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Increased Efficacies of an Individual Catalytic Site in Clustered Multivalent Dendritic Catalysts

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Abstract: In the studies reported so far on dendrimer-mediated catalysis, the efficacies of the catalytic units were studied and compared primarily across the generations. In order to identify the efficacy of an individual catalytic unit with respect to the number of such units present within a given generation, a series of catalysts were prepared within a generation. Dendrimers incorporated with phosphine-metal complexes were chosen for the study and as many as 11 catalysts within three generations were synthesized. The C–C bond-forming reactions, namely, the Heck and the Suzuki coupling reactions, were then selected to study the catalytic efficiencies of the series of partially and fully phosphine-metal complex functionalized dendrimers. The efficacies of the formation of cinnamate and biphenyl, catalyzed by the dendritic catalysts, were compared. The comparative analyses show that an individual catalytic site is far more effective in its catalytic activity when presented in multiple numbers, i.e., in a multivalent dendritic system, than as a single unit within the same generation, i.e., in a monovalent dendritic system. The study identifies the beneficial effects of the multivalent presentation of the catalytic moieties, both within and across the dendrimer generations.

Keywords: C–C bond formation; dendrimers; Heck reaction; multivalency; organometallic catalysis; palladium

Introduction

Dendrimers exhibit uniformly distributed functional groups at their peripheries.[1] Incorporation of catalytically active moieties at the peripheries of dendrimers and studies of their organometallic catalysis are attractive, in order to explore the properties of these new types of macromolecules.[2] Pioneering works of van Koten and co-workers,[3] Reetz and co-workers,[a] Astruc and co-workers[5] and a number of other groups have established that dendrimers are effective macromolecular carriers of catalysts.[6–19] Stereoselective reactions using dendritic catalysts were reported, wherein the stereoselective conversion resulted due to a co-operativity between the adjacent catalytic sites present at the dendrimer peripheries.[20] The first examples of a dendritic catalyst directing the stereoselectivity of a catalytic reaction, assisted through conformational chirality transfer of the dendritic structure to the catalytic center was demonstrated recently.[15] In addition, "dendrimer effects" were also reported, resulting from an autocatalysis, with the increase in the catalytic units from lower to higher generations of the dendrimer series.[7] In the studies reported so far, the efficacies of the catalytic units are studied most primarily across the generations, and comparisons on the catalysis profiles are performed among the dendrimer generations. Such dendritic catalysts include both the types wherein the catalytic units are placed either at the peripheries of the dendrimer, or at the interiors of the dendritic structures. It has been observed that the efficiency of the dendritic catalysts increases with higher generations, and the effect was ascribed due to a positive dendritic effect. An early report of van Koten and co-workers[3b] showed a negative dendritic effect on atom-transfer radical addition reaction, using carbosilane-supported arylnickel(II) catalysts. This effect was attributed to a "proximity effect" between the peripheral Ni(II) sites, that led to lower catalytic efficiencies and irreversible formation of inactive Ni(III) species. Reetz and co-workers[4] observed an enhanced catalytic activity of Pd(0)-containing dendritic catalysts compared with the corresponding monomeric cata-

lysts, which was attributed to the higher thermal stabilities of the dendritic metal complexes. Recently, Astruc and co-workers[5] reported a series of poly(propylene imine)-based dendritic catalysts and a negative dendritic effect was observed in a carbon-carbon coupling reactions, resulting from an increase in the steric hindrance around the active metal centres, as the dendrimer generations advanced. Such a negative dendritic effect was also reported by Gade and coworkers[8] on asymmetric hydrogenation reactions, although the effect was rationalized as being due to back-folding of the catalyst and the resulting steric hindrance.

With a number of examples that exist on dendritic catalysts, primarily across the generations, it was surmised how the individual catalytic unit would behave in a dendrimer whose peripheries are functionalized with many such units. In this query, we were interested particularly to investigate the catalytic activities of an organometallic catalyst when the catalytic moiety is present in varying numbers within a given dendrimer generation. The poly(ether imine) (PETIM) dendrimers were chosen for this study.[21] It was desired to study (i) how the catalytic activity of an individual catalytic site is modified due to the dendritic backbone and (ii) how the catalytic activity of the individual site is modified as a result of clustering of many catalytic sites at the peripheries of the dendrimer. An effort was thus undertaken and systematic studies with a number of partially and fully metal complex functionalized dendritic catalysts have shown that the catalytic activities are significantly higher for the multivalent catalytic moiety substituted dendritic catalysts, than the monovalent homologues, within a given dendrimer generation. The details of the synthesis of a number of multivalent dendritic catalysts, evaluation and discussion of the catalytic profiles are presented herein.

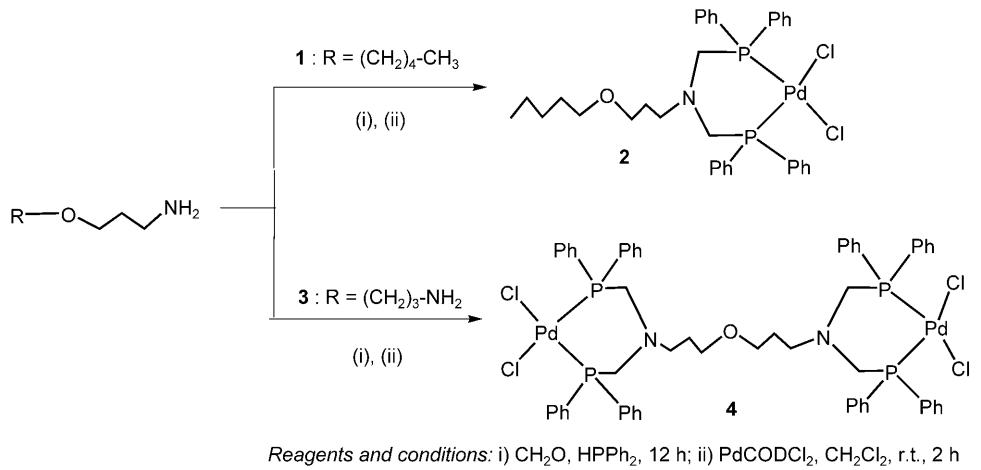
Results and Discussion

Synthesis and Characterization of Multivalent Dendritic Catalysts

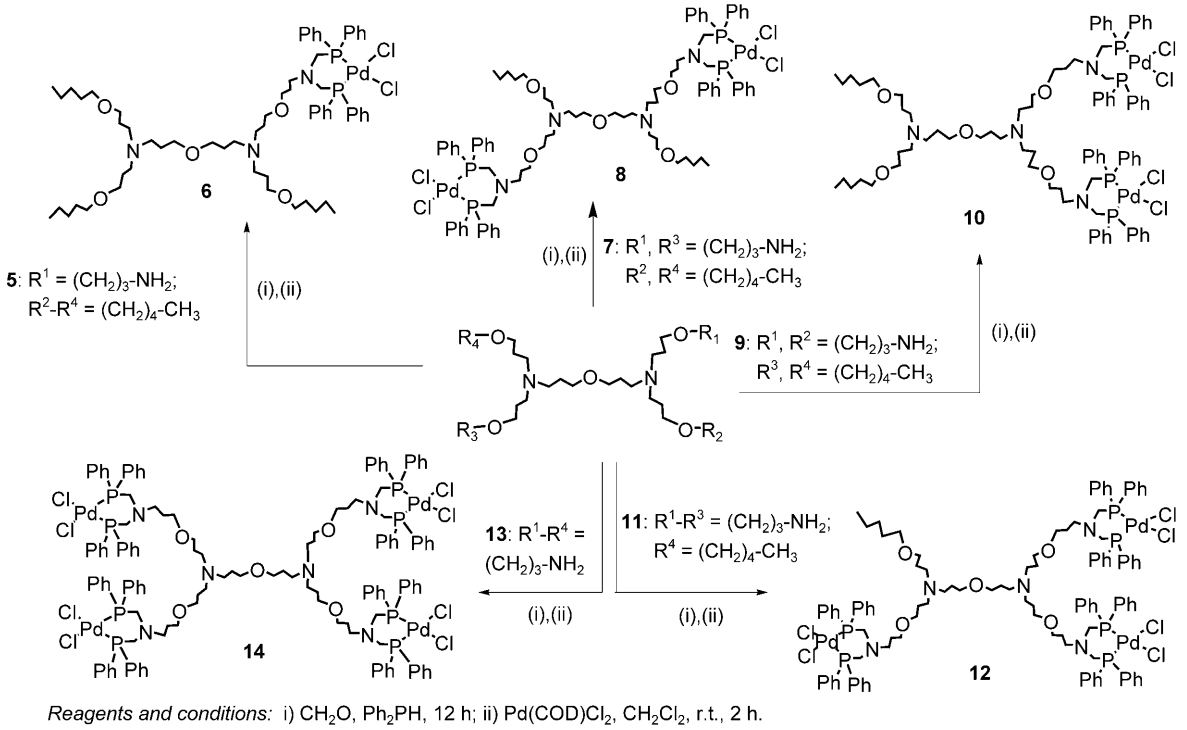
The PETIM dendrimers, chosen for the studies of the dendritic catalysts, are constituted with tertiary amine as the branching sites and an ether as the linking functionality, interspaced with a propyl group as the spacer. The synthesis of this series of dendrimers was established previously.[21] The alcohol-terminated PETIM dendrimers were chosen for further modifications in the present study. It was desired to install catalytic units in varying numbers within each generation. Thus, a first generation dendrimer can, in principle, present four distinct catalysts, one each with one, two, three and four catalytic sites. Second generation dendrimer can, in principle, lead to eight such distinct catalysts. The early synthetic efforts required synthesizing the partially and the fully ligand functionalized dendrimers. The catalysis study was planned using the bis(diphenylphosphinomethyl)amine-palladium complex. The optimal formation of a six-membered metal complex with the above ligand is attractive in the studies of the dendritic catalysts. Functionalization with alkyldiphenylphosphine moieties was conducted through a Mannich reaction of the amine functionalities, present at the peripheries of dendrimer, with formaldehyde and diphenylphosphine.[4,22] The number of the primary amine groups led to define the number of phosphine groups at the peripheries of the dendrimers. The primary amine groups were, in turn, prepared by Michael addition of acrylonitrile with hydroxy groups, followed by a reduction. The first and second generation PETIM dendrimers present up to four and eight hydroxy groups at their peripheries. A partial etherification was exercised in order to mask a few hydroxy groups, useful to prepare the dendrimers with partially substituted phosphine groups. *n*-Pentyl ether substituted dendrimers were prepared, in differing numbers, in each generation. Subsequent Michael addition of acrylonitrile with the remaining hydroxy groups, led to 2-cyanoethyl ethers, and a metal-mediated reduction of the nitrile provided the amine functionalized dendrimers. Preparations of the partial pentyl ether substituted dendrimers and their Michael addition and reduction reactions are summarized in the Supporting Information.

The synthesis of phosphine-Pd(II) metal complexes, having one and two catalytic sites, corresponding to the lowest members in the dendritic catalyst series, is presented in Scheme 1. Mono-amine **1** and bis-amine **3** were subjected to Mannich reaction with Ph_2PCH_2OH, prepared *in situ* from CH_2O and $HPPh_2$, to afford the free phosphine ligands. The ligands were complexed with $Pd(COD)Cl_2$ to form the complexes **2** and **4**, presenting one and two catalytic sites, respectively. The complexes **2** and **4** are yellow solids and are soluble in solvents such as 1,4-dioxane and CH_2Cl_2. The identities of the free ligands and the Pd(II) metal complexes were established by NMR spectroscopic and elemental composition analyses. Mass spectrometric characterization of free ligands confirmed further the constitution of the ligands.

Four partial and a full phosphine-metal complex substituted first generation dendritic catalysts were synthesized by double phosphinomethylation of primary amines to afford the phosphine ligand functionalized dendrimers (Scheme 2). The partial *O*-pentyl group attached dendritic amines **5**, **7**, **9** and **11** afforded partially functionalized ligands, that upon Pd(II) metal complexation led to formation of the catalysts **6**, **8**, **10** and **12**. The fully phosphine-Pd(II) complex substituted catalyst **14** was prepared using the amine



Scheme 1. Synthesis of the zero generation dendritic catalysts.



Scheme 2. Synthesis of the first generation dendritic catalysts.

functionalized dendrimer **13**. The free phosphine ligand containing dendrimers were generally glassy or foamy solids, whereas the corresponding metal complexes were yellow solids. ^{31}P NMR analysis of the free phosphine ligands and the corresponding Pd(II) complexes showed shift of a signal from ~−28 ppm for the free ligand to ~8 ppm for the metal complex. The constitution of the phosphine ligand dendrimers were confirmed further through mass spectrometric analysis and the metal complexes through the elemental composition analysis. The *trans*-**7** and *cis*-**9** orientations of the substitutions were identified through analysis of ^{1}H NMR spectral patterns of the derivatives, wherein the C*H*$_2$OH resonance in the *trans*-derivative appeared at 3.78 ppm, whereas in the *cis*-derivative, it appeared at 3.73 ppm (Figure 1). Subsequent reactions led to the formation of the catalysts with *trans*- and *cis*-orientations. This particular analysis was applicable to higher generations also.

Preparations of second generation catalysts, presenting varying numbers of catalytic sites, were initiated using a few partially *O*-pentyl substituted dendrimers, namely, **15**, **17**, **19** and **21** (Scheme 3). Double phosphinomethylation of primary amine groups af-

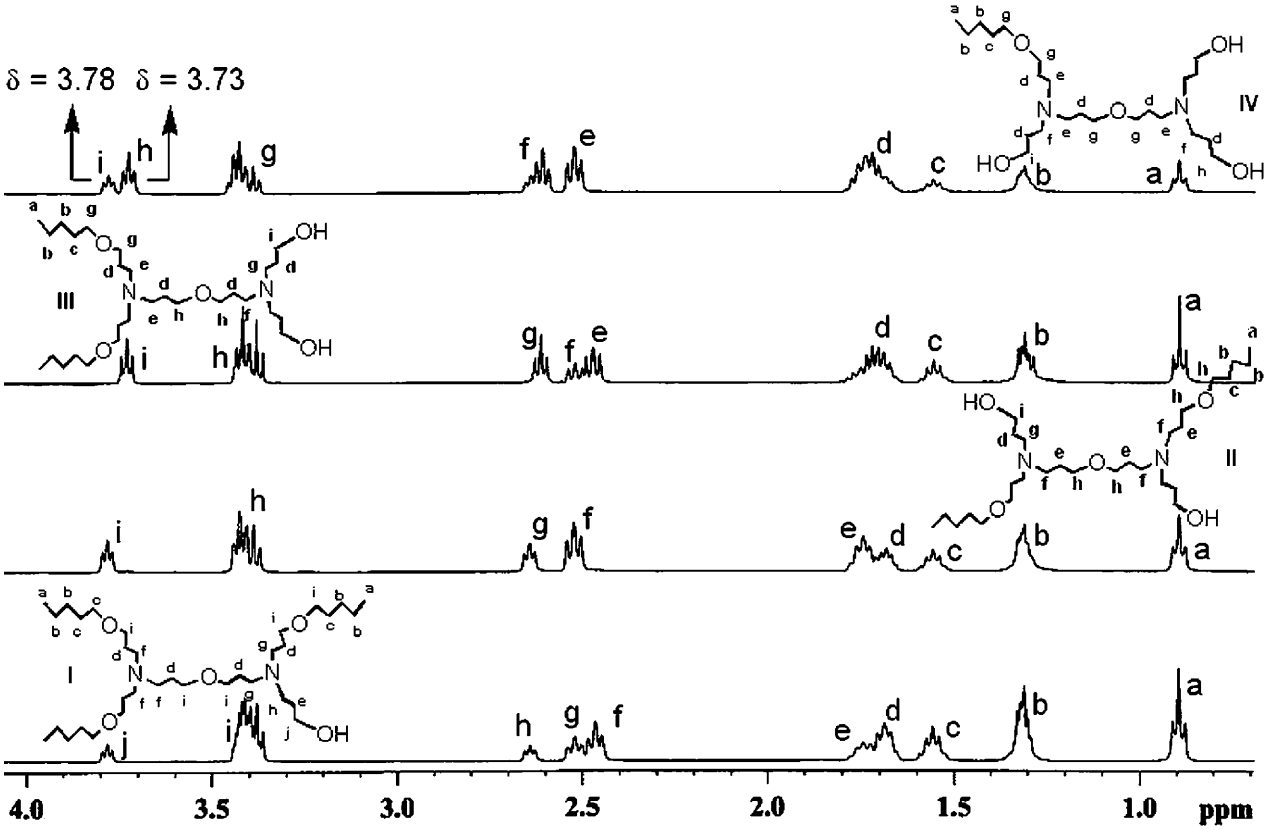
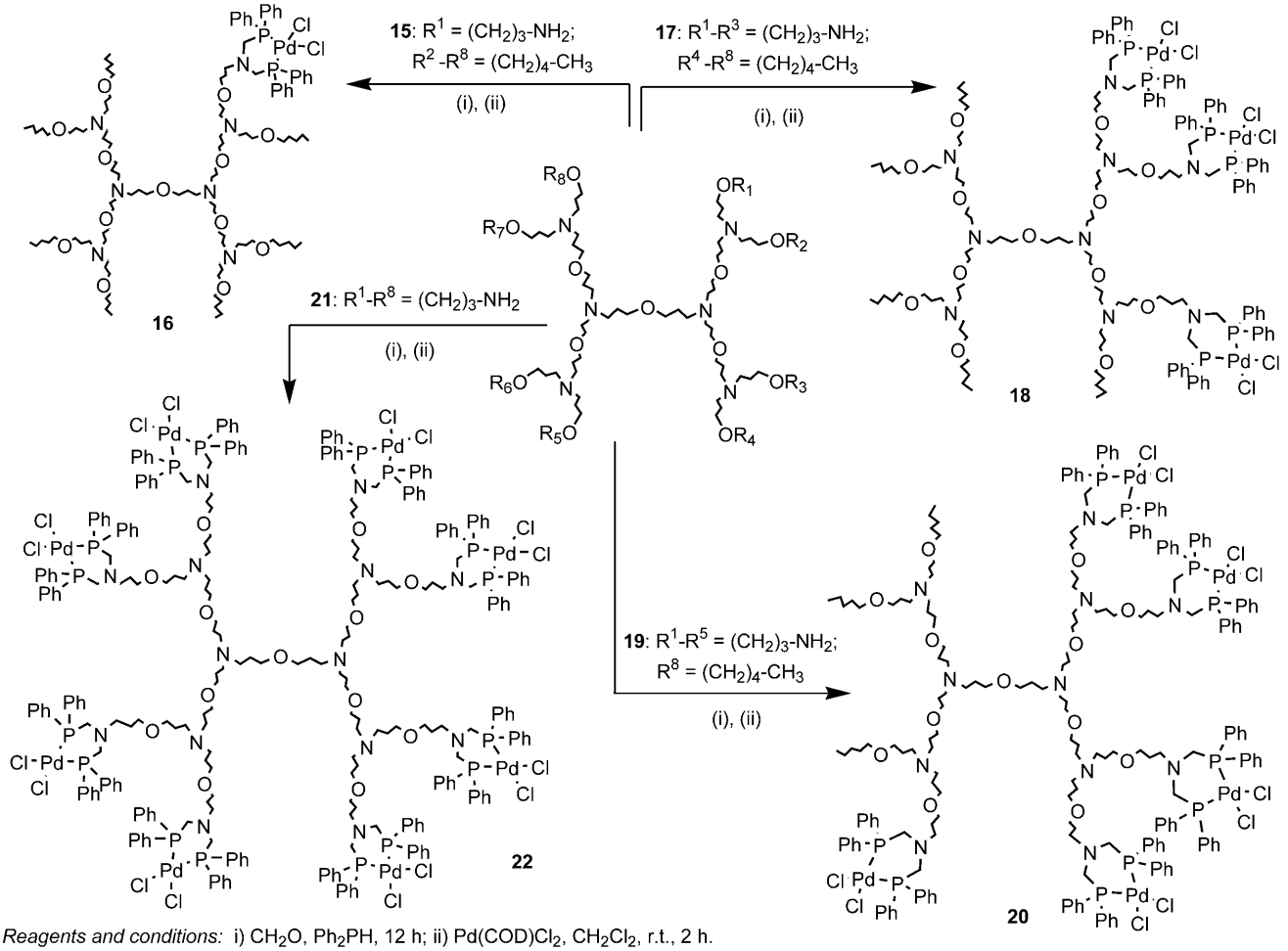


Figure 1. Comparison of ^{1}H NMR spectra of partial alkylated first generation alcohol terminated PETIM dendrimers.

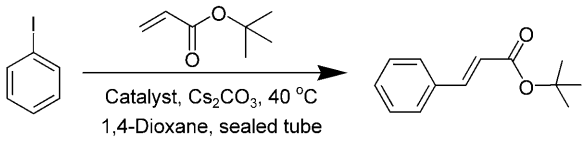
forded the free phosphine ligands, in excellent yields, in each case. Subsequent metal complexation afforded the dendritic phosphine-Pd(II) complexes **16**, **18**, **20** and **22**, containing one, three, five and eight catalytic centres, respectively. The purities and structural homogeneities of the ligands and the metal complexes were ascertained by IR, ^{1}H, ^{13}C and ^{31}P NMR spectroscopies and elemental composition analysis. Further, it was also possible to secure the mass spectral analysis of a few dendritic phosphine ligands.

Efficacies of the Multivalent Dendritic Catalysts in the Heck and Suzuki Coupling Reactions

The following catalytic studies were undertaken, in order to analyze and compare the catalytic efficiencies of the partially and fully catalytic sites substituted dendrimers, both within and across generations. The C–C bond forming Heck coupling reaction was chosen in order to analyze the catalytic efficiencies. The Heck coupling reaction is a Pd-catalyzed reaction and is well studied.[23] A C–C bond-forming Heck coupling reaction, between iodobenzene and *tert*-butyl acrylate, was tested using the dendritic catalysts (Scheme 4). The reaction was conducted in the presence of Cs_2CO_3 as the base and in 1,4-dioxane. The molar equivalents of the olefin and base were 1.5 times with respect to iodobenzene. Each individual catalytic centre was considered as an independent unit, such that the dendritic catalysts presenting more than one catalytic centre, was considered in multiples according to the number of the catalytic sites within the dendrimer. Thus, the studies were conducted on the basis of a *per* catalytic site, and the number of moles of the phosphine-metal complex was normalized, so as to maintain a uniform molar equivalent of the phosphine-metal complex in each catalytic reaction, irrespective of the number of catalytic sites in each dendritic catalyst. After few trial coupling reactions, the mole ratio of iodobenzene *vs.* one catalytic site was fixed at 0.5 mol%, i.e., the substrate *per* one catalytic site was 200:1. The progress of the reaction was monitored by the HPLC method. Formation of only *tert*-butyl cinnamate was observed with all catalysts. Figure 2 shows the formation of *tert*-butyl cinnamate after 1 h of the reaction, in the presence of different catalysts. A product formation of >70% could be observed with most catalysts within 1 h of the reaction. All catalysts, however, showed a nearly quantitative conversion after 24 h. Using only $Pd(OAc)_2$ as the catalyst and at a mole ratio of 0.5 mol%, the reaction led to ~44% conversion, after 24 h. Thus, a significantly higher catalytic activity



Scheme 3. Synthesis of the second generation dendritic catalysts.



Scheme 4. The Heck coupling reaction, employed to test the dendritic catalysts.

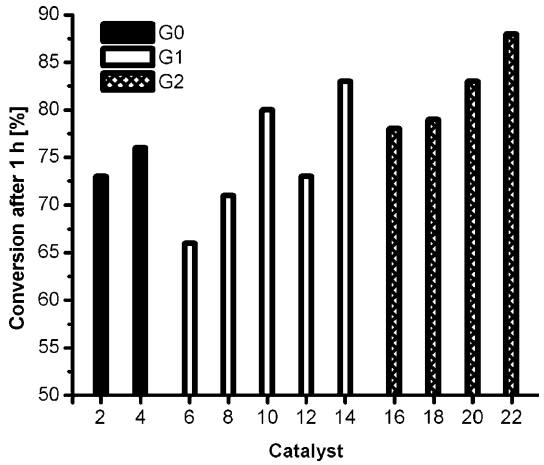
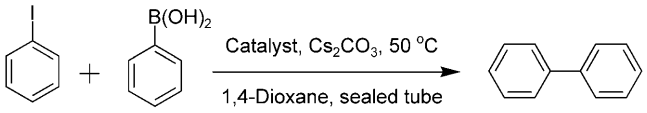


Figure 2. Product formation in Heck coupling reaction, after 1 h, employing the dendritic catalysts.

could be observed generally for the bis-phosphine-metal catalysts.

An analysis of Figure 2 show the following trends: (i) the activity of an individual catalytic site is better in catalysts presenting more than one catalytic site within the molecule; (ii) across the generations, the individual catalytic sites in higher generation dendrimers show higher catalytic activity than the individual catalytic sites in the lower generations; (iii) the individual catalytic site in *cis*-oriented **10** is better as a catalyst than the *trans*-oriented catalyst **8** and (iv) even within partially substituted catalysts **12** and **18**, each having three catalytic sites, the catalytic activity of each individual site is considerably better for the second generation catalyst **18**, than the individual catalytic sites in the first generation catalyst **12**. Across the generations zero **4**, first **14** and second **22** genera-



Scheme 5. The Suzuki coupling reaction, employed to test the dendritic catalysts.

tion catalysts, the product formation after 1 h was 77%, 84% and 89%, respectively. On the other hand, with zero **2**, first **6** and second generation **16** catalysts, each with one catalytic unit, the product formation in 1 h was 73%, 67% and 77%, respectively. With a nearly equivalent accessibility of the catalytic site in each case, the higher catalytic activity of an individual catalytic site in **14** and **22**, in comparison to **6** and **16** would correspond to the nature of the dendritic catalyst. Further, within each dendrimer generation, the individual catalytic site catalyzes considerably improved product formation with the multivalent dendritic catalyst than the partially substituted and monovalent dendritic catalysts. Thus, in addition to the role played by the dendritic scaffold, there is also a beneficial effect experienced by an individual catalytic site due to the presence multiple numbers of catalytic sites placed within the molecule.

In order to assess the observations of the catalytic efficacies in the Heck coupling reaction, the dendritic catalysts were also employed to catalyze the Suzuki coupling reaction of an aryl iodide with a phenylboronic acid, leading to the formation of biphenyl (Scheme 5). In this reaction too, the dendritic catalysts having more than one catalytic site within the molecule were considered in multiples of one catalytic site. As the catalyst to substrate ratio was based on the individual catalytic site, catalysts having more than one catalytic site were considered according to the number of catalytic sites that the molecule possesses while calculating the molar ratios required for the catalysis. The mole ratio of iodobenzene to an individual catalytic centre was maintained at 200:1. Figure 3 shows the trend in the formation of biphenyl in each case of the catalysts. Significant differences were observed in the product formation among the catalysts, both within and across the generations. For example, each individual catalytic site efficacy in the case of the second generation catalyst **22** is superior to the individual catalytic site in the case of the second generation catalyst **16**. Such a trend has been observed with other catalysts too within the generation, as well as, across the generations. The catalytic efficacy of the individual catalytic centers in *cis*-**10** was observed to be better than *trans*-**8** in the Suzuki reaction, as in the case of Heck coupling reaction. Analysis of the trend in the case of the Suzuki reaction was nearly the same as with the Heck coupling reaction. Further, a conversion of ~28% was only observed for the non-dendritic catalyst $PdCl_2(PPh_3)_2$, with the mole ratio of 200:1 for substrate:catalyst.

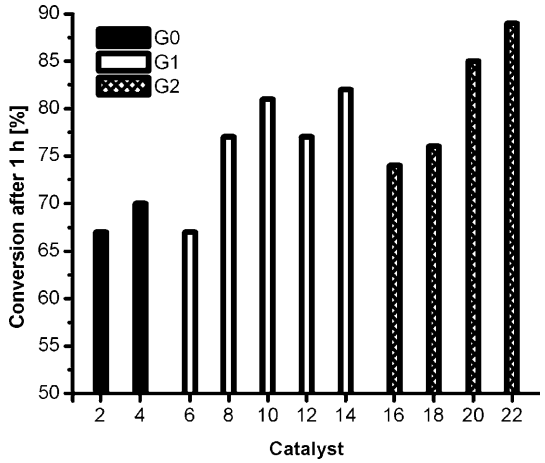


Figure 3. Product formation in Suzuki reaction, after 1 h, employing the dendritic catalysts.

The status of the catalysts in both Heck and Suzuki coupling reactions were examined after the completion of the reaction. Nearly quantitative recovery of the catalysts was possible in the most and fully catalytic site containing catalysts, through the differential solubilization of the catalysts, substrates and the products. Thus, whereas the substrates and products were fully soluble in hexane, the catalysts were insoluble and this differential solubilization was sufficient to recover the catalysts. On the other hand, the monovalent catalytic site populated dendritic catalysts, **2**, **6**, **16** and **18**, could not be recovered fully due to their solubilization in hexane.[24] With the ability to recover the multivalent catalytic site loaded catalysts, the absence of both leaching and the metal nanoparticle formation were inferred. Further, the absence of the metal nanoparticle formation was also inferred from the observation of the initiation of the reaction and the product formation, without an induction period. Evolution of S-shaped curves, with an induction period, is known previously[25] for reactions involving the metallic particle formation.

It is pertinent to compare the results we observed with that known previously on the dendritic catalysts. Specifically, the dendrimer peripheries fully substituted with ligand-metal complex have been studied in several occasions previously, ever since the first report of Reetz and co-workers a decade ago.[4a] Various types of dendrimers have been utilized, that include, (i) poly(propylene imine) dendrimers;[4,5,8,14] (ii) poly(amidoamine) dendrimers;[10,20] (iii) poly(aryl ether) dendrimers;[9,12,13] (iv) carbosilane dendrimers;[3,16,17] phosphorus-containing dendrimers[6] and (iv) poly(propyl ether imine) dendrimers.[19] In the later case, concerning the use of poly(propyl ether imine) dendrimers, reported previously by us, the

ligand constitution was (bis-diphenylphosphinopropyl)amine ligand attached to the dendrimer backbone. A comparison of the above ligand-metal complex and the (bis-diphenylphosphinomethyl)amine-metal complex reported herein showed that the dendritic catalysts of this report are far more effective, likely due to the differences in the ligand constitution, base and the solvent used for the reaction. On the other hand, the (bis-diphenylphosphinomethyl)amino ligand, attached to dendritic backbone, has been studied previously, across the generations, by fully substituting the peripheries with the ligand-metal complex.[4-6,10,14] In the light of these reports, the present investigation addresses the catalysis behaviour of catalysts within a given generation. Synthesis of the series of partially and fully catalytic site incorporated dendrimers, reported herein, could be accomplished in a facile manner. The most important outcome of our catalysis study is the observation that a considerable increase in the catalytic efficacy of an individual catalytic site results, as the number of the catalytic site increases, within a given generation and with identical dendritic backbone. We rule out the possibility of formation and stability of metal nanoparticles for reasons that (i) the mole ratio of the catalytic site employed to conduct the reactions was normalized to *per* catalytic site, thereby we applied a uniform molar equivalence of catalytic site for all the studied catalysts, irrespective of the number of such sites available in a dendrimer generation; (ii) the homogeneous catalysts could be recovered nearly quantitatively through differential solubilizations and (iii) the absence of S-shaped curves of the product formation, without an induction period. $Pd(0)L_2$ is known to be the catalyst for the coupling reactions, for which $Pd(II)L_2$ formed as the pre-catalyst. Investigations of Amatore and Jutand have shown that anionic $Pd(0)L_2X^-$ ($X^- =$ anion) species also forms as a catalytic intermediate.[26,27] We undertook an effort to follow the changes in the pre-catalyst **10** during the active catalyst formation and observed that (i) the yellow colour of the pre-catalyst in 1,4-dioxane and in the presence of Cs_2CO_3, at 70 °C, changed to a reddish-brown solution, and (ii) the ^{31}P NMR spectrum of the active Pd(0) catalyst exhibited resonances at 26.1 ppm and 24.3 ppm. These resonances appeared to correspond to the phosphine ligand co-ordinated Pd(0) catalyst. It has been reported previously that the $Pd(0)(PPh_3)_2$ complex exhibits the resonance for the phosphorus nucleus at 23.0 ppm.[28] The resonance at ~8.4 ppm, relating to the ^{31}P nuclei of the pre-catalyst **10**, disappeared completely. Further, the absence of peaks at ~−28.5 ppm and ~28.6 ppm, corresponding to the free ligand alkyldiphenylphosphine and the alkyldiphenylphosphine oxide, respectively, indicated that these species were not present in the reaction mixture. The chelation of bis-phosphine with the metal centre is important for the stability, recoverability and re-use of the dendritic catalysts.[5d]

It appears that the kinetics of catalysis lead to the observed increases in the catalytic behaviour of the individual catalytic sites in the mostly or fully ligand-metal substituted dendrimers. For example, when comparing the *cis*-**10** and *trans*-**8**, both with identical constitutions, but with differing spatial proximities, each catalytic site in *cis*-**10** is more effective than *trans*-**8**. Furthermore, the dendritic backbone also provides a positive effect on catalysis, as for example, a comparison of the catalysts **6** and **16**, each having one catalytic site. This trend among **6** and **16** is likely to be due to a higher association or even an encapsulation of the substrate with the higher generation dendrimer scaffold, than the lower generation scaffold. We presume that the rate constants associated with individual catalytic centre are modified systematically, during catalysis, as the number of the catalytic units increases within a generation of the dendrimer. Intermediates within the catalytic cycle may assist the multivalent catalysts more than the monovalent catalysts, which contributes positively to the catalytic efficacy of an individual catalytic site. The fact that the individual catalytic site efficacies increase as the number of catalytic sites increases within the dendritic molecule indicates that there is no inactive and aggregative species formation in the multivalent catalysts. The absence of aggregative species formation would allow each individual catalytic site to exhibit higher catalytic efficacies. The higher efficacies of catalysts with lower absolute concentrations were demonstrated by detailed kinetic studies of Blackmond and co-workers.[29] Overall, from the studies within and across the dendrimer generations, it emerges that the efficacies of each individual catalytic site increase with a multivalent catalyst system, than with a monovalent dendritic catalyst.

Conclusions

A large number of dendritic catalysts has been studied previously, primarily by utilizing fully ligand-metal substituted dendritic catalysts and across the generations. This study shows the catalytic activities of individual sites, as a function of the number of such catalytic sites within the dendrimer generation. The chosen catalytic reactions, namely, the Heck and the Suzuki coupling reactions, are among the most widely used C−C bond forming reactions. The study shows primarily the important increases in the catalytic activities of individual catalytic sites in the partially and fully substituted dendritic catalysts. The observations of this study address some of the pertinent queries relating to the efficiencies of the multivalent dendritic catalysts.

Experimental Section

General Methods

Analytical TLC was performed on commercial Merck plates coated with aluminium oxide 60 F254 neutral (type E, 0.2 mm). I_2 was used as staining agent for TLC. Neutral alumina was used for column chromatography. The full alcohol and amine functionalized dendrimers were synthesized by known procedures.[21] Phosphination reactions were performed using standard Schlenk techniques under an argon atmosphere. The solvents were dried according to literature procedures and saturated with N_2. The deutrated solvents used for NMR spectroscopic measurements were degassed by successive "freeze-pump-thaw" cycles and dried over 4 Å molecular sieves. 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; band, several overlapping signals; b, broad. The IR spectra were recorded as neat samples on a Perkin–Elmer 1600 spectrometer. The other starting material were commercially available and used without further purification.

General Procedure for Phosphinomethylation of Amine (I)

A mixture of $(CH_2O)_n$ (2.1 molar equiv. *per* amine group) and Ph_2PH (2.2 molar equiv. *per* amine group) in MeOH was heated at 70 °C for 10 min and then cooled to room temperature. The reaction mixture was added to a solution of dendritic amine in MeOH and stirred for 30 min, diluted with PhMe (12 mL) and heated at 70 °C for 0.5 h. The reaction mixture was stirred for an additional 12 h at room temperature, concentrated and MeOH (~20 mL) was added, so as to precipitate the product, which was dried subsequently under vacuum for 10 h at 65 °C.

General Procedure for the Preparation of Pd Catalyst (II)

A mixture of the dendritic phosphine and $Pd(COD)Cl_2$ (1 molar equiv. *per* bis-phosphine unit) in CH_2Cl_2 was stirred at room temperature for 2 h. The solvents were then removed, the residue washed with hexane and Et_2O, dried to afford the desired Pd complex.

2: A mixture of $(CH_2O)_n$ (0.08 g, 2.77 mmol) and Ph_2PH (0.54 g, 2.91 mmol) in MeOH (4 mL) was heated at 70 °C for 10 min. and then cooled. To this reaction mixture, a solution of the dendritic amine **1** (0.19 g, 1.32 mmol) in MeOH (4 mL) was added and the reaction was followed further as given in the general procedure I, to afford the bisphosphinomethyl intermediate as a glassy solid; yield: 0.68 g (95%),. FT-IR (neat): $\nu = 3056$, 2954, 2931, 2859, 1968, 1909, 1830, 1672, 1434, 1180, 1119, 945, 741, 695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.42$–7.38 (m, 8H) 7.27–7.26 (m, 12H), 3.60 (band, 4H), 3.26–3.20 (m, 4H), 2.94 (band, 2H), 1.67 (band, 2H), 1.52–1.46 (m, 2H), 1.33–1.26 (m, 4H), 0.89 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 138.0$, 137.6, 133.1, 132.9, 128.5, 128.3, 128.2, 70.9, 68.5, 58.5, 53.2, 29.3, 28.3, 22.5, 14.0; ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = -28.5$; HR-MS: $m/z = 574.2618$ $[M+2O+H]^+$, calcd. for $C_{34}H_{42}NO_3P_2$: 574.2640.

To a solution of the above intermediate (0.19 g, 0.35 mmol) in CH_2Cl_2 (6 mL), $Pd(COD)Cl_2$ (0.10 g, 0.35 mmol) was added and the reaction was followed as given in the general procedure II, to afford the dendritic phosphine-Pd complex **2**, as a pale yellow solid; yield: 0.24 g (96%); mp 120–122 °C; FT-IR (neat): $\nu = 3073$, 3055, 2974, 2927, 2856,1483, 1436, 1307, 1187, 1102, 873, 846, 740, 691, 560, 512 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 7.88$–7.81 (m, 8H) 7.57–7.42 (m, 12H), 3.40–3.37 (m, 4H), 3.20 (t, $J = 6.6$ Hz, 2H), 3.08 (t, $J = 5.7$ Hz, 2H), 2.70 (t, $J = 7.2$ Hz, 2H) 1.59–1.42 (m, 4H), 1.31–1.23 (m, 4H), 0.88 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (75.5 MHz, CD_2Cl_2): $\delta = 134.4$, 134.3, 132.0, 129.0, 128.9, 71.4, 68.0, 59.7, 57.4, 56.8, 29.8, 28.8, 26.4, 22.9, 14.21; ^{31}P NMR (162 MHz, CD_2Cl_2): $\delta = 8.3$; elemental analysis calcd. (%) for $C_{34}H_{41}Cl_2NOP_2Pd$: C 56.80, H 5.75, N 1.95; found: C 56.30, H 5.65, N 1.94.

4: A mixture of $(CH_2O)_n$ (0.17 g, 5.63 mmol) and Ph_2PH (1.1 g, 5.9 mmol) in MeOH (4 mL) was heated at 70 °C for 10 min and then cooled. To this reaction mixture, a solution of the dendritic amine **3**[20] (0.18 g, 1.34 mmol) in MeOH (4 mL) was added and the reaction was followed further as given in the general procedure I, to afford the bisphosphinomethyl intermediate as a foamy solid; yield: 1.2 g (97%); FT-IR (neat): $\nu = 3069$, 3052, 2944, 2856, 2794, 1585, 1481, 1434, 1097, 1070, 864, 740, 695, 506, 480 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.42$–7.35 (m, 16H), 7.25–7.20 (m, 24H), 3.56 (band, 8H), 3.10 (t, $J = 6.0$ Hz, 4H), 2.89 (t, $J = 6.6$ Hz, 4H), 1.64–1.56 (m, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 138.2$, 138.0, 133.1, 132.9, 128.4, 128.3, 128.2, 68.6, 58.7, 58.6, 58.5, 53.2, 53.1, 53.0, 26.7; ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = -28.5$; HR-MS: $m/z = 989.3505$ $[M+4O+H]^+$, calcd. for $C_{58}H_{61}N_2O_5P_4$: 989.3531.

To a solution of the above intermediate (0.11 g, 0.12 mmol) in CH_2Cl_2 (5 mL), $Pd(COD)Cl_2$ (0.066 g, 0.23 mmol) was added and the reaction was followed as given in the general procedure II, to afford the dendritic phosphine-Pd complex **4**, as a yellow solid; yield: 0.15 g (98%); mp 167–169 °C; FT-IR (neat): $\nu = 3073$, 3055, 2974, 2927, 2856, 1483, 1436, 1307, 1187, 1102, 873, 846, 740, 691, 560, 512 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 7.75$–7.69 (m, 16H) 7.44–7.31 (m, 24H), 3.25 (band, 8H), 2.82 (t, $J = 5.7$ Hz, 4H), 2.51 (t, $J = 6.0$ Hz, 4H), 1.39–1.33 (m, 4H); ^{13}C NMR (75.5 MHz, CD_2Cl_2): $\delta = 134.4$, 134.2, 132.0, 129.7, 129.1, 128.9, 68.2, 59.5, 57.3, 56.7, 26.3; ^{31}P NMR (162 MHz, CD_2Cl_2): $\delta = 8.5$; elemental analysis calcd. (%) for $C_{58}H_{60}Cl_4N_2OP_4Pd_2$: C 54.44, H 4.73, N 2.19; found: C 53.55, H 4.53, N 2.29.

6: A mixture of $(CH_2O)_n$ (0.057 g, 1.89 mmol) and Ph_2PH (0.37 g, 1.98 mmol) in MeOH (4 mL) was heated at 70 °C for 10 min. and then cooled. To this reaction mixture, a solution of the dendritic amine **5** (0.57 g, 0.90 mmol) in MeOH was added and stirred for 30 min. The reaction mixture was diluted with PhMe (12 mL), heated at 70 °C for 0.5 h. The mixture was stirred for an additional 12 h at room temperature, concentrated and hexane (~20 mL) was added, hexane layer was filtered, concentrated and dried under vacuum for 10 h at 65 °C, to afford the bisphosphinomethyl intermediate as a glassy liquid; yield: 0.89 g (96%). FT-IR (neat): $\nu =$ 3059, 2952, 2931, 2857, 2801, 1463, 1436, 1371, 1161, 1116,

738, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.41–7.35$ (m, 8H) 7.28–7.26 (m, 12H), 3.56 (d, $J = 2.5$ Hz, 4H), 3.43–3.36 (m, 16H), 3.28 (t, $J = 4.9$ Hz, 2H), 3.21 (t, $J = 5.2$ Hz, 2H) 2.91 (t, $J = 5.4$ Hz, 2H), 2.47 (band, 12H), 1.70–1.53 (m, 20H), 1.31 (band, 12H), 0.89 (t, $J = 6.4$ Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 138.2$, 138.1, 133.1, 133.0, 128.5, 128.4, 128.3, 71.0, 68.8, 50.7, 29.6, 28.4, 27.3, 22.5, 14.0; ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = -28.5$; HR-MS: $m/z =$ 1044.7251 $[M+2O+H]^+$, calcd. for $C_{62}H_{100}N_3O_5P_2$: 1044.7087.

To a solution of the above intermediate (0.115 g, 0.112 mmol) in CH_2Cl_2 (5 mL), $Pd(COD)Cl_2$ (0.032 g, 0.112 mmol) was added and the reaction was stirred for 2 h at room temperature, solvent removed and the residue was extracted with hexane, concentrated and dried to afford the dendritic phosphine-Pd complex **6**, as a brownish yellow liquid; yield: 0.12 g (89%). FT-IR (neat): $\nu = 3073$, 3055, 2974, 2927, 2856,1483, 1436, 1307, 1187, 1102, 873, 846, 740, 691, 560, 512 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.82–7.73$ (m, 8H) 7.51–7.35 (m, 12H), 3.43–3.36 (m, 22H), 3.17 (t, $J = 6.5$ Hz, 2H), 2.67 (b, 2H), 2.51 (band, 12H), 1.71 (band, 14H), 1.61–1.53 (m, 6H), 1.31 (band, 12H), 0.89 (t, $J = 5.9$ Hz, 9H); ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 134.3$, 134.2, 131.9, 131.3, 131.2, 129.6, 129.0, 128.9, 71.5, 68.3, 68.0, 59.5, 57.2, 56.7, 50.9, 29.7, 28.7, 27.2, 22.9, 14.2; ^{31}P NMR (162 MHz, CD_2Cl_2): $\delta = 8.5$; elemental analysis calcd. (%) for $C_{62}H_{99}Cl_2N_3O_5P_2Pd$: C 61.7, H 8.28, N 3.49; found: C 60.9, H 8.25, N 3.51.

8: A mixture of $(CH_2O)_n$ (0.116 g, 3.86 mmol) and Ph_2PH (0.75 g, 4.05 mmol) in MeOH (4 mL) was heated at 70 °C for 10 min and then cooled. To this reaction mixture, a solution of the dendritic amine **7** (0.57 g, 0.92 mmol) in MeOH (4 mL) was added and the reaction was followed further as given in the general procedure I, to afford the bisphosphinomethyl intermediate as a glassy liquid; 1.25 g (96%). FT-IR (neat): $\nu = 3070$, 3053, 2931, 2856, 2800, 1950, 1890, 1736, 1586, 1481, 1434, 1158, 1114, 741, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.41–7.37$ (m, 16H) 7.27–7.26 (m, 24H), 3.55 (d, $J = 3.2$ Hz, 8H), 3.41–3.34 (m, 12H), 3.27 (t, $J = 6.4$ Hz, 4H), 3.21 (t, $J = 6.6$ Hz, 4H), 2.91 (t, $J = 6.8$ Hz, 4H), 2.45 (band, 12H), 1.70–1.52 (m, 20H), 1.32–1.28 (m, 8H), 0.88 (t, $J = 6.7$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 138.2$, 138.1, 133.2, 133.0, 128.4, 128.3, 128.2, 71.0, 69.1, 69.0, 68.8, 58.8, 58.7, 58.6, 53.2, 50.8, 50.7, 29.4, 28.4, 26.8, 22.5, 14.0; ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = -28.5$; ES-MS: $m/z = 1427.8180$ $[M+2O+H]^+$; calcd. for $C_{86}H_{119}N_4O_6P_4$: 1427.8080.

To a solution of the above intermediate (0.124 g, 87.9 μmol) in CH_2Cl_2 (5 mL), $Pd(COD)Cl_2$ (0.05 g, 0.176 mmol) was added and the reaction was followed as given in the general procedure II, to afford the dendritic phosphine-Pd complex **8**, as a yellow-orange solid; yield: 0.15 g (94%); mp 85–87 °C; FT-IR (neat): $\nu = 3073$, 3055, 2974, 2927, 2856,1483, 1436, 1307, 1187, 1102, 873, 846, 740, 691, 560, 512 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 7.86–7.79$ (m, 16H) 7.55–7.41 (m, 24H), 3.36–3.29 (m, 20H), 3.23 (t, $J =$ 6.6 Hz, 4H), 3.03 (t, $J = 5.7$ Hz, 4H), 2.68 (t, $J = 6.0$ Hz, 4H), 2.38 (band, 12H), 1.66–1.47 (m, 20H), 1.29–1.26 (m, 8H), 0.87 (t, $J = 6.8$ Hz, 6H); ^{13}C NMR (75.5 MHz, CD_2Cl_2): $\delta =$ 134.4, 134.3, 132.0, 129.0, 128.9, 71.3, 69.4, 69.2, 68.1, 59.7, 57.4, 56.8, 51.3, 29.9, 28.8, 26.4, 23.0, 14.2; ^{31}P NMR (162 MHz, CD_2Cl_2): $\delta = 8.4$; elemental analysis calcd. (%) for $C_{86}H_{118}Cl_4N_4O_5P_4Pd_2$: C 58.48, H 6.73, N 3.17; found: C 57.80, H 6.78, N 3.18.

10: A mixture of $(CH_2O)_n$ (0.067 g, 2.23 mmol) and Ph_2PH (0.44 g, 2.34 mmol) in MeOH (4 mL) was heated at 70 °C for 10 min. and then cooled. To this reaction mixture, a solution of the dendritic amine **9** (0.33 g, 0.53 mmol) in MeOH (4 mL) was added and the reaction was followed further as given in the general procedure I, to afford the bisphosphinomethyl intermediate as a glassy liquid; yield: 0.73 g (97%). FT-IR (neat): $\nu = 3053$, 2932, 2858, 2801, 1482, 1465, 1438, 1368, 1166, 1116, 741, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.40–7.37$ (m, 16H) 7.27–7.25 (m, 24H), 3.55 (d, $J = 3.0$ Hz, 8H), 3.42–3.35 (m, 12H), 3.27 (t, $J = 6.3$ Hz, 4H), 3.20 (t, $J = 6.5$ Hz, 4H), 2.90 (t, $J = 6.9$ Hz, 4H), 2.47–2.42 (m, 12H), 1.70–1.53 (m, 20H), 1.32–1.28 (m, 8H), 0.89 (t, $J = 6.7$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 138.2$, 138.1, 133.2, 133.0, 128.4, 128.3,128.2, 71.0, 69.2, 69.0, 68.8, 58.8, 58.7, 58.6, 53.2, 50.9, 50.8, 29.5, 28.4, 27.4, 26.8, 22.5, 14.0; ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = -28.5$; ES-MS: $m/z = 1411.8140$ $[M+O+H]^+$, calcd. for $C_{86}H_{119}N_4O_5P_4$: 1411.8131.

To a solution of the above intermediate (0.132 g, 0.093 mmol) in CH_2Cl_2 (5 mL), $Pd(COD)Cl_2$ (0.053 g, 0.187 mmol) was added and the reaction was followed as given in the general procedure II, to afford the dendritic phosphine-Pd complex **10**, as a yellow-orange solid; yield: 0.16 g (97%); mp 112–115 °C; FT-IR (neat): $\nu = 3073$, 3055, 2974, 2927, 2856, 1483, 1436, 1307, 1187, 1102, 873, 846, 740, 691, 560, 512 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 7.78–7.72$ (m, 16H) 7.47–7.33 (m, 24H), 3.34–3.25 (m, 28H), 3.15 (t, $J = 5.7$ Hz, 4H), 2.95 (t, $J = 5.7$ Hz, 4H), 2.59 (t, $J =$ 6.3 Hz, 12H), 1.74 (band, 8H), 1.44–1.42 (m, 8H), 1.23–1.18 (m, 8H), 0.80 (t, $J = 6.9$ Hz, 6H); ^{13}C NMR (75.5 MHz, CD_2Cl_2): $\delta = 134.4$, 134.3, 131.9, 129.7, 129.0, 128.9, 71.4, 69.1, 68.4, 68.2, 59.7, 59.5, 59.4, 57.3, 56.7, 51.0, 29.8, 28.8, 26.3, 22.9, 14.2; ^{31}P NMR (162 MHz, CD_2Cl_2): $\delta = 8.4$; elemental analysis calcd. (%) for $C_{86}H_{118}Cl_4N_4O_5P_4Pd_2$: C 58.48, H 6.73, N 3.17; found: C 57.80, H 6.78, N 3.18.

12: A mixture of $(CH_2O)_n$ (0.16 g, 5.2 mmol) and Ph_2PH (1.0 g, 5.42 mmol) in MeOH (4 mL) was heated at 70 °C for 10 min. and then cooled. To this reaction mixture, a solution of the dendritic amine **11** (0.50 g, 0.82 mmol) in MeOH (4 mL) was added and the reaction was followed further as given in the general procedure I, to afford the bisphosphinomethyl intermediate as a foamy solid; yield: 1.4 g (95%). FT-IR (neat): $\nu = 3053$, 2952, 2932, 2861, 2801, 1480, 1437, 1176, 1120, 741, 749, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.40–7.34$ (m, 24H) 7.27–7.25 (m, 36H), 3.54 (band, 12H), 3.40–3.33 (m, 8H), 3.27–3.24 (m, 6H), 3.20–3.16 (m, 6H), 2.90 (t, $J = 6.6$ Hz, 6H), 2.48 (band, 12H), 1.68–1.52 (m, 20H), 1.31–1.25 (m, 4H), 0.88 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 138.2$, 138.1, 133.0, 128.5, 128.3, 128.2, 71.0, 68.8, 58.7, 50.8, 29.4, 28.3, 26.8, 22.5, 14.0; ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = -28.5$; ES-MS: $m/z =$ 1826.9000 $[M+2O+H]^+$, calcd. for $C_{110}H_{138}N_5O_7P_6$: 1826.9022.

To a solution of the above intermediate (0.15 g, 0.083 mmol) in CH_2Cl_2 (5 mL), $Pd(COD)Cl_2$ (0.071 g, 0.25 mmol) was added and the reaction was followed as given in the general procedure II, to afford the dendritic phosphine-Pd complex **12**, as a yellow solid; yield: 0.18 g (94%); mp 187–189 °C; FT-IR (neat): $\nu = 3073$, 3055, 2974,

2927, 2856,1483, 1436, 1307, 1187, 1102, 873, 846, 740, 691, 560, 512 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 7.78–7.72$ (m, 24H) 7.46–7.33 (m, 36H), 3.29–3.22 (m, 32H), 3.17–3.11 (m, 6H), 2.94–2.91 (m, 6H), 2.58 (band, 6H), 1.52–1.39 (m, 20H), 1.22–1.18 (m, 4H), 0.79 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (75.5 MHz, CD_2Cl_2): $\delta = 134.3$, 134.2, 131.8, 129.6, 128.9, 128.8, 128.7, 71.2, 69.2, 68.9, 68.0, 59.5, 59.3, 59.2, 57.2, 56.6, 29.8, 28.7, 28.3, 27.4, 26.2, 22.8, 14.2; ^{31}P NMR (162 MHz, CD_2Cl_2): $\delta = 8.5$; elemental analysis calcd. (%) for $C_{110}H_{137}Cl_6N_5O_5P_6Pd_3$: C 56.77, H 5.93, N 3.01; found: C 56.01, H 5.85, N 3.08.

14: A mixture of $(CH_2O)_n$ (0.18 g, 5.96 mmol) and Ph_2PH (1.16 g, 6.2 mmol) in MeOH (4 mL) was heated at 70 °C for 10 min. and then cooled. To this reaction mixture, a solution of the dendritic amine **13**[21] (0.419 g, 0.71 mmol) in MeOH (4 mL) was added and the reaction was followed further as given in the general procedure I, to afford the bisphosphinomethyl intermediate as a foamy solid; yield: 1.51 g (98%). FT-IR (neat): $\nu = 3069$, 3052, 2944, 2857, 2799, 1956, 1888, 1813, 1585, 1481, 1434, 1370, 1114, 741, 695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.41–7.35$ (m, 32H) 7.27–7.25 (m, 48H), 3.54 (d, $J = 3.0$ Hz, 16H), 3.34 (band, 4H), 3.24 (t, $J = 5.6$ Hz, 8H), 3.18 (t, $J = 6.3$ Hz, 8H), 2.89 (t, $J = 6.7$ Hz, 8H), 2.43 (band, 12H), 1.63–1.59 (m, 20H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 138.2$, 138.1, 133.2, 133.0, 128.4, 128.3, 128.2, 68.8, 58.7, 53.1, 50.8, 26.8; ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = -28.4$; MALDI-TOF-MS (dihydroxybenzoic acid matrix): $m/z = 2327.8$ $[M+8O+Na]^+$, calcd. for $C_{134}H_{156}N_6O_{13}P_8Na$: 2327.9.

To a solution of the above intermediate (0.12 g, 0.056 mmol) in CH_2Cl_2 (5 mL), $Pd(COD)Cl_2$ (0.064 g, 0.23 mmol) was added and the reaction was followed as given in the general procedure II, to afford the dendritic phosphine-Pd complex **14**, as a yellow-orange solid; yield: 0.16 g (96%); mp 178–182 °C; FT-IR (neat): $\nu = 3053$, 2927, 2862, 1483, 1436, 1306, 1267, 1102, 738, 691 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 7.85–7.79$ (m, 32H) 7.51–7.42 (m, 48H), 3.37 (band, 20H), 3.20 (band, 8H), 3.00–2.97 (m, 8H), 2.64 (band, 20H), 1.88 (band, 12H), 1.47 (band, 8H); ^{13}C NMR (75.5 MHz, CD_2Cl_2): $\delta = 134.4$, 134.2, 132.0, 129.7, 129.0, 128.9, 68.3, 59.4, 57.3, 56.7, 51.1, 50.9, 26.4; ^{31}P NMR (162 MHz, CD_2Cl_2): $\delta = 8.7$; elemental analysis calcd. (%) for $C_{134}H_{156}Cl_8N_6O_5P_8Pd_4$: C 55.73, H 5.44, N 2.91; found: C 53.18, H 5.16, N 3.02.

16: A mixture of $(CH_2O)_n$ (0.015 g, 0.51 mmol) and Ph_2PH (0.098 g, 0.53 mmol) in MeOH (4 mL) was heated at 70 °C for 10 min. and then cooled. To this reaction mixture, a solution of the dendritic amine **15** (0.38 g, 0.24 mmol) in MeOH (4 mL) was added and stirred for 30 min. The reaction mixture was diluted with PhMe (12 mL), heated at 70 °C for 0.5 h. The mixture was stirred for an additional 12 h at room temperature, concentrated and hexane (~20 mL) was added, hexane layer was filtered, concentrated and dried under vacuum for 10 h at 65 °C, to afford the bisphosphinomethyl intermediate as a gum; yield: 0.45 g (94%). FT-IR (neat): $\nu = 3054$, 2953, 2932, 2857, 2802, 1482, 1466, 1367, 1163, 1116, 741, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.42–7.37$ (m, 8H) 7.28–7.27 (m, 12H), 3.55 (d, $J = 3.4$ Hz, 4H), 3.43–3.36 (m, 48H), 3.28 (t, $J = 6.4$ Hz, 2H), 3.21 (t, $J = 6.7$ Hz, 2H), 2.91 (t, $J = 6.9$ Hz, 2H), 2.47–2.41 (m, 36H), 1.70–1.53 (m, 52H), 1.33–1.29 (m, 28H), 0.90 (t, $J = 6.7$ Hz, 21H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 138.2$, 138.1, 133.2, 133.0, 128.4, 128.3, 71.0, 69.2, 69.0, 68.8, 50.9, 50.8, 29.5, 28.4, 27.4, 22.5, 14.0; ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = -28.5$; ES-MS: $m/z = 2040.6240$ $[M+O+Na+H]^+$, calcd. for $C_{118}H_{216}N_7O_{14}P_2Na$: 2040.5778.

To a solution of the above intermediate (0.265 g, 0.13 mmol) in CH_2Cl_2 (5 mL) was added with $Pd(COD)Cl_2$ (0.038 g, 0.13 mmol) and was stirred for 2 h at room temperature, solvent removed and the residue was extracted with hexane, concentrated and dried to afford the dendritic phosphine-Pd complex **16**, as a brownish yellow liquid; yield: 0.25 g (88%). FT-IR (neat): $\nu = 3073$, 3055, 2974, 2927, 2856,1483, 1436, 1307, 1187, 1102, 873, 846, 740, 691, 560, 512 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.88–7.80$ (m, 8H) 7.51–7.39 (m, 12H), 3.44–3.28 (m, 52H), 3.23 (t, $J = 5.4$ Hz, 2H), 3.11 (t, $J = 5.8$ Hz, 2H), 2.72 (t, $J = 6.7$ Hz, 2H), 2.56 (band, 36H), 1.82–1.66 (m, 38H), 1.59–1.50 (m, 14H), 1.31 (b, 28H), 0.90 (t, $J = 6.7$ Hz, 21H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 134.0$, 133.9, 133.8, 131.9, 128.7, 128.5, 71.0, 69.0, 68.8, 67.7, 59.4, 56.9, 56.5, 50.8, 50.7, 29.4, 28.3, 22.5, 14.0; ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = 8.3$; elemental analysis calcd. (%) for $C_{118}H_{215}Cl_2N_7O_{13}P_2Pd$: C 65.03, H 9.94, N 4.50; found: C 65.54, H 9.99, N 4.46.

18: A mixture of $(CH_2O)_n$ (0.06 g, 1.97 mmol) and Ph_2PH (0.38 g, 2.06 mmol) in MeOH (4 mL) was heated at 70 °C for 10 min. and then cooled. To this reaction mixture, a solution of the dendritic amine **17** (0.49 g, 0.312 mmol) in MeOH (4 mL) was added and the reaction was followed further as given in the general procedure I, to afford the bisphosphinomethyl intermediate as a glassy liquid; yield: 0.82 g (95%). FT-IR (neat): $\nu = 3069$, 3051, 2928, 2855, 2800, 1480, 1458, 1433, 1375, 1165, 1114, 740, 695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.44–7.37$ (m, 24H) 7.27 (band, 36H), 3.55 (d, $J = 2.9$ Hz, 12H), 3.43–3.31 (m, 40H), 3.26 (t, $J = 5.7$ Hz, 6H), 3.21 (t, $J = 6.2$ Hz, 6H), 2.91 (t, $J = 6.8$ Hz, 6H), 2.46 (band, 36H), 1.70–1.53 (m, 52H), 1.32–1.29 (m, 20H), 0.89 (band, 15H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 138.2$, 138.1, 133.2, 133.0, 128.5, 128.3, 128.2, 71.0, 69.2, 69.0, 68.8, 58.8, 58.7, 58.6, 53.1, 50.8, 50.7, 29.7, 28.4, 27.3, 26.8, 22.5, 14.0; ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = -28.5$; ES-MS: $m/z = 2767.8743$ $[M+H]^+$; calcd. for $C_{166}H_{254}N_9O_{13}P_6$: 2767.7917.

To a solution of the above intermediate (0.153 g, 0.055 mmol) in CH_2Cl_2 (5 mL), $Pd(COD)Cl_2$ (0.047 g, 0.166 mmol) was added and the reaction was followed as given in the general procedure II, to afford the dendritic phosphine-Pd complex **18**, as a pale yellow gummy solid; yield: 0.17 g (92%). FT-IR (neat): $\nu = 3073$, 3055, 2974, 2927, 2856,1483, 1436, 1307, 1187, 1102, 873, 846, 740, 691, 560, 512 cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 7.78–7.73$ (m, 24H) 7.46–7.32 (m, 36H), 3.32–3.23 (m, 54H), 3.17 (band, 6H), 2.96 (band, 6H), 2.60–2.50 (m, 42H), 1.66 (band, 40H), 1.45–1.42 (m, 10H), 1.22 (band, 20H), 0.82–0.78 (m, 15H); ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 134.3$, 134.2, 131.9, 129.5, 129.0, 128.9, 128.8, 71.3, 68.7, 68.0, 59.3, 57.2, 56.7, 51.0, 29.8, 28.7, 26.2, 22.9, 14.2; ^{31}P NMR (162 MHz, CD_2Cl_2): $\delta = 8.5$; elemental analysis calcd. (%) for $C_{166}H_{253}Cl_6N_9O_{13}P_6Pd_3$: C 60.41, H 7.73, N 3.82; found: C 59.8, H 7.72, N 3.84.

20: A mixture of $(CH_2O)_n$ (0.048 g, 1.61 mmol) and Ph_2PH (0.31 g, 1.69 mmol) in MeOH (4 mL) was heated at 70 °C for 10 min. and then cooled. To this reaction mixture, a solution of the dendritic amine **19** (0.24 g, 0.153 mmol) in MeOH (4 mL) was added and the reaction was followed fur-

ther as given in the general procedure I, to afford the bisphosphinomethyl intermediate as a glassy liquid; yield: 0.52 g (96%). FT-IR (neat): $\nu = 3065, 2957, 2857, 2796, 1659, 1472, 1440, 1372, 1110, 1030, 742, 695\ cm^{-1}$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.43–7.37$ (m, 40H) 7.27 (band, 60H), 3.54 (band, 20H), 3.41–3.31 (m, 32H), 3.28–3.24 (m, 10H), 3.20 (t, $J = 5.0$ Hz, 10H), 2.90 (band, 10H), 2.45 (band, 36H), 1.70–1.53 (m, 52H), 1.30–1.28 (band, 12H), 0.88 (band, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 138.2, 138.1, 133.2, 133.0, 128.4, 128.3, 128.2, 71.0, 69.2, 68.8, 58.7, 50.8, 29.5, 28.3, 27.3, 26.8, 22.5, 14.0$; ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = -28.5$.

To a solution of the above intermediate (0.16 g, 0.046 μmol) in CH_2Cl_2 (5 mL), $Pd(COD)Cl_2$ (0.066 g, 0.23 mmol) was added and the reaction was followed as given in the general procedure II, to afford the dendritic phosphine-Pd complex **20**, as a pale yellow sticky solid; yield: 0.19 g (93%). FT-IR (neat): $\nu = 3073, 3055, 2974, 2927, 2856, 1483, 1436, 1307, 1187, 1102, 873, 846, 740, 691, 560, 512\ cm^{-1}$; ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 7.78–7.62$ (m, 40H) 7.43–7.24 (m, 60H), 3.29–3.17 (m, 62H), 2.95 (band, 10H), 2.58 (band, 46H), 1.64 (band, 46H), 1.44 (band, 6H), 1.21–1.18 (m, 12H), 0.8 (band, 9H); ^{13}C NMR (75.5 MHz, CD_2Cl_2): $\delta = 134.4, 134.2, 131.9, 131.5, 131.4, 129.0, 128.8, 128.7, 71.3, 69.1, 69.0, 68.9, 68.8, 59.5, 57.3, 56.7, 51.0, 29.8, 28.8, 23.0, 14.2$; ^{31}P NMR (162 MHz, CD_2Cl_2): $\delta = 8.5$; elemental analysis calcd. (%) for $C_{214}H_{291}Cl_{10}N_{11}O_{13}P_{10}Pd_5$: C 58.12, H 6.63, N 3.48; found: C 59.51, H 7.13, N 3.82.

22: A mixture of $(CH_2O)_n$ (0.072 g, 2.39 mmol) and Ph_2PH (0.46 g, 2.49 mmol) in MeOH (4 mL) was heated at 70 °C for 10 min. and then cooled. To this reaction mixture, a solution of the dendritic amine **21**[21] (0.21 g, 0.142 mmol) in MeOH (4 mL) was added and the reaction was followed further as given in the general procedure I, to afford the bisphosphinomethyl intermediate as a foamy solid; yield: 0.64 g (97%). FT-IR (neat): $\nu = 3064, 3048, 2948, 2852, 2796, 1583, 1480, 1429, 1113, 739, 691\ cm^{-1}$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.41–7.36$ (m, 64H) 7.26 (band, 96H), 3.54 (d, $J = 3.0$ Hz, 32H), 3.36 (band, 20H), 3.28–3.17 (m, 32H), 2.90 (t, $J = 6.9$ Hz, 16H), 2.45 (band, 36H), 1.67–1.62 (m, 52H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 138.2, 138.1, 133.1, 132.9, 128.5, 128.4, 128.3, 68.8, 58.8, 58.7, 58.6, 53.1, 50.8, 26.6$; ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = -28.5$.

To a solution of the above intermediate (0.23 g, 0.049 mmol) in CH_2Cl_2 (5 mL), $Pd(COD)Cl_2$ (0.11 g, 0.39 mmol) was added and the reaction was followed as given in the general procedure II, to afford the dendritic phosphine-Pd complex **22**, as an orange solid; yield: 0.29 g (96%); mp 159–162 °C; FT-IR (neat): $\nu = 3054, 2944, 2861, 1483, 1436, 1309, 1184, 1103, 738, 737, 693\ cm^{-1}$; ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 7.86–7.79$ (m, 64H) 7.52–7.42 (m, 96H), 3.38 (band, 52H), 3.20 (band, 16H), 3.00 (band, 16H), 2.65–2.54 (m, 52H), 1.71 (band, 36H), 1.48 (band, 16H); ^{13}C NMR (75.5 MHz, CD_2Cl_2): $\delta = 134.4, 134.3, 132.0, 129.7, 129.0, 128.9, 68.1, 59.4, 57.3, 56.7, 51.1, 50.9, 26.4$; ^{31}P NMR (162 MHz, CD_2Cl_2): $\delta = 8.5$; elemental analysis calcd. (%) for $C_{286}H_{348}Cl_{16}N_{14}O_{13}P_{16}Pd_8$: C 56.27, H 5.75, N 3.21; found: C 55.71, H 5.49, N 3.33.

General Procedure for the Heck Coupling Reaction (III)

Iodobenzene (1 mmol), olefin (1.5 mmol), Cs_2CO_3 (1.5 mmol) and dendritic Pd(II) catalyst (0.6–5.0 μmol) in dry 1, 4-dioxane (2 mL) were taken in a sealed tube, fitted with a teflon cap. The tube was evacuated, flushed with argon gas, after which the reaction mixture heated with stirring at 40 °C. For analysis, an aliquot was taken, diluted in hexane (2 mL) and washed with water (2 mL), the hexane layer was filtered and analyzed by HPLC (silica gel, UV detector λ_{max} 260).

General Procedure for the Suzuki Coupling Reaction (IV)

Iodobenzene (1 mmol), phenylboronic acid (1.5 mmol), Cs_2CO_3 (1.5 mmol) and dendritic Pd(II) catalyst (0.6–5.0 μmol) in dry 1, 4-dioxane (3 mL) were taken in a sealed tube, fitted with a teflon cap. The tube was evacuated, flushed with argon gas, after which the reaction mixture heated with stirring at 50 °C. For analysis, an aliquot was taken, diluted in hexane (2 mL) and washed with water (2 mL), the hexane layer filtered and analyzed by HPLC (silica gel, UV detector λ_{max} 260).

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