Identification of Suitable Ligands for a Transition Metal-Catalyzed Reaction: Screening of a Modular Ligand Library in the Enantioselective Hydroboration of Styrene

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Abstract: Based on a general modular synthetic scheme, a variety of chiral bidentate P/P-, P/S-, P/N-, and P/Se-ligands is accessible in an efficient divergent manner starting from phenol or naphthol derived backbone systems. A library of 20 selected ligands was tested in the Rh-catalyzed asymmetric hydroboration of styrene to give 1-phenylethanol in up to 91% ee after oxidative work-up. It was demonstrated that small variations of the ligand structures lead to pronounced, unpredictable differences in the performance of the *in situ* generated rhodium complexes. The modular approach should be applicable for the identification and optimization of suitable ligands for other transition metal-catalyzed transformations with comparably low effort.

Keywords: enantioselectivity; homogeneous catalysis; hydroboration; ligand effects; P ligands; rhodium

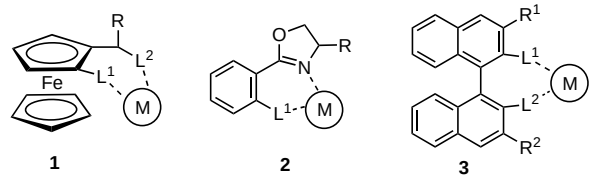
Introduction

Homogeneous transition metal catalysis has proven to be extremely valuable in a number of synthetic transformations.[1] The efficiency of a given catalytic system depends, among other factors, on a subtle interplay between the metal center and its coordinated ligand(s). Steric, geometric and electronic ligand effects are important but not easily predictable factors, especially in enantioselective catalysis. Therefore, the process of variation and selection (or trial and error) is still commonly applied in the discovery and optimization of chiral catalysts.

In order to minimize the effort connected to the synthesis of many different ligands (structural variation), a modular ligand design is highly desirable. This offers the possibility for a flexible, divergent (or even combinatorial)[2] generation of whole ligand libraries, which can then be entered into a screening process. The easy manipulation enhances the chances to find systems with optimum performance concerning both reactivity and selectivity.

While modularity can be relatively easily achieved utilizing established peptide chemistry,[3] the design of non-peptidic modular ligands for low-valent transition metals is still a challenge. Prominent examples for enantioselective catalysts based on such ligands are those of types **1**,[4] **2**,[5] and **3**[6] shown in Figure 1.[7]

Recently, we introduced a new modularly designed class of bidentate chelate ligands based on a hydroquinone backbone, demonstrated their ease of synthesis, and detailed the scope of our approach.[8] A variety of P/P-, P/S-, P/Se, and P/N-ligands were synthesized and characterized, partly as their Pd(II) complexes (Scheme 1).

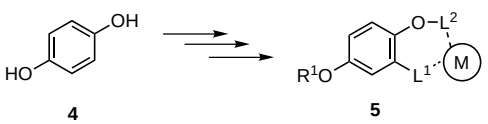


1 2 3

Figure 1. Examples of prominent catalyst architectures based on modular ligands.

Starting from hydroquinone (**4**), two donor moieties (L^1, L^2) can be independently introduced in a straightforward synthetic sequence to give access to complexes of type **5** with high structural diversity.

In this paper, we demonstrate that ligands of type **6** (Figure 2) synthesized via this strategy – also employing



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Scheme 1.

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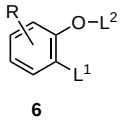

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Figure 2.

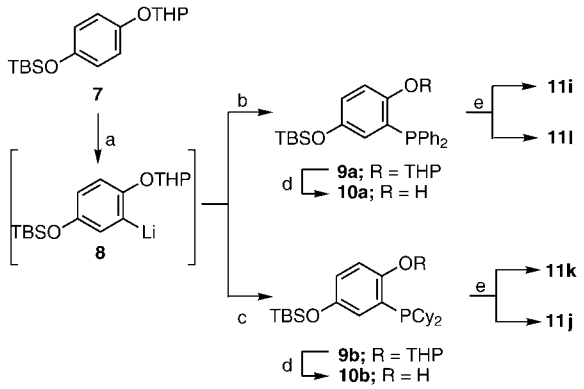
modified backbones – possess a considerable potential for enantioselective transition metal catalysis.

Specifically, screening of a small ligand library led to the identification of a few new useful ligands for the asymmetric, Rh-catalyzed hydroboration of styrene.

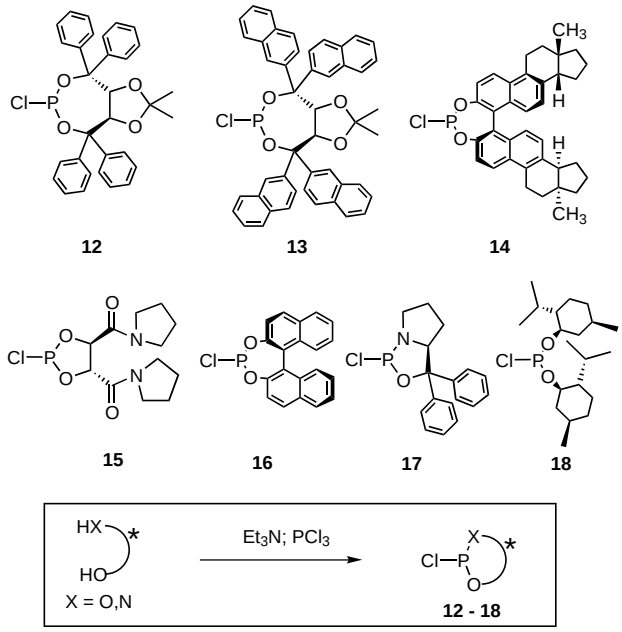
Results and Discussion

Synthesis of Ligands

The various bidentate ligands used in this study are shown in Figure 3. Ligands **11a – h** were prepared as described previously.[8] The related new ligands **11i – l** were prepared in a similar fashion following the established general procedures (Scheme 2). The first donor functionality (PR_2) was introduced by *ortho*-lithiation of the diprotected hydroquinone building block **7** and subsequent reaction with a chlorophosphane. Deprotection of the THP moiety proceeded smoothly in case of the diphenylphosphane derivative **9a** (0.05 equiv. of *p*-TsOH in MeOH, rt) but required harsher conditions (1.5 equiv. of *p*-TsOH in MeOH, reflux, 4 h) for the more basic dicyclohexylphosphane derivative **9b.** The resulting phenols **10a** and **10b** were converted to P/P-ligands **11i** – **l** by treatment with a chlorophosphite, which was freshly prepared from the corresponding diol or aminoalcohol and PCl_3 in the presence of triethylamine according to an established literature procedure (Scheme 3).[8,9]



Scheme 2. (a) −78 °C, *n*-BuLi, rt; (b) −78 °C, $ClPPh_2$, rt, 73%; (c) −78 °C, $ClPCy_2$, rt, 72%; (d) *p*-TsOH, MeOH, (54 – 72%); (e) THF, Et_3N, $ClP(OR)_2$, 51 – 99%.



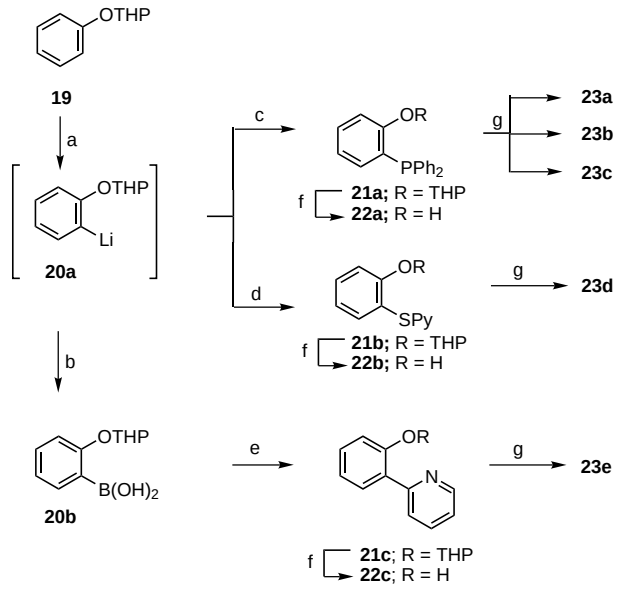
Scheme 3. Preparation of P(III) electrophiles **12** – **18.**

The more or less air-sensitive bidentate ligands (**11i** – **l**) were purified by silica gel chromatography and their purity was confirmed by various spectroscopic methods. Interestingly, the $^4J_{PP}$ coupling constants are markedly different in the two series: while the PPh_2 substituted compounds (e.g., **11i** and **11l**) exhibit a $^4J_{PP}$ coupling constant of about 15 Hz, the PCy_2 derivatives (e.g. **11j** and **11k**) show a significantly larger coupling (~27 Hz).

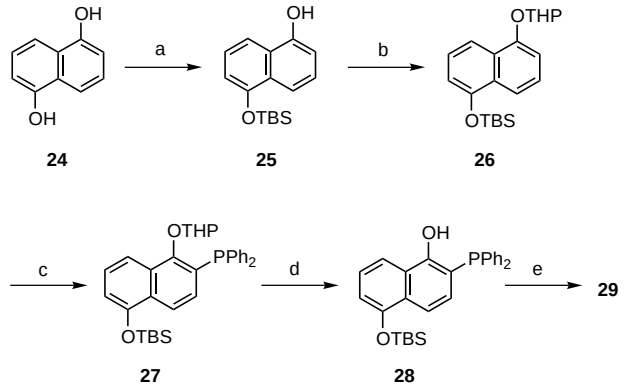
The second, TBS-protected hydroxy functionality of the hydroquinone-derived ligands of type **11** described above was originally introduced to allow a potential immobilization of the backbone at a later stage of the project.[8] As simplified analogues (and to investigate the effect of the electron-donating OTBS functionality on their performance in catalysis) some ligands of type **23** were prepared in a similar reaction sequence starting from the THP-protected phenol **19** (Scheme 4).

The lithiated intermediate **20a** was either subjected directly to different electrophiles to give the diphenylphosphane, or 2-pyridyl sulfide derivatives **21a** and **21b**, respectively, or transformed to the corresponding boronic acid **20b**. The latter was subsequently used in a Suzuki coupling[10] with 2-bromopyridine to yield **21c**. Cleavage of the THP group of compounds **21a – c** (using *p*-TsOH in MeOH) went smoothly in all cases with yields of 70 – 90%. The subsequent transformation of the resulting phenols **22a – c** with a variety of chlorophosphites (Scheme 3) furnished the bidentate ligands **23a – e**.

Besides the variation of the ligand teeth, we were also interested in varying the nature of the ligand backbone. As an alternative backbone system, 1,5-naphthalenediol (**24**) instead of hydroquinone (**4**) was investigated



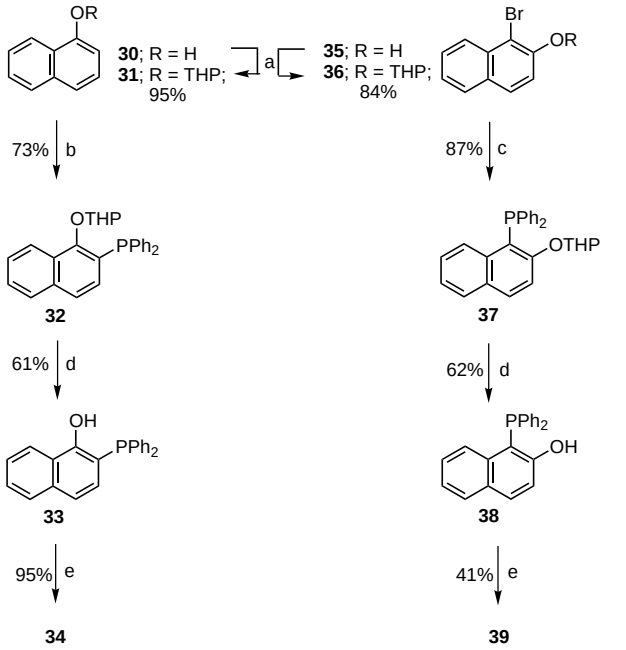
Scheme 4. (a) −78 °C, *n*-BuLi, rt; (b) −78 °C, B(O-*i*-Pr)$_3$, rt, H_2O; (c) −78 °C, $ClPPh_2$, rt, 61%; (d) −78 °C, PySSPy, rt, 91%; (e) Na_2CO_3, toluene, EtOH, 2-bromopyridine, cat. $Pd(PPh_3)_4$, 80 °C, 70%; (f) *p*-TsOH, MeOH, 70–79%; (g) $ClP(OR)_2$, Et_3N, THF, rt, 77–98%.



Scheme 5. (a) TBSCl, imidazole, DMF, rt, 68%; (b) dihydropyran, cat. PPTS, CH_2Cl_2, rt, 99%; (c) *n*-BuLi, THF, −78 °C to rt, then −78 °C, $ClPPh_2$, rt, 82%; (d) *p*-TsOH (1.5 equiv.), MeOH, rt, 0.5 h, 87%; (e) **12**, Et_3N, THF, rt, 94%.

(Scheme 5). This readily available compound[11] was, after purification by flash-chromatography, first monosilylated to yield **25**, which was then THP-protected to furnish derivative **26**. From this building block the bidentate P/P-ligand **29** was obtained via the established three-step sequence consisting of *ortho*-phosphanylation, THP deprotection, and coupling with the chlorophosphite **12** (46% overall yield from **24**).

In a related fashion, the simplified ligand **34** was synthesized from α-naphthol **30** in 4 steps with an overall yield of 42% (Scheme 6, left). The isomeric ligand **39** with a switched placement of the two donor functionalities was prepared from 1-bromo-2-hydroxy-

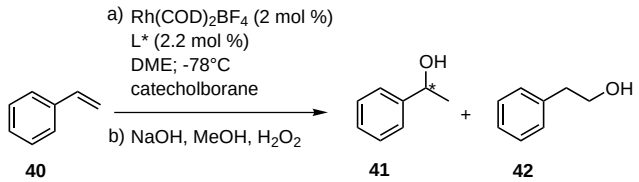


Scheme 6. (a) Dihydropyran, cat. PPTS, CH_2Cl_2, rt; (b) −78 °C, *n*-BuLi, rt, −78 °C, $ClPPh_2$, rt; (c) *n*-BuLi, −78 °C, $ClPPh_2$, rt; (d) *p*-TsOH (1.5 equiv.), MeOH, rt, 0.5 h; (e) **12**, Et_3N, THF, rt.

naphthalene (**35**) utilizing a bromine/lithium exchange to regioselectively generate the 1-lithiated intermediate. The remaining steps proceeded according to the established protocol (Scheme 6, right). It may be noteworthy that ligand **39** is rather labile (as compared to **34**) which leads to substantial losses during the purification by column chromatography.

Screening of Ligands

Having succeeded in developing a rather flexible synthetic scheme for the preparation of a broad variety of new ligands, we were interested in evaluating their potential (activity and selectivity) in asymmetric transition metal catalysis. As a first test reaction, we chose the Rh-catalyzed asymmetric hydroboration of styrene (Scheme 7).[12] After oxidation of the intermediate borane adduct(s), the chiral alcohol **41** is usually obtained as the main regioisomer.



Scheme 7.

In this reaction, the job of the chiral catalyst is to control both the regioselectivity (**41** versus **42**) and the enantioselectivity in the formation of **41**.

Following the established protocol,[12b] the catalysts were generated *in situ* from $Rh(COD)_2BF_4$ (2 mol %) and the ligands (2.2 mol %) shown in Figure 3 using 1,2-dimethoxyethane (DME) as a solvent. Screening commenced with the addition of styrene and catecholborane at −78 °C. The reactions were quenched at this temperature after the time indicated in Table 1 by addition of MeOH, 3 M aqueous NaOH, and 35% aqueous H_2O_2. Only then was the reaction mixture removed from the cold bath, thus preventing unreacted styrene to undergo less selective hydroboration at higher temperatures. In some cases, the products (**41**/**42**) were isolated, and yields and selectivities determined after chromatographic purification. In other cases, a more convenient work-up/analysis procedure was used: After addition of methyl *tert*-butyl ether (MTBE) and dodecane (internal standard) to the crude reaction mixture, an aliquot of the organic layer was passed through a small plug of alumina (alox-N). Product yield and enantiomeric excess (ee) were then determined by means of chiral GC or HPLC.

The results of the various experiments, summarized in Table 1, show that chelating bidentate P/P-ligands are especially suited in the Rh-catalyzed asymmetric hydroboration, which is in accordance to the findings of other authors.[12] While ligands with either a selenide- (**11b**) or a sulfur-containing moiety (**11c, d** and **23d**) in the L^1-position showed only little activity and selectivity, some P/N-ligands, such as **11e** (59% ee) and **23e** (49% ee), also gave quite promising results.[13]

A closer look at the performance of the different P/P-ligands reveals some interesting trends:

(1) Generally, ligands having a TADDOL[14]-derived L^2-position performed better than those derived from the other chiral diols (or aminoalcohols) employed. For example, **11a** outperformed **11f** − **h** and **11l**; **23a** was more selective than **23b, c**.

(2) Changing the PPh_2 group in L^1-position to a more bulky (and more electron-rich) PCy_2 group (**11a** → **11k** and **11i** → **11j**) leads to catalysts, giving the enantiomeric product, albeit with lower ee.

(3) Exchanging the phenyl-TADDOL-derived L^2-ligand tooth with the corresponding 2-naphthyl-TADDOL-derived phosphite (**11a** → **11i** and **11k** → **11j**) leads to significantly less active catalysts, possibly due to steric crowding.

(4) Variations within the aromatic ligand backbone also cause pronounced effects. For instance, the hydroquinone-derived ligands (type **11**) were both more active and more selective than their phenol-derived counterparts of type **23**. Thus, **11a** performed better than **23a, 11e** better than **23e**, and **11f** better than **23b**. The overall best catalytic performance was seen with the 1,5-

Table 1. Results of the screening experiments according to Scheme 7.

Entry	Ligand	t [h]	Ratio **41/42**[a]	Yield of **41** [%]	ee [%] of **41** (config.)
1	**11a**	2.5	95/5	81[b]	77 (*R*)
2	**11a**	2.5	98/2	98[c]	81 (*R*)
3	**11b**	5	64/36	31[b]	3 (*S*)
4	**11c**	5	80/20	56[b]	6 (*S*)
5	**11d**	5	83/17	25[b]	5 (*S*)
6	**11e**	2.5	77/23	52[b]	59 (*R*)
7	**11f**	2.5	92/8	71[b]	28 (*S*)
8	**11g**	2.5	95/5	80[b]	13 (*R*)
9	**11h**	2.5	88/12	78[b]	9 (*R*)
10	**11i**	2.5	94/6	24[c]	87 (*R*)
11	**11j**	2.5	95/5	25[c]	38 (*S*)
12	**11k**	2.5	97/3	92[c]	49 (*S*)
13	**11l**	2.5	89/11	75[c]	17 (*S*)
14	**11m**	2.5	86/14	77[c]	30 (*S*)
15	**23a**	2.5	88/12	62[b]	65 (*R*)
16	**23b**	5	86/14	60[b]	28 (*S*)
17	**23c**	5	88/12	60[b]	22 (*R*)
18	**23d**	5	70/30	45[b]	3 (*S*)
19	**23e**	5	77/23	54[b]	49 (*R*)
20	**29**	3.5	96/4	97[c]	88 (*R*)
21	**34**	3.5	95/5	63[c]	91 (*R*)
22	**39**	3.5	85/15	7[c]	61 (*R*)

[a] Determined by GC and/or ^1H NMR.
[b] Isolated yields.
[c] Yields determined by GC (with internal standard).

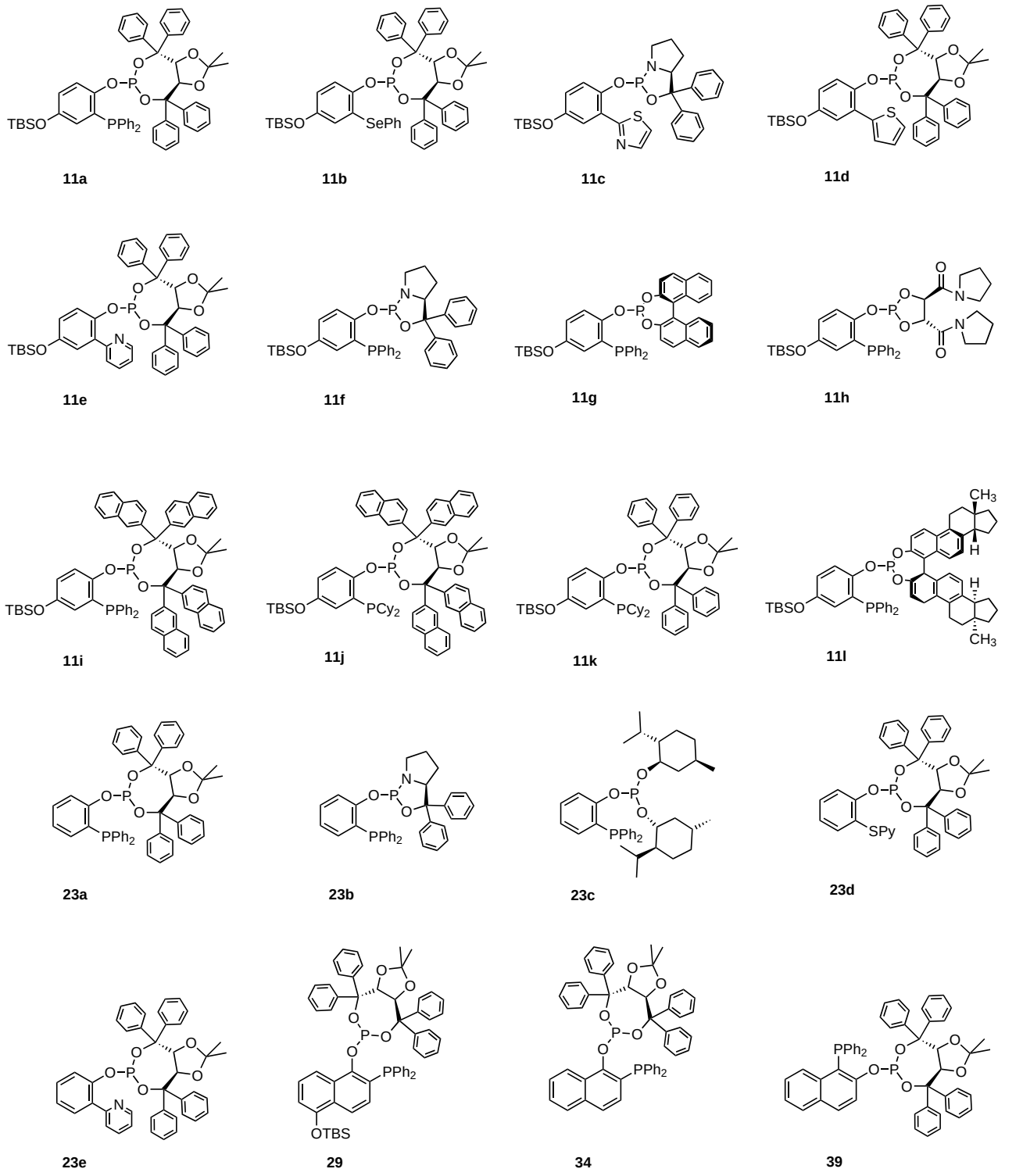


Figure 3. Overview on the chiral bidentate ligands used in this study.

naphthalenediol derived ligand **29**, furnishing 1-phenylethanol in 97% yield with high regio- and enantioselectivity (88% ee). Its simplified analogue **34**, lacking the TBSO-moiety, was even slightly more selective (91% ee) but considerably less active. As compared to **34**, the regioisomer **39** was markedly different in its activity (7% vs. 64% yield) and selectivity (61% vs. 91% ee) than **34**. The better performance of the naphthalenediol-derived ligand **29** in comparison to its hydroquinone-derived competitor **11a** may result from steric interaction between the proton in the 8-position of **29** and the L^2-ligand teeth (stronger pre-organization).

Conclusion

We have developed a general synthetic scheme, which, due to its modularity and efficiency, allows for the synthesis of a broad variety of structurally diverse bidentate ligands in a divergent manner with comparatively low effort.

Taking the Rh-catalyzed hydroboration of styrene as a test case, it was demonstrated that these ligands possess a real potential for asymmetric catalysis. In addition, it was demonstrated that even subtle variations of the ligand structure have rather dramatic (unpredictable) consequences for both the activity and the selectivity (including the absolute configuration of the product) of the resulting catalysts. Therefore, we are optimistic that further optimization of the systems will allow the development of even better ligands with this general architecture, which can be applied to other types of transition metal catalyzed processes.[15]

Ongoing efforts in this laboratory are also focusing on establishing a solid-phase approach to synthesize modular ligands. Thus, combinatorial solid-phase techniques could be applied to the generation and screening of polymer supported catalysts from previously synthesized ligand libraries. Those results will be reported separately.

Experimental Section

General Remarks

Manipulations involving air-sensitive compounds were carried out in an argon atmosphere using Schlenk and syringe techniques. Anhydrous solvents were obtained by distillation from sodium benzophenone ketyl (THF and DME) or by refluxing for 4 h with CaH_2 followed by distillation and storage over 3 Å molecular sieves (dichloromethane). Reagents (generally >99%) were used as provided by commercial sources without further purification unless otherwise stated. The concentration of *n*-BuLi solutions was determined by titration with menthol in THF in the presence of 1,10-phenantroline.[16] Reactions were monitored by analytical thin-layer chromatography (TLC) using Merck silica gel 60 F 254 glass plates. The chromatograms were visualized with UV light and by staining with a cerium reagent [prepared by dissolving 2 g of phosphomolybdic acid and 1 g of cerium(IV)-sulfate in a mixture of 10 mL conc. H_2SO_4 and 90 mL EtOH] followed by heating. Flash chromatography[17] was performed with silica gel 60 (230–400 mesh) from E. Merck. Preparative thin layer chromatography (PTLC) was carried out using a Chromatotron (Harrison Research Model 7924 T) on glass plates coated with 1–4 mm layers of silica gel containing gypsum (E. Merck PF 60 F 254). NMR spectra were obtained in $CDCl_3$ on Bruker instruments (AM 270 or AM 400) using residual undeuterated solvent as an internal reference. The spectra are reported in ppm using the following abbreviations to express the multiplicities: s = singlet; d = doublet; t = triplet; q = quartet; b = broad. ^{13}C chemical shifts were determined using ^{1}H-decoupled spectra, the number of protons bound directly was determined employing the DEPT sequence[18] (q = CH_3; t = CH_2; d = CH; s = quaternary carbons). For ^{13}C signals which are split due to coupling to ^{31}P atoms, J_{CP} is additionally given. Some of the assignments are based on 2-dimensional spectra. Mass spectroscopy was performed on a Finnigan Incos 500 (EI) or a Finnigan MAT 900S (ESI). Each dataset is preceded by the method in brackets. Infrared spectra were recorded on a Perkin-Elmer Paragon 1000 FT-IR spectrometer using the ATR technique. Optical rotations were measured with a Perkin Elmer 343plus polarimeter, concentrations *c* are given in g/100 mL. Melting points were measured in open capillary tubes and are uncorrected.

General Procedure I: Introduction of the First Donor Functionality *via* Lithiation Starting from Compounds 7, 19, 26, 31, or 36

In a flame-dried Schlenk flask under argon a solution of **7**, **19**, **26**, **31**, or **36** (1 equiv.) in absolute THF was cooled to −78 °C and treated dropwise with *n*–BuLi-solution in hexane (1.2 or 1.5 equiv.). The resulting yellow solution was stirred for 15 min. at −78 °C before the cooling bath was removed and the reaction mixture was stirred at rt for another 30 to 60 min. The yellow solution was recooled to −78 °C and the electrophile (1.2 or 2 equiv.) was added. Liquid electrophiles were used directly, in the case of solid electrophiles a THF-solution of the electrophile was prepared. Stirring was continued for 4 to 18 hours. In the case of sulfur-containing electrophiles, water was added and the mixture was quenched with 1 N aqueous NaOH. When using phosphorus electrophiles the mixture was quenched with degassed aqueous $NaHCO_3$-solution. The aqueous phase was extracted with EtOAc (3 ×) and the combined organic phases were washed with saturated aqueous NaCl solution and dried ($MgSO_4$). The solvent was removed and the crude product was purified by chromatography.

General Procedure II: Preparation of the $ClP(OR)_2$ Electrophiles 12 − 18 from Diols (or Aminoalcohols)

In an atmosphere of argon a solution of Et_3N (2.02 equiv.) in THF was cooled to −50 to −55 °C. After addition of PCl_3 (1.05 equiv.) a solution of the diol (1 equiv.) in THF was added dropwise. After 30 min the mixture was allowed to warm to rt and stirring was continued for another 2 h. Under argon, the precipitate was filtered off through a short pad of celite and washed with THF. The filtrate was concentrated and all volatiles were removed under vacuum (oil pump) to give the crude product, which was used without further purification.

General Procedure III: Synthesis of Ligands of Type 11i–l, 23a–e, 29, 34, 39 from the Corresponding Phenolic Precursors

In an argon atmosphere a solution of the phenol (**10a–b**, **22a–c**, **28**, **33** or **38**; 1 equiv.) in THF was treated at rt with Et_3N (15 or 20 equiv.). After stirring for 15 to 30 min a solution of the phosphorus electrophile (1.5 or 2 equiv.) in THF was added dropwise at 0 °C. The resulting milky suspension was stirred overnight at rt. The mixture was filtered under argon through a

short plug of celite eluting with THF. All volatiles were removed under vacuum. The crude product was purified by flash chromatography under nitrogen.

[5-(*tert*-Butyldimethylsilanoxy)-2-(tetrahydropyran-2-yloxy)phenyl]diphenylphosphane (9a)

According to general procedure I, a solution of **7** (307 mg, 0.99 mmol) in THF (7 mL) was reacted with *n*-BuLi (1.6 M, 940 μL, 1.50 mmol) and chlorodiphenylphosphane (360 μL, 2.00 mmol). The crude product was purified by flash chromatography (hexane/EtOAc 20 + 1) to afford **9a** as a white solid; yield: 358 mg (0.73 mmol, 73%); mp 70 – 71 °C; TLC (hexane / EtOAc, 20:1): $R_f = 0.41$; ^{1}H NMR (400 MHz, $CDCl_3$): δ = −0.05 (s, 6H, $SiCH_3$), 0.85 (s, 9H, $SiCCH_3$), 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, $^3J_{HP} = 4$ Hz, $^4J_{HH} = 3$ Hz, 1H, H-C6), 6.75 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H, H-C4), 7.00 (dd, $^3J_{HH} = 9$ Hz, $^4J_{HP} = 5$ Hz, 1H, H-C3), 7.29 – 7.44 (m, 10H, H-C_{ar}); ^{31}P NMR (81 MHz, $CDCl_3$): δ = -15.0 (s); ^{13}C NMR (75 MHz, $CDCl_3$): δ = −4.7 (q, $SiCH_3$), 17.8 (t, CH_2), 18.1 (s, SiC), 25.2 (t, CH_2), 25.6 (q, $SiC\underline{C}H_3$), 30.0 (t, CH_2), 61.1 (t, OCH_2), 96.4 (d, OCH), 114.7 (d, $^3J_{CP} = 1.8$ Hz, $C3_{ar}$-H), 121.1 (d, $C4_{ar}$-H), 124.0 (d, $^2J_{CP} = 1.4$ Hz, $C6_{ar}$-H), 127.5 (s, $^1J_{CP} = 13.0$ Hz, C1-P), 128.34 (d, $^3J_{CP} = 7.3$ Hz, C_{ar}H), 128.39 (d, $^3J_{CP} = 7.2$ Hz, C_{ar}H), 128.64 (d, C_{ar}H), 128.68 (d, C_{ar}H), 134.04 (d, $^2J_{CP} = 20.5$ Hz, C_{ar}H), 134.08 (d, $^2J_{CP} = 20.6$ Hz, C_{ar}H), 136.61 (s, $^1J_{CP} = 10.3$ Hz, C_{ar}P), 136.68 (s, $^1J_{CP} = 10.5$ Hz, C_{ar}P), 150.0 (s, $C5_{ar}$-O), 152.8 (s, $^2J_{CP} = 14.4$ Hz, $C2_{ar}$-O); IR (ATR): $\tilde{\nu} = 3069$ (w), 3053 (w), 2948 (m), 2929 (m), 2895 (w), 2883 (w), 2857 (m), 1586 (w), 1572 (w), 1503 (w), 1470 (s), 1434 (m), 1393 (m), 1356 (m), 1324 (w), 1275 (m), 1259 (m), 1218 (s), 1200 (s), 1182 (m), 1135 (w), 1124 (m), 1108 (m), 1049 (w), 1038 (m), 1020 (m), 965 (s), 950 (s), 921 (s), 887 (w), 872 (m), 839 (s), 825 (m), 781 (m), 743 (m), 697 cm^{-1} (s); MS (EI): *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 (EI): calcd. for $C_{29}H_{37}O_3PSi$: 492.2249; found: 492.2251.

[5-(*tert*-Butyldimethylsilanoxy)-2-(tetrahydropyran-2-yloxy)phenyl]dicyclohexylphosphane (9b)

According to general procedure I, a solution of **7** (660 mg, 2.15 mmol) in THF (40 mL) was treated with *n*-BuLi (1.54 M, 2.10 mL, 3.22 mmol) and chlorodicyclohexylphosphane (1.00 g, 4.30 mmol). The crude product was purified by chromatography (cyclohexane/EtOAc, 20:1) to afford **9b** as a colorless oil; yield: 780 mg (1.55 mmol, 72%); TLC (cyclohexane/EtOAc, 20:1): $R_f = 0.41$; ^{1}H NMR (300 MHz, $CDCl_3$, −10 °C): δ = 0.12 (s, 6H, $SiCH_3$), 0.92 (s, 9H, $SiCCH_3$), 0.86 – 1.37 (m, 11H, CH_2), 1.57 – 2.02 (m, 17H, CH_2, CH), 3.60 (br d, $J = 10$ Hz, 1H, OCH_2), 3.88 (br td, $J_1 = 11$ Hz, $J_2 = 3$ Hz, 1H, OCH_2), 5.32 (br s, 1H, OCH), 6.72 (dd, $^3J_{HH} = 9$ Hz, $^4J_{HH} = 3$ Hz, 1H, H-C4), 6.83 (dd, $^3J_{HP} = 7$ Hz, $^4J_{HH} = 3$ Hz, 1H, H-C6), 6.97 (dd, $^3J_{HH} = 9$ Hz, $^4J_{HP} = 3$ Hz, 1H, H-C3); ^{31}P NMR (121 MHz, $CDCl_3$): δ = −2.4 (s); ^{13}C NMR (75 MHz, $CDCl_3$, −10 °C): δ = −4.6 (q, $SiCH_3$), 18.2 (s, SiC), 18.6 (t, CH_2), 25.2 (t, CH_2), 25.6 (q, $SiC\underline{C}H_3$), 26.2 (t, CH_2), 27.0 – 27.3 (mt, CH_2), 29.2 (t, $^2J_{CP} = 19$ Hz, CH_2), 29.3 (t, $^2J_{CP} = 21$ Hz, CH_2), 30.3 (t, CH_2), 30.3 (t, $^2J_{CP} = 26$ Hz, CH_2), 30.6 (t, $^2J_{CP} = 25$ Hz, CH_2), 32.7 (d, $^1J_{CP} = 11$ Hz, CHP), 33.2 (d, $^1J_{CP} = 12$ Hz, CHP), 61.6 (t, OCH_2), 96.6 (d, OCH), 114.9 (d, $C3_{ar}$-H), 121.2 (d, $C4_{ar}$-H), 124.2 (s, $^1J_{CP} = 21$ Hz, $C1_{ar}$-P), 126.4 (d, $C6_{ar}$-H), 148.9 (s, $^3J_{CP} = 6$ Hz, $C5_{ar}$-O), 154.7 (s, $^2J_{CP} = 9$ Hz, $C2_{ar}$-O); MS (EI): *m/z* (%) = 505 (7) $[M + H]^+$, 504 (4) $[M]^+$, 448 (8), 421 (13), 420 (26), 339 (27), 338 (98), 281 (20), 256 (27), 199 (43), 197 (38), 167 (17), 115 (17), 85 (100), 73 (72), 57 (22), 55 (36); HRMS (EI): calcd. for $C_{29}H_{49}O_3PSi$: 504.3189; found: 504.3171.

[5-(*tert*-Butyldimethylsilanoxy)-2-(hydroxyphenyl)]diphenylphosphane (10a)

p-Toluenesulfonic acid monohydrate (*p*-TsOH) (78 mg, 0.40 mmol) was added to a solution of **9a** (1.00 g, 2.00 mmol), stirred in degassed MeOH (50 mL) under an argon atmosphere. After 2 h at 40 °C the reaction solution was quenched by the addition of half saturated brine. The aqueous layer was extracted with EtOAc, the combined organic layers were dried over $MgSO_4$, and the solvent was removed under vacuum. The crude product was purified by flash chromatography (hexane/EtOAc, 10:1) to afford **10a** as a white solid, solutions of which proved to be rather sensitive towards oxidation; yield: 602 mg (1.47 mmol, 72%); mp 104 – 105 °C; TLC (hexane/EtOAc, 10:1): $R_f = 0.17$; ^{1}H NMR (400 MHz, $CDCl_3$): δ = −0.03 (s, 6H, $SiCH_3$), 0.85 (s, 9H, $SiCCH_3$), 5.76 (d, $^4J_{HP} = 6$ Hz, 1H, OH, exchanges with D_2O), 6.32 – 6.37 (m, 1H, H-C6), 6.78 – 6.83 (m, 2H, H-$C4_{ar}$, H-$C3_{ar}$), 7.29 – 7.42 (m, 10H, H_{Ph}); ^{31}P NMR (81 MHz, $CDCl_3$): δ = −27.3 (s); ^{13}C NMR (75 MHz, $CDCl_3$): δ = −4.7 (q, $SiCH_3$), 18.2 (s, SiC), 25.7 (q, $SiC\underline{C}H_3$), 116.3 (d, $^3J_{CP} = 2$ Hz, $C3_{ar}$-H), 121.6 (s, $^1J_{CP} = 7$ Hz, $C1_{ar}$-P), 123.4 (d, $C4_{ar}$-H), 124.8 (d, $^2J_{CP} = 3$ Hz, $C6_{ar}$-H), 128.7 (d, $^3J_{CP} = 7$ Hz, C_{ar}H), 129.0 (d, C_{ar}H), 133.4 (d, $^2J_{CP} = 19$ Hz, C_{ar}H), 135.0 (s, $^1J_{CP} = 6$ Hz, CP), 149.4 (s, $^3J_{CP} = 2$ Hz, $C5_{ar}$-O), 153.4 (s, $^2J_{CP} = 19$ Hz, $C2_{ar}$-O); IR (ATR): $\tilde{\nu} = 3432$ (br w), 3070 (w), 3054 (w), 2955 (m), 2929 (m), 2895 (w), 2885 (w), 2857 (w), 1585 (w), 1492 (m), 1479, 1471 (s), 1434 (m), 1398 (m), 1362 (w), 1325 (w), 1257 (s), 1212 (m), 1182 (m), 1123 (w), 1092 (w), 1027 (w), 1000 (w), 946 (s), 885 (w), 839 (s), 781 (s), 744 (s), 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 (EI): calcd. for $C_{24}H_{29}O_2PSi$: 408.1674; found: 408.1675; anal. calcd. for $C_{24}H_{29}O_2PSi$: C 70.56, H 7.15; found C 70.20, H 7.33.

[5-(*tert*-Butyldimethylsilanoxy)-2-(hydroxyphenyl)]dicyclohexylphosphane (10b)

A solution of **9b** (750 mg, 1.49 mmol) dissolved in 1 mL THF and *p*-TsOH (341 mg, 1.79 mmol) in degassed MeOH (50 mL) was refluxed under argon for 1 h. The reaction was quenched by addition of saturated aqueous $NaHCO_3$, and the aqueous layer was extracted with EtOAc (3 ×), the combined organic layers were dried over $mgSO_4$, and the solvent was evaporated under vacuum. The crude product was purified by flash chromatography (hexane/ EtOAc = 10 + 1) under nitrogen to afford **10b** as a colorless oil; yield: 340 mg (0.81 mmol, 54%); TLC (cyclohexane/EtOAc, 10:1): $R_f = 0.29 – 0.36$; ^{1}H NMR (300 MHz, C_7D_8): δ = 0.15 (s, 6H, $SiCH_3$), 0.99 (s, 9H, $SiCCH_3$), 0.89 – 1.24 (m, 10H, CH_2), 1.50 – 1.88 (m, 12H, CH_2, CH), 6.72

(dd, $^3J_{HH}=9$ Hz, $^4J_{HH}=3$ Hz, 1H, H-C4$_{ar}$), 6.89–6.96 (m, 3H, H-C3$_{ar}$, H-C6$_{ar}$, OH exchanges with D_2O); ^{31}P NMR (121 MHz, C_7D_8): δ = −31.4 (s); ^{13}C NMR (75 MHz, C_7D_8): δ = −4.4 (q, $SiCH_3$), 18.5 (s, SiC), 25.9 (q, $SiC\underline{C}H_3$), 26.6 (t, $^4J_{CP}=1$ Hz, CH_2), 27.1-27.4 (mt, CH_2), 29.0 (t, $^2J_{CP}=6$ Hz, CH_2), 30.6 (t, $^2J_{CP}=16$ Hz, CH_2), 33.1 (d, $^1J_{CP}=8$ Hz, CHP), 116.2 (d, $^3J_{CP}=2$ Hz, C3$_{ar}$-H), 118.5 (s, $^1J_{CP}=10$ Hz; C1$_{ar}$-P), 123.3 (d, $^2J_{CP}=2$ Hz, C6$_{ar}$-H), 123.5 (d, C4$_{ar}$-H), 148.7 (s, C5$_{ar}$-O), 156.9 (s, $^2J_{CP}=19$ Hz, C2$_{ar}$-O); MS (EI): *m/z* (%) = 421 (9) $[M+H]^+$, 420 (29) $[M]^+$, 403 (7), 339 (14), 338 (48), 281 (14), 256 (11), 199 (28), 197 (18), 183 (11), 167 (10), 115 (12), 83 (28), 73 (93), 57 (31), 55 (100); HRMS (ESI): calcd. for $[C_{24}H_{41}O_2PSi+H]^+$: 421.2692; found: 421.2690.

(*3aR*,*8aR*)-6-[4-(*tert*-Butyldimethylsilanoxy)-2-diphenylphosphanylphenoxy]-2,2-dimethyl-4,4,8,8-tetra(naphth-2-yl)tetrahydro-1,3,5,7-tetraoxa-6-phosphaazulene (11i)

Following general procedure III, a solution of **13**[19] in THF (10 mL) was added at 0 °C to a stirred mixture of the phenol **10a** (350 mg, 0.86 mmol) and Et_3N (2.4 mL, 17.1 mmol) in THF (10 mL). The obtained crude product was purified by flash chromatography (cyclohexane/EtOAc, 20:1) to afford **11i** as a fluffy yellow foam; yield: 939 mg (0.85 mmol, 99%); mp 139–141 °C; TLC (cyclohexane/EtOAc, 10:1): $R_f=0.47$; $[\alpha]_{589}$: −184° (*c* 0.95, $CHCl_3$, 20 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ = −0.07 (s, 6H, $SiCH_3$), 0.36 (s, 3H, CH_3), 0.85 (s, 9H, $SiCCH_3$), 1.09 (s, 3H, CH_3), 5.44 (s, 2H, HCO), 6.13 (dd, 1H, $^3J_{HP}=4$ Hz, $^4J_{HH}=3$ Hz, H-C3′), 6.60 (dd, 1H, $^3J_{HH}=9$ Hz, $^4J_{HH}=3$ Hz, H-C5′), 6.96 (ddd, 1H, $^3J_{HH}=9$ Hz, $^4J_{HP}=5$ Hz, $^4J_{HP}=1$ Hz, H-C6′), 7.12–7.93 (m, 34H, H$_{ar}$), 8.02 (d, 1H, $J_{HH}=2$ Hz, H$_{Naph}$), 8.07 (d, 1H, $J_{HH}=1$ Hz, H$_{Naph}$), 8.23 (d, 1H, $J_{HH}=2$ Hz, H$_{Naph}$), 8.41 (d, 1H, $J_{HH}=1$ Hz, H$_{Naph}$); ^{31}P NMR (121 MHz, $CDCl_3$): δ = −15.8 (d, $^4J_{PP}=15.6$ Hz, PPh_2), 137.5 [d, $^4J_{PP}=15.6$ Hz, $P(OR)_2$]; ^{13}C NMR (75 MHz, $CDCl_3$): δ = −4.7 (q, $SiCH_3$), 18.1 (s, SiC), 25.6 (q, $SiC\underline{C}H_3$), 26.1 (q, CH_3), 27.4 (q, CH_3), 81.2 (d, $^3J_{CP}=4$ Hz, HCO), 82.5 (d, $^3J_{CP}=16$ Hz, HCO), 83.5 (sσ, CPh_2O), 86.0 (s, $^2J_{CP}=8$ Hz, CPh_2O), 113.4 (s, COO), 121.2 (d, C5′-H$_{ar}$), 122.0 (d, C6′-H$_{ar}$), 124.5 (d, C3′-H$_{ar}$), 125.2-129.0 (md, CH$_{ar}$), 132.5-132.9 (ms, C$_{ar}$), 133.4 (s, $^1J_{CP}=19$ Hz, C2′-P), 133.7 (d, $^2J_{CP}=5$ Hz, CH$_{ar}$), 134.0 (d, $^2J_{CP}=5$ Hz, CH$_{ar}$), 136.5 (s, $^1J_{CP}=13$ Hz, CP), 138.3 (s, C$_{ar}$), 138.9 (s, $^3J_{CP}=3$ Hz, C$_{ar}$), 142.3 (s, C$_{ar}$), 142.9 (s, C$_{ar}$), 148.4 (s, $^2J_{CP}=20$ Hz, C1′-O), 152.1 (s, C4′-O); IR (KBr): $\tilde{\nu}=3055$ (w), 2952 (w), 2927 (w), 2856 (w), 1733 (w), 1584 (w), 1506 (m), 1464 (s), 1433 (m), 1382 (m), 1270 (m), 1253 (m), 1180 (br m), 1163 (m), 1126 (w), 1093 (m), 1063 (m), 1027 (m), 944 (m), 886 (s), 860 (s), 827 (m), 776 (w), 741 (m), 694 (m), 667 (s), 476 cm^{-1} (m); MS (ESI): *m/z* (%) = 1103 (36) $[M+H]^+$, 1045 (95), 1027 (13), 767 (50), 738 (75), 631 (53), 611 (12), 557 (16), 489 (100), 471 (32), 455 (12), 429 (21), 409 (20), 393 (16); HRMS (ESI): calcd. for $[C_{71}H_{64}O_6PSi+H]^+$: 1103.4026; found: 1103.4024.

(*3aR*,*8aR*)-6-[4-(*tert*-Butyldimethylsilanoxy)-2-dicyclohexylphosphanylphenoxy]-2,2-dimethyl-4,4,8,8-tetra(naphth-2-yl)-tetrahydro-1,3,5,7-tetraoxa-6-phosphaazulene (11j)

Following general procedure III, this a solution of **13**[19] (1.26 mmol) was added at 0 °C to a stirred mixture of the phenol **10b** (265 mg, 0.63 mmol) and Et_3N (1.8 mL, 12.6 mmol) in THF (10 mL). The obtained crude product was purified by chromatography (cyclohexane/EtOAc, 20:1) to afford **11j** as a fluffy yellow solid; yield: 354 mg (0.32 mmol, 51%); mp 122–124 °C; TLC (cyclohexane/EtOAc, 10:1): $R_f=0.53$; $[\alpha]_{589}$: −178° (*c* 1.00, 20 °C, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.15 (s, 6H, $SiCH_3$), 0.40 (s, 3H, CH_3), 0.80–2.09 (m, 22H, CH_2, CH), 0.96 (s, 9H, $SiCCH_3$), 1.05 (s, 3H, CH_3), 5.49 (d, $^3J_{HH}=8$ Hz, 1H, HCO), 5.57 (br dd, $^3J_{HH}=8$ Hz, $J=4$ Hz, 1H, HCO), 6.42 (dd, $^3J_{HP}=11$ Hz, $^4J_{HH}=3$ Hz, 1H, H-C3′), 6.59 (br dd, $^3J_{HH}=9$ Hz, $^4J_{HP}=2$ Hz, 1H, H-C6′), 6.68 (dd, $^3J_{HH}=9$ Hz, $^4J_{HH}=3$ Hz, 1H, H-C5′), 7.38–7.94 (m, 24H, H$_{ar}$), 8.08 (br d, $J_{HH}=3$ Hz, 1H, H$_{Naph}$), 8.19 (br d, $J_{HH}=5$ Hz, 1H, H$_{Naph}$), 8.26 (s, 1H, H$_{Naph}$), 8.43 (s, 1H, H$_{Naph}$); ^{31}P NMR (121 MHz, $CDCl_3$): δ = −10.9 (br s, PCy_2), 138.6 [d, $^4J_{PP}=28.8$ Hz, $P(OR)_2$]; ^{13}C NMR (75 MHz, $CDCl_3$): δ = −4.5 (q, $SiCH_3$), 18.2 (s, SiC), 25.6 (q, $SiC\underline{C}H_3$), 26.0 (q, CH_3), 26.2–26.4 (mt, CH_2), 26.5–27.1 (mt, CH_2), 27.3 (q, CH_3), 28.7 (t, CH_2), 30.0 (t, $^2J_{CP}=17$ Hz, CH_2), 32.4 (d, CHP), 32.8 (d, $^1J_{CP}=15$ Hz, CHP), 80.8 (d, HCO), 82.4 (d, $^3J_{CP}=15$ Hz, HCO), 83.1 (s, CPh_2O), 85.8 (s, $^2J_{CP}=8$ Hz; CPh_2O), 113.5 (s, COO), 119.0 (d, $^2J_{CP}=8$ Hz, C3′-H$_{ar}$), 119.8 (d, $^3J_{CP}=9$ Hz, C6′-H$_{ar}$), 121.0 (d, C5′-H$_{ar}$), 124.8–129.7 (md, CH$_{ar}$), 132.1-133.1 (s, C$_{ar}$), 136.2 (s, $^1J_{CP}=13$ Hz, C2′-P), 138.2 (s, C$_{ar}$), 139.5 (s, C$_{ar}$), 140.4 (s, $^3J_{CP}=7$ Hz, C$_{ar}$), 142.8 (s, C$_{ar}$), 147.0 (s, $^2J_{CP}=14$ Hz, C1′$_{ar}$-O), 150.9 (s, C4′$_{ar}$-O); IR (KBr): $\tilde{\nu}=3055$ (w), 2926 (s), 2851 (m), 1734 (w), 1627 (w), 1599 (w), 1564 (w), 1504 (m), 1470 (s), 1443 (m), 1382 (m), 1266 (m), 1253 (s), 1212 (m), 1170 (br m), 1122 (w), 1096 (w), 1063 (m), 1033 (m), 944 (m), 887 (s), 860 (s), 835 (s), 820 (s), 772 (m), 757 (m), 742 (m), 667 (s), 476 cm^{-1} (m); MS (ESI): *m/z* (%) = 1115 (22) $[M+H]^+$, 1057 (1), 779 (6), 631 (11), 573 (3), 545 (3), 485 (100), 421 (7), 403 (2); HRMS (ESI): calcd. for $[C_{71}H_{76}O_6PSi+H]^+$, 1115.4965; found: 1115.4965.

(*3aR*,*8aR*)-6-[4-(*tert*-Butyldimethylsilanoxy)-2-dicyclohexylphosphanylphenoxy]-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro-1,3,5,7-tetraoxa-6-phosphaazulene (11k)

Following general procedure III, a solution of **12** (1.36 mmol) was added at 0 °C to a stirred mixture of the phenol **10b** (285 mg, 0.68 mmol) and Et_3N (1.9 mL, 13.6 mmol) in THF (10 mL). The obtained crude product was purified by chromatography (cyclohexane/EtOAc, 20:1) to afford **11k** as a fluffy white solid; yield: 544 mg (0.59 mmol, 88%); mp 98–99 °C; TLC (cyclohexane/EtOAc, 10:1): $R_f=0.64$; $[\alpha]_{589}$: −123° (*c* 1.00, 20 °C, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.15 (s, 6H, $SiCH_3$), 0.40 (s, 3H, CH_3), 0.86–1.30 (m, 10H, CH_2), 0.95 (s, 9H, $SiCCH_3$), 1.23 (s, 3H, CH_3), 1.38–2.02 (m, 12H, CH_2, CH), 5.16 (d, $^3J_{HH}=8$ Hz, 1H, HCO), 5.26 (d, $^3J_{HH}=8$ Hz, 1H, HCO), 6.61 (dd, $^3J_{HH}=9$ Hz, $^4J_{HH}=3$ Hz, 1H, H- C5′), 6.72 (br dd, $^3J_{HH}=9$ Hz, $^4J_{HP}=2$ Hz, 1H, H-C6′), 6.82 (br dd, $^3J_{HP}=5$ Hz, $^4J_{HH}=3$ Hz, 1H, H-C3′), 7.15–7.40 (m, 12H, H$_{Ph}$), 7.43 (br d, $J_{HH}=7$ Hz, 2H, H$_{Ph}$), 7.49 (br dd, $J_{HH}=8$ Hz, $J_{HH}=1$ Hz, 2H, H$_{Ph}$), 7.55–7.60 (m, 2H, H$_{Ph}$), 7.72 (br d, $J_{HH}=7$ Hz, 2H, H$_{Ph}$); ^{31}P NMR (121 MHz, $CDCl_3$): δ = −7.4 (br s, PCy_2), 138.2 [d, $^4J_{PP}=25.7$ Hz, $P(OR)_2$]; ^{13}C NMR (75 MHz, $CDCl_3$): δ = −4.5 (q, $SiCH_3$), 18.3 (s, SiC), 25.7 (q, $SiC\underline{C}H_3$), 25.9 (q, CH_3), 26.2–26.4 (mt, CH_2), 26.7–27.0 (mt, CH_2), 27.2 (q, CH_3), 29.4 (t, $^2J_{CP}=9$ Hz, CH_2), 30.6 (t, $^2J_{CP}=18$ Hz, CH_2), 33.3 (d, $^1J_{CP}=13$ Hz, CHP), 33.6 (d, $^1J_{CP}=14$ Hz, CHP), 80.6 (d, $^3J_{CP}=4$ Hz,

HCO), 82.1 (d, $^3J_{CP}=15$ Hz, HCO), 83.4 (s, CPh_2O), 85.8 (dσ, $^2J_{CP}=9$ Hz, CPh_2O), 113.2 (s, COO), 121.0 (d, C5′$_{ar}$-H), 121.2 (d, C6′$_{ar}$-H), 126.0 (s, C2′$_{ar}$-P), 126.8 (d, $^2J_{CP}=6$ Hz, C3′$_{ar}$-H), 127.0–129.0 (md, $C_{ar}H$), 141.0 (s, $^3J_{CP}=1$ Hz, C_{ar}), 141.7 (s, C_{ar}), 145.3 (s, $^3J_{CP}=1$ Hz, C_{ar}), 145.8 (s, C_{ar}), 150.9 (s, C4′$_{ar}$-O), 151.4 (s, $^2J_{CP}=11$ Hz, C1′$_{ar}$-O); IR (KBr): $\tilde{\nu}=3062$ (w), 3025 (w), 2988 (w), 2926 (s), 2851 (m), 1741 (w), 1649 (w), 1587 (w), 1564 (w), 1491 (m), 1470 (s), 1447 (s), 1382 (m), 1253 (m), 1196 (br m), 1166 (m), 1088 (m), 1036 (m), 1019 (m), 945 (m), 887 (s), 837 (s), 783 (w), 739 (m), 697 (s), 667 cm^{-1} (s); MS (ESI): *m/z* (%) = 915 (6) $[M+H]^+$, 679 (6), 485 (100), 467 (3), 431 (8), 421 (5), 345 (5); HRMS (ESI): calcd. for $[C_{55}H_{68}O_6PSi+H]^+$: 915.4339; found 915.4336; anal. calcd. for $C_{55}H_{68}O_6PSi$: C 72.18, H 7.49; found C 71.39, H 7.51.

(R_a)-6-[4-(*tert*-Butyldimethylsilanoxy)-2-diphenylphosphanylphenoxy]-5,7-dioxa-6-phosphacyclohepta-[1,2-*c*;4,3-*c'*]-di-[(14β)-estra-1,3,5,7,9-pentaene] (11l)

Following general procedure III, a solution of **14** (1.00 mmol) was added at 0 °C to a stirred mixture of the phenol **10a** (203 mg, 0.50 mmol) and Et_3N (1.4 mL, 9.95 mmol) in THF (8 mL). The crude product was purified by chromatography (cyclohexane/EtOAc, 20:1) to afford **11l** as a fluffy white solid; yield: 374 mg (0.40 mmol, 80%); mp 172 °C; TLC (cyclohexane/EtOAc, 10:1): $R_f=0.72$; $[\alpha]_{589}$: −111° (*c* 1.13, 20 °C, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = −0.07 (s, 6H, $SiCH_3$), 0.82 (s, 9H, $SiCCH_3$), 1.03 (s, 6H, CH_3), 1.68–1.92 (m, 14H, CH_2), 2.24–2.30 (m, 2H, CH_2), 2.66–2.68 (m, 2H, CH), 3.00–3.26 (m, 4H, CH_2), 6.12 (dd, $^3J_{HP}=4$ Hz, $^4J_{HH}=3$ Hz, 1H, H-C3′), 6.73 (ddd, $^3J_{HH}=9$ Hz, $^4J_{HH}=3$ Hz, $^5J_{HP}=1$ Hz, 1H, H-C5′), 6.94 (d, $^3J_{HH}=9$ Hz, 1H, H_{ar}), 6.98 (d, $^3J_{HH}=9$ Hz, 1H, H_{ar}), 7.00–7.10 (m, 1H, H-C6′), 7.14 (d, $^3J_{HH}=9$ Hz, 1H, H_{ar}), 7.19 (d, $^3J_{HH}=9$ Hz, 1H, H_{ar}), 7.28–7.68 (m, 11H, H_{ar}), 7.87 (d, $^3J_{HH}=9$ Hz, 1H, H_{ar}), 8.08 (d, $^3J_{HH}=9$ Hz, 1H, H_{ar}), 8.19 (dd, $^3J_{HH}=9$ Hz, $^4J_{HP}=3$ Hz, 1H, H_{ar}); ^{31}P NMR (121 MHz, $CDCl_3$): δ = −14.8 (d, $^4J_{PP}=15.4$ Hz, -PPh_2), 144.1 [d, $^4J_{PP}=15.4$ Hz, -$P(OR)_2$]; ^{13}C NMR (75 MHz, $CDCl_3$): δ = −4.7 (q, $SiCH_3$), 18.2 (σ, SiC), 22.8 (t, CH_2), 23.6 (t, CH_2), 25.3 (q, $SiC\underline{C}H_3$), 25.6 (q, $SiC\underline{C}H_3$), 31.5 (t, CH_2), 35.5 (t, CH_2), 39.3 (s, $\underline{C}CH_3$), 41.0 (t, CH_2), 50.8 (d, CH), 119.5 (s, C_{ar}), 121.1 (d, C5′$_{ar}$-H), 121.3 (s, C_{ar}), 121.4 (d, C6′$_{ar}$-H), 124.7 (d, C3′$_{ar}$-H), 125.1 (d, $J_{CP}=10$ Hz, $C_{ar}H$), 128.5–129.2 (md, $C_{ar}H$), 129.9 (s, C_{ar}), 130.0 (s, $^1J_{CP}=20$ Hz, C2′-P), 130.4 (s, C_{ar}), 131.8 (s, C_{ar}), 134.0 (d, $^2J_{CP}=20$ Hz, $C_{ar}H$), 134.3 (d, $^2J_{CP}=20$ Hz, $C_{ar}H$), 135.8 (s, C_{ar}), 136.2 (s, $C_{ar}P$), 136.6 (s, $C_{ar}P$), 146.2 (s, $^2J_{CP}=15$ Hz, CO), 146.8 (s, $^2J_{CP}=15$ Hz, $C_{ar}O$), 148.3 (s, $^2J_{CP}=20$ Hz, C1′$_{ar}$-O), 152.5 (s, C4′$_{ar}$-O); IR (KBr): $\tilde{\nu}=3055$ (w), 2944 (s), 2925 (s), 2856 (s), 1738 (w), 1657 (w), 1585 (m), 1498 (m), 1464 (s), 1432 (m), 1386 (m), 1340 (w), 1303 (w), 1270 (m), 1253 (m), 1233 (m), 1189 (s), 1137 (w), 1085 (w), 1045 (w), 979 (s), 941 (m), 881 (s), 838 (s), 780 (m), 742 (m), 694 (m), 667 cm^{-1} (s); MS (ESI): *m/z* (%) = 939 (6) $[M+H]^+$, 861 (15), 549 (100), 531 (2), 484 (15), 468 (7); HRMS (ESI): calcd. for $[C_{60}H_{64}O_4PSi+H]^+$: 939.4128; found: 939.4430.

2-Phenoxy-tetrahydropyran (19)

In a flame-dried 500 mL Schlenk flask, phenol (6.8 g, 72 mmol), 3,4-*2H*-dihydropyran (13.2 mL, 144 mmol) and pyridinium *p*-toluenesulfonate (1.82 g, 7.2 mmol) were dissolved in dichloromethane (220 mL) and stirred for 18 h at rt under argon. The mixture was washed with half concentrated aqueous NaCl solution and the aqueous phase was extracted with MTBE (3 × 100 mL). The combined organic phases were washed with half concentrated aqueous NaCl solution and dried over K_2CO_3.The solvent was removed and the crude product was purified by flash-chromatography (hexane/EtOAc, 20:1) to afford **19** as a colorless oil; yield: 12.5 g (97%); TLC (hexane/EtOAc, 10:1): $R_f=0.33$; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.56–1.75 (m, 3H, CH_2), 1.82–1.93 (m, 2H, CH_2), 1.94–2.09 (m, 1H, CH_2), 3.6 (dψtd, 1H, $J_1=11$ Hz, $J_2=4$ Hz, $J_3=2$ Hz, OCH_2), 3.93 (ddd, 1H, J_1=11 Hz, $J_2=9$ Hz, $J_3=3$ Hz, OCH_2), 5.43 (ψt, 1H, $J=3$ Hz, OCH), 6.98 (ψtt , 1H, J_1=7 Hz, $J_2=1$ Hz, H-C4′$_{ar}$), 7.03–7.1 (m, 2H, H-C2′$_{ar}$), 7.25–7.34 (m, 2H, H-C3′$_{ar}$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.7 (t, CH_2), 25.1 (t, CH_2), 30.3 (t, CH_2), 61.9 (t, OCH_2), 96.2 (d, OCH), 116.3 (d, $C_{ar}H$), 121.4 (d, $C_{ar}H$), 129.4 (d, $C_{ar}H$), 157.0 (s, C_{ar}); IR (ATR): $\tilde{\nu}=3064$ (w), 3041 (w), 3029 (w), 2943 (s), 2874 (m), 2851 (m), 1599 (s), 1588 (s), 1495 (s), 1468 (m), 1454 (m), 1441 (m), 1289 (m), 1230, 1201 (s), 1183, 1172 (m), 1124 (s), 1110 (s), 1078 (s), 1037 (s), 1021 (s), 872 (s), 815 (m), 962 (s), 921 (s), 753 (s), 691 cm^{-1} (s); MS: *m/z* (%) = 178 (4, M^+), 94 (27, $M^+-C_5H_9O+H$), 85 (100, $C_5H_9O^+$), 77 (9, $C_6H_5^+$); HRMS (EI): calcd. for $C_{11}H_{14}O_2$: 178.0993; found: 178.0992.

2-(Tetrahydropyran-2-yloxy)-phenylboronic Acid (20b)

In a flame-dried Schlenk flask argon, **19** (399 mg, 2.24 mmol) was dissolved in THF (10 mL), cooled to −78 °C and treated dropwise with *n*-BuLi (2.24 mL, 3.36 mmol). After stirring for 15 min at −78 °C stirring was continued for 75 min at rt. The reaction mixture was recooled to −78 °C and triisopropyl borate (1.3 mL, 5.66 mmol) was added over a period of 30 min. The resulting white suspension was stirred for 3 h at rt, water was added and the aqueous phase was extracted with EtOAc (3 ×). The combined organic phases were washed with saturated aqueous NaCl solution and dried ($MgSO_4$). The solvent was removed under vacuum and the resulting crude product **20b** was used directly (pale yellow oil) without further purification in the following Suzuki-coupling; TLC (hexane/EtOAc, 10:1): $R_f=0.08$.

Preparation of 2-(2-Diphenylphosphanyl-phenoxy)-tetrahydropyran (21a)

According to general procedure I, a solution of **19** (1.5 g, 8.4 mmol) in THF (40 mL) was reacted with *n*-BuLi (8.4 mL, 12.6 mmol) and diphenylchlorophosphane (3.0 mL, 16.8 mmol). The crude product was purified by flash chromatography (hexane/EtOAc, 20:1) to give **21a** as a white solid; yield: 1.85 g (61%); TLC (hexane/EtOAc, 10:1): $R_f=0.29$; mp 107–108 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.24–1.33 (m, 1H, CH_2), 1.33–1.65 (m, 5H, CH_2), 3.40–3.53 (m, 2H, OCH_2), 5.43 (bs, 1H, OCH), 6.67 (ddd, 1H, $J_1=7$ Hz, $J_{PH}=5$ Hz, $J_3=2$ Hz, H-C3′$_{ar}$), 6.88 (bψt, 1H, $J_1=7$ Hz, H-C4′$_{ar}$), 7.13 (bdd, 1H, $J_1=8$ Hz, $J_{PH}=5$ Hz, H-C6′$_{ar}$), 7.23–7.43 (m, 11H, H-C5′$_{ar}$/PPh_2); ^{31}P NMR (81 MHz, $CDCl_3$): δ = −15.4; IR (ATR): $\tilde{\nu}$ =

3052 (w), 3012 (w), 3001 (w), 2943 (m), 2874 (w), 2849 (w), 1583 (m), 1573 (m), 1468 (s), 1434 (s), 1439 (s), 1389 (w), 1356 (m), 1276 (m), 1232 (s), 1201 (s), 1163 (w), 1182 (m), 1122 (s), 1108 (s), 1068 (w), 1049 (m), 1037 (s), 1021 (s), 961 (s), 921 (s), 872 (m), 817 (m), 745 (bs), 696 cm^{-1} (s); MS: *m/z* (%) = 362 (10, M^+), 278 (100, $M^+ - C_5H_9O + H$), 199 (33, $M^+ - C_5H_9O - C_6H_5 + H$), 183 (18), 85 (7, $C_5H_9O^+$); HRMS (EI): calcd. for $C_{23}H_{23}O_2P$: 362.1435; found: 362.1437; anal. calcd. for $C_{23}H_{23}O_2P$ (%): C 76.23, H 6.40; found: C 75.86, H 6.48.

2-[2-(Tetrahydropyran-2-yloxy)-phenylsulfanyl]-pyridine (21b)

Following the general procedure I **19** (1.06 g, 5.95 mmol) was dissolved in THF (15 mL) and *n*-BuLi (6.0 mL, 8.9 mmol) was added. After stirring for 30 min at rt dipyridyl disulfide (2.44 g, 11.1 mmol) in THF (15 mL) was added. The yellow suspension was stirred overnight. After work-up the crude product was purified by flash-chromatography (hexane/EtOAc = 4 + 1) to give **21b** as a white solid; yield: 1.56 g (91%); TLC (hexane/EtOAc, 4:1): $R_f = 0.19$; mp 90 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.35 - 1.50$ (m, 2H, CH_2), 1.50-1.72 (m, 4H, CH_2), 3.52 (m, 1H, OCH_2), 3.71 (ψtd, 1H, $J_1 = 11$ Hz, $J_2 = 3$ Hz, OCH_2), 5.45 (bs, 1H, OCH), 6.94 (bd, 1H, J_1=8 Hz, H-C3$_{Pyr}$), 6.98 (ddd, 1H, $J_1 = 7$ Hz, $J_2 = 5$ Hz, $J_3 = 1$ Hz, H-C5$_{Pyr}$), 7.03 (ψtd, 1H, $J_1 = 7$ Hz, $J_2 = 1$ Hz, H-C5′), 7.19 – 7.26 (m, 1H, H-C3′$_{ar}$), 7.38 (ddd, $J_1 = 8$ Hz, $J_2 = 7$ Hz, $J_3 = 2$ Hz, H-C4$_{Pyr}$), 7.44 (ψtd, 1H, $J_1 = 7$ Hz, $J_2 = 2$ Hz, H-C4′), 7.59 (dd, 1H, $J_1 = 8$ Hz, $J_2 = 2$ Hz, H-C6′), 8.42 (bd, 1H, $J_1 = 5$ Hz, H-C6$_{Pyr}$); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 17.8$ (t, CH_2), 25.1 (t, CH_2), 30.0 (t, CH_2), 61.5 (t, OCH_2), 96.3 (d, OCH), 115.5 (d, $C_{ar}H$), 119.6 (d, $C_{ar}H$), 120.1 (s, $C_{ar}1'$), 121.4 (d, $C_{ar}H$), 122.1 (d, $C_{ar}H$), 131.0 (d, $C_{ar}H$), 136.1 (d, $C_{ar}H$), 136.3 (d, $C_{ar}H$), 149.3 (s, $C_{ar}S$), 157.1 (s, C2′$_{ar}$); IR (ATR): $\tilde{\nu} = 3061$ (w), 3042 (w), 2943 (m), 2871 (w), 2849 (w), 1573 (s), 1558 (s), 1473 (s), 1447 (s), 1416 (s), 1389 (w), 1355 (m), 1276 (m), 1238 (s), 1200 (s), 1182 (m), 1162 (w), 1120 (s), 1109 (s), 1076 (w), 1065 (m), 1035 (s), 1020 (s), 955 (s), 918 (s), 871 (m), 816 (m), 751 (s), 721 cm^{-1} (m); MS: *m/z* (%) = 203 (42, $M^+ - C_5H_9O^+ + H$); 186 (100, $M^+ - SPy + H$); 85 (21, $C_5H_9O^+$); HRMS (EI): calcd. for $C_{16}H_{17}O_2SN$: 287.0980; found: 287.0981; anal. calcd. for $C_{16}H_{17}O_2SN$: C 66.87, H 5.96, N 4.87; found C 66.86, H 5.96, N 4.98.

2-[2-(Tetrahydro-pyran-2-yloxy)-phenyl]-pyridine (21c)

A 25 mL 2-neck flask equipped with a reflux condenser was charged with the boronic acid **20b** (=2.24 mmol, *vide supra*) and toluene (20 mL) under argon. 2 M aqueous Na_2CO_3-solution (2.4 mL, 6.4 mmol), EtOH (2 mL), $Pd(PPh_3)_4$ (78 mg, 3 mol %) and 2-bromopyridine (0.27 mL, 2.8 mmol) were added. The mixture was degassed and stirred for 15 hours at 80 °C. The brownish mixture was quenched with water and the aqueous phase was extracted with toluene (3 ×). The combined organic phases were washed with water followed by saturated aqueous NaCl solution. The extract was dried ($MgSO_4$) and the solvent was removed under reduced pressure and the crude product was purified by preparative rotational chromatography (hexane/MTBE, 3:1) to afford **21c** as a pale yellow oil (fluorescent in high dilution); yield: 395 mg (70% over two steps); TLC (hexane/EtOAc, 4:1): $R_f = 0.08$. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.45 - 1.88$ (m, 6H, CH_2), 3.56 – 3.64 (m, 1H, OCH_2), 3.79 – 3.88 (ψtd, 1H, $J_1 = 11$ Hz, $J_2 = 3$ Hz , OCH_2), 5.48 (bs, 1H, OCH), 7.12 (ψtd, 1 H, $J_1 = 7$ Hz, $J_2 = 1$ Hz, H-C5′$_{ar}$), 7.21 (ddd, 1H, $J_1 = 7$ Hz, $J_2 = 5$ Hz, $J_3 = 1$ Hz, H-C5$_{Pyr}$), 7.26 (bd, 1H, $J_1 = 8$ Hz, H-C3$_{Pyr}$), 7.35 (ddd, 1 H, $J_1 = 8$ Hz, $J_2 = 7$ Hz, $J_3 = 2$ Hz, H-C4$_{Pyr}$), 7.71 (ψtd, 1H, $J_1 = 8$ Hz, $J_2 = 2$ Hz, H-C4′$_{ar}$), 7.79 (dd, 1H, $J_1 = 8$ Hz, $J_2 = 2$ Hz, H-C6′$_{ar}$), 7.88 (d, 1H, $J_1 = 8$ Hz, H-C3′$_{ar}$), 8.71 (bd, 1H, $J_1 = 5$ Hz, H-C6$_{Pyr}$); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 18.6$ (t, CH_2), 25.1 (t, CH_2), 30.3 (t, CH_2), 61.9 (t, OCH_2), 96.7 (d, OCH), 115.5 (d, $C_{ar}H$), 121.6 (d, $C_{ar}H$), 122.0, (d, $C_{ar}H$), 125.2 (d, $C_{ar}H$), 129.8 (d, $C_{ar}H$), 129.9 (s, C1′$_{ar}$), 131.0 (d, $C_{ar}H$), 135.3 (d, $C_{ar}H$), 149.4 (d, $C_{ar}H$), 154.3 (s, C_{Py}), 156.2 (s, C2′$_{ar}$); IR (ATR): $\tilde{\nu} = 3059$ (w), 3007 (w), 2942 (m), 2869 (w), 2850 (w), 1600 (s), 1585 (s), 1492 (s), 1462 (s), 1453 (s), 1424 (s), 1388(w), 1355 (m), 1324 (w), 1301 (m), 1256 (m), 1225 (s), 1200 (s), 1181 (m), 1162 (w), 1146 (w), 1126 (s), 1120 (s), 1107 (s), 1074 (m), 1060 (m), 1049 (m), 1036, 1023 (s), 957 (s), 918 (s), 872 (m), 817 (m), 792 (m), 750 (bs), 732 cm^{-1} (m); MS: *m/z* (%) = 255 (2, M^+), 172 (36, $MH^+ - C_5H_9O + H$), 171 (100, $M^+ - C_5H_9O + H$), 85 (64, $C_5H_9O^+$); HRMS: calcd. for $C_{16}H_{17}O_2N$: 255.1259; found: 255.1255.

2-Diphenylphosphanylphenol (22a)

In an argon atmosphere **21a** (1.88 g, 5.19 mmol) was taken up in MeOH (120 mL) and stirred for 4.5 hours with *p*-TsOH (250 mg, 1.31 mmol, 25 mol %). After extractive work-up, the crude product was subjected to preparative rotational chromatography (hexane/EtOAc, 10:1) to give compound **22a** as a white solid; yield: 1.01 g (70%); TLC (hexane/EtOAc, 10:1): $R_f = 0.11$; mp 146 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 6.20$ (bs, 1H, OH), 6.90 (bψt, 1H, $J = 7$ Hz, H-C4$_{ar}$), 6.91 (bdd, 1H, $J_1 = 8$ Hz, $J_{P\text{-}H} = 5$ Hz, H-C6$_{ar}$), 7.00 (ddd, 1H, $J_1 = 7$ Hz, $J_{P\text{-}H} = 6$ Hz $J_3 = 2$ Hz, H-C3$_{ar}$), 7.28 – 7.43 (m, 11H, H-C5$_{ar}$, PPh_2); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 115.6$ (d, $C_{ar}H$), 120.9 (d, C2$_{ar}$, $J_{PC} = 5.6$ Hz), 121.1 (d, $C_{ar}H$, $J_{PC} = 2.7$ Hz), 128.7 (d, $C_{ar}H$, $J_{PC} = 7.2$ Hz), 129.0 (d, $C_{ar}H$), 131.6 (d, $C_{ar}H$), 133.4 (d, $C_{ar}H$, $J_{PC} = 18.2$ Hz), 134.7 (d, $C_{ar}H$, $J_{PC} = 2.2$ Hz), 134.9 (d, $C_{ar}P$, $J_{PC} = 5.6$ Hz), 159.1 (d, C1$_{ar}$, $J_{PC} = 19.1$ Hz); ^{31}P NMR (81 MHz, $CDCl_3$): $\delta = -29.5$; IR (ATR): $\tilde{\nu} = 3520$ (m), 3268 (bm), 3068 (m), 3056 (m), 3013 (w), 1590 (m), 1578 (m), 1477 (m), 1469 (m), 1434 (s), 1345 (m), 1322 (w), 1308 (w), 1285 (m), 1252 (w), 1210, 1181 (m), 1158 (w), 1122 (m), 1090 (w), 1069 (w), 1027 (m), 999, 855 (w), 825 (m), 747 (s), 697 cm^{-1} (s); MS (EI): *m/z* (%) = 278 (100, M^+), 261 (2, $M^+ - OH$), 199 (49), 183 (29, M^+); HRMS (EI): calcd. for $C_{18}H_{15}OP$: 278.0860; found: 278.0861; anal. calcd. for $C_{18}H_{15}OP$: C 77.69, H 5.43; found: C 77.21, H 5.52.

2-(Pyridin-2-yl-sulfanyl)-phenol (22b)

As described above, **21b** (1.35 g, 4.69 mmol) was dissolved in MeOH (110 mL) and treated with *p*-TsOH (491 mg, 2.58 mmol, 55 mol %). After 3.5 hours the mixture was worked-up. Recrystallization from hexane gave **22b** as white crystals; yield: 0.76 g (79%); TLC (hexane/EtOAc, 4:1): $R_f = 0.13$; mp 116 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 6.91$ (ψtd, 1H, $J_1 = 8$ Hz, $J_2 = 2$ Hz, H-C5$_{ar}$), 7.08 – 7.16 (m, 2H, H-C3$_{ar}$ or C3′$_{Pyr}$, H-C5′$_{Pyr}$), 7.23 (d, 1H, $J_1 = 8$ Hz, H-C3′$_{Pyr}$ or C3$_{ar}$), 7.36

(bψtd, 1H, $J_1 = 8$ Hz, $J_2 = 2$ Hz, H-C4′$_{Pyr}$), 7.52 (dd, 1H, $J_1 = 8$ Hz, $J_2 = 1$ Hz, H-C6$_{ar}$), 7.59 (ψtd, 1H, $J_1 = 8$ Hz, $J_2 = 2$ Hz, H-C4$_{ar}$), 8.42 (bdd, 1H, $J_1 = 5$ Hz, $J_2 = 1$ Hz, H-C6‘$_{Pyr}$), 9.81 (bs, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 117.6 (s, C1$_{ar}$), 118.1 (d, C$_{ar}$H), 120.7 (d, C$_{ar}$H), 121.1 (d, C$_{ar}$H), 122.8 (d, C$_{ar}$H), 132.0 (d, C$_{ar}$H), 135.4 (d, C$_{ar}$H), 137.6 (d, C$_{ar}$H), 148.9 (d, C$_{ar}$H), 158.5 (s, C$_{PyS}$), 159.7 (s, C2$_{ar}$); IR (ATR): $\tilde{\nu}$ = 3421 (bw), 3053 (bm), 2922 (w), 2842 (w), 2695 (w), 2575 (bw), 1580 (s), 1560 (s), 1470 (s), 1446 (s), 1418 (s), 1369 (m), 1294 (m), 1279 (m), 1243, 1183 (m), 1152 (m), 1126 (m), 1087 (w), 1047 (w), 1030 (w), 998 (w), 836 (w), 753 (s), 723 cm^{-1} (m); MS (EI): *m/z* (%) = 203 (20, M^+), 202 (10, $M^+ - H$), 186 (100, $M^+ - OH$); HRMS (EI): calcd. for $C_{11}H_9ONS$: 203.0404; found: 203.0404; anal. calcd. for $C_{11}H_9ONS$: C 65.00, H 4.46, N 6.89; found: C 64.90, H 4.53, N 7.00.

2-Pyridin-2-ylphenol (22c):

Following the general procedure **21c** (0.40 g, 1.57 mmol) was dissolved in MeOH (30 mL) and *p*-TsOH (15 mg, 78 μmol, 5 mol %) was added. The solution was stirred for 1.5 h. After extractive work-up and chromatographic purification (hexane/EtOAc, 2:1) **22c** was isolated as a yellow solid; yield: 202 mg (76%); TLC (hexane/EtOAc, 2:1): R_f = 0.44; mp 55–56 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.92 (ψtd, 1H, $J_1 = 7$ Hz, $J_2 = 1$ Hz, H-C5$_{ar}$), 7.04 (dd, 1H, $J_1 = 8$ Hz, $J_2 = 1$ Hz, H-C3′$_{Pyr}$), 7.21–7.28 (m, 1H, H-C5′$_{Pyr}$), 7.31 (ddd, 1H, $J_1 = 8$ Hz, $J_2 = 7$ Hz, $J_3 = 1$ Hz, H-C4′$_{Pyr}$), 7.81 (ψtd, 1H, $J_1 = 8$ Hz, $J_2 = 2$ Hz, H-C4$_{ar}$), 7.85 (dd, 1H, $J_1 = 8$ Hz, $J_2 = 1$ Hz, H-C6$_{ar}$), 7.92 (d, 1H, $J = 8$ Hz, H- C3), 8.52 (bd, 1H, $J = 5$ Hz, H-C6′$_{Pyr}$), 14.39 (bs, 1 H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 118.6 (d, C$_{ar}$H), 118.7 (d, C$_{ar}$H), 119.0 (d, C$_{ar}$H), 121.5 (d, C$_{ar}$H), 126.1 (d, C$_{ar}$H), 131.5 (d, C$_{ar}$H), 137.7 (d, C$_{ar}$H), 145.8 (d, C$_{ar}$H), 157.9 (s, C$_{Py}$), 160.0 (s, C2$_{ar}$); IR (ATR): $\tilde{\nu}$ = 3057 (w), 3009 (w), 2928 (w), 2855 (w), 2688 (w), 2629 (bw), 1723 (w), 1593 (s), 1562 (m), 1502 (m), 1477 (s), 1430 (s), 1399 (m), 1304 (m), 1270 (s), 1243 (s), 1224 (m), 1165 (w), 1154 (w), 1118 (w), 1098 (w), 1074 (w), 1055 (w), 1045 (w), 1022 (w), 1111 (w), 937 (w), 884 (w), 853 (w), 834 (m), 750 (s), 734 (s), 725 cm^{-1} (s); MS: *m/z* (%) = 172 (15, MH^+), 171 (100, M^+), 143 (15), 117 (26), 78 (4, $C_5NH_5^+$); HRMS: calcd. for $C_{11}H_9ON$: 171.0684; found: 171.0682; anal. calcd. for $C_{11}H_9ON$: C 77.17, H 5.30, N 8.18; found: C 77.14, H 5.46, N 8.16.

(3*R*,9*R*)-6-(2-Diphenylphosphanyl-phenoxy)-2,2-dimethyl-4,4,8,8-tetraphenyl-tetrahydro-1,3,5,7-tetraoxa-6-phosphaazulene (23a)

Following the general procedure III **22a** (100 mg, 0.36 mmol) in THF (4 mL) was treated with Et_3N (1.0 mL, 7.2 mmol) and **12** (2 equiv.) in THF (4 mL) was added dropwise. The crude product was purified by chromatography (hexane/EtOAc, 10:1) to give **23a** as a white foam; yield: 251 mg (90%); TLC (hexane/EtOAc, 10:1): R_f 0.29; mp 147 °C; $[\alpha]_\lambda$ (*c* 1.00; 20 °C, $CHCl_3$): $[\alpha]_{589}$: −155.6; $[\alpha]_{578}$: −163.6; $[\alpha]_{546}$: −188.0; $[\alpha]_{436}$: −343.4; $[\alpha]_{365}$: −600.2; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.39 (s, 3H, CH_3), 0.95 (s, 3H, CH_3), 5.12 (d, 1H, $J = 9$ Hz, CH), 5.20 (d, 1H, $J = 9$ Hz, CH), 6.66–6.72 (m, 1H, H-C3′), 6.92–7.01 (m, 2H, H-C$_{ar}$), 7.12–7.34 (m, 25H, H-C$_{ar}$), 7.39–7.45 (m, 2H, H-C$_{ar}$), 7.47–7.54 (m, 2H, H-C$_{ar}$), 7.57 (bd, 2H, $J = 8$ Hz, H-C$_{ar}$); ^{31}P NMR (81 MHz, $CDCl_3$): δ = −17.2 (bs), 134.9 (d, J_{PP} = 13 Hz); MS: *m/z* (%) = 772 (1%, M^+); 341 (100, $M^+ - C_{31}H_{27}O_2$); 237 (4); 207 (14); 179 (19, $C_{14}H_{11}^+$); HRMS: calcd. for $C_{49}H_{42}O_5P_2$: 772.2507; found: 772.2514; IR (ATR): $\tilde{\nu}$ = 3088 (w), 3058 (w), 3026 (w), 2988 (w), 2935 (w), 1714 (w), 1692 (w), 1599 (w), 1585 (w), 1569 (w), 1494 (m), 1465 (m), 1447 (s), 1434 (s), 1382 (m), 1371 (m), 1351 (w), 1320 (w), 1216 (bs), 1166 (m), 1089 (s), 1050 (s), 1036 (s), 1019 (s), 977 (m), 888 (s), 849 (s), 769 (m), 741 (s), 725 (m), 696 cm^{-1} (s); anal.: calcd. for $C_{49}H_{42}O_5P_2$: C 76.16, H 5.48; found: C 74.95, H 5.82.

(3a*S*)-1-(2-Diphenylphosphanylphenoxy)-3,3-diphenyltetrahydro-2-oxa-6a–aza-1-phosphapentalene (23b)

According to general procedure III **22a** (100 mg, 0.36 mmol) was dissolved in THF (5 mL) and treated with Et_3N (1.0 mL, 7.2 mmol) followed by **17** (2 equiv.) in THF (5 mL). The crude product was purified by filtration through a short column packed with alumina N under a flow of argon eluting with hexane/EtOAc, 10:1 (75 mL) followed by hexane/EtOAc, 3:1 (25 mL). The solvent was removed under vacuum to afford **23b** as a white foam; yield: 169 mg (84%); TLC (alumina N; hexane/EtOAc, 10:1): R_f = 0.52; mp 133 °C; $[\alpha]_\lambda$ (*c* 1.00, 20 °C, $CHCl_3$): $[\alpha]_{589}$: −208.1, $[\alpha]_{578}$: −219.1, $[\alpha]_{546}$: −253.6, $[\alpha]_{436}$: −486.2, $[\alpha]_{365}$: −920.7; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.82–1.00 (m, 2H, CH_2), 1.23–1.37 (m, 1H, CH_2), 1.69 (m, 1H, CH_2), 2.76–2.87 (m, 1H, CH_2), 3.14–3.24 (m, 1H, CH_2), 4.13 (dd, 1H, $J_1 = 7$ Hz, J_2=5 Hz, N-CH), 6.66 (ddd, 1H, $J_1 = 7$ Hz, $J_{P\text{-}H} = 4$ Hz, $J_3 = 2$ Hz, H-C3′), 6.88 (bψt, 1H, $J = 7$ Hz, H-C4′), 6.95 (dd, 1H, $J_1 = 8$ Hz, $J_{P\text{-}H} = 5$ Hz, H-C6′), 7.05 (ψtd, 1H, $J_1 = 8$ Hz, $J_2 = 2$ Hz, H-C5′), 7.09 (bd, 2H, $J = 7$ Hz, H-C$_{ar}$ 7.16–7.35 (m, 16H, H-C$_{ar}$), 7.39 (bd, 2H, J=8 Hz, H-C$_{ar}$); ^{31}P NMR (81 MHz, $CDCl_3$): δ = −16.6, 138.4; IR (ATR): $\tilde{\nu}$ = 3056, 3027, 3001 (w), 2970, 2945, 2872 (w), 1584, 1568 (w), 1493, 1478 (w), 1464, 1447 (m), 1434 (s), 1346 (w), 1261 (w), 1212 (bm), 1197 (m), 1157, 1121, 1104, 1066 (w), 1027 (m), 980 (m), 913 (w), 867, 856, 817 (m), 765 (m), 746 (s), 699 cm^{-1} (s); MS (EI): *m/z* (%) = 559 (88, M^+), 352 (39), 324 (88, $M^+ - C_{17}H_{17}N$), 278 (13, $MH^+ - C_{17}H_{17}NOP$), 264 (29), 235 (100, $C_{17}H_{17}N^+$), 199 (26), 183 (26); HRMS (EI): calcd. for $C_{35}H_{31}O_2P_2N$: 559.1830; found: 559.1831; anal. calcd. for $C_{35}H_{31}O_2P_2N$: C 75.12, H 5.58, N 2.50; found: C 75.21, H 5.96, N 2.70.

(1*R*,2*S*,5*R*)-(2-Diphenylphosphanylphenoxy)-dimenthyloxyphosphane (23c)

Following the general procedure III **22a** (100 mg, 0.36 mmol) was dissolved in THF (5 mL) and Et_3N (1.0 mL, 7.2 mmol) was added followed by **18** (2 equiv.) in THF (5 mL). The crude product was purified by preparative rotational chromatography (hexane/EtOAc, 30 + 1) to afford **23c** as a clear, colorless, viscous oil; yield: 214 mg (96%); TLC (hexane/EtOAc, 10:1): R_f = 0.62; $[\alpha]_\lambda$ (*c* 1.00, 20 °C, $CHCl_3$): $[\alpha]_{589}$: −25.3, $[\alpha]_{578}$: −27.0, $[\alpha]_{546}$: −30.6, $[\alpha]_{436}$: −57.4, $[\alpha]_{365}$: −116.0; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.61 (d, 3H, $J = 7$ Hz, CH_3), 0.66 (d, 3H, $J = 7$ Hz, CH_3), 0.74–1.38 (m, 22H, CH_3, CH_2, CH), 1.51–1.65 (m, 4H, CH_2, CH), 1.98–2.14 (m, 4H, CH_2, CH), 3.58 (bqd, 1H, J_1 = 10 Hz, $J_2 = 5$ Hz, PO-CH), 4.12–4.23 (m, 1H, PO-CH), 6.64 (bdd, 1H, $J_1 = 8$ Hz, $J_{P\text{-}H} = 4$ Hz, H-C3′), 6.91–6.97 (m, 1H, H-C$_{ar}$), 7.12–7.38 (m, 12H, H-C$_{ar}$); ^{31}P NMR (81 MHz, $CDCl_3$):

$\delta = -17.4$, 134.3; IR (ATR): $\tilde{\nu} = 3070$ (w), 3054 (w), 2954 (s), 2925 (s), 2869 (m), 1730 (w), 1583 (m), 1570 (m), 1467 (s), 1455 (m), 1434 (s), 1369 (m), 1325 (w), 1270 (m), 1218 (m), 1180 (w), 1095 (w), 1069 (w), 1038 (w), 1018 (m), 1007 (m), 997 (m), 974 (s), 964 (s), 928 (m), 855 (s), 817 (m), 799 (m), 760 (m), 743 (s), 712 (m), 696 (s), 667 cm^{-1} (m); **MS**: *m/z* (%) = 618 (2, M^+), 479 (7, $M^+ - C_{10}H_{19}$), 341 (100, $C_{20}H_{38}O_2P^+$), 325 (16), 278 (37, $M^+ - C_{20}H_{38}O_2P + H$), 265 (19); 199 (31), 183 (17), 139 (71, $C_{10}H_{19}^+$); HRMS: calcd. for $C_{38}H_{52}O_3P_2$;: 618.3391; found: 618.3395.

(3*R*,9*R*)-2-[2-(2,2)-Dimethyl-4,4,8,8-tetraphenyltetrahydro-1,3,5,7-tetraoxa-6-phosphaazulene-6-yloxy)-phenylsulfanyl]-pyridine (23d)

A solution of **22b** (100 mg, 0.49 mmol) in THF (5 mL) was deprotonated with Et_3N (1.4 mL, 9.8 mmol) and reacted with **12** (2 equiv.) in THF (5 mL). The suspension was stirred for 3.5 hours at rt. The crude product was purified by chromatography (hexane/EtOAc, 4:1) to afford **23d** as a pale brown foam; yield: 371 mg (98%); TLC (hexane/EtOAc, 4:1): $R_f = 0.22$; mp 114 °C; $[\alpha]_\lambda$ (*c* 1.00, 20 °C, $CHCl_3$): $[\alpha]_{589}$: −207.8; $[\alpha]_{578}$: −218.4; $[\alpha]_{546}$: −250.7; $[\alpha]_{436}$: −456.8; $[\alpha]_{365}$: −798.0; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.54$ (s, 3H, CH_3), 0.75 (s, 3H, CH_3), 5.09 (d, 1H, $J = 8$ Hz, CH), 5.44 (d, 1H, $J = 8$ Hz, CH), 6.64 (d, 1H, $J = 8$ Hz, H-C_{ar}), 6.89 (bd, 1H, $J = 8$ Hz, H-C_{ar}), 6.91 (bdd, 1H, $J_1 = 5$ Hz, $J_2 = 7$ Hz, H-C_{ar}), 7.06 (bψt, 1H, $J = 7$ Hz, H-C_{ar}), 7.10 – 7.38 (m, 16H, H-C_{ar}), 7.38 – 7.52 (m, 5H, H-C_{ar}), 7.58 (bd, 2H, H-C_{ar}), 8.38 (bd, 1H, $J = 5$ Hz, H-C6′$_{Pyr}$); ^{31}P NMR (81 MHz, $CDCl_3$): $\delta = 128.9$; IR (ATR): $\tilde{\nu} = 3089$, 3060, 3036 (w); 2989, 2935 (w), 1713, 1661, 1599 (w), 1574 (m), 1560 (w), 1494, 1468 (m), 1447 (s), 1417 (m), 1382, 1371 (m), 1217 (bm), 1166 (m), 1118, 1089 (m), 1051, 1035, 1018 (s), 984, 977, 967 (m), 888 (s), 853 (m), 750, 741, 725 (s), 698 cm^{-1} (s); MS: *m/z* (%) = 698 (1%, MH^+), 431 (2, $C_{31}H_{27}O_2^+$), 266 (100, $M^+ - C_{31}H_{27}O_2$), 237 (13), 207 (29), 186 (93), 179 (72, $C_{14}H_{11}^+$); HRMS: calcd. for $C_{42}H_{37}O_5PSN$ (MH^+): 698.2130; found: 698.2137; anal. calcd. for $C_{42}H_{37}O_5PSN$: C 72.29, H 5.20, N 2.01; found: C 72.47, H 5.72, N 1.75.

(3*R*,9*R*)-2-[2-(2,2-Dimethyl-4,4,8,8-tetraphenyltetrahydro-1,3,5,7-tetraoxa-6-phosphaazulene-6-yloxy)-phenyl]-pyridine (23e)

Following the general procedure III **22c** (80 mg, 0.47 mmol) in THF (5 mL) was reacted with Et_3N (1.0 mL, 7.2 mmol) followed by **12** (2 equiv.) in THF (5 mL). The crude product was purified by chromatography (hexane/EtOAc, 4:1) to give **23e** as a white foam; yield: 242 mg (77%); TLC (hexane/EtOAc, 4:1): $R_f = 0.19$; mp 94 °C; $[\alpha]_\lambda$ (*c* 1.00, 20 °C, $CHCl_3$): $[\alpha]_{589}$: −241.1; $[\alpha]_{578}$: −252.9; $[\alpha]_{546}$: −290.6; $[\alpha]_{436}$: −531.2; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.41$ (s, 3H, CH_3), 0.86 (s, 3H,CH_3), 5.14 (d, 1H, $J = 9$ Hz, CH), 5.20 (d, 1H, $J = 9$ Hz, CH), 7.08 – 7.34 (m, 14H, H-C_{ar}), 7.34 – 7.56 (m, 8H, H-C_{ar}), 7.64 (bψtd, 1H, $J_1 = 8$ Hz, $J_2 = 1$ Hz, H-C_{ar}), 7.80 (bdd, 1H, $J_1 = 7$ Hz, $J_2 = 2$ Hz, H-C_{ar}), 8.68 (bd, 1H, $J = 5$ Hz, H-C6$_{Pyr}$); ^{31}P NMR (81 MHz, $CDCl_3$): $\delta = 135.4$; IR (ATR): $\tilde{\nu} = 3059$ (w), 3035 (w), 2933 (w), 1955 (w), 1814 (w), 1713 (w), 1601 (w), 1586 (m), 1564 (w), 1492 (m), 1462 (m), 1448 (s), 1424 (m), 1382 (m), 1371 (m), 1302 (w), 1248 (m), 1215 (bm), 1166 (m), 1089 (m), 1050 (s), 1035 (s), 1019 (s), 978 (m), 887 (s), 852 (m), 792 (m), 772 (m), 749 (s), 740 (s), 725 (m), 698 cm^{-1} (s); MS: *m/z* (%) = 666 (86, MH^+), 431 (64, $C_{31}H_{27}O_2^+$), 234 (100, $M^+ - C_{31}H_{27}O_2$), 207 (17), 179 (64, $C_{14}H_{11}^+$); 167 (13, $C_{13}H_{11}^+$); 77 (4, $C_6H_5^+$); HRMS: calcd. for $[C_{42}H_{36}O_5PN + H^+]$: 666.2409; found: 666.2409; anal. calcd. for $C_{42}H_{36}O_5PN$: C 75.78, H 5.45, N 2.10; found: C 75.54, H 6.10, N 1.96.

5-(*tert*-Butyldimethylsilanoxy)-1-naphthol (25)

In a 250 mL three-necked round-bottom flask equipped with an addition funnel, a solution of chloro-*tert*-butyldimethylsilane (5.00 g, 33 mmol) and **24** (8.00 g, 50 mmol) in DMF (100 mL) was prepared under an argon atmosphere. A solution of imidazole (2.72 g, 40 mmol) in DMF (30 mL) was added dropwise, and the reaction was stirred for 15 h at rt. After addition of 50 mL water the aqueous phase was extracted with MTBE (3 × 100 mL). The combined organic phases were washed with water (1 ×) and brine (1 ×), and subsequently dried over $MgSO_4$. After removal of the solvent under vacuum, the crude product was purified by chromatography (cyclohexane/EtOAc, 10:1) to afford **25** as a white solid; yield: 6.15 g (68%); TLC (cyclohexane/EtOAc, 4:1): $R_f = 0.44$; mp 86 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.27$ (s, 6H, $SiCH_3$), 1.08 (s, 9H, $SiCCH_3$), 5.17 (bs, 1H, OH), 6.80 (dd, J_1=7.5 Hz, J_2=1.0 Hz, 1H, H-C_{ar}), 6.88 (dd, J_1=7.5 Hz, J_2=1.0 Hz, 1 H, H-C_{ar}), 7.27 (m, 2H, H-C_{ar}), 7.76 (Ωt, J_1=8.5 Hz, 2H, H-C_{ar}); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -4.3$ (q, $SiCH_3$), 18.4 (s, SiC), 25.9 (q, $SiC\underline{C}H_3$), 109.1 (d, $C_{ar}H$), 113.3 (d, $C_{ar}H$), 114.3 (d, $C_{ar}H$), 115.5 (d, $C_{ar}H$), 124.9 (d, $C_{ar}H$), 125.3 (d, $C_{ar}H$),125.8 (s, C_{ar}), 129.3 (s, C_{ar}), 151.2 (s, C_{ar}), 151.7 (s, C_{ar}); IR (ATR): $\tilde{\nu} = 3397$ (m, OH), 2952 (m), 2926 (m), 2855 (m), 1592 (s), 1513 (s), 1403 (s), 1344 (w), 1270 (s), 962 (s), 828 (s), 775 cm^{-1} (s); MS (EI): *m/z* (%) = 274 (70), 218 (25), 217 (100), 201 (25); HRMS (EI): calcd. for $C_{16}H_{22}O_2Si$: 274.139; found: 274.139.

tert-Butyldimethyl-[5-(tetrahydropyran-2-yloxy)-1-naphthyloxy]silane (26)

A solution of **25** (2.74 g, 10.0 mmol), 3,4-dihydro-2*H*-pyran (2.71 mL, 30.0 mmol) and PPTS (0.25 mg, 1.0 mmol) in dichloromethane (50 mL) was stirred for 10 h under an argon atmosphere. The reaction was quenched by addition of aqueous concentrated $NaHCO_3$ (50 mL). After a standard work-up with MTBE, the combined organic phases were dried over $MgSO_4$. After removal of the solvent under vacuum, the crude product was purified by flash-chromatography (cyclohexane/EtOAc, 10:1) to afford **26** as a faint yellow solid; yield: 3.55 g (99%); TLC (cyclohexane/EtOAc, 10:1): $R_f = 0.62$; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.26$ (s, 6H, $SiCH_3$); 1.08 (s, 9H, $SiCCH_3$); 1.58 – 1.84 (m, 3H, CH_2), 1.88 – 2.15 (m 3H, CH_2), 3.63 (ddt, 1H, $J_1 = 11$ Hz, $J_2 = 3$ Hz, $J_3 = 1$ Hz, OCH_2), 3.94 (Ωtd, 1H, J_1 =11 Hz, $J_2 = 3$ Hz, OCH_2), 5.62 (Ωt, 1H, $J = 3$ Hz, OCH), 6.85 (dd, 1H, J_1 =8 Hz, J_2 =1 Hz, H-C_{ar}); 7.13 (dd, 1H, J_1 = 8 Hz, $J_2 = 1$ Hz, H-C_{ar}), 7.33 (dd, 1H, $J_1 = 8$ Hz, $J_2 = 1$ Hz, H-C_{ar}), 7.30 (dd, 1H, $J = 8$ Hz, $J_2 = 1$ Hz, H-C_{ar}), 7.80 (d, 1H, $J =$ 8 Hz, H-C_{ar}), 7.89 (d, 1H, $J = 8$ Hz, H-C_{ar}); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -4.3$ (q, $SiCH_3$), 18.4 (s, SiC), 18.8 (t, CH_2), 25.3 (t, CH_2), 25.9 (q, $SiC\underline{C}H_3$), 30.5 (t, CH_2), 61.9 (t, OCH_2), 96.3 (d, OCH, 108.6 (d, $C_{ar}H$), 113.1(d, $C_{ar}H$), 114.9 (d,

$C_{ar}H$), 115.8 (d, $C_{ar}H$), 124.9 (d, $C_{ar}H$), 125.1 (d, $C_{ar}H$), 127.6 (s, C_{ar}), 129.1 (s, C_{ar}), 151.5 (s, C_{ar}), 152.4 (s, C_{ar}); IR (ATR): $\tilde{\nu}$ = 3052 (w), 2928 (s), 2854 (m), 1590 (s), 1505 (s), 1409 (s), 1354 (w), 1267 (s), 1257 (s), 1200 (w), 1112 (w), 986 (s), 830 (s), 776 (s), 674 (w); M/S: *m/z* (%) = 358 (5), 331 (10), 274 (85), 217 (100), 201 (14), 115 cm^{-1} (6); HRMS: calcd. for $C_{21}H_{30}O_3Si$: 358.1164; found: 358.1960; anal. calcd. for $C_{21}H_{30}O_3Si$: C 70.35, H 8.43; found: C 70.19, H 8.61.

[5-*tert*-Butyldimethylsilanoxy)-1-(tetrahydropyran-2-yloxy)-2-naphthyl]-diphenylphosphane (27)

According to general procedure III, a solution of **26** (1.08 g, 3.0 mmol) in THF (15 mL) was treated with *n*-BuLi (2.2 mL, 3.6 mmol) and chlorodiphenylphosphane (0.79 g, 0.67 mL, 3.6 mmol). The crude product was purified by chromatography (cyclohexane/EtOAc/Et_3N, 30:1:1) to afford **27** as a faint yellow foam; yield: 1.33 g (82%); TLC (cyclohexane/EtOAc/Et_3N, 10:1:1): R_f = 0.8; ^1H NMR (300 MHz, $CDCl_3$): δ = 0.25 (s, 3H, $SiCH_3$), 0.27 (s, 3H, $SiCH_3$), 1.04 (s, 9H, $SiCCH_3$), 1.45 – 1.58 (m, 3H, CH_2), 1.98 – 2.07 (m, 3H, CH_2), 3.25 (m, 1H, OCH_2), 4.05 (m, 1H, OCH_2), 5.24 (m, 1H, *J* = 3 Hz, OCH), 6.85 (dd, 1H, J_1 = 8 Hz, J_2 = 1 Hz, H-C_{ar}), 6.90 (dd, 1H, J_1 = 8 Hz, J_2 = 4 Hz, H-C_{ar}), 7.25 – 7.37 (m, 11H, H-C_{ar}), 7.86 (dd, 1H, J_1 = 9 Hz, J_2 = 1 Hz, H-C_{ar}), 7.94 (dt, 1 H, J_1 = 9 Hz, J_2 = 1 Hz, H-C_{ar}); ^{13}C NMR (100 MHz, $CDCl_3$): δ = −4.3 (q, $SiCH_3$), −4.2 (q, $SiCH_3$), 18.4 (s, SiC), 20.4 (t, CH_2), 25.0 (t, CH_2), 25.8 (q, $SiC\underline{C}H_3$), 31.0 (t, CH_2), 64.6 (t, OCH_2), 104.3 (d, OCH), 104.4 (d, $C\underline{H}_{ar}$), 113.3 (d, $C_{ar}H$), 116.8 (d, $C_{ar}H$), 119.0 (d, $C_{ar}H$), 125.9 (d, $C_{ar}H$), 128.3 (d, $C_{ar}H$, J_{CP} = 12 Hz), 129.4 (s, C_{ar}), 129.8 (s, C_{ar}), 133.4 (d, J_P = 20 Hz, $C_{ar}H$), 133.9 (d, J_{CP} = 20 Hz, $C_{ar}H$), 137.3 (s, J_{CP} = 12 Hz, C_{ar}), 137.6 (s, J_{CP} = 12 Hz, C_{ar}), 151.5 (s, C_{ar}), 157.5 (s, J_{CP} = 20 Hz, C_{ar}-O); ^{31}P NMR (121 MHz): δ = −16.06 (s); IR (ATR): $\tilde{\nu}$ = 3052 (m), 2951 (s), 2855 (m), 1582 (w), 1491 (s), 1359 (m), 1269 (s), 1031 (w), 988 (s), 840 (s), 740 (m), 696 cm^{-1} (m); HRMS: calcd. for $[C_{33}H_{39}O_3PSi + H]^+$: 543.2484; found: 543.2490.

5-(*tert*-Butyldimethylsilanoxy)-2-diphenylphosphanyl-1-naphthol (28)

A solution of **27** (1.08 g, 2.0 mmol), and *p*-TsOH (0.594 g, 3.0 mmol) in THF (15 mL) and methanol (5 mL) was stirred for 30 min in an argon atmosphere. The reaction was quenched by addition of brine (10 mL). After a standard work-up with dichloromethane, the combined organic phases were dried over $MgSO_4$. After removal of the solvent, the crude product was purified by chromatography (cyclohexane/EtOAc/Et_3N, 20:1:1) to afford **28** as a faint yellow oil; yield: 0.795 g (88%); ^1H NMR (300 MHz, $CDCl_3$): δ = 0.26 (s, 6H, $SiCH_3$), 1.05 (s, 9H, $SiCCH_3$); 3.39 (s, 1H, OH), 6.89 (dd, 1H, J_1 = 8 Hz, J_2 = 1 Hz, H-C_{ar}), 7.05 (dd, 1H, J_1 = 8 Hz, J_2 = 5 Hz, H-C_{ar}), 7.25 – 7.40 (m, 11H, H-C_{ar}), 7.67 (d, 1H, *J* = 8 Hz, H-C_{ar}), 7.87 (d, *J* = 8 Hz, H-C_{ar}); ^{13}C NMR (100 MHz, $CDCl_3$): δ = −4.5 (q, $SiCH_3$), 18.2 (s, SiC), 25.6 (q, $SiC\underline{C}H_3$), 104.6 (d, $C_{ar}H$), 112.7 (s, C_{ar}), 114.4 (d, $C_{ar}H$), 115.3 (d, $C_{ar}H$), 115.7 (d, $C_{ar}H$), 125.4 (s, C_{ar}), 125.7 (d, $C_{ar}H$), 128.7 (d, $C_{ar}H$), 128.8 (d, J_{CP} = 11 Hz, $C_{ar}H$), 128.9 (s, C_{ar}), 129.9 (s, C_{ar}), 133.2 (d, J_{CP} = 18 Hz, $C_{ar}H$), 135.1 (s, C_{ar}), 151.5 (s, C_{ar}), 156.8 (s, J_{CP} = 11 Hz, C_{ar}); ^{31}P NMR (300 MHz): δ = −32.4 (s); IR (ATR): $\tilde{\nu}$ = 3394 (s, OH), 3052 (m), 2953 (s), 2928 (s), 2855 (m), 1585 (s), 1492 (s), 1401 (s), 1271 (s), 1189 (w), 985 (s), 840 (s), 742 (s), 694 cm^{-1} (m); HRMS: calcd. for $[C_{28}H_{30}O_2PSi + H]^+$: 458.1901; found: 458.1895.

(3*R*,9*R*)-6-[5-(*tert*-Butyldimethylsilanoxy)-2-diphenylphosphanyl-1-naphthyloxy]-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro-1,3,5,7-tetraoxa-6-phosphaazulene (29)

According to general procedure III, a solution of **28** (0.79 g, 1.72 mmol) in THF (10 mL) was treated with Et_3N (3.60 mL, 25.8 mmol) and **12** (1.83 g, 3.44 mmol) in THF (10 mL). The crude product was purified by chromatography (hexane/EtOAc/Et_3N, 20:1:1) to afford **29** as a white foam; yield: 1.54 g (94%); mp 106 °C; $[\alpha]_\lambda$ (*c* 1.00, 20 °C, $CHCl_3$): $[\alpha]_{589}$: −190, $[\alpha]_{546}$: −230, $[\alpha]_{405}$: −562; ^1H NMR (300 MHz, benzene-d_6): δ = 0.09 (s, 6H, $SiCH_3$), 0.52 (s, 3H, CH_3), 0.69 (s, 3H, CH_3), 0.98 (s, 9H, $SiCCH_3$), 5.60 (dd, 1H, OCH, J_1 = 8.0 Hz, J_2 = 1.0 Hz), 5.72 (m, 1H, OCH), 6.81 (d, 1H, *J* = 7.5 Hz, H-C_{ar}), 6.83 – 7.37 (m, 20H, H-C_{ar}), 7.48 (m, 2H, H-C_{ar}), 7.64 (d, 2H, *J* = 7.5 Hz, H-C_{ar}), 7.73 (m, 4H, H-C_{ar}), 7.91 (d, 2H, *J* = 7.0 Hz, H-C_{ar}), 8.00 (d, 2H, *J* = 7.5 Hz, H-C_{ar}), 8.07 (d, 1H, *J* = 8.5 Hz, H-C_{ar}), 8.54 (d, 1H, *J* = 8.0 Hz, H-C_{ar}); ^{31}P NMR (300 Hz, benzene-d_6): δ = −17.2 (d, *J* = 65.5 Hz), 147.4 (d, *J* = 65.5 Hz); IR (ATR): $\tilde{\nu}$ = 3056 (s), 2927 (s), 2854 (s), 1710 (s), 1587 (m), 1493 (s), 1408 (s), 1271 (s), 1217 (s), 984 (s), 742 (s), 696 cm^{-1}; MS (ESI): *m/z* (%) = 1061 (41), 1059 (77), 826 (8), 523 (28), 489 (59), 459 (100), 431 (46), 345 (18); HRMS (ESI): calcd. for $[C_{59}H_{58}O_6P_2Si + Ag]^+$: 1059.253; found: 1059.253.

2-(1-Naphthyloxy)-tetrahydropyran (31)

A solution of **30** (5.00 g, 34.7 mmol), 3,4-dihydro-2*H*-pyran (9.46 mL, 104.0 mmol) and PPTS (0.87 mg, 3.47 mmol) in dichloromethane (100 mL) was stirred for 3 h under an argon atmosphere. The reaction was quenched by addition of half saturated brine (50 mL), and conc. aqueous $NaHCO_3$ (50 mL). The aqueous phase was extracted with dichloromethane. The combined organic phases were dried over $MgSO_4$ and the solvent was removed under vacuum. The crude product was purified by chromatography (cyclohexane/EtOAc, 10:1) to afford **31** as a white oil; yield: 7.54 g (95%); TLC (hexane/EtOAc, 10:1): R_f = 0.73; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.59 – 1.82 (m, 3H, CH_2), 1.90 – 2.23 (m, 3H, CH_2), 3.64 (ddt, 1H, J_1 = 11.5 Hz, J_2 = 4.0 Hz, J_3 = 1.5 Hz, OCH_2), 3.93 (Ωtd, 1H, J_1 = 11.5 Hz, J_2 = 3.0 Hz, OCH_2), 5.64 (Ωt, 1H, *J* = 3.0 Hz, OCH), 7.12 (dd, 1H, J_1 = 7.5 Hz, J_2 = 1.0 Hz, H-C_{ar}), 7.36 (Ωt, 1H, *J* = 8.0 Hz, H-C_{ar}), 7.42 – 7.50 (m, 2H, H-C_{ar}), 7.79 (m, 1H, H-C_{ar}), 8.29 (m, 1H, H-C_{ar}); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.8 (t, CH_2), 25.3 (t, CH_2), 30.5 (t, CH_2), 61.9 (t, OCH_2), 96.3 (d, OCH), 108.2 (d, $C_{ar}H$), 121.0 (d, $C_{ar}H$), 122.0 (d, $C_{ar}H$), 125.2 (d, $C_{ar}H$), 126.0 (d, $C_{ar}H$), 126.2 (d, $C_{ar}H$), 127.5 (d, $C_{ar}H$), 134.5 (s, C_{ar}), 152.5 (s, C_{ar}-O); M/S (EI): *m/z* (%) = 208 (4), 185 (4), 129 (8), 111 (12), 97 (31), 84 (23), 83 (32), 69 (51), 57 (73), 55 (100); HRMS (EI): calcd. for $C_{15}H_{16}O_2$: 228.115; found: 228.116; anal. calcd. for $C_{15}H_{16}O_2$: C 78.92, H 7.06; found: C 78.88, H 7.15.

Diphenyl-[1-(tetrahydropyran-2-yloxy)-2-naphthyl]-phosphane (32)

According to general procedure I, a solution of **31** (3.00 g, 13.1 mmol) in THF (45 mL) was reacted with *n*-BuLi (15.8 mmol) and chlorodiphenylphosphane (3.48 g, 2.91 mL, 15.8 mmol). The crude product was purified by chromatography (cyclohexane/EtOAc, 20:1) to afford **32** as a faint yellow foam; yield: 3.75 g (73%); TLC (hexane/EtOAc, 10:1): $R_f = 0.60$; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.45-1.58$ (m, 3H, CH_2), 1.88–2.07 (m, 3H, CH_2), 3.30 (m, 1H, OCH_2), 4.00 (m, 1H, OCH_2), 5.20 (m, 1H, OCH), 6.90 (dd, 1H, $J_1 = 7.5$ Hz, $J_2 = 3.5$ Hz, H-C_{ar}), 7.24 (m, 4H, H-C_{ar}), 7.31 (m, 6H, H-C_{ar}), 7.41–7.49 (m, 2H, H-C_{ar}), 7.52 (m, 1H, H-C_{ar}), 8.34 (m, 1H, H-C_{ar}); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 20.5$ (t, CH_2), 25.1 (t, CH_2), 31.1 (t, CH_2), 64.8 (t, OCH_2), 104.5 (d, OCH), 123.8 (d, CH_{ar}), 124.0 (d, $C_{ar}H$), 125.6 (d, $C_{ar}H$), 126.7 (d, $C_{ar}H$), 127.2 (d, $C_{ar}H$), 128.0–128.3 (md, $C_{ar}H$), 130.2 (d, $C_{ar}H$), 133.5 (d, $J_{CP} = 20.0$ Hz, $C_{ar}H$), 134.1 (d, $^2J_{CP} = 20.0$ Hz, $C_{ar}H$), 135.8 (s, C_{ar}), 137.3 (s, $J_{CP} = 6.5$ Hz, C_{ar}), 137.3 (s, $J_{CP} = 10.0$ Hz, C_{ar}), 158.1 (s, $^2J_{CP} = 20.0$ Hz, $C1_{ar}$-O); ^{31}P NMR (121 MHz): $\delta = -16.22$ (s); IR (ATR): $\tilde{\nu} = 3048$ (m), 2940 (s), 2848 (m), 1580 (m), 1557 (m), 1496 (w), 1477 (m), 1432 (s), 1355 (s), 1256 (m), 1195 (m), 1116 (m), 1071 (s), 1030 (s), 937 (m), 904 (s), 813 (m), 744 (s), 695 cm^{-1} (s); M/S (EI): *m/z* (%) = 412 (10), 328 (100, -THP), 249 (60), 199 (39), 183 (28), 144 (84); HRMS (EI): calcd. for $[C_{27}H_{25}O_2P + H]^+$: 412.159; found: 412.158.

2-Diphenylphosphanyl-1-naphthol (33)

A solution of **32** (1.74 g, 4.22 mmol) and *p*-TsOH (1.20 g, 6.33 mmol) in MeOH (30 mL) was stirred for 2 h under an argon atmosphere. The reaction was quenched by addition of brine (30 mL). After a standard work-up with MTBE, the combined organic phases were dried over $MgSO_4$. After removal of the solvent under vacuum, the crude product was purified by flash-chromatography (cyclohexane/EtOAc, 30:1) to afford **33** as a yellow solid; yield: 0.84 g (61%); TLC (hexane/EtOAc, 10:1): $R_f = 0.48$; mp 90 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.08$ (dd, 1H, $J_1 = 8.5$ Hz, $J_2 = 4.5$ Hz, H-C_{ar}), 7.25–7.42 (m, 10H, H-C_{ar}), 7.51 (m, 2H, H-C_{ar}), 7.63 (m, 1H, H-C_{ar}), 8.29 (m, 1H, H-C_{ar}); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 112.6 (s, C_{ar}-P), 120.6 (d, $J_{PP} = 2.0$ Hz, $C_{ar}H$), 123.0 (d, $J_{PP} = 3.0$ Hz, $C_{ar}H$), 123.9 (s, C_{ar}-P), 125.7 (d, $C_{ar}H$), 127.6 (d, $J_{PP} = 22.0$ Hz, $C_{ar}H$), 128.7 (d, $J_{PP} = 7.0$ Hz, $C_{ar}H$), 128.9 (d, $C_{ar}H$), 129.8 (d, $C_{ar}H$), 133.2 (d, $J_{CP} = 18.0$ Hz, $C_{ar}H$), 135.1 (s, C_{ar}), 135.5 (s, C_{ar}), 157.0 (s, $^2J_{CP} = 20.5$ Hz, C_{ar}-1); ^{31}P NMR (121 MHz): $\delta = -32.47$ (s); IR (ATR, cm^{-1}): $\tilde{\nu} = 3393$ (bs, OH), 3049 (s), 2922 (w), 1954 (w), 1816 (w), 1623 (m), 1584 (m), 1565 (s), 1499 (m), 1477 (m), 1432 (s), 1383 (s), 1259 (s), 1246 (s), 1195 (m), 1129 (m), 1090 (m), 1068 (s), 1024 (m), 804 (s), 741 (s), 693 (s), 663 cm^{-1} (m); MS (EI): *m/z* (%) = 328 (4), 266 (100), 249 (37), 220 (40), 201 (88), 189 (27), 126 (15), 77 (20), 47 (11); HRMS (EI): calcd. for $C_{22}H_{17}OP$: 328.102; found: 328.101.

(3R,9R)-6-(2-Diphenylphosphanyl-1-naphthyloxy)-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro-1,3,5,7-tetraoxa-6-phosphaazulene (34)

According to general procedure III, a solution of **33** (0.28 g, 0.85 mmol) in THF (10 mL) under argon was treated with Et_3N (1.73 g, 2.38 mL, 17.06 mmol) and **12** (0.90 g, 1.70 mmol) in THF (4 mL). The crude product was purified by chromatography (hexane/EtOAc, 10:1) to afford **34** as a white foam; yield: 0.66 g (95%); TLC (hexane/EtOAc, 10:1): $R_f = 0.67$; mp 119 °C; $[\alpha]_\lambda$ (*c* 1.00, 20 °C, $CHCl_3$): $[\alpha]_{589}$: −94, $[\alpha]_{546}$: −146, $[\alpha]_{405}$: −593, $[\alpha]_{405}$: −1028; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.37$ (s, 3H, CH_3), 1.06 (s, 3H, CH_3), 5.09 (dd, 1H, $J_1 = 8.5$, $J_2 = 2.0$ Hz, CH), 5.17 (d, 1H, $J = 8.5$ Hz, CH), 6.91 (dd, 1H, $J_1 = 8.5$ Hz, J_2=3.0 Hz, CH_{ar}), 7.10–7.29 (m, 20H, H-C_{ar}), 7.31–7.50 (m, 10H, H-C_{ar}), 7.56 (m, 1H, H-C_{ar}), 7.72 (m, 3H, H-C_{ar}), 8.42 (d, 1H, $J = 8.5$ Hz, H-C_{ar}); ^{31}P NMR (121 MHz): $\delta = -17.9$ (d, $^4J_{PP} = 60.5$ Hz, PPh_2), 147.3 [d, $^4J_{PP} = 60.5$ Hz, $P(OR)_2$]; IR (ATR): $\tilde{\nu} = 3053$ (m), 2986 (w), 2929 (w), 1952 (w), 1814 (w), 1582 (w), 1558 (m), 1492 (m), 1445 (s), 1432 (m), 1359 (m), 1247 (m), 1214 (s), 1163 (m), 1087 (m), 1031 (s), 1012 (s), 887 (s), 740 (s), 694 (s), 664 (m); MS (ESI): *m/z* (%) = 931 (100), 929 (89), 765 (9), 467 (8), 431 (16), 329 cm^{-1} (11); HRMS (ESI): calcd. for $[C_{22}H_{17}OP + Ag]^+$: 929.171; found: 929.172.

2-(1-Bromo-2-naphthyloxy)-tetrahydropyran (36):

A solution of **35** (4.46 g, 22.0 mmol), 3,4-dihydro-*2H*-pyran (5.43 mL, 60.0 mmol) and PPTS (0.50 g, 2.0 mmol) in dry dichloromethane (100 mL) was stirred for 5 h under an argon atmosphere. The reaction was quenched by addition of half saturated brine (50 mL). The aqueous phase was extracted with dichloromethane. The combined organic phases were dried over $MgSO_4$. After removal of the solvent under vacuum, the crude product was purified by chromatography (cyclohexane/EtOAc, 25:1) to afford **36** as a yellow oil; yield: 5.15 g (84%); TLC (hexane/EtOAc, 10:1): $R_f = 0.46$; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.60-1.80$ (m, 3H, CH_2), 1.85–2.30 (m 3H, CH_2), 3.60 (m, 1H, OCH_2), 3.97 (Ωtd, 1H, J_1 =11.0 Hz, $J_2 = 3.0$ Hz, OCH_2), 5.65 (Ωt, 1H, $J = 3.0$ Hz, OCH), 7.36–7.44 (m, 2H, H-C_{ar}), 7.55 (Ωdt, 1H, $J_1 = 8.0$ Hz, $J_2 = 1.0$ Hz, H-C_{ar}), 7.73–7.80 (m, 2H, H-C_{ar}), 8.23 (d, 1H, $J = 8.5$ Hz, H-C_{ar}); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 18.3$ (t, CH_2), 25.2 (t, CH_2), 30.2 (t, CH_2), 61.9 (t, OCH_2), 97.1 (d, OCH), 110.5 (s, C_{ar}-Br), 117.4 (d, $C_{ar}H$), 124.5 (d, $C_{ar}H$), 126.3 (d, $C_{ar}H$), 127.4 (d, $C_{ar}H$), 128.0 (d, $C_{ar}H$), 128.6 (d, $C_{ar}H$), 130.3 (d, $C_{ar}H$), 133.2 (s, C_{ar}), 151.4 (s, C_{ar}); IR (ATR): $\tilde{\nu} = 3058$ (w), 2941 (s), 2868 (m), 1622 (s), 1595 (s), 1500 (s), 1462 (s), 1428 (m), 1382 (m), 1349 (s), 1239 (m), 1255 (s), 1200 (s), 1119 (s), 1020 (s), 999 (s), 962 (s), 895 (s), 871 (s), 804 (s), 744 cm^{-1} (s); M/S (EI): *m/z* (%) = 306 (1), 224 (98), 222 (100), 194 (17), 192 (17), 144 (76), 115 (72), 114 (77), 85 (77), 55 (48); HRMS (EI): calcd. for $C_{15}H_{15}BrO_2$: 306.026; found: 306.026.

Diphenyl-[2-(tetrahydropyran-2-yloxy)-1-naphthyl]-phosphane (37)

According to general procedure I, a solution of **36** (3.07 g, 10.0 mmol) in THF (50 mL) was reacted with *n*-BuLi (12.0 mmol) and chlorodiphenylphosphane (0.33 g, 15.0 mL, 3.6 mmol). However, the mixture was not warmed up prior to the addition of the chlorophosphane at −78 °C. The crude product was purified by flash-chromatography (cyclohexane/EtOAc, 25:1) to afford **37** as a faint yellow foam; yield: 3.58 g (87%); TLC (hexane/EtOAc, 10:1): $R_f = 0.28$; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.83-0.88$ (m, 1H, CH_2), 1.12–1.35

(m, 4H, CH_2), 1.37 – 1.55 (m, 1H, CH_2), 3.50 (ψdt, J_1 = 11.0 Hz, J_2 = 4.0 Hz, 1H, OCH_2), 3.62 (ψdt, J_1 = 11.0 Hz, J_2 = 3.0 Hz, 1H, OCH_2), 5.20 (ψt, J = 3.0 Hz, 1H, OCH), 7.16 – 7.59 (m, 12H, H-C_{ar}), 7.80 (d, J = 8.0 Hz, 1H, H-C_{ar}), 7.95 (d, J = 9.0 Hz, 1H, H-C_{ar}), 8.96 (ψt, J = 8.0 Hz, 1H, H-C_{ar}); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.8 (t, CH_2), 25.0 (t, CH_2), 29.3 (t, CH_2), 61.6 (t, OCH_2), 96.9 (d, OCH), 116.2 (d, $C_{ar}H$), 123.7 (d, $C_{ar}H$), 126.5 – 128.3 (md, $C_{ar}H$), 129.6 (s, J_{CP} = 6.0 Hz, C_{ar}), 131.0 (d, J_{CP} = 18.5 Hz, $C_{ar}H$), 132.3 (d, J_{CP} = 19.0 Hz, $C_{ar}H$), 133.1 (d, $C_{ar}H$), 136.2 (dσ, J_{CP} = 20.0 Hz, C_{ar}), 138.2 (s, J_{CP} = 11.5 Hz, C_{ar}), 138.7 (s, J_{CP} = 25.5 Hz, C_{ar}), 159.0 (s, C_{ar}); ^{31}P NMR (121 MHz): δ = −22.68 (s); IR (ATR): $\tilde{\nu}$ = 3050 (m), 2940 (s), 2869 (m), 2846 (m), 1616 (m), 1589 (m), 1503 (s), 1478 (m), 1455 (m), 1431 (s), 1316 (m), 1257 (m), 1234 (s), 1200 (m), 1117 (s), 1074 (w), 1029 (s), 1005 (s), 965 (s), 897 (s), 871 (s), 818 (s), 744 (s), 694 cm^{-1} (s); M/S (EI): *m/z* (%) = 412 (10), 327 (79), 328 (100, M – THP), 249 (36), 202 (18), 183 (20), 85 (25), 56 (18); HRMS (EI): calcd. for $C_{27}H_{25}O_2P$: 412.1592; found: 412.159.

1-Diphenylphosphanyl-2-naphthol (38)

A solution of **37** (3.12 g, 7.56 mmol) and *p*-TsOH (2.16 g, 11.35 mmol) in MeOH (100 mL) was stirred for 30 min under an argon atmosphere. The solution was passed through a plug of alumina N. After removal of the solvent under vacuum, the crude product was purified by flash-chromatography (cyclohexane/EtOAc, 20:1) to afford **38** as a yellow foam; yield: 1.53 g (62%); TLC (hexane/EtOAc, 10:1): R_f = 0.28; mp 118 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.15 – 7.27 (m, 4H, H-C_{ar}), 7.26 – 7.32 (m, 4H, H-C_{ar}), 7.39 – 7.47 (m, 4H, H-C_{ar}), 7.71 – 7.82 (m, 2H, H-C_{ar}), 7.88 (d, 1H, J = 10.0 Hz, H-C_{ar}), 8.04 (m, 1H, H-C_{ar}), 13.3 (1H, OH); ^{31}P NMR (121 MHz): δ = −36.6 (s); IR (ATR): $\tilde{\nu}$ = 3469 (m), 3289 (w), 3100 (bs, OH), 3051 (s), 2951 (w), 1953 (w), 1814 (w), 1615 (s), 1595 (s), 1566 (m), 1504 (m), 1478 (m), 1456 (m), 1433 (s), 1383 (m), 1339 (s), 1238 (m), 1200 (s), 1125 (s), 1068 (m), 1026 (w), 997 (m), 906 (m), 820 (s), 776 (m), 742 (s), 693 cm^{-1} (s); MS (EI): *m/z* (%) = 328 (100), 249 (98), 202 (60), 201 (69), 183 (57), 115 (41), 77 (56), 50 (31); HRMS (EI): calcd. for $C_{22}H_{17}OP$: 328.102; found: 328.102.

(3*R*,9*R*)-6-(1-Diphenylphosphanyl-2-naphthyloxy)-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro-1,3,5,7-tetraoxa-6-phosphaazulene (39)

According to general procedure III, a solution of **38** (0.24 g, 0.73 mmol) was treated with Et_3N (1.11 g, 1.53 mL, 10.95 mmol) in THF (10 mL) and **12** (0.775 g, 1.46 mmol) in THF (2 mL). The crude product was purified by chromatography (hexane/EtOAc, 20:1) to afford **39** as a white foam; yield: 0.245 g (41%); TLC (hexane/EtOAc, 10:1): R_f = 0.65; mp 95 °C; $[\alpha]_\lambda$ (*c* 1.00, 20 °C, $CHCl_3$): $[\alpha]_{589}$: +51, $[\alpha]_{546}$: +33, $[\alpha]_{405}$: −101; ^{1}H NMR (300 MHz, benzene-d_6): δ = 0.79 (s, 3H, CH_3), 0.86 (s, 3H, CH_3), 5.56 (d, 1H, J = 8.0, CHO), 6.01 (d, 1H, J = 8.0 Hz, CHO), 6.93 – 7.19 (m, 20H, H-C_{ar}), 7.47 – 7.62 (m, 8H, H-C_{ar}), 7.69 (ψd, 2H, J = 8.0 Hz, H-C_{ar}), 7.79 (ψd, 2H, J = 8.0 Hz, H-C_{ar}), 7.87 (m, 3H, H-C_{ar}), 8.42 (d, 1H, J = 8.5 Hz, H-C_{ar}); ^{31}P NMR (121 MHz): δ = −22.6 (d, $^4J_{PP}$ = 59.0 Hz, PPh_2), 134.8 [d, $^4J_{PP}$ = 59.0 Hz, $P(OR)_2$]; IR (ATR): $\tilde{\nu}$ = 3464 (w) 3053 (m), 2987 (w), 2931 (w), 1953 (w), 1890 (w), 1615 (m), 1588 (m), 1493 (m), 1446 (s), 1432 (s), 1369 (m), 1343 (w), 1212 (s), 1163 (m), 1087 (m), 1050 (m), 1028 (m), 994 (s), 823 (s), 796 (m), 740 (s), 695 (s), 661 cm^{-1} (m); MS (ESI): *m/z* (%) = 931 (92), 929 (84), 885 (63), 877 (100), 535 (54), 447 (48), 431 (39), 345 (16); HRMS (ESI): calcd. for $[C_{22}H_{17}OP + Ag]^+$: 929.171; found: 929.173.

General Procedure for the Enantioselective Hydroboration of Styrene: Preparation of 1-Phenylethanol (41)

A flame-dried and argon-flushed Schlenk tube was charged with bis(1,5-cyclooctadiene)rhodium(I) tetrafluoroborate (8.1 mg, 0.02 mmol) and the chiral ligand (0.022 mmol). The flask was evacuated and flushed with argon (3 ×). Then DME (1 mL) was added and the mixture was stirred for 0.5 hours at rt (usually orange to red suspensions). After addition of styrene **40** (114 μL, 1 mmol) the mixture was cooled to −78 °C and catecholborane (128 μL, 1.2 mmol) was added. *Note: Since catecholborane is a low melting compound and tends to solidify, the addition should occur relatively fast using a large diameter cannula.* Stirring was continued for the time indicated at −78 °C and quenched with MeOH (2 mL), 3 M aqueous NaOH (2.4 mL,) and aqueous H_2O_2 (35%, 208 μL, 2.4 mmol). The green-brownish suspension was stirred for 3 hours at rt.

Method A: The reaction mixture was transferred to a separation funnel and extracted with MTBE (3 ×). The combined organic layers were washed with 1 M aqueous NaOH and saturated aqueous NH_4Cl, and dried over $MgSO_4$. The solvent was removed under vacuum and the crude product was subjected to preparative rotational chromatography (hexane/EtOAc, 3:1) to afford **41** as a pale yellow oil. The enantiomeric excess was determined by HPLC using a chiral stationary phase (Chiralcel O*J*, hexane/2-propanol, 9:1, 0.8 mL min^{-1}).

Method B: To the reaction mixture was added MTBE (3 mL), and dodecane (114 μL, 0.5 mmol) as an internal standard. An aliquot of the organic layer was passed through a plug of alumina N, which was washed with MTBE. The resulting sample was analyzed by GC using a chiral column (Macherey-Nagel, Lipodex A, 100 °C).

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