, not intended to prepare and characterize all possible combinations: on the one hand the goal was to develop and to evaluate experimental procedures giving access to a broad structural diversity, on the other hand the structural characterization of representative metal complexes was projected.



Scheme 1. Retrosynthetic analysis of modular complexes of type **IV**.

Results and Discussion

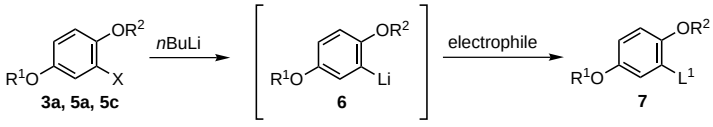
Synthesis of the ligand backbone: Following the strategy outlined above (Scheme 1), the first task was to convert hydroquinone (**1**) into a suitable functionalized and orthogonally bis-protected derivative (**3** or **5**) that would allow the regioselective introduction of L^1 in *ortho* position to one of the oxygen functions. As the protecting group R^1 (which would be replaced by a linker group in the projected solid-phase synthesis) two rather stable groups were selected as suitable candidates: 1) the *tert*-butyldimethylsilyl (TBS) and the simple benzyl protecting group.[12] While the benzyl ether **2b** is a commercially available compound, the TBS derivative **2a** was prepared from **1** in 64% yield under standard conditions (Scheme 2). As a protecting group (R^2) for the second hydroxy functionality, the tetrahydropyranyl (THP) and methoxymethyl (MOM) ethers were chosen because the resulting acetals (OTHP, OMOM) are stable under basic conditions, but can be selectively cleaved under mild (acidic) conditions.[12] In addition, these groups exhibit a strong *ortho*-directing effect in metallation reactions (vide infra).[13] The conversion of **2a** into the diprotected hydroquinone **3a** was achieved in high yield under the conditions given in Scheme 2. As an alternative to prepare for the regioselective introduction of L^1 a bromine/lithium exchange was taken into consideration. Therefore, the phenols **2a** and **2b** were



Scheme 2. i) TBSCl, imidazole, DMF, RT (**1** → **2a**, 64%); ii) 3,4-dihydro-*2H*-pyrane, CH_2Cl_2, cat. PPTS, RT (**2a** → **3a**, 93%); iii) *t*$BuNH_2$/Br_2, toluene, −78 °C to RT (**2a** → **4a**, 60%); Br_2, $CHCl_3$, RT (**2b** → **4b**, 74%); iv) 3,4-dihydro-*2H*-pyrane, CH_2Cl_2, cat. PPTS, RT (**4a** → **5a**, 92%); $CH_2(OMe)_2$, CH_2Cl_2, molecular sieves, rfl. (**4a** → **5c**, 92%); $CH_2(OMe)_2$, CH_2Cl_2, P_2O_5(**4b** → **5b**, 88%).

converted into the bromides **4a** and **4b**, respectively. While the conversion of **2b** to **4b** was best performed with bromine in chloroform following the procedure of Dodsworth,[14] the bromination of the HBr-sensitive substrate **2a** was achieved by employing the reagent prepared in situ from bromine and *tert*-butylamine.[15] In both cases, a 2,6-dibrominated compound was formed as a by-product that had to be removed by chromatography. Finally, the protection of the free phenolic OH function of **4a** and **4b** under standard conditions provided the acetals **5a–c**. The reaction sequences thus developed (Scheme 2) could easily be performed on a multigram scale and open an efficient access to the backbone part of the projected ligands.

Introduction and variation of L^1: The first general method to introduce a donor functionality L^1 starts with the conversion of compounds of type **3** or **5** into a metallated intermediate of type **6** and subsequent reaction with an electrophilic (L^1-X) reagent (Scheme 3). Lithiation of **3** was achieved by *ortho*

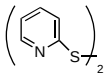
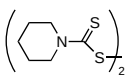
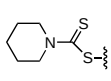


Scheme 3.

metallation (1.5 equivalents *n*-butyllithium, THF, −78 °C to room temperature), while substrates **5a** and **5b** smoothly underwent bromine–lithium exchange by treatment with 1.2 equivalents of *n*-butyllithium in THF at −78 °C.[16]

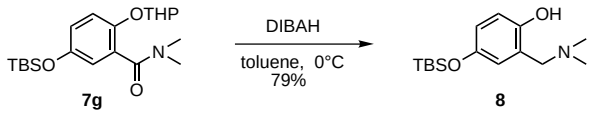
The lithiated intermediates of type **6** were successfully treated with a variety of electrophiles including disulfides, diselenides, chlorophosphanes, and carbamoyl chlorides (Table 1). Usually, these reactions proceeded smoothly according to TLC analysis. However, as the yields given in Table 1 reflect, some of the products proved to be rather sensitive towards oxidation causing some losses during workup. All attempts to use chlorophosphites ($ClP(OR)_2$) or diaminochlorophosphanes ($ClP(NR_2)_2$) as electrophiles only afforded product mixtures, probably due to the sensitivity of the initial products towards further nucleophilic attack. Certainly because of steric reasons, di-*tert*-butyldisulfide did not react with **6** at all.

Table 1. Preparation of products of type **7** according to Scheme 3.

	Reactant	R^1	R^2	Lithiation conditions[a]	Electrophile	L^1	Product (yield)
1	**5a**	TBS	THP	A	Ph_2S_2	SPh	**7a**[b] (89%)
2	**5a**	TBS	THP	A			**7b** (82%)
3	**5a**	TBS	THP	A			**7c** (67%)
4	**5a**	TBS	THP	A	Ph_2Se_2	SePh	**7d**[b] (87%)
5	**5a**	TBS	THP	A	$ClPPh_2$	PPh_2	**7e**[b] (79%)
6	**3a**	TBS	THP	B	Ph_2S_2	SPh	**7a** (94%)
7	**3a**	TBS	THP	B	Ph_2Se_2	SePh	**7d** (93%)
8	**3a**	TBS	THP	B	$ClPPh_2$	PPh_2	**7e** (73%)
9	**3a**	TBS	THP	B	$ClP(iPr)_2$	$P(iPr)_2$	**7f** (68%)
10	**3a**	TBS	THP	B	$ClCONMe_2$	$CONMe_2$	**7g** (85%)
11	**5c**	TBS	MOM	A	Ph_2S_2	SPh	**7h**[c] (90%)
12	**5c**	TBS	MOM	A	$ClPPh_2$	PPh_2	**7i** (69%)

[a] Lithiation conditions: A: 1.2 equiv *n*BuLi, THF, −78 °C, 1 h, then 2 equiv electrophile, warm up to RT; B: 1.5 equiv *n*BuLi, THF, −78 °C,15 min, RT, 30 min, then 2 equiv electrophile at −78 °C, 15 min, warm up to RT. [b] The isolated product contained minor amounts of **3a**. [c] The isolated product contained minor amounts of **3b**.

The clean reaction of the lithiated intermediate **6** with a carbamoyl chloride ($ClCONMe_2$) deserves special notice, because the resulting amide could easily be reduced with diisobutyl aluminum hydride to the corresponding amine (**8**) with concomitant deprotection of R^2 (Scheme 4). This paves



Scheme 4.

the way for the preparation of a broad variety of amine side chains, because many (including chiral) amines are available which can easily be converted into the corresponding carbamoyl chlorides (or isocyanates) by treatment with phosgene.

As a second general possibility for the variation of L^1 it was envisioned to attach hetero arenes by means of a Pd-catalyzed cross-coupling reaction.[17] In a first series of experiments, we converted **5a** into the Grignard derivative and the lithiated intermediates of type **6** into the corresponding zinc or tin organic species by addition of zinc bromide or tributyltin chloride, respectively. However, the subsequent Pd-catalyzed coupling reactions employing heteroarylbromides proceeded only sluggishly. Much better results were obtained under the conditions of the Suzuki coupling.[18] In the presence of $[Pd(PPh_3)_4]$ as a catalyst and aqueous Na_2CO_3 as a base, the boronic acid, prepared from **3a** by successive treatment with butyllithium, triisopropylborate, and water, treated with 2-bromopyridine, 2-bromopyrimidine, 2-bromothiophene, and 2-bromothiazol in toluene to afford the desired products (**10a–10e**) in acceptable yields (Scheme 5, Table 2). For the analogous transformations of the boronic ester derived from the MOM-protected starting material **5b**, the use of $Ba(OH)_2$ as a base in dimethoxyethane/water[19] proved to be most effective. As one would have expected, higher yields were generally observed with the more electron-deficient six-membered heterocycles. It must be emphasized that the THP protecting group was not stable under the conditions of the Suzuki coupling. In some cases, when the cleavage of the THP group was not complete, brief treatment of the crude reaction mixture with methanolic *p*-toluene sulfonic acid (*p*-TsOH) completed the conversion to the (desired) deprotected compounds.

As a third general possibility for the introduction and variation of L^1 the Pd-catalyzed amination according to Buchwald[20] and Hartwig[21] was investigated. After preliminary experiments had indicated that THP-protected substrates are not suitable for these transformations,[22] all reactions were carried out with the MOM-protected substrate

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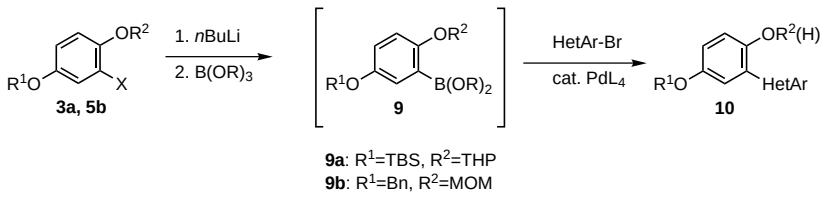
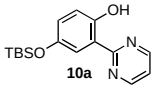
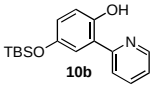
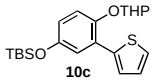
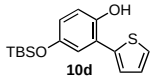
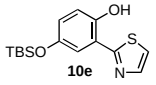
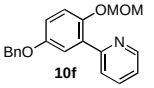
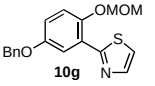


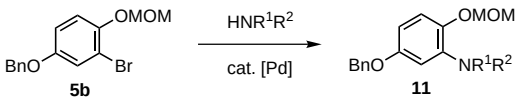
Scheme 5.

Table 2. Preparation of products of type **10** by Suzuki coupling according to Scheme 5.

	Reactant	Reaction conditions[a]	HetAr-Br	Product[b]	Yield
1	**3a**	A		 **10a**	85 %
2	**3a**	A		 **10b**	81 %
3	**3a**	A		 **10c**	48 %
				 **10d**	33 %
4	**3a**	A		 **10e**	56 %
5	**5b**	B		 **10f**	72 %
6	**5b**	B		 **10g**	55 %

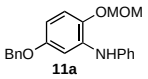
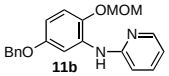
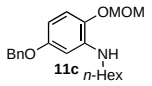
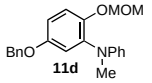
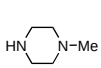
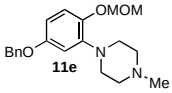
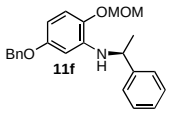
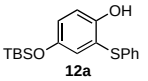
[a] Reaction conditions: A: i) 1.5 equiv *n*BuLi, THF, −78 °C, 15 min, RT 30 min, then 2.5 equiv $B(O\mathit{i}Pr)_3$ over a period of 30 min at −78 °C, warm up to RT, 2 h, then H_2O; ii) 1.25 equiv HetAr-Br, 2.5 equiv 2 M aqueous Na_2CO_3, 3 mol % $[Pd(PPh_3)_4]$, toluene, EtOH, reflux. B: i) 1.05 equiv *n*BuLi, THF, −78 °C, 30 min, then 1.5 equiv $B(OMe)_3$, −78 °C, 30 min, RT, 1 h; ii) 1.1 equiv HetAr-Br, 1.2 equiv $Ba(OH)_2 \cdot 8H_2O$, 3 mol % $[Pd(PPh_3)_4]$, DME/H_2O, 80 °C, 4 h. [b] In some cases the OTHP function (R^2 = THP) was not completely cleaved under the conditions of the Suzuki coupling; however, the cleavage can be easily completed by exposure to methanolic *p*-TsOH.

5b (Scheme 6). The results, summarized in Table 3, show that both primary and secondary amines bearing either arylic or aliphatic substituents can be employed. However, it must be emphasized that the choice of the ligand was found to be absolutely crucial. While different ligands (dppf or BINAP) had to be used in the reactions of different primary amines, the Buchwald ligand 1-dicyclohexylphosphino-1′-dimethylaminobiphenyl[23] proved to be superior for the reactions of all secondary amines. Thus, the Pd-catalyzed amination of the electron-rich[24] substrate **5b** allows the introduction of many different, including chiral, amino side chains as L^1.



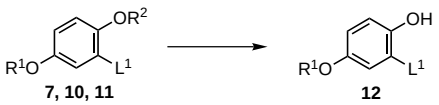
Scheme 6.

Table 3. Preparation of products of type **11** by Pd-catalyzed amination of **5b** according to Scheme 6.

	Conditions[a]	Amine	Product	Yield
1	A	$PhNH_2$	 **11a**	98 %
2	B		 **11b**	98 %
3	B	*n*-Hex-NH_2	 **11c**	95 %
4	C	PhNHMe	 **11d**	90 %
5	C		 **11e**	95 %
6	B		 **11f**	92 %
7	C	Ph_2NH	 **12a**	78 %

[a] Conditions: Reactions were run with 1.0 equiv of **5b**, 1.2 equiv amine, 1.4 equiv of NaO*t*Bu, 1–2 mol % $Pd_2(dba)_3$, 3–6 mol % ligand, toluene (3 mL) at 80 °C. A: 1 mol % $[Pd_2(dba)_3]$, 3 mol % DPPF; B: 1–2 mol % $[Pd_2(dba)_3]$, 3–4 mol % (*rac*)-BINAP; C: 1–2 mol % $[Pd_2(dba)_3]$, 3–6 mol % 1-(*N*,*N*-dimethylamino)-1′-(dicyclohexylphosphino)biphenyl.

Variation of L^2: In order to prepare for the introduction of the second donor function (L^2) to the ligand backbone, the protecting group (R^2) adjacent to the first ligand tooth (L^1) of the prepared monodentate ligands had to be removed (Scheme 7). While the deprotection of the THP ethers usually

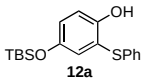
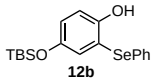
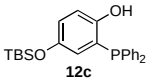
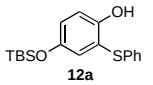
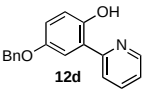
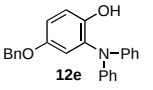


Scheme 7.

proceeded smoothly either with ethanolic HCl or with *p*-TsOH in methanol, the cleavage of the MOM protecting group required much more severe conditions (NaI, acetone, aqueous HCl).[25] For unknown reasons, the phosphane **7i** could not be cleaved under these conditions.

The results of several deprotection reactions are summarized in Table 4. In some cases the yields were lowered due to

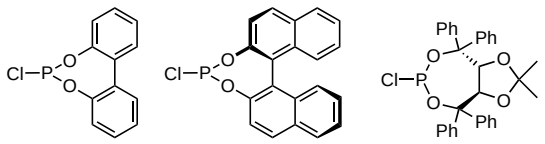
Table 4. Cleavage of the protecting group R^2 according to Scheme 7.

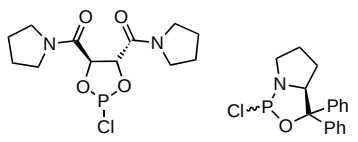
	Reactant	R^1	R^2	Conditions[a]	Product	Yield
1	**7a**	TBS	THP	A	 **12a**	93%
2	**7d**	TBS	THP	A	 **12b**	86%
3	**7e**	TBS	THP	B	 **12c**	72%
4	**7h**	TBS	MOM	C	 **12a**	78%
5	**10f**	Bn	MOM	D	 **12d**	85%
6	**11g**	Bn	MOM	D	 **12e**	52%

[a] Cleavage conditions: A: 5 mol% *p*-$TsOHH_2O$, MeOH, RT; B: 20 mol% *p*-$TsOHH_2O$, MeOH, 40 °C; C: 1.05 equiv NaI, 0.16 M HCl/acetone, reflux; D: 1.0 equiv NaI, cat. 2 N aqueous HCl, acetone, 50 °C.

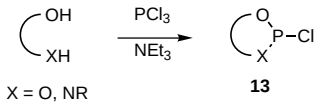
difficulties during product isolation, a problem that would not appear with polymer-bound substrates. During the cleavage of the THP group of the phosphane **7e** it was necessary to strictly exclude oxygen in order to prevent oxidation of the phosphorous center.

Having prepared a variety of deprotected phenols of type **12**, we turned our attention to the *O*-phosphorylation of these substrates. Though a couple of chlorophosphanes (R_2PCl) and chlorophosphites ($(RO)_2PCl$) are commercially available, many more reagents of type **13** (e.g., those shown below)


13a **13b** **13c**

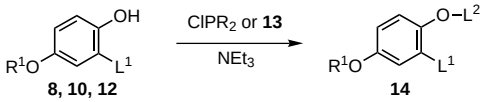

13d **13e**

are easily accessible from the corresponding diols or amino alcohols by treatment with PCl_3 in the presence of an amine base (Scheme 8).[26]


X = O, NR **13**

Scheme 8.

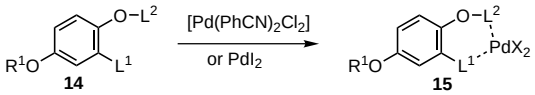
Starting from the phenols of type **12**, various *O*-phosphorylation reactions were carried out under standard conditions according to Scheme 9. In order to obtain a high conversion,


8, 10, 12 **14**

Scheme 9.

two equivalents of the P electrophile were usually employed in the presence of a large excess (15–20 equivalents) of NEt_3 in THF. As Table 5 reflects, a decent number of new bidentate P/S, P/Se, P/P and P/N ligands of type **14** were prepared by this means, most of which were fully characterized by spectroscopic methods (see experimental section). However, as indicated in Table 5, some of the products were found to be highly sensitive towards oxidation and/or hydrolysis.[27] In such cases, the ligands were directly converted to the corresponding Pd-complexes (vide infra).

Preparation and characterization of selected Pd^{II} complexes: To exemplify the general ability of the bidentate ligands of type **14** to form stable and well-defined complexes with transition metals, we converted several of them to the corresponding palladium(II) complexes (**15**) following a standard procedure (Scheme 10) generally using the bis(benzonitrile)dichloro-Pd^{II} complex as a soluble source of Pd^{II}.[28] Usually a mixture of this reagent and the respective chelate ligand were stirred in benzene or toluene (in some cases at 80 °C) before hexane was injected causing the $PdCl_2$ complex to precipitate as a yellow solid, which was isolated in good to excellent yield by simple filtration. As an alternative, the ligands could be complexed by employing PdI_2 to give the respective PdI_2 complexes as red solids. The crude complexes showed only traces of impurities in the ^1H NMR spectrum. It should be mentioned that the characterization of the complexes by ^{13}C NMR was meaningless in several cases due to the complexity of the spectra caused by the P–C coupling. The various complexes prepared are listed in Figure 1.


14 **15**

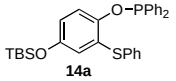
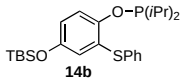
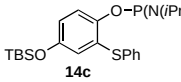
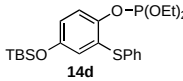
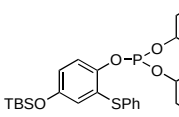
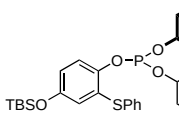
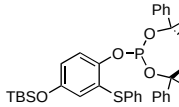
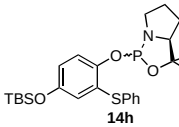
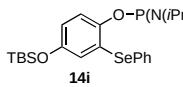
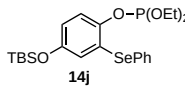
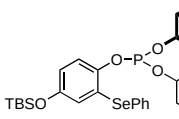
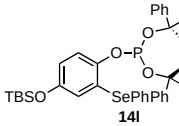
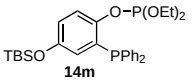
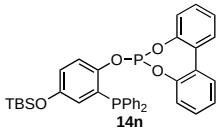
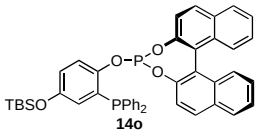
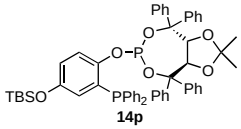
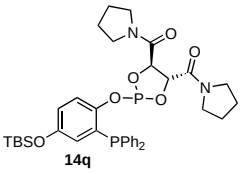
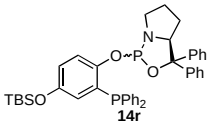
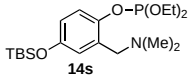
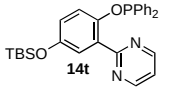
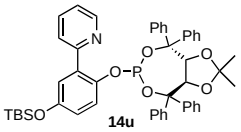
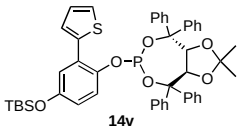
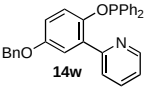
Scheme 10.

In most cases, our attempts to grow single crystals of the complexes **15** failed. However, when we tried to recrystallize **15a** from a hot mixture of THF and dichloromethane, we obtained crystals of the desilylated derivative **15a′** that were suitable for an X-ray crystallographic investigation.[29]

The structure of **15a′** (Figure 2) shows the Pd atom in a slightly distorted square-planar coordination. The Pd–Cl bond, which is *trans* to the Pd–P bond, is significantly longer (2.37 Å) than the other Pd–Cl bond (2.29 Å). Similar differences in Pd–Cl bond lengths have been observed in other dichlorophosphinothiolatopalladium(II) complexes.[30] The an-

0947-6539/00/0615-2878 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 15

Table 5. Preparation of ligands of type **14** according to Scheme 9.

	Reactant	R^1	L^1	$ClPR_2$	Product	Yield
1	**12a**	TBS	SPh	$ClPPh_2$	 **14a**	90 %
2	**12a**	TBS	SPh	$ClP(iPr)_2$	 **14b**	98 %
3	**12a**	TBS	SPh	$ClP(N(iPr)_2)_2$	 **14c**	65 %
4	**12a**	TBS	SPh	$ClP(OEt)_2$	 **14d**	79 %
5	**12a**	TBS	SPh	**13a**	 **14e**	99 %
6	**12a**	TBS	SPh	**13b**	 **14f**	99 %
7	**12a**	TBS	SPh	**13c**	 **14g**	99 %
8	**12a**	TBS	SPh	**13e**	 **14h**	93 %
9	**12b**	TBS	SePh	$ClP(N(iPr)_2)_2$	 **14i**	94 %
10	**12b**	TBS	SePh	$ClP(OEt)_2$	 **14j**	54 %
11	**12b**	TBS	SePh	**13b**	 **14k**	32 %
12	**12b**	TBS	SePh	**13c**	 **14l**	64 %
13	**12c**	TBS	PPh_2	$ClP(OEt)_2$	 **14m**	94 %
14	**12c**	TBS	PPh_2	**13a**	 **14n**	37 %
15	**12c**	TBS	PPh_2	**13b**	 **14o**	84 %
16	**12c**	TBS	PPh_2	**13c**	 **14p**	99 %
17	**12c**	TBS	PPh_2	**13d**	 **14q**	90 %
18	**12c**	TBS	PPh_2	**13e**	 **14r**	69 %
19	**8**	TBS	CH_2NMe_2	$ClP(OEt)_2$	 **14s**	96 %
20	**10a**	TBS	2-pyrimidyl	$ClPPh_2$	 **14t**	a)
21	**10b**	TBS	2-pyridyl	**13c**	 **14u**	85 %
22	**10d**	TBS	2-thiophenyl	**13c**	 **14v**	67 %
23	**12d**	OBn	2-pyridyl	$ClPPh_2$	 **14w**	[a]

[a] The ligand could only be isolated as the corresponding Pd^{II} complex **15**.

gle between the two phenyl rings of the biphenyl group is 38.4 (1)°. The molecule shows no short intermolecular distances. In the crystal the molecules are connected by intermolcular hydrogen bonding between the hydroxyl group and a Cl atom of a neighboring molecule. The second complex we were able to crystallize is **15f**. Its crystal structure (Figure 3)[31] also shows the typical slightly distorted square-planar coordination mode of the Pd^{II} atom with the Pd–Cl bond *trans* to the phosphorous being longer (2.35 Å) than the other Pd–Cl bond (2.29 Å). In both complexes (**15a′** and **15f**) the metal is located outside the plane defined by the aromatic backbone rendering the whole chelate substructure chiral. The P-Pd-S coordination angle in **15a′** is 93.0° and the P–Pd–N angle in **15f** is 85.2°.

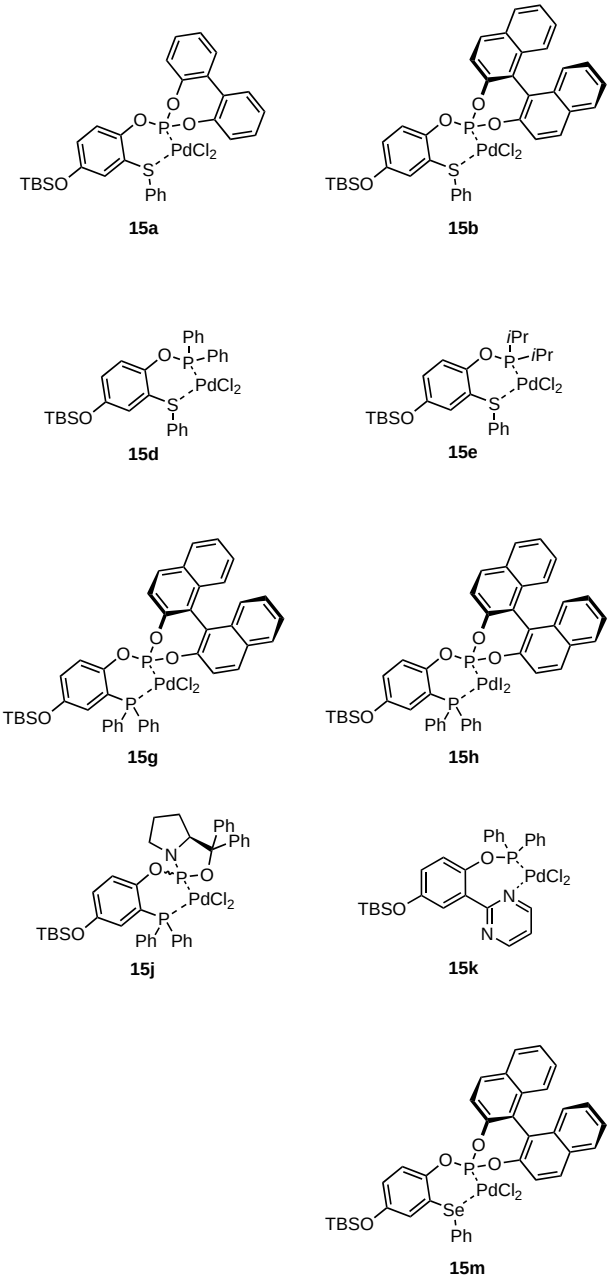


Figure 1. Various Pd^{II} complexes prepared according to Scheme 10.

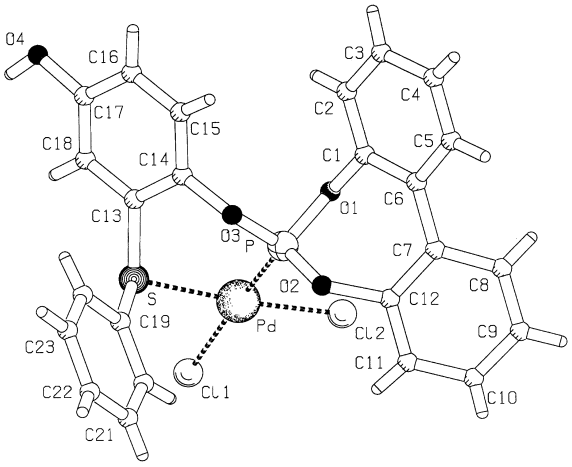


Figure 2. Structure of complex **15a′** in the crystal.

Conclusion

We have introduced a concept for the modular synthesis of new (chiral) bidentate chelate ligands and their respective transition metal complexes. The general validity of the approach was demonstrated by synthesis and characterization of a variety of structurally diverse compounds. Further variations of the ligand backbone, the ligand teeth, and the metal fragment are possible. Thus, the methodology developed opens a rather general access to a broad variety of new chiral and achiral transition metal complexes. Furthermore, it is generally suited for the automated solid-phase synthesis of combinatorial libraries, as will be reported separately. Also, the testing of the new ligands in (asymmetric) metal catalysis is under current investigation. We are optimistic that our modular approach will lead to the discovery of new, efficient, homogeneous transition metal catalysts in the future.

Experimental Section

General: Manipulations involving air-sensitive compounds were carried out in an argon atmosphere by using Schlenk and syringe techniques. Anhydrous solvents were obtained by distillation from sodium benzophenone ketyl (THF and diethyl ether) or by refluxing for 4 h with CaH_2 followed by distillation and storage over 3 Å molecular sieves (toluene and DMF). Reagents (generally $\geq 99\,\%$) were used as provided by Aldrich, Fluka, Merck, Acros, and Chemetall without further purification unless otherwise stated. The concentration of organolithium solutions was determined by titration with menthol in THF in the presence of 1,10-phenantroline.[32] Reactions were monitored by analytical thin-layer chromatography (TLC) by using Merck silica gel 60 F254 glass plates. The chromatograms were visualized with UV light and by staining with a cerium reagent [prepared by dissolving phosphomolybdic acid (2 g) and cerium(IV) sulfate (1 g) in a mixture of conc. H_2SO_4 (10 mL) and EtOH (90 mL)] followed by heating. Flash chromatography[33] was performed with silica gel 60 (230–400 mesh) from Merck. Preparative thin-layer chromatography (PTLC) was carried out by using a chromatotron (Harrison Research Model 7924T) on glass plates coated with 1–4 mm layers of silica-gel-containing gypsum (Merck PF60 F254). NMR spectra were obtained in $CDCl_3$ on Bruker instruments (AM270 or AM400) with a residual undeuterated solvent as an internal reference. The spectra are reported in ppm relative to tetramethylsilane with the following abbreviations to express the multiplicities: s = singlet; d = doublet; t = triplet; q =

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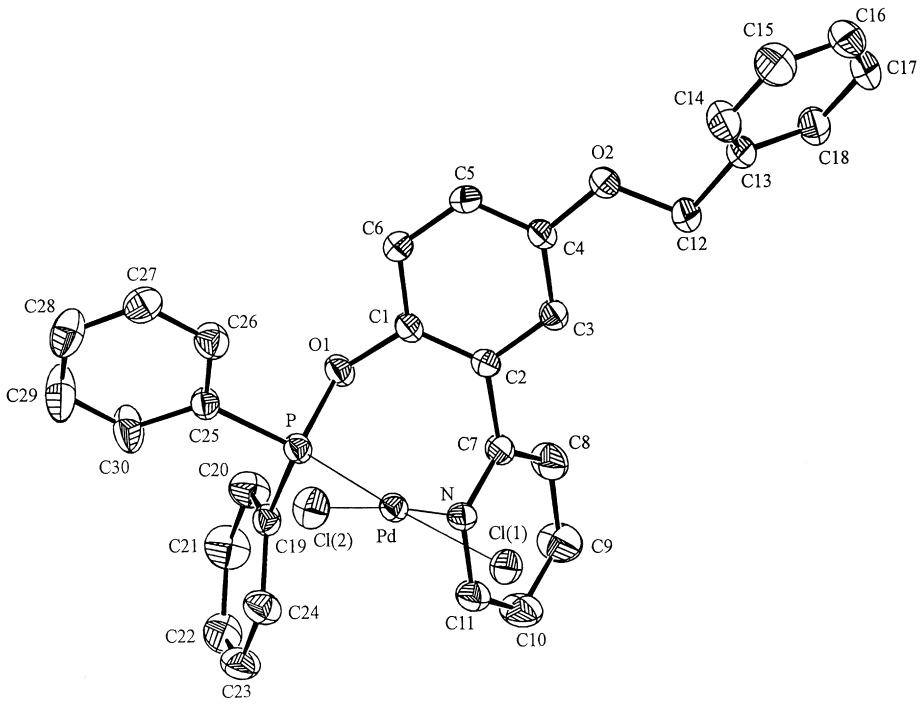

Figure 3. Structure of complex **15 f** in the crystal.

quartet; br = broad. ^{13}C chemical shifts were determined using ^{1}H-decoupled spectra, the number of protons bound directly was determined by employing the DEPT sequence[34] (q = CH_3; t = CH_2; d = CH; s = quarternary carbons). Mass spectroscopy was carried out at 70 eV with a Finnigan MAT 95 ST instrument. Infrared spectra were usually recorded on a Magna FT IR 750 instrument (Nicolet) by using the ATR technique. Optical rotations were measured with a Perkin–Elmer 241 polarimeter, concentrations *c* are given in g 100 mL^{-1}. Melting points were measured in open capillary tubes and are uncorrected.

4-(*tert*-Butyldimethylsilanoxy)phenol (2a): Hydroquinone (**1**, 10 g, 91 mmol) and TBSCl (14 g, 93 mmol) were dissolved in DMF (120 mL), and a solution of imidazol (7.5 g, 110 mmol) in DMF (40 mL) was added dropwise. The clear colorless solution obtained was stirred for 17 h in an argon atmosphere and then quenched with H_2O (40 mL). The layers were separated and the aqueous layer was extracted with MTB ether (3150 mL). The combined organic layers were washed with water and brine, and dried ($MgSO_4$). The solvent was evaporated and the crude product was purified by flash-chromatography (hexane/EtOAc 10:1) to afford **2a** (13 g, 58 mmol, 64 %) as a white solid. M.p. 58 °C; TLC (hexane/EtOAc 10:1): $R_f = 0.22$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.17$ (s, 6H; $SiCH_3$), 0.97 (s, 9H; $SiCCH_3$), 4.41 (br s, 1H; OH), 6.71 (s, 4H; H_{ar}); ^{13}C NMR (67 MHz, $CDCl_3$): $\delta = -4.5$ (q, $SiCH_3$), 18.2 (s, SiC), 25.7 (q, $SiCCH_3$), 116.0 (d, CH_{ar}), 120.8 (d, CH_{ar}), 149.3 (s, C_{ar}), 149.7 (s, C_{ar}); IR (ATR): $\tilde{\nu} = 3334$ (w, OH), 2957 (w), 2930 (w), 2896 (w), 2886 (w), 2859 (w), 1506 (s), 1254 (m), 1238 (m), 1213 (m), 912 (m), 829 (s), 780 cm^{-1} (m); MS: *m*/*z* (%): 224 (20), 167 (100); HRMS $C_{12}H_{20}O_2Si$: calcd 224.1233; found 224.1219.[35]

[4-(Tetrahydropyran-2-yloxy)phenoxy]-*tert*-butyldimethylsilane (3a): A solution of **2a** (8.03 g, 36 mmol), 3,4-dihydro-2*H*-pyran (9.6 mL, 105 mmol), and pyridinium *p*-toluene sulfonate (PPTS) (890 mg, 3.54 mmol)[36] in dichloromethane (110 mL) was stirred at RT for 4.5 h in an argon atmosphere. The reaction mixture was washed then with half-saturated brine (100 mL), the layers were separated, and the organic layer was dried ($MgSO_4$). After solvent evaporation the crude product was purified by flash chromatography (hexane/EtOAc 10:1) to afford **3a** (10.32 g, 33.5 mmol, 93 %) as a colorless oil. TLC (hexane/EtOAc 10:1): $R_f = 0.52$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.17$ (s, 6H; $SiCH_3$), 0.98 (s, 9H; $SiCCH_3$), 1.52–1.74 (m, 3H; CH_2), 1.77–1.91 (m, 2H; CH_2), 1.91–2.07 (m, 1H; CH_2), 3.53–3.65 (m, 1H; OCH_2), 3.94 (td, $J_1 = 10.5$ Hz, $J_2 = 3$ Hz, 1H; OCH_2), 5.28 (br t, $J = 3.5$ Hz, 1H; OCH), 6.75 (dt, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 2H; H-C3), 6.92 (dt, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 2H; H-C2); ^{13}C NMR (67 MHz, $CDCl_3$): $\delta = -4.5$ (q, $SiCH_3$), 18.1 (s, SiC), 19.0 (t, CH_2), 25.3 (t, CH_2), 25.7 (q, $SiCCH_3$), 30.3 (t, CH_2), 62.1 (t, OCH_2), 97.2 (d, OCH), 117.5 (d, CH_{ar}), 120.5 (d, CH_{ar}), 150.1 (s, C_{ar}), 151.5 (s, C_{ar}); IR (ATR): $\tilde{\nu} = 3044$ (w), 2949 (m), 2930 (m), 2895 (w), 2883 (w), 2858 (m), 1736 (w), 1503 (s), 1472 (w), 1463 (w), 1441 (w), 1389 (w), 1385 (w), 1325 (w), 1255 (s), 1227 (s), 1219 (s), 1201 (s), 1182 (m), 1147 (w), 1126 (m), 1110 (m), 1077 (w), 1049 (w), 1038 (m), 1021 (m), 1010 (w), 971 (s), 915 (s), 872 (m), 838 (s), 794 (w), 780 (m), 707 (w), 679 cm^{-1} (w); MS: *m*/*z* (%): 308 (1) $[M]^+$, 1225 (12), 224 (67), 166 (25), 167 (100), 85 (14); HRMS $C_{17}H_{28}O_3Si$: calcd 308.1808; found 308.1813.

2-Bromo-4-(*tert*-butyldimethylsilanoxy)phenol (4a): A solution of *tert*-butylamine (15.6 mL, 148 mmol) in toluene (130 mL) was cooled to −40 °C and bromine (3.30 mL, 64.5 mmol) was added dropwise. The mixture was stirred for 1 h at −25 °C and then cooled to −78 °C before a separately prepared, cooled (0 °C) solution of **2a** (12.9 g, 57.5 mmol) in toluene (110 mL) was added by means of a transfer needle under argon. The obtained mixture was allowed to warm up to −50 °C over a period of 2.5 h. The cooling bath was removed and stirring was continued for 1 h. A mixture of H_2O (30 mL) and saturated aqueous $Na_2S_2O_3$ (30 mL) was added, and the aqueous layer was extracted with MTB ether (310 mL). The combined organic layers were washed with water and twice with brine. The solvent was evaporated, and the crude product was purified by flash chromatography (hexane/EtOAc 20:1) to afford **4a** (10.4 g, 34.3 mmol, 60 %) as a pale orange oil. TLC (hexane/EtOAc 10:1): $R_f = 0.29$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.17$ (s, 6H; $SiCH_3$), 0.97 (s, 9H; $SiCCH_3$), 5.14 (s, 1H; OH), 6.71 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; H-C5), 6.88 (d, $J = 9$ Hz, 1H; H-C6), 6.96 (d, $J = 3$ Hz, 1H; H-C3); ^{13}C NMR (67 MHz, $CDCl_3$): $\delta = -4.6$ (q, $SiCH_3$), 18.1 (s, SiC), 25.6 (q, $SiCCH_3$), 109.6 (s, CBr), 116.0 (d, CH_{ar}), 120.7 (d, CH_{ar}), 123.0 (d, CH_{ar}), 146.9 (s, C_{ar}), 149.4 (s, C_{ar}); IR (ATR): $\tilde{\nu} = 3524$ (w, OH), 2955 (m), 2930 (w), 2897 (w), 2858 (w), 1488 (s), 1257 (m), 1209 (m), 934 (m), 840 (s), 781 cm^{-1} (m); MS: *m*/*z* (%): 304 (36), 302 (34), 247 (100), 245 (98), 166 (76); HRMS $C_{12}H_{19}BrO_2Si$: calcd 302.0338; found 302.0335.

4-Benzyloxy-2-bromophenol (4b): Following the procedure of Dodsworth and Sammes,[37] 4-benzyloxyphenol **2b** (20.0 g, 0.1 mol) was treated with bromine (15.6 g, 0.1 mol). After extractive workup, the crude product was filtered through a short pad of silica gel with hexane/dichloromethane (1:1). The product was recrystallized from hot hexane to afford **4b** (20.7 g, 74.2 mmol, 74 %) as a white solid. M.p. 68 °C; TLC (hexane/dichloromethane 1:1): $R_f = 0.39$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5.00$ (s, 2H; CH_2), 5.20 (br s, 1H; OH), 6.88 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; ArH), 6.95 (d, $J = 9$ Hz, 1H; ArH), 7.11 (d, $J = 3$ Hz, 1H; ArH), 7.33–7.44 (m, 5H; ArH); the regioselectivity of the bromination was verified by NOE measurements; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 70.9$ (t, CH_2), 109.9 (s, $C_{ar}Br$), 116.2 (d, CH_{ar}), 116.3 (d, CH_{ar}), 118.1 (d, CH_{ar}), 127.5 (d, CH_{ar}), 128.1 (d, CH_{ar}), 128.6 (d, CH_{ar}), 136.6 (s, C_{ar}), 146.7 (s, $C_{ar}O$), 152.9 (s, $C_{ar}O$); IR (ATR): $\tilde{\nu} = 3511$ (w, OH), 3032 (w), 1490 (s), 1203 (m), 1015 cm^{-1} (m); MS (EI) *m*/*z* (%): 280 (19) $[M+2]^+$, 278 (20) $[M]^+$, 91 (100) $[C_7H_7]^+$; HRMS $C_{13}H_{11}BrO_2$: calcd 277.9943; found 277.9939; elemental analysis calcd (%) for $C_{13}H_{11}BrO_2$: C 55.94, H 3.97; found C 56.13, H 3.94.

[3-Bromo-4-(tetrahydropyran-2-yloxy)phenoxy]-*tert*-butyldimethylsilane (5a): A solution of **4a** (8.9 g, 29 mmol), 3,4-dihydro-2*H*-pyran (5.5 mL, 61 mmol) and pyridinium *p*-toluene sulfonate (PPTS) (745 mg, 2.96 mmol) in dichloromethane (330 mL) was stirred for 19 h in an argon atmosphere. The mixture was then quenched with H_2O (30 mL) and brine (30 mL), and the aqueous layer was extracted with MTB ether. The combined organic layers were dried (K_2CO_3), and the solvent was evaporated. The crude product was purified by flash chromatography (hexane/EtOAc 50:1) to

afford **5a** (10.2 g, 26 mmol, 92%) as a colorless oil. TLC (hexane/EtOAc 10:1): $R_f = 0.51$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.17$ (s, 6H; $SiCH_3$), 0.97 (s, 9H; $SiCCH_3$), 1.58–1.76 (m, 3H; CH_2), 1.76–2.13 (m, 3H; CH_2), 3.60 (dtd, $J_1 = 11$ Hz, $J_2 = 3$ Hz, $J_3 = 1$ Hz, 1H; OCH_2), 3.96 (td, $J_1 = 11$ Hz, $J_2 = 3$ Hz, 1H; OCH_2), 5.34 (t, $J = 3$ Hz, 1H; OCH), 6.70 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; H-C6), 7.01 (d, $J = 9$ Hz, 1H; H-C5), 7.04 (d, $J = 3$ Hz, 1H; H-C2); ^{13}C NMR (67 MHz, $CDCl_3$): $\delta = -4.5$ (q, $SiCH_3$), 18.1 (s, SiC), 18.4 (t, CH_2), 25.2 (t, CH_2), 25.6 (q, $SiCCH_3$), 30.3 (t, CH_2), 61.8 (t, OCH_2), 97.6 (d, OCH), 113.3 (s, CBr), 117.8 (d, CH_{ar}), 119.5 (d, CH_{ar}), 124.5 (d, CH_{ar}), 148.1 (s, C_{ar}), 150.6 (s, C_{ar}); IR (ATR): $\tilde{\nu} = 2949$ (m), 2930 (w), 2858 (w), 1600 (w), 1487 (s), 1254 (m), 1200 (m), 938 (m), 920 (m), 840 (m), 781 cm^{-1} (m); MS: *m*/*z* (%): 304 (50), 302 (53), 247 (100), 245 (97), 166 (54), 85 (68); HRMS $C_{17}H_{27}BrO_3Si$: calcd 386.0913; found 386.0911.

5-Benzyloxy-2-methoxymethyloxybromobenzene (5b): A 50 mL two-necked-flask equipped with a mechanical stirrer was charged with **4b** (5.0 g, 17.9 mmol, 1.0 equiv), dimethoxymethane (31.6 mL, 358 mmol, 20.0 equiv) and dry dichloromethane (35 mL). Phosphorus pentoxide (7.6 g, 53.7 mmol, 3.0 equiv) was added through a powder funnel, and the suspension was stirred at RT for 30 min. The mixture was carefully poured into a cold saturated solution of Na_2CO_3 and extracted with dichloromethane (3×90 mL). The combined organic layers were washed with aqueous NaOH (1M, 1×90 mL), water (1×90 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo to give a white solid. The solid was recrystallized from hot hexane to afford **5b** (5.1 g, 15.8 mmol, 88%) as a white solid. M.p. 60 °C; TLC (hexane/EtOAc 10:1): $R_f = 0.31$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.53$ (s, 3H; OCH_3), 4.96 (s, 2H; OCH_2), 5.17 (s, 2H; OCH_2), 6.87 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; ArH), 7.08 (d, $J = 9$ Hz, 1H; ArH), 7.21 (d, $J = 3$ Hz, 1H; ArH), 7.25–7.44 (m, 5H; ArH); ^{13}C NMR (67.5 MHz, $CDCl_3$): $\delta = 56.3$ (q, OCH_3), 70.6 (t, OCH_2), 95.9 (t, OCH_2), 113.5 (s, $C_{ar}Br$), 114.8 (d, CH_{ar}), 117.9 (d, CH_{ar}), 119.6 (d, CH_{ar}), 127.4 (d, CH_{ar}), 128.0 (d, CH_{ar}), 128.5 (d, CH_{ar}), 136.5 (s, C_{ar}), 148.1 (s, $C_{ar}O$), 154.1 (s, $C_{ar}O$); IR (ATR): $\tilde{\nu} = 2936$ (w), 1490 (s), 1196 (m), 1155 (m), 1034 (m), 992 (m), 739 cm^{-1} (m); MS (EI) *m*/*z* (%): 324 (43) $[M+1]^+$, 322 (44) $[M-1]^+$, 244 (18), 91 (100) $[C_7H_7]^+$; HRMS $C_{15}H_{15}BrO_3$: calcd 322.0205; found 322.0205; elemental analysis calcd (%) for $C_{15}H_{15}BrO_3$: C 55.75, H 4.68; found C 55.69, H 4.70.

[3-Bromo-4-(methoxymethyloxy)phenoxy]-*tert*-butyldimethylsilane (5c): The phenol **4a** (5.00 g, 16.5 mmol), dimethoxymethane (8.5 mL, 96 mmol), and *p*-toluenesulfonic acid monohydrate (30 mg, 0.16 mmol) in dichloromethane (15 mL) were refluxed in an argon atmosphere for 66 h in a flask equipped with a pressure-equalizing dropping funnel, which was charged with molecular sieves 4 Å and topped with a reflux condenser. For workup saturated aqueous $NaHCO_3$ was added at RT, and the mixture was extracted with EtOAc (350 mL). The combined organic layers were washed with brine ($2 \times$) and dried ($MgSO_4$). The solvent was evaporated, and the crude product was purified by flash chromatography (hexane/EtOAc 20:1) to afford **5c** (5.35 g, 15.3 mmol, 92%) as a pale yellow oil. TLC (hexane/EtOAc 10:1): $R_f = 0.47$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.18$ (s, 6H; $SiCH_3$), 0.97 (s, 9H; $SiCCH_3$), 3.53 (s, 3H; OCH_3), 5.16 (s, 2H; OCH_2), 6.72 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; H-C6), 7.02 (d, $J = 9$ Hz, 1H; H-C5), 7.05 (d, $J = 3$ Hz, 1H; H-C2); IR (ATR): $\tilde{\nu} = 2956$ (m), 2930 (m), 2896 (m), 2858 (w), 1600 (w), 1489 (s), 1254 (m), 1215 (m), 1197 (m), 1156 (m), 937 (s), 836 (s), 781 cm^{-1} (m); MS: *m*/*z* (%): 348 (100), 346 (96), 291 (82), 289 (79), 267 (53), 261 (45), 259 (58), 165 (56), 73 (66); HRMS $C_{14}H_{23}BrO_3Si$: calcd 346.0600; found 346.0602.

General procedure Ia—lithiation of 5a/5c and subsequent reaction with electrophiles: In an argon atmosphere a solution of the bromide **5a** or **5c** (1 equiv) in THF was cooled to −78 °C and *n*BuLi (1.2 equiv, 1.6M in hexane) was added dropwise. The resulting yellow solution was stirred for 1 h at −78 °C before a solution of the electrophile (2 equiv) in THF was added at the same temperature; stirring was continued for some hours before the mixture was quenched with water. The aqueous layer was extracted with MTB ether ($3 \times$), and the combined organic layers were washed with water ($2 \times$) and brine, and dried ($MgSO_4$). The solvent was evaporated and the crude product was purified by chromatography.

General procedure Ib—lithiation of 3a and subsequent reaction with electrophiles: *n*BuLi (1.5 equiv, ca. 1.5M in hexane) was added dropwise to a solution of of **3a** (1 equiv) in THF at −78 °C in a dry argon atmosphere. The resulting solution was stirred for 15 min at this temperature and 30 min at RT before the electrophile (2 equiv) was added at −78 °C. Stirring was continued for 15 min at this temperature and for an indicated period at RT before the resulting mixture was quenched (usually with water). The aqueous layer was extracted with EtOAc ($3 \times$), and the combined organic layers were washed with water ($2 \times$) and brine, and dried ($MgSO_4$). The solvent was evaporated and the crude product was purified by chromatography.

***tert*-Butyldimethyl[3-phenylsulfanyl-4-(tetrahydropyran-2-yloxy)phenoxy]silane (7a) from 5a**: According to the general procedure Ia, *n*BuLi (10 mL, 16 mmol) was added to a solution of **5a** (5.00 g, 12.9 mmol) in THF (20 mL), followed by a solution of diphenyldisulfide (5.64 g, 25.8 mmol) in THF (20 mL), and the mixture was stirred overnight. The reaction mixture was cooled to 0 °C and quenched with H_2O (30 mL). The crude product was purified by flash chromatography (hexane/EtOAc 10:1) to yield 5.10 g of a 15:1 mixture (^{1}H NMR) of **7a** (89%) and **3a** (6%) as a pale yellow oil. TLC (hexane/EtOAc 10:1): $R_f = 0.35$; for the data of the main product (**7a**) see the following experiment.

***tert*-Butyldimethyl[3-phenylsulfanyl-4-(tetrahydropyran-2-yloxy)phenoxy]silane (7a) from 3a**: According to the general procedure Ib, **3a** was treated with diphenyldisulfide on an 1 mmol scale to give **7a** in 94% yield. TLC (hexane/EtOAc 10:1): $R_f = 0.35$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.06$ (s, 6H; $SiCH_3$), 0.91 (s, 9H; $SiCCH_3$), 1.46–1.98 (m, 6H; CH_2), 3.57 60 (dbt, $J_1 = 11$ Hz, $J_2 = 3$ Hz, 1H; OCH_2), 3.88 (td, $J_1 = 11$ Hz, $J_2 = 3$ Hz, 1H; OCH_2), 5.35 (t, $J_1 = 3$ Hz, 1H; OCH), 6.51 (d, $J = 3$ Hz, 1H; H-C2), 6.65 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; H-C6), 7.01 (d, $J = 9$ Hz, 1H; H-C5), 7.27 (tt, $J_1 = 7$ Hz, $J_2 = 1.5$ Hz, 1H; *p*-Ph), 7.32 (td, $J_1 = 7$ Hz, $J_2 = 1$ Hz, 2H; *m*-Ph), 7.40 (dt, $J_1 = 7$ Hz, $J_2 = 1.5$ Hz, 2H; *o*-Ph); ^{13}C NMR (67 MHz, $CDCl_3$): $\delta = -4.6$ (q, $SiCH_3$), 18.1 (s, SiC), 18.3 (t, CH_2), 25.3 (t,CH_2), 25.6 (q, $SiCCH_3$), 30.3 (t, CH_2), 61.7 (t, OCH_2), 97.2 (d, OCH), 116.6 (d, CH_{ar}, *p*-SPh), 119.0 (d, CH_{ar}), 121.8 (d, CH_{ar}), 126.7 (s, $C_{ar}S$), 127.3 (d, CH_{ar}), 129.1 (d, CH_{ar}, SPh), 132.1 (d, CH_{ar}, SPh), 134.4 (s, SPh), 149.0 (s, C_{ar}), 150.4 (s, C_{ar}); IR (ATR): $\tilde{\nu} = 3059$ (w), 2948 (m), 2930 (m), 2895 (w), 2883 (w), 2857 (w), 1582 (w), 1574 (w), 1482 (s), 1440 (w), 1390 (w), 1357 (w), 1276 (m), 1254 (m), 1214 (m), 1199 (s), 1182 (m), 1123 (w), 1110 (w), 1049 (w), 1037 (w), 1021 (w), 952 (s), 921 (s), 872 (w), 840 (s), 825 (w), 781 (m), 753 (w), 741 (w), 690 cm^{-1} (w); MS: *m*/*z* (%): 416 (1) $[M]^+$, 333 (44), 332 (100), 276 (44), 275 (92), 224 (14), 167 (22), 166 (24), 85 (17), 73 (34); HRMS $C_{23}H_{32}O_3SSi$: calcd 416.1841; found 416.1843.

2-[5-(*tert*-Butyldimethylsilanoxy)-2-(tetrahydropyran-2-yloxy)phenylsulfanyl]pyridine (7b): According to the general procedure Ia, a solution of **5a** (100 mg, 0.26 mmol) in THF (2 mL) was treated with *n*BuLi (200 µL, 0.32 mmol) and dipyridyldisulfide (116 mg, 0.53 mmol) in THF (1 mL), and the mixture was stirred for 1 h in the cooling bath and 1 h at RT. The crude product was purified by preparative radial chromatography (hexane/EtOAc 20:1, then 10:1) to yield **7b** (88 mg, 0.21 mmol, 82%) as a pale yellow oil. TLC (hexane/EtOAc 10:1): $R_f = 0.11$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.17$ (s, 6H; $SiCH_3$), 0.96 (s, 9H; $SiCCH_3$), 1.39–1.50 (m, 2H; CH_2), 1.59–1.78 (m, 4H; CH_2), 3.49–3.56 (m, 1H; OCH_2), 3.74–3.82 (m, 1H; OCH_2), 5.30–5.33 (m, 1H; OCH), 6.83 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; H-C4), 6.92 (br d, $J = 8$ Hz, 1H; H-C3, py-H), 6.98 (ddd, $J_1 = 8$ Hz, $J_2 = 5$ Hz, $J_3 = 1$ Hz, 1H; H-C5, py-H), 7.06 (d, $J = 3$ Hz, 1H; H-C6), 7.10 (d, $J = 9$ Hz, 1H; H-C3), 7.44 (Ψtd, $J_1 = 8$ Hz, $J_2 = 2$ Hz, 1H; H-C4, py-H), 8.42 (br d, $J = 5$ Hz, 1H; H-C6, py-H); ^{13}C NMR (67 MHz, $CDCl_3$): $\delta = -4.5$ (q, $SiCH_3$), 18.0 (s, SiC), 18.1 (t, CH_2), 25.1 (t, CH_2), 25.6 (q, $SiCCH_3$), 30.1 (t, CH_2), 61.6 (t, OCH_2), 97.2 (d, OCH), 117.0 (d, CH_{ar}), 119.8 (d, CH_{ar}), 120.5 (s, C_{ar}), 121.8 (d, CH_{ar}), 122.2 (d, CH_{ar}), 126.9 (d, CH_{ar}), 136.9 (d, CH_{ar}), 148.7 (d, CH_{ar}), 150.2 (s, C_{ar}), 151.7 (s, C_{ar}), 160.8 (s, SPy); IR (ATR): $\tilde{\nu} = 2952$ (m), 2930 (m), 2895 (w), 2884 (w), 2857 (w), 1685 (w), 1575 (w), 1560 (w), 1484 (s), 1449 (m), 1418 (m), 1357 (w), 1277 (m), 1255 (m), 1214 (m), 1200 (s), 1122 (w), 1037 (w), 952 (s), 920 (m), 840 (s), 781 cm^{-1} (m); MS: *m*/*z* (%): 333 (86), 316 (100), 300 (20), 276 (36), 260 (18), 202 (24), 165 (87), 73 (27); HRMS $C_{22}H_{31}NO_3SSi$: calcd 417.1794; found 417.1799.

5-[*tert*-Butyldimethylsilanoxy-2-(tetrahydropyran-2-yloxy)phenyl]piperidine-1-carbodithionic acid ester (7c): According to the general procedure Ia, a solution of **5a** (200 mg, 0.52 mmol) in THF (2 mL) was treated with *n*BuLi (400 µL, 0.64 mmol) and dicyclopentamethylenthiuramdisulfide (330 mg, 1.02 mmol) in THF (5 mL), and the mixture was stirred for 1 h in the cooling bath and 1 h at RT. In order to remove a white precipitate, the mixture was filtrated through Celite with hexane/EtOAc 3:1. After the usual workup, the crude product was purified by preparative radial chromatography (hexane/EtOAc 6:1) to yield **7c** (167 mg, 0.35 mmol, 67%) as a light brownish oil. TLC (hexane/EtOAc 10:1): $R_f = 0.16$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.19$ (s, 6H; CH_3), 0.96 (s, 9H; $SiCCH_3$),

0947-6539/00/0615-2882 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 15

1.63–2.03 (m, 12H; CH_2), 3.55–3.63 (m, 1H; OCH_2), 3.95–4.36 (m, 1H; OCH_2), 5.30–5.34 (m, 1H; OCH), 6.98 (dd, $J_1=9$ Hz, $J_2=3$ Hz, 1H; H-C4), 6.93 (d, $J=3$ Hz, 1H; H-C6), 7.13 (d, $J=9$ Hz, 1H; H-C3); ^{13}C NMR (67 MHz, $CDCl_3$): $\delta=-4.5$ (q, $SiCH_3$), 18.1 (s, SiC), 18.6 (t, CH_2), 24.1 (t,CH_2), 25.3 (t,CH_2), 25.7 (q, Si*C*CH_3), 30.5 (t, CH_2), 61.9 (t, OCH_2), 97.7 (d, OCH), 116.8 (d, CH_{ar}), 121.6 (s, C_{ar}S), 123.2 (d, CH_{ar}), 129.1 (d, CH_{ar}), 149.9 (s, C_{ar}), 152.8 (s, C_{ar}), 195.4 (s, C=S); IR (ATR): $\tilde{\nu}=2937$ (m), 2857 (m), 1484 (s), 1452 (m), 1356 (w), 1278 (m), 1256 (m), 1243 (m), 1225 (m), 1214 (m), 1199 (m), 1122 (w), 1111 (m), 1020 (w), 950 (s), 921 (m), 840 (s), 781 cm^{-1} (m); MS: *m*/*z* (%): 350 (12), 298 (48), 128 (100), 112 (11), 85 (17), 69 (34); HRMS $C_{23}H_{37}NO_3S_2Si$: calcd 467.1984; found 467.1985.

***tert*-Butyldimethyl[3-phenylselenyl-4-(tetrahydropyran-2-yloxy)phenoxy]-silane (7d) from 5a**: According to the general procedure Ia, a solution of **5a** (100 mg, 0.26 mmol) in THF (1.5 mL) was treated with *n*BuLi (200 µL, 0.32 mmol) and a solution of diphenyldiselenide (164 mg, 0.53 mmol) in THF (2 mL), and the mixture was stirred for 1 h in the cooling bath and 1 h at RT. The crude product was purified by preparative radial chromatography (hexane/EtOAc 50:1) to yield 112 mg of a 8:1 mixture of **7d** (87%) and **3a** (11%) as a pale yellow oil. TLC (hexane/EtOAc 10:1): $R_f=0.40$; for the data of the main product (**7d**) see the following experiment.

***tert*-Butyldimethyl[3-phenylselenyl-4-(tetrahydropyran-2-yloxy)phenoxy]-silane (7d) from 3a**: According to the general procedure Ib, **3a** was treated with diphenyldiselenide on a 1 mmol scale to give **7d** in 93% yield. TLC (hexane/EtOAc 10:1): $R_f=0.40$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.00$ (s, 6H; $SiCH_3$), 0.86 (s, 9H; $SiCCH_3$), 1.52–1.75 (m, 3H; CH_2), 1.77–1.94 (m, 2H; CH_2), 1.94–2.09 (m, 1H; CH_2), 3.60 (dtd, $J_1=11$ Hz, $J_2=3$ Hz, $J_3=1.5$ Hz, 1H; OCH_2), 3.94 (td, $J_1=11$ Hz, $J_2=3$ Hz, 1H; OCH_2), 5.39 (t, $J=3$ Hz, 1H; OCH), 6.33 (d, $J=3$ Hz, 1H; H-C2), 6.60 (dd, $J_1=9$ Hz, $J_2=3$ Hz, 1H; H-C6), 6.96 (d, $J=9$ Hz, 1H; H-C5), 7.30–7.41 (m, 3H; *o*-, *p*-Ph), 7.58–7.66 (m, 2H; *m*-Ph); ^{13}C NMR (67 MHz, $CDCl_3$): $\delta=-4.7$ (q, $SiCH_3$), 18.1 (s, SiC), 18.5 (t, CH_2), 25.3 (t, CH_2), 25.6 (q, Si*C*CH_3), 30.4 (t, CH_2), 61.7 (t, OCH_2), 97.1 (d, OCH), 115.7 (d, CH_{ar}), 118.5 (d, CH_{ar}), 121.1 (d, CH_{ar}), 124.1 (s, C_{ar}Se), 128.1 (s, SePh), 128.3 (d, CH_{ar}), 129.5 (d, CH_{ar}), 135.9 (d, CH_{ar}), 148.4 (s, C_{ar}), 150.8 (s, C_{ar}); IR (ATR): $\tilde{\nu}=3071$ (w), 3058 (w), 2948 (m), 2930 (m), 2895 (w), 2882 (w), 2857 (w), 1591 (w), 1570 (w), 1480 (s), 1438 (w), 1390 (w), 1356 (w), 1274 (m), 1254 (m), 1213 (m), 1199 (s), 1182 (m), 1123 (w), 1110 (w), 1074 (w), 1037 (m), 1021 (m), 963 (m), 938 (m), 920 (s), 872 (w), 839 (s), 781 (m), 742 (m), 692 cm^{-1} (w); MS: *m*/*z* (%): 464 (1) $[M]^+$, 380 (100), 323 (58), 224 (35), 167 (68), 166 (32), 85 (22), 73 (43); HRMS $C_{23}H_{32}O_3SeSi$: calcd 464.1286; found 464.1287.

[5-(*tert*-Butyldimethylsilanoxy)-2-(tetrahydropyran-2-yloxy)phenyl]diphenylphosphane (7e) from 3a: According to the general procedure Ib, a solution of **3a** (307 mg, 0.99 mmol) in THF (7 mL) was treated with *n*BuLi (1.6 M, 940 µL, 1.50 mmol) and chlorodiphenylphosphane (360 µL, 2.00 mmol) and the mixture was stirred for 2.5 h before it was quenched with saturated aqueous $NaHCO_3$ (5 mL). The crude product was purified by preparative radial chromatography (hexane/EtOAc 20:1) to yield **7e** (358 mg, 0.73 mmol, 73%) as a white solid. M.p. 70–71 °C; TLC (hexane/EtOAc 20:1): $R_f=0.41$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=-0.05$ (s, 6H; $SiMe_2$), 0.85 (s, 9H; $SiCMe_3$), 1.18–1.67 (m, 6H; CH_2), 3.44 (br d, $J=11$ Hz, 1H; OCH_2), 3.54 (br td, $J_1=11$ Hz, $J_2=2$ Hz, 1H; OCH_2), 5.27 (br s, 1H; OCH), 6.08 (dd, $J_{HH}=3$ Hz, $J_{PH}=4$ Hz, 1H; H-C6), 6.75 (dd, $J_1=3$ Hz, $J_2=9$ Hz, 1H; H-C4), 7.00 (dd, $J_{PH}=5$ Hz, $J_{HH}=9$ Hz, 1H; H-C3), 7.29–7.44 (m, 10H; Ph); ^{31}P NMR (81.0 MHz, $CDCl_3$): $\delta=-15.0$ (s); IR (ATR): $\tilde{\nu}=3069$, 3053 (w), 2948, 2929 (m), 2895, 2883 (w), 2857 (m), 1586, 1572, 1503 (w), 1470 (s), 1434, 1393, 1356 (m), 1324 (w), 1275, 1259 (m), 1218, 1200 (s), 1182 (m), 1135 (w), 1124, 1108 (m), 1049 (w), 1038, 1020 (m), 965, 950, 921 (s), 887 (w), 872 (m), 839 (s), 825 (m), 781, 743 (m), 697 cm^{-1} (s); MS: *m*/*z* (%): 492 (12) $[M]^+$, 409 (29), 408 (90), 351 (15), 273 (10), 225 (13), 224 (80), 185 (11), 183 (12), 168 (31), 167 (100), 85 (18), 73 (18); HRMS $C_{29}H_{37}O_3PSi$: calcd 492.2249; found 492.2251.

[5-(*tert*-Butyldimethylsilanoxy)-2-(tetrahydropyran-2-yloxy)phenyl]diphenylphosphane (7e) from 5a: According to the general procedure Ia, a solution of **5a** (1.60 g, 4.13 mmol) in THF (25 mL) was treated with *n*BuLi (1.6 M, 3.1 mL, 4.96 mmol) and chlorodiphenylphosphane (1.5 mL, 8.37 mmol), and the mixture was stirred for 4 h before it was quenched with saturated aqueous $NaHCO_3$ (5 mL). The crude product was purified by preparative radial chromatography (hexane/EtOAc 50:1, later 20:1) to yield **7e** (1.62 g, 3.29 mmol, 79%) as a white solid. The spectroscopic data were identical to those described above.

[5-(*tert*-Butyldimethylsilanoxy)-2-(tetrahydropyran-2-yloxy)phenyl]diisopropylphosphane (7f): According to the general procedure Ib, a solution of **3a** (306 mg, 0.99 mmol) in THF (7 mL) was treated with *n*BuLi (1.6 M, 930 µL, 1.49 mmol) and chlorodiisopropylphosphane (320 µL, 2.01 mmol) and the mixture was stirred for 1.5 h before it was quenched with saturated aqueous $NaHCO_3$ (5 mL). The crude product was purified by preparative radial chromatography (hexane/EtOAc 20:1) to yield **7f** (285 mg, 0.67 mmol, 68%) as a redish-brown oil. TLC (hexane/EtOAc 10:1): $R_f=0.54$; ^{1}H NMR (270 MHz, $CDCl_3$): $\delta=0.17$ (s, 6H; $SiCH_3$), 0.79–1.06 (m, 15H; $SiCCH_3$, CH_3), 1.12 (d, $J=7$ Hz, 3H; CH_3), 1.17 (d, $J=7$ Hz, 3H; CH_3), 1.52–2.34 (m, 8H; CH_2, CH), 3.54–3.70 (br m, 1H; OCH_2), 3.94 (br td, $J_1=10.5$ Hz, $J_2=3$ Hz, 1H; OCH_2), 5.31 (br t, $J=3$ Hz, 1H; OCH), 6.75 (br d, $J=9$ Hz, 1H; H-C3), 6.88 (br s, 1H; H-C6), 7.03 (br dd, $J_1=9$ Hz, $J_2=3$ Hz, 1H; H-C4); ^{31}P NMR (81.0 MHz, $CDCl_3$): $\delta=4.9$ (s); IR (ATR): $\tilde{\nu}=2948$ (s), 2929 (s), 2896 (m), 2884 (m), 2862 (m), 1736 (w), 1591 (w), 1570 (w), 1503 (w), 1472 (s), 1390 (m), 1382 (m), 1361 (m), 1323 (w), 1275 (m), 1254 (m), 1232 (m), 1212 (m), 1199 (s), 1181 (m), 1140 (m), 1124 (m), 1108 (m), 1078 (w), 1048 (w), 1038 (m), 1021 (m), 965 (s), 953 (s), 921 (s), 873 (m), 839 (s), 824 (m), 796 (m), 780 (m), 741 (w), 725 (w), 684 (w), 658 cm^{-1} (w); MS: *m*/*z* (%): 424 (29) $[M]^+$, 381 (10), 341 (25), 340 (100), 298 (31), 241 (28), 167 (14), 85 (12),73 (26); HRMS $C_{23}H_{41}O_3PSi$: calcd 424.2563; found 424.2561.

5-(*tert*-Butyldimethylsilanoxy)-*N*,*N*-dimethyl-2-(tetrahydropyran-2-yloxy)benzamide (7g): According to the general procedure Ib, a solution of **3a** (310 mg, 1.00 mmol) in THF (6 mL) was treated with *n*BuLi (1.6 M, 940 µL, 1.50 mmol) and dimethylcarbamoyl chloride (185 µL, 2.01 mmol), and the mixture was stirred for 4 h before it was quenched with water (5 mL). The crude product was purified by preparative radial chromatography (hexane/EtOAc 1:1) to yield **7g** (322 mg, 0.85 mmol, 85%) as a white solid. M.p. 89 °C; TLC (hexane/EtOAc 1:1): $R_f=0.39$; ^{1}H NMR (400 MHz, $CDCl_3$, 60 °C): $\delta=0.19$ (s, 6H; $SiCH_3$), 0.99 (s, 9H; $SiCCH_3$), 1.52–2.05 (br m, 6H; CH_2), 2.88 (s, 3H; NCH_3), 3.10 (s, 3H; NCH_3), 3.59 (br d, $J=10.5$ Hz, 1H; OCH_2), 3.94 (br t, $J=10.5$ Hz, 1H; OCH_2), 5.28 (br s, 1H; OCH), 6.72 (d, $J=3$ Hz, 1H; H-C6), 6.76 (dd, $J_1=9$ Hz, $J_2=3$ Hz, 1H; H-C4), 7.03 (d, $J=9$ Hz, 1H; H-C3); at RT some of the signals were very broad due to coalescense; IR (ATR): $\tilde{\nu}=3041$ (w), 2950 (s), 2930 (s), 2895 (w), 2884 (w), 2858 (m), 1642 (s), 1608 (w), 1583 (w), 1485 (s), 1473 (m), 1454 (m), 1443 (m), 1416 (m), 1389 (m), 1360 (w), 1324 (w), 1290 (m), 1255 (m), 1216 (s), 1200 (s), 1181 (m), 1146 (w), 1122 (m), 1110 (m), 1065 (m), 1049 (w), 1037 (m), 1021 (m), 974 (s), 921 (m), 907 (s), 873 (m), 840 (s), 826 (m), 814 (m), 798 (w), 781 (m), 739 (w), 693 (w), 678 cm^{-1} (w); MS: *m*/*z* (%): 296 (19), 295 (100), 250 (31), 238 (47), 193 (21); HRMS $C_{20}H_{33}NO_4Si$: calcd 379.2179; found 379.2159; elemental analysis calcd (%) for $C_{20}H_{33}NO_4Si$: C 63.29, H 8.77, N 3.69; found C 62.83, H 8.64, N 3.78.

***tert*-Butyldimethyl[3-phenylsulfanyl-4-(methoxymethyloxy)phenoxy]silane (7h)**: According to the general procedure Ia, a solution of **5c** (203 mg, 0.59 mmol) in THF (2 mL) was treated with *n*BuLi (440 µL, 0.70 mmol) and a solution of diphenyldisulfide (269 mg, 1.23 mmol) in THF (1 mL), and the mixture was stirred overnight. The crude product was purified by preparative radial chromatography (hexane/EtOAc 25:1) to yield 200 mg of a 15:1 mixture of **7h** (90%) and **3b** (6%) as a pale yellow oil. TLC (hexane/EtOAc 10:1): $R_f=0.41$.

*Data for the main product (**7h**)*: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.05$ (s, 6H; $SiCH_3$), 0.89 (s, 9H; $SiCCH_3$), 3.45 (s, 3H; OCH_3), 5.14 (s, 2H; OCH_2), 6.48 (d, $J=3$ Hz, 1H; H-C2), 6.63 (dd, $J_1=9$ Hz, $J_2=3$ Hz, 1H; H-C6), 6.99 (d, $J=9$ Hz, 1H; H-C5), 7.27–7.41 (m, 5H; Ph); ^{13}C NMR (67 MHz, $CDCl_3$): $\delta=-4.6$ (q, $SiCH_3$), 18.1 (s, SiC), 25.6 (q, Si*C*CH_3), 56.2 (q, OCH_3), 95.6 (d, OCH_2), 116.5 (d, CH_{ar}, *p*-SPh), 119.1 (d, CH_{ar}), 121.9 (d, CH_{ar}), 126.9 (s, SPh), 127.5 (d, CH_{ar}), 129.2 (d, CH_{ar}, SPh), 132.3 (d, CH_{ar}, SPh), 134.0 (s, C_{ar}), 149.2 (s, C_{ar}), 150.8 (s, C_{ar}); IR (ATR): $\tilde{\nu}=3073$ (w), 3060 (w), 2955 (m), 2929 (m), 2896 (m), 2858 (m), 1583 (w), 1484 (s), 1277 (m), 1254 (m), 1217 (s), 1195 (s), 1155 (s), 999 (s), 949 (s), 838 (s), 781 cm^{-1} (m); MS: *m*/*z* (%): 376 (76), 331 (97), 268 (90), 218 (27), 211 (100), 179 (44), 73 (32); HRMS $C_{20}H_{28}O_3SSi$: calcd 376.1528; found 376.1532.

*Data of the side product (**3b**)*: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.16$ (s, 6H; $SiCH_3$), 0.97 (s, 9H; $SiCCH_3$), 3.48 (s, 3H; OCH_3), 5.10 (s, 2H; OCH_2), 6.75 (d, $J=9$ Hz, 2H; H_{ar}), 6.90 (d, $J=9$ Hz, 2H; H_{ar}).

[5-(*tert*-Butyldimethylsilanoxy)-2-(methoxymethyloxy)phenyl]diphenylphosphane (7i): According to the general procedure Ia, a solution of **5c** (2.45 g, 7.06 mmol) in THF (25 mL) was treated with *n*BuLi (5.3 mL,

8.48 mmol) and a solution of chlorodiphenylphosphane (2.55 mL, 14.12 mmol) in THF (5 mL), and the mixture was stirred overnight. The crude product was purified by flash chromatography (hexane/EtOAc 50:1, 20:1, 15:1) to give **7i** (2.20 g, 4.86 mmol, 69%) as a white solid. M.p. 119 °C; TLC (hexane/EtOAc 20:1): $R_f = 0.27$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = -0.07$ (s, 9H; $SiCH_3$), 0.84 (s, 9H; $SiCCH_3$), 3.22 (s, 3H; OCH_3), 5.00 (s, 2H; OCH_2), 6.10 (br t, $J = 3$ Hz, 1H; H-C6), 6.77 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; H-C4), 6.99 (dd, $J_{HH} = 9$ Hz, $J_{PH} = 5$ Hz, 1H; H-C3), 7.27–7.38 (m, 10H; Ph); ^{13}C NMR (67 MHz, $CDCl_3$): $\delta = -4.7$ (q, $SiCH_3$), 18.1 (s, SiC), 25.6 (q, Si*C*CH_3), 55.8 (q, OCH_3), 94.8 (t, OCH_2), 115.1 (dd, $J_{PC} = 2$ Hz, C_{ar}), 121.4 (d, CH_{ar}), 124.4 (d, CH_{ar}), 127.7 (dd, $J_{PC} = 13$ Hz, C_{ar}), 128.3 (d, CH_{ar}), 128.5 (dd, $J_{PC} = 15$ Hz, CH_{ar}), 133.7 (dd, $J_{PC} = 20$ Hz, CH_{ar}), 136.6 (dd, $J_{PC} = 11$ Hz, C_{ar}), 150.5 (s, C_{ar}), 153.2 (dd, $J_{PC} = 15$ Hz, C_{ar}); IR (ATR): $\tilde{\nu} = 3068$ (w), 3054 (w), 2992 (w), 2952 (m), 2929 (m), 2905 (w), 2857 (w), 2820 (w), 1584 (w), 1573 (w), 1482 (s), 1472 (m), 1442 (w), 1433 (m), 1388 (w), 1361 (w), 1323 (w), 1302 (w), 1284 (m), 1265 (w), 1255 (w), 1229 (s), 1199 (m), 1156 (m), 1133 (m), 1081 (m), 1057 (w), 1026 (w), 998 (s), 950 (m), 923 (m), 890 (w), 874 (w), 839 (s), 826 (w), 780 (m), 753 (m), 748 (m), 744 (m), 725 (w), 695 (m), 681 cm^{-1} (w); MS: *m/z* (%): 453 (26) $[M+H]^+$, 452 (78) $[M]^+$, 438 (32), 437 (100), 410 (20), 407 (12), 391 (25), 183 (11); HRMS $C_{26}H_{33}O_3PSi$: calcd 452.1937; found 452.1931; elemental analysis calcd (%) for $C_{26}H_{33}O_3PSi$: C 69.00, H 7.35; found C 68.79, H 7.19.

4-(*tert*-Butyldimethylsilanoxy)-2-dimethylaminomethylphenol (8): A solution of DIBAH in toluene (1.5 M, 1.45 mL, 2.17 mmol) was added at 0 °C under argon over a period of 20 min by means of a gas-tight syringe to a stirred solution of the benzamide **7g** (200 mg, 0.53 mmol) in dry toluene (4 mL). After 1 h at 0 °C the conversion was complete. The reaction solution was quenched with saturated aqueous $NaHCO_3$, and the precipitate was filtered off. The resulting mixture was extracted with EtOAc (3 ×), and the combined organic layers were washed with water (1 ×) and brine (1 ×), and dried ($MgSO_4$). After evaporation of the solvent the residue was purified by preparative radial chromatography (EtOAc/hexane 1:1) to yield the amine **8** (119 mg, 0.42 mmol, 79%) as a beige solid. M.p. 55 °C; TLC (hexane/EtOAc 1:1): R_f 0.25; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.15$ (s, 6H; $SiCH_3$), 0.98 (s, 9H; $SiCCH_3$), 2.31 (s, 6H; NCH_3), 3.55 (s, 2H; CH_2), 6.46 (d, $J = 3$ Hz, 1H; H-C3), 6.64 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; H-C5), 6.67 (d, $J = 9$ Hz, 1H; H-C6), 10.6 (very br s, OH); ^{13}C NMR (67 MHz, $CDCl_3$): $\delta = -4.5$ (q, $SiCH_3$), 18.1 (s, SiC), 25.7 (q, Si*C*CH_3), 44.5 (q, NCH_3), 62.8 (t, CH_2), 116.3 (d, CH_{ar}), 119.7 (d, CH_{ar}), 119.8 (d, CH_{ar}), 122.5 (s, C_{ar}), 147.8 (s, C_{ar}), 152.6 (s, C_{ar}); IR (ATR): $\tilde{\nu} = 3032$ (w), 2955 (m), 2930 (m), 2885 (w), 2858 (m), 2828 (w), 2785 (w), 1645 (w), 1625 (w), 1593 (w), 1492 (s), 1472 (m), 1463 (m), 1426 (w), 1390 (w), 1362 (w), 1353 (w), 1293 (w), 1285 (w), 1250 (s), 1213 (m), 1179 (w), 1148 (w), 1104 (w), 1042 (w), 1023 (w), 987 (m), 958 (m), 880 (m), 868 (m), 840 (m), 817 (w), 780 (m), 698 cm^{-1} (w); MS: *m/z* (%): 282 (12) $[M+H]^+$, 281 (68) $[M]^+$, 236 (30), 180 (33), 179 (100), 73 (14); HRMS $C_{15}H_{27}NO_2Si$: calcd 281.1811; found 281.1813; elemental analysis calcd (%) for $C_{15}H_{27}NO_2Si$: C 64.01, H 9.67, N 4.98; found C 64.08, H 9.51, N 4.94.

[5-(*tert*-Butyldimethylsilanoxy)-2-(tetrahydropyran-2-yloxy)]boronic acid (9a): According to the general procedure Ib, a solution of **3a** (501 mg, 1.62 mmol) in THF (5 mL) was treated with *n*BuLi (1.6 M, 1.50 mL, 2.40 mmol) and the mixture was stirred for 15 min at −78 °C and 30 min at RT before triisopropylborate (940 μL, 4.09 mmol) was added over a period of 30 min at −78 °C by using a syringe pump. The mixture was stirred for 2 h at RT before it was quenched with water and extracted with EtOAc (3 ×). The combined organic layers were washed with brine and dried ($MgSO_4$). After evaporation of the solvent the crude product **9** (colorless oil, 600 mg) was used in the Suzuki couplings described below without further purification. TLC (hexane/EtOAc 4:1): $R_f = 0.28$.

4-(*tert*-Butyldimethylsilanoxy)-2-pyrimidin-2-ylphenol (10a): A 50 mL two necked flask equipped with a reflux condenser was set under argon and subsequently charged with the boronic acid **9a** (freshly prepared from 501 mg, 1.62 mmol **3a** as described above), toluene (10 mL), EtOH (1.5 mL), aqueous Na_2CO_3 (2 M, 2 mL, 4.0 mmol), Pd[$(PPh_3)_4$] (56 mg, 3 mol%), and a solution of 2-bromopyrimidine (322 mg, 2.02 mmol) in toluene (13 mL). Under strict exclusion of air, the mixture was stirred at 80 °C for 2.5 h before it was cooled to RT and partitioned between water and toluene. The aqueous layer was extracted with toluene (3 ×), and the combined organic layers were washed with water (1 ×) and brine (1 ×), and dried ($MgSO_4$). After evaporation of the solvent, the residue was purified by preparative radial chromatography (EtOAc/hexane 1:6) to give **10a** (433 mg, 1.43 mmol, 85% from **3a**) as a light yellow solid. M.p. 88 °C; TLC (hexane/EtOAc 1:3): $R_f = 0.41$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.23$ (s, 6H; $SiCH_3$), 1.00 (s, 9H; $SiCCH_3$), 6.90 (d, $J = 9$ Hz, 1H; H-C6), 6.94 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; H-C5), 7.20 (t, $J = 5$ Hz, 1H; pym-H), 7.96 (d, $J = 3$ Hz, 1H; H-C3), 8.79 (d, $J = 5$ Hz, 2H; pym-H), 12.66 (s, 1H; OH, exchanges with D_2O); ^{13}C NMR (67 MHz, $CDCl_3$): $\delta = -4.5$ (q, $SiCH_3$), 18.2 (s, SiC), 25.7 (q, Si*C*CH_3), 118.2 (d, CH_{ar}), 118.5 (d, CH_{ar}), 118.7 (s, C_{ar}), 119.0 (d, CH_{ar}), 125.9 (d, pym-CH_{ar}), 147.8 (s, C_{ar}), 155.2 (s, C_{ar}), 156.1 (d, NCH), 164.9 (s, NC); IR (ATR): $\tilde{\nu} = 3066$ (w), 3041 (w), 2948 (m), 2928 (m), 2893 (w), 2857 (m), 2802 (w), 1579 (m), 1558 (s), 1508 (w), 1487 (s), 1469 (m), 1431 (s), 1381 (m), 1361 (w), 1337 (w), 1279 (m), 1266 (w), 1246 (m), 1230 (s), 1214 (m), 1207 (m), 1118 (w), 1093 (w), 1085 (w), 1004 (w), 959 (m), 945 (m), 901 (w), 864 (m), 837 (s), 794 (w), 777 (m), 704 (w), 674 cm^{-1} (w); MS: *m/z* (%): 303 (11) $[M+H]^+$, 302 (52) $[M]^+$, 246 (26), 245 (100), 217 (10); HRMS $C_{16}H_{22}N_2O_2Si$: calcd 302.1451; found 302.1447; elemental analysis calcd (%) for $C_{16}H_{22}N_2O_2Si$: C 63.54, H 7.33, N 9.26; found C 63.12, H 7.31, N 9.08.

4-(*tert*-Butyldimethylsilanoxy)-2-pyridin-2-ylphenol (10b): EtOH (1.0 mL), aqueous Na_2CO_3 (2 M, 1.2 mL, 2.4 mmol), Pd(PPh_3)$_4$ (35 mg, 3 mol%), and 2-bromopyridine (120 μL, 1.26 mmol) was to a stirred solution of the boronic acid **9a** (354 mg, 1.00 mmol) in toluene (15 mL) under argon. Under strict exclusion of air the mixture was heated under reflux for 6 h before it was cooled to RT and partitioned between water and toluene. The aqueous layer was extracted with toluene (3 ×) and the combined organic layers were washed with water (1 ×) and brine (1 ×), and dried ($MgSO_4$). After evaporation of the solvent the residue was purified by preparative radial chromatography (EtOAc/hexane 1:10) to give **10b** (244 mg, 0.81 mmol) as a yellow solid (yield: 81% from **3a**). M.p. 41 °C; TLC (hexane/EtOAc 1:10): $R_f = 0.29$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.21$ (s, 6H; $SiCH_3$), 1.02 (s, 9H; $SiCCH_3$), 6.82 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; H-C5), 6.89 (d, $J = 9$ Hz, 1H; H-C6), 7.21–7.30 (m, 2H; py-H, H-C3), 7.81–7.87 (m, 2H; py-H), 8.93 (br d, $J = 5$ Hz, 1H; py-H), 13.84 (br s, 1H; OH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -4.4$ (q, $SiCH_3$), 18.2 (s, SiC), 25.6 (q, Si*C*CH_3), 116.7 (d, CH_{ar}), 118.8 (s, C_{ar}), 119.0 (d, CH_{ar}), 119.1 (d, CH_{ar}), 121.5 (d, CH_{ar}), 123.6 (d, CH_{ar}), 137.7 (d, py-CH_{ar}), 146.0 (d, CH_{ar}), 147.6 (s, C_{ar}), 154.4 (s, C_{ar}), 157.6 (s, py-C_{ar}); IR (ATR): $\tilde{\nu} = 3043$ (w), 2955 (m), 2929 (m), 2895 (w), 2885 (w), 2857 (m), 1595 (m), 1562 (m), 1490 (s), 1482 (s), 1462 (m), 1418 (m), 1389 (w), 1362 (w), 1320 (w), 1276 (m), 1247 (s), 1213 (s), 1159 (w), 1097 (w), 1055 (w), 1035 (w), 1005 (w), 939 (s), 851 (s), 839 (s), 822 (m), 781 (m), 736 (m), 718 (w), 698 cm^{-1} (w); MS: *m/z* (%): 302 (12) $[M+H]^+$, 301 (58) $[M]^+$, 245 (26), 244 (100), 216 (11); HRMS $C_{17}H_{23}NO_2Si$: calcd 301.1498; found 301.1496; elemental analysis calcd (%) for $C_{17}H_{23}NO_2Si$: C 67.73, H 7.69, N 4.65; found C 67.59, H 7.65, N 4.58.

2-(4-*tert*-Butyldimethylsilanoxy-2-thiophen-2-ylphenoxy)tetrahydropyran (10c) and 4-(*tert*-Butyldimethylsilanoxy)-2-thiophen-2-ylphenol (10d): EtOH (1.5 mL), aqueous Na_2CO_3 (2 M, 1.8 mL, 4.0 mmol), Pd(PPh_3)$_4$ (51 mg, 3 mol%), and 2-bromothiophene (280 μL, 2.89 mmol) was added to a stirred solution of the boronic acid **9a** (freshly prepared from 450 mg, 1.46 mmol **3a** as described above) in toluene (20 mL) under argon. Under strict exclusion of air, the mixture was stirred at 80 °C for 6 h before it was cooled to RT and partitioned between water and toluene. The aqueous layer was extracted with toluene (3 ×), and the combined organic layers were washed with water (1 ×) and brine (1 ×), and dried ($MgSO_4$). After evaporation of the solvent the residue was purified by preparative radial chromatography (EtOAc/hexane 1:10, later 1:6) to afford **10c** (274 mg, 0.70 mmol, 48% from **3a**) and **10d** (146 mg, 0.48 mmol, 33% from **3a**), both as yellow oils.

*Data for **10c***: TLC (hexane/EtOAc 1:10): $R_f = 0.38$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.21$ (s, 6H; $SiCH_3$), 1.00 (s, 9H; $SiCCH_3$), 1.55–1.79 (m, 3H; CH_2), 1.82–1.96 (m, 1H; CH_2), 1.96–2.07 (m, 1H; CH_2), 2.07–2.23 (m, 1H; CH_2), 3.63 (dtbd, $J_1 = 11$ Hz, $J_2 = 4$ Hz, $J_3 = 2$ Hz, 1H; OCH_2), 3.92 (td, $J_1 = 11$ Hz, $J_2 = 3$ Hz, 1H; OCH_2), 5.44 (t, $J = 3$ Hz, 1H; OCH), 6.71 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; H-C5), 7.09 (dd, $J_1 = 5$ Hz, $J_2 = 4$ Hz, 1H; thiophen-H), 7.14 (d, $J = 9$ Hz, 1H; H-C6), 7.29 (d, $J = 3$ Hz, 1H; H-C3), 7.34 (dd, $J_1 = 5$ Hz, $J_2 = 1$ Hz, 1H; thiophen-H), 7.48 (dd, $J_1 = 4$ Hz, $J_2 = 1$ Hz, 1H; thiophen-H).

*Data for **10d***: TLC (hexane/EtOAc 1:10): $R_f = 0.11$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.19$ (s, 6H; $SiCH_3$), 0.99 (s, 9H; $SiCCH_3$), 5.12 (br s, 1H; OH, exchanges with D_2O), 6.72 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; H-C5), 6.83 (d, $J = 9$ Hz, 1H; H-C6), 6.92 (d, $J = 3$ Hz, 1H; H-C3), 7.14 (dd, $J_1 = 5$ Hz, $J_2 = 3.5$ Hz, 1H; thiophen-H), 7.29 (dd, $J_1 = 3.5$ Hz, $J_2 = 1$ Hz, 1H; thiophen-H),

0947-6539/00/0615-2884 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 15

7.39 (dd, $J_1 = 5$ Hz, $J_2 = 1$ Hz, 1H; thiophen-H); ^{13}C NMR (67 MHz, $CDCl_3$): $\delta = -4.5$ (q, $SiCH_3$), 18.2 (s, SiC), 25.7 (q, $SiCCH_3$), 116.8 (d, CH_{ar}), 120.6 (d, CH_{ar}), 120.8 (d, CH_{ar}), 121.4 (s, C_{ar}), 125.9 (d, thiophen-CH_{ar}), 126.1 (d, thiophen-CH_{ar}), 127.7 (d, thiophen-CH_{ar}), 138.8 (s, SC), 146.7 (s, C_{ar}), 149.2 (s, C_{ar}); IR (ATR): $\tilde{\nu} = 3532$, 3392 (w, br), 3104 (w), 3073 (w), 2955 (m), 2929 (m), 2895 (w), 2858 (m), 1608 (w), 1525 (w), 1505 (m), 1490 (s), 1463 (m), 1440 (m), 1410 (m), 1390 (w), 1361 (w), 1355 (w), 1325 (w), 1293 (w), 1259 (m), 1226 (m), 1199 (m), 1162 (w), 1108 (w), 1071 (w), 1015 (w), 1000 (m), 965 (w), 915 (s), 873 (w), 854 (m), 834 (s), 781 (m), 696 cm^{-1} (m); MS: *m*/*z* (%): 306 (34) $[M]^+$, 251 (13), 250 (37), 249 (100), 233 (37), 85 (10); HRMS $C_{16}H_{22}O_2SSi$: calcd 306.1110; found 306.1103.

4-(*tert*-Butyldimethylsilanoxy)-2-thiazol-2-ylphenol (10e): EtOH (1 mL), aqueous Na_2CO_3 (2 M, 1.25 mL, 2.50 mmol), $Pd(PPh_3)_4$ (36 mg, 3 mol%), and 2-bromothiazol (120 μL, 1.34 mmol) was added to a stirred solution of the boronic acid **9a** (prepared from 332 mg, 1.07 mmol **3a** as described above) in toluene (15 mL) under an atmosphere of argon. Under strict exclusion of air the mixture was heated under reflux for 6 h before it was cooled to RT and partitioned between water and toluene. The aqueous layer was extracted with toluene (3 ×), and the combined organic layers were washed with water (1 ×) and brine (1 ×), and dried ($MgSO_4$). After evaporation of the solvent, the residue was purified by preparative radial chromatography (EtOAc/hexane 1:20) to yield **10e** (184 mg, 0.60 mmol, 56% from **3a**) as a colorless oil. TLC (hexane/EtOAc 1:10): $R_f = 0.49$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.21$ (s, 6H; $SiCH_3$), 1.01 (s, 9H; $SiCCH_3$), 6.84 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; H-C5), 6.94 (d, $J = 9$ Hz, 1H; H-C6), 7.09 (d, $J = 3$ Hz, 1H; H-C3), 7.29 (d, $J = 3$ Hz, 1H; SCH), 7.80 (d, $J = 3$ Hz, 1H; NCH), 11.87 (s, 1H; OH, exchanges with D_2O); ^{13}C NMR (67 MHz, $CDCl_3$): $\delta = -4.5$ (q, $SiCH_3$), 18.2 (s, SiC), 25.7 (q, $SiCCH_3$), 116.7 (s, C_{ar}), 117.0 (d, CH_{ar}), 117.4 (d, CH_{ar}), 118.4 (d, CH_{ar}), 124.0 (d, CH_{ar}), 141.4 (d, CH_{ar}), 147.9 (s, C_{ar}), 151.5 (s, C_{ar}), 169.1 (s, CN); IR (ATR): $\tilde{\nu} = 3120$ (w), 3092 (w), 3039 (w), 2956 (m), 2929 (m), 2894 (w), 2885 (w), 2858 (m), 1627 (w), 1591 (w), 1498 (s), 1486 (s), 1472 (m), 1463 (w), 1449 (m), 1390 (w), 1362 (w), 1324 (w), 1301 (w), 1268 (s), 1217 (m), 1201 (s), 1141 (m), 1066 (w), 1004 (m), 927 (s), 878 (m), 863 (m), 838 (s), 801 (w), 781 (m), 715 (m), 686 cm^{-1} (w); MS: *m*/*z* (%): 308 (11) $[M+H]^+$, 307 (56) $[M]^+$, 251 (27), 250 (100), 247 (17), 245 (16), 224 (16), 167 (36), 166 (18), 73 (13); HRMS $C_{15}H_{21}NO_2SSi$: calcd 307.1062; found 307.1066.

2-(5-Benzyloxy-2-methoxymethylphenyl)pyridine (10f): An oven-dried Schlenk tube was cooled under argon and charged with **5b** (646 mg, 2.0 mmol, 1.0 equiv) and dry THF (5 mL). The tube was purged with argon, tightly capped with a septum and cooled to −78 °C. A solution of *n*BuLi in hexane (1.5 M, 1.38 mL, 2.1 mmol, 1.05 equiv) was added dropwise and the reaction mixture was stirred for 30 min at this temperature. After the addition of trimethyl borate (0.334 mL, 3.0 mmol, 1.5 equiv) by a syringe, the solution was stirred for 30 min at −78 °C and for 1 h at RT. The clear solution was concentrated in vacuo to give a white solid of the boronic ester (**9b**). The Schlenk tube was then charged with $Ba(OH)_2 \cdot 8H_2O$ (757 mg, 2.4 mmol, 1.2 equiv), 2-bromopyridine (0.210 mL, 2.2 mmol, 1.1 equiv), tetrakis(triphenylphosphine)palladium(0) (69 mg, 0.06 mmol, 3 mol%), and a DME/water mixture (12:2, 14 mL), and purged with argon. The mixture was heated at 80 °C for 4 h and then allowed to cool to RT. The layers were separated and the aqueuos phase was extracted twice with diethyl ether (5 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography to give **10f** (470 mg, 1.46 mmol, 73%) as a white solid. M.p. 65 °C; TLC (hexane/EtOAc 4:1): $R_f = 0.11$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.40$ (s, 3H; OCH_3), 5.09 (Ψs, 2H; OCH_2), 5.10 (Ψs, 2H; OCH_2), 6.97 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; ArH), 7.16 (d, $J = 9$ Hz, 1H; ArH), 7.21–7.26 (m, 1H; ArH), 7.29–7.35 (m, 1H; ArH), 7.38 (Ψt, $J = 7$ Hz, 2H; ArH), 7.43–7.48 (m, 3H; ArH), 7.72 (td, $J_1 = 8$ Hz, $J_2 = 2$ Hz, 1H; ArH), 7.84 (Ψd, $J = 8$ Hz, 1H; ArH), 8.70–8.74 (m, 1H; ArH); ^{13}C NMR (67.5 MHz, $CDCl_3$): $\delta = 56.0$ (q, OCH_3), 70.4 (t, OCH_2), 95.9 (t, OCH_2), 116.4 (d, CH_{ar}), 116.5 (d, CH_{ar}), 117.5 (d, CH_{ar}), 121.8 (d, CH_{ar}), 125.0 (d, CH_{ar}), 127.4 (d, CH_{ar}), 127.7 (d, CH_{ar}), 128.4 (d, CH_{ar}), 131.1 (s, C_{ar}-Pyr), 135.5 (d, CH_{ar}), 137.0 (s, C_{ar}), 148.8 (s, $C_{ar}O$), 149.3 (d, CH_{ar}), 154.05 (s, $C_{ar}O$), 155.6 (s, $C_{ar}N$); IR (ATR): $\tilde{\nu} = 2898$ (w), 1585 (m), 1498 (s), 1461 (s), 1189 (m), 1153 (m), 1056 (w), 991 cm^{-1} (s); MS (EI) *m*/*z* (%): 321 (10) $[M]^+$, 230 (91), 186 (53), 91 (100) $[C_7H_7]^+$; HRMS $C_{20}H_{19}NO_3$: calcd 321.1365; found 321.1355.

2-(5-Benzyloxy-2-methoxymethyloxyphenyl)thiazole (10g): By following the procedure described above for the preparation of **10f**, the boronic ester **9b** (2.0 mmol) was treated with 2-bromothiazole (2.2 mmol) to give **10g** (425 mg, 1.3 mmol, 65%) as a yellow solid. M.p. 52 °C; TLC (hexane/EtOAc 10:1): $R_f = 0.34$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5.54$ (s, 3H; OCH_3), 5.13 (s, 2H; OCH_2), 5.34 (s, 2H; OCH_2), 7.01 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; ArH), 7.20 (d, $J = 9$ Hz, 1H; ArH), 7.33 (Ψt, $J = 7$ Hz, 1H; ArH), 7.36–7.50 (m, 5H; Ar), 7.93 (d, $J = 3$ Hz, 1H; ArH), 8.08 (d, $J = 3$ Hz, 1H; ArH); ^{13}C NMR (67.5 MHz, $CDCl_3$): $\delta = 56.3$ (q, OCH_3), 70.4 (t, OCH_2), 94.7 (t, OCH_2), 112.5 (d, CH_{ar}), 116.1 (d, CH_{ar}), 118.2 (d, CH_{ar}), 120.1 (d, CH_{ar}), 120.9 (d, CH_{ar}), 123.4 (d, CH_{ar}), 127.4 (d, CH_{ar}), 127.8 (d, CH_{ar}), 128.4 (d, CH_{ar}), 136.8 (s, C_{ar}), 141.7 (d, CH_{ar}), 143.7 (s, C_{ar}-thiazol), 148.3 (s, $C_{ar}O$), 153.6 (s, $C_{ar}O$), 161.9 (s, $C_{ar}NS$); IR (ATR): $\tilde{\nu} = 3077$ (w), 2899 (w), 1502 (s), 1426 (m), 1281 (m), 1223 (m), 1149 (m), 1079 (m), 985 cm^{-1} (m); MS (EI) *m*/*z* (%): 327 (17) $[M]^+$, 236 (100) $[M - C_7H_7]^+$, 91 (57) $[C_7H_7]^+$; HRMS $C_{18}H_{17}NO_3S$: calcd 327.0929; found 327.0931.

General procedure II—Pd-catalyzed amination of 5b with primary and secondary amines: An oven-dried Schlenk tube was charged under argon with **5b** (1.0 mmol), the respective amine (1.2 mmol), sodium *tert*-butoxide (1.4 mmol), $[Pd_2(dba)_3]$ (1-2 mol%), the respective ligand (2–6 mol%), and dry toluene (3 mL). The tube was purged with argon and tightly capped with a septum. The mixture was heated at 80 °C for 18 h. The solution was then allowed to cool to RT, diluted with dichloromethane (15 mL), filtered through a short plug of Celite and silica gel, and concentrated in vacuo. The crude product was purified, if neccesary, by flash chromatography.

***N*-(5-Benzyloxy-2-methoxymethylphenyl)aniline (11a)**: Following general procedure II, **5b** (1.0 mmol) was treated with aniline (1.2 mmol) in the presence of $[Pd_2(dba)_3]$ (1.0 mol%), 1,1′-bis(diphenlyphosphino)ferrocene (3.0 mol%), and sodium *tert*-butoxide (1.4 mmol) to give **11a** (329 mg, 0.98 mmol, 98%) as a yellow oil. TLC (hexane/EtOAc 10:1): $R_f = 0.24$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.52$ (s, 3H; OCH_3), 4.99 (s, 2H; OCH_2), 5.16 (s, 2H; OCH_2), 6.23 (br s, 1H; NH), 6.42 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; ArH), 6.95 (d, $J = 3$ Hz, 1H; ArH), 6.98 (Ψd, $J = 8$ Hz, 1H; ArH), 7.03 (d, $J = 9$ Hz, 1H; ArH), 7.11 (Ψd, $J = 8$ Hz, 2H; ArH), 7.24–7.43 (m, 7H; ArH); ^{13}C NMR (67.5 MHz, $CDCl_3$): $\delta = 56.1$ (q, OCH_3), 70.2 (t, OCH_2), 96.1 (t, OCH_2Ph), 102.3 (d, CH_{ar}), 104.7 (d, CH_{ar}), 116.1 (d, CH_{ar}), 119.0 (d, CH_{ar}), 121.5 (d, CH_{ar}), 127.4 (d, CH_{ar}), 127.7 (d, CH_{ar}), 128.4 (d, CH_{ar}), 129.2 (d, CH_{ar}), 134.9 (s, C_{ar}), 137.1 (s, $C_{ar}OBn$), 140.2 (s, $C_{ar}N$), 141.9 (s, $C_{ar}N$), 154.2 (s, $C_{ar}OMOM$); IR (ATR): $\tilde{\nu} = 3408$ (w, NH), 2929 (w), 1594 (s), 1520 (s), 1496 (s), 1188 (m), 1151 (m), 1076 (w), 995 cm^{-1} (m); MS (EI) *m*/*z* (%): 335 (12) $[M]^+$, 290 (28) $[M - C_2H_5O]^+$, 28), 91 (100) $[C_7H_7]^+$; HRMS $C_{21}H_{21}NO_3$: calcd 335.1521; found 335.1518; elemental analysis calcd (%) for $C_{21}H_{21}NO_3$: C 75.20, H 6.31, N 4.18; found C 74.81, H 6.42, N 4.18.

***N*-(5-Benzyloxy-2-methoxymethyloxyphenyl)-2-aminopyridine (11b)**: Following general procedure II, **5b** (1.0 mmol) was treated with 2-aminopyridine (1.2 mmol) in the presence of $[Pd_2(dba)_3]$ (2.0 mol%), *rac*-BINAP (4.0 mol%) and sodium *tert*-butoxide (1.4 mmol) to give **11b** (330 mg, 0.98 mmol, 98%) as an orange oil. TLC (hexane/EtOAc 2:1): $R_f = 0.40$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.51$ (s, 3H; OCH_3), 5.08 (s, 2H; OCH_2), 5.17 (s, 2H; OCH_2), 6.55 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; ArH), 6.76 (dd, $J_1 = 7$ Hz, $J_2 = 6$ Hz, 1H; ArH), 6.83 (d, $J = 9$ Hz, 1H; ArH), 7.08 (d, $J = 9$ Hz, 1H; ArH), 7.12 (br s, 1H; NH), 7.31–7.53 (m, 6H; ArH), 7.90 (d, $J = 3$ Hz, 1H; ArH), 8.27 (dd, $J_1 = 5$ Hz, $J_2 = 1$ Hz, 1H; ArH); ^{13}C NMR (67.5 MHz, $CDCl_3$): $\delta = 56.1$ (q, OCH_3), 70.3 (t, OCH_2), 96.0 (t, OCH_2Ph), 105.6 (d, CH_{ar}), 106.4 (d, CH_{ar}), 109.6 (d, CH_{ar}), 115.1 (d, CH_{ar}), 115.6 (d, CH_{ar}), 127.4 (d, CH_{ar}), 127.7 (d, CH_{ar}), 128.4 (d, CH_{ar}), 132.0 (s, C_{ar}), 137.2 (s, $C_{ar}OBn$), 137.3 (d, CH_{ar}), 140.5 (s, $C_{ar}N$), 148.0 (d, CH_{ar}), 154.0 (s, $C_{ar}OMOM$), 155.0 (s, $CarN_2$); IR (ATR): $\tilde{\nu} = 3417$ (w, NH), 2932 (w), 1594 (s), 1525 (s), 1474 (s), 1446 (s), 1189 (m), 1152 (s), 1077 (m), 986 cm^{-1} (m); MS (EI) *m*/*z* (%): 336 (29) $[M]^+$, 291 (33) $[M - C_2H_5O]^+$, 275 (38), 213 (39), 91 (100) $[C_7H_7]^+$; HRMS $C_{20}H_{20}N_2O_3$: calcd 336.1474; found 336.1472; elemental analysis calcd (%) for $C_{20}H_{20}N_2O_3$: C 71.41, H 5.99, N 8.33; found C 71.12, H 5.61, N 8.30.

***N*-(5-Benzyloxy-2-methoxymethyloxyphenyl)hexylamine (11c)**: Following general procedure II, **5b** (1.0 mmol) was treated with hexylamine (1.2 mmol) in the presence of $[Pd_2(dba)_3]$ (1.0 mol%), *rac*-BINAP (3.0 mol%) and sodium *tert*-butoxide (1.4 mmol) to give **11c** (326 mg, 0.95 mmol, 95%) as a yellow oil. TLC (hexane/EtOAc 20:1): $R_f = 0.14$; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0.90$ (Ψt, 3H; CH_3), 1.28–1.44 (m, 6H; $(CH_2)_3CH_3$), 1.63 (quint, 2H; $NHCH_2CH_2$), 3.08 (t, $J = 7$ Hz, 2H; $NHCH_2$), 3.71 (s, 3H; OCH_3), 4.23 (br s, 1H; NH), 5.00 (s, 2H; OCH_2), 5.11 (s, 2H; OCH_2), 6.18 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; ArH), 6.30 (d, $J = 3$ Hz, 1H; ArH), 6.89 (d, $J = 9$ Hz, 1H; Ar), 7.32 (Ψd, $J = 7$ Hz, 1H; ArH), 7.38; Ψt,

2H; ArH), 7.44 (Ψd, $J = 7$ Hz, 2H; ArH); ^{13}C NMR (67.5 MHz, $CDCl_3$): $\delta = 13.9$ (q, CH_3), 22.5 (t, CH_2), 26.7 (t, CH_2), 29.2 (t, CH_2), 31.4 (t, CH_2), 43.4 (t, CH_2), 55.8 (q, OCH_3), 70.0 (t, OCH_2), 95.8 (t, OCH_2Ph), 98.6 (d, CH_{ar}), 99.6 (d, CH_{ar}), 114.8 (d, CH_{ar}), 127.3 (d, CH_{ar}), 127.5 (d, CH_{ar}), 128.2 (d, CH_{ar}), 137.4 (s, C_{ar}), 138.9 (s, $C_{ar}OBn$), 140.2 (s, $C_{ar}N$), 155.0 (s, $C_{ar}OMOM$); IR (ATR): $\tilde{\nu} = 3427$ (w, NH), 2928 (m), 1615 (m), 1520 (s), 1454 (m), 1188 (m), 1153 (m), 1077 (w), 1003 cm^{-1} (m); MS (EI) m/z (%): 343 (61) $[M]^+$, 298 (85) $[M - C_2H_5O]^+$, 91 (100) $[C_7H_7]^+$; HRMS $C_{21}H_{29}NO_3$: calcd 343.2147; found 343.2153.

***N*-(5-Benzyloxy-2-methoxymethyloxyphenyl)-*N*-methylaniline (11d)**: Following general procedure II, **5b** (1.0 mmol) was treated with *N*-methylaniline (1.2 mmol) in the presence of $Pd_2(dba)_3$ (1.0 mol%), 1-(*N*,*N*-dimethylamino)-1′-(dicyclohexylphosphino)biphenyl (3.0 mol%) and sodium *tert*-butoxide (1.4 mmol) to give **11d** (314 mg, 0.90 mmol, 90%) as an orange oil. TLC (hexane/EtOAc = 20:1): $R_f = 0.12$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.23$ (s, 3H), 3.36 (s, 3H), 4.99 (s, 2H; OCH_2), 5.00 (s, 2H; OCH_2), 6.71 (d, $J = 8$ Hz, 2H; ArH), 6.75 (Ψt, $J = 8$ Hz, 1H; ArH), 6.82 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; ArH), 6.87 (d, $J = 3$ Hz, 1H; ArH), 7.13 (d, $J = 9$ Hz, 1H; ArH), 7.19 (Ψt, $J = 8$ Hz, 2H; ArH), 7.30–7.46 (m, 5H; ArH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 39.2$ (q, N-CH_3), 56.0 (q, OCH_3), 70.5 (t, OCH_2), 95.7 (t, OCH_2), 112.7 (d, CH_{ar}), 114.0 (d, CH_{ar}), 115.3 (d, CH_{ar}), 117.6 (d, CH_{ar}), 118. 6 (d, CH_{ar}), 127.5 (d, CH_{ar}), 127.9 (d, CH_{ar}), 128.5 (d, CH_{ar}), 128.7 (d, CH_{ar}), 136.9 (s, C_{ar}), 139.0 (s, $C_{ar}OBn$), 147.5 (s, $C_{ar}N$), 149.1 (s, $C_{ar}N$), 154.5 (s, $C_{ar}OMOM$); IR (ATR): $\tilde{\nu} = 2898$ (w), 1596 (s), 1499 (vs), 1191 (s), 1154 (m), 1064 (m), 1001 (s), 747 cm^{-1} (m); MS (EI) m/z (%): 349 (53) $[M]^+$, 304 (70) $[M - C_2H_5O]^+$, 244 (77) $[M - C_7H_7N]^+$, 106 (68) $[C_7H_8N]^+$, 91 (100) $[C_7H_7]^+$; HRMS $C_{22}H_{23}NO_3$: calcd 349.1678; found 349.1675.

***N*-(5-Benzyloxy-2-methoxymethyloxyphenyl)-*N*-methylpiperazine (11e)**: Following general procedure II, **5b** (1.0 mmol) was treated with *N*-methylpiperazine (1.2 mmol) in the presence of $[Pd_2(dba)_3]$ (1.0 mol%), 1-(*N*,*N*-dimethylamino)-1′-(dicyclohexylphosphino)biphenyl (3.0 mol%), and sodium *tert*-butoxide (1.4 mmol) to give **11e** (325 mg, 0.95 mmol, 95%) as a brown-red oil. The crude product was filtered with EtOAc through a short column of alumina N. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.35$ (s, 3H; N-CH_3), 2.59 (br s, 4H; N-CH_2, 3.11 (br s, 4H; N-CH_2), 3.53 (s, 3H; OCH_3), 5.00 (s, 2H; OCH_2), 5.15 (s, 2H; OCH_2), 6.53 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; ArH), 6.61 (d, $J = 3$ Hz, 1H; ArH), 6.98 (d, $J = 9$ Hz, 1H; ArH), 7.31–7.46 (m, 5H; ArH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 46.1$ (q, N-CH_3), 50.4 (t, N-CH_2), 55.4 (t, N-CH_2), 56.1 (q, OCH_3), 70.3 (t, OCH_2), 95.9 (t, OCH_2Ph), 106.6 (d, CH_{ar}), 107.0 (d, CH_{ar}), 118.3 (d, CH_{ar}), 127.5 (d, CH_{ar}), 127.8 (d, CH_{ar}), 128.5 (d, CH_{ar}), 137.1 (s, C_{ar}), 143.8 (s, C_{ar}), 144.0 (s, $C_{ar}N$), 154.7 (s, $C_{ar}OMOM$); IR (ATR): 2936 (w), 2793 (w), 1606 (w), 1505 (vs), 1453 (m), 1225 (m), 1189 (s), 1151 (s), 1077 (m), 1011 cm^{-1} (s); MS (EI) m/z (%): 342 (25) $[M]^+$, 297 (32) $[M - C_2H_5O]^+$, 244 (20) $[M - C_5H_{10}N_2]^+$, 91 (100) $[C_7H_7]^+$; HRMS $C_{20}H_{26}N_2O_3$: calcd 342.1943; found 342.1944.

(*S*)-*N*-(5-Benzyloxy-2-methoxymethyloxyphenyl)-1-phenylethylamine (11f): Following general procedure II, **5b** (1.0 mmol) was treated with (*S*)-1-phenylethylamine (1.2 mmol) in the presence of $[Pd_2(dba)_3]$ (2.0 mol%), rac-BINAP (4.0 mol%), and sodium *tert*-butoxide (1.4 mmol) to give **11f** (334 mg, 0.92 mmol, 92%) as a yellow oil. TLC (hexane/EtOAc 10:1): $R_f = 0.23$; $[\alpha]_{589}^{20} = -42.1$ ($c = 0.95$ in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.57$ (d, J = 7 Hz, 3H; CH_3), 3.56 (s, 3H; OCH_3), 4.46 (q, J = 7 Hz, 1H; CH), 4.72 (br s, 1H; NH), 4.87 (s, 2H; OCH_2), 5.18 (s, 2H; OCH_2), 6.10 (d, J = 3 Hz, 1H; ArH), 6.19 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; ArH), 6.93 (d, $J = 9$ Hz, 1H; ArH), 7.22–7.40 (m, 10H; 2 × PhH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 24.6$ (q, CH_3), 52.8 (d, CH), 55.7 (q, OCH_3), 69.7 (t, OCH_2), 95.8 (t, OCH_2Ph), 99.7 (d, CH_{ar}), 100.5 (d, CH_{ar}), 114.8 (d, CH_{ar}), 125.5 (d, CH_{ar}), 126.6 (d, CH_{ar}), 127.1 (d, CH_{ar}), 127.3 (d, CH_{ar}), 128.1 (d, CH_{ar}), 128.3 (d, CH_{ar}), 137.2 (s, C_{ar}), 138.7 (s, C_{ar}), 138.8 (s, C_{ar}), 144.8 (s, $C_{ar}N$), 154.6 (s, $C_{ar}OMOM$); IR (ATR): $\tilde{\nu} = 3425$ (w), 2958 (w), 1613 (w), 1517 (vs), 1434 (w), 1218 (m), 1189 (s), 1152 (s), 1076 (m) 999 cm^{-1} (m); MS (EI) m/z (%): 363 (30) $[M]^+$, 318 (22) $[M - C_2H_5O]^+$, 214 (10), 105 (87), 91 (100) $[C_7H_7]^+$; HRMS $C_{23}H_{25}NO_3$: calcd 363.1834; found 363.1833.

***N*-(5-Benzyloxy-2-methoxymethyloxyphenyl)-*N*-phenylaniline (11g)**: Following general procedure II, **5b** (1.0 mmol) was treated with *N*-phenylaniline (1.2 mmol) in the presence of $[Pd_2(dba)_3]$ (2.0 mol%), 1-(*N*,*N*-dimethylamino)-1′-(dicyclohexylphosphino)biphenyl (6.0 mol%), and sodium *tert*-butoxide (1.4 mmol) to give **11g** (321 mg, 0.78 mmol, 78%) as a yellow oil. TLC (hexane/EtOAc 10:1): $R_f = 0.24$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.22$ (s, 3H; OCH_3), 4.84 (s, 2H; OCH_2), 4.94 (s, 2H; OCH_2), 6.79 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; ArH), 6.82 (d, $J = 3$ Hz, 1H; ArH), 6.94 (Ψt, $J = 8$ Hz, 2H; ArH), 7.02 (d, $J = 8$ Hz, 4H; ArH), 7.08 (d, $J = 9$ Hz, 1H; ArH), 7.20 (Ψt, $J = 8$ Hz, 4H; ArH), 7.28–7.40 (m, 5H; ArH); ^{13}C NMR (67.5 MHz, $CDCl_3$): $\delta = 55.8$ (q, OCH_3), 70.3 (t, OCH_2), 95.4 (t, OCH_2Ph), 112.3 (d, CH_{ar}), 116.2 (d, CH_{ar}), 119.0 (d, CH_{ar}), 121.7 (d, CH_{ar}), 121.8 (d, CH_{ar}), 127.5 (d, CH_{ar}), 127.8 (d, CH_{ar}), 128.4 (d, CH_{ar}), 128.8 (d, CH_{ar}), 136.7 (s, C_{ar}), 137.6 (s, $C_{ar}OBn$), 147.2 (s, $C_{ar}N$), 147.4 (s, $C_{ar}N$), 154.6 (s, $C_{ar}OMOM$); IR (ATR): $\tilde{\nu} = 3034$ (w), 2897 (w), 1586 (m), 1492 (s), 1267 (m), 1212 (m), 1149 (m), 1075 (m), 996 cm^{-1} (m); MS (EI) m/z (%): 411 (16) $[M]^+$, 366 (20) $[M - C_2H_5O]^+$, 91 (100) $[C_7H_7]^+$; HRMS $C_{27}H_{25}NO_3$: calcd 411.1834; found 411.1837.

4-(*tert*-Butyldimethylsilanoxy)-2-phenylsulfanylphenol (12a) from 7a: *p*-Toluenesulfonic acid monohydrate (27 mg, 0.14 mmol) was added to a stirred solution of **7a** (1.12 g, 2.68 mmol) in MeOH (65 mL) under an argon atmosphere. After 40 min the mixture was partitioned between EtOAc and half-saturated brine. The aqueous layer was extracted with EtOAc (2 ×) and the combined organic layers were dried ($MgSO_4$). The solvent was evaporated and the residue purified by preparative radial chromatography (EtOAc/hexane 1:10) to yield **12a** (834 mg, 2.51 mmol, 93%) as a colorless oil. TLC (hexane/EtOAc 10:1): $R_f = 0.32$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.17$ (s, 6H; $SiCH_3$), 0.97 (s, 9H; $SiCCH_3$), 6.14 (br s, 1H; OH, exchanges with D_2O), 6.88 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; H-C5), 6.95 (d, $J = 9$ Hz, 1H; H-C6), 7.02 (d, $J = 3$ Hz, 1H; H-C3), 7.10 (d, $J = 8$ Hz, 2H; *o*-SPh), 7.16 (t, $J = 7.5$ Hz, 1H; *p*-SPh), 7.23 (dd, $J_1 = 8$ Hz, $J_2 = 7.5$ Hz, 2H; *m*-SPh); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -4.5$ (q, $SiCH_3$), 18.2 (s, SiC), 25.7 (q, $SiCCH_3$), 115.9 (d, CH_{ar}), 116.2 (s, $C_{ar}S$), 124.1 (d, CH_{ar}), 126.1 (d, CH_{ar}), 126.9 (d, CH_{ar}), 127.1 (d, CH_{ar}), 129.2 (d, CH_{ar}), 135.8 (s, SPh), 149.1 (s, C_{ar}), 151.8 (s, C_{ar}); IR (ATR): $\tilde{\nu} = 3445$ (br w), 3060 (w), 2955 (m), 2929 (m), 2895 (w), 2885 (w), 2857 (m), 1604 (w), 1582 (w), 1484 (s), 1472 (s), 1440 (w), 1408 (w), 1390 (w), 1362 (w), 1328 (w), 1285 (w), 1256 (s), 1213 (s), 1184 (m), 1122 (w), 1080 (w), 1047 (w), 1024 (w), 1006 (w), 999 (w), 940 (s), 876 (m), 840 (s), 798 (w), 780 (m), 738 (m), 715 (w), 688 (m), 652 (w).); MS: m/z (%): 333 (21) $[M+H]^+$, 332 (83) $[M]^+$, 276 (38), 275 (100), 166 (34), 73 (14); HRMS 332.1266: calcd for $C_{18}H_{24}O_2SSi$; found 332.1269.

4-(*tert*-Butyldimethylsilanoxy)-2-phenylsulfanylphenol (12a) from 7h: A mixture of the MOM ether **7h** (101 mg, 0.27 mmol), NaI (42 mg, 0.28 mmol), acetone (6 mL), and hydrochloric acid (2 M, 0.5 mL) was heated to reflux for 75 min. After addition of saturated aqueous $NaHCO_3$ (10 mL), the aqueous layer was extracted with EtOAc (320 mL) and the combined organic layers were washed with brine and dried ($MgSO_4$). The solvent was evaporated and the crude product was purified by flash chromatography (hexane/EtOAc 25:1) to give **12a** (69 mg, 0.21 mmol, 78%) as a colorless oil. The spectroscopic data were identical to those described above.

4-(*tert*-Butyldimethylsilanoxy)-2-phenylselenylphenol (12b): A solution of **7d** (1.28 g, 2.76 mmol) and *p*-toluenesulfonic acid monohydrate (27 mg, 0.14 mmol) in MeOH (67 mL) was stirred under argon for 90 min at RT. The mixture was partitioned between EtOAc and half-saturated brine. The aqueous layer was extracted with EtOAc (2 ×), and the combined organic layers were dried ($MgSO_4$). The solvent was evaporated, and the residue was purified by preparative radial chromatography (EtOAc/hexane 1:10) to yield **12b** (910 mg, 2.39 mmol, 86%) as a pale yellow oil. TLC (hexane/EtOAc 10:1): $R_f = 0.32$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.17$ (s, 6H; $SiCH_3$), 0.98 (s, 9H; $SiCCH_3$), 6.03 (s, 1H; OH, exchanges with D_2O), 6.86 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; H-C5), 6.96 (d, $J = 9$ Hz, 1H; H-C6), 7.12 (d, $J = 3$ Hz, 1H; H-C3), 7.17–7.29 (m, 5H; SePh); ^{13}C NMR (67 MHz, $CDCl_3$): $\delta = -4.5$ (q, $SiCH_3$), 18.1 (s, SiC), 25.7 (q, $SiCCH_3$), 114.5 (s, $C_{ar}Se$), 115.3 (d, CH_{ar}), 123.8 (d, CH_{ar}), 126.8 (d, CH_{ar}), 128.2 (d, CH_{ar}), 129.4 (d, CH_{ar}), 129.7 (d, CH_{ar}), 130.7 (s, SePh), 149.0 (s, C_{ar}), 151.2 (s, C_{ar}); IR (ATR): $\tilde{\nu} = 3428$ (w, b), 3072 (w), 3058 (w), 2954 (w), 2928 (w), 2895 (w), 2885 (w), 2857 (w), 1600 (w), 1578 (w), 1478 (s), 1438 (w), 1405 (w), 1390 (w), 1362 (w), 1327 (w), 1281 (w), 1255 (s), 1211 (s), 1185 (w), 1118 (w), 1068 (w), 1021 (w), 999 (w), 933 (m), 875 (w), 839 (s), 780 (m), 733 (m), 707 (w), 688 (w), 678 (w), 666 cm^{-1} (w); MS: m/z (%): 380 (91) $[M]^+$, 323 (99), 246 (10), 167 (16), 166 (100), 151 (20), 73 (36); HRMS $C_{18}H_{24}O_2SeSi$: calcd 380.0711; found 380.0711.

[5-(*tert*-Butyldimethylsilanoxy)-2-(hydroxyphenyl)]diphenylphosphane (12c): *p*-Toluenesulfonic acid monohydrate (78 mg, 0.40 mmol) was added to a solution of **7e** (1.00 g, 2.00 mmol), stirred in degassed MeOH (50 mL) under an argon atmosphere. After 2 h at 40 °C the conversion was

0947-6539/00/0615-2886 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 15

complete. The reaction solution was partitioned between EtOAc and half-saturated brine, the aqueous layer was extracted with EtOAc, and the combined organic layers were dried ($MgSO_4$). The solvent was evaporated and the residue purified by preparative radial chromatography (EtOAc/hexane 1:10) to yield **12c** (602 mg, 1.47 mmol, 72%) as a white solid, solutions of which proved to be rather sensitive towards oxidation. M.p. 104–105 °C; TLC (hexane/EtOAc 10:1): $R_f = 0.17$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = -0.03$ (s, 6H; $SiCH_3$), 0.85 (s, 9H; $SiCCH_3$), 5.76 (d, $J = 6$ Hz, 1H; OH, exchanges with D_2O), 6.32–6.37 (m, 1H; H-C4), 6.78–6.83 (m, 2H; H-C3, H-C6), 7.29–7.42 (m, 10H; Ph); ^{31}P NMR (81.0 MHz, $CDCl_3$): $\delta = -27.3$; IR (ATR): $\tilde{\nu} = 3432$ (br w), 3070, 3054 (w), 2955, 2929 (m), 2895, 2885 (w), 2857 (w), 1585 (w), 1492 (m), 1479, 1471 (s), 1434, 1398 (m), 1362, 1325 (w), 1257 (s), 1212, 1182 (m), 1123, 1092, 1027, 1000 (w), 946 (s), 885 (w), 839 (s), 781, 744, 696 cm^{-1} (s); MS: *m*/*z* (%): 409 (30) $[M+H]^+$, 408 (100) $[M]^+$, 351 (32), 273 (20), 256 (15), 185 (21), 183 (22), 137 (14), 111 (11), 109 (12), 97 (19), 95 (18), 83 (21), 81 (33), 73 (30), 71 (17), 69 (70), 60 (20), 57 (31), 55 (38); HRMS $C_{24}H_{29}O_2PSi$: calcd 408.1674; found 408.1675; elemental analysis calcd (%) for $C_{24}H_{29}O_2PSi$: C 70.56, H 7.15; found C 70.20, H 7.33.

2-(5-Benzyloxy-2-hydroxyphenyl)pyridine (12d): A 100 mL flask equipped with a reflux condenser was charged with **10f** (2.4 g, 7.6 mmol, 1.0 equiv), sodium iodide (1.1 g, 7.6 mmol, 1.0 equiv), hydrochloric acid (2N, 1.8 mL), and acetone (40 mL). The reaction mixture was heated at 50 °C for 2 h, allowed to cool to RT, and filtered. After evaporation of the solvent in vacuo, the crude product was purified by flash chromatography (hexane/EtOAc = 6:1) to afford **12d** (1.8 g, 6.4 mmol, 85%) as a bright yellow solid. M.p. 90 °C; TLC (hexane/EtOAc 6:1): $R_f = 0.24$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5.08$ (s, 2H; OCH_2), 6.97 (d, $J = 8$ Hz, 1H; ArH), 7.01 (dd, $J_1 = 8$ Hz, $J_2 = 3$ Hz, 1H; ArH), 7.25 (Ψdd, $J_1 = 8$ Hz, $J_2 = 4$ Hz, 1H; ArH), 7.34 (Ψt, $J = 7$ Hz, 1H; ArH), 7.37–7.44 (m, 3H; ArH), 7.47 (Ψd, $J = 7$ Hz, 2H; ArH), 7.83 (Ψd, $J = 3$ Hz, 2H; ArH), 8.52 (Ψd, $J = 5$ Hz, 1H; ArH), 13.88 (br s, 1H; OH); ^{13}C NMR (67.5 MHz, $CDCl_3$): $\delta = 70.9$ (t, OCH_2), 112.4 (d, CH_{ar}), 118.8 (d, CH_{ar}), 119.0 (d, CH_{ar}), 119.0 (d, CH_{ar}), 121.5 (d, CH_{ar}), 127.5 (d, CH_{ar}), 127.9 (d, CH_{ar}), 128.5 (d, CH_{ar}), 137.2 (s, C_{ar}), 137.7 (d, CH_{ar}), 145.9 (d, CH_{ar}), 151.2 (s, C_{ar}-Pyr), 154.2 (s, C_{ar}N), 157.4 (s, C_{ar}OH), IR (ATR): 3031 (w), 1594 (m), 1564 (m), 1485 (s), 1421 (m), 1381 (w), 1215 (m), 1025 (w), 813 cm^{-1} (m); MS (EI) *m*/*z* (%): 277 (20) $[M]^+$, 186 (100), 158 (9), 130 (16), 91 (18) $[C_7H_7]^+$; HRMS $C_{18}H_{15}NO_2$: calcd 277.1103; found 277.1107; elemental analysis calcd (%) for $C_{18}H_{15}NO_2$: C 77.96, H 5.45, N 5.05; found C 77.74, H 5.45, N 5.01.

***N*-(5-Benzyloxy-2-hydroxy)-*N*-phenylaniline (12e)**: Following the procedure described above for the preparation of **12d**, the MOM-protected compound **11g** (211 mg, 0.51 mmol, 1.0 equiv) was treated with sodium iodide (77 mg, 0.51 mmol, 1.0 equiv) and hydrochloric acid (2N, 3 drops) in acetone (10 mL) to afford **12e** (97 mg, 0.26 mmol, 52%) as a pink oil after flash chromatography (hexane/EtOAc 10:1). TLC (hexane/EtOAc 10:1): $R_f = 0.16$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.93$ (s, 2H; OCH_2), 5.18 (br s, 1H; OH), 6.72 (d, $J = 3$ Hz, 1H; ArH), 6.83 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; ArH), 6.95 (d, $J = 8$ Hz, 1H; ArH), 6.99–7.06 (m, 5H; Ar), 7.22–7.30 (m, 4H; ArH), 7.29–7.40 (m, 5H; ArH); ^{13}C NMR (67.5 MHz, $CDCl_3$): $\delta = 70.6$ (t, OCH_2), 114.1 (d, CH_{ar}), 115.6 (d, CH_{ar}), 117.0 (d, CH_{ar}), 121.7 (d, CH_{ar}), 122.7 (d, CH_{ar}), 127.6 (d, CH_{ar}), 127.9 (d, CH_{ar}), 128.5 (d, CH_{ar}), 129.4 (d, CH_{ar}), 133.3 (s, C_{ar}), 136.8 (s, C_{ar}OBn), 146.4 (s, C_{ar}N), 146.4 (s, C_{ar}N), 153.1 (s, C_{ar}OH); IR (ATR): 3534 (w), 3035 (w), 1589 (m), 1494 (s), 1272 (m), 1215 (m), 1027 cm^{-1} (w); MS (EI) *m*/*z* (%): 367 (100) $[M]^+$, 276 (72) $[M - C_7H_7]^+$, 91 (78) $[C_7H_7]^+$; HRMS $C_{25}H_{21}NO_2$: calcd 367.1572; found 367.1577.

General procedure III—preparation of the RR′P-Cl electrophiles (13) from diols or aminoalcohols:[26a, 26d] In an atmosphere of argon, a solution of NEt_3 (2 equiv) in THF was cooled to −40 to −65 °C. After addition of PCl_3 (1.05 equiv) a solution of the diol or aminoalcohol (1 equiv) was added dropwise. After 15 min the mixture was allowed to warm to RT and stirring was continued for further 3–4 h. The white precipitate was filtered off through a short pad of Celite and washed with THF. The filtrate was concentrated and all volatiles were removed in vacuo (oil pump) to give the crude product of type **13** which was used without further purification.

General procedure IV—synthesis of ligands of type 14 from the corresponding phenolic precursors: In an argon atmosphere, a solution of the phenol (**8**, **10**, or **12**, 1 equiv) in THF was treated at RT with NEt_3 (usually 15 or 20 equiv). After stirring for 10 min a solution of the phosphorous electrophile (usually 2 equiv) in THF was added dropwise at RT and the resulting milky suspension was stirred for 4–12 h. The mixture was filtered under argon through a short column of Alox N (ICN) with dry, degassed solvents. Finally, all volatiles were removed in vacuo. In general, the products proved to be rather sensitive towards oxidation and hydrolysis. Only in some cases was chromatographic purification possible.

[4-(*tert*-Butyldimethylsilanoxy)-2-phenylsulfanylphenoxy]diphenylphosphane (14a): According to general procedure IV, the phenol **12a** (502 mg, 1.51 mmol) in THF (5 mL) was treated with NEt_3 (4.3 mL, 30.9 mmol) and a solution of $ClPPh_2$ (540 μL, 3.01 mmol) in THF (5 mL). The mixture was stirred overnight and filtered through Alox N with hexane/EtOAc/CH_2Cl_2 10:1:1 (360 mL). After evaporation of the solvent the crude product was purified by preparative radial chromatography (hexane/EtOAc 10:1) to give **14a** (705 mg, 1.36 mmol, 90%) as a colorless oil. TLC (hexane/EtOAc/CH_2Cl_2 10:1:1): $R_f = 0.52$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.04$ (s, 6H; $SiCH_3$), 0.88 (s, 9H; $SiCCH_3$), 6.53 (d, $J = 3$ Hz, 1H; H-C3), 6.57 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; H-C5), 6.92 (dd, $J_{HH} = 9$ Hz, $J_{PH} = 2$ Hz, 1H; H-C6), 7.24–7.42 (m, 11H; Ph), 7.54–7.62 (m, 4H; Ph); MS: *m*/*z* (%): 519 (7), 439 (22), 332 (70), 275 (100), 202 (15), 185 (39), 183 (83), 166 (52), 73 (44); HRMS $C_{30}H_{33}O_2PSSi$: calcd 516.1708; found 516.1709.

[4-(*tert*-Butyldimethylsilanoxy)-2-phenylsulfanylphenoxy]diisopropylphosphane (14b): According to the general procedure IV, the phenol **12a** (762 mg, 2.29 mmol) in THF (8 mL) was treated with NEt_3 (6.5 mL, 46.6 mmol) and a solution of $ClP(iPr)_2$ (730 μL, 4.59 mmol) in THF (7 mL). The mixture was stirred for 3 h and then filtered through Alox N with hexane/EtOAc/CH_2Cl_2 10:1:1 (360 mL). Evaporation of the solvent afforded **14b** (1.01 g, 2.25 mmol, 98%) as a colorless oil (>90% purity according to ^{1}H NMR). Due to the instability, **14b** was not further purified. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.04$ (s, 6H; $SiCH_3$), 0.88 (s, 9H; $SiCCH_3$), 1.07 (dd, $J_{HH} = 7$ Hz, $J_{PH} = 16$ Hz, 6H; CH_3), 1.14 (dd, $J_{HH} = 7$ Hz, $J_{PH} = 11$ Hz, 3H; CH_3), 1.90 (dsept, $J_d = 3$ Hz, $J_{sept} = 7$ Hz, 2H; PCH), 6.40 (d, $J = 3$ Hz, 1H; H-C3), 6.60 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; H C5), 7.12 (dd, $J_{HH} = 9$ Hz, $J_{PH} = 2$ Hz, 1H; H-C6), 7.27–7.34 (m, 3H; Ph), 7.36–7.40 (m, 2H; Ph); MS (oxidized product): *m*/*z* (%): 464 (8) $[M + O]^+$, 407 (69), 332 (69), 275 (100), 166 (35), 73 (16).

[4-(*tert*-Butyldimethylsilanoxy)-2-phenylsulfanylphenoxy]bis(diisopropylamino)phosphane (14c): According to the general procedure IV, a solution of the phenol **12a** (100 mg, 0.3 mmol) in THF (2 mL) was treated at RT with NEt_3 (850 μL, 0.61 mmol) and a solution of $ClP(N(iPr)_2)_2$ (160 mg, 0.6 mmol) in THF (2 mL). The mixture was stirred overnight before it was filtered through a pad of Alox N with hexane/EtOAc 10:1 (100 mL) and EtOAc (20 mL). The solvent was evaporated and the crude product purified by preparative radial chromatography (hexane/EtOAc 10:1) to give **14c** (110 mg, 0.20 mmol, 65%) as a colorless oil (>90% purity according to ^{1}H NMR). TLC (hexane/EtOAc 5:1): $R_f = 0.62$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.03$ (s, 6H; $SiCH_3$), 0.88 (s, 9H; $SiCCH_3$), 1.11 (d, $J = 7$ Hz, 12H; CH_3), 1.18 (d, $J = 7$ Hz, 12H; CH_3), 3.58 (Ψsept, $J = 7$ Hz, 4H; NCH), 6.42 (d, $J = 3$ Hz, 1H; H-C3), 6.60 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; H-C5), 7.12 (dd, $J_{HH} = 9$ Hz, $J_{PH} = 4$ Hz, 1H; H-C6), 7.21–7.36 (m, 5H; Ph); MS: *m*/*z* (%): 562 (3), 462 (51), 363 (7), 331 (11), 231 (100), 132 (98), 88 (36), 73 (58); HRMS $C_{30}H_{51}N_2O_2PSSi$: calcd 562.3178; found 562.3176.

[4-(*tert*-Butyldimethylsilanoxy)-2-phenylsulfanylphenoxy]diethoxyphosphane (14d): According to general procedure IV, the phenol **12a** (100 mg, 0.30 mmol) in THF (2 mL) was treated with NEt_3 (0.85 mL, 0.61 mmol) and a solution of $ClP(OEt)_2$ (87 μL, 0.60 mmol) in THF (1 mL). The mixture was stirred overnight and then filtered through Alox N with hexane/EtOAc 10:1 (70 mL). The solvent was evaporated and the crude product was purified by preparative radial chromatography (hexane/EtOAc 10:1) to give **14d** (107 mg, 0.24 mmol, 79%) as a colorless oil (>95% purity according to ^{1}H NMR). TLC (hexane/EtOAc 5:1): $R_f = 0.64$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.04$ (s, 6H; $SiCH_3$), 0.99 (s, 9H; $SiCCH_3$), 1.28 (t, $J = 7$ Hz, 6H; CH_3), 4.01 (Ψquint, 4H; $J = 7$ Hz, 6H; CH_2), 6.47 (d, $J = 3$ Hz, 1H; H-C3), 6.62 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; H-C5), 6.96 (dd, $J_1 = 9$ Hz, $J_2 = 1$ Hz, 1H; H-C6), 7.26–7.39 (m, 5H; Ph); MS: *m*/*z* (%): 452 (100), 407 (11), 375 (16), 339 (18), 332 (36), 319 (24), 275 (56), 209 (68), 166 (26), 121 (36), 93 (46), 73 (75), 65 (57); HRMS $C_{22}H_{33}O_4PSSi$: calcd 452.1606; found 452.1606.

6-[4-*tert*-Butyldimethylsilanoxy)-2-phenylsulfanylphenoxy]-5,7-dioxa-6-phosphadibenzo[*a*,*c*]cycloheptene (14e): According to general procedure III (vide supra) the chlorophosphite **13a** was prepared from 2,2′-biphenol (1.86 g, 10 mmol), NEt_3 (2.9 mL, 20.8 mol), and PCl_3 (890 μL, 10.2 mmol)$_3$ in THF (40 mL). After removal of all volatiles, the residue

(crude **13a**, colorless oil) was dissolved in THF (20 mL) to give a 0.5 M solution. Following general procedure IV, the solution of **13a** (7.30 mL, 3.57 mmol) was added to a stirred mixture of the phenol **12a** (794 mg, 2.39 mmol) and NEt_3 (670 μL, 4.6 mmol) in THF (12 mL), and stirring was continued overnight. The precipitate was filtered off and washed with hexane/EtOAc 10:1 (350 mL). The filtrate was concentrated in vacuo to give **14e** (1.30 g, 2.37 mmol, 99 %) as a colorless oil (> 95 % purity according to ^{1}H NMR), which could be further purified by preparative radial chromatography (hexane/EtOAc 10:1). TLC (hexane/EtOAc 10:1): $R_f = 0.47$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.07$ (s, 6H; $SiCH_3$), 0.90 (s, 9H; $SiCCH_3$), 6.57 (d, $J = 3$ Hz, 1H; H-C3), 6.65 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; H-C5), 7.01 (d, $J = 9$ Hz, 1H; H-C6), 7.20 (br d, $J = 8$ Hz, 2H; H_{ar}), 7.27 – 7.38 (m, 7H; H_{ar}), 7.39 – 7.42 (m, 2H; H_{ar}), 7.47 (dd, $J_1 = 8$ Hz, $J_2 = 2$ Hz, 2H; H_{ar}); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -4.6$ (q, $SiCH_3$), 18.2 (s, SiC), 25.6 (q, $SiCCH_3$), 119.5 (d, CH_2), 121.9 (d, $J_{PC} = 8$ Hz), 122.3 (d), 122.7 (d), 125.3 (d), 127.6 (d), 129.1 (d), 129.4 (d), 129.9 (d), 131.1 (ds, $J_{PC} = 3$ Hz), 132.1 (d), 133.9 (s), 144.1 (ds, $J_{PC} = 6$ Hz), 149.1 (ds, $J_{PC} = 6$ Hz), 152.7 (s); IR (ATR): $\tilde{\nu} = 3062$ (w), 2955 (w), 2929 (w), 2885 (w), 2857 (w), 1583 (w), 1476 (s), 1435 (m), 1279 (w), 1252 (m), 1190 (s), 1096 (m), 947 (m), 914 (m), 878 (s), 854 (s), 768 (m), 690 cm^{-1} (w); MS: *m*/*z* (%): 546 (100), 489 (98), 215 (26), 168 (22); HRMS $C_{30}H_{31}O_4PSSi$: calcd 546.1450; found 546.1441.

(*S*)-4-[4-(*tert*-Butyldimethylsilanoxy)-2-phenylsulfanylphenoxy]-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalene (14f): According to general procedure III (vide supra) the chlorophosphite **13b** was prepared from (*S*)-2,2′-binaphthol (800 mg, 2.79 mmol), NEt_3 (810 μL, 5.81 mmol), and PCl_3 (250 μL, 2.86 mmol) in THF (25 mL). After filtration the solvent was removed in vacuo to give **13b** as a fluffy white solid, which was dissolved in THF (5 mL). Following general procedure IV, this solution was added to a stirred mixture of the phenol **12a** (449 mg, 1.35 mmol) and NEt_3 (4 mL, 28.7 mmol) in THF (5 mL). After 3 h the precipitate was filtered off and washed with hexane/EtOAc 10:1 (330 mL). The filtrate was concentrated in vacuo to give **14f** (865 mg, 1.34 mmol, 99 %) as a fluffy white solid (> 95 % purity according to ^{1}H NMR). Due to the instability no further purification was performed. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.07$ (s, 6H; $SiCH_3$), 0.90 (s, 9H; $SiCCH_3$), 6.58 (d, $J = 3$ Hz, 1H; H-C3), 6.65 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; H-C5), 7.08 (d, $J = 9$ Hz, 1H; H-C6), 7.20 – 7.47 (m, 12H; H_{ar}), 7.52 (d, $J = 9$ Hz, 1H; H_{ar}), 7.88 (t, $J = 9$ Hz, 2H; H_{ar}), 7.93 (d, $J = 9$ Hz, 1H; H_{ar}), 7.98 (d, $J = 9$ Hz, 1H; H_{ar}); IR (ATR): $\tilde{\nu} = 3056$ (w), 2954 (w), 2928 (w), 2884 (w), 2856 (w), 1725 (w), 1620 (w), 1589 (m), 1476 (s), 1471 (s), 1463 (s), 1326 (m), 1255 (m), 1229 (m), 1198 (s), 1187 (s), 1071 (m), 954 (s), 868 (s), 829 (m), 749 cm^{-1} (m); MS: *m*/*z* (%): 646 (16) $[M]^+$, 589 (8), 389 (18), 332 (89), 275 (72), 268 (100), 239 (66), 166 (45), 73 (60); HRMS $C_{38}H_{35}O_4PSSi$: calcd 646.1763; found 646.1764.

(3*R*,9*R*)-4-[4-(*tert*-Butyldimethylsilanoxy)-2-phenylsulfanylphenoxy]-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro-1,3,5,7-tetraoxa-6-phosphaazulene (14g): According to general procedure III (vide supra) the chlorophosphite **13c** was prepared from the corresponding (*R*,*R*)-TADDOL (625 mg, 1.34 mmol, 90 % *ee*), NEt_3 (375 μL, 2.69 mmol), and PCl_3 (120 μL, 1.34 mmol) in THF (3 mL) to give **13c** as a fluffy white solid, which was dissolved in THF (3 mL). Following general procedure IV, this solution was added to a stirred mixture of the phenol **12a** (222 mg, 0.67 mmol) and NEt_3 (1.8 mL, 12.9 mmol) in THF (2 mL). After stirring overnight the precipitate was filtered off and washed with hexane/EtOAc 10:1 (100 mL). The filtrate was concentrated in vacuo to give crude **14g** (587 mg, 0.7 mmol) as fluffy white solid (> 90 % purity according to ^{1}H NMR) which was employed for the complexation experiments (vide infra) without further purification. An analytical sample of **14g** was obtained by preparative radial chromatography (hexane/EtOAc 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.04$ (s, 6H; $SiCH_3$), 0.46 (s, 3H; CH_3), 0.89 (s, 9H; $SiCCH_3$), 0.92 (s, 3H; CH_3), 5.13 (br d, $J = 9$ Hz, 1H; OCH), 5.29 (d, $J = 9$ Hz, 1H; OCH), 6.40 (d, $J = 3$ Hz, 1H; H-C3), 6.48 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; H-C5), 6.69 (dd, $J_{HH} = 9$ Hz, $J_{PH} = 1$ Hz, 1H; H-C6), 7.17 – 7.70 (m, 25H; Ph); IR (ATR): $\tilde{\nu} = 3086$ (w), 3060 (w), 3026 (w), 2989 (w), 2955 (m), 2930 (m), 2885 (w), 2858 (w), 1704 (w), 1584 (w), 1494 (m), 1478 (s), 1448 (s), 1387 (m), 1372 (m), 1127 (m), 1254 (s), 1166 (m), 1088 (m), 1035 (s), 1018 (s), 949 (m), 887 (s), 837 (s), 740 (s), 697 cm^{-1} (s); MS: *m*/*z* (%): 573 (7), 431 (7), 395 (79), 378 (10), 332 (8), 237 (48), 207 (18), 179 (100), 167 (28), 105 (15), 73 (16); HRMS $C_{49}H_{51}O_6PSSi$: calcd 826.2913; found 826.2915.

(3a*S*)-1-[4-(*tert*-Butyldimethylsilanoxy)-2-phenylsulfanylphenoxy]-3,3-diphenyltetrahydro-2-oxa-6a-aza-1-phosphapentalene (14h): According to general procedure III (vide supra) the phosphorous electrophile **13e** was prepared from (*S*)-2-(1-hydroxy-1,1-diphenylmethyl)-pyrrolidin (153 mg, 0.60 mmol), NEt_3 (170 μL, 1.22 mmol), and PCl_3 (60 μL, 0.68 mmol) in THF (6 mL) to give **13e** as a colorless oil, which was dissolved in THF (4 mL). Following general procedure IV, this solution was added to a stirred mixture of the phenol **12a** (100 mg, 0.30 mmol) and NEt_3 (630 μL, 4.52 mmol) in THF (2 mL). After 19 h at RT the reaction mixture was filtered through Celite, the solvent was evaporated in vacuo, and the residue was eluted through a small pad of Alox N with hexane/EtOAc (10:1). The solvent was evaporated to give **14h** (172 mg, 0.28 mmol, 93 %) as a colorless viscous oil (> 95 % purity according to ^{1}H NMR). TLC (hexane/EtOAc 10:1): $R_f = 0.39$; $[\alpha]_{589}^{20} = -189$ ($c = 0.81$ in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.01$ (s, 6H; $SiCH_3$), 0.81 – 0.96 (m, 10H; $SiCCH_3$, CH_2), 1.36 – 1.46 (m, 1H; CH_2), 1.48 – 1.60 (m, 1H; CH_2), 1.67 – 1.80 (m, 1H; CH_2), 3.07 – 3.19 (m, 1H; NCH_2), 3.40 – 3.52 (m, 1H; NCH_2), 3.97 (dd, $J_1 = 8$ Hz, $J_2 = 4$ Hz, 1H; NCH), 6.21 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; H-C5′), 6.41 (d, $J = 3$ Hz, 1H; H-C3′), 7.61 (d, $J = 9$ Hz, 1H; H-C6′), 7.11 (br d, $J = 8$ Hz, 2H; Ph) 7.16 – 7.37 (m, 11H; Ph), 7.40 (dd, $J_1 = 7$ Hz, $J_2 = 1$ Hz, 2H; Ph); ^{31}P NMR (81.0 MHz, $CDCl_3$): $\delta = 139.4$ (s); IR (ATR): $\tilde{\nu} = 3059$ (w), 3025 (w), 2955 (m), 2928 (m), 2882 (w), 2858 (m), 2396 (w, b), 1584 (w), 1495 (m), 1471 (s), 1448 (m), 1391 (w), 1362 (w), 1254 (m), 1199 (s), 1105 (w), 1053 (w), 1025 (m), 981 (m), 949 (m), 914 (w), 858 (s), 838 (s), 782 (m), 749 (m), 701 (s), 656 cm^{-1} (w); MS: *m*/*z* (%): 614 (24) $[M+H]^+$, 613 (55) $[M]^+$, 544 (10), 378 (23), 363 (20), 362 (81), ,333 (12), 332 (44), 321 (23), 283 (18), 282 (100), 281 (26), 276 (13), 275 (60), 265 (17), 264 (89), 236 (13), 235 (50), 234 (36), 206 (14), 167 (16), 166 (30), 165 (31), 73 (53); HRMS $C_{35}H_{40}NO_3PSSi$: calcd 613.2236; found 613.2233.

[4-(*tert*-Butyldimethylsilanoxy)-2-phenylselenylphenoxy]bis(diisopropylamino)phosphane (14i): According to general procedure IV, the phenol **12b** (99 mg, 0.26 mmol) in THF/DMF (1:1, 4 mL) was treated with NEt_3 (550 μL, 3.94 mmol) and $ClP(NiPr_2)_2$ (150 mg, 0.56 mmol). The mixture was stirred for 4.5 h at RT and then filtered through Celite with THF. After evaporation of all volatiles in vacuo the residue was filtered through a short column of Alox N with hexane/EtOAc (10:1). The solvent was evaporated to give **14i** (150 mg, 0.25 mmol, 94 %) as a white solid which was not further purified. M.p. 62 °C; TLC (hexane/EtOAc 10:1): $R_f = 0.71$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = -0.04$ (s, 6H; $SiCH_3$), 0.85 (s, 9H; $SiCCH_3$), 1.14 (d, $J = 6.5$ Hz, 12H; CH_3), 1.21 (d, $J = 6.5$ Hz, 12H; CH_3), 3.62 (sept, $J = 6.5$ Hz, 4H; NCH), 6.27 (d, $J = 3$ Hz, 1H; H-C3), 6.55 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; H-C5), 7.09 (dd, $J_{HH} = 9$ Hz, $J_{PH} = 4$ Hz, 1H; H-C6), 7.29 – 7.40 (m, 3H; *o*-, *p*-Ph), 7.55 – 7.64 (m, 2H; *m*-Ph); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -4.7$ (q, $SiCH_3$), 18.1 (s, SiC), 24.0 (dq, $J_{PC} = 9$ Hz, CH_3), 24.2 (dq, $J_{PC} = 6$ Hz, C′H_3), 25.7 (q, $SiCCH_3$), 45.1 (dd, $J_{PC} = 12$ Hz, NCH), 116.7 (dd, $J_{PC} = 23$ Hz, CH_{ar}), 118.0 (d, CH_{ar}), 120.9 (d, CH_{ar}), 124.2 (s, $C_{ar}Se$), 128.1 (d, CH_{ar}, SePh), 128.7 (s, SePh), 129.4 (d, CH_{ar}, SePh), 136.0 (d, CH_{ar}, SePh), 147.4 (s, C_{ar}), 149.6 (s, C_{ar}); ^{31}P NMR (81.0 MHz, $CDCl_3$): $\delta = 115.7$ (s); IR (ATR): $\tilde{\nu} = 3071$ (w), 3060 (w), 2965 (m), 2929 (m), 2896 (w), 2859 (w), 1722 (w), 1591 (w), 1580 (w), 1565 (w), 1476 (s), 1438 (w), 1391 (w), 1363 (w), 1265 (w), 1253 (m), 1209 (m), 1197 (m), 1180 (m), 1157 (w), 1117 (m), 1065 (w), 1041 (w), 1023 (m), 956 (m), 937 (m), 870 (m), 852 (s), 839 (m), 811 (w), 780 (m), 741 (m), 692 (w), 665 cm^{-1} (w); MS: *m*/*z* (%): 231 (35) $[C_{12}H_{28}N_2P]^+$, 132 (100) $[C_6H_{15}NP]^+$, 90 (14), 73 (16); HRMS $C_{30}H_{51}N_2O_2PSeSi$: calcd 610.2623; found 610.2621; elemental analysis calcd (%) for $C_{30}H_{51}N_2O_2PSeSi$: C 59.09, H 8.43, N 4.59; found C 58.99, H 8.20, N 4.46.

[4-(*tert*-Butyldimethylsilanoxy)-2-phenylselenylphenoxy]diethoxyphosphane (14j): According to general procedure IV, the phenol **12b** (104 mg, 0.27 mmol) in THF (5 mL) was treated with NEt_3 (520 μL, 3.73 mmol) and $ClP(OEt)_2$ (72 μL, 0.50 mmol). The mixture was stirred for 30 min at RT and then filtered through Alox N with hexane/EtOAc (10:1). The solvent was evaporated to give **14j** (73 mg, 0.15 mmol, 54 %) as a colorless oil (> 95 % purity according to ^{1}H NMR). TLC (hexane/EtOAc 10:1): $R_f = 0.45$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = -0.01$ (s, 6H; $SiCH_3$), 0.86 (s, 9H; $SiCCH_3$), 1.32 (t, $J = 7$ Hz, 6H; CH_3), 4.08 (quint, $J = 7$ Hz, 4H; CH_2), 6.37 (d, $J = 3$ Hz, 1H; H-C3), 6.59 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; H-C5), 6.94 (d, $J = 9$ Hz, 1H; H-C6), 7.30 – 7.41 (m, 3H; *o*-, *p*-Ph), 7.54 – 7.65 (m, 2H; *m*-Ph); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -4.7$ (q, $SiCH_3$), 16.8 (dq, $J_{PC} = 4.5$ Hz, CH_3), 18.1 (s, SiC), 25.6 (q, $SiCCH_3$), 58.8 (dt, $J_{PC} = 8$ Hz, CH_2), 118.7 (d, CH_{ar}), 119.9 (dd, $J_{PC} = 11$ Hz, CH_{ar}), 121.8 (d, CH_{ar}), 126.4 (d, $J_{PC} = 3$ Hz, $C_{ar}Se$), 128.3 (s, SePh), 128.3 (d, CH_{ar}, SePh), 129.5 (d, CH_{ar}, SePh), 135.6 (d, CH_{ar}, SePh), 144.3 (d, $J_{PC} = 6$ Hz, C_{ar}), 152.0 (s, C_{ar}); IR (ATR): $\tilde{\nu} = 3430$ (w, b) 3071 (w), 3059 (w), 2955 (w), 2929 (w), 2895 (w), 2885 (w), 2857 (w), 1600 (w), 1578 (w), 1479 (s), 1439 (w), 1407 (w), 1391

0947-6539/00/0615-2888 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 15

(w), 1362 (w), 1327 (w), 1281 (w), 1256 (m), 1212 (m), 1119 (w), 1067 (w), 1036 (w), 1022 (w), 935 (m), 874 (w), 840 (s), 781 (m), 735 (m), 689 cm^{-1} (w); MS: *m*/*z* (%): 500 (67) $[M]^+$, 423 (81), 380 (18), 367 (54), 323 (21), 166 (33), 121 (26), 93 (43), 73 (100), 65 (53); HRMS $C_{22}H_{33}O_4PSeSi$: calcd 500.1051; found 500.1054.

(*S*)-4-[4-(*tert*-Butyldimethylsilanoxy)-2-phenylselenylphenoxy]-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalene (14k): According to general procedure III (vide supra) the chlorophosphite **13b** was prepared from (*S*)-2,2′-binaphthol (151 mg, 0.53 mmol), NEt_3 (150 μL, 1.08 mmol), and PCl_3 (50 μL, 0.57 mmol) in THF (5 mL) to give **13b** as a fluffy white solid, which was dissolved in THF (4 mL). Following general procedure IV, this solution was added to a stirred mixture of the phenol **12b** (100 mg, 0.26 mmol) and NEt_3 (550 μL, 3.95 mmol) in THF (3 mL). After 3.5 h at RT the reaction mixture was filtered through Celite with THF, the solvent was evaporated in vacuo and the residue was filtered through a short column of Alox N with hexane/EtOAc (10:1). The solvent was evaporated to give **14k** (59 mg, 0.085 mmol, 32%) as a fluffy white solid. M.p. 73–74 °C; TLC (hexane/EtOAc 10:1): $R_f = 0.37$; $[\alpha]_{589}^{20} = +77$ ($c = 0.71$ in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.03$ (s, 6H; $SiCH_3$), 0.88 (s, 9H; $SiCCH_3$), 6.50 (d, $J = 3$ Hz, 1H; H-C3′), 6.63 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; H-C5′), 7.09 (d, $J = 9$ Hz, 1H; H-C6′), 7.22–7.49 (m, 9H; H_{ar}), 7.52 (d, $J = 9$ Hz, 1H; H_{ar}), 7.58 (d, $J = 9$ Hz, 1H; H_{ar}), 7.60–7.65 (m, 2H; H_{ar}), 7.88–7.98 (m, 3H; H_{ar}), 8.01 (d, $J = 9$ Hz, 1H; H_{ar}); ^{31}P NMR (81.0 MHz, $CDCl_3$): $\delta = 144.5$ (s); IR (ATR): $\tilde{\nu} = 3058$ (w), 2954 (w), 2928 (w), 2885 (w), 2857 (w), 1620 (w), 1589 (w), 1578 (w), 1510 (w), 1477 (s), 1463 (m), 1438 (w), 1391 (w), 1361 (w), 1326 (w), 1277 (w), 1257 (w), 1230 (w), 1198 (s), 1187 (s), 1155 (w), 1071 (w), 1041 (w), 1022 (w), 979 (w), 955 (m), 939 (m), 878 (m), 868 (m), 852 (w), 830 (s), 783 (w), 749 (w), 691 (w), 676 cm^{-1} (w); MS: *m*/*z* (%): 694 (84) $[M]^+$, 617 (53), 380 (16), 323 (18), 315 (53), 269 (23), 268 (100), 252 (33), 166 (20), 81 (12), 73 (50), 69 (24), 57 (10); HRMS $C_{38}H_{35}O_4PSeSi$: calcd 694.1207; found 694.1212; elemental analysis calcd (%) for $C_{38}H_{35}O_4PSeSi$: C 65.79, H 5.09; found C 65.72, H 5.41.

(3*R*,9*R*)-4-[4-(*tert*-Butyldimethylsilanoxy)-2-phenylselenylphenoxy]-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro-1,3,5,7-tetraoxa-6-phosphaazulene (14l): According to general procedure III (vide supra), the chlorophospite **13c** was prepared from the corresponding (*R*,*R*)-TADDOL (246 mg, 0.53 mmol, 90% *ee*), NEt_3 (150 μL, 1.08 mmol), and PCl_3 (50 μL, 0.57 mmol) in THF (5 mL) to give **13c** as a fluffy white solid, which was dissolved in THF (4 mL). Following general procedure IV, this solution was added to a stirred mixture of the phenol **12b** (99 mg, 0.26 mmol) and NEt_3 (550 μL, 3.95 mmol) in THF (3 mL). After 1.5 h at RT the reaction mixture was filtered through Celite with THF, all volatiles were evaporated in vacuo, and the residue was filtered through a short column of Alox N with hexane/EtOAc (10:1). The solvent was evaporated to give **14l** (147 mg, 0.17 mmol, 64%) as a fluffy white solid. M.p. 82–83 °C; TLC (hexane/EtOAc 10:1): $R_f = 0.40$; $[\alpha]_{589}^{20} = -129$ ($c = 1.00$ in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = -0.01$ (s, 6H; $SiCH_3$), 0.47 (s, 3H; CH_3), 0.87 (s, 9H; $SiCCH_3$), 0.94 (s, 3H; CH_3), 5.16 (d, $J = 8$ Hz, 1H; OCH), 5.32 (d, $J = 8$ Hz, 1H; OCH), 6.33 (d, $J = 3$ Hz, 1H; H-C3′), 6.47 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; H-C5′), 6.78 (dd, $J_{HH} = 9$ Hz, $J_{PH} = 2$ Hz, 1H; H-C6′), 7.16–7.40 (m, 15H; Ph), 7.43 (dd, $J_1 = 7$ Hz, $J_2 = 1$ Hz, 2H; Ph), 7.48–7.56 (m, 4H; Ph), 7.58 (dd, $J_1 = 8$ Hz, $J_2 = 1$ Hz, 2H; Ph), 7.69 (d, $J = 8$ Hz, 2H; Ph); ^{31}P NMR (81.0 MHz, $CDCl_3$): $\delta = 134.3$ (s); IR (ATR): $\tilde{\nu} = 3089$ (w), 3059 (w), 3036 (w), 3026 (w), 2989 (w), 2955 (w), 2929 (w), 2896 (w), 2857 (w), 1588 (w), 1494 (w), 1476 (s), 1448 (m), 1438 (w), 1382 (w), 1371 (w), 1274 (w), 1254 (m), 1197 (m), 1166 (w), 1089 (w), 1052 (m), 1034 (m), 1019 (m), 977 (w), 933 (m), 888 (s), 838 (s), 782 (w), 740 (m), 725 (w), 698 (s), 672 cm^{-1} (w); MS: *m*/*z* (%): 890 (9) $[M+O]^+$, 874 (12) $[M]^+$, 443 (63), 431 (31), 380 (84), 345 (100), 323 (84), 265 (29), 207 (24), 179 (39), 178 (42), 166 (28); HRMS $C_{49}H_{51}O_6PSeSi$: calcd 874.2358; found 874.2355; elemental analysis calcd (%) for $C_{49}H_{51}O_6PSeSi$: C 67.34, H 5.88; found C 67.52, H 5.92.

[4-(*tert*-Butyldimethylsilanoxy)-2-diphenylphosphanylphenoxy]diethoxyphosphane (14m): According to general procedure IV, the phenol **12c** (200 mg, 0.49 mmol) in THF (10 mL) was treated with NEt_3 (1.05 mL, 7.53 mmol) and $ClP(OEt)_2$ (145 μL, 1.00 mmol). The mixture was stirred for 20 min at RT and then filtered through Alox N with hexane/EtOAc (10:1). After evaporation of the solvent the product **14m** (244 mg, 0.46 mmol, 94%) was obtained as a colorless oil (>95% purity according to ^{1}H NMR). TLC (hexane/EtOAc 10:1): $R_f = 0.35$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = -0.07$ (s, 6H; $SiCH_3$), 0.83 (s, 9H; $SiCCH_3$), 1.16 (t, $J = 7$ Hz, 6H; CH_3), 3.78 (quint, $J = 7$ Hz, 4H; CH_2), 6.09 (dd, $J_{HH} = 4$ Hz, $J_{PH} = 3$ Hz, 1H; H-C3), 6.74 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; H-C5), 7.00 (ddd, $J_{HH} = 9$ Hz, $J_{PH} = 5$ Hz, $J_{PH} = 1$ Hz, 1H; H-C6), 7.22–7.39 (m, 10H; Ph); ^{31}P NMR (81.0 MHz, $CDCl_3$): $\delta = -16.0$ (d, $J_{PP} = 6.9$ Hz, PPh_2), 132.3 (d, $J_{PP} = 6.9$ Hz, $P(OEt)_2$); IR (ATR): $\tilde{\nu} = 3070$ (w), 3054 (w), 2975 (w), 2956 (m), 2929 (m), 2896 (w), 2858 (w), 1586 (w), 1570 (w), 1501 (w), 1468 (s), 1434 (m), 1389 (m), 1362 (w), 1273 (m), 1255 (m), 1207 (s), 1159 (w), 1129 (w), 1095 (w), 1045 (m), 1024 (s), 947 (s), 864 (s), 838 (s), 780 (m), 745 (s), 696 (m), 678 cm^{-1} (m); MS: *m*/*z* (%): 528 (22) $[M]^+$, 499 (18), 345 (19), 344 (89), 287 (20), 213 (11), 195 (17), 167 (48), 139 (44), 121 (100), 93 (68), 73 (29), 65 (35); HRMS $C_{28}H_{38}O_4P_2Si$: calcd 528.2015; found 528.2019.

6-[(4-*tert*-Butyldimethylsilanoxy)-2-diphenylphosphanylphenoxy]-5,7-dioxa-6-phosphadibenzo[*a*,*c*]cycloheptene (14n): According to general procedure III (vide supra), the chlorophosphite **13a** was prepared from 2,2′-biphenol (154 mg, 0.83 mmol), NEt_3 (235 μL, 1.68 mmol), and PCl_3 (76 μL, 0.87 mmol) in THF (9 mL) to give **13a** as a colorless oil, which was dissolved in THF (6 mL). Following general procedure IV, this solution was added to a stirred mixture of the phenol **12c** (160 mg, 0.39 mmol) and NEt_3 (870 μL, 6.24 mmol) in THF (5 mL). After 4 h at RT the mixture was filtered through Alox N with hexane/EtOAc (10:1), and all volatiles were removed in vacuo to give **14n** (90 mg, 0.14 mmol, 37%) as a colorless oil (>90% purity according to ^{1}H NMR). TLC (hexane/EtOAc 10:1): $R_f = 0.34$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = -0.03$ (s, 6H; $SiCH_3$), 0.87 (s, 9H; $SiCCH_3$), 6.18 (t, $J_{HH,PH} = 3.5$ Hz, 1H; H-C3′), 6.80 (dd, $J_1 = 9$ Hz, $J_2 = 3.5$ Hz, 1H; H-C5′), 7.03 (d, $J = 7.5$ Hz, 2H; H_{ar}), 7.12 (dd, $J_{HH} = 9$ Hz, $J_{PH} = 5$ Hz, 1H; H-C6′), 7.19–7.33 (m, 4H; H), 7.33–7.41 (m, 10H; Ph), 7.43 (dd, $J_1 = 7$ Hz $J_2 = 2$ Hz, 2H; H_{ar}); IR (ATR): $\tilde{\nu} = 3069$ (w), 3055 (w), 3028 (w), 3001 (w), 2955 (w), 2928 (w), 2885 (w), 2857 (w), 1585 (w), 1570 (w), 1499 (m), 1467 (s), 1434 (s), 1389 (w), 1362 (w), 1272 (m), 1252 (m), 1213 (w), 1187 (s), 1121 (w), 1096 (m), 1069 (w), 1057 (w), 1044 (w), 1027 (w), 1010 (w), 1000 (w), 945 (m), 914 (m), 878 (s), 854 (s), 838 (m), 769 (s), 747 (m), 696 cm^{-1} (m); MS: *m*/*z* (%): 623 (42) $[M+H]^+$, 622 (100) $[M]^+$, 621 (16), 546 (27), 545 (76), 483 (24), 482 (62), 481 (15), 408 (28), 407 (15), 273 (17), 215 (46), 185 (18), 183 (29), 168 (53), 73 (41); HRMS $C_{36}H_{36}O_4P_2Si$: calcd 622.1858; found 622.1859.

(*S*)-4-[4-(*tert*-Butyldimethylsilanoxy)-2-diphenylphosphanylphenoxy]-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalene (14o): According to general procedure III (vide supra) the chlorophosphite **13b** was prepared from (*S*)-2,2′-binaphthol (418 mg, 1.46 mmol), NEt_3 (410 μL, 2.94 mmol), and PCl_3 (135 μL, 1.53 mmol) in THF (12 mL) to give **13b** as a fluffy white solid, which was dissolved in THF (8 mL). Following general procedure IV, this solution was added to a stirred mixture of the phenol **12c** (300 mg, 0.73 mmol) and NEt_3 (1.50 mL, 10.76 mmol) in THF (5 mL). After 8 h at RT the mixture was filtered through Celite and silicagel with THF. Removal of the solvent in vacuo and purification of the crude product by preparative radial chromatography (EtOAc/hexane 1:10) afforded **14o** (443 mg, 0.61 mmol, 84%) as a fluffy white solid. M.p. 88–90 °C; TLC (hexane/EtOAc 10:1): $R_f = 0.38$; $[\alpha]_{589}^{20} = +122$ ($c = 1.01$ in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = -0.03$ (s, 6H; $SiCH_3$), 0.86 (s, 9H; $SiCCH_3$), 6.17 (t, $J_{HH,PH} = 3$ Hz, 1H; H-C3′), 6.78 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; H-C5′), 7.11 (dd, $J_{HH} = 9$ Hz, $J_{PH} = 5$ Hz, 1H; H-C6′), 7.18–7.31 (m, 3H; H_{ar}), 7.32–7.48 (m, 15H; Ph, H_{ar}), 7.75 (d, $J = 9$ Hz, 1H; H_{ar}), 7.86 (d, $J = 8$ Hz, 1H; H_{ar}), 7.92 (d, $J = 8$ Hz, 1H; H_{ar}), 7.95 (d, $J = 9$ Hz, 1H; H_{ar}); ^{31}P NMR (145.8 MHz, $CDCl_3$): $\delta = -15.3$ (d, $J_{PP} = 15.3$ Hz, $-PPh_2$), 144.5 (d, $J_{PP} = 15.3$ Hz, $-P(OR)_2$); IR (ATR): $\tilde{\nu} = 3052$, 2953, 2884, 2856 (m), 1696, 1620 (w), 1587 (m), 1570, 1509 (w), 1462 (s), 1434, 1389 (m), 1361 (w), 1326, 1271, 1255, 1230 (m), 1197, 1186 (s), 1155, 1071 (m), 979 (w), 955 (s), 940 (m), 880 (s), 852 (m), 831 (s), 783, 769 (m), 747, 695 cm^{-1} (s); MS: *m*/*z* (%): 409 (30), 408 (100), 351 (32), 273 (20), 256 (15), 185 (21), 183 (22), 137 (14), 111 (11), 109 (12), 97 (19), 95 (18), 83 (21), 81 (33), 73 (30), 71 (17), 69 (70), 60 (20), 57 (31), 55 (38); HRMS $C_{44}H_{40}O_4P_2Si$: calcd 722.2171; found 722.2168; elemental analysis calcd (%) for $C_{44}H_{40}O_4P_2Si$: C 73.11, H 5.58; found C 72.86, H 5.77.

(3*R*,9*R*)-4-[4-(*tert*-Butyldimethylsilanoxy)-2-diphenylphosphanylphenoxy]-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro-1,3,5,7-tetraoxa-6-phosphaazulene (14p): According to general procedure III (vide supra), the chlorophosphite **13c** was prepared from the corresponding (*R*,*R*)-TADDOL (570 mg, 1.22 mmol, 90% *ee*), NEt_3 (340 μL, 2.44 mmol), and PCl_3 (115 μL, 1.28 mmol) in THF (10 mL) to give **13c** as a fluffy white solid, which was dissolved in THF (7 mL). Following general procedure IV, this solution was added at 0 °C to a stirred mixture of the phenol **12c** (250 mg, 0.61 mmol) and NEt_3 (1.3 mL, 9.15 mmol) in THF (4 mL). After 24 h at RT

the mixture was filtered through Celite and silicagel, the solvent was removed in vacuo, and the crude product was purified by preparative radial chromatography (EtOAc/hexane 1:10) to yield **14p** (545 mg, 0.60 mmol, 99%) as a fluffy white solid. M.p. 140–145 °C; TLC (hexane/EtOAc 10:1): $R_f = 0.38$; $[\alpha]_{589}^{20} = -125$ ($c = 1.04$ in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = -0.05$ (s, 6H; $SiCH_3$), 0.39 (s, 3H; CH_3), 0.86 (s, 9H; $SiCCH_3$), 1.00 (s, 3H; CH_3), 5.14 (d, $J = 8$ Hz, 1H; OCH), 5.17 (d, $J = 8$ Hz, 1H; OCH), 6.12 (t, $J_{HH} = J_{PH} = 3$ Hz, 1H; H-C3′), 6.65 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; H-C5′), 6.86 (dd, $J_{HH} = 9$ Hz, $J_{PH} = 5$ Hz, 1H; H-C6′), 7.12–7.39 (m, 24H; Ph), 7.39–7.46 (m, 2H; Ph), 7.51–7.57 (m, 2H; Ph), 7.62 (br d, $J = 8$ Hz, 2H; Ph); ^{31}P NMR (81.0 MHz, $CDCl_3$): $\delta = -16.3$ (d, $J_{PP} = 13.5$ Hz, PPh_2), 136.1 (d, $J_{PP} = 13.5$ Hz, $-P(OR)_2$); IR (ATR): $\tilde{\nu} = 3088$ (w), 3057 (w), 3035 (w), 2988 (w), 2955 (w), 2929 (w), 2857 (w), 1705 (w), 1585 (w), 1570 (w), 1494 (w), 1466 (s), 1448 (m), 1434 (w), 1382 (w), 1371 (w), 1362 (w), 1273 (w), 1254 (m), 1197 (m), 1166 (w), 1089 (m), 1050 (m), 1036 (m), 1020 (m), 948 (w), 887 (s), 837 (s), 782 (w), 741 (m), 725 (w), 696 cm^{-1} (s); MS: m/z (%): 903 (15) $[M+H]^+$, 902 (<1) $[M]^+$, 472 (25), 471 (100), 208 (12), 207 (40), 179 (44), 178 (18), 167 (18), 165 (13), 105 (17), 73 (21), 57 (18); HRMS $C_{55}H_{56}O_6P_2Si$: calcd 902.3321; found 902.3327; elemental analysis calcd (%) for $C_{55}H_{56}O_6P_2Si$: C 73.15, H 6.25; found C 73.40, H 6.52.

(4a*R*,5a*R*)-[2-(4-(*tert*-Butyldimethylsilanoxy)-2-diphenylphosphanylphenoxy)-5-pyrrolidin-1-carbonyl)[1,3,2]dioxaphospholan-4-yl]pyrrolidin-1-ylmethanone (14q): According to general procedure III (vide supra), the chlorophosphite **13d** was prepared from (*R*,*R*)-*N*,*N*,*N*′*N*′-bistetramethylenetartaramide[38] (128 mg, 0.50 mmol), NEt_3 (140 μL, 1.00 mmol), and PCl_3 (48 μL, 0.55 mmol) in THF (5 mL) to give **13d** as a fluffy white solid, which was dissolved in THF (4 mL). Following general procedure IV, this solution was added to stirred mixture of the phenol **12c** (102 mg, 0.25 mmol) and NEt_3 (520 μL, 3.73 mmol) in THF (4 mL). After 4 h at RT the mixture was filtered through Celite with THF, the solvent was removed, and the crude product was purified by preparative radial chromatography (EtOAc) to yield **14q** (157 mg, 0.23 mmol, 90%) as a fluffy white solid. M.p. 59–61 °C; TLC (EtOAc): $R_f = 0.31$; $[\alpha]_{589}^{20} = -81$ ($c = 0.95$ in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = -0.09$ (s, 6H; $SiCH_3$), 0.82 (s, 9H; $SiCCH_3$), 1.72–2.02 (m, 8H; CH_2), 3.33–3.51 (m, 4H; NCH), 3.51–3.77 (m, 4H; NCH), 5.12 (dd, $J_{HH} = 8$ Hz, $J_{PH} = 6$ Hz, 1H; OCH), 5.48 (d, $J = 8$ Hz, 1H; OCH), 6.09 (t, $J_{HH,PH} = 3$ Hz, 1H; H-C3), 6.73 (dd, $J_1 = 8.5$ Hz, $J_2 = 3$ Hz, 1H; H-C5), 6.91 (dd, $J_{HH} = 8.5$ Hz, $J_{PH} = 5$ Hz, 1H; H-C6), 7.16–7.40 (m, 10H; Ph); ^{31}P NMR (81.0 MHz, $CDCl_3$): $\delta = -15.2$ (d, $J_{PP} = 18.7$ Hz, PPh_2), 137.4 (d, $J_{PP} = 18.7$ Hz, $-P(OR)_2$); IR (ATR): $\tilde{\nu} = 3069$ (w), 3053 (w), 2954 (m), 2929 (m), 2881 (m), 2858 (w), 1650 (s), 1585 (w), 1570 (w), 1465 (s), 1450 (m), 1435 (m), 1389 (w), 1361 (w), 1342 (w), 1313 (w), 1273 (m), 1255 (m), 1226 (w), 1197 (m), 1123 (w), 1091 (w), 1069 (w), 1039 (w), 1026 (w), 1008 (m), 974 (w), 948 (m), 869 (m), 842 (s), 781 (m), 747 (m), 696 cm^{-1} (m); MS: m/z (%): 692 (2) $[M]^+$, 471 (28), 455 (13), 408 (12), 286 (12), 285 (100), 268 (10), 206 (44), 158 (10), 98 (12), 81 (12), 69 (18); HRMS $C_{36}H_{46}N_2O_6P_2Si$: calcd 692.2600; found 692.2612; elemental analysis calcd (%) for $C_{36}H_{46}N_2O_6P_2Si$: C 62.41, H 6.69, N 4.04; found C 62.13, H 6.70, N 4.16.

(3a*S*)-1-[4-(*tert*-Butyldimethylsilanoxy)-2-diphenylphosphanylphenoxy]-3,3-diphenyltetrahydro-2-oxa-6a-aza-1-phosphapentalene (14r): According to general procedure III (vide supra), the phosphorous electrophile **13e** was prepared from (*S*)-2-(1-hydroxy-1,1-diphenylmethyl)pyrrolidin (125 mg, 0.49 mmol), NEt_3 (140 μL, 1.00 mmol), and PCl_3 (45 μL, 0.51 mmol) in THF (5 mL) to give **13e** as a colorless oil, which was dissolved in THF (4 mL). Following general procedure IV, this solution was added to a stirred mixture of the phenol **12c** (100 mg, 0.24 mmol) and NEt_3 (520 μL, 3.73 mmol) in THF (3 mL). After 4 h at RT the mixture filtered through Celite with THF, the solvent was evaporated in vacuo and the residue was filtered through a short column of Alox N with hexane/EtOAc (10:1). The solvent was evaporated to give **14r** (115 mg, 0.17 mmol, 69%) as a fluffy white solid (>95% purity according to ^{1}H NMR). M.p. 53-54 °C; TLC (hexane/EtOAc 10:1): $R_f = 0.33$; $[\alpha]_{589}^{20} = -170$ ($c = 1.02$ in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = -0.06$ (s, 6H; $SiCH_3$), 0.88–0.96 (m, 10H; $SiCCH_3$, CH_2), 1.32–1.43 (m, 1H; CH_2), 1.43–1.55 (m, 1H; CH_2), 1.68 (dq, $J_1 = 12$ Hz, $J_2 = 8$ Hz, 1H; CH_2), 2.79–2.92 (m, 1H; NCH_2), 3.15–3.30 (m, 1H; NCH_2), 4.09 (dd, $J_1 = 8$ Hz, $J_2 = 5$ Hz, 1H; NCH), 6.12 (t, $J_{HH,PH} = 3$ Hz, 1H; H-C3′), 6.48 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; H-C5′), 6.77 (dd, $J_{HH} = 9$ Hz, $J_{PH} = 5$ Hz, 1H; H-C6′), 7.11 (br d, $J = 8$ Hz, 2H; Ph) 7.17–7.39 (m, 16H; Ph), 7.41 (d, $J = 8$ Hz, 2H; Ph); ^{31}P NMR (81.0 MHz, $CDCl_3$): $\delta = -15.9$ (d, $J_{PP} = 14.1$ Hz, PPh_2), 139.1 (d, $J_{PP} = 14.1$ Hz, $-P_{Het}$); IR (ATR): $\tilde{\nu} = 3056$ (w), 3027 (w), 3000 (w), 2955 (m), 2928 (m), 2883 (w), 2857 (m), 1585 (w), 1568 (w), 1493 (w), 1465 (s), 1447 (m), 1434 (m), 1389 (m), 1361 (w), 1255 (m), 1200 (m), 1188 (m), 1122 (w), 1104 (w), 1069 (w), 1054 (w), 1027 (w), 982 (m), 947 (m), 913 (w), 861 (s), 837 (s), 781 (m), 745 (s), 697 (s), 680 (m), 656 cm^{-1} (w); MS: m/z (%): 690 (40) $[M+H]^+$, 689 (81) $[M]^+$, 482 (32), 456 (17), 455 (58), 454 (53), 453 (31), 438 (18), 408 (22), 407 (26), 282 (24), 264 (59), 236 (20), 235 (100), 183 (16), 165 (14), 90 (13), 73 (36); HRMS $C_{41}H_{45}NO_3P_2Si$: calcd 689.2644; found 689.2641; elemental analysis calcd (%) for $C_{41}H_{45}NO_3P_2Si$: C 71.39, H 6.57, N 2.03; found C 70.79, H 6.63, N 2.22.

[4-(*tert*-Butyldimethylsilanoxy)-2-*N*,*N*-dimethylaminomethylphenoxy]diethoxyphosphane (14s): According to general procedure IV, the phenol **8** (77 mg, 0.27 mmol) in THF (4.5 mL) was treated with NEt_3 (570 μL, 4.09 mmol) and $ClP(OEt)_2$ (78 μL, 0.54 mmol). The mixture was stirred for 1 h at RT and then filtered through Alox N with hexane/EtOAc (2:1). After evaporation of the solvent the product **14s** (104 mg, 0.26 mmol, 96%) was obtained as a colorless oil (>95% purity according to ^{1}H NMR). TLC (hexane/EtOAc 1:1): $R_f = 0.25$ (br); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.16$ (s, 6H; $SiCH_3$), 0.96 (s, 9H; $SiCCH_3$), 1.30 (t, $J = 7$ Hz, 6H; CH_3), 2.25 (s, 6H; NCH_3), 3.43 (s, 2H; NCH_2), 4.01 (quint, $J = 7$ Hz, 4H; OCH_2), 6.64 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; H-C5′), 6.86 (d, $J = 3$ Hz, 1H; H-C3′), 6.92 (dd, $J_{HH} = 9$ Hz, $J_{PH} = 1$ Hz, 1H; H-C6′); ^{13}C NMR (67 MHz, $CDCl_3$): $\delta = -4.5$ (q, $SiCH_3$), 16.8 (dq, $J_{PC} = 5$ Hz, CH_3), 18.1 (s, SiC), 25.7 (q, $SiCCH_3$), 45.4(q, NCH_3), 57.8 (t, NCH_2), 58.4 (dt, $J_{PC} = 8.5$ Hz, OCH_2), 118.9 (d, CH_{ar}), 120.5 (dd, $J_{PC} = 11$ Hz, CH_{ar}), 122.1 (d, CH_{ar}), 130.9 (d, $J_{PC} = 1.5$ Hz, C_{ar}), 145.1 (d, $J_{PC} = 6$ Hz, C_{ar}), 151.3 (s, C_{ar}); IR (ATR): $\tilde{\nu} = 3034$ (w), 2975 (w), 2954 (m), 2930 (m), 2895 (w), 2885 (w), 2858 (w), 2826 (w), 2784 (w), 2711 (w), 1641 (w), 1608 (w), 1492 (s), 1472 (m), 1463 (m), 1426 (w), 1389 (w), 1362 (w), 1286 (w), 1250 (s), 1211 (m), 1200 (m), 1147 (m), 1098 (w), 1049 (m), 1024 (m), 986 (m), 957 (m), 940 (m), 922 (m), 870 (s), 839 (s), 818 (m), 779 (m), 698 cm^{-1} (w); MS: m/z (%): 401 (1) $[M]^+$, 372 (12), 282 (16), 281 (88), 263 (35), 262 (92), 236 (34), 180 (33), 179 (100), 73 (15); HRMS $C_{19}H_{36}NO_4PSi$: calcd 401.2151; found 401.2156.

[4-(*tert*-Butyldimethylsilanoxy)-2-pyrimidin-2-ylphenoxy]diphenylphosphane (14t): According to general procedure IV, the phenol **10a** (100 mg, 0.33 mmol) in THF (5 mL) was treated with NEt_3 (690 μL, 4.95 mmol) and $ClPPh_2$ (120 μL, 0.67 mmol). The mixture was stirred for 6 h at RT and then filtered through Alox N with hexane/EtOAc (3:1). The solvent was evaporated to give crude **14t** (183 mg) as a colorless semi-crystalline residue, which (due to its instability) was used directly whithout further purification (vide infra). TLC (hexane/EtOAc 3:1): $R_f = 0.38$.

(3a*R*,8a*R*)-6-[4-(*tert*-Butyldimethylsilanoxy)-2-pyridin-2-ylphenoxy]-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro-1,3,5,7-tetraoxa-6-phosphaazulene (14u): According to general procedure III (vide supra), the chlorophosphite **13c** was prepared from the corresponding (*R*,*R*)-TADDOL (329 mg, 0.71 mmol, 90% *ee*), NEt_3 (200 μL, 1.43 mmol), and PCl_3 (68 μL, 0.78 mmol) in THF (7 mL) to give **13c** as a fluffy white solid, which was dissolved in THF (6 mL). Following general procedure IV, this solution was added to a stirred mixture of phenol **10b** (108 mg, 0.36 mmol) and NEt_3 (750 μL, 5.38 mmol) in THF (5 mL). After 16 h at RT the mixture was filtered through Celite with THF, the solvent was removed, and the crude product was purified by preparative radial chromatography (EtOAc/hexane 1:20; later 1:10) to yield **14u** (246 mg, 0.31 mmol, 85%) as a fluffy white solid. M.p. 94–95 °C; TLC (hexane/EtOAc 10:1): $R_f = 0.17$; $[\alpha]_{589}^{20} = -182$ ($c = 1.05$ in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.22$ (s, 6H; $SiCH_3$), 0.38 (s, 3H; CH_3), 0.91 (s, 3H; CH_3), 1.00 (s, 9H; $SiCCH_3$), 5.11 (d, $J = 8$ Hz, 1H; OCH), 5.15 (d, $J = 8$ Hz, 1H; OCH), 6.71 (ddd, $J_1 = 8.5$ Hz, $J_2 = 3$ Hz, $J_{PH} = 1$ Hz, 1H; H-C5′), 6.96 (d, $J = 8.5$ Hz, 1H; H-C6′), 7.08–7.54 (m, 22H; H-C3′, py-H, Ph), 7.54–7.67 (m, 2H; py-H), 8.66 (br d, $J = 5$ Hz, 1H; py-H); ^{31}P NMR (81.0 MHz, $CDCl_3$): $\delta = 137.0$ (s); IR (ATR): $\tilde{\nu} = 3089$ (w), 3059 (w), 3037 (w), 2989 (w), 2955 (w), 2930 (w), 2885 (w), 2857 (w), 1586 (w), 1565 (w), 1490 (s), 1471 (w), 1462 (m), 1448 (m), 1440 (w), 1401 (w), 1382 (w), 1371 (w), 1314 (w), 1290 (w), 1253 (m), 1216 (m), 1195 (m), 1166 (m), 1089 (m), 1050 (m), 1034 (m), 1019 (m), 991 (m), 939 (m), 885 (s), 837 (s), 788 (m), 781 (m), 740 (m), 724 (m), 699 (s), 666 cm^{-1} (w); MS: m/z (%): 797 (8) $[M+H]^+$, 431 (12), 366 (25), 365 (21), 364 (100), 179 (21), 178 (38); HRMS calcd for $C_{48}H_{51}NO_6PSi$ $[M+H]$: 796.3223; found 796.3227; elemental analysis calcd (%) for $C_{48}H_{50}NO_6PSi$: C 72.42, H 6.34, N 1.76; found C 72.99, H 6.81, N 1.77.

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(3a*R*,8a*R*)-6-[4-(*tert*-Butyldimethylsilanoxy)-2-thiophen-2-ylphenoxy]-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro-1,3,5,7-tetraoxa-6-phosphaazulene (14v): According to general procedures III (vide supra), the chlorophosphite **13c** was prepared from the corresponding (*R*,*R*)-TADDOL (344 mg, 0.74 mmol, 90% *ee*), NEt_3 (210 μL, 1.50 mmol), and PCl_3 (70 μL, 0.80 mmol) in THF (7 mL) to give **13c** as a fluffy white solid, which was dissolved in THF (6 mL). Following general procedure IV, this solution was added to a stirred mixture of the phenol **10d** (113 mg, 0.37 mmol) and NEt_3 (780 μL, 5.60 mmol) in THF (4 mL). After 5 h at RT the mixture was filtered through Celite with THF, the solvent was evaporated in vacuo, and the residue was filtered through a short Alox N column with hexane/EtOAc (10:1). The solvent was evaporated to give **14v** (203 mg, 0.25 mmol, 67%) as a fluffy white solid. M.p. 94–96 °C; TLC (hexane/EtOAc 10:1): $R_f = 0.40$; $[\alpha]_{589}^{20} = -177$ ($c = 0.99$ in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.24$ (s, 6H; $SiCH_3$), 0.35 (s, 3H; CH_3), 1.03 (s, 12H; $SiCCH_3$, CH_3), 5.06 (d, $J = 8$ Hz, 1H; OCH), 5.13 (dd, $J_{HH} = 8$ Hz, $J_{PH} = 1.5$ Hz, 1H; OCH), 6.62 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; H-C5′), 6.98 (dd, $J_{HH} = 9$ Hz, $J_{PH} = 1.5$ Hz, 1H; H-C6′), 7.03–7.09 (m, 2H; thiophene-H, H-C3′), 7.14–7.46 (m, 20H; H_{ar}), 7.46–7.55 (m, 2H; Ph); ^{31}P NMR (81.0 MHz, $CDCl_3$): $\delta = 137.4$ (s); IR (ATR): $\tilde{\nu} = 3089$ (w), 3059 (w), 3036 (w), 2989 (w), 2955 (w), 2930 (w), 2885 (w), 2858 (w), 1602 (w), 1577 (w), 1525 (w), 1484 (s), 1447 (m), 1437 (m), 1401 (w), 1382 (w), 1371 (w), 1295 (w), 1254 (m), 1226 (m), 1191 (m), 1166 (m), 1088 (m), 1050 (m), 1037 (m), 1020 (w), 1014 (m), 1000 (m), 916 (s), 885 (s), 837 (s), 781 (m), 740 (m), 725 (w), 698 (s), 652 cm^{-1} (w); MS: *m*/*z* (%): 800 (<1) $[M]^+$, 605 (10), 564 (19), 369 (50), 295 (16), 265 (23), 238 (18), 237 (87), 236 (28), 180 (23), 179 (100), 178 (37), 167 (59), 165 (20), 105 (15), 73 (29); HRMS $C_{47}H_{49}O_6PSSi$: calcd 800.2757; found 800.2757; elemental analysis calcd (%) for $C_{47}H_{49}O_6PSSi$: C 70.47, H 6.17; found C 70.30, H 6.25.

[4-Benzyloxy-2-(2′-pyridyl)phenoxy]diphenylphosphane (14w): An oven-dried 25 mL Schlenk tube equipped with a reflux condenser and a septum was cooled under argon and charged with **12d** (400 mg, 1.44 mmol, 1.0 equiv), triethylamine (4.0 mL, 28.8 mmol, 20.0 equiv), and dry THF (10 mL). The tube was purged with argon and tightly capped with a septum and cooled in an ice-bath. Chlorodiphenylphosphine (0.52 mL, 2.88 mmol, 2.0 equiv) was added by a syringe to give a white suspension. After stirring for 1 h at RT the white precipitate was removed by filtration under argon through Alox N and was washed with diethyl ether. Evaporation of the solvent gave **14w** as a yellow oil, which due to its sensitivity was directly further converted to the complex **15f** (see below).

General procedure V—generation of $PdCl_2$ complexes: A solution of the corresponding ligand of type **14** (1.05 equiv) in benzene or toluene was added to a solution of $[PdCl_2(PhCN)_2]$ (1 equiv) in benzene or toluene under an argon atmosphere. The mixture was stirred at RT or 80 °C for an indicated period. Hexane was then added to precipitate the Pd^{II} complex (**15**). After filtration, the precipitate (product) was washed with hexane and dried in vacuo.

{6-[4-(*tert*-Butyldimethylsilanoxy)-2-phenylsulfanylphenoxy]-5,7-dioxa-6-phosphadibenzo[*a*,*c*]cycloheptene}dichloropalladium(II) (15a): According to general procedure V, ligand **14e** (200 mg, 0.37 mmol) was treated with $[PdCl_2(PhCN)_2]$ (137 mg, 0.36 mmol) in benzene (7 mL). After 5 min at RT, the mixture refluxed for 20 min before hexane (20 mL) was added. After cooling to RT, the complex **15a** (253 mg, 0.35 mmol, 95%) was isolated as a yellow solid (>95% purity according to ^{1}H NMR). M.p. (decomp) >230 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.28$ (s, 6H; $SiCH_3$), 1.10 (s, 9H; $SiCCH_3$), 7.06 (dd, $J_1 = 9$ Hz, $J_2 = 1$ Hz, 1H; H_{ar}), 7.12–7.17 (m, 3H; H_{ar}), 7.34–7.47 (m, 8H; H_{ar}), 7.52 (dd, $J_1 = 7$ Hz, $J_2 = 2$ Hz, 2H; *o*-SPh), 7.70–7.74 (m, 2H; H_{ar}); IR (ATR): $\tilde{\nu} = 3062$ (w), 2955 (w), 2929 (w), 2885 (w), 2857 (w), 1583 (w), 1476 (s), 1435 (m), 1279 (w), 1252 (m), 1190 (s), 1096 (m), 947 (m), 914 (m), 878 (s), 854 (s), 768 (m), 690 (w); FAB-MS (*m*-nitrobenzylalcohol): *m*/*z* (%): 689 (100) $[M - Cl]^+$, 653 (26) $[M - 2Cl]^+$; HRMS $C_{30}H_{30}O_4SSiPPdCl^+$ $[M - Cl]^+$: calcd 686.0094; found 686.0101.

[6-(4-Hydroxy-2-phenylsulfanylphenoxy)-5,7-dioxa-6-phosphadibenzo[*a*,*c*]cyclohepten]dichloropalladium(II) (15a′): Recrystallization of **15a** from hot CH_2Cl_2/THF yielded the desilylated compound **15a′** ($R^1 = H$) as yellow transparent crystals which were characterized by X-ray crystallographic analysis.

(*S*)-{4-[4-(*tert*-Butyldimethylsilanoxy)-2-phenylsulfanylphenoxy]-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalene}dichloropalladium(II) (15b): According to general procedure V, ligand **14f** (290 mg, 0.45 mmol) was treated with $[PdCl_2(PhCN)_2]$ (165 mg, 0.43 mmol) in benzene (8 mL). The mixture was heated to reflux for 30 min and then diluted with hexane (20 mL). After cooling, the complex **15b** (318 mg, 0.39 mmol, 90%) was isolated as a yellow solid (>95% purity according to ^{1}H NMR). M.p. (decomp) >225 °C; $[\alpha]_{589}^{20} = +101$ ($c = 0.405$ in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.28$ (s, 6H; $SiCH_3$), 1.02 (s, 9H; $SiCCH_3$), 6.95–7.05 (br m, 1H), 7.10–7.18 (br m, 1H), 7.21 (Ψt, $J = 9$ Hz, 2H), 7.32 (d, $J = 3$ Hz, 2H), 7.37 (s, 2H), 7.42–7.59 (m, 6H), 7.68–7.75 (br m, 2H), 7.92–8.05 (br m, 4H); a high-temperature measurement together with a selective decoupling experiment was used for a better assignment: ^{1}H NMR (400 MHz, $CDCl_3$, 60 °C): $\delta = 0.28$ (s, 6H; $SiCH_3$), 1.03 (s, 9H; $SiCCH_3$), 6.96 (d, $J = 9$ Hz, 1H; H-C6), 7.11 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; H-C5), 7.15–7.26 (m, 3H; H_{ar}), 7.29–7.33 (m, 2H; H_{ar}), 7.34 (d, $J = 3$ Hz, 1H; H-C3), 7.43–7.49 (m, 4H; H_{ar}), 7.49–7.54 (m, 1H; H_{ar}), 7.57 (d, $J = 9$ Hz, 1H; H_{ar}), 7.72–7.77 (m, 2H; *o*-SPh), 7.93 (d, $J = 8$ Hz, 1H; H_{ar}), 7.96 (d, $J = 8$ Hz, 1H; H_{ar}), 8.00 (d, $J = 9$ Hz, 2H; H_{ar}); IR (ATR): $\tilde{\nu} = 3058$ (w), 2953 (w), 2929 (w), 2885 (w), 2857 (w), 1702 (w), 1592 (w), 1481 (s), 1472 (s), 1464 (s), 1291 (w), 1257 (m), 1219 (m), 1197 (s), 1185 (s), 1071 (m), 959 (s), 921 (s), 830 (s), 814 (s), 748 (m); FAB-MS (*m*-nitrobenzylalcohol): *m*/*z* (%): 788 (77) $[M - Cl]^+$, 768 (20), 751 (18), 332 (18), 268 (58).

{(3*R*,9*R*)-4-[4-(*tert*-Butyldimethylsilanoxy)-2-phenylsulfanylphenoxy]-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro-1,3,5,7-tetraoxa-6-phosphaazulene}dichloropalladium(II) (15c): According to general procedure V, ligand **14g** (330 mg, 0.40 mmol) was treated with $[PdCl_2(PhCN)_2]$ (152 mg, 0.40 mmol) in benzene (6 mL). The mixture was heated to reflux for 30 min and then diluted with hexane (10 mL). The complex **15c** (208 mg, 0.21 mmol, 52%) was isolated as a yellow solid (>90% purity according to ^{1}H NMR). M.p. (decomp) >190 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.17$ (s, 6H; $SiCH_3$), 0.22 (s, 3H; CH_3), 0.95 (s, 9H; $SiCCH_3$), 1.36 (s, 3H; CH_3), 5.15 (d, $J = 8$ Hz, 1H; OCH), 5.25–5.37 (br m, 1H), 5.58–5.90 (br m, 1H), 6.34–6.48 (br m, 1H), 6.90–7.80 (m, 26H); a high-temperature measurement gave a better resolution: ^{1}H NMR (400 MHz, $CDCl_3$, 60 °C): $\delta = 0.19$ (s, 6H; $SiCH_3$), 0.31 (s, 3H; CH_3), 0.97 (s, 9H; $SiCCH_3$), 1.39 (s, 3H; CH_3), 5.26 (d, $J = 8$ Hz, 1H; OCH), 5.40 (br d, $J = 9$ Hz, 1H; H-C6), 5,78 (d, $J = 8$ Hz, 1H; OCH), 6.46 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; H-C5), 7.07 (d, $J = 3$ Hz, 1H; H-C3), 7.11–7.36 (m, 15H; Ph), 7.39 (br d, $J = 8$ Hz, 2H; SPh), 7.44–7.52 (m, 6H; Ph), 7.63–7.69 (br d, $J = 8$ Hz, 2H; SPh); FAB-MS (*m*-nitrobenzylalcohol): *m*/*z* (%): 1003 (3) $[M]^+$, 680 (6), 538 (12), 480 (5), 432 (26), 345 (10), 268 (11), 195 (15), 179 (100).

{[4-(*tert*-Butyldimethylsilanoxy)-2-phenylsulfanylphenoxy]diphenylphosphane}dichloropalladium(II) (15d): According to general procedure V the ligand **14a** (199 mg, 0.385 mmol) was treated with $[PdCl_2(PhCN)_2]$ (140 mg, 0.365 mmol) in benzene (4 mL). The mixture was heated to reflux for 1 h and then diluted with hexane (10 mL). The complex **15d** (202 mg, 0.29 mmol, 80%) was isolated as a yellow solid (>95% purity according to ^{1}H NMR). M.p. (decomp) >160 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.21$ (s, 6H; $SiCH_3$), 0.96 (s, 9H; $SiCCH_3$), 6.63 (br d, $J = 9$ Hz, 1H; H-C6), 6.88 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; H-C5), 7.17 (br d, $J = 8$ Hz, 1H), 7.30–7.45 (m, 9H), 7.54 (br t, $J = 7$ Hz, 3H), 7.65 (br d, $J = 8$ Hz, 2H), 7.68–7.95 (br m, 2H); a high-temperature measurement gave a better resolution: ^{1}H NMR (400 MHz, $CDCl_3$, 60 °C): $\delta = 0.21$ (s, 6H; $SiCH_3$), 0.98 (s, 9H; $SiCCH_3$), 6.64 (dd, $J_{HH} = 9$ Hz, $J_{PH} = 1$ Hz, 1H; H-C6), 6.87 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; H-C5), 7.12–7.26 (m, 1H; Ph), 7.32 (d, $J = 3$ Hz, 1H; H-C3), 7.33–7.42 (m, 7H; Ph), 7.55 (Ψtd, $J_1 = 8$ Hz, $J_2 = 2$ Hz, 2H; Ph), 7.64–7.77 (m, 5H; Ph); FAB-MS (*m*-nitrobenzylalcohol) *m*/*z* (%): 659 (54) $[M - Cl]^+$, 515 (22), 439 (56), 407 (15), 183 (16).

{[4-(*tert*-Butyldimethylsilanoxy)-2-phenylsulfanylphenoxy]diisopropylphosphane}dichloropalladium(II) (15e): According to general procedure V, the ligand **14b** (205 mg, 0.46 mmol) was treated with $[PdCl_2(PhCN)_2]$ (162 mg, 0.42 mmol) in toluene (4 mL). The mixture was heated to reflux for 1 h and then diluted with hexane (10 mL). The complex **15e** (221 mg, 0.35 mmol, 84%) was isolated as a yellow solid (>95% purity according to ^{1}H NMR). M.p. (decomp) >185 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.23$ (s, 6H; $SiCH_3$), 0.98 (s, 9H; $SiCCH_3$), 1.08–1.21 (m, 6H; CH_3), 1.24 (d, $J = 7$ Hz, 3H; CH_3), 1.29 (d, $J = 7$ Hz, 3H; CH_3), 2.68 (Ψsext, $J = 7$ Hz, 2H; PCH), 7.12 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; H-C5), 7.15–7.19 (m, 2H), 7.19–7.28 (m, 2H), 7.31–7.36 (m, 2H), 7.31–7.36 (m, 2H), 7.47–7.53 (m, 1H); a high-temperature measurement gave a better resolution: ^{1}H NMR (400 MHz, $CDCl_3$, 60 °C): $\delta = 0.24$ (s, 6H; $SiCH_3$), 1.00 (s, 9H; $SiCCH_3$), 1.18 (d, $J = 7$ Hz, 3H; CH_3), 1.22 (d, $J = 7$ Hz, 3H; CH_3), 1.29 (d, $J = 7$ Hz, 3H; CH_3), 1.33 (d, $J = 7$ Hz, 3H; CH_3), 2.68 (Ψoctet d, $J_1 = 7$ Hz, $J_2 = 2$ Hz,

2H; PCH), 7.10 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; H-C5), 7.13–7.19 (m, 2H; H_{ar}), 7.21–7.27 (m, 2H; H_{ar}), 7.36–7.41 (m, 2H; H_{ar}), 7.52–7.58 (m, 1H; H_{ar}); FAB-MS (*m*-nitrobenzylalcohol): *m*/*z* (%): 589 (100) $[M-Cl]^+$, 554 (3), 483 (6), 445 (16), 405 (6), 371 (25), 285 (8).

{[4-Benzyloxy-2-(2′-pyridyl)phenoxy]diphenylphosphane}dichloropalladium(II) (15f): An oven-dried Schlenk tube was cooled under argon, charged with $[PdCl_2(PhCN)_2]$ (622 mg, 1.8 mmol, 1.3 equiv) and dry benzene (25 mL) and stirred for 15 min under reflux to give a brown solution. A solution of the crude phosphine ligand **14w** in benzene (3 mL) was added dropwise by syringe. After stirring for 2 h at this temperature, the hot orange solution was poured into hexane (100 mL, RT). The yellow precipitate was filtered, dried, and recrystallized from dichloromethane/hexane to afford **15f** (580 mg, 0.91 mmol, 63%) as a bright yellow solid. M.p. (decomp) >230 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5.12$ (s, 2H; OCH_2), 6.04 (Ψd, $J = 9$ Hz, 1H; ArH), 6.88 (dd, $J = 3$ Hz, 1H; ArH), 7.12 (d, $J = 3$ Hz, 1H; ArH), 7.32 (dd, $J_1 = 8$ Hz, $J_2 = 6$ Hz, 1H; ArH), 7.64–7.50 (m, 8H; ArH), 7.51–7.61 (m, 3H; ArH), 7.61–7.70 (m, 3H; ArH), 7.92 (t, $J = 8$ Hz, 2H; ArH), 7.96 (d, $J = 8$ Hz, 1H; ArH), 9.12 (d, J = 6 Hz, 1H; ArH); ^{31}P NMR (81.0 MHz, $CDCl_3$): $\delta = 121.4$; IR (ATR): $\tilde{\nu} = 3468$ (w), 3059 (w), 1699 (w), 1482 (s), 1436 (m), 1188 (s), 1112 (m), 999 (w), 869 (m), 751 (m); MS (FAB): *m*/*z* (%): 604 (27) $[M-{}^{35}Cl]^+$, 602 (26) $[M-{}^{37}Cl]^+$, 307 (22), 154 (100), 136 (66).

{(*S*)-4-[4-(*tert*-Butyldimethylsilanoxy)-2-diphenylphosphanylphenoxy]-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalene}dichloropalladium(II) (15g): According to general procedure V the ligand **14o** (101 mg, 0.14 mmol) was treated with $[PdCl_2(PhCN)_2]$ (51 mg, 0.13 mmol) in benzene (5.5 mL). The mixture was stirred for 1.5 h at RT and then diluted with hexane (20 mL). The complex **15g** (15 g 88 mg, 0.10 mmol, 75%) was isolated as a yellow solid. M.p. 235 °C; $[\alpha]_{589}^{20} = +145$ ($c = 0.99$ in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = -0.03$ (s, 3H; $SiCH_3$), −0.01 (s, 3H; $SiCH_3$), 0.87 (s, 9H; $SiCCH_3$), 6.18 (dd, $J_{HH} = 3$ Hz, $J_{PH} = 11$ Hz, 1H; H-C3), 6.84 (dd, $J_{PH} = 6$ Hz, $J_{HH} = 9$ Hz, 1H; H-C6), 7.06 (dd, $J_1 = 3$ Hz, $J_2 = 9$ Hz, 1H; H-C5), 7.16–7.37 (m, 5H; H_{ar}), 7.44 (br t, $J = 7$ Hz, 1H; H_{ar}), 7.48–7.57 (m, 5H; H_{ar}), 7.57–7.67 (m, 5H; H_{ar}), 7.75 (d, $J = 8$ Hz, 1H; H_{ar}), 7.79 (d, $J = 8$ Hz, 1H; H_{ar}), 7.92 (d, $J = 8$ Hz, 1H; H_{ar}), 7.97 (d, $J = 10$ Hz, 1H; H_{ar}), 7.99 (d, $J = 10$ Hz, 1H; H_{ar}), 8.02 (d, $J = 10$ Hz, 1H; H_{ar}); ^{31}P NMR (81.0 MHz, $CDCl_3$): $\delta = 13.8$ (d, $J_{PP} = 14.8$ Hz, PPh_2), 121.3 (d, $J_{PP} = 14.8$ Hz, $-P(OR)_2$); IR (ATR): $\tilde{\nu} = 3057$ (w), 2954 (w), 2929 (w), 2884 (w), 2857 (w), 1619 (w), 1592 (w), 1572 (w), 1508 (w), 1479 (m), 1464 (s), 1437 (m), 1390 (w), 1362 (w), 1317 (w), 1287 (w), 1265 (m), 1221 (m), 1183 (s), 1156 (w), 1126 (w), 1100 (w), 1072 (m), 1028 (w), 959 (s), 917 (s), 883 (m), 871 (m), 829 (m), 813 (m), 785 (w), 773 (w), 749 (m), 717 (w), 710 (w), 697 (m), 655 cm^{-1} (w); FAB-MS (*m*-nitrobenzylalcohol): *m*/*z* (%): 900 (9) $[M]^+$, 865 (100) $[M-Cl]^+$, 844 (34), 827 (18), 407 (30), 391 (10), 289 (19), 268 (64), 239 (22), 183 (24), 154 (70), 136 (59), 73 (93); elemental analysis calcd (%) for $C_{44}H_{40}O_4Cl_2P_2PdSi$: C 58.71, H 4.48; found C 58.55, H 4.58.

{(*S*)-4-[4-(*tert*-Butyldimethylsilanoxy)-2-diphenylphosphanylphenoxy]-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalene}diiodopalladium(II) (15h): PdI_2 (49 mg, 0.135 mmol) was added to a solution of **14o** (98 mg, 0.135 mmol) in CH_2Cl_2 (0.8 mL). The dark red mixture was stirred under exclusion of light for 19 h at RT and then filtered through Celite before the solvent was evaporated. The complex **15h** (146 mg, 0.135 mmol, 99%) was isolated as a red solid. M.p. (decomp) >203 °C; $[\alpha]_{589}^{20} +115$ ($c =$ 0.05 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = -0.01$ (s, 3H; $SiCH_3$), 0.03 (s, 3H; $SiCH_3$), 0.87 (s, 9H; $SiCCH_3$), 6.27 (dd, $J_{PH} = 10$ Hz, $J_{HH} = 3$ Hz, 1H; H-C3′), 6.83 (dd, $J_{HH} = 9$ Hz, $J_{PH} = 6$ Hz, 1H; H-C6′), 7.04 (dd, $J_1 =$ 3 Hz, $J_2 = 9$ Hz, 1H; H-C5′), 7.23–7.33 (m, 6H; H_{ar}), 7.42–7.65 (m, 10H; H_{ar}), 7.76 (dd, $J_1 = 8$ Hz, $J_2 = 1.5$ Hz, 1H; H_{ar}), 7.80 (dd, $J_1 = 8$ Hz, $J_2 =$ 1.5 Hz, 1H; H_{ar}), 7.94 (d, $J = 7.5$ Hz, 1H; H_{ar}), 7.97 (d, $J = 8$ Hz, 1H; H_{ar}), 8.00 (d, $J = 9$ Hz, 1H; H_{ar}), 8.02 (d, $J = 9$ Hz, 1H; H_{ar}); ^{31}P NMR (81.0 MHz, $CDCl_3$): $\delta = 9.8$ (d, $J_{PP} = 5.3$ Hz, PPh_2), 124.7 (d, $J_{PP} = 5.3$ Hz, $-P(OR)_2$); IR (ATR): $\tilde{\nu} = 3054$ (w), 2954 (w), 2928 (w), 2884 (w), 2856 (w), 1619 (w), 1591 (m), 1572 (w), 1508 (w), 1478 (m), 1464 (s), 1436 (m), 1390 (w), 1362 (w), 1322 (w), 1286 (w), 1265 (m), 1221 (m), 1184 (s), 1155 (w), 1124 (w), 1098 (w), 1072 (m), 1028 (w), 998 (w), 957 (s), 912 (s), 870 (m), 859 (m), 842 (s), 829 (m), 812 (m), 784 (w), 772 (w), 748 (m), 726 (w), 709 (w), 696 (m), 654 cm^{-1} (w); FAB-MS (*m*-nitrobenzylalcohol): *m*/*z* (%): 1082 (4) $[M]^+$, 955 (100) $[M-I]^+$, 846 (20), 829 (14), 407 (11), 268 (17), 183 (10), 154 (16), 136 (16), 81 (16), 73 (50), 57 (30); elemental analysis calcd (%) for $C_{44}H_{40}O_4I_2P_2PdSi$: C 48.80, H 3.72; found C 48.54, H 3.94.

{(3*R*,9*R*)-4-[4-(*tert*-Butyldimethylsilanoxy)-2-diphenylphosphanylphenoxy]-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro-1,3,5,7-tetraoxa-6-phosphaazulene}dichloropalladium(II) (15i): According to general procedure V, the ligand **14p** (104 mg, 0.115 mmol) was treated with $[PdCl_2(PhCN)_2]$ (42 mg, 0.11 mmol) in benzene (5 mL). The mixture was stirred for 1 h at RT and then diluted with hexane (20 mL). The precipitate (product) was collected by filtration through a short pad of Celite. After washing with hexane for several times, the product was isolated by dissolving it in CH_2Cl_2 and subsequent evaporation. The complex **15i** (106 mg, 0.10 mmol, 89%) was obtained as a yellow solid. M.p. 184–186 °C; $[\alpha]_{589}^{20} = -65$ ($c = 0.98$ in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = -0.15$ (s, 3H; $SiCH_3$), −0.12 (s, 3H; $SiCH_3$), 0.18 (s, 3H; CH_3), 0.80 (s, 9H; $SiCCH_3$), 1.30 (s, 3H; CH_3), 5.13 (d, $J = 8$ Hz, 1H; OCH), 5.16 (dd, $J_{HH} = 9$ Hz, $J_{PH} = 7$ Hz, 1H; H-C6′), 5.89 (dd, $J_{PH} = 11$ Hz, $J_{HH} = 3$ Hz, 1H; H-C3′), 5.91 (d, $J = 8$ Hz, 1H; OCH), 6.33 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; H-C5′), 6.99 (Ψt, $J = 7.5$ Hz, 2H; Ph), 7.08 (d, $J = 8$ Hz, 1H; Ph), 7.13 (Ψt, $J = 8$ Hz, 2H; Ph), 7.17–7.34 (m, 8H; Ph), 7.37–7.58 (m, 15H; Ph), 7.63 (d, $J = 7$ Hz, 2H; Ph); ^{31}P NMR (81.0 MHz, $CDCl_3$): $\delta = 13.6$ (d, $J_{PP} = 5.7$ Hz, PPh_2), 85.2 (d, $J_{PP} = 5.7$ Hz, $-P(OR)_2$); IR (ATR): $\tilde{\nu} = 3059$ (w), 2991 (w), 2954 (w), 2930 (w), 2897 (q), 2858 (w), 1594 (w), 1571 (w), 1495 (w), 1479 (m), 1469 (s), 1448 (m), 1437 (m), 1385 (m), 1374 (w), 1362 (w), 1286 (w), 1262 (m), 1215 (m), 1193 (m), 1164 (w), 1126 (w), 1100 (m), 1086 (m), 1052 (m), 1032 (s), 1010 (s), 997 (s), 909 (s), 835 (m), 786 (m), 750 (m), 740 (m), 730 (m), 699 (s), 657 (w); FAB-MS (*m*-nitrobenzylalcohol): *m*/*z* (%): 1043 (8) $[M-Cl]^+$, 577 (29), 431 (42), 345 (10), 265 (14), 178 (97), 177 (50), 167 (100), 105 (35), 69 (50), 55 (68); elemental analysis calcd (%) for $C_{55}H_{56}O_6Cl_2P_2PdSi$: C 61.14, H 5.22; found C 59.80, H 5.16.

{(3a*S*)-1-[4-(*tert*-Butyldimethylsilanoxy)-2-diphenylphosphanylphenoxy]-3,3-diphenyltetrahydro-2-oxa-6a-aza-1-phosphapentalene}dichloropalladium(II) (15j): According to general procedure V, the ligand **14r** (86 mg, 0.125 mmol) was treated with $[PdCl_2(PhCN)_2]$ (46 mg, 0.12 mmol) in toluene (5 mL) for 1 h at RT before hexane (20 mL) was added. The precipitate (product) was isolated by filtration through Celite and washed with hexane and diethyl ether several times. It was then dissolved in $CHCl_3$. After evaporation of the solvent the complex **15j** (98 mg, 0.11 mmol, 94%) was obtained as a yellow solid. M.p. 175–176 °C; $[\alpha]_{589}^{20} = -134$ ($c = 0.7$ in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = -0.11$ (s, 3H; $SiCH_3$), −0.08 (s, 3H; $SiCH_3$), 0.81 (s, 9H; $SiCCH_3$), 1.11 (dt, $J_1 = 12$ Hz, $J_2 = 6$ Hz, 1H; CH_2), 1.67–1.84 (br m, 1H; CH_2), 1.97 (qd, $J_1 = 12$ Hz, $J_2 = 6$ Hz, 1H; CH_2), 2.17 (br dtd, $J_1 = 12$ Hz, $J_2 = 8$ Hz, $J_3 = 5$ Hz, 1H; CH_2), 3.07 (dtd, $J_1 = 12$ Hz, $J_2 = 10$ Hz, $J_3 = 3$ Hz, 1H; NCH), 4.43 (dq, $J_1 = 18$ Hz, $J_2 = 9$ Hz, 1H; NCH_2), 4.70 (ddd, $J_1 = 18$ Hz, $J_2 = 12$ Hz, $J_3 = 5$ Hz, 1H; NCH_2), 5.12 (ddd, $J_{HH} = 9$ Hz, $J_{PH} = 5$ Hz, $J_{PH} = 1$ Hz, 1H; H-C6′), 5.97 (dd, $J_{PH} = 11$ Hz, $J_{HH} = 3$ Hz, 1H; H-C3′), 6.68 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; H-C5′), 7.20–7.36 (m, 4H; Ph), 7.36–7.65 (m, 14H; Ph), 7.71 (d, $J = 7$ Hz, 1H; Ph), 7.75 (d, $J = 7$ Hz, 1H; Ph); ^{31}P NMR (81.0 MHz, $CDCl_3$): $\delta = 15.3$ (d, $J_{PP} = 18.4$ Hz, PPh_2), 134.2 (d, $J_{PP} = 18.4$ Hz, $-P(NO)$); IR (ATR): $\tilde{\nu} = 3058$ (w), 3028 (w), 2953 (m), 2929 (m), 2885 (w), 2858 (w), 1592 (w), 1570 (w), 1477 (s), 1468 (s), 1448 (m), 1437 (m), 1391 (m), 1362 (w), 1333 (w), 1285 (m), 1265 (m), 1197 (m), 1159 (w), 1125 (m), 1101 (m), 1065 (m), 1030 (w), 999 (w), 966 (s), 940 (m), 915 (s), 890 (s), 878 (s), 838 (s), 812 (m), 784 (m), 751 (s), 698 (s), 664 cm^{-1} (w); FAB-MS (*m*-nitrobenzylalcohol): *m*/*z* (%): 830 (1) $[M-Cl]^+$, 795 (17) $[M-2Cl]^+$, 236 (11), 169 (64), 95 (24), 81 (30), 69 (100); elemental analysis calcd (%) for $C_{41}H_{45}NO_3Cl_2P_2PdSi$: C 56.79, H 5.23, N 1.62; found C 53.22, H 4.94, N 1.71.

{[4-(*tert*-Butyldimethylsilanoxy)-2-pyrimidin-2-ylphenoxy]diphenylphosphane}dichloropalladium(II) (15k): According to general procedure V, the crude ligand **14t** (183 mg, 0.3 mmol) was treated with $[PdCl_2(PhCN)_2]$ (126 mg, 0.33 mmol) in toluene (14 mL) for 4 h at RT, and the mixture was filtered through Celite. On addition of hexane (25 mL) to the orange filtrate a precipitate (product) formed which was isolated by filtration and washed with hexane several times. Elution with $CHCl_3$ and evaporation of the solvent afforded complex **15k** (184 mg, 0.26 mmol, 80%) as an orange solid. M.p. 140–145 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.27$ (s, 3H; $SiCH_3$), 0.28 (s, 3H; $SiCH_3$), 1.01 (s, 9H; $SiCCH_3$), 5.88 (dd, $J_{HH} = 9$ Hz, $J_{PH} = 2$ Hz, 1H; H-C6′), 6.74 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H; H-C5′), 7.35 (d, $J = 3$ Hz, 1H; H-C3′), 7.37 (Ψt, $J = 6$ Hz, 1H; pym-H), 7.42 (Ψtd, $J_1 = 8$ Hz, $J_2 = 3$ Hz, 2H; Ph), 7.54–7.63 (br m, 3H; Ph), 7.63–7.74 (m, 3H; Ph), 8.03 (d, $J = 8$ Hz, 1H; Ph), 8.06 (d, $J = 8$ Hz, 1H; Ph), 8.95 (br dd, $J_1 = 5$ Hz, $J_2 =$ 2 Hz, 1H; pym-H), 9.43 (dd, $J_1 = 6$ Hz, $J_2 = 2$ Hz, 1H; pym-H); ^{31}P NMR (81.0 MHz, $CDCl_3$): $\delta = 126.2$ (s); IR (ATR): $\tilde{\nu} = 3293$ (w, br), 3057 (w),

0947-6539/00/0615-2892 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 15

2955 (w), 2929 (w), 2884 (w), 2857 (w), 1700 (w), 1607 (w), 1582 (m), 1555 (m), 1488 (m), 1472 (w), 1447 (s), 1437 (s), 1400 (w), 1362 (w), 1326 (w), 1275 (w), 1254 (m), 1186 (m), 1129 (w), 1111 (m), 1102 (m), 1027 (w), 998 (w), 946 (w), 879 (m), 838 (s), 798 (w), 784 (w), 745 (w), 718 (w), 704 (w), 690 cm^{-1} (m); FAB-MS (*m*-nitrobenzylalcohol): *m*/*z* (%): 629 (42), 515 (16), 485 (16), 409 (100), 393 (17), 291 (14), 201 (12), 183 (21), 154 (23), 136 (20), 77 (15), 73 (75); elemental analysis calcd (%) for $C_{28}H_{31}N_2O_2Cl_2PPdSi$: C 50.65, H 4.71, N 4.22; found C 49.75, H 4.66, N 3.60.

{[4-(*tert*-Butyldimethylsilanoxy)-2-diphenylphosphanylphenoxy]diethoxyphosphane}dichloropalladium(II) (15l): According to general procedure V, the ligand **14m** (244 mg, 0.46 mmol) was treated with $[PdCl_2(PhCN)_2]$ (168 mg, 0.44 mmol) in toluene (16 mL) for 3 h at RT before the solvent was evaporated. The solid residue was washed with hexane several times to give the complex **15l** (166 mg, 0.24 mmol, 53%) as a beige white solid. M.p. 105–107 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = -0.06$ (br s, 6H; $SiCH_3$), 0.83 (br s, 9H; $SiCCH_3$), 1.19 (br t, $J = 7$ Hz, 6H; CH_3), 4.31–4.43 (m, 2H; OCH_2), 4.43–4.56 (m, 2H; OCH_2), 6.12 (br dd, $J_1 = 10$ Hz, $J_2 = 2$ Hz, 1H; H_{ar}), 7.02–7.10 (m, 2H; H_{ar}), 7.32–7.76 (m, 10H; H_{ar}); ^{31}P NMR (81.0 MHz, $CDCl_3$): $\delta = 14.3$ (d, $J_{PP} = 22.2$ Hz, PPh_2), 111.1 (d, $J_{PP} = 22.2$ Hz, $-P(OEt)_2$); IR (ATR): $\tilde{\nu} = 3056$ (w), 2955 (w), 2930 (w), 2896 (w), 2858 (w), 1728 (w), 1592 (w), 1571 (w), 1478 (m), 1469 (s), 1437 (m), 1390 (w), 1363 (w), 1285 (m), 1264 (m), 1197 (m), 1161 (w), 1124 (w), 1100 (m), 1065 (w), 1018 (s), 950 (m), 885 (m), 839 (m), 813 (w), 784 (m), 751 (w), 708 (m), 692 cm^{-1} (m); FAB-MS (*m*-nitrobenzylalcohol): *m*/*z* (%): 671 (32) $[M - Cl]^+$, 605 (19), 513 (18), 499 (26), 471 (16), 407 (26), 291 (15), 183 (14), 154 (17), 136 (17), 73 (100), 57 (19);elemental analysis calcd (%) for $C_{28}H_{38}O_4Cl_2P_2PdSi$: C 47.64, H 5.43; found C 49.00, H 5.51.

{(*S*)-4-[4-(*tert*-Butyldimethylsilanoxy)-2-phenylselenylphenoxy]-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalene}dichloropalladium(II) (15m): According to general procedure V, the ligand **14k** (43 mg, 0.06 mmol) was treated with $[PdCl_2(PhCN)_2]$ (22 mg, 0.06 mmol) in toluene (4 mL) for 1 h at RT. After addition of hexane (20 mL) the mixture was filtered through Celite, and the precipitate (product) was washed several times with hexane and then dissolved in $CHCl_3$. After evaporation of the solvent the complex **15m** (38 mg, 0.04 mmol, 73%) was isolated as an orange solid. M.p. 203 °C; IR (ATR): $\tilde{\nu} = 3057$ (w), 2954 (w), 2929 (w), 2884 (w), 2857 (w), 1700 (w), 1620 (w), 1592 (m), 1507 (w), 1478 (s), 1464 (m), 1441 (w), 1434 (w), 1390 (w), 1362 (w), 1323 (w), 1286 (w), 1257 (m), 1220 (m), 1185 (s), 1156 (w), 1144 (w), 1127 (w), 1071 (m), 1029 (w), 1019 (w), 998 (w), 959 (s), 923 (s), 885 (m), 871 (m), 828 (m), 813 (m), 784 (m), 710 (w), 698 (w), 685 (w), 653 cm^{-1} (w); FAB-MS (*m*-nitrobenzylalcohol): *m*/*z* (%): 837 (11) $[M - Cl]^+$, 817 (17), 268 (41), 73 (100).

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