PAPER

Synthesis of hybrid dendritic molecules with diazaphospholidine oxide grafted at the surface of octavinylsilsesquioxane (OVS)†

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A range of dendritic molecules was made using the monodentate SEMI-ESPHOS phosphine oxide ligand, which was derivatised with a series of functional groups including bromide, vinyl, allyl and terminal alkyne. Several methods to attach the resulting precursors onto octavinylsilsesquioxane (OVS), ranging from hydrosilylation, Suzuki, Heck, Grubbs or Sonogashira coupling reactions, have been investigated. Cross-metathesis of SEMI-ESPHOS oxide dendrons containing vinyl end groups with OVS catalyzed by Grubbs' catalyst was proven to be effective in the formation of precursors for dendritic molecules based on OVS.

Introduction

Dendrimers are tree-like compounds with the possibility of structural control and location of functional groups throughout the molecule. They usually consist of a core, and dendron arms, which in turn have head groups attached to them. They have several potentially important uses including light emitting materials,[1–8] membrane components,[9] MRI contrast agents,[10] DNA intercalation compounds,[11] drug delivery systems[12] and catalyst supports.[13–16] In recent years, several groups have investigated the incorporation or complexation of transition metal fragments within the dendritic architecture, leading to a variety of metallodendritic species.[17] Among them, dendrimer-supported catalysts[18] combine the main advantages of both homogeneous and heterogeneous catalysts.[19] On the one hand, they present excellent solubility in common organic solvents, good activity resulting from the high availability of the catalytic centres, and a well-defined structure allowing thorough characterisation and better mechanistic understanding. On the other hand, their persistent shape and large size allow suitable membranes to separate them from the reaction products and solvents by ultrafiltration after homogeneous catalytic reactions.[20–25] Thus, they offer a neat solution to the separation problem, which has dogged the com-

mercialisation of some homogeneous catalysts.[19] Another striking feature of dendrimers concerns the use of their well-defined architecture to control the chemical and physical properties not only of the core but also of the peripheral groups or the linkers in the dendron arms. This control can lead to so-called "dendritic effects", which lead to changes in the activity, stability and/or selectivity of the catalyst on increasing the generations of the dendrimers. Such dendritic effects are the subject of an excellent review by Helms and Fréchet.[26] In particular, during extensive studies of polyhedral oligomeric silsesquioxane (POSS) based dendrimers[27–40] we discovered that a dendrimer with 16 terminal PPh_2P- groups gave much higher selectivity to the desired linear product (linear:branched ratio (l : b) = 13.9) in the oct-1-ene hydroformylation reaction than any of its small molecule analogues (l : b typically 2–5).[30,31] This was very specific for a dendrimer in which the Ph_2P groups were separated by a $-(CH_2)_2Si(CH_2)_2$ spacer. Shorter or longer chains, or replacing a C atom in the spacer by O were ineffective. Modelling studies using molecular mechanics[27] suggest that the reason for the enhanced selectivity is that crowding on the dendrimer periphery forces the phosphines into a position that is ideal for coordination in two equatorial sites of trigonal bipyramidal intermediates, which is known[41] to give increased linear selectivity for hydroformylation reactions. Bearing in mind that these peripheral constraints can change the selectivity of catalytic reactions so that the selectivities normally associated with bidentate ligands can be obtained with unidentate analogues, we postulated that inactive monodentate ligands could be turned into active bidentates upon attachment to the periphery of POSS cored dendrimers. Such an example is well illustrated by ESPHOS, a bidentate C_2 symmetric ligand, which is capable of catalysing the asymmetric hydroformylation of vinyl acetate with regio- and stereo-selectivities that are amongst the highest yet reported, whilst its unidentate analogue SEMI-ESPHOS, is a very poor ligand for this reaction.[42,43] We thus investigated the

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attachment of the inactive monodentate SEMI-ESPHOS ligand onto the periphery of a POSS cored dendrimer, anticipating that two or more of the SEMI-ESPHOS moieties might be held in such a way that they can effectively promote bidentate binding. In the end, we successfully synthesised several POSS based dendrimers bearing SEMI-ESPHOS peripheral groups and found that one, with 24 SEMI-ESPHOS groups, successfully reproduced some of the properties of ESPHOS, although not all of them.[37,40] During the course of these studies on SEMI-ESPHOS bearing dendrimers, we attempted various synthetic strategies towards their synthesis. Some of these strategies involved the synthesis of dendrimers bearing SEMI-ESPHOS oxide dendrimers, some of which subsequently turned out to have interesting and tuneable luminescent properties. We have reported the photophysical properties[44] but now report full details of the syntheses of these dendrimers.

Results and discussions

Synthesis of diazaphospholidine oxides

In order to attach SEMI-ESPHOS oxide ligands onto the POSS cube, we investigated three main routes to derivatise the standard SEMI-ESPHOS backbone, including the aromatic halogenation of a benzene ring and the tether of vinyl or alkyne groups to this backbone.

Octavinylsilsesquioxane-based dendrimer cores containing terminal alkynes and aryl borate esters synthesized in our group,[35] offer an ideal platform for C–C coupling reactions, such as Heck, Suzuki or Sonogashira. Aromatic halogenated SEMI-ESPHOS ligands have thus become target compounds in the grafting of this ligand onto a POSS cube.

Brominated SEMI-ESPHOS oxide ligands have already been synthesized,[46] giving rise to interesting precursors for the above couplings. It was reported that tetrabutylammonium tribromide (TBABr₃) was an efficient regioselective bromination agent for the monobromination of aromatic amines, affording predominantly parabromoaniline in high yield at 20 °C in CH₂Cl₂.[47] However, using this method in a solution of CH₂Cl₂–MeOH, the direct bromination of SEMI-ESPHOS oxide **3** (Scheme 1), prepared by oxidation of SEMI-ESPHOS **2** with *t*-BuOOH at room temperature,[48] led to a complicated mixture of products as assessed by $^{31}P\{^1H\}$ NMR. X-ray quality crystals, obtained from this solution, showed that the five membered diazaphospholidine ring was broken, producing the dibrominated product **4** (Scheme 1, c)) (see ESI for details on crystallographic data†). Nevertheless, in the absence of methanol, *para*-monobromination of SEMI-ESPHOS oxide **3** occurred on the *N*-benzene ring in CH₂Cl₂ with TBABr₃ offering compound **5** in 40% yield (Scheme 1, d)).

An alternative method to introduce a bromine group onto the *P*-benzene ring, affording SEMI-ESPHOS oxide
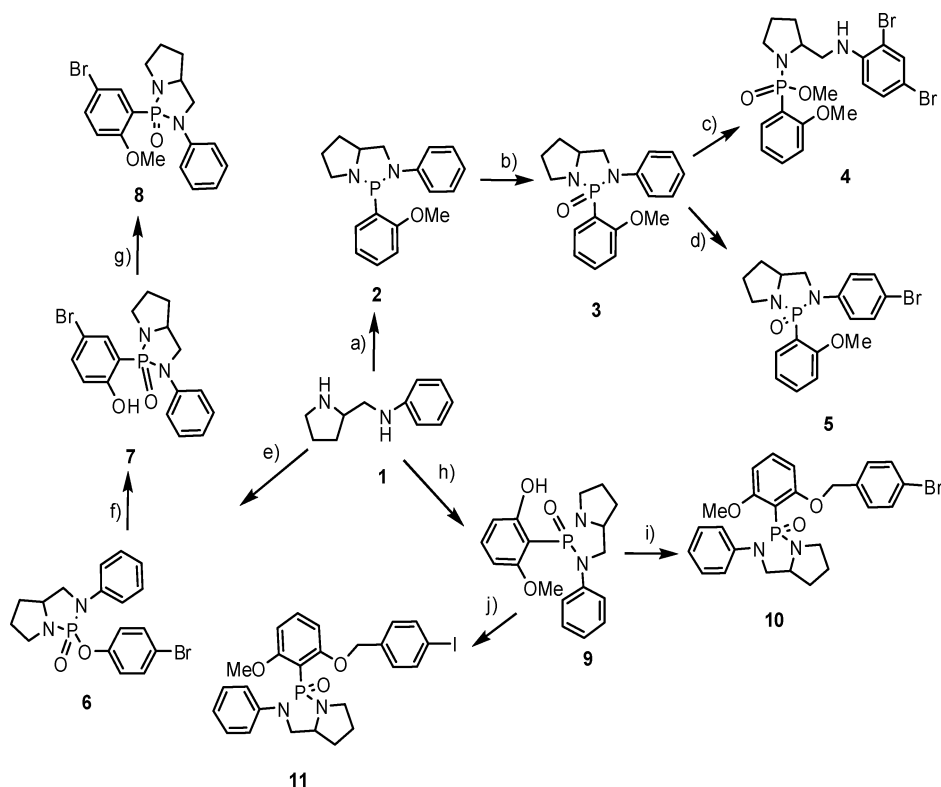
Scheme 1 Synthesis of SEMI-ESPHOS oxides functionalised with halides. Reagents and conditions: a) bis(dimethylamino)(*o*-methoxyphenyl)-phosphine,[45] toluene, reflux, 72 h, (55%); b) *t*-BuOOH, THF, room temperature, 3 h (84%); c) tetra-*n*-butylammonium tribromide (TBABr₃), CH₂Cl₂–MeOH; d) tetra-*n*-butylammonium tribromide (TBABr₃), CH₂Cl₂, room temperature, 18 h → reflux, 4 h, (40%); e) P(NMe₃)₃, toluene, reflux, 14 h → 4-bromophenol, reflux, 12 h → cooling to 0 °C, *t*- BuOOH, CH₂Cl₂ → room temperature, 8 h, (62%); f) −78 °C, THF, LDA, 4 h, → room temperature, (14%); g) MeI, K₂CO₃, acetone, 60 °C, 12 h, (94%); h) P(NMe₃)₃, toluene, reflux, 14 h → 3-methoxyphenol, reflux, 12 h → cooling to 0 °C, *t*-BuOOH, CH₂Cl₂ and room temperature, 8 h → −78 °C, THF, LDA, 4 h → room temperature, (70%); i) 4-bromobenzylbromide, 18-crown-6, THF, K₂CO₃, 60 h, (91%); j) 4-iodobenzylbromide, 18-crown-6, THF, K₂CO₃, 76 h, (80%).
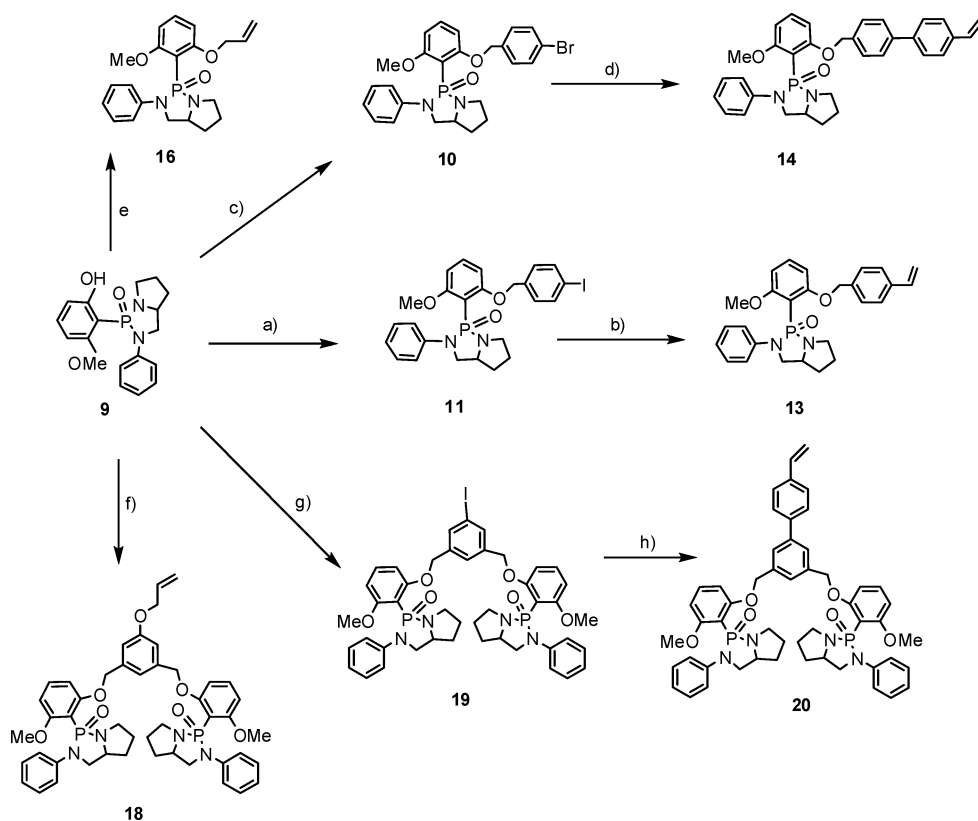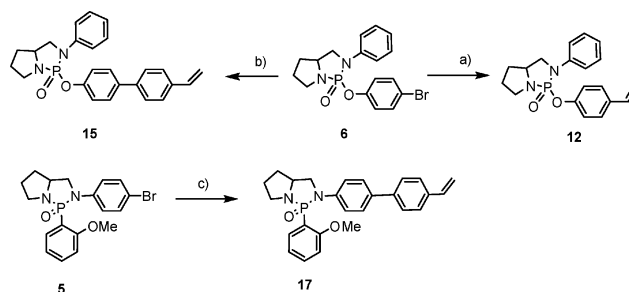
Scheme 2 Synthesis of SEMI-ESPHOS oxides functionalised with 4-vinyl groups (I). Reagents and conditions: a) 4-iodobenzylbromide, 18-crown-6, THF, K$_2$CO$_3$, 76 h, (80%); b) toluene, vinyltributylstannane, Pd(PPh$_3$)$_4$, 80 °C, 40 h, (88%); c) 4-bromobenzylic bromide, 18-crown-6, THF, K$_2$CO$_3$, 60 h, (91%); d) 4-styrene boronic acid, Pd(PPh$_3$)$_4$, 2 M K$_2$CO$_3$, THF, reflux, 48 h, (90%); e) allyl bromide, K$_2$CO$_3$, KI, acetone, 80 °C, 7 days, (72%); f) 1,3-bis(bromomethyl)-5-allyloxybenzene,[50] K$_2$CO$_3$, 18-crown-6, THF, reflux, 60 h, (73%); g) 1,3-bis(bromomethyl)-5-iodobenzene,[51] K$_2$CO$_3$, 18-crown-6, THF, reflux, 72 h, (64%); h) 4-styreneboronic acid, Pd(PPh$_3$)$_4$, K$_2$CO$_3$ (2 M), THF, reflux, 60 h, (70%).

8 (Scheme 1, e)–g)), involved a multi-step synthesis with a total yield of 8%. First, the thermodynamically driven reaction between tris(dimethylamino)phosphine and (*R*)-2-anilinomethylpyrrolidine (**1**) was carried out in refluxing toluene, releasing gaseous dimethylamine. After the addition of 4-bromophenol, the intermediate phosphine was oxidised with *t*-BuOOH at room temperature yielding **6** in 62% yield. Treatment of compound **6** with LDA in THF at −78 °C, led to a P–O to P–C rearrangement[49] giving the corresponding phosphine oxide **7** in very low yield (14%), presumably because of the undesirable metal-bromo exchange reaction between lithium and arylbromide. Methylation of **7** with MeI in refluxing acetone afforded **8**, for which X-ray structural details appear in the ESI†.

Eventually, the introduction of bromo or iodo groups was performed *via* the phosphine oxide ligand, **9**, synthesized according to literature procedures.[49] *O*-Alkylation of **9** with 4-bromobenzylbromide and 4-iodobenzylbromide, in the presence of K$_2$CO$_3$ and 18-crown-6 as a phase transfer agent afforded respectively, brominated SEMI-ESPHOS oxide **10** and iodinated SEMI-ESPHOS oxide **11** with total yields, based on (*R*)-2-anilinomethylpyrrolidine, of 47% and 41% (Scheme 1, h)–j)). The X-ray structure of **11** is shown in the supporting information.† We have previously shown the efficient functionalization of the eight terminal vinyl groups around octavinylsilsesquioxane *via* cross-metathesis (Grubbs' catalyst) and hydrosilylation (Karstedt's

catalyst).[35,38] In both cases, vinyl terminated dendrons were needed to achieve such couplings with OVS.

Whilst palladium-catalyzed Stille reactions of vinyltributylstannane with **6** and **11** afforded respectively the vinyl terminated compounds **12** (Scheme 3, a)) and **13** (Scheme 2, b)), Suzuki coupling of styrene-4-boronic acid with **5**, **6** and **10** gave 4-vinylbiphenyl tethered SEMI-ESPHOS oxides **14** (Scheme 2, d)), **15** and **17** (Scheme 3, b) and c)), respectively.

Scheme 3 Synthesis of SEMI-ESPHOS oxides functionalised with 4-vinyl groups (II). Reagents and conditions: a) toluene, vinyltributylstannane, Pd(PPh$_3$)$_4$, 80 °C, 40 h, (78%); b) 4-styreneboronic acid, Pd(PPh$_3$)$_4$, 2 M K$_2$CO$_3$, THF, reflux, 48 h, (77%); c) 4-styreneboronic acid, Pd(PPh$_3$)$_4$, K$_2$CO$_3$ (2 M), THF, reflux, 48 h, (56%).
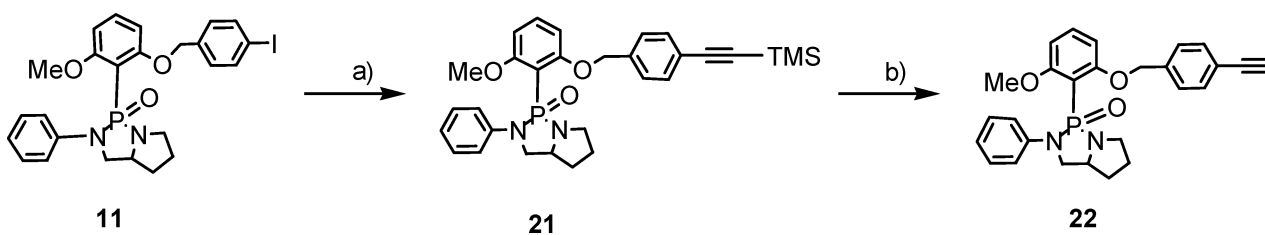
Scheme 4 Synthesis of SEMI-ESPHOS oxide functionalised with terminal alkynes. Reagents and conditions: a) trimethylsilylacetylene (TMSA), Pd(PPh$_3$)$_2$ Cl$_2$, CuI, PPh$_3$, Et$_3$N/THF, (60 °C), 16 h, (83%); b) K$_2$CO$_3$, CH$_2$Cl$_2$–MeOH, 4 h, room temperature, (86%).

The reaction of **9** with allyl bromide, carried out in THF in the presence of potassium carbonate and 18-crown-6, afforded the allyl terminated SEMI-ESPHOS oxide **16** in 72% yield (Scheme 2, e)). In addition, the 'pincer'-type ligands **18**, and **20** were designed using Fréchet type building blocks, 1,3-bis(bromomethyl)-5-allyloxybenzene[50] and 1,3-bis(bromomethyl)-5-iodobenzene,[51] synthesized via the sequence of reactions depicted in Scheme 2, f), g) and h).

Bromophenyl terminated octavinylsilsesquioxanes have already been synthesized[35] offering the possibility for C–C couplings such as a Sonogashira reaction with an alkyne terminated dendron. This group was attached onto SEMI-ESPHOS oxide **9** in two steps, via a Sonogashira reaction of **11** with trimethylsilylacetylene, followed by deprotection with methanolic K$_2$CO$_3$ in a mixture of CH$_2$Cl$_2$–MeOH at room temperature afforded compound **22** in 86% yield (Scheme 4).

Synthesis of dendritic molecules

The attachment of the halogenated, vinyl and alkyne terminated SEMI-ESPHOS oxides onto the POSS cube was then investigated via standard C–C coupling reactions, hydrosilylation and cross metathesis.

Both Suzuki cross-coupling reaction of **10** with an aryl borate ester decorated POSS core[35] and Sonogashira reaction of **22** with a bromophenyl terminated POSS[35] failed, as only partial substitution was obtained as indicated by MALDI-TOF mass spectrometry. Basic solutions together with long reaction times and high temperatures may have promoted the base-catalyzed ring-opening polymerization of the silsesquioxane cage resulting in the destruction of the dendritic structures.[52] Similarly, the failure in the Heck coupling of octavinylsilsesquioxane with dendron **11** resulted in only partial substitution of the cube as already observed by Sellinger et al. in a similar reaction.[53]

The hydrosilylation of allyl SEMI-ESPHOS oxide **16** onto the eight Si–H groups of a POSS cube, synthesised according to literature methods,[54] catalyzed by Karstedt's catalyst was monitored by ^{31}P{^{1}H} NMR. A new strong peak at 35.7 ppm appeared together with the disappearance of the peak at 26.09 ppm attributed to **16**. However, the former peak at 35.7 ppm characterized the hydroxyl SEMI-ESPHOS oxide **9**, so that the cleavage of the O-allyl bond in **16** impeded the hydrosilylation reaction of **9** with the POSS cube.

Eventually, we investigated the cross-metathesis of OVS with alkene terminated SEMI-ESPHOS catalyzed by Grubbs' catalyst. Hybrid dendritic molecules **23**, **24**, **25**, **26**, **27** and **28** were synthesized by metathesis of octavinylsilsesquioxane with dendrons **12**, **15**, **17**, **13**, **14** and **20** (Scheme 5). These reactions, carried out under a gentle reflux in dry CH$_2$Cl$_2$, were monitored by ^{1}H NMR

spectroscopy. After total disappearance of the vinylsilyl signal, the desired cube was purified by repeated precipitation, followed by column chromatography on silica gel to remove traces of side-products, mainly the homo-metathesis of SEMI-ESPHOS oxide arms. One of them, the homo-metathesis side product, **29**, has also been synthesised independently by homo-metathesis of **14**. (Fig. 1)
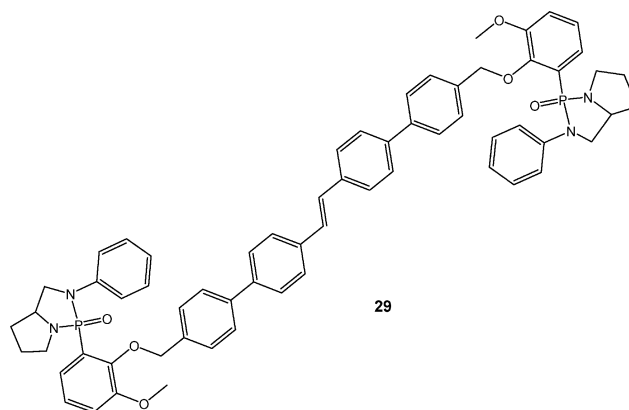
Fig. 1 Homo-metathesis side product **29** from self condensation of a vinylbiphenyl decorated SEMI-ESPHOS oxide, **14**.

The microanalyses were generally slightly higher in C than expected. This may be because of residual solvent trapped in the dendrimers. For dendrimers **23** and **28**, small amounts of petroleum are observed in the ^{1}HNMR spectra (see experimental). ^{1}H, ^{13}C NMR spectra and MALDI-TOF MS measurements (see ESI for the actual spectra†) on those compounds generally showed that the syntheses had been successful.

In all cases, except dendrimer **24**, peaks assigned to [M+Na]$^+$ are observed from the dendrimers with all 8 arms functionalised with SEMI-ESPHOS oxide. Despite the low excess of functionalised SEMI-ESPHOS oxide used in the cross metathesis, no significant peaks are observed for dendrimers with less than 8 arms functionalised. Peaks to lower mass are observed, but, where we are able to offer tentative assignments, these seem to be fragments of the fully functionalised dendrimer where sections of the SEMI-ESPHOS oxide have been lost. For **23**, this fragmentation appears to occur by cleavage of a C–O bond, whilst for **25** and **28**, the C–C bond of a biphenyl unit appears to break. This is particularly dramatic for **28**, where the parent ion and fragments assigned to cleavage of 1, 2, 3 and 4 biphenyl C–C bonds are observed. For **24**, the calculated molecular mass is 3740.29, but the parent ion is observed at 3800.50. We very tentatively assign this to [M + Na + 2H$_2$O]$^+$. Dendritic molecules **25** and **27** constructed on the chromophore 4-vinyl biphenyl bridges display strong blue light luminescence even
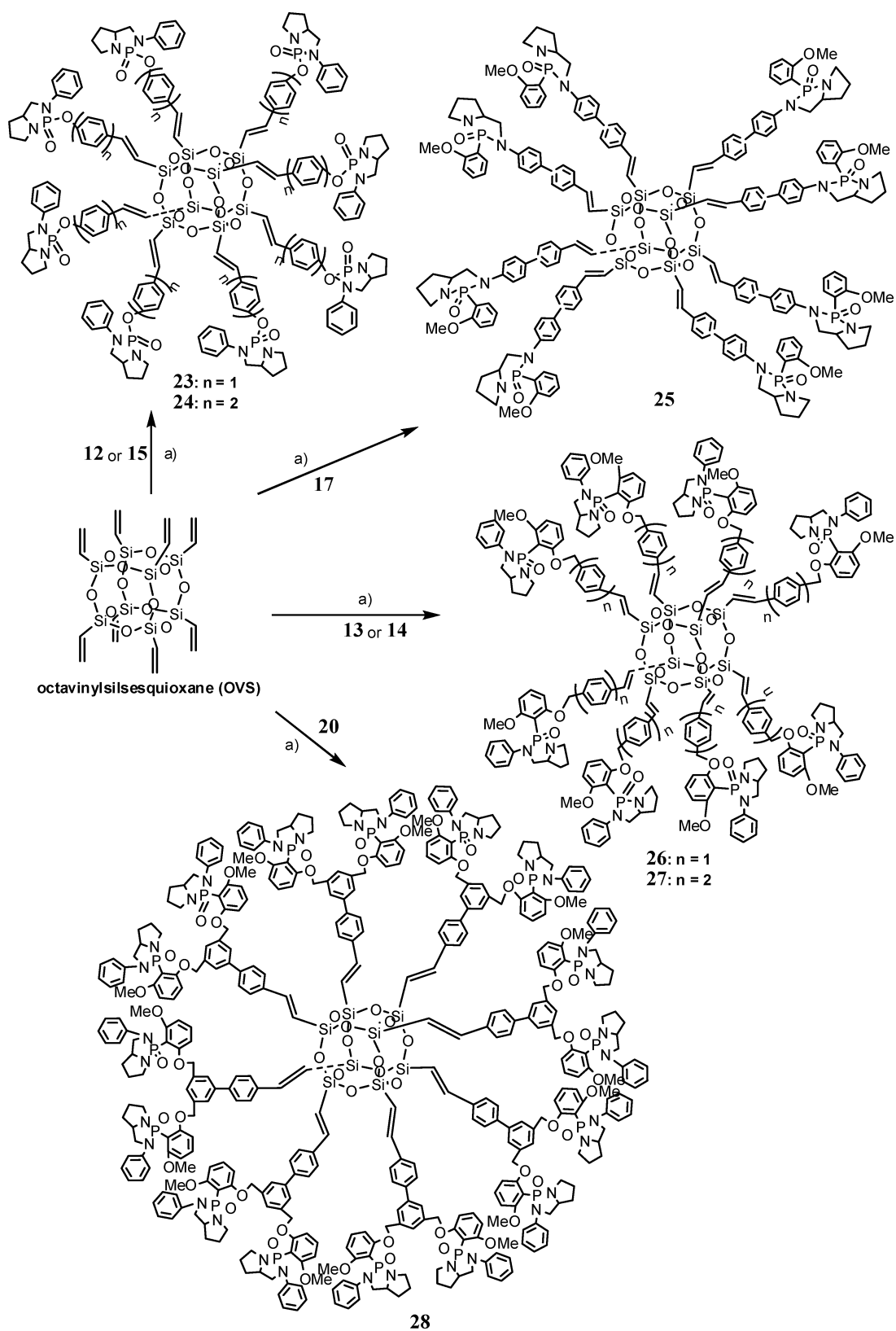
Scheme 5 Synthesis of hybrid dendritic molecules by cross-metathesis. Reagents and conditions: a) Grubbs' catalyst (1st gen.), CH₂Cl₂, reflux.

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under irradiation of sunlight. A detailed study of this blue light-emitting property based on photoluminescence quantum yields, steady state and time resolved solution spectroscopy along with molecular dynamics investigation and DFT calculation, showed that the bulky diazaphospholidine oxide groups bound on the tail of the chromophoric arms along with their connecting pattern produced effective steric hindrance at the peripheral surface of the dendritic structures, subsequently acting as a trigger to tune the photophysical properties of the resulting precursors of OVS based dendritic catalysts. Particularly, enhanced PL efficiency ($\Phi = 58\%$) was obtained for **25**, since successfully reducing intra-molecular degrees of freedom by the steric hindrance, resulting from the so-called dendritic effect, has favoured the radiative relaxation.[44]

Conclusions

The elaboration of octavinylsilsesquioxane (OVS) with halogenated, vinyl or alkyne modified SEMI-ESPHOS oxides at its surface is described. While standard C–C cross couplings and hydrosilylation reactions have failed to attach these ligands onto OVS, metathesis catalyzed by Grubbs' catalyst has proven to be a successful method for this purpose.

Experimental

General

All manipulations were carried out under dry and deoxygenated argon (treated by a column filled with Cr(II) on silica) using standard Schlenk techniques and moisture–sensitive reactions were conducted in oven-dried glassware. Column chromatography was performed using Merck 9385 silica 60. THF, diethyl ether, and light petroleum were degassed and dried by distillation from sodium diphenyl ketyl before use; toluene from sodium; CH_2Cl_2 from calcium hydride; and methanol or ethanol from magnesium alkoxide. Melting points were carried out with Gallenhamp Melting Point Apparatus and uncorrected. Microanalyses were carried out on a Carlo Erba 1110 CHNS analyzer. The ^1H, ^{13}C and ^{29}Si NMR spectra were recorded on a Bruker Avance 300 or a Bruker Avance II 400 NMR spectrometer. Matrix assisted laser desorption/ionization (MALDI) mass spectra were obtained using a Micromass TOF Spec 2E mass spectrometer system equipped with a 337 nm N_2 laser operating in the positive ion detection mode. Samples were generated by addition to the matrix (α-cyano-4-hydroxycinnamic acid or 2,5-dihydroxybenzoic acid, with NaI as an ionization promoter) and dissolved in a suitable solvent (THF or CH_2Cl_2) before being transferred to the sample holder and dried. The spectra were calibrated using a mixture of 4 peptides, angiotensin I & II, Renin substrate & ACTH clip (18–39). X-Ray diffraction studies on crystals were performed at 293 K using a Bruker SMART diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). All reagents were purchased from Aldrich. Octavinylsilsesquioxane,[55] (R)-5-oxopyrrolidine-2-carboxanilide,[56] bis(dimethylamino)(o-methoxyphenyl)phosphine,[45] (R)-2-anilinomethylpyrrolidine 1,[56] SEMI-ESPHOS 2,[48] 1,3-bis(bromomethyl)-5-allyloxybenzene,[50] and 1,3-bis(bromomethyl)-5-iodobenzene,[51] were prepared as described in the literature.

SEMI-ESPHOS oxide (3). To a solution of semi-ESPHOS, **2**, (8.65 g, 27.6 mmol) in THF (80 mL), t-butyl hydroperoxide (11 mL, 3 M, 33 mmol) was slowly added at 0 °C and the resulting mixture was stirred overnight. The solvent was removed in vacuo and the crude product collected by filtration and crystallized from toluene to give **3** as colorless crystals (7.6 g, 84%). Mp 146–148 °C. ^1H NMR (CDCl$_3$): δ_H (ppm) 1.76 (m, 1H), 1.92 (m, 1H), 2.12 (m, 2H), 2.96 (m, 1H), 3.50 (m, 1H), 3.74 (s, 3H), 3.88 (m, 2H), 3.92 (m, 1H), 6.82 (m, 2H), 7.03 (m, 3H), 7.14 (m, 2H, 7.39 (dd, 1H, $J = 7.4$ Hz, 1.0 Hz), 8.12 (dd, 1H, $J = 9.1$ Hz, 1.8 Hz). $^{13}C\{^1H\}$ NMR (CDCl$_3$): δ_H (ppm) 26.9 (d, $J = 2.2$ Hz), 33.8, 45.5, 49.1 (d, $J = 15.7$ Hz), 56.2, 59.6 (d, $J = 6.0$ Hz), 111.2 (d, $J = 8.2$ Hz), 116.1 (d, $J = 4.5$ Hz), 120.8 (d, $J = 14.2$ Hz), 120.9, 121.0, 129.3, 133.9 (d, $J = 1.5$ Hz), 137.0 (d, $J = 7.5$ Hz), 142.9, 160.9. $^{31}P\{^1H\}$ NMR (CDCl$_3$): δ_P (ppm) 26.56. MS calcd [M + Na]$^+$: = 351.1; found: 351.1; Anal. calcd for C$_{18}$H$_{21}$N$_2$O$_2$P: C 65.84, H 6.45, N 8.53. Found: C 65.78, H 6.53, N 8.53.

Modified SEMI-ESPHOS oxide (5). A solution of tetra-n-butylammonium tribromide (TBABr$_3$) (4.7 g, 9.7 mmol) in CH$_2$Cl$_2$ (20 mL) was added dropwise over 6 h at room temperature to a solution of **3** (3.1 g, 9.45 mmol) in CH$_2$Cl$_2$ (50 mL). The mixture was stirred overnight and refluxed for 4 h. After cooling to room temperature the reaction mixture was washed with 10% sodium thiosulfate solution, brine and water. The organic layer was separated and dried over MgSO$_4$. The solvent was evaporated in vacuo and the crude product purified by column chromatography on silica gel using ethyl acetate. Crystallization from ethyl acetate/petroleum ether afforded **5** as a white powder (1.5 g, 40%). Mp 174–176 °C. ^1H NMR (CDCl$_3$): δ_H (ppm) 1.76 (m, 2H), 2.01 (m, 2H), 2.94 (m, 1H), 3.39 (m, 1H), 3.68 (s, 3H), 3.78 (m, 2H), 3.90 (m, 1H), 6.72 (t, 1H, $J = 6.5$ Hz), 6.86 (d, 2H, $J = 8.4$ Hz), 6.96 (m, 1H), 7.19 (d, 2H, $J = 8.4$ Hz), 7.35 (t, 1 H, $J = 8.4$ Hz), 8.00 (qd, 1H, $J = 7.6$ Hz, 1.8 Hz). $^{13}C\{^1H\}$ NMR (CDCl$_3$): δ_C (ppm) 26.83, 33.75, 45.40, 49.16 (d, $J = 15.7$ Hz), 56.25, 59.61 (d, $J = 6$ Hz), 111.26 (d, $J = 8.2$ Hz), 113.53 117.68 (d, $J = 4.5$ Hz), 120.85, 121.04, 132.08, 134.19, 137.02 (d, $J = 7.5$ Hz), 141.25, 161.14. $^{31}P\{^1H\}$ NMR (C$_6$D$_6$): δ_P (ppm) 25.37. MS calcd [M]$^+$: 406.04; found: 406.9 (Br^{79}), 408.9(Br^{81}); Anal. calcd for C$_{18}$H$_{20}$BrN$_2$O$_2$P: C 53.09, H 4.95, N 6.88. Found: C 52.72, H 4.78, N 6.76.

Modified SEMI-ESPHOS oxide (6). A two-necked, round-bottomed flask containing dry toluene (40 mL) was charged with tris(dimethylamino)phosphine (7.67 g, 47 mmol) and (R)-2-anilinomethylpyrrolidine **1** (8.28 g, 47 mmol) under argon and the mixture was heated at 110 °C for 14 h. After cooling to room temperature, 4-bromophenol (8.1 g, 47 mmol) was added under argon and the mixture was heated at 110 °C for 12 h. After cooling to room temperature, the solvent was removed in vacuo. The crude phosphane was taken up in CH$_2$Cl$_2$ (50 mL) and this solution was cooled to 0 °C. Then t-butyl hydroperoxide (25 mL, 2 M, 50 mmol) was slowly added and the resulting mixture stirred for 8 h. After removal of the solvent in vacuo, the crude product was purified by crystallization from ethyl acetate/petroleum ether affording **6** as a white solid (11.5 g, 62%). Mp 108–110 °C. ^1H NMR (CDCl$_3$): δ_H (ppm) 1.73 (m, 2H), 2.07 (m, 2H), 3.10 (m, 1H), 3.34 (m, 1H), 3.56 (m, 2H), 3.88 (m, 1H), 6.92 (m, 2H), 7.03 (tt, 1H, $J = 7.2$ Hz, 1.1 Hz), 7.22 (d, 2H, $J = 8.6$ Hz), 7.35 (m, 4H). $^{13}C\{^1H\}$ NMR (CDCl$_3$): δ_C (ppm) 26.5 (d, $J = 3.0$ Hz), 32.8, 47.0

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(d, J = 3.0 Hz), 50.0 (d, J = 18.0 Hz), 57.4 (d, J = 9.8 Hz), 116.6, 116.6, 118.2, 122.2, 123.4, 123.5, 129.8, 132.9. ^{31}P{^{1}H} NMR (CDCl$_3$): δ_P (ppm) 18.80. MS calcd [M + H]$^+$: 393.04, [M + Na]$^+$: 415.02; found: 393.1, 415.1; Anal. calcd for C$_{17}$H$_{18}$BrN$_2$O$_2$P: C 51.93, H 4.61, N 7.12. Found: C 52.26, H 4.48, N 7.08.

Modified SEMI-ESPHOS oxide (7). A solution of LDA (2.5 mL, 2 M, 5 mmol) was slowly added to a stirred solution of **6** (982 mg, 2.5 mmol) in dry THF (25 mL) under argon at −78 °C. The mixture was stirred for 4 h and allowed to warm to room temperature. Then the mixture was quenched by addition of a saturated NH$_4$Cl solution (20 mL). The product was extracted with ethyl acetate. The combined organic layers were dried over MgSO$_4$, filtered, and concentrated to dryness *in vacuo*. The crude product was purified by column chromatography on silica gel using EtOAc, followed by crystallization from ethyl acetate/petroleum ether to afford **7** as a white solid (136 mg, 14%). Mp 124–126 °C. ^{1}H NMR (CDCl$_3$): δ_H (ppm) 1.69 (m, 1H), 1.97 (m, 3H), 2.91 (m, 1H), 3.52 (m, 1H), 3.67 (m, 1H), 4.03 (m, 2H), 6.76 (dd, 1H, J = 8.4, 6.7 Hz), 6.89 (t, 3H, J = 7.6 Hz), 7.19 (m, 3H), 7.33 (dd, 1H, J = 4.9 Hz, 1.8 Hz), 11.11 (s, 1H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ_C (ppm) 27.1, 32.7, 44.8, 49.9 (d, J = 14.0 Hz), 60.4, 116.9 (d, J = 6.3 Hz), 120.1 (d, J = 12.1 Hz), 122.6, 129.8, 133.8 (d, J = 8.4 Hz), 137.5, 138.3, 140.4, 160.8, 162.1. ^{31}P{^{1}H} NMR (CDCl$_3$): δ_P (ppm) 33.36. MS calcd [M]$^+$: 394.03 (Br^{81}), [M + Na]$^+$: 417.02; found: 394.96 (Br^{81}), 416.93; Anal. calcd for C$_{17}$H$_{18}$BrN$_2$O$_2$P: C 51.93, H 4.61, N 7.12. Found: C 52.32, H 4.88, N 6.86.

Modified SEMI-ESPHOS oxide (8). MeI (429 mg, 3 mmol) and K$_2$CO$_3$ (414 mg, 3 mmol) under argon were added to a solution of **7** (116 mg, 0.3 mmol) in acetone (15 mL). The mixture was stirred at 60 °C overnight under argon. After cooling to room temperature, it was filtered and evaporated *in vacuo*. The crude product was purified by crystallization from ethyl acetate/petroleum ether to afford **8** as a white solid (115 mg, 94%). Mp 196–198 °C. ^{1}H NMR (CDCl$_3$): δ_H (ppm) 1.72 (m, 1H), 1.85 (m, 1H), 2.10 (m, 2H), 2.94 (m, 1H), 3.46 (m, 1H), 3.65 (s, 3H), 3.79 (m, 2H),3.92 (m, 1H), 6.58 (dd, 1H, J = 8.8 Hz, 6.4 Hz), 6.79 (t, 1H, J = 7.2 Hz), 6.98 (d, 2H, J = 7.7 Hz), 7.09 (m, 2H), 7.41 (q, 1H, J = 8.8 Hz), 8.18 (m, 1H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ_C (ppm) 26.9, 33.7, 45.3, 49.2 (d, J = 15.8 Hz), 56.5, 59.7 (d, J = 6.1 Hz), 113.2 (d, J = 8.8 Hz), 116.3 (d, J = 4.6 Hz), 121.4, 129.4, 136.4, 139.4 (d, J = 8.2 Hz), 140.9, 142.1, 160.8, 162.0. ^{31}P{^{1}H} NMR (CDCl$_3$): δ_P (ppm) 24.18. MS calcd [M + H]$^+$: 407.05, [M + Na]$^+$: 430.04; found: 407.27, 430.27. Anal. calcd for C$_{18}$H$_{20}$BrN$_2$O$_2$P: C 53.09, H 4.95, N 6.88. Found: C 52.52, H 5.18, N 7.18.

Modified SEMI-ESPHOS oxide (9). A two-necked, round-bottomed flask containing dry toluene (30 mL) was charged with tris(dimethylamino)phosphine (4.7 g, 28.75 mmol) and (*R*)-2-anilinomethylpyrrolidine **1** (5.06 g, 28.75 mmol) under argon and the mixture was heated at 110 °C for 10 h. After cooling to room temperature, 3-methoxyphenol (3.56 g, 28.75 mmol) was added under argon and the mixture was heated at 110 °C for 12 h. After cooling to room temperature, the solvent was removed *in vacuo*. The crude phosphane was taken up in CH$_2$Cl$_2$ (40 mL) and this solution was cooled to 0 °C. *Tert*-butyl hydroperoxide (16 mL, 2 M, 32 mmol) was slowly added and the resulting mixture was stirred for 8 h. After the solvent was removed *in vacuo*, the crude product was collected by filtration and crystallized from ethyl

acetate/petroleum ether to afford a diazaphospholidine oxide intermediate as white needles (6.9 g, 70%). Mp 108–110 °C. ^{1}H NMR (CDCl$_3$): δ_H (ppm) 1.58 (m, 1H), 1.86 (m, 3H), 2.96 (m, 1H), 3.16 (m, 1H), 3.32 (m, 1H), 3.41 (m, 1H), 3.48 (s, 3H), 3.73 (m, 1H), 6.38 (dd, 1H, J = 3.6 Hz, J = 2.3 Hz), 6.49 (m, 2H), 6.86 (t, 1H, J = 7.2 Hz), 7.19 (m, 5H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ_C (ppm) 26.5 (d, J = 3.6 Hz), 32.8, 47.0 (d, J = 2.8 Hz), 50.1 (d, J = 17.8 Hz), 55.6, 57.5 (d, J = 10.3 Hz), 107.4 (d, J = 4.6 Hz), 111.2, 113.7 (d, J = 4.0 Hz), 116.6 (d, J = 4.7 Hz), 121.9, 129.7, 130.1, 141.7, 160.8, 161.8. ^{31}P{^{1}H} NMR (CDCl$_3$): δ_P (ppm) 18.56. MS calcd [M + H]$^+$: 345.13; found: 345.2.

A solution of LDA (17 mL, 2 M in THF, 34 mmol) was dropwise added to a stirred solution of the resulting intermediate (5.9 g, 17 mmol) in dry THF (100 mL) under argon at −78 °C. After the addition was complete, the mixture was allowed to warm to room temperature and quenched by slow addition of a saturated NH$_4$Cl solution (50 mL). The organic layer was separated and the aqueous layer extracted with ethyl acetate. The combined organic layers were dried over MgSO$_4$, filtered, and concentrated to dryness *in vacuo*. The crude product was purified by crystallization from ethyl acetate/petroleum ether to afford **9** as white crystals (4.3 g, 74%). Mp 194–196 °C. ^{1}H NMR (CDCl$_3$): δ_H (ppm) 1.77 (m, 1H), 1.95 (m, 1H), 2.15 (m, 2H), 3.03 (m, 1H), 3.54 (m, 1H), 3.71 (s, 3H), 3.80 (m, 1H), 3.90 (m, 1H), 4.02 (m, 1H), 6.20 (dd, 1H, J = 8.1 Hz, 5.9 Hz), 6.57 (dd, 1H, J = 8.3 Hz, 5.3 Hz), 6.88 (t, 1H, J = 7.2 Hz), 7.01 (d, 2H, J = 8.6 Hz), 7.26 (m, 3H), 12.08 (s, 1H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ_C (ppm) 26.8, 33.8, 45.1, 49.2 (d, J = 15.6 Hz), 56.6, 60.0 (d, J = 7.0 Hz), 100.6, 101.4 (d, J = 7.6 Hz), 110.9 (d, J = 11.2 Hz), 116.1 (d, J = 5.0 Hz), 121.7, 129.5, 135.1, 142.1, 161.8, 163.9. ^{31}P{^{1}H} NMR (CDCl$_3$): δ_P (ppm) 35.56. MS calcd [M + H]$^+$: 345.13, [M + Na]$^+$: 368.12; found: 345.2, 368.2.

Modified SEMI-ESPHOS oxide (10). 4-Bromobenzyl bromide (1.16 g, 4.6 mmol), 18-crown-6 (148 mg, 0.56 mmol), and K$_2$CO$_3$ (1.1 g, 7.96 mmol) were added under argon to a solution of **9** (1.55 g, 4.5 mmol) in THF (50 mL). The resulting mixture was refluxed and monitored by ^{31}P{^{1}H} NMR. After 60 h, compound **9** was consumed as the signal of 35.56 ppm completely disappeared. After cooling to room temperature, the mixture was filtered through a glass filter, concentrated and crystallized from ethyl acetate/petroleum ether to afford **10** as colorless crystals (2.1 g, 91%). Mp 142–144 °C. ^{1}H NMR (CDCl$_3$): δ_H (ppm) 1.55 (m, 1H), 1.67 (m, 1H), 1.89 (m, 2H), 2.78 (m, 1H), 3.37 (s, 3H), 3.39 (m, 1H), 3.54 (m, 2H), 3.73 (m, 1H), 4.76 (ABq, 2H, J = 12.5 Hz), 6.30 (dd, 2H, J = 8.4 Hz, J = 2.4 Hz), 6.71 (m, 1H), 7.10 (m, 7H), 7.66 (dd, 2H, J = 8.4 Hz, J = 2.4 Hz). ^{13}C{^{1}H} NMR (CDCl$_3$): δ_C (ppm) 26.6, 33.8, 46.5, 47.8 (d, J = 16.0 Hz), 56.3, 58.7 (d, J = 5.6 Hz), 70.5, 105.0 (d, J = 8.2 Hz), 105.9 (d, J = 8.2 Hz), 116.5 (d, J = 4.3 Hz), 120.7, 122.0, 129.1, 129.3, 132.0, 133.4, 136.3, 144.3 (d, J = 6.8 Hz), 161.6, 162.1. ^{31}P{^{1}H} NMR (CDCl$_3$): δ_P (ppm) 25.83. MS calcd [M + H]$^+$: 514.37, [M + Na]$^+$: 537.36; found: 514.9, 537.0. Anal. calcd for C$_{25}$H$_{26}$BrN$_2$O$_3$P: C 58.49, H 5.10, N 5.46. Found: C 58.82, H 4.92, N 5.11.

Modified SEMI-ESPHOS oxide (11). 4-Iodobenzylic bromide (2.0 g, 6.73 mmol), 18-crown-6 (300 mg, 1.13 mmol), and K$_2$CO$_3$ (2.0 g, 14.47 mmol) were added to a solution of **9** (2.02 g, 5.88 mmol) in THF (70 mL) under argon. The resulting mixture was refluxed and monitored by ^{31}P{^{1}H} NMR. After 76 h compound **9** was consumed as the signal at 35.56 ppm completely

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disappeared. The solvent was removed *in vacuo*. CH_2Cl_2 (30 mL) and brine (30 mL) were added to the residue and stirred for 15 min. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were dried over $MgSO_4$, filtered through a glass filter and concentrated *in vacuo*. The crude product was purified by crystallization from ethyl acetate/petroleum ether to afford **11** as colorless crystals (2.66 g, 80%). Mp 126–128 °C. ^1H NMR ($CDCl_3$) δ_H (ppm) 1.85 (m, 1H), 1.95 (m, 1H), 2.05 (m, 2H), 2.96 (m, 1H), 3.53 (s, 3H), 3.55 (m, 1H), 3.70 (m, 2H), 3.93 (m, 1H), 4.90 (ABq, 2H, $J = 12.7$ Hz), 6.45 (dd, 2H, $J = 8.4$ Hz, 2.2 Hz), 6.88 (m, 1H), 7.21 (m, 7H), 7.66 (dd, 2H, $J = 8.4$ Hz, 2.2 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ_C (ppm) 26.6, 33.8, 46.6, 47.9 (d, $J = 16.5$ Hz), 56.3, 58.8 (d, $J = 6.0$ Hz), 70.5, 93.6, 105.0 (d, $J = 8.2$ Hz), 106.0 (d, $J = 8.2$ Hz), 116.5 (d, $J = 4.5$ Hz), 120.7, 129.1, 129.5, 133.4, 137.0, 138.0, 144.2 (d, $J = 6.7$ Hz), 161.6, 162.1. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ_P (ppm) 25.97. MS calcd $[M]^+$: 560.07; found: 560.1; Anal. calcd for $C_{25}H_{26}IN_2O_3P$: C 53.58, H 4.68, N 5.00. Found: C 53.83, H 4.54, N 4.92.

Modified SEMI-ESPHOS oxide (12). Vinyltributylstannane (874 mg, 2.72 mmol) was added with a syringe to a solution of **6** (1.07 g, 2.72 mmol) and $[Pd(PPh_3)_4]$ (62 mg, 0.054 mmol) in toluene (15 mL) under argon. The mixture was heated at 80 °C for 40 h. After cooling to room temperature, it was diluted with CH_2Cl_2 (20 mL) and successively with water, a 10% ammonium hydroxide solution and brine. The organic layer was separated and dried over $MgSO_4$. After the solvent was removed *in vacuo*, the crude product was purified by column chromatography on silica gel using ethyl acetate to afford **12** as a white powder (816 mg, 88%). ^1H NMR ($CDCl_3$): δ_H (ppm) 1.62 (m, 2H), 1.92 (m, 2H), 3.04 (m, 1H), 3.25 (m, 1H), 3.45 (m, 2H), 3.79 (m, 1H), 5.15 (d, 1H, $J = 10.8$ Hz), 5.61 (d, 1H, $J = 17.6$ Hz), 6.59 (dd, 1H, $J = 17.6$ Hz, 10.8 Hz), 6.91 (m, 3H), 7.19 (m, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ_C (ppm) 26.6 (d, $J = 3.0$ Hz), 32.8 (d, $J = 3.0$ Hz), 47.0 (d, $J = 3.0$ Hz), 50.3 (d, $J = 18.0$ Hz), 57.5 (d, $J = 9.8$ Hz), 114.0, 116.6 (d, $J = 5.2$ Hz), 121.6 (d, $J = 4.5$ Hz), 122.0, 127.6, 130.0, 134.7, 136.3, 141.5, 151.0 (d, $J = 8.8$ Hz). $^{31}P\{^1H\}$ NMR (C_6D_6): δ_P (ppm) 18.72. MS calcd $[M + Na]^+$: 463.09; found: 363.09. Anal. calcd for $C_{19}H_{21}N_2O_2P$: C 67.03, H 6.22, N 8.23. Found: C 66.22, H 6.70, N 8.08.

Modified SEMI-ESPHOS oxide (13). Vinyltributylstannane (642.43 mg, 2.00 mmol) was added with a syringe to a solution of **11** (1.12 g, 2.00 mmol) and $[Pd(PPh_3)_4]$ (46 mg, 0.04 mmol) in toluene (15 mL) under argon. The mixture was heated to 80 °C for 40 h. After cooling to room temperature, it was diluted with CH_2Cl_2 (20 mL) and successively with water, a 10% ammonium hydroxide solution and brine. The organic layer was separated and dried over $MgSO_4$. After the solvent was removed *in vacuo*, the crude product was purified by column chromatography on silica gel using ethyl acetate to afford **13** as a white powder (754.40 mg, 82%). ^1H NMR ($CDCl_3$): δ_H (ppm) 2.02 (m, 2H), 2.94 (m, 1H), 3.50 (m, 3H), 3.54 (s, 3H), 3.66 (m, 2H), 3.93 (m, 1H), 4.93 (ABq, 2H, $J = 12.4$ Hz), 5.27 (d, 1H, $J = 10.8$ Hz), 5.78 (d, 1H, $J = 17.6$ Hz), 6.48 (m, 2H), 6.76 (dd, 1H, $J = 10.8$ Hz, 17.6 Hz), 6.87 (m, 1H), 7.23 (m, 5H), 7.36 (m, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ_C (ppm) 26.6, 33.8, 46.5, 48.1 (d, $J = 15.7$ Hz), 56.3, 58.8 (d, $J = 5.2$ Hz), 71.0, 104.8 (d, $J = 8.2$ Hz), 106.0 (d, $J = 8.2$ Hz), 114.3, 116.6 (d, $J = 3.7$ Hz), 120.7, 126.7, 127.9, 129.1, 129.4, 133.4, 136.8 (d $J = 6$ Hz), 137.4, 144.3, 144.4, 161.8, 162.3. $^{31}P\{^1H\}$ NMR ($CDCl_3$):

δ_P (ppm) 26.04. MS calcd $[M + Na]^+$: 483.18; found: 483.09. Anal. calcd for $C_{27}H_{29}N_2O_3P$: C 70.42, H 6.35, N 6.08. Found: C 69.82, H 6.71, N 5.91.

Modified SEMI-ESPHOS oxide (14). 4-styrene boronic acid (370 mg, 2.5 mmol), $[Pd(PPh_3)_4]$ (70 mg, 0.06 mmol) and a solution of K_2CO_3 (2 M, 3.5 mL) were added under argon to a solution of **10** (1.12 g, 2.0 mmol) in THF (18 mL). The mixture was heated at 75 °C for 48 h. After cooling to room temperature, the mixture was filtered through a glass filter and diluted with CH_2Cl_2 (40 mL) and water (10 mL). The aqueous layer was separated and extracted with CH_2Cl_2. The combined organic layers were washed with brine, water and dried over $MgSO_4$. After removal of the solvent *in vacuo*, the crude product was purified by column chromatography on silica gel using a gradient from CH_2Cl_2 to ethyl acetate and then acetone to afford **14** as a white powder (973 mg, 90%). ^1H NMR ($CDCl_3$): δ_H (ppm) 2.01 (m, 2H), 2.95 (m, 1H), 3.48 (m, 3H), 3.55 (s, 3H), 3.68 (m, 2H), 3.95 (m, 1H), 5.05 (ABq, 2H, $J = 12.8$ Hz), 5.30 (d, 1H, $J = 10.8$ Hz), 5.83 (d, 1H, $J = 17.6$ Hz), 6.49 (m, 2H), 6.75 (dd, 1H, $J = 10.8$ Hz, 17.6 Hz), 6.88 (m, 1H), 7.20 (m, 5H), 7.48 (m, 5H), 7.58 (m, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ_C (ppm) 26.62, 33.77, 46.55, 48.07 (d, $J = 15.7$ Hz), 56.27, 58.84 (d, $J = 5.2$ Hz), 70.93, 104.86 (d, $J = 8.2$ Hz), 105.99 (d, $J = 8.2$ Hz), 112.45, 114.36, 116.58 (d, $J = 4.5$ Hz), 120.69, 127.07, 127.35, 127.52, 128.18, 129.09, 132.44, 133.41, 136.38, 136.76, 137.06, 140.46, 144.31, 161.79, 162.28. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ_P (ppm) 26.04. MS calcd $[M + Na]^+$: 559.21; found: 559.17. Anal. calcd for $C_{33}H_{33}N_2O_3P$: C 73.86, H 6.20, N 5.22. Found: C 73.11, H 5.92, N 4.89.

Modified SEMI-ESPHOS oxide (15).[44] A mixture of **6** (1.04 g, 2.64 mmol), 4-styrene boronic acid (0.49 g, mmol), $[Pd(PPh_3)_4]$ (91 mg, mmol), K_2CO_3 (2 M, 3.2 mL), and THF (20 mL) was heated under argon at 75 °C for 48 h. After cooling to room temperature, CH_2Cl_2 (30 mL) and water (10 ml) were added, and the layers were separated. The aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with brine, water, and dried over $MgSO_4$. After evaporation of the solvent, flash column chromatograpy with CH_2Cl_2–ethyl acetate (4 : 1) afforded **15** as a white powder (850 mg, 77%). Mp 146–148 °C; $[M+Na]$ = 439.15; ^1H NMR ($CDCl_3$) δ_H (ppm) 1.72 (m, 2H), 2.05 (m, 2H), 3.15 (m, 1H), 3.36 (m, 1H), 3.59 (m, 2H), 3.90 (m, 1H), 5.29 (d, 1H, $J = 11.04$ Hz), 5.82 (d, 1H, $J = 17.6$ Hz), 6.76 (dd, 1H, $J = 17.6$ Hz, 11.04 Hz), 7.03 (tt, 1H, $J = 7.2$ Hz, 1.1 Hz), 7.11 (m, 2H), 7.27 (m, 2H), 7.36 (m, 2H), 7.50 (m, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ_C (ppm) 26.55 (d, $J = 3$ Hz), 32.79, 47.11, 50.31 (d, $J = 18$ Hz), 57.54 (d, $J = 9.8$ Hz), 114.37, 116.58, 116.64, 121.81, 121.87, 122.00, 127.06, 127.40, 128.31, 129.78, 136.70, 136.96, 137.72, 140.00; $^{31}P\{^1H\}$ NMR (C_6D_6): δ_P (ppm) 18.89; Anal. calcd for $C_{25}H_{25}N_2O_2P$: C 72.03, H 6.05, N 6.73. Found: C 71.41, H 5.63, N 6.25.

Modified SEMI-ESPHOS oxide (16). Allyl bromide (1.5 g, 12.4 mmol), K_2CO_3 (820 mg, 5.9 mmol) and KI (100 mg, 0.59 mmol) were added under argon to the solution of **9** (1.36 g, 3.95 mmol) in acetone (100 mL). The resulting mixture was refluxed at 80 °C and monitored by $^{31}P\{^1H\}$ NMR spectroscopy. After 7 days compound **9** was consumed (disappearance of the signal at 35.56 ppm). The solvent and excess allyl bromide were removed by distillation. CH_2Cl_2 (50 mL) and brine (30 mL) were added to the residue and the solution was stirred for 15 min. The

organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel using CH_2Cl_2 and crystallization from ethyl acetate/petroleum ether afforded **16** as colorless crystals (1.1 g, 72%). Mp 120–122 °C. ^{1}H NMR (CDCl$_3$): δ_H (ppm) 1.63 (m, 1H), 1.83 (m, 1H), 2.03 (m, 2H), 3.03 (m, 1H), 3.48 (s, 3H), 3.51 (m, 1H), 3.66 (m, 2H), 3.97 (m, 1H), 4.38 (dt, 2H, J = 7.0 Hz, 1.6 Hz), 5.31 (dq, 1H, J = 10.5 Hz, 1.6 Hz), 5.79 (dq, 1H, J = 17.2 Hz, 1.6 Hz), 6.39 (m, 3H), 6.79 (t, 1H, J = 7.2 Hz), 7.13 (m, 5 H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ_C (ppm) 26.57, 33.79, 46.60, 47.71 (d, J = 16 Hz), 56.23, 58.79 (d, J = 5.6 Hz), 70.12, 104.63 (d, J = 8.2 Hz), 105.82 (d, J = 8.2 Hz), 116.54 (d, J = 4.4 Hz), 118.08, 120.60, 129.00, 133.22, 133.45, 148.46, 153.58, 161.55, 162.25. ^{31}P{^{1}H} NMR (CDCl$_3$): δ_P (ppm) 26.08. MS calcd [M + H]$^+$: 385.17, [M + Na]$^+$: 407.15; found: 385.1, 407.1; Anal. calcd for $C_{21}H_{25}N_2O_3P$: C 65.61, H 6.55, N 7.29. Found: C 65.66, H 6.44, N 7.21.

Modified SEMI-ESPHOS oxide (17)[44]. A mixture of **5** (750 mg, 1.85 mmol), 4-styrene boronic acid (0.34 g, mmol), [Pd(PPh$_3$)$_4$] (65 mg, mmol), K$_2$CO$_3$ (2 M, 3.2 mL), and THF (16 mL) was heated under argon at 75 °C for 48 h. After cooling to room temperature, CH_2Cl_2 (30 mL) and water (10 mL) were added, and the layers were separated. The aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with brine, water, and dried over $MgSO_4$. After evaporation of the solvent, flash column chromatography with ethyl acetate afforded **17** as a pale yellow powder (440 mg, 56%). Mp 192–194 °C [M+Na] = 453.11; ^{1}H NMR (CDCl$_3$) δ_C (ppm) 1.79 (m, 2H), 2.12 (m, 2H), 3.02 (m, 1H), 3.55 (m, 1H), 3.78 (s, 3H), 3.94 (m, 3H), 5.25 (d, 1H, J = 17.4 Hz, 10.78 Hz), 5.72 (d, 1H, J = 18.47), 6.77 (dd, 1H, J = 17.4 Hz, 10.78 Hz), 6.81 (m, 1H), 7.04 (m, 1H), 7.13 (d, 2H, J = 8.3 Hz), 7.42 (m, 7 H), 8.11 (qd, 1H, J = 7.5 Hz, 1.8 Hz); ^{13}C{^{1}H} NMR (CDCl$_3$): δ_C (ppm) 26.89, 33.77, 45.47, 49.50 (d, J = 15 Hz), 56.27, 59.75 (d, J = 6 Hz), 111.42 (d, J = 8.2 Hz), 113.80, 116.40, 116.46, 120.83, 121.01, 126.86, 126.94, 127.68, 134.01, 136.21, 136.85, 136.94, 137.05, 140.48, 160.90; ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ_P (ppm) 26.44; Anal. calcd for $C_{26}H_{27}N_2O_2P$: C 72.54, H 6.32, N 6.51. Found: C 71.60, H 6.10, N 6.26.

Modified SEMI-ESPHOS oxide (18). 1,3-bis(bromomethyl)-5-allyloxybenzene (320 mg, 1 mmol),[50] 18-crown-6 (81 mg, 0.3 mmol) and K$_2$CO$_3$ (800 mg, 5.8 mmol) were added under argon to a solution of **9** (688.6 mg, 2 mmol) in THF (25 mL). The resulting mixture was refluxed and monitored by ^{31}P{^{1}H} NMR spectroscopy. After 60 h compound **9** was consumed (disappearance of the signal at 35.56 ppm). After cooling to room temperature, CH_2Cl_2 (60 mL) and brine (40 mL) were added and the solution was stirred for 15 min. Then the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were dried over $MgSO_4$, filtered through a glass filter and concentrated *in vacuo*. The residue was dissolved in a small amount of ethyl acetate and precipitated in petroleum ether. After filtration the crude product was purified by column chromatography on silica gel using a gradient from ethyl acetate to acetone affording **18** as a white solid (620 mg, 73%). Mp 88–92 °C. ^{1}H NMR (CDCl$_3$): δ_H (ppm) 1.74 (m, 4H), 1.98 (m, 4H), 2.90 (m, 2H), 3.41 (m, 2H), 3.47 (s, 6H), 3.59 (m, 4H), 3.87 (m, 2H), 4.44 (m, 2H), 4.95 (ABq, 4H. J =

8.4), 5.33 (m, 2H), 5.95 (m, 1H), 6.37 (m, 4H), 6.78 (m, 3H), 6.86 (d, 2H, J = 3.4 Hz), 7.14 (m, 10H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ_C (ppm) 26.62, 33.76, 46.52, 47.86 (d, J = 16.5 Hz), 56.27, 58.72, 69.15, 70.86, 104.78 (d, J = 8.2 Hz), 106.05 (d, J = 8.2 Hz), 113.07 (d, J = 5.3 Hz), 116.45 (d, J = 4.5 Hz), 117.90 (d, J = 6.7 Hz), 118.10, 120.65, 129.10, 129.46, 133.39, 133.60, 139.11, 144.31(d, J = 6.7 Hz), 159.43, 161.59, 162.29. ^{31}P{^{1}H} NMR (CDCl$_3$): δ_P (ppm) 25.94. MS calcd [M + H]$^+$: 847.33, [M + Na]$^+$: 849.32; Found: 847.30, 869.23. Anal. calcd for $C_{47}H_{52}N_4O_7P_2$: C 66.66, H 6.19, N 6.62. Found: C 66.10, H 6.17, N 6.48.

Modified SEMI-ESPHOS oxide (19). 1,3-bis(bromomethyl)-5-iodobenzene,[51] (389 mg, 1 mmol), 18-crown-6 (81 mg, 0.3 mmol), and K$_2$CO$_3$ (800 mg, 5.7 mmol) were added to a solution of **9** (688.6 mg, 2 mmol) in THF (30 mL) under argon. The resulting mixture was refluxed and monitored by ^{31}P{^{1}H} NMR spectroscopy. After 72 h compound **9** was consumed (disappearance of the signal at 35.56 ppm). After cooling to room temperature, CH_2Cl_2 (60 mL) and brine (40 mL) were added and the solution stirred for 15 min. Then the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were dried over $MgSO_4$, filtered through a glass filter and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel using a gradient from ethyl acetate to acetone to afford **19** as a white solid (585 mg, 64%). Mp 122–126 °C. ^{1}H NMR (CDCl$_3$): δ_H (ppm) 1.85 (m, 4H), 2.05 (m, 4H), 2.98 (m, 2H), 3.51 (m, 2H), 3.57 (br s, 6H), 3.67 (m, 4H), 3.97 (m, 2H), 4.98 (q, 4H, J = 8.2 Hz), 6.40 (m, 2H), 6.50 (m, 2H), 6.86 (m, 2H), 7.26 (m, 11H), 7.65 (d, 2H, J = 2.2 Hz). ^{13}C{^{1}H} NMR (CDCl$_3$): δ_C (ppm) 26.60, 33.74, 46.60, 47.91 (d, J = 16.5 Hz), 56.31, 58.73, 69.99, 94.97, 105.05 (d, J = 7.5 Hz), 105.97 (d, J = 8.2 Hz), 116.44 (d, J = 4.5 Hz), 120.72, 125.13, 125.24, 129.15, 133.44, 135.57 (d, J = 4.5 Hz), 139.79, 144.33, 161.21,162.19. ^{31}P{^{1}H} NMR (CDCl$_3$): δ_P (ppm) 26.01. MS calcd [M + H]$^+$: 917.21, [M + Na]$^+$: 939.19; found: 917.17, 939.16. Anal. calcd for $C_{44}H_{47}IN_4O_6P_2$: C 57.65, H 5.17, N 6.11. Found: C 56.83, H 5.02, N 5.77.

Modified SEMI-ESPHOS oxide (20). 4-styrene boronic acid (90 mg, 0.60 mmol), [Pd(PPh$_3$)$_4$] (20 mg, 0.017 mmol) and a solution of K$_2$CO$_3$ (2 M, 2.0 mL) were added under argon to a solution of **19** (500 mg, 0.55 mmol) in THF (10 mL). The mixture was heated at 75 °C for 48 h. After cooling to room temperature, the mixture was filtered through a glass filter and diluted with CH_2Cl_2 (40 mL) and water (10 mL). The aqueous layer was separated and extracted with CH_2Cl_2. The combined organic layers were washed with brine, water and dried over $MgSO_4$. After removal of the solvent, the crude product was purified by column chromatography on silica gel using a gradient from CH_2Cl_2 to ethyl acetate and then acetone to afford **20** as a white powder (304.5 mg, 62%). ^{1}H NMR (CDCl$_3$): δ_H (ppm) 1.65 (m, 4H), 1.91 (m, 4H), 2.88 (m, 2H), 3.49 (m, 8H), 3.57 (m, 4H), 3.86 (m, 2H), 4.85 (ABq, 4H, J = 12.6 Hz), 5.22 (d, 1 H, J = 10.8 Hz), 5.75 (d, 1 H, J = 17.6 Hz), 6.40 (m, 4H), 6.67 (dd, 1 H, J = 10.8 Hz, 17.6 Hz), 6.75 (m, 2H), 7.14 (m, 11 H), 7.40 (d, 2H, J = 8.6 Hz), 7.50 (m, 4 H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ_C (ppm) 26.57, 33.72, 46.61, 47.83, 56.28, 58.71, 71.05, 104.98, 106.20, 112.68, 114.78, 116.54, 120.68, 125.38, 127.07, 127.59, 128.01, 129.11, 132.64, 133.45, 136.12, 136.79,137.22, 140.78, 144.65, 161.56, 162.34. ^{31}P{^{1}H} NMR (CDCl$_3$): δ_P (ppm) 25.99. MS calcd [M]$^+$: 892.35; found:

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892.97. Anal. calcd for $C_{52}H_{54}N_4O_6P_2$: C 69.94, H 6.09, N 6.27. Found: C 69.24, H 5.77, N 5.76.

Modified SEMI-ESPHOS oxide (21). A Schlenk flask containing THF (30 mL) and Et$_3$N (10 mL) was charged with **11** (1.12 g, 2 mmol), [Pd(PPh$_3$)$_2$Cl$_2$] (100 mg, 0.14 mmol), CuI (10 mg, 0.05 mmol), and PPh$_3$ (15 mg, 0.057 mmol) under argon. The mixture was stirred at room temperature for 90 min. Trimethylsilylacetylene (245 mg, 2.5 mmol) was added with a syringe and the mixture was stirred at 60 °C for 16 h under argon. After cooling to room temperature the reaction mixture was filtered through a glass filter to remove the insoluble salts and the solvent was removed *in vacuo*. The crude product was purified by column chromatography on silica gel using EtOAc affording **21** as a white powder (880 mg, 83%). [M] = 530; ^{1}H NMR (CDCl$_3$): δ_H (ppm) 0.25 (s, 9H), 1.63 (m, 1H), 1.85 (m, 1H), 2.05 (m, 2H), 2.92 (m, 1H), 3.49 (m, 1H), 3.54 (s, 3H), 3.68 (m, 2H), 3.95 (m, 1H), 5.05 (br d, 2H, J = 3 Hz), 6.45 (dt, 2H, J = 8.4 Hz, 5.5 Hz), 6.87 (t, 1H, J = 6.8 Hz), 7.27 (m, 5H), 7.40 (br q, 4H, J = 8.4 Hz); ^{13}C{^{1}H} NMR (CDCl$_3$): δ_C (ppm) 0.01, 26.20, 33.38, 46.18, 47.45 (d, J = 16 Hz), 55.88, 58.35 (d, J = 5.6 Hz), 70.42, 94.31, 104.58 (d, J = 8.2 Hz), 104.93, 105.56 (d, J = 8.2 Hz), 116.12 (d, J = 4.4 Hz), 120.32, 122.42, 127.07, 128.71, 132.09, 133.02, 137.31, 143.86 (d, J = 7.0 Hz), 161.24, 161.83; ^{31}P{^{1}H} NMR (CDCl$_3$): δ_P (ppm) 26.03.

Modified SEMI-ESPHOS oxide (22). K$_2$CO$_3$ (1.62 g, 11.7 mmol) was added at room temperature under argon to a solution of **21** (880 mg, 1.67 mmol) in CH$_2$Cl$_2$–MeOH (20 mL/20 mL). After the reaction mixture was stirred for 4 h at room temperature, it was filtered and the solvent was removed *in vacuo*. The residue was purified by column chromatography on silica gel using EtOAc affording **22** as a white powder (652 mg, 86%). Mp 140–142 °C. ^{1}H NMR (CDCl$_3$): δ_H (ppm) 1.72 (m, 2H), 1.93 (m, 2H), 3.08 (m, 2H), 3.66 (br d, 3H, J = 11.8 Hz), 3.85 (s, 3H), 4.18 (m, 1H), 5.12 (br d, 2H, J = 2 Hz), 6.61 (m, 5H), 7.15 (q, 2H, J = 7.1 Hz), 7.35 (t, 1H, J = 8.3 Hz), 7.48 (dq, 4H, J = 8.4 Hz, 2.6 Hz). ^{13}C{^{1}H} NMR (CDCl$_3$): δ_C (ppm) 25.50 (d, J = 7.5 Hz), 31.04 (d, J = 7.5 Hz), 46.76 (d, J = 5.2 Hz), 50.53 (d, J = 8.2 Hz), 56.60, 58.20 (d, J = 5.2 Hz), 71.11, 83.82, 104.92, 105.03, 106.70, 106.82, 112.62, 116.47, 121.89, 127.49, 129.49, 132.62, 134.06, 137.99, 149.32, 162.56, 163.12. ^{31}P{^{1}H} NMR (CDCl$_3$): δ_P (ppm) 24.48. MS calcd [M]$^+$: 458.18; found: 458.04; Anal. calcd for $C_{27}H_{27}N_2O_3P$: C 70.73, H 5.94, N 6.11. Found: C 68.87, H 6.41, N 5.59.

Synthesis of Grubbs self metathesis product (29). An oven-dried flask equipped with a condenser and a magnetic stirring bar was charged under nitrogen with **14** (154 mg, 0.29 mmol) in CH$_2$Cl$_2$ (10 ml). The solution of Grubbs' catalyst (16.5 mg, 0.02 mmol) in CH$_2$Cl$_2$ (3 ml) was injected in the mixture heated at 55 °C to maintain a gentle reflux. The reaction was stopped and cooled down to room temperature after disappearance of the vinyl signals in ^{1}H NMR (90 h). The solvent was removed *in vacuo* and the residue loaded onto a silica gel column. The first fraction was removed with EtOAc as eluent whilst the desired product was eluted with acetone to afford **29** as a white powder (205 mg, 68%). ^{1}H NMR (400.13 MHz, CDCl$_3$, 296 K): δ_H (ppm) = 1.61 (m, 2H), 1.75 (m, 2H), 2.02 (m, 4H), 2.96 (m, 2H), 3.51 (m, 2H), 3.55 (s, 6H, OCH$_3$), 3.69 (m, 4H), 3.96 (m, 2H, NCH), 4.98 (d, 2H, $^2J_{HH}$ = 12.6 Hz), 5.14 (d, 2H, $^2J_{HH}$ = 12.6 Hz), 6.50 (m, 4H), 6.89 (t, 2H,

$^3J_{HH}$ = 7.3 Hz), 7.19 (s, 2H CH=CH), 7.23 (m, 14H), 7.48 (d, 4H, $^3J_{HH}$ = 8.4 Hz), 7.61 (d, 4H, $^3J_{HH}$ = 8.4 Hz), 7.62 (br, 4H); ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$, 296 K): δ_C (ppm) = 26.6, 32.8, 46.9, 48.1, 56.7, 58.9, 71.1, 105.4, 106.0, 112.8, 117.6, 120.6, 126.8, 127.4, 127.4, 127.6, 128.3, 129.1, 132.5, 136.6, 137.4, 139.7, 140.5, 161.8, 162.3; ^{31}P{^{1}H} NMR (162.0 MHz, CDCl$_3$, 296 K): δ_P (ppm) = 24.8; found: C 72.9, H 6.0, N 5.0, $C_{64}H_{62}O_6P_2N_4$ requires C 73.4, H 5.9, N 5.3.

Synthesis of dendritic molecules (23), (24), (25), (26), (27) and (28).

Typical Procedure. In an oven-dried flask equipped with a condenser and a magnetic stirring bar were charged under argon octavinylsilsesquioxane (50 mg, 0.08 mmol) and **12** (340 mg, 1.00 mmol) in CH$_2$Cl$_2$ (8 mL). The solution was stirred and heated to maintain a gentle reflux at 55 °C. A solution of Grubbs' catalyst (30 mg, 0.036 mmol in 3 mL CH$_2$Cl$_2$) was injected with syringe. The reaction mixture was refluxed and monitored by ^{1}H NMR spectroscopy. The proton resonances of vinylsilyl groups disappeared after 90 h and the reaction was cooled to room temperature. After the mixture was filtered, the solution was concentrated and precipitated from a mixture of ethyl acetate (120 mL)/petroleum ether (300 mL). The precipitation procedure was repeated twice followed by column chromatography on silica gel using a gradient from dichloromethane/acetone (1:2) to dichloromethane–methanol (1:8) to afford **23** as an off-white powder (180 mg, 72%). ^{1}H NMR (CDCl$_3$): δ_H (ppm) 1.67 (m, 16H), 1.98 (m, 16H), 3.12 (m, 8H), 3.32 (m, 8H), 3.54 (m, 16H), 3.86 (m, 8H), 6.14 (d, 8H, J = 19.2 Hz), 6.96 (d, 8H, J = 19.2 Hz), 7.04 (m, 16H), 7.30 (m, 48H). Peaks arising from small amounts of petroleum ether are observed at δ 1.28 and 0.90 ppm and from CH$_2$Cl$_2$ at 5.3 ppm ^{13}C{^{1}H} NMR (CDCl$_3$): δ_C (ppm) 26.52, 32.80, 47.11, 50.25 (d, J = 18 Hz), 57.52 (d, J = 9.8 Hz), 116.63 (d, J = 4.5 Hz), 117.22, 121.63, 127.81, 128.45, 129.78, 134.32, 141.49, 148.54, 152.13. ^{31}P{^{1}H} NMR (CDCl$_3$): δ_P (ppm) 18.84. MS calcd [M+Na]$^+$: 3154.49; found: (MALDI-TOF) 3154.87. Anal. calcd for $C_{152}H_{160}N_{16}O_{28}P_8Si_8$: C 58.30, H 5.15, N 7.16. Found: C 59.53, H 4.96, N 7.13.

Dendritic molecule (24)[44]. The synthesis has already been reported.[44]

^{1}H NMR (CDCl$_3$) δ_H (ppm) 1.71 (m, 16H), 2.04 (m, 16H), 3.14 (m, 8H), 3.36 (m, 8H), 3.61 (m, 16H), 3.89 (m, 8H), 6.40 (d, 8H, J = 19.2 Hz), 7.03 (tt, 8H, J = 7.3 Hz), 7.26 (m, 16H), 7.35 (m, 24H), 7.54 (m, 48H); ^{13}C{^{1}H} NMR (CDCl$_3$): δ_C (ppm) 26.15 (d, J = 3 Hz), 33.43, 46.72, 29.92 (d, J = 18 Hz), 57.15 (d, J = 9.8 Hz), 116.21, 116.27, 117.41, 121.44, 121.49, 121.64, 127.09, 127.44, 127.99, 129.39, 136.28, 137.01, 141.18, 149.06; ^{31}P{^{1}H} NMR (CDCl$_3$): δ_P (ppm) 18.97; ^{29}Si NMR (CDCl$_3$): δ_{Si} (ppm) −78.22; MS calcd [M + Na + 2 H$_2$O]$^+$: 3799.25; found: (MALDI-TOF) 3800.45; Anal. calcd for $C_{200}H_{192}N_{16}O_{28}P_8Si_8$: C 64.23, H 5.17, N 5.99. Found: C 62.80, H 4.68, N 5.71.

Dendritic molecule (25). The synthesis has already been reported.[44]

^{1}H NMR (CDCl$_3$) δ_H (ppm) 1.82 (m, 16H), 2.15 (m, 16H), 3.01 (m, 8H), 3.55 (m, 8H), 3.77 (s, 24H), 3.96 (m, 24H), 6.31 (d, 8H, J = 19.2 Hz), 6.80 (m, 8H), 7.03 (m, 8H), 7.11 (d, 16H, J = 8.6 Hz), 7.46 (m, 64 H), 8.13 (qd, 8H, J = 7.4 Hz, 1.8 Hz); ^{13}C{^{1}H} NMR (CDCl$_3$): δ_C (ppm) 26.89, 33.77, 45.47, 49.47 (d, J = 15 Hz), 56.29,

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59.76 (d, J = 5.2 Hz), 111.43 (d, J = 8.2 Hz), 116.39, 116.45, 117.22, 120.83, 121.02, 126.85, 127.73, 132.95, 134.04, 136.01, 136.96, 137.06, 141.45, 149.12, 160.87; $^{31}P\{^1H\}$ NMR (CDCl$_3$): δ_P (ppm) 26.52; ^{29}Si NMR (CDCl$_3$): δ_{Si} (ppm) −78.22; MS calcd [M+Na]$^+$: 3875.43; found: (MALDI-TOF) 3875.29; Anal. calcd for C$_{208}$H$_{208}$N$_{16}$O$_{28}$P$_8$Si$_8$: C 64.85, H 5.44, N 5.82. Found: C 63.57, H 3.83, N 5.26.

Dendritic molecule (26). ^1H NMR (CDCl$_3$) δ_H (ppm) 1.80 (m,16H), 1.99 (m, 8H), 2.91 (m, 8H), 3.46 (m, 16 H), 3.53 (s, 24H), 3.64 (m, 16H), 3.91 (m, 8H), 4.93 (ABq, 16H, J = 12.7 Hz), 6.34 (d, 8H, J = 19.2 Hz), 6.45 (m, 16H), 6.84 (m, 8H), 7.22 (m, 48H), 7.33 (d, 8H, J = 19.2 Hz), 7.48 (q, 24H, J = 8.4 Hz).$^{13}C\{^1H\}$ NMR (CDCl$_3$): δ_C (ppm) 26.58, 33.76, 46.53, 48.00 (d, J = 15.7 Hz), 56.25, 58.78, 70.91, 104.87 (d, J = 8.2 Hz), 105.95 (d, J = 8.2 Hz), 116.61 (d, J = 4.5 Hz), 117.74, 120.66, 127.47, 127.97, 129.07, 133.39, 137.15, 138.09, 144.31, 144.41, 149.24, 161.68, 162.23. $^{31}P\{^1H\}$ NMR (CDCl$_3$): δ_P (ppm) 26.05. MS calcd [M + Na]$^+$: 4115.64; found: (MALDI-TOF) 4114.69. Anal. calcd for C$_{216}$H$_{224}$N$_{16}$O$_{36}$P$_8$Si$_8$: C 63.39, H 5.52, N 5.47. Found: C 63.18, H 5.43, N 5.24.

Dendritic molecule (27). ^1H NMR (CDCl$_3$): δ_H (ppm) 1.92 (m, 16H), 2.87 (m, 8H), 3.40 (m, 24H), 3.47 (s, 24H), 3.59 (m, 16H), 3.86 (m, 8H), 4.97 (ABq, 16H, J = 12.7 Hz), 6.29 (d, 8H, J = 19 Hz), 6.40 (m, 16H), 6.81 (m, 8H), 7.18 (m, 48H), 7.39 (m, 24H), 7.53 (m, 48H). $^{13}C\{^1H\}$ NMR (CDCl$_3$): δ_C (ppm) 26.61, 33.76, 46.54, 48.08 (d, J = 16.5 Hz), 56.27, 58.76, 70.90, 104.86 (d, J = 8.2 Hz), 105.99 (d, J = 8.2 Hz), 112.43, 116.56 (d, J = 4.5 Hz), 117.85, 120.69, 127.32, 127.61, 128.18, 128.64, 129.09, 133.42, 136.59, 136.83, 140.24, 141.64, 144.30, 149.13, 161.74, 162.30. $^{31}P\{^1H\}$ NMR (CDCl$_3$):δ_P (ppm) 26.06. ^{29}Si NMR (CDCl$_3$): δ_{Si} (ppm) −78.21; MS calcd [M + Na]$^+$: 4724.47; found: (MALDI-TOF) 4727.39; Anal. calcd for C$_{264}$H$_{256}$N$_{16}$O$_{36}$P$_8$Si$_8$: C 67.44, H 5.49, N 4.77. Found: C 68.08, H 5.27, N 4.55

Dendritic molecule (28). ^1H NMR (CDCl$_3$): δ_H (ppm) 1.65 (br, 32H), 1.91 (br, 32H), 2.88 (br, 16H), 3.58 (br, 96H), 3.86 (m, 16H), 4.85 (ABq, 32H, J = 12.6 Hz), 6.45 (br, 40H), 6.75 (br, 16H), 7.14 (br, 96 H), 7.60 (br, 48 H). $^{13}C\{^1H\}$ NMR (CDCl$_3$). Peaks arising from small amounts of petroleum ether are observed at δ 0.80–0.90 and 1.28–1.30 ppm. δ_C (ppm) 26.58, 33.71, 46.51, 48.07, 56.29, 58.73, 71.00, 104.87, 104.98, 106.20, 116.46, 117.78, 120.62, 125.38, 127.40, 127.73, 127.86, 129.09, 133.41, 136.54, 137. 44, 138.32, 141.20, 144.38, 149.17, 161.59, 162.37. $^{31}P\{^1H\}$ NMR (CDCl$_3$): δ_P (ppm) 25.95, 26.01, 26.03. MS calcd [M + Na]$^+$: 7575.25; found (MALDI-TOF) 7576.98, 6787.45, 5999.10, 5209.38, 4419.58; Anal. calcd for C$_{416}$H$_{424}$N$_{32}$O$_{60}$P$_{16}$Si$_8$: C 66.16, H 5.66, N 5.93. Found: C 64.77, H 5.64, N 5.25.

Acknowledgements

Notes and references

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