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Synthesis and studies of Rh(I) catalysts within and across poly(alkyl aryl ether) dendrimers

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ABSTRACT

In order to study the efficiencies of catalytic moieties within and across dendrimer generations, partially and fully functionalized dendrimers were synthesized. Poly(alkyl aryl ether) dendrimers from zero to three generations, presenting 3 to 24 peripheral functionalities, were utilized to prepare as many as 12 catalysts. The dendrimer peripheries were partially and fully functionalized with triphenylphosphine in the first instance. A rhodium(I) metal complexation was performed subsequently to afford multivalent dendritic catalysts, both within and across generations. Upon synthesis, the dendritic catalysts were tested in the hydrogenation of styrene, in a substrate-to-catalyst ratio of 1:0.001. Turn-over-numbers were evaluated for each catalyst, from which significant increases in the catalytic activities were identified for multivalent catalysts than monovalent catalysts, both within and across generations.

1. Introduction

Interfacing organometallic catalysis with dendrimers was explored on many occasions, in an effort to assess the effect of dendritic structural features in organometallic catalysis [1–5]. The catalytic moieties are incorporated generally at the interior or at the peripheries of dendritic structures [6–25]. Both positive and negative effects in catalysis were reported, either due to a co-operativity or a stabilization assisting the catalysis and steric hindrances affecting the catalysis. It is accepted generally that dendritic catalysts function as supported homogeneous catalysts. In an effort to identify the effect of dendritic scaffolds, we reported recently multivalent poly(ether imine) dendritic catalysts, wherein each dendrimer generation was presented with varying number of catalytic moieties [26]. When organometallic catalysis was performed on the basis of molar equivalents of the catalytic sites, a considerable increase in the catalytic activities was observed for dendritic structures presented with more catalytic units than that presented with lesser units. The beneficial effect of clustering the catalytic units was presumed to arise from altered kinetic profiles of association-dissociation of the intermediates involved in the catalytic cycle. In continuing this effort, we undertook to study organometallic catalysis mediated by a constitutionally different poly(alkyl aryl ether) dendrimer-based multivalent catalysts. Specifically, the studies were focused on varying the number of catalytic sites within each generation and also across the generations. Rhodium(I)-mediated catalysis was studied upon synthesis of a number of monovalent and multivalent catalysts. This report describes synthesis of these catalysts and an evaluation of their catalytic profiles.

2. Results and discussion

2.1. Synthesis and characterization of multivalent dendritic catalysts

Phloroglucinol-based poly(alkyl aryl ether) dendrimers [27] were chosen for the present study. The first generation dendrimer of this type can provide 1 to 6 catalytic moieties when the moieties are presented at its periphery. Second generation and third generation dendrimers can provide 1 to 12 and 1 to 24 catalytic moieties at their peripheries, respectively. Pre-formed poly (alkyl aryl ether) dendrimers were synthesized as previously reported [27]. These dendrimers are constituted with phloroglucinol which formed as the core, branch point functionalities and n-pentyl group as the linker between the branch points. Dendrimer generations 0, 1, 2 and 3 presenting 3, 6, 12 and 24 peripheral functionalities, respectively, were chosen for the preparation of multivalent dendritic organometallic catalysts. Whereas complete functionalization with catalytic moieties involved least chemical modifications at the peripheries of pre-formed dendrimers, partial substitution with catalytic moieties required

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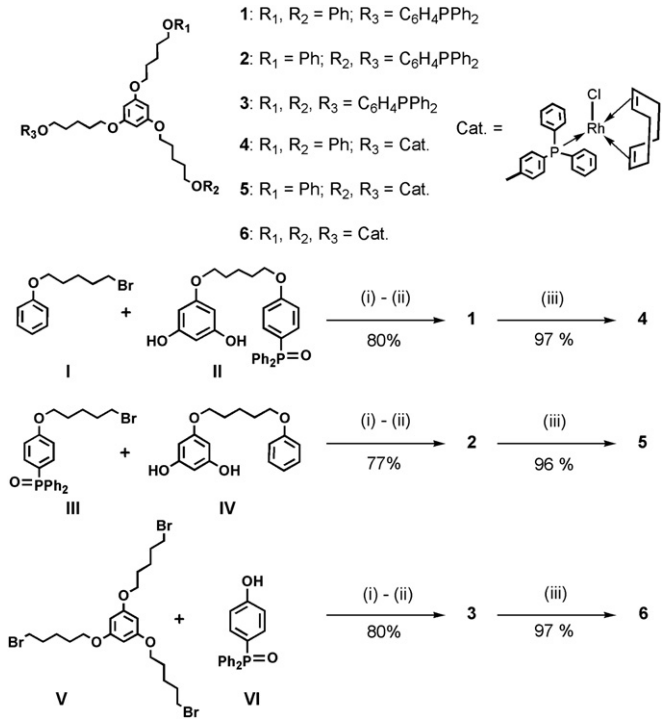
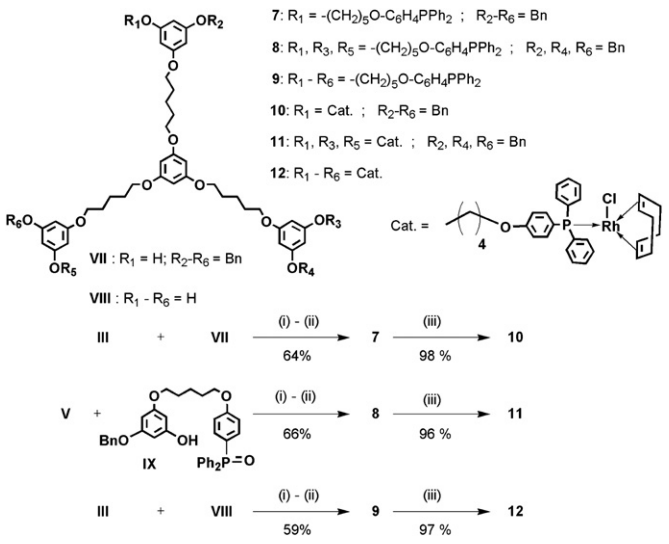
protection of defined number peripheral functionalities. Thus, modification with required number of peripheral hydroxyl groups formed the initial efforts towards synthesis of multivalent catalysts.

A triphenylphosphine ligand, wherein one of the phenyl groups emanating from dendrimer peripheries, was chosen for complexation with Rh(I) metal and subsequent catalysis studies. Key monomer building blocks for elaboration of dendrimer peripheries with phosphine ligand were derivatives **I**–**VI** (Scheme 1). These were prepared by phenolic *O*-alkylation with appropriate alkyl bromides, details of which are provided in the Supporting Information. Zero generation dendritic catalysts providing 1–3 catalytic moieties were prepared by *O*-alkylations of appropriate monomer building blocks, followed by a reduction [28,29] of phosphine oxides to afford phosphines **1**, **2** and **3** and their subsequent metal complexations with Rh(I) (Scheme 1), leading to the formation of catalysts **4**, **5** and **6**, respectively. *O*-Alkylation and subsequent reduction reactions led to moderate to good yields of phosphine oxides and phosphines **1**–**3**. On the other hand, metal complexations, using dimeric Rh(cod)Cl (cod: 1,5-cyclooctadiene) were facile and the products formed in good yields. Whereas phosphine oxides and phosphines were colorless oils, the corresponding metal complexes were yellow gums.

A similar strategy was adopted for the synthesis of first generation catalysts, possessing one, three and six catalytic sites at their peripheries. Dendrimer **VII** with partial functionalization of hydroxyl groups at its peripherey and fully hydroxyl group functionalized dendrimer **VIII** were secured through deprotections of the corresponding fully protected dendrimer. Details of synthesis and characterization are provided in the Supporting Information. Phosphine-functionalized dendrimers were obtained through *O*-alkylations with appropriate phosphine oxide containing derivatives, followed by $LiAlH_4/CeCl_3$ mediated reduction to phosphines **7**–**9** (Scheme 2). Rh(I) complexation with dendritic phosphines was performed using Rh(cod)Cl dimer in CH_2Cl_2 and complexes **10**–**12** were obtained as orange gums or semi-solids. Metal co-ordinations



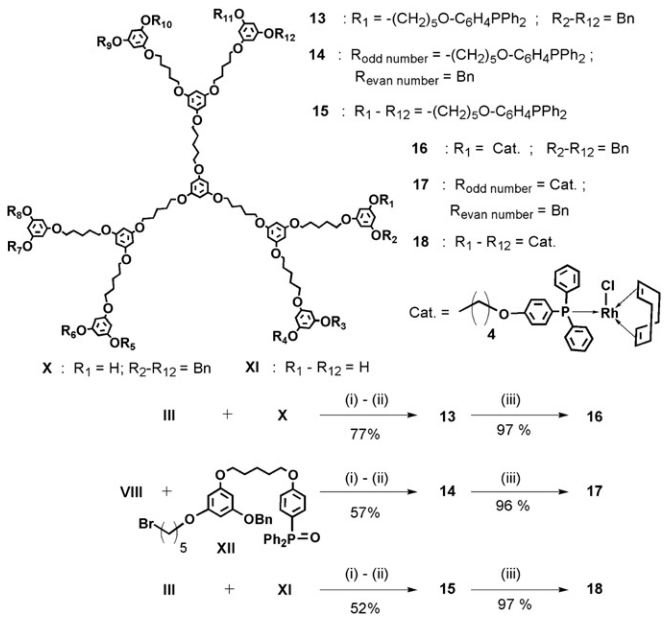
Scheme 1. Reagents and conditions. (i) K_2CO_3, 18-C-6 (cat.), DMF, 70 °C; (ii) $LiAlH_4$, $CeCl_3$, THF, 60 °C; (iii) $[Rh(cod)Cl]_2$, CH_2Cl_2, rt.



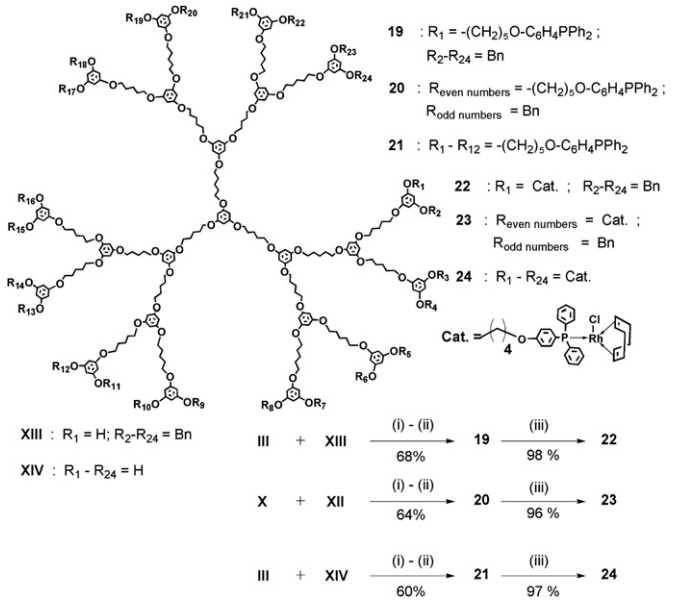
Scheme 2. Reagents and conditions. (i) K_2CO_3, 18-C-6 (cat.), DMF, 70 °C; (ii) $LiAlH_4$, $CeCl_3$, THF, 60 °C; (iii) $[Rh(cod)Cl]_2$, CH_2Cl_2, rt.

by phosphines were confirmed by the absence of a resonance at ~ − 6.9 ppm, corresponding to metal-free phosphine resonance and the appearance of a doublet at ~29.5 ppm (J ~ 150 Hz), corresponding to metal co-ordinated phosphine resonance. Elemental analysis and metal analysis, performed using inductively coupled plasma-optical emission spectrometer (ICP-OES), further confirmed the constitutions of **10**–**12**. Synthesis of partially and fully functionalized second and third generation dendrimers were undertaken by utilizing pre-formed dendrimers.

Schemes 3 and 4 provide synthetic sequences to prepare second and third generation dendrimers phosphine–metal complexes. In these instances too, the number of hydroxyl groups at the peripheries of dendrimers defined the number of phosphines and catalytic moieties. Three catalysts within each generation was prepared through *O*-alkylation, using appropriate phosphine oxide



Scheme 3. Reagents and conditions. (i) NaH, DMF, 70 °C; (ii) $LiAlH_4$, $CeCl_3$, THF, 60 °C; (iii) $[Rh(cod)Cl]_2$, CH_2Cl_2, rt.



Scheme 4. Reagents and conditions. (i) NaH, DMF, 70 °C; (ii) $LiAlH_4$, $CeCl_3$, THF, 60 °C; (iii) $[Rh(cod)Cl]_2$, CH_2Cl_2, rt.

monomer building blocks, followed by reduction to phosphines and metal complexations with Rh(I). Whereas *O*-alkylation reaction yields were moderate, reduction of phosphine oxide to phosphine and the metal complexation were facile and good yields were obtained. Molecular structures of third generation catalysts **23** and **24** are shown in Fig. 1, whereas molecular structures of remaining catalysts are presented in the Supporting Information. The metal complexes and phosphine intermediates were characterized for their identities and homogeneities by routine physical methods. Disappearance of ^{31}P resonance at ~– 6.9 ppm and the appearance of a doublet at ~29.5 ppm, with phosphorus–metal coupling constant of ~150 Hz, confirmed complete complexation of all phosphine moieties to metal. Metal content stoichiometries in the complexes were confirmed through atomic absorption analysis. Further, ^1H and ^{31}P NMR resonances for phosphine oxides, phosphines and the metal complexes were observed to have the following trend. Aromatic moieties in phosphine oxides showed resonances in the region of 7.30–7.70 ppm, that in phosphines were between 7.15 and 7.30 ppm. In the metal complexes, aromatic moieties were observed between 7.25 and 7.75 ppm. Corresponding ^{31}P NMR values were observed in the region of: phosphine oxides 29.3–29.4 ppm; phosphines ~– 6.9 ppm and metal complexes ~29.5 ppm as a doublet, with a coupling constant of 150 Hz.

2.2. Assessment of catalytic activities

Catalytic activities of multivalent dendritic Rh(I) organometallic catalysts, **4**–**6**, **10**–**12**, **16**–**18** and **22**–**24** were assessed in a case study involving hydrogenation of styrene, monitored by gas chromatography. In assessing catalytic activities, the reactions were conducted on the basis of *per* catalytic site, so as to treat multivalent catalysts with respect to the number of catalytic sites. Dendritic catalysts having more than one catalytic site were considered in multiples according to the number of such sites within the dendrimer. Studies were thus performed with uniform molar equivalent of the metal in each catalytic reaction. After few trial reactions, the substrate-to-one catalytic moiety mole ratio of 1:0.001 was chosen, and the studies were performed in 1,4-dioxane, at a H_2 (g) pressure of 10 bar. The formation of ethyl benzene was monitored at varying time interval. The reactions proceeded generally without an induction period and a complete conversion to product occurred at varying durations. Significant differences in the catalytic profiles were noticed during initial periods of the reaction. Catalytic efficiencies, measured as turn-over-number (TON), are presented in Fig. 2 for each catalyst during 30 and 60 min reaction durations.

Upon completion of hydrogenation, the catalyst was recovered, by removing the solvent *in vacuo* and washing the catalyst with n-hexane, and re-used in order to assess the efficacy of recovered

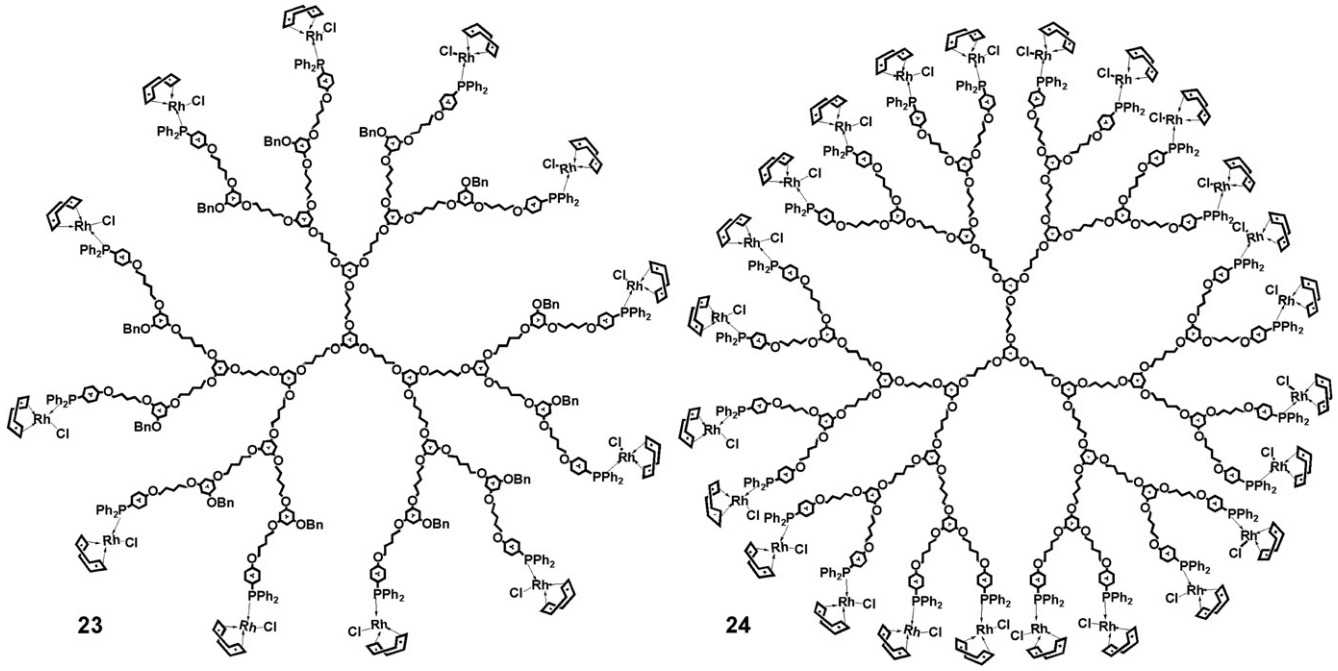


Fig. 1. Molecular structures of third generation catalysts **23** and **24**.

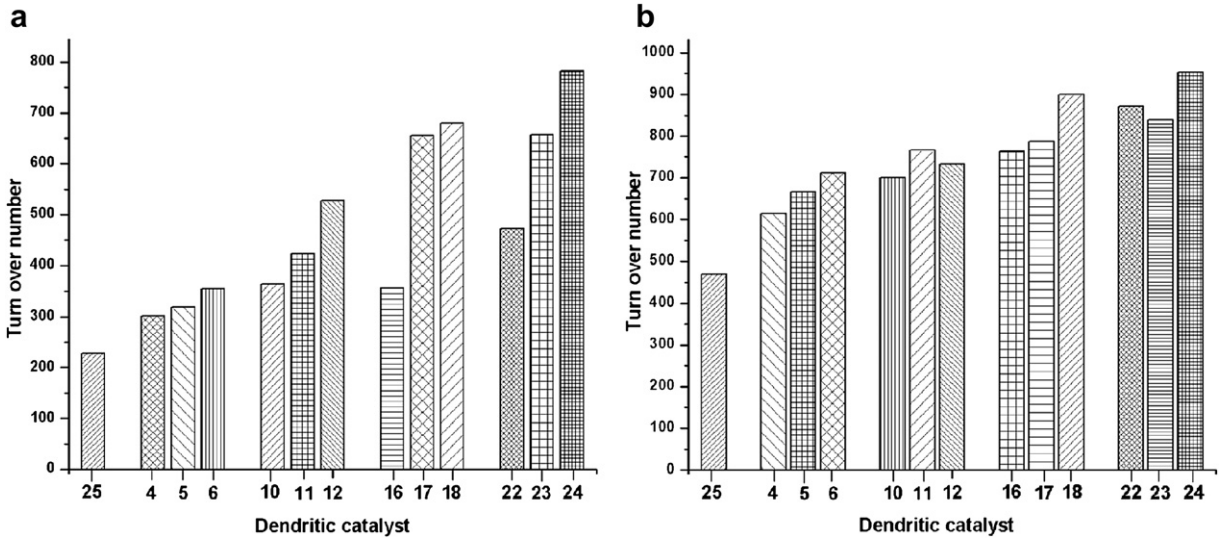


Fig. 2. Turn-over-number (TON) during (a) 30 min reaction duration and (b) 60 min reaction duration of hydrogenation of styrene.

catalysts. Catalysts **11** and **24** were undertaken for recovery and re-use studies. A second time use of the catalysts led to hydrogenations, with more than 80% of catalytic efficiencies as judged after 60 min, thereby ascertaining that the catalysts largely retained their efficacies for reusability. Impediment to recovery and re-use was encountered when the catalysts were exposed to hydrogenation conditions for several hours, during which period catalysts precipitated, possibly due to loss of (cod) ligand upon hydrogenation. Stability of catalysts was also assessed by heating catalysts **6** and **24** in 1,4-dioxane at 50 °C for ~2 h, followed by characterizing the complexes by ^{1}H and ^{31}P NMR spectroscopies. Spectral comparisons showed that catalysts were intact. Further, catalysis mediated by $(Ph_3P)Rh(cod)Cl$ (**25**) was conducted in the presence of excess triphenylphosphine, in order to identify whether an alternate mode of metal complexation during the catalytic reaction might contribute to increased catalytic efficiencies. Presence of externally added 2 and 4 M equivalents of triphenylphosphine along with **25** led to marginal decrease in the catalytic activities. Formation of higher stoichiometric *in situ* Rh–P complexes thus appeared to be unlikely.

An analysis of the hydrogenation reaction showed that (i) of the twelve dendritic catalysts, three in each zero, first, second and third generations, and also **25**, a higher catalytic activity was observed for higher generations; (ii) within a given generation, multivalent catalysts mediated the reaction considerably more effectively than monovalent catalysts; (iii) across generations, monovalent catalysts **4**, **10**, **16** and **22** led to considerable increases in catalytic activities in the increasing order and (iv) among fully functionalized multivalent catalysts **6**, **12**, **18** and **24**, the increase in catalytic activities was more significant with higher generations. When comparing these results, it is important to note that the reactions are performed on the basis of individual catalytic site basis. The observations of increased catalytic activities by multivalent catalysts are in line with our earlier studies involving poly (ether imine) dendrimer type, presented with partial and complete substitution of Pd-based catalytic units at the peripheries [26]. Increases in activities of individual catalytic sites were either significant across the generations, or considerable within the generations, thereby indicating beneficial effects of clustering the catalytic sites.

The basis of present study was to identify catalytic effects upon clustering dendritic ligands and metal complexes in spatially and topologically well-defined dendritic structures. In such an effort, initial requirement was to synthesize dendrimers capable to present varying number of such ligands and metal complexes within the generation. The present study focused on identifying the effect of dendritic backbone, when catalysis is mediated by varying number of catalysts within a given dendrimer generation. Thus, when comparing monovalent catalysts **4**, **10**, **16** and **22**, each with one catalytic center across zero, first, second and third generations, the activities of styrene hydrogenation increased as the generations advanced. Higher catalytic activities of higher generations appeared to be in part due the effect of dendrimer backbone. The origin of higher catalytic effects is unclear. We presume that the observed effects arise due to several catalytic moieties available within the same dendritic structure, that alter kinetic association–dissociation rate constants, as opposed to least number of catalytic moieties present on the same generation. Comparable results observed with un-related poly(ether imine) dendrimer catalysts and their efficacies to mediate C–C bond forming reactions[26] reiterate that activities of individual catalytic moieties are moderate to significantly higher when the moieties are clustered on a dendrimer structure.

3. Conclusion

Synthesis and evaluation of catalytic activities of Rh(I) catalysts presented both within and across dendrimer generations was undertaken. Phloroglucinol-based poly(alkyl aryl ether) dendrimers, in the generation series **0**–**3**, presenting **3**, **6**, **12** and **24** peripheral functional groups, were chosen for installation of varying number of catalytic moieties at their peripheries. Twelve catalysts with varying number phosphine ligands and Rh(I) complexes with above dendrimer generations were thus prepared. Upon synthesis, the catalysts were studied in a hydrogenation reaction with styrene as the substrate. A comparison of the catalytic activities, measured as TON, of each dendritic catalyst showed that moderate to significant increases in the efficacies of individual catalytic moiety occurred when the moiety was presented along with several such moieties at the peripheries of a dendrimer structure, than as isolated moiety within the same dendrimer structure. The observations verify not only a role of dendritic backbone, but also an effect of clustering the catalytic moieties within and across dendrimer generations.

4. Experimental

4.1. General methods

Chemicals were purchased from commercial sources and were used without further purification. K_2CO_3 (AR grade) was dried at 120 °C for 24 h before being used. Solvents were dried and distilled according literature procedures and saturated with Ar. Analytical TLC was performed on commercial Merck plates coated with silica gel GF_{254} (0.25 mm) and I_2 was used as staining agent for TLC. Silica gel (230–400 mesh) was used for column chromatography. The ^1H, ^{13}C and ^{31}P NMR spectra were recorded on the following spectrometers: Jeol AC 300 FT NMR spectrometer (^1H: 300 MHz, ^{13}C: 75.5 MHz), Bruker AMX 400 (^1H: 400 MHz, ^{13}C: 100 MHz, ^{31}P: 162 MHz), with TMS or H_3PO_4 as a reference. The following abbreviations are used to explain the multiplicities: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad; band, several overlapping signals. Atomic absorption spectroscopic measurements of metal content were conducted using Thermo iCAB 6500 DUO ICP-OES instrument.

4.2. General procedures. Synthesis of phosphine oxides

A solution of phenol (1 M equiv.), bromide functionalized monomer (1.2 M equiv. *per* hydroxyl group), K_2CO_3 (1.2 M equiv. *per* hydroxyl group) and 18-C-6 (cat.) in DMF was stirred for 24–48 h at 70 °C. Solvents were removed *in vacuo*, the resulting residue was dissolved in CH_2Cl_2, washed with water, dried, concentrated and purified (SiO_2), using PhMe/EtOAc gradient elution, to afford dendritic phosphine oxide. Alternatively a solution of phenol (1 M equiv.), bromide functionalized monomer (1.2 M equiv. *per* hydroxyl group), NaH (60% in mineral oil, 1.2 M equiv. *per* hydroxyl group) in DMF was stirred for 48–72 h at 70 °C. Solvents were removed *in vacuo*, the resulting residue was dissolved in CH_2Cl_2, washed with water, dried, concentrated and purified (SiO_2), using $CHCl_3$/MeOH gradient elution, to afford dendritic phosphine oxide.

4.3. Reduction of phosphine oxides

$LiAlH_4$ (3.0 M equiv. *per* phosphine oxide) was added to a stirred suspension of $CeCl_3$ (2.0 M equiv. *per* phosphine oxide) in THF, followed by the addition of dendritic phosphine oxide in THF. The reaction mixture was warmed at 70 °C for 7 h, quenched with water, filtered, concentrated and purified (SiO_2, PhMe/EtOAc) to afford dendritic phosphine.

4.4. Preparation of dendritic Rh catalysts

A mixture of dendritic phosphine and $[Rh(cod)Cl]_2$ (0.5 M equiv. *per* phosphine group) in CH_2Cl_2 was stirred for 10 min at room temperature under an Ar atmosphere. The solvents were evaporated *in vacuo*, washed with hexane and Et_2O to afford the desired dendritic Rh catalyst.

4.5. Hydrogenation reactions

The dendritic catalyst (0.005 mmol of Rh content) and styrene (5 mmol) in 1,4-dioxane (10 mL) were charged into an autoclave, flushed twice with H_2 (g) and pressurized (10 bar). At defined time intervals, aliquot of the reaction mixture were withdrawn, filtered (0.45 μ) and analyzed by GC. GC parameters: silica capillary column; N_2 carrier gas; column initial temperature, 80 °C; column final temperature, 200 °C; column temperature rate, 20 °C/min. The TON was calculated as: mole of product formed/mole of catalyst used.

1. A mixture of **I** (0.3 g, 1.25 mmol), **II** (0.2 g, 0.42 mmol), K_2CO_3 (0.23 g, 1.67 mmol) and 18-C-6 (cat.) in DMF (10 mL) was stirred at 70 °C for 24 h and proceeded as described in general procedure to afford phosphine oxide, as a colorless gum (0.28 g, 82%). TLC: R_f 0.5 (PhMe/EtOAc = 25:75). ^1H NMR ($CDCl_3$, 300 MHz) δ 1.64 (m, 6 H), 1.83 (m, 12 H), 3.97 (m, 12 H), 6.06 (s, 3 H), 6.93 (m, 8 H), 7.26 (m, 4 H), 7.41–7.69 (m, 12 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 22.7, 28.8, 28.9, 67.5, 67.6, 67.8, 93.8, 114.4, 114.6, 120.5, 128.4 (d, J = 11.3 Hz), 129.4, 131.7, 132.0 (d, J = 9.8 Hz), 132.3, 133.6, 133.9 (d, J = 9.8 Hz), 158.9, 160.8; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 29.42; ESI-MS m/*z*: calcd. for $C_{51}H_{57}O_7P$ $[M+H]^+$: 813.3920; found: 813.3945. Anal. calcd. for $C_{51}H_{57}O_7P$: C,75.35; H,7.07; found C,75.45; H,7.17.

A solution of above intermediate (0.18 g, 0.22 mmol) in THF (5 mL) was added to the stirred suspension of $CeCl_3$ (0.16 g, 0.65 mmol) and LAH (0.05 g, 1.29 mmol) in THF (20 mL) and proceeded as described in general procedure to afford **1**, as a colorless gum (0.17 g, 98%). TLC: R_f 0.6 (PhMe/EtOAc = 98:2). ^1H NMR ($CDCl_3$, 300 MHz) δ 1.63 (br, 6 H), 1.84 (br, 12 H), 3.94 (m, 12 H), 6.06 (s, 3 H), 6.90 (m, 8 H); 7.24–7.30 (m, 16 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 22.7, 28.9, 67.6, 67.7, 93.7, 114.4, 114.6 (d, J = 7.5 Hz), 120.5, 127.2 (d, J = 9.0 Hz), 128.4 (d, J = 7.5 Hz), 129.4, 133.4 (d, J = 18.8 Hz), 135.5 (d, J = 22.6 Hz), 137.8 (d, J = 9.8 Hz), 158.9, 159.8, 160.8; ^{31}P NMR ($CDCl_3$, 162 MHz) δ −6.88; Anal. calcd. for $C_{51}H_{57}O_6P$: C, 76.86; H, 7.21; found C, 76.57; H, 7.01.

2. A mixture of **IV** (0.25 g, 0.86 mmol), **III** (0.96 g, 2.16 mmol), K_2CO_3 (0.30 g, 2.16 mmol) and 18-C-6 (cat.) in DMF (20 mL) was stirred at 70 °C for 24 h and proceeded as described in general procedure to afford phosphine oxide, as a colorless gum (0.69 g, 79%). TLC: R_f 0.4 ($CHCl_3$/MeOH = 95:5). ^1H NMR ($CDCl_3$, 300 MHz) δ 1.65 (m, 6 H), 1.85 (m, 12 H), 4.03 (m, 12 H), 6.06 (s, 3 H), 6.93 (m, 7 H), 7.26 (m, 2 H), 7.41–7.69 (m, 24 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 22.7, 28.8, 28.9, 67.5, 67.6, 67.8, 93.7, 114.4, 114.5, 120.5, 128.4 (d, J = 11.3 Hz), 129.4, 131.7, 132.0 (d, J = 9.8 Hz), 132.3, 133.6, 133.9 (d, J = 9.8 Hz), 158.9, 160.8; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 29.39; ESI-MS m/*z*: calcd. for $C_{63}H_{66}O_8P_2$ $[M]^+$: 1012.42; found: 1013.5; Anal. calcd. for $C_{63}H_{66}O_8P_2$: C,74.69; H, 6.57; found C, 74.55; H, 6.70.

A solution of above intermediate (0.34 g, 0.33 mmol) in THF (5 mL) was added to the stirred suspension of $CeCl_3$ (0.5 g, 2.0 mmol) and LAH (0.15 g, excess) in THF (25 mL) and proceeded as described in general procedure to afford **2**, as a colorless gum (0.32 g, 97%). TLC: R_f 0.7 (PhMe/EtOAc = 98:2). ^1H NMR ($CDCl_3$, 300 MHz) δ 1.63 (br, 6 H), 1.84 (br, 12 H), 3.94 (m, 12 H), 6.06 (s, 3 H), 6.89 (m, 7 H), 7.15–7.30 (m, 26 H); ^{13}C NMR(75.5 MHz, $CDCl_3$) δ 22.7, 28.9, 67.6, 67.7, 93.7, 114.4, 114.7 (d, J = 7.5 Hz), 120.5, 127.3 (d, J = 9.0 Hz), 128.4 (d, J = 7.5 Hz), 129.0, 129.4, 133.4 (d, J = 19.6 Hz), 135.5 (d, J = 21.1 Hz), 137.8 (d, J = 9.8 Hz), 158.9, 159.8, 160.8; ^{31}P NMR ($CDCl_3$, 162 MHz) δ −6.91; Anal. calcd. for $C_{63}H_{66}O_6P_2$: C,77.12; H,6.78; found C,77.09; H, 6.66.

3. A mixture of **V** (0.32 g, 0.56 mmol), **VI** (0.6 g, 2.0 mmol), K_2CO_3 (0.31 g, 2.2 mmol) and 18-C-6 (cat.) in DMF (15 mL) was stirred at 70 °C for 24 h and proceeded as described in general procedure to afford phosphine oxide, as a colorless gum (0.55 g, 82%). TLC: R_f 0.5 ($CHCl_3$/MeOH = 93:7). ^1H NMR ($CDCl_3$, 300 MHz) δ 1.64 (m, 6 H), 1.85 (m, 12 H), 3.93 (t, J = 6.3 Hz, 6 H), 4.01 (t, J = 6.3 Hz, 6 H), 6.06 (s, 3 H), 6.95 (d, J = 8.7 Hz, 6 H), 7.27–7.69 (m, 36 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 22.7, 28.8, 28.9, 67.6, 67.8, 93.7, 114.4 (d, J = 13.6 Hz), 128.4 (d, J = 12.0 Hz), 131.7, 132.0 (d, J = 9.8 Hz), 132.2, 133.6, 133.9
(d, J = 11.3 Hz), 160.8, 161.9; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 29.3; ESI-MS m/*z*: calcd. for $C_{75}H_{75}O_9P_3$ $[M]^+$: 1212.46; found: 1213.366. Anal. calcd. for $C_{75}H_{75}O_9P_3$: C,74.24; H, 6.23; found C,74.03; H,6.63.

A solution of above intermediate (0.1 g, 0.08 mmol) in THF (3 mL) was added to the stirred suspension of $CeCl_3$ (0.1 g, 0.37 mmol) and LAH (0.04 g, excess) in THF (20 mL) and proceeded as described in general procedure to afford **3**, as a colorless gum (0.32 g, 97%). TLC: R_f 0.7 (PhMe/EtOAc = 98:2). ^1H NMR ($CDCl_3$, 300 MHz) δ 1.60 (br, 6 H), 1.84 (br, 12 H), 3.94 (m, 12 H), 6.05 (s, 3 H),

6.87 (d, J = 8.4 Hz, 6 H), 7.23–7.30 (m, 36 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 22.7, 28.9, 67.6, 67.7, 93.8, 114.7 (d, J = 7.5 Hz), 128.4 (d, J = 7.5 Hz), 133.4 (d, J = 19.6 Hz), 135.6 (d, J = 21.1 Hz), 137.9 (d, J = 10.6 Hz), 159.8, 160.8; ^{31}P NMR ($CDCl_3$, 162 MHz) δ −6.93; Anal. calcd. for $C_{75}H_{75}O_6P_3$: C,77.30; H,6.49; found C,77.43; H,6.59.

4. A mixture of **1** (0.034 g, 0.043 mmol) and $[Rh(cod)Cl]_2$ (0.010 g, 0.021 mmol) in CH_2Cl_2 (1 mL) was stirred at room temperature for 10 min and proceeded as described in general procedure to afford **4**, as a yellow gum (0.044 g, 98%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.62 (br, 6 H), 1.83–2.05 (br, 16 H), 2.39 (br, 4 H), 3.13 (s, 2 H), 3.96 (m, 12 H), 5.55 (s, 2 H), 6.06 (s, 3 H), 6.91 (m, 8 H), 7.25–7.76 (m, 16 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 22.7, 29.0, 33.0, 67.6, 67.8, 70.5 (d, J = 13.6 Hz), 94.0, 104.9 (m, J = 7.5 Hz), 114.4–114.5 (d, J = 10.8 Hz), 120.5, 128.0 (d, J = 10.5 Hz), 129.4, 129.9, 132.0, 132.5, 134.5 (d, J = 10.5 Hz), 136.9 (d, J = 12.8 Hz), 159.0, 160.7, 160.9; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 29.5 (d, J_{PRh} = 150 Hz); Anal. calcd. for $C_{59}H_{69}ClO_6PRh$: C, 67.91; H, 6.66; Rh, 9.86; found C, 67.70; H, 6.74; Rh, 9.5.

5. A mixture of **2** (0.04 g, 0.04 mmol) and $[Rh(cod)Cl]_2$ (0.02 g, 0.04 mmol) in CH_2Cl_2 (1 mL) was stirred at room temperature for 10 min and proceeded as described in general procedure to afford **5**, as a yellow foam (0.057 g, 96%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.63 (br, 6 H), 1.83–2.05 (br, 20 H), 2.42 (br, 8 H), 3.13 (s, 4 H), 3.96 (m, 12 H), 5.55 (s, 4 H) 6.06 (s, 3 H), 6.91 (m, 7 H), 7.25–7.95 (m, 26 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 22.7, 28.9, 33.0, 67.7, 67.8, 70.5 (d, J = 13.6 Hz), 93.8, 104.9 (m, J = 7.5 Hz), 114.2, 114.3 (d, J = 10.8 Hz), 120.5, 128.0 (d, J = 10.5 Hz), 129.4, 129.9, 132.0, 132.5, 134.4 (d, J = 10.5 Hz), 136.9 (d, J = 12.8 Hz), 159.1, 160.7, 160.8; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 29.5 (d, J_{PRh} = 150 Hz). Anal. calcd. for $C_{79}H_{90}Cl_2O_6P_2Rh_2$: C, 64.36; H, 6.15; Rh, 13.8; found C, 64.08; H, 6.17; Rh, 14.4.

6. A mixture of **3** (0.05 g, 0.043 mmol) and $[Rh(cod)Cl]_2$ (0.032 g, 0.064 mmol) in CH_2Cl_2 (1 mL) was stirred at room temperature for 10 min and proceeded as described in general procedure to afford **6,** as a yellow foam (0.080 g, 98%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.62 (br, 6 H), 1.73–2.05 (m, 24 H), 2.40 (br, 12 H), 3.13 (s, 6 H), 3.93 (t, J = 6.0 Hz, 6 H), 3.99 (t, J = 6.4 Hz, 6 H), 5.55 (s, 6 H) 6.06 (s, 3 H), 6.91 (d, J = 8.0 Hz, 6 H), 7.18–7.77 (m, 36 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.7, 28.9, 33.0, 67.7, 70.5 (d, J = 13.7 Hz), 93.8, 104.9 (m, J = 7.0 Hz), 114.2 (d, J = 10.8 Hz), 128.0 (d, J = 9.8 Hz), 129.9, 131.9, 132.4, 134.4 (d, J = 11.1 Hz), 136.8 (d, J = 12.9 Hz), 160.6, 160.8; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 29.5 (d, J_{PRh} = 149 Hz); Anal. calcd. for $C_{99}H_{111}Cl_3O_6P_3Rh_3$: C, 62.42; H, 5.87; Rh, 16.2; found C, 61.25; H, 6.04; Rh, 17.1.

7. A mixture of **VII** (0.7 g, 0.61 mmol), phosphine monomer **III** (0.41 g, 0.92 mmol), K_2CO_3 (0.17 g, 1.23 mmol) and 18-C-6 (cat.) in DMF (15 mL) was stirred at 70 °C for 24 h and proceeded as described in general procedure to afford phosphine oxide, as a colorless gum (0.69 g, 74%). TLC: R_f 0.5 (PhMe/EtOAc = 50:50). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.64 (m, 8 H), 1.83 (m, 16 H), 3.91 (t, J = 6.0 Hz, 14 H), 3.99 (t, J = 6.0 Hz, 2 H), 4.98 (s, 10 H), 6.06–6.23 (m, 12 H), 6.95 (d, J = 8.7 Hz, 2 H), 7.29–7.67 (m, 37 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.7, 28.9, 67.7, 67.8, 70.0, 93.8, 94.1, 94.5, 114.5 (d, J = 12.9 Hz), 127.5, 127.9, 128.4 (d, J = 11.9 Hz), 128.5, 131.7, 132.0 (d, J = 9.8 Hz), 132.4, 133.6, 133.9 (d, J = 11.2 Hz), 136.8, 160.6, 160.8; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 29.35; MALDI-TOF-MS m/z: calcd. for $C_{97}H_{101}O_{14}P$ $[M + H]^+$: 1522.70; found: 1522.61. Anal. calcd. for $C_{97}H_{101}O_{14}P$: C, 76.56; H, 6.69; found C,76.30; H, 6.57.

A solution of above intermediate (0.28 g, 0.18 mmol) in THF (4 mL) was added to the stirred suspension of $CeCl_3$ (0.1 g, 0.37 mmol) and LAH (0.05 g, excess) in THF (25 mL) and proceeded as described in general procedure to afford **7**, as a colorless gum (0.23 g, 86%). TLC: R_f 0.65 (PhMe/EtOAc = 98:2). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.61 (m, 8 H), 1.82 (m, 16 H), 3.92 (m, 16 H), 4.98 (s, 10 H), 6.06–6.23 (m, 12 H) 6.87 (d, J = 8.0 Hz, 2 H), 7.22–7.41 (m, 37 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.7, 28.9, 67.6, 67.7, 70.0, 93.7, 94.0, 94.4, 114.6 (d, J = 8.0 Hz), 127.5, 127.9, 128.4 (d, J = 8.8 Hz), 128.5, 133.3 (d, J = 19.0 Hz), 135.6 (d, J = 21.2 Hz), 136.8, 160.6, 160.8; ^{31}P NMR ($CDCl_3$, 162 MHz) δ −6.94; Anal. calcd. for $C_{97}H_{101}O_{13}P$: C, 77.37; H, 6.76; found C, 77.80; H, 6.46.

8. A mixture of **V** (0.28 g, 0.49 mmol), **IX** (1.1 g, 1.95 mmol), K_2CO_3 (0.4 g, 2.9 mmol) and 18-C-6 (cat.) in DMF (10 mL) was stirred at 70 °C for 36 h and proceeded as described in general procedure to afford phosphine oxide, as a yellow oil (0.73 g, 72%). TLC: R_f 0.4 ($CHCl_3$/MeOH = 95:5). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.61 (br, 12 H), 1.81 (br, 24 H), 3.93 (t, J = 6.0 Hz, 18 H), 4.00 (t, J = 6.0 Hz, 6 H), 4.98 (s, 6 H), 6.06–6.15 (m, 12 H), 6.95 (d, J = 8.4 Hz, 6 H), 7.30–7.68 (m, 51 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 22.7, 28.8, 28.9, 67.7, 67.8, 70.0, 93.7, 94.1, 114.5 (d, J = 12.0 Hz), 127.5, 127.9, 128.4 (d, J = 12.8 Hz), 128.5, 131.7 (d, J = 3.0 Hz), 132.0 (d, J = 9.8 Hz), 132.4, 133.4, 134.0 (d, J = 11.3 Hz), 136.8, 160.6, 160.8, 162.0; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 29.4; MALDI-TOF-MS m/z: calcd. for $C_{129}H_{135}O_{18}P_3$ $[M + H]^+$: 2065.36; found: 2065.487. Anal. calcd. for $C_{129}H_{135}O_{18}P_3$: C,74.98; H,6.59; found C,74.63; H, 6.92.

A solution of above intermediate (0.2 g, 0.1 mmol) in THF (5 mL) was added to the stirred suspension of $CeCl_3$ (0.14 g, 0.57 mmol) and LAH (0.06 g, excess) in THF (25 mL) and proceeded as described in general procedure to afford **8**, as a colorless gum (0.18 g, 92%). TLC: R_f 0.7 (PhMe/EtOAc = 98:2). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.59 (br, 12 H), 1.81 (br, 24 H), 3.94 (m, 24 H), 4.98 (s, 6 H), 6.05–6.14 (m, 12 H), 6.86 (d, J = 8.4 Hz, 6 H), 7.22–7.41 (m, 51 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 22.7, 29.0, 67.6, 67.7, 70.0, 94.2, 114.7 (d, J = 7.6 Hz), 127.5, 127.9, 128.4 (d, J = 7.5 Hz), 128.6, 133.4 (d, J = 18.8 Hz), 135.6 (d, J = 21.1 Hz), 136.8, 137.9 (d, J = 10.5 Hz), 159.8, 160.6, 160.8; ^{31}P NMR ($CDCl_3$, 162 MHz) δ − 6.96; Anal. calcd. for $C_{129}H_{135}O_{15}P_3$: C,76.76; H, 6.74; found C,76.88; H, 6.73.

9. A mixture of **VIII** (0.21 g, 0.27 mmol), **III** (0.86 g, 1.9 mmol), K_2CO_3 (0.34 g, 2.4 mmol) and 18-C-6 (cat.) in DMF (25 mL) was stirred at 70 °C for 48 h and proceeded as described in general procedure to afford phosphine oxide, as a brown oil (0.55 g, 70%). TLC: R_f 0.5 ($CHCl_3$/MeOH = 93:7). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.62 (br, 18 H), 1.82 (br, 36 H), 3.92 (t, J = 6.6 Hz, 24 H), 4.00 (t, J = 6.6 Hz, 12 H), 6.05 (s, 12 H), 6.95 (d, J = 8.7 Hz, 12 H), 7.42–7.68 (m, 72 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 22.7, 28.8, 28.9, 67.7, 67.8, 93.8, 114.5 (d, J = 13.6 Hz), 128.4 (d, J = 12.8 Hz), 131.7, 132.0 (d, J = 9.8 Hz), 132.2, 133.5, 133.8 (d, J = 11.3 Hz), 160.8, 161.9; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 29.44; MALDI-TOF-MS m/z: calcd. for $C_{177}H_{186}O_{24}P_6$ $[M + Na]^+$: 2904.17 Found: 2904.65; Anal. calcd. for $C_{177}H_{186}O_{24}P_6$: C, 72.32; H, 6.54; found C, 72.14; H, 6.72.

A solution of above intermediate (0.25 g, 0.086 mmol) in THF (5 mL) was added to the stirred suspension of $CeCl_3$ (0.19 g, 0.8 mmol) and LAH(0.08 g, excess) in THF (25 mL) and proceeded as described in general procedure to afford **9**, as a colorless gum (0.2 g, 84%). TLC: R_f 0.7 (PhMe/EtOAc = 95:5). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.63 (m, 18 H), 1.83 (m, 36 H), 3.93 (m, 36 H), 6.05 (s, 12 H), 6.86 (d, J = 7.8 Hz, 12 H), 7.15–7.30 (m, 72 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 22.7, 29.0, 67.6, 67.7, 93.9, 114.7 (d, J = 8.2 Hz), 128.4 (d, J = 7.5 Hz), 129.0, 133.4 (d, J = 19.6 Hz), 135.6 (d, J = 21.2 Hz), 138.0 (d, J = 11.3 Hz), 159.9, 160.9; ^{31}P NMR ($CDCl_3$, 162 MHz) δ − 6.97; Anal. calcd. for $C_{177}H_{186}O_{18}P_6$: C, 76.27; H, 6.73; found C, 76.52; H, 6.51.

10. A mixture of **7** (0.04 g, 0.026 mmol) and $[Rh(cod)Cl]_2$ dimer (0.0065 g, 0.013 mmol) in CH_2Cl_2 (1 mL) was stirred at room temperature for 10 min and proceeded as described in general procedure to afford **10**, as a yellow gum (0.044 g, 97%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.62 (br, 8 H), 1.79–2.05 (br, 20 H), 2.40 (br, 4 H), 3.12 (s, 2 H), 3.92 (t, J = 6.1 Hz, 14 H), 3.98 (t, J = 6.1 Hz, 2 H), 4.98 (s, 10 H), 5.55 (s, 2 H), 6.06–6.23 (m, 12 H), 6.90 (d, J = 8.6 Hz, 2 H), 7.29–7.73 (m, 37 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.7, 28.9, 33.0, 67.7, 67.8, 70.0, 70.5 (d, J = 13.6 Hz), 93.7, 94.0, 94.4, 104.9 (m, J = 7.1 Hz), 114.3 (d, J = 10.8 Hz), 127.5, 127.9, 128.3 (d, J = 12.0 Hz), 128.5, 129.9, 132.0, 132.3, 134.4 (d, J = 11.2 Hz), 136.8, 136.9 (d, J = 7.8 Hz), 160.6, 160.8; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 29.6 (d,

J_{PRh} = 149 Hz). Anal. calcd. for $C_{105}H_{113}ClO_{13}PRh$: C, 71.97; H, 6.50; Rh, 5.86; Found C, 73.34; H, 6.82; Rh, 5.40.

11. A mixture of **8** (0.056 g, 0.027 mmol) and $[Rh(cod)Cl]_2$ (0.02 g, 0.041 mmol) in CH_2Cl_2 (1 mL) was stirred at room temperature for 10 min and proceeded as described in general procedure to afford **11**, as a yellow foam (0.073 g, 98%). ^1H NMR ($CDCl_3$, 400 MHz) δ 1.61 (br, 12 H), 1.79–2.05 (br, 36 H), 2.38 (br, 12 H), 3.13 (s, 6 H), 3.92 (t, J = 6.0 Hz, 18 H), 3.98 (t, J = 6.0 Hz, 6 H), 4.99 (s, 6 H), 5.55 (s, 6 H), 6.06–6.15 (m, 12 H), 6.90 (d, J = 8.4 Hz, 6 H), 7.30–7.76 (m, 51 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.7, 28.9, 33.0, 67.6, 67.7, 70.0, 70.5 (d, J = 13.8 Hz), 93.7, 94.1, 104.9 (m, J = 7.0 Hz), 114.2 (d, J = 10.9 Hz), 127.5, 127.9, 128.0 (d, J = 9.8 Hz), 128.5, 129.9, 131.9, 132.2, 134.4 (d, J = 11.1 Hz), 136.8, 136.9 (d, J = 7.9 Hz), 160.7, 160.8; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 29.5 (d, J_{PRh} = 149 Hz). Anal. calcd. for $C_{153}H_{171}Cl_3O_{15}P_3Rh_3$: C, 66.63; H, 6.25; Rh, 11.14; found C, 66.58; H, 6.06, Rh, 9.60.

12. A mixture of **9** (0.036 g, 0.013 mmol) and $[Rh(cod)Cl]_2$ (0.019 g, 0.04 mmol) in CH_2Cl_2 (1 mL) was stirred at room temperature for 10 min and proceeded as described in general procedure to afford **12**, as a yellow foam (0.053 g, 96%). ^1H NMR ($CDCl_3$, 300 MHz) δ 1.63 (br, 18 H), 1.82–2.08 (br, 60 H), 2.39 (br, 24 H), 3.13 (s, 12 H), 3.92 (t, J = 6.0 Hz, 24 H), 4.00 (t, J = 6.0 Hz, 12 H), 5.55 (s, 12 H) 6.06 (s, 12 H), 6.90 (d, J = 8.1 Hz, 12 H), 7.35–7.77 (m, 72 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 22.7, 28.9, 33.0, 67.7, 70.5 (d, J = 13.6 Hz), 93.8, 104.9 (m, J = 7.5 Hz), 114.2 (d, J = 10.5 Hz), 128.0 (d, J = 9.8 Hz), 129.9, 131.8, 132.4, 134.4 (d, J = 11.3 Hz), 136.8 (d, J = 12.8 Hz), 160.7, 160.8; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 29.5 (d, J_{PRh} = 149 Hz); Anal. calcd. for $C_{225}H_{258}Cl_6O_{18}P_6Rh_6$: C, 63.34; H, 6.10; Rh, 14.48; found C, 63.69; H, 6.11; Rh, 14.84.

13. A mixture of **X** (0.65 g, 0.23 mmol), phosphine monomer **III** (0.2 g, 0.46 mmol), K_2CO_3 (0.062 g, 0.46 mmol) and 18-C-6 (cat.) in DMF (20 mL) was stirred at 70 °C for 36 h and proceeded as described in general procedure to afford phosphine oxide, as a colorless gum (0.62 g, 85%). TLC: R_f 0.6 (PhMe/EtOAc = 50:50). ^1H NMR ($CDCl_3$, 400 MHz) δ 1.59 (m, 20 H), 1.80 (m, 40 H), 3.90 (t, J = 6.0 Hz, 38 H), 3.99 (t, J = 6.0 Hz, 2 H), 4.97 (s, 22 H), 6.05–6.23 (m, 30 H) 6.87 (d, J = 8.4 Hz, 2 H), 7.22–7.67 (m, 67 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.7, 28.8, 28.9, 67.7, 67.8, 70.0, 93.8, 94.1, 94.5, 114.5 (d, J = 12.9 Hz), 127.5, 127.9, 128.4 (d, J = 12.1 Hz), 128.5, 131.7, 132.0 (d, J = 9.8 Hz), 132.3, 133.5, 133.9 (d, J = 11.2 Hz), 136.8, 160.6, 160.9; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 28.9; Anal. calcd. for $C_{205}H_{221}O_{32}P$:C, 76.28; H, 6.90; found C, 76.47; H, 6.96.

A solution of above intermediate (0.19 g, 0.086 mmol) in THF (3 mL) was added to the stirred suspension of $CeCl_3$ (0.05 g, 0.18 mmol) and LAH (0.03 g, excess) in THF (20 mL) and proceeded as described in general procedure to afford **13**, as a colorless gum (0.17 g, 91%). TLC: R_f 0.65 (PhMe/EtOAc = 98:2). ^1H NMR ($CDCl_3$, 400 MHz) δ 1.59 (br, 20 H), 1.80 (br, 40 H), 3.92 (br, 40 H), 4.97 (s, 22 H), 6.05–6.23 (m, 30 H) 6.87 (d, J = 8.1 Hz, 2 H), 7.23–7.41 (m, 67 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.7, 28.9, 67.7, 70.0, 93.7, 94.0, 94.4, 114.6 (d, J = 8.0 Hz), 127.5, 127.9, 128.4 (d, J = 8.1 Hz), 128.5, 133.3 (d, J = 18.9 Hz), 135.5 (d, J = 21.2 Hz), 136.8, 160.6, 160.8; ^{31}P NMR ($CDCl_3$, 162 MHz) δ − 6.9; Anal. calcd. for $C_{205}H_{221}O_{31}P$: C, 76.66; H, 6.94; found C, 76.65; H, 6.89.

14. A mixture of **VIII** (0.19 g, 0.24 mmol), **XII** (1.3 g, 1.75 mmol), NaH (0.1 g, 2.4 mmol, 60% in mineral oil) in DMF (10 mL) was stirred at 70 °C for 48 h and proceeded as described in general procedure to afford phosphine oxide, as a brown oil (0.77 g, 69%). TLC: R_f 0.4 ($CHCl_3$/MeOH = 9:1). ^1H NMR ($CDCl_3$, 400 MHz) δ 1.62 (br, 30 H), 1.84 (br, 60 H), 3.90 (t, J = 6.0 Hz, 48 H), 4.00 (t, J = 6.0 Hz, 12 H), 4.99 (s, 12 H), 6.05–6.24 (m, 30 H), 6.95 (d, J = 8.4 Hz, 12 H), 7.31–7.68 (m, 102 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.7, 28.8, 28.9, 67.7, 67.8, 70.0, 93.7, 94.1, 114.5 (d, J = 13.0 Hz), 127.5, 127.9, 128.4 (d, J = 12.2 Hz), 128.5, 131.7, 132.0 (d, J = 9.7 Hz), 132.4, 133.4, 133.8 (d, J = 11.2 Hz), 136.7, 160.6, 160.8, 162.0; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 29.34.

A solution of above intermediate (0.25 g, 0.05 mmol) in THF (6 mL) was added to the stirred suspension of $CeCl_3$ (0.1 g, 0.4 mmol) and LAH (0.06 g, excess) in THF (25 mL) and proceeded as described in general procedure to afford **14**, as a colorless gum (0.2 g, 82%). TLC: R_f 0.7 (PhMe/EtOAc = 95:5). ^1H NMR ($CDCl_3$, 300 MHz) δ 1.59 (br, 30 H), 1.80 (br, 60 H), 3.92 (br, 60 H), 4.98 (s, 12 H), 6.05–6.14 (m, 30 H), 6.86 (d, J = 8.1 Hz, 12 H), 7.25–7.39 (m, 102 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 22.7, 28.8, 28.9, 67.5, 67.6, 70.0, 93.8, 94.1, 114.6 (d, J = 8.4 Hz), 127.5, 127.9, 128.3 (d, J = 7.5 Hz), 128.6, 133.4 (d, J = 19.2 Hz), 135.6 (d, J = 21.2 Hz), 136.8, 137.9 (d, J = 10.5 Hz), 159.8, 160.6, 160.8; ^{31}P NMR ($CDCl_3$, 162 MHz) δ −6.99; Anal. calcd. for $C_{285}H_{306}O_{36}P_6$:C,76.18; H, 6.86; found C, 75.88; H,7.06.

15. A mixture of **XI** (0.35 g, 0.187 mmol), **III** (1.25 g, 2.8 mmol), NaH (0.12 g, 2.8 mmol, 60% in mineral oil) in DMF (15 mL) was heated at 70 °C for 72 h and proceeded as described in general procedure to afford phosphine oxide, as a brown oil (0.75 g, 65%). TLC: R_f 0.5 ($CHCl_3$/MeOH = 80:20). ^1H NMR (300 MHz, $CDCl_3$) δ 1.61 (br, 42 H), 1.82 (br, 84 H), 3.91 (br, 60 H), 3.98 (t, J = 6.6 Hz, 24 H), 6.05 (s, 30 H), 6.94 (d, J = 8.0 Hz, 24 H), 7.44–7.67 (m, 144 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 22.7, 28.8, 28.9, 67.6, 67.7, 93.8, 114.4 (d, J = 13.6), 128.4 (d, J = 12.0 Hz), 131.7, 132.0 (d, J = 9.7 Hz), 132.3, 133.5, 133.9 (d, J = 11.3 Hz), 160.8, 162.0; ^{31}P NMR ($CDCl_3$, 162.0 MHz) δ 29.4.

A solution of above intermediate (0.26 g, 0.04 mmol) in THF (6 mL) was added to the stirred suspension of $CeCl_3$ (0.15 g, 0.6 mmol) and LAH (0.06 g, excess) in THF (25 mL) and proceeded as described in general procedure to afford **15**, as a colorless gum (0.2 g, 80%). TLC: R_f 0.41 (PhMe/EtOAc = 95:5). ^1H NMR (300 MHz, $CDCl_3$) δ 1.60 (br, 42 H), 1.80 (br, 84 H), 3.95 (br, 84 H), 6.05 (s, 30 H), 6.94 (d, J = 8.1 Hz, 24 H), 7.15–7.32 (m, 144 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 22.7, 28.9, 67.6, 67.7, 93.8, 114.6 (d, J = 9.0 Hz), 128.4 (d, J = 7.5 Hz), 129.0, 133.4 (d, J = 18.1 Hz), 135.5 (d, J = 21.1 Hz), 138.0 (d, J = 10.6 Hz), 159.8, 160.8; ^{31}P NMR ($CDCl_3$, 162.0 MHz) δ − 7.0; Anal. calcd. for $C_{381}H_{408}O_{42}P_{12}$: C, 75.88; H, 6.82; found: C, 75.84; H, 6.54.

16. A mixture of **13** (0.063 g, 0.02 mmol) and $[Rh(cod)Cl]_2$ (0.005 g, 0.01 mmol) in CH_2Cl_2 (1 mL) was stirred at room temperature for 10 min and proceeded as described in general procedure to afford **16**, as a yellow foam (0.066 g, 97%). ^1H NMR ($CDCl_3$, 400 MHz) δ 1.59 (br, 20 H), 1.77–2.05 (br, 44 H), 2.36–2.50 (br, 4 H), 3.13 (s, 2 H), 3.90 (t, J = 6.0 Hz, 38 H), 3.98 (t, J = 6.0 Hz, 2 H), 4.97 (s, 22 H), 5.55 (s, 2 H), 6.05–6.22 (m, 30 H), 6.93 (d, J = 8.4 Hz, 2 H), 7.28–7.67 (m, 67 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 22.7, 29.0, 33.1, 67.7, 67.8, 70.0, 70.5 (d, J = 13.5 Hz), 94.0, 94.4, 94.7, 104.9 (m, J = 6.8 Hz), 114.3 (d, J = 10.5 Hz), 127.5, 127.9, 128.3 (d, J = 12.0 Hz), 128.5, 129.9, 131.9, 132.3, 134.4 (d, J = 11.1 Hz), 136.8, 136.9 (d, J = 7.7 Hz), 160.7, 160.9; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 29.6 (d, J_{PRh} = 149 Hz). Anal. calcd. for $C_{213}H_{233}ClO_{31}PRh$: C, 73.97; H, 6.79; Rh, 2.96; found C, 73.59; H, 6.71; Rh, 2.98.

17. A mixture of **14** (0.034 g, 0.0076 mmol) and $[Rh(cod)Cl]_2$ (0.011 g, 0.023 mmol) in CH_2Cl_2 (1 mL) was stirred at room temperature for 10 min and proceeded as described in general procedure to afford **17**, as a yellow foam (0.043 g, 96%). ^1H NMR ($CDCl_3$, 300 MHz) δ 1.63 (br, 30 H), 1.84–2.05 (br, 84 H), 2.39 (br, 24 H), 3.13 (s, 12 H), 3.97 (br, 60 H), 4.99 (s, 12 H), 5.54 (s, 12 H) 6.05–6.16 (m, 30 H), 6.91 (d, J = 8.4 Hz, 12 H), 7.33–7.77 (m, 102 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 22.7, 28.9, 33.0, 67.7, 67.8, 70.0, 70.5 (d, J = 13.6 Hz), 93.8, 94.3, 104.9 (m, J = 6.8 Hz), 114.3 (d, J = 11.2 Hz), 127.5, 127.9, 128.0 (d, J = 9.8 Hz), 128.5, 130.0, 132.0, 132.5, 134.4 (d, J = 11.1 Hz), 136.8, 136.9 (d, J = 7.9 Hz), 160.7, 160.9; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 29.5 (d, J_{PRh} = 149 Hz). Anal. calcd. for $C_{333}H_{378}Cl_6O_{36}P_6Rh_6$: C, 66.97; H, 6.38; Rh, 10.34; found C, 67.11; H, 6.14; Rh, 9.80.

18. A mixture of **15** (0.047 g, 0.0077 mmol) and $[Rh(cod)Cl]_2$ (0.023 g, 0.047 mmol) in CH_2Cl_2 (1 mL) was stirred at room temperature for 10 min and proceeded as described in general

procedure to afford **18**, as a yellow foam (0.067 g, 97%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.62 (br, 42 H), 1.82–2.05 (br, 132 H), 2.38 (br, 48 H), 3.13 (s, 24 H), 3.97 (m, 84 H), 5.54 (s, 24 H) 6.05 (s, 30 H), 6.90 (d, J = 8.4 Hz, 24 H), 7.36–7.77 (m, 144 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 22.7, 28.9, 33.0, 67.7, 67.8, 70.5 (d, J = 13.6 Hz), 93.8, 104.9 (m, J = 7.1 Hz), 114.2 (d, J = 11.2 Hz), 128.0 (d, J = 9.8 Hz), 130.0, 131.8, 132.4, 134.4 (d, J = 11.3 Hz), 136.8 (d, J = 13.6 Hz), 160.7, 160.8; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 29.5 (d, J_{PRh} = 149 Hz); Anal. calcd. for $C_{477}H_{552}Cl_{12}O_{42}P_{12}Rh_{12}$: C, 63.73; H, 6.19; Rh, 13.72; found C, 64.21; H, 6.33; Rh, 12.48.

19. A mixture of **XIII** (0.19 g, 0.03 mmol), phosphine monomer **III** (0.027 g, 0.06 mmol) and NaH (0.003 g, 60% in mineral oil, 0.06 mmol) in DMF (15 mL) was stirred at 70 °C for 24 h and proceeded as described in general procedure to afford phosphine oxide, as a colorless gum (0.16 g, 80%). TLC: R_f 0.6 (PhMe/EtOAc = 60:40). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.60 (br, 44 H), 1.79 (br, 88 H), 3.90 (t, J = 6.0 Hz, 86 H), 4.00 (t, J = 6.0 Hz, 2 H), 4.97 (s, 46 H), 6.05–6.22 (m, 66 H), 6.94 (d, J = 8.4 Hz, 2 H), 7.16–7.44 (m, 127 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.7, 28.9, 29.0, 67.7, 67.8, 70.0, 93.8, 94.5, 127.5, 127.9, 128.4 (d, J = 12.1 Hz), 128.5, 132.0 (d, J = 9.8 Hz), 132.3, 133.5, 133.9,136.8, 160.6, 160.8; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 29.9; Anal. calcd. for $C_{421}H_{461}O_{68}$P:C, 76.15; H, 7.00; found C,76.30; H, 6.77.

A solution of above intermediate (0.32 g, 0.048 mmol) in THF (5 mL) was added to the stirred suspension of $CeCl_3$ (0.024 g, 0.1 mmol) and LAH (0.02 g, excess) in THF (20 mL) and proceeded as described in general procedure to afford **19**, as a colorless gum (0.28 g, 86%). TLC: R_f 0.65 (PhMe/EtOAc = 96:4). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.59 (br, 44 H), 1.80 (br, 88 H), 3.92 (br, 88 H), 4.97 (s, 46 H), 6.05–6.23 (m, 66 H) 6.86 (d, J = 8.4 Hz, 2 H), 7.22–7.40 (m, 127 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.7, 28.8, 67.6, 67.7, 70.0, 93.7, 94.0, 94.4, 114.6 (d, J = 8.0 Hz) 127.5, 127.9, 128.2, 128.4 (d, J = 7.0 Hz), 128.5, 133.3 (d, J = 18.9 Hz), 135.5 (d, J = 21.7 Hz), 136.8, 160.5, 160.8; ^{31}P NMR ($CDCl_3$, 162 MHz) δ −6.94; Anal. calcd. for $C_{421}H_{461}O_{67}$P:C, 76.33; H, 7.01; found C, 76.16; H, 6.89.

20. A mixture of **XI** (0.11 g, 0.06 mmol), **XII** (0.65 g, 0.88 mmol), K_2CO_3 (0.14 g, 1.0 mmol) and 18-C-6 (cat.) in DMF (20 mL) was stirred at 70 °C for 72 h and proceeded as described in general procedure to afford phosphine oxide, as a brown oil (0.41 g, 72%). TLC: R_f 0.4 ($CHCl_3$/MeOH = 9:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.61 (br, 66 H), 1.82 (br, 132 H), 3.90 (t, J = 6.0 Hz, 108 H), 4.00 (t, J = 6.0 Hz, 24 H), 4.99 (s, 24 H), 6.01–6.14 (m, 66 H), 6.95 (d, J = 8.6 Hz, 24 H), 7.31–7.68 (m, 204 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.7, 28.8, 28.9, 67.7, 67.8, 70.0, 93.8, 94.2, 114.6 (d, J = 13.0 Hz), 127.5, 127.9, 128.4 (d, J = 12.8 Hz), 128.5, 131.7, 132.0 (d, J = 9.8 Hz), 132.4, 133.5, 134.0 (d, J = 11.3 Hz), 136.8, 160.6, 160.8, 161.9; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 29.34; Anal. calcd. for $C_{597}H_{648}O_{90}P_{12}$:C,74.42; H,6.78; found C,74.26; H, 6.52.

A solution of above intermediate (0.16 g, 0.016 mmol) in THF (5 mL) was added to the stirred suspension of $CeCl_3$ (0.1 g, 0.4 mmol) and LAH (0.024 g, excess) in THF (20 mL) and proceeded as described in general procedure to afford **20**, as a colorless gum (0.14 g, 89%). TLC: R_f 0.6 (PhMe/EtOAc = 95:5). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.60 (br, 66 H), 1.81 (br, 132 H), 3.92 (br, 132 H), 4.99 (s, 24 H), 6.06–6.15 (m, 66 H), 6.86 (d, J = 8.4 Hz, 24 H), 7.25–7.39 (m, 204 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.7, 28.9, 67.5, 67.6, 70.0, 93.8, 94.1, 114.5 (d, J = 8.4 Hz), 127.5, 127.9, 128.4 (d, J = 7.5 Hz), 128.6, 133.4 (d, J = 18.8 Hz), 135.6 (d, J = 21.1 Hz), 136.8, 137.9 (d, J = 10.5 Hz), 159.8, 160.6, 160.8; ^{31}P NMR ($CDCl_3$, 162 MHz) δ − 6.99; Anal. calcd. for $C_{597}H_{648}O_{78}P_{12}$: C, 75.93; H, 6.92; found C, 75.46; H, 6.67.

21. A mixture of **XIV** (0.21 g, 0.05 mmol), **III** (0.62 g, 1.4 mmol), NaH (0.071 g, 60% in mineral oil, 1.8 mmol) in DMF (30 mL) was heated at 90 °C for 72 h and proceeded as described in general procedure to afford phosphine oxide, as a brown oil (0.48 g, 74%). TLC: R_f 0.4 ($CHCl_3$/MeOH = 80:20). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.60 (br, 90 H), 1.81 (br, 180 H), 3.91 (br, 180 H), 6.05 (s, 66 H), 6.93 (d, J = 8.4 Hz, 48 H), 7.43–7.67 (m, 288 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 22.7, 28.9, 29.6, 67.7, 67.8, 93.7, 114.5 (d, J = 12.0 Hz), 128.4 (d, J = 12.0 Hz), 131.7, 132.0 (d, J = 9.8 Hz), 132.3, 133.4, 133.9 (d, J = 11.2 Hz), 160.8, 162.0; ^{31}P NMR ($CDCl_3$, 162.0 MHz) δ 29.2. Anal. calcd. for $C_{789}H_{852}O_{114}P_{24}$: C, 73.45; H, 6.66; found: C, 73.23; H, 7.11.

A solution of above intermediate (0.215 g, 0.016 mmol) in THF (3 mL) DMF (0.1 mL) was added to the stirred suspension of $CeCl_3$ (0.2 g, 0.83 mmol) and LAH (0.1 g, excess) in THF (25 mL) and proceeded as described in general procedure to afford **21**, as a brown gum (0.17 g, 81%). TLC: R_f 0.30 (PhMe/EtOAc = 90:10). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.60 (br, 90 H), 1.82 (br, 180 H), 3.94 (br, 180 H), 6.05 (s, 66 H), 6.85 (d, J = 8.4 Hz, 48 H), 7.15–7.38 (br, 288 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.7, 28.9, 67.6, 67.7, 93.8, 114.7 (d, J = 8.0 Hz), 128.2, 128.4 (d, J = 7.5 Hz), 129.0, 133.4 (d, J = 19.0 Hz), 135.5 (d, J = 21.3 Hz), 137.7 (d, J = 10.2 Hz), 159.9, 160.9; ^{31}P NMR ($CDCl_3$, 162.0 MHz) δ - 6.9. Anal. calcd. for $C_{789}H_{852}O_{90}P_{24}$: C, 75.7; H, 6.86; found: C, 75.29; H, 6.52.

22. A mixture of **19** (0.1 g, 0.015 mmol) and $[Rh(cod)Cl]_2$ (0.0037 g, 0.0075 mmol) in CH_2Cl_2 (1 mL) was stirred at room temperature for 10 min and proceeded as described in general procedure to afford **22**, as a yellow gum (0.102 g, 98%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.59 (m, 44 H), 1.78–2.05 (m, 90 H), 2.40 (br, 4 H), 3.13 (s, 2 H), 3.92 (br, 88 H), 4.98 (s, 46 H), 5.55 (s, 2 H), 6.05–6.23 (m, 66 H), 6.90 (d, J = 8.6 Hz, 2 H), 7.24–7.67 (m, 127 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.7, 28.9, 67.7, 67.8, 70.0, 93.7, 94.5, 127.5, 127.9, 128.0, 128.5, 130.0, 134.4 (d, J = 11.1 Hz), 136.8, 160.6, 160.8; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 29.5 (d, J_{PRh} = 150 Hz). Anal. calcd. for $C_{422}H_{467}ClO_{67}PRh$: C, 74.75; H, 6.94; Rh, 1.52. Found C, 73.94; H, 6.95; Rh, 1.57.

23. A mixture of **20** (0.03 g, 0.0032 mmol) and $[Rh(cod)Cl]_2$ (0.0094 g, 0.019 mmol) in CH_2Cl_2 (1 mL) was stirred at room temperature for 10 min and proceeded as described in general procedure to afford **23**, as a yellow foam (0.038 g, 96%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.62 (br, 66 H), 1.83–2.05 (br, 180 H), 2.39 (br, 48 H), 3.13 (s, 24 H), 3.98 (br, 132 H), 4.99 (s, 24 H), 5.55 (s, 24 H) 6.06–6.17 (m, 66 H), 6.92 (d, J = 8.6 Hz, 24 H), 7.34–7.78 (m, 204 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.7, 28.9, 33.0, 67.7, 67.8, 70.0, 70.5 (d, J = 13.7 Hz), 93.8, 94.3, 104.9 (m, J = 7.1 Hz), 114.2 (d, J = 11.2 Hz), 127.5, 127.9, 128.0 (d, J = 9.8 Hz), 128.5, 129.9, 131.9, 132.2, 134.4 (d, J = 11.2 Hz), 136.7, 136.8 (d, J = 8.1 Hz), 160.7, 160.9; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 29.5 (d, J_{PRh} = 149 Hz). Anal. calcd. for $C_{693}H_{792}Cl_{12}O_{78}P_{12}Rh_{12}$: C, 67.12; H, 6.44; Rh, 9.96; found C, 67.04; H, 6.26; Rh, 10.2.

24. A mixture of **21** (0.05 g, 0.004 mmol) and $[Rh(cod)Cl]_2$ (0.024 g, 0.048 mmol) in CH_2Cl_2 (1 mL) was stirred at room temperature for 10 min and proceeded as described in general procedure to afford **24**, as a yellow foam (0.072 g, 97%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.62 (br, 90 H), 1.73–2.05 (br, 276 H), 2.38 (br, 96 H), 3.12 (s, 48 H), 3.97 (br, 180 H), 5.54 (s, 48 H) 6.05 (s, 66 H), 6.90 (d, J = 8.4 Hz, 48 H), 7.29–7.76 (m, 288 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.7, 28.8, 28.9, 33.0, 67.7, 67.8, 70.5 (d, J = 13.5 Hz), 93.8, 104.9 (m, J = 6.8 Hz), 114.2 (d, J = 11.0 Hz), 128.0 (d, J = 9.8 Hz), 130.0, 131.9, 132.3, 134.4 (d, J = 11.0 Hz), 136.8 (d, J = 13.1 Hz), 160.7, 160.8; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 29.5 (d, J_{PRh} = 150 Hz). Anal. calcd. for $C_{981}H_{1140}Cl_{24}O_{90}P_{24}Rh_{24}$: C, 63.91; H, 6.23; Rh, 13.40; found C, 64.07; H, 6.41; Rh, 13.70.

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Appendix. Supplementary material

Supplementary material associated with this article can be found in the online version, at doi:10.1016/j.jorganchem.2010.09.054.

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