Supporting information

All manipulations were performed under an inert-gas atmosphere of dried nitrogen in standard (Schlenk) glassware. Solvents were dried according to standard procedures and saturated with N_2. Water, hydrochloric acid and KOH-solution were degassed by stirring under vacuum for three times 10 min. The deuterated solvents used for the NMR spectroscopic measurements were degassed by three successive "freeze-pump-thaw" cycles and dried over 4-Å molecular sieves. Solids were separated from suspensions by centrifugation thus avoiding filtration procedures. The centrifuge employed was a Rotina 48 (Hettich Zentrifugen, Tuttlingen, Germany) which was equipped with a specially designed Schlenk tube rotor.[1]

The ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on the following spectrometers: A Bruker AC 200 FT NMR spectrometer (^{1}H: 200.13, ^{13}C: 50.3 MHz), a Bruker AC 300 FT NMR spectrometer (^{1}H: 300.17, ^{13}C: 75.5, ^{31}P: 121.5 MHz), a Bruker AMX 400 resp. Avance 400 FT NMR spectrometer (^{1}H: 400.16, ^{13}C: 100.6 MHz) or a Bruker ARX 500 FT NMR spectrometer (^{1}H: 500.13, ^{13}C: 125.8 MHz) with tetramethylsilane or H_3PO_4 as references. The IR spectra were recorded on a Perkin-Elmer 1600 spectrometer. Melting points were determined using an Electrothermal IA 9100 apparatus and are not corrected. Mass spectrometric measurements (FAB, ESI, MALDI-TOF) were executed by the Service Commun de la Spectrometrie de Masse at the Université Louis Pasteur Strasbourg. $[\alpha]_D$-values were determined using a Perkin-Elmer 241 Polarimeter. Elemental analyses were carried out in the microanalytical laboratory of the chemistry department at Strasbourg. Hydodynamic radii (R_H) were determined in the Laboratoire de dynamique des fluides complexes at Strasbourg by light diffuson using a laser at 488 nm. N-(4-Carboxylbutanoyl)-Pyrphos,[2] 1,3-diphenyl-1-acetatopropene[3] and $(PhCN)_2PdCl_2$[4] were synthesized according to the literature. The other starting materials were obtained commercially and used without further purification.

[1] K. W. Hellmann, L. H. Gade, *Verfahrenstechnik* **1997**, *31*, 70.
[2] U. Nagel, E. Kinzel, J. Andrade, G. Prescher, *Chem. Ber.* **1986**, *119*, 3326.
[3] A. L Gemal, J.-L. Luche, *J. Am. Chem. Soc*. **1981**, *103*, 5454
G. Hoelfe, W. Steglich, H. Vorbruegen, *Angew. Chem. Int. Ed. Engl*. **1978**, *17*, 569.
[4] G. K. Anderson, M. Lin, *Inorg. Synth.* **1990**, *28*, 61.

1. General procedure for the syntheses of the phosphane dendrimers:

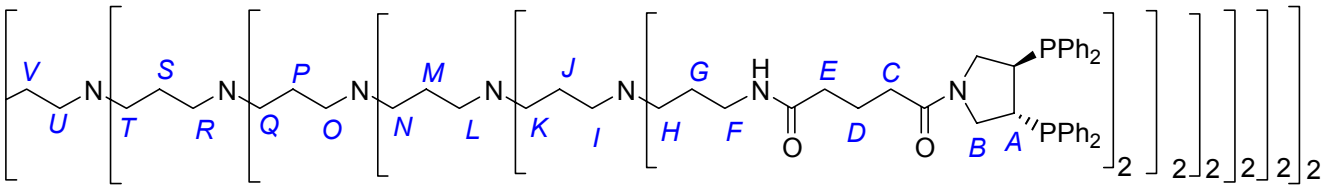
A mixture of N-(4-Carboxylbutanoyl)-Pyrphos (1.15 eq.), EDC·HCl (1.27 eq.), 1-HOBT (1.73 eq.) and triethylamine (1.85 eq) was stirred in DMF for 40 min. To the suspension was added the dendrimer dissolved in DMF. The solution was stirred at room temperature for 48 to 90 h. All volatiles were completely removed in vacuo. The residue was taken up in 20 mL CH_2Cl_2 and thoroughly extracted with 15 mL 0.2 N hydrochloric acid (3 x), 15 mL H_2O, 15 mL 0.2 N KOH (2 x) and 15 mL H_2O (2-3 times). The solvent was removed in vacuo. The residue was dissolved in toluene which was afterwards removed under vaccuum. This drying procedure was repeated several times. Finally, the resulting white solid was washed with *n*-pentane and dried in vacuo yielding the phosphane dendrimers as off-white powders.

A) PPI dendrimers

The pyrphos-functionalized dendrimers **PPI(Pyrphos)$_4$ - PPI(Pyrphos)$_{32}$** have been previously characterized.[5]

PPI(Pyrphos)$_{64}$: Yield 483 mg (11.6 µmol, 92 %); **^{1}H-NMR** (500.14 MHz, 283 K, $CDCl_3$): δ = 7.60 - 7.40 (m, 64 H, N*H*) 7.38 - 7.11 (m, 1280 H, $H_{aromat.}$), 4.00 - 3.75 (m, 128 H, $H^B{}_{trans}$), 3.72 – 3.55 (m, 64 H, $H^B{}_{cis}$), 3.40 – 3.05 (m, 128 H, $H^{B'}{}_{cis}$, H^F), 2.98 – 2.76 (m, 128 H, H^A), 2.55 – 2.95 (m, 756 H, $H^{H+I+K+L+N+O+Q+R+T+U+E+C}$), 1.92 – 1.72 (m, 128 H, H^D), 1.66 - 1.38 (m, 248 H, $H^{G+J+M+P+S}$), 1.26 (m, 4 H, H^V); **^{13}C{^{1}H}-NMR** (75.5 MHz, 298 K, $CDCl_3$): δ = 172.9 (C_q, HN*C*), 171.1 (C_q, O=*C*N(ring)), 136.5 - 135.5 (m, C_q, $C_{i, aromat.}$), 133.8 - 133.4 (m, CH, $C_{m, aromat.}$), 129.5 - 128.4 (m, CH, $C_{o+p, aromat.}$), 52.4 - 50.8 (m, CH_2, $C^{H+I+K+L+N+O+Q+R+T+U}$), 48.8 (m, CH_2, C^B), 48.1 (m, CH_2, $C^{B'}$), 38.9 (m, CH, C^A), 37.8 (br, CH_2, C^F), 37.2 (m, CH, $C^{A'}$), 35.5 (CH_2, $C^{C/E}$), 33.9 (CH_2, $C^{E/C}$), 27.1 (CH_2, C^G), 24.4 - 24.8 (br, CH_2, $C^{J+M+P+S+V}$), 21.0 (CH_2, C^D); **^{31}P{^{1}H}-NMR** (121.51 MHz, 297 K, $CDCl_3$): δ = -10.8 (s, br);

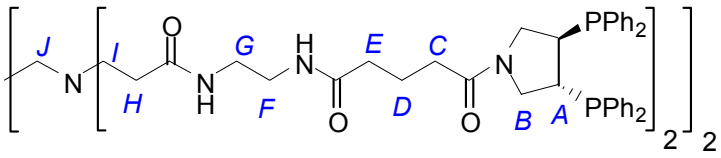
[5] G. D. Engel, L. H. Gade, *Chem. Eur. J.* 2002, **8**, 4319.



B) PAMAM dendrimers

PAMAM(Pyrphos)$_4$: Yield 325 mg (122.2 μmol, 78%);

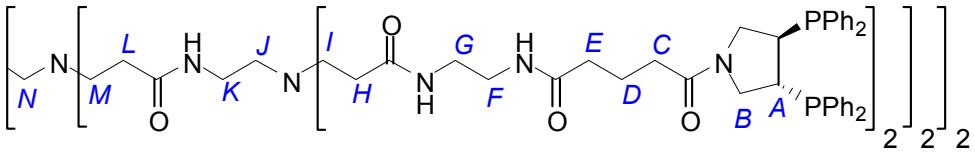
^{1}H-NMR (300.16 MHz, 295 K, $CDCl_3$): δ = 7.81- 7.65 (s broad, 4H, N*H*), 7.35 - 7.05 (m, 84 H, H-$_{aromat}$, N*H*.), 3.98-3.82 (m, 8H, $H^B{}_{trans}$); 3.61 (pseudo-t, 4H, $^2J_{HH}$ = 12.5 Hz, $^3J_{HP}$ = 12.5 Hz, $H^B{}_{cis}$); 3.39-3.20 (m, 20H, $H^B{}_{cis}$, H^F, H^G); 2.99-2.80 (m, 8H, H^A); 2.70-2.56 (m, 8H, H^I); 2.45-2.35 (m, 4H, H^J); 2.35-2.23 (m, 8H, H^H); 2.23-2.11 (m, 16H, H^E, H^C); 1.94-1.79 (m, 8H, H^D); **{^{1}H}^{13}C-NMR** (50.3 MHz, 297 K, $CDCl_3$): δ = 172.4-172.3 (m, C_q, HN*C*=O), 170.1 (C_q, O=*C*N (ring)), 135.3 - 134.3 (m, C_q, $C_{i,\ aromat.}$), 133.5 (d, $|^2J_{CP}|$ = 21 Hz, CH, $C_{m,\ aromat.}$), 128.3 - 129.6 (m, CH, $C_{o+p,\ aromat.}$), 50.1 (CH_2, C^J), 49.3 (CH_2, C^I), 47.7 (m, CH_2, C^B), 47.0 (CH_2, $C^{B'}$), 38.7 (CH_2, $C^{F/G}$), 38.1 (CH_2, $C^{F/G}$), 37.9 (CH, C^A), 36.1 (CH, $C^{A'}$), 34.5 (CH_2, $C^{E/C}$), 33.1 (CH_2, $C^{E/C}$), 32.6 (CH_2, C^H), 19.7 (CH_2, C^D); **{^{1}H}^{31}P-NMR** (121.5 MHz, $CDCl_3$, 295 K): δ = -11.0 (s, br); **IR** (KBr): 3289 s (br, ν N-H), 3051 m, 2930 m, 1642 vs (br, ν C=O), 1544 s, 1433 vs (ν P-Ph), 1250 m, 1157 w, 1093 w, 1026 w, 999 w, 741 s (δ C-$H_{aromat.}$), 696 vs (δ C-$H_{aromat.}$), 506 m ; $[a]_D^{20}$ = + 112.0 ° (c = 0.342, $CHCl_3$);. **MS** (FAB) m/z (%):2675 (30) $[M+H+O]^+$ (oxidation in the matrix), 2659 (40) $[M+H]^+$, 2473 (10)$[M-PPh_2+H]^+$,1328 (50) $[M+2H]^{2+}$, 2288 (16) $[M-2PPh_2+H]^+$, 185 (100) $[PPh_2]^+$; **elemental analysis** calcd (%) for $C_{154}H_{172}N_{14}O_{12}P_8$ (2658.94): C 69.57, H 6.52, N 7.37; found: C 68.85, H 6.58, N 7.06.



PAMAM(Pyrphos)$_8$: Yield 446 mg (78.0 μmol, 84%);

^{1}H-NMR (300.16 MHz, 295 K, $CDCl_3$): δ = 7.90 – 7.75 (m, 8H, N*H*), 7.55 – 7.45 (s broad, 4H, N*H*), 7.32 – 6.90 (m, 168 H, H-$_{aromat}$, N*H*), 3.98-3.80 (m, 16H, $H^B{}_{trans}$); 3.62- 3.57 (m,

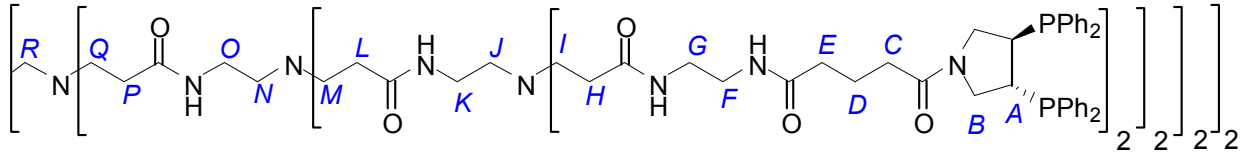
8H, H^{B}_{cis}); 3.41-3.15 (m, 48H, H^{B}_{cis}, H^{F}, H^{G}, H^{K}); 3.00-2.80 (m, 16H, H^{A}); 2.75-2.58 (m, 24H, H^{I}, H^{M}); 2.55-2.35 (m, 12H, H^{J}, H^{N}); 2.35-2.23 (m, 24H, H^{H}, H^{L}); 2.23-2.11 (m, 32H, H^{E}, H^{C}); 1.95-1.75 (m, 16H, H^{D}); **{^{1}H}^{13}C-NMR** (50.3 MHz, 297 K, $CDCl_3$): δ = 173.4 (m, C_q, HN*C*=O), 171.4 (m, C_q, HN*C*=O),169.8 (C_q, O=*C*N (ring)), 136.4 - 135.3 (m, C_q, $C_{i,\ aromat.}$), 133.7 - 133.3 (m, CH, $C_{m,\ aromat.}$), 129.5 - 128.6 (m, CH, $C_{o+p,\ aromat.}$), 52.9 (br, CH_2, C^{N}, C^{J}), 50.1 (br, CH_2, C^{I}, C^{M}), 48.8 (m, CH_2, C^{B}), 48.1 (m, CH_2, $C^{B'}$), 39.6 (br, CH_2, C^{G}), 38.8 (m, CH_2, $C^{F/G}$), 37.9 (m, CH_2, C^{K} ,$C^{F/G}$, CH, C^{A}), 37.1 (m, CH, $C^{A'}$), 35.5 (CH_2, $C^{E/C}$), 34.1 (CH_2, C^{L}, C^{H}), 33.7 (CH_2, $C^{E/C}$), 20.8 (CH_2, C^{D}); **{^{1}H}^{31}P-NMR** (121.5 MHz, $CDCl_3$, 295 K): δ = -11.1 (s, br); **IR** (KBr): 3292 m (ν N-H), 3069 w, 2930 w, 1650 vs (br, ν C=O), 1548 s, 1433 vs (ν P-Ph), 1250 w 1093 m, 1026 m, 741 s (δ C-$H_{aromat.}$), 696 (δ C-$H_{aromat.}$), 506 m; $[a]_D^{20}$ = + 105.2 ° (c = 0.370, $CHCl_3$); $\mathbf{R_H}$ = 1.6 nm; **MS** (MALDI-TOF, 1,8,9-trihydroxyanthracene) m/z: 5748 $[M+K]^+$, 5733 $[M+Na]^+$, 5716 $[M+Li]^+$, 2856 $[M+2H]^{2+}$; **elemental analysis** calcd (%) for $C_{326}H_{376}N_{34}O_{28}P_{16}$ (5714.33): C 68.52, H 6.63, N 8.33; found: C 68.37, H 6.85, N 7.91.



PAMAM(Pyrphos)$_{16}$: Yield 305 mg (25.8 μmol, 80%);

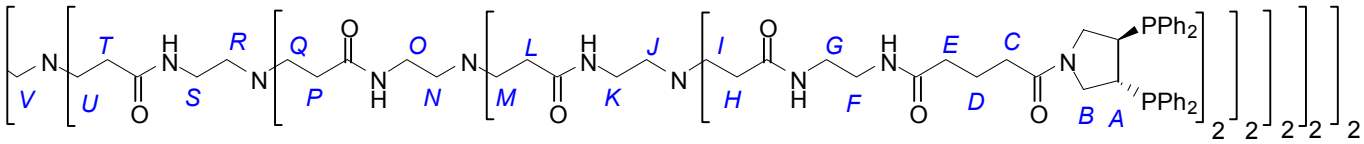
^{1}H-NMR (300.16 MHz, 295 K, $CDCl_3$): δ = 7.95 – 7.70 (m, 32H, N*H*), 7.52 – 7.00 (m, 332 H, H-$_{aromat}$, N*H*), 4.05 -3.75 (m, 32H, H^{B}_{trans}); 3.68- 3.52 (m, 16H, H^{B}_{cis}); 3.42-3.12 (m, 104H, H^{B}_{cis}, H^{F}, H^{G}, H^{K}, H^{O}); 2.95-2.78 (m, 32H, H^{A}); 2.75-2.55 (m, 56H, H^{I}, H^{M}, H^{Q}); 2.55-2.40 (m, 28H, H^{J}, H^{N}, H^{R}); 2.40-2.05 (m, 120H, H^{H}, H^{L}, H^{P}, H^{E}, H^{C}); 1.95-1.75 (m, 32H, H^{D}); **{^{1}H}^{13}C-NMR** (50.3 MHz, 297 K, $CDCl_3$): δ = 173.4 (m, C_q, HN*C*=O), 173.2 (m, C_q, HN*C*=O), 172.6 (m, C_q, HN*C*=O), 171.2 (C_q, O=*C*N (ring)), 136.4 - 135.3 (m, C_q, $C_{i,\ aromat.}$), 133.7 - 133.4 (m, CH, $C_{m,\ aromat.}$), 129.5 - 128.5 (m, CH, $C_{o+p,\ aromat.}$), 52.3 (br, CH_2, C^{N}, C^{J}, C^{R}), 50.3 (br, CH_2, C^{I}, C^{M}, C^{Q}), 48.8 (m, CH_2, C^{B}), 48.1 (m, CH_2, $C^{B'}$), 39.7-38.6 (m, CH_2, C^{F}, C^{G}, C^{K}, C^{O}, CH, C^{A}), 37.1 (m, CH, $C^{A'}$), 35.5 (CH_2, $C^{E/C}$), 34.1 (CH_2, C^{L}, C^{H}, C^{P}), 33.7

(CH_2, $C^{E/C}$), 20.8 (CH_2, C^D); **{^{1}H}^{31}P-NMR** (121.5 MHz, $CDCl_3$, 295 K): δ = -11.0 (s, br); **IR** (KBr): 3293 s (vbr, ν N-H), 3069 m, 2930 m, 2235 w, 1645 vs (br, ν C=O), 1545 s, 1480 w, 1433 vs (ν P-Ph), 1341 w, 1250 w, 1156 w, 1093 w, 1026 w, 999 w, 910 w, 740 s (δ C-$H_{aromat.}$), 697 (δ C-$H_{aromat.}$), 506 m; $[a]_D^{20}$ = + 102.2 ° (c = 0.370, $CHCl_3$); $\mathbf{R_H}$ = 2.0 nm; **MS** (MALDI-TOF, 1,8,9-trihydroxyanthracene) m/z: 11839 $[M+ Na]^+$, 11824 $[M+Li]^+$; **elemental analysis** calcd (%) for $C_{670}H_{784}N_{74}O_{60}P_{32}$ (11825.2): C 68.05, H 6.68, N 8.76; found: C 67.02, H 6.58, N 8.12.



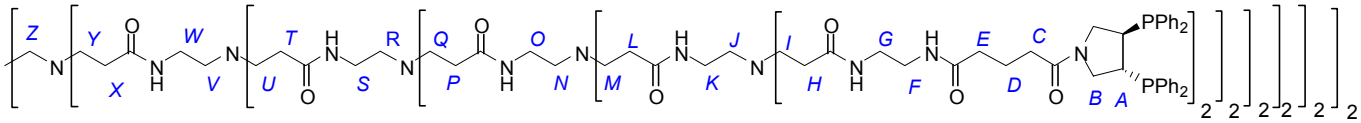
PAMAM(Pyrphos)$_{32}$: Yield 314 mg (13.0 μmol, 89%);

^{1}H-NMR (300.16 MHz, 295 K, $CDCl_3$): δ = 7.95 – 7.70 (m, 64H, N*H*), 7.65 – 7.05 (m, 668 H, H-$_{aromat}$, N*H*), 4.00 -3.75 (m, 64H, $H^B{}_{trans}$); 3.70- 3.50 (m, 32H, $H^B{}_{cis}$); 3.40-3.00 (m, 184H, $H^B{}_{cis}$, H^F, H^G, H^K, H^O, H^S); 2.95-1.95 (m, 612H, H^A, H^I, H^M, H^Q, H^U, H^J, H^N, H^R, H^V, H^H, H^L, H^P, H^T, H^E, H^C); 1.95-1.70 (m, 64H, H^D); **{^{1}H}^{13}C-NMR** (50.3 MHz, 297 K, $CDCl_3$): δ = 173.4 (m, C_q, HN*C*=O), 173.2 (m, C_q, HN*C*=O), 172.6 (m, C_q, HN*C*=O), 171.2 (C_q, O=*C*N (ring)), 136.2 - 135.5 (m, C_q, $C_{i,\ aromat.}$), 133.7 - 133.4 (m, CH, $C_{m,\ aromat.}$), 129.5 - 128.6 (m, CH, $C_{o+p,\ aromat.}$), 52.4 (br, CH_2, C^N, C^J, C^R,C^V), 50.3 (br, CH_2, C^I, C^M, C^Q, C^U), 48.8 (m, CH_2, C^B), 48.1 (m, CH_2, $C^{B'}$), 39.7-38.6 (m, CH_2, C^F, C^G, C^K, C^O,C^S, CH, C^A), 37.1 (m, CH, $C^{A'}$), 35.4 (CH_2, $C^{E/C}$), 34.1 (CH_2, C^H, C^L, C^P, C^T), 33.7 (CH_2, $C^{E/C}$), 20.8 (CH_2, C^D); **{^{1}H}^{31}P-NMR** (121.5 MHz, $CDCl_3$, 295 K): δ = -11.0 (s, br); **IR** (KBr): 3295 s (vbr, ν N-H), 3065 m, 2931 m, 1643 vs (br, ν C=O), 1544 s, 1432 s (ν P-Ph), 1337 w, 1251 m, 1092 w, 915 w, 740 s (δ C-$H_{aromat.}$), 697 (δ C-$H_{aromat.}$), 505 m; $[a]_D^{20}$ = + 111.1 ° (c = 0.340, $CHCl_3$); $\mathbf{R_H}$ = 2.7 nm; **elemental analysis** calcd (%) for $C_{1358}H_{1600}N_{154}O_{124}P_{64}$ (24046.9): C 67.83, H 6.70, N 8.97; found: C 67.19, H 7.03, N 8.39.



PAMAM(Pyrphos)$_{64}$: Yield 162 mg (3.3 μmol, 78%);

^{1}H-NMR (300.16 MHz, 295 K, $CDCl_3$): δ = 8.00 – 7.65 (m, 128H, N*H*), 7.65 – 7.40 (m, 60H, N*H*), 7.40-6.90 (m, 1280 H, H-$_{aromat}$), 4.00 -3.75 (m, 128H, H^{B}_{trans}); 3.75- 3.45 (m, 64H, H^{B}_{cis}); 3.40-3.00 (m, 440H, H^{B}_{cis}, H^{F}, H^{G}, H^{K}, H^{O}, H^{S}, H^{W}); 2.95-1.95 (m, 1004H, H^{A}, H^{I}, H^{M}, H^{Q}, H^{U}, H^{Y}, H^{J}, H^{N}, H^{R}, H^{V}, H^{Z}, H^{H}, H^{L}, H^{P}, H^{T}, H^{X}, H^{E}, H^{C}); 1.95-1.70 (m, 128H, H^{D}); **{^{1}H}^{13}C-NMR** (50.3 MHz, 297 K, $CDCl_3$): δ = 173.4 (m, C_q, HN*C*=O), 173.2 (m, C_q, HN*C*=O), 172.6 (m, C_q, HN*C*=O), 171.2 (C_q, O=*C*N (ring)), 136.3 - 135.4 (m, C_q, $C_{i,\ aromat.}$), 133.7 - 133.3 (m, CH, $C_{m,\ aromat.}$), 129.6 - 128.6 (m, CH, $C_{o+p,\ aromat.}$), 52.4 (br, CH_2, C^{N}, C^{J}, C^{R},C^{V}, C^{Z}), 50.3 (br, CH_2, C^{I}, C^{M}, C^{Q}, C^{U}, C^{Y}), 48.8 (m, CH_2, C^{B}), 48.1 (m, CH_2, $C^{B'}$), 39.7-38.6 (m, CH_2, C^{F}, C^{G}, C^{K}, C^{O},C^{S},C^{W}, CH, C^{A}), 37.1 (m, CH, $C^{A'}$), 35.4 (CH_2, $C^{E/C}$), 34.1 (CH_2, C^{H}, C^{L}, C^{P}, C^{T}, C^{X}), 33.7 (CH_2, $C^{E/C}$), 20.8 (CH_2, C^{D}); **{^{1}H}^{31}P-NMR** (121.5 MHz, $CDCl_3$, 295 K): δ = -11.0 (s, br); **IR** (KBr): 3291 s (vbr, ν N-H), 3069 m, 2929 m, 1646 vs (br, ν C=O), 1544 s, 1433 s (ν P-Ph), 1341 w, 1250 m, 1155 w, 1093 w, 1026 w, 911 w, 740 s (δ C-H$_{aromat.}$), 696 (δ C-H$_{aromat.}$), 505 m; $[a]_D^{20}$ = + 90.8 ° (c = 0.340, $CHCl_3$); **R_H** = 4.7 nm; **elemental analysis** calcd (%) for $C_{1358}H_{1600}N_{154}O_{124}P_{64}$ (24046.9): C 67.72, H 6.72, N 9.07; found: C 68.17, H 6.89, N 8.48.



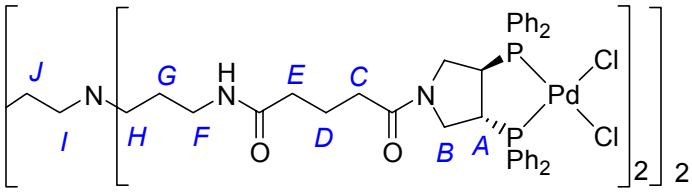
2. General procedure for the metalation of the phosphane dendrimers:

To a solution of the dendritic phosphane (80 - 120 mg) in CH_2Cl_2 (10 ml) was added a solution of $(PhCN)_2PdCl_2$ (1.0 - 1.05 eq. per phosphane unit) in CH_2Cl_2 (20 ml). For the higher dendrimers, a solid started to precipitate. The mixture was stirred for 24 - 72 h at room temperature, then the solvent was reduced in vacuo to 8 ml. The precipitation was completed

by addition of diethyl ether (30 ml). The solid was separated by centrifugation, thoroughly washed with toluene, n-pentane and dried in vacuo.

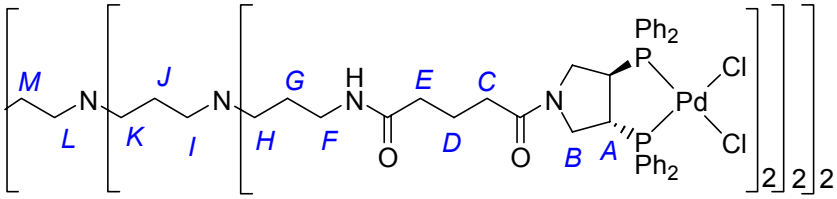
A) PPI dendrimers

PPI(PyrphosPdCl$_2$)$_4$: Yield: 165 mg (52.1 µmol, 76 %); m. p. decomposition > 230 °C; **^{1}H-NMR** (300.17 MHz, 298 K, d$_6$-DMSO): δ = 8.10 - 7.50 (m, 84 H, H$_{aromat.}$, N*H*), 3.85 - 3.74 (m, 4 H, H^B), 3.74 - 3.55 (m, 4 H, H^B), 3.45 - 3.27 (m, 8 H, H^F), 2.96 - 2.85 (m, 12 H, H$^{A/B}$), 2.74 - 2.61 (m, 4 H, H$^{A/B}$), 2.41 - 2.11 (m, 12 H, H^{H+I}), 2.07 - 1.83 (m, 16 H, H^{C+E}), 1.62 - 1.45 (m, 8 H, H^D), 1.44 - 1.30 (m, 8 H, H^G), 1.30 - 1.24 (m, 4 H, H^J); **^{13}C{^{1}H}-NMR** (75.5 MHz, 298 K, d$_6$-DMSO): δ = 171.6 (br, C$_q$, HN*C*=O), 170.6 (C$_q$, O=*C*N-ring), 136.2 (CH, C$_{aromat.}$), 134.4 (CH, C$_{aromat.}$), 132.1 (CH, C$_{aromat.}$), 129.8 - 128.7 (m, CH, C$_{aromat.}$), 127.7 (C$_q$, C$_{i,\ aromat.}$), 123.7 (C$_q$, C$_i$', $_{aromat.}$), 52.9 (CH$_2$, C^I), 50.8 (br, CH$_2$, C^H), 44.8 - 42.5 (several multipletts, CH$_2$ and CH, C^{A+B}, (2 rotamers)), 36.6 (CH$_2$, C^F), 34.5 (CH$_2$, C$^{C/E}$), 32.5 (CH$_2$, C$^{E/C}$), 26.1 (br, CH$_2$, C^{G+J}), 20.3 (CH$_2$, C^D); **^{31}P{^{1}H}-NMR** (121.5 MHz, 297 K, d$_6$-DMSO): δ = 42.4 (s, br); **IR** (KBr): 3422 m (ν N-H), 3053 w, 2937 w, 2863 w, 1640 vs (br, ν C=O), 1540 w, 1480 w, 1435 vs (ν P-Ph), 1334 w, 1183 w, 1101 s, 998 m, 828 w, 746 s (δ C-H$_{aromat.}$), 690 s (δ C-H$_{aromat.}$), 542 s, 520 s, 496 m; **MS** (FAB) m/z (%): 3133 (84) [M-Cl]$^+$, 1549 (100) [M-2 Cl]$^{2+}$; **elemental analysis** calcd (%) for C$_{148}$H$_{164}$Cl$_8$N$_{10}$O$_8$P$_8$Pd$_4$ (3168.08): C 56.11, H 5.22, N 4.42; found: C 55.76, H 5.38, N 4.89.

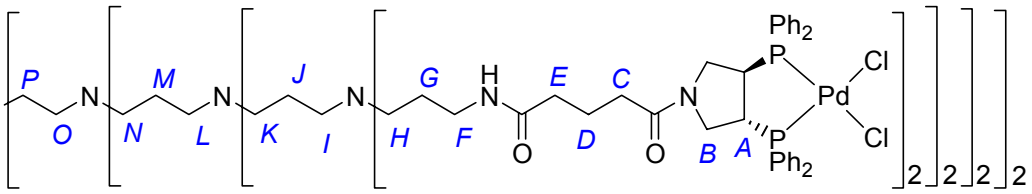


PPI(PyrphosPdCl$_2$)$_8$: Yield 80.1 mg (12.4 µmol, 75 %); m. p. decomposition > 217 °C; **^{1}H-NMR** (300.17 MHz, 300 K, d$_6$-DMSO): δ = 8.02 - 7.49 (m, 168 H, H$_{aromat.}$, N*H*), 3.85 - 3.48 (m, br, 32 H, H^B), 3.31 - 3.24 (m, 16 H, H^F), 2.95 - 2.79 (m, br, 16 H, H^A), 2.60 - 2.10 (m, vbr, 36 H, H$^{H+I+K+L}$), 2.03 - 1.83 (m, 32 H, H^{C+E}), 1.58 - 1.20 (m, vbr, 44 H, H$^{D+G+J+M}$); **^{13}C{^{1}H}-NMR** (75.5 MHz, 300 K, d$_6$-DMSO): δ = 171.6 (br, C$_q$, HN*C*=O), 170.5 (C$_q$, O=*C*N-ring), 136.2 (CH, C$_{aromat.}$), 133.2 (CH, C$_{aromat.}$), 132.0 (CH, C$_{aromat.}$), 129.5 - 128.2 (m, CH, C$_{aromat.}$), 127.1 (C$_q$, C$_{i,\ aromat.}$), 123.6 (C$_q$, C$_i$', $_{aromat.}$), 54.8 (CH$_2$, C^L), 50.6 (br, CH$_2$,

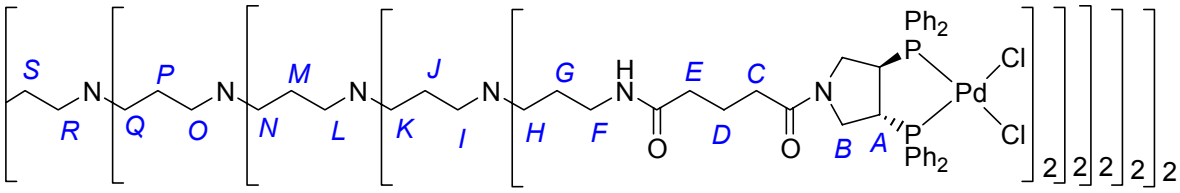
C^{H+I+K}), 45.0 - 42.0 (several multipletts, CH_2 and. CH, C^{A+B}, (2 rotamers)), 36.5 (CH_2, C^{F}), 34.5 (CH_2, $C^{C/E}$), 32.5 (CH_2, $C^{E/C}$), 26.1 (br, CH_2, C^{G+J}), 20.2 (CH_2, C^{D}); **$^{31}P\{^1H\}$-NMR** (121.5 MHz, 298 K, d_6-DMSO): δ = 42.8 (s, br); **IR** (KBr): 3422 m (ν N-H), 3052 w, 2929 w, 2863 w, 1637 vs (br, ν C=O), 1542 w, 1435 vs (ν P-Ph), 1333 w, 1183 w, 1101 s, 998 m, 828 w, 746 s (δ C-$H_{aromat.}$), 690 s (δ C-$H_{aromat.}$), 542 s, 520 s, 496 m; **elemental analysis** calcd (%) for $C_{304}H_{344}Cl_{16}N_{22}O_{16}P_{16}Pd_8$ (6476.40): C 56.38, H 5.35, N 4.75; found: C 56.11, H 5.22, N 4.42.



PPI(PyrphosPdCl$_2$)$_{16}$: Yield 117 mg (8.93 µmol, 84 %); m. p. decomposition > 220 °C; **^{1}H-NMR** (300.17 MHz, 300 K, d_6-DMSO): δ = 8.01 - 7.38 (m, 336 H, $H_{aromat.}$, N*H*), 3.84 - 3.49 (m, br, 64 H, H^{B}), 3.37 - 3.27 (m, 32 H, H^{F}), 2.95 - 2.78 (m, br, 32 H, H^{A}), 2.72 - 2.05 (m, vbr, 84 H, $H^{H+I+K+L+N+O}$), 2.05 - 1.79 (m, 64 H, H^{C+E}), 1.63 - 1.20 (m, vbr, 92 H, $H^{D+G+J+M+P}$); **$^{13}C\{^1H\}$-NMR** (75.5 MHz, 300 K, d_6-DMSO): δ = 171.6 (br, C_q, HN*C*=O), 170.5 (C_q, O=*C*N-ring), 136.2 (CH, $C_{aromat.}$), 133.2 (CH, $C_{aromat.}$), 132.1 (CH, $C_{aromat.}$), 129.4 - 128.2 (m, CH, $C_{aromat.}$), 127.2 (C_q, $C_{i,\ aromat.}$), 123.8 (C_q, C_i', $_{aromat.}$), 54.9 (CH_2, C^{O}), 50.8 (br, CH_2, $C^{H+I+K+L+N}$), 44.8 - 42.1 (several multipletts, CH_2 and CH, C^{A+B}, (2 rotamers)), 36.6 (CH_2, C^{F}), 34.5 (CH_2, $C^{C/E}$), 32.5 (CH_2, $C^{E/C}$), 26.2 (br, CH_2, $C^{G+J+M+P}$), 20.2 (CH_2, C^{D}); **$^{31}P\{^1H\}$-NMR** (121.5 MHz, 300 K, d_6-DMSO): δ = 42.8 (s, br); **IR** (KBr): 3426 m (ν N-H), 3053 w, 2929 w, 2863 w, 1640 vs (br, ν C=O), 1543 w, 1480 w, 1435 vs (ν P-Ph), 1334 w, 1183 w, 1101 s, 998 m, 828 w, 746 s (δ C-$H_{aromat.}$), 690 s (δ C-$H_{aromat.}$), 542 s, 520 s, 496 m; **elemental analysis** calcd (%) for $C_{616}H_{704}Cl_{32}N_{46}O_{32}P_{32}Pd_{16}$ (13092.71): C 56.51, H 5.42, N 4.92; found: C 56.76, H 5.62, N 4.41.



PPI(PyrphosPdCl$_2$)$_{32}$: Yield 102 mg (3.87 µmol, 89 %); m. p. decomposition > 223 °C; **^{1}H-NMR** (300.17 MHz, 300 K, d$_6$-DMSO): δ = 8.02 - 7.30 (m, 672 H, H$_{aromat.}$, N*H*), 3.84 - 3.43 (m, br, 128 H, H^B), 3.37 - 3.27 (m, 64 H, H^F), 3.02 - 2.75 (m, br, 64 H, H^A), 2.72 - 1.75 (several multipletts, vbr, 308 H, H$^{H+I+K+L+N+O+Q+R+C+E}$), 1.60 - 1.20 (m, vbr, 188 H, H$^{D+G+J+M+P+S}$), signals very broad, integration uncertain; **^{13}C{^{1}H}-NMR** (75.5 MHz, 300 K, d$_6$-DMSO): δ = 171.6 (br, C$_q$, HN*C*=O), 170.4 (C$_q$, O=*C*N-ring), 136.1 (CH, C$_{aromat.}$), 133.2 (CH, C$_{aromat.}$), 132.1 (CH, C$_{aromat.}$), 129.4 - 128.0 (m, CH, C$_{aromat.}$), 127.2 (C$_q$, C$_{i,\ aromat.}$), 123.9 (C$_q$, C$_i$', $_{aromat.}$), 54.9 (CH$_2$, C^R), 52.5 - 50.8 (br, CH$_2$, C$^{H+I+K+L+N+O+Q}$), 44.7 - 42.5 (several multipletts, CH$_2$ and CH, C^{A+B}, (2 rotamers)), 36.7 (CH$_2$, C^F), 34.5 (CH$_2$, C$^{C/E}$), 32.6 (CH$_2$, C$^{E/C}$), 26.6 (br, CH$_2$, C$^{G+J+M+P+S}$), 20.2 (CH$_2$, C^D); **^{31}P{^{1}H}-NMR** (121.5 MHz, 300 K, d$_6$-DMSO): δ = 42.7 (s, br); **IR** (KBr): 3422 m (ν N-H), 3052 w, 2928 w, 2863 w, 2803 w, 1637 vs (br, ν C=O), 1542 w, 1480 w, 1434 vs (ν P-Ph), 1333 w, 1182 w, 1100 s, 1038 m, 998 m, 828 w, 745 s (δ C-H$_{aromat.}$), 690 s (δ C-H$_{aromat.}$), 542 s, 519 s, 483 m; **elemental analysis** calcd (%) for C$_{1240}$H$_{1424}$Cl$_{64}$N$_{94}$O$_{64}$P$_{64}$Pd$_{32}$ (26326.62): C 56.57, H 5.45, N 5.00; found: C 55.68, H 5.58, N 4.62.

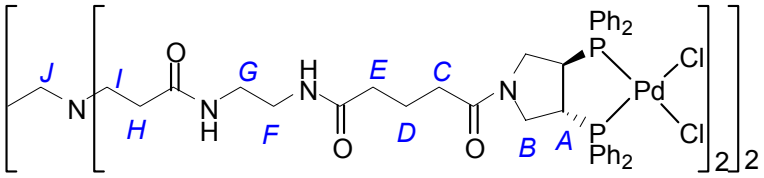


B) PAMAM dendrimers

PAMAM(PyrphosPdCl$_2$)$_4$: Yield 325 mg (122.2 µmol, 78%);

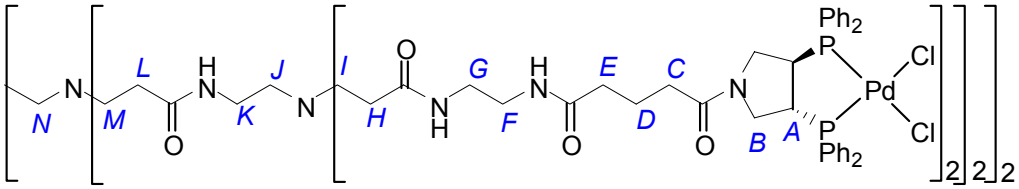
^{1}H-NMR (300.16 MHz, 295 K, d$_6$-DMSO): δ = 8.15 – 8.07 (s broad, 4H, N*H*), 8.00 - 7.48 (m, 84 H, H-$_{aromat}$, N*H*), 3.86 - 3.56 (m, 16H, H^B, H^A); 3.38 – 1.86 (m, H$^{B/A}$, H^F, H^G, H^I, H^J, H^H, H^E, H^C); 1.64-1.44 (m, 8H, H^D) signals very broad, integration uncertain; **{^{1}H}^{13}C-NMR** (50.3 MHz, 297 K, d$_6$-DMSO): δ = 172.4 (C$_q$, HN*C*=O), 171.2 (br, C$_q$, HN*C*=O), 170.1 (C$_q$,

O=*C*N (ring)), 137.0 – 136.4 (m, CH, $C_{aromat.}$), 134.2 – 133.4 (m, CH, $C_{aromat.}$), 132.8 – 132.2 (m, CH, $C_{aromat.}$), 130.0 – 128.8 (m, CH, $C_{aromat.}$), 128.4 - 127.0 (m, C_q, $C_{i,\ aromat.}$), 125.0 - 123.6 (m, C_q, $C_{i,\ aromat.}$), 55.8 – 54.8 (CH_2, C^J), 50.4 – 49.8 (CH_2, C^I), 45.4 – 42.8 (m, CH_2, C^B, CH, C^A), 38.8 – 38.4 (CH_2, C^{F+G}), 35.0 (CH_2, $C^{E/C}$), 32.9 (CH_2, $C^{E/C}$), 32.4 (CH_2, C^H), 20.6 (CH_2, C^D); **{^{1}H}^{31}P-NMR** (121.5 MHz, d_6-DMSO, 295 K): δ = 43.0 (s, br); **IR** (KBr): 3308 s (br, ν N-H), 2926 m, 1642 vs (br, ν C=O), 1535 s, 14374 vs (ν P-Ph), 1333 w, 1182 w, 1099 s, 1036 w, 997 w, 828 w, 746 s (δ C-$H_{aromat.}$), 689 s (δ C-$H_{aromat.}$), 542 m, 519 s, 482 m ;



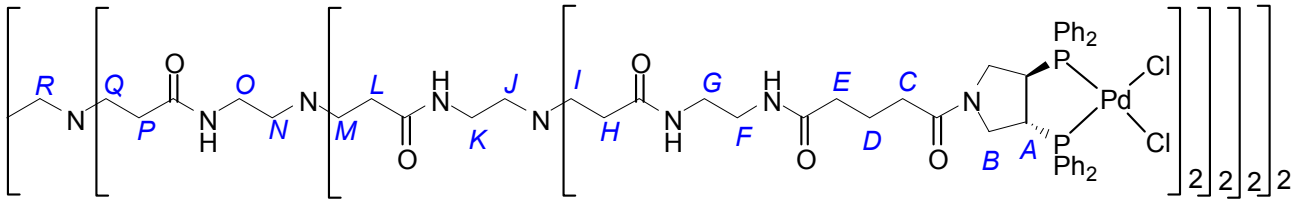
PAMAM(PyrphosPdCl$_2$)$_8$: Yield 75 mg (10.5 μmol, 85%);

^{1}H-NMR (300.16 MHz, 295 K, d_6-DMSO): δ = 7.95 – 7.45 (m, 180 H, H-$_{aromat}$, N*H*), 3.85-3.45 (m, 24H, H^B), 3.40- 3.15 (m, 8H, H^B), 3.10 – 2.75 (m, 56H, H^A, H^F, H^G, H^K), 2.75-2.50 (m, 24H, H^I, H^M), 2.55 - 1.80 (m, 68H, H^J, H^N, H^H, H^L, H^E, H^C); 1.60-1.40 (m, 16H, H^D), signals very broad, integration uncertain; **{^{1}H}^{13}C-NMR** (50.3 MHz, 297 K, d_6-DMSO): δ = 172.4 (C_q, HN*C*=O), 171.8 (br, C_q, HN*C*=O),171.1 (C_q, O=*C*N (ring)), 136.7 (m, CH, $C_{aromat.}$), 133.7 (m, CH, $C_{aromat.}$), 132.5 (m, CH, $C_{aromat.}$), 129.7 - 129.1 (m, CH, $C_{aromat.}$), 128.2 – 127.2 (m, C_q, $C_{i,\ aromat.}$), 124.8 – 123.9 (m, C_q, C_i', $_{aromat.}$), 52.4 (br, CH_2, C^N, C^J), 49.9 (br, CH_2, C^I, C^M), 45.4 – 42.8 (several multipletts, CH_2 and CH, C^{A+B}, (2 rotamers)), 38.7 (m, CH_2, C^K, C^F, C^G), 35.0 (CH_2, $C^{E/C}$), 33.5 (m, CH_2, C^L, C^H), 32.9 (CH_2, $C^{E/C}$), 20.6 (CH_2, C^D); **{^{1}H}^{31}P-NMR** (121.5 MHz, d_6-DMSO, 295 K): δ = 43.0 (s, br); **IR** (KBr): 3427 m (ν N-H), 1644 vs (br, ν C=O), 1538 s, 1434 vs (ν P-Ph), 1099 m, 997 m, 828 w, 746 s (δ C-$H_{aromat.}$), 690 s (δ C-$H_{aromat.}$), 543 m, 519 s, 483 m;



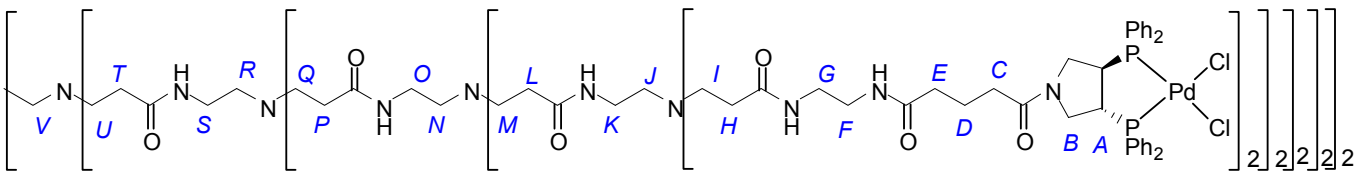
PAMAM(PyrphosPdCl$_2$)$_{16}$: Yield 74 mg (5.04 µmol, 84%);

^{1}H-NMR (300.16 MHz, 295 K, d$_6$-DMSO): δ = 8.10 – 7.45 (m, 364 H, H-$_{aromat}$, N*H*), 3.90 – 1.80 (several multipletts, vbr, 404H, H^B, H^F, H^G, H^K, H^O,H^A, H^I, H^M, H^Q,H^J, H^N, H^R, H^H, H^L, H^P, H^E, H^C); 1.60 -1.35 (m, 32H, H^D), signals very broad, integration uncertain **{^{1}H}^{31}P-NMR** (121.5 MHz, CDCl$_3$, 295 K): δ = 43.0 (s, br); **IR** (KBr): 3426 s (vbr, ν N-H), 1651 vs (br, ν C=O), 1538 s, 1434 s (ν P-Ph), 1100 m, 746 m (δ C-H$_{aromat.}$), 690 (δ C-H$_{aromat.}$), 543 m, 520 m;



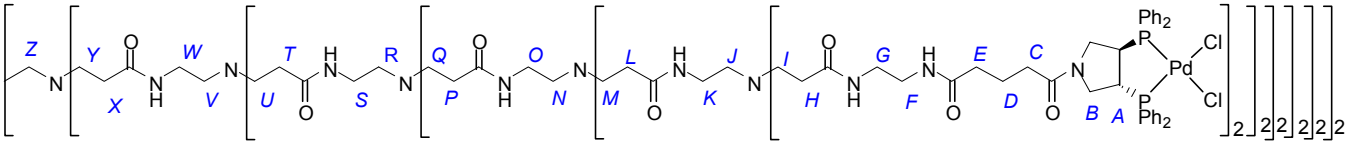
PAMAM(PyrphosPdCl$_2$)$_{32}$: Yield 90 mg (3.02 µmol, 83%);

^{1}H-NMR (300.16 MHz, 295 K, CDCl$_3$): δ = 8.10 – 7.10 (m, 732 H, H-$_{aromat}$, N*H*), 4.00 -1.70 (m, 772H, H^B, H^F, H^G, H^K, H^O, H^S, H^A, H^I, H^M, H^Q, H^U, H^J, H^N, H^R, H^V, H^H, H^L, H^P, H^T, H^E, H^C); 1.60 -1.40 (m, 64H, H^D), signals very broad, integration uncertain; **{^{1}H}^{13}C-NMR** (50.3 MHz, 297 K, CDCl$_3$): δ = 172.4 (br, C$_q$, HN*C*=O), 171.1 (br, C$_q$, HN*C*=O), 136.7 (CH, C$_{aromat.}$), 133.7 (CH, C$_{aromat.}$), 132.5 (CH, C$_{aromat.}$), 129.8 - 128.9 (m, CH, C$_{aromat.}$), 128.2 – 127.2 (C$_q$, C$_{i,\ aromat.}$), 124.9 – 123.8 (C$_q$, C$_i$', $_{aromat.}$),52.3 (br, CH$_2$, C^N, C^J, C^R,C^V), 49.8 (br, CH$_2$, C^I, C^M, C^Q, C^U), 45.1 – 43.2 (several multipletts, CH$_2$ and CH, C^{A+B}, (2 rotamers)), 38.9 – 38.5 (m, CH$_2$, C^F, C^G, C^K, C^O,C^S,), 35.0 (CH$_2$, C$^{E/C}$), 33.4 (CH$_2$, C^H, C^L, C^P, C^T), 32.9 (CH$_2$, C$^{E/C}$), 20.6 (CH$_2$, C^D); **{^{1}H}^{31}P-NMR** (121.5 MHz, CDCl$_3$, 295 K): δ = 43.0 (s, br); **IR** (KBr): 3304 s (vbr, ν N-H), 3054 m, 2935 m, 1647 vs (br, ν C=O), 1545 s, 1434 s (ν P-Ph), 1335 w, 1259 m, 1184 w, 1100 m, 998 w, 746 s (δ C-H$_{aromat.}$), 691 s (δ C-H$_{aromat.}$), 543 m, 519 s;



PAMAM(PyrphosPdCl$_2$)$_{64}$: Yield 96 mg (1.60 μmol, 78%);

^{1}H-NMR (300.16 MHz, 295 K, $CDCl_3$): δ = 8.00 – 7.10 (m, 1468 H, H-$_{aromat}$, N*H*), 3.90 – 1.40 (several multipletts, vbr, 1764H, H^B, H^F, H^G, H^K, H^O, H^S, H^W, H^A, H^I, H^M, H^Q, H^U, H^Y, H^J, H^N, H^R, H^V, H^Z, H^H, H^L, H^P, H^T, H^X, H^E, H^C, H^D); **{^{1}H}^{31}P-NMR** (121.5 MHz, $CDCl_3$, 295 K): δ = 43.0 (s, br); **IR** (KBr): 3308 s (vbr, ν N-H), 1648 vs (br, ν C=O), 1546 s, 1435 s (ν P-Ph), 1261 m, 1101 w, 747 s (δ C-H$_{aromat.}$), 691 (δ C-H$_{aromat.}$), 520 m;



3. Catalytic studies

General:

The determination of the enantiomeric excesses of 1,3-diphenyl-1-acetatopropene was carried out by HPLC with a chiral column (chiralcel-OD).Method: iPrOH/Hexane (15/85); 1 ml/min; tr_1 = 5.7 min; tr_2 = 12.9 min; UV detector at λ = 240, 250, 257, 265 nm.

General procedure for the allylic amination experiments:

The ratio Pd/substrate was 1:300 in all cases. In the air, about 4 mg of catalyst precursor and 360 mg of substrate was placed in a Schlenk tube. The Schlenk tube was then subjected to three vacuum-N_2 cycles, the solids were dissolved in 5ml of DMSO and morpholine was added. The mixture was warmed to 45°C and stirred over a period of 20 h. After removal of the solvent in vacuo and the residue was purified by column chromatography (silica gel, Ethyl ether/ pentane (1/1)). The product was dried under vacuum to obtained a colourless viscous oil.

	% ee	% Yield
PyrBoc $PdCl_2$	11	81
PPI(PyrphosPdCl_2)$_4$	19	85
PPI(PyrphosPdCl_2)$_8$	31	80
PPI(PyrphosPdCl_2)$_{16}$	40	95
PPI(PyrphosPdCl_2)$_{32}$	42	78
PPI(PyrphosPdCl_2)$_{64}$	40	96
PAMAM(PyrphosPdCl_2)$_4$	31	93
PAMAM(PyrphosPdCl_2)$_8$	51	90
PAMAM(PyrphosPdCl_2)$_{16}$	58	87
PAMAM(PyrphosPdCl_2)$_{32}$	64	79
PAMAM(PyrphosPdCl_2)$_{64}$	69	82