

Supporting Information

Sequence Isomerism in [3]Rotaxanes

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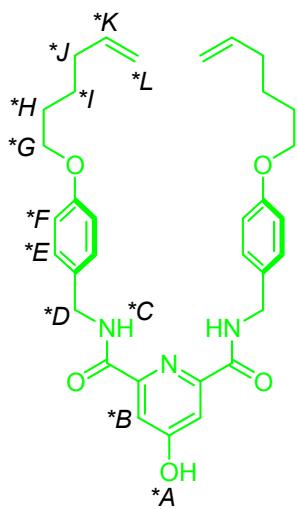
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General experimental procedures

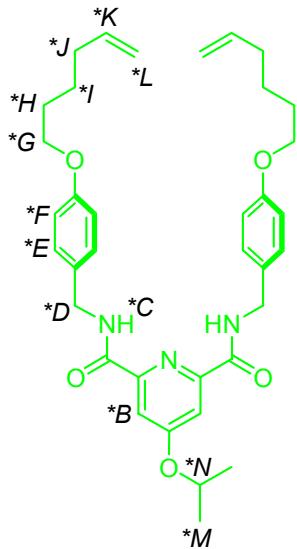
Unless stated otherwise, all reagents and anhydrous solvents were purchased from Aldrich Chemicals and used without further purification. 4-(hex-5-enyloxy)phenylmethanamine¹, **L1**Pd(CH₃CN)² and *o*-nitrobenzenesulfonylhydrazide³ were prepared according to literature procedures. Column chromatography was carried out using Kieselgel C60 (Merck, Germany) as the stationary phase, and TLC was performed on precoated silica gel plates (0.25 mm thick, 60F₂₅₄, Merck, Germany) and observed under UV light. All ¹H and ¹³C NMR spectra were recorded on a Bruker AV 400 instrument, at a constant temperature of 300 K. Chemical shifts are reported in parts per million from high to low field. Coupling constants (*J*) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: m = multiplet, b = broad, d = doublet, dd = double doublet, t = triplet, s = singlet. Melting points were determined using a Sanyo Gallenkamp apparatus. FAB mass spectrometry was carried out by the services at the University of Edinburgh.



2

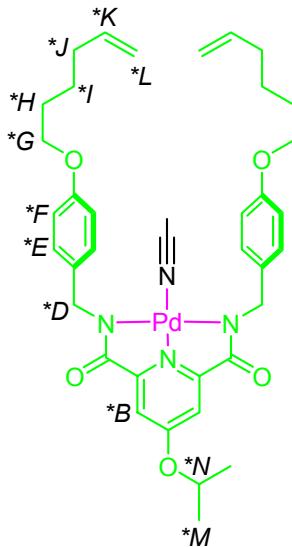
To a suspension of chelidamic acid **1** (3.0 g, 15 mmol) and pentafluorophenol (PFP) (6.1 g, 33 mmol) in dichloromethane (75 mL) at 0°C, a solution of 1-ethyl-3-(3'-dimethylaminopropyl)carbodiimide (EDCI) (6.3 g, 33 mmol) in dichloromethane (75

mL) was added drop wise. The reaction mixture was stirred for 3-5 hours until the solution became homogenous, after which it was concentrated under reduced pressure and passed through a short plug of silica (ethyl acetate: 40-60 petroleum ether; 2: 3). The resultant colorless solid was then dissolved in chloroform (25 mL) and the solution cooled to 0°C, after which a solution of 4-(hex-5-enyloxy)phenyl)methanamine¹ (6.0 g, 29 mmol) in chloroform (25 mL) was added drop wise. The resulting solid was filtered off and recrystallized from acetonitrile to yield **2** as a colorless solid (7.4 g, 89%). Mp. 182-184 °C; ¹H NMR (400 MHz, CDCl₃): δ = 1.48-1.59 (m, 4H, H_{*I}), 1.69-1.80 (m, 4H, H_{*H}), 2.05-2.15 (m, 4H, H_{*J}), 3.83 (t, 4H, J = 6.5 Hz, H_{*G}), 4.40 (d, 4H, J = 5.7 Hz, H_{*D}), 4.93-5.07 (m, 4H, H_{*L}), 5.75-5.88 (m, 2H, H_{*K}), 6.71 (d, 4H, J = 8.6 Hz, H_{*F}), 7.10 (d, 4H, J = 8.6 Hz, H_{*E}), 7.77 (s, 2H, H_{*B}), 8.61 (bs, 2H, H_{*C}), 10.87 (bs, 1H, H_{*A}); ¹³C NMR (100 MHz, CDCl₃): δ = 25.3, 28.7, 33.4, 43.1, 67.7, 112.9, 114.5, 114.7, 129.0, 129.4, 138.5, 149.9, 158.5, 164.1, 167.1; LRMS (FAB, NOBA): m/z = 558 [MH]⁺; HRMS (FAB, NOBA): m/z = 558.29898 [MH]⁺ (calc. for C₃₃H₄₀N₃O₅, 558.29680).

**L1**

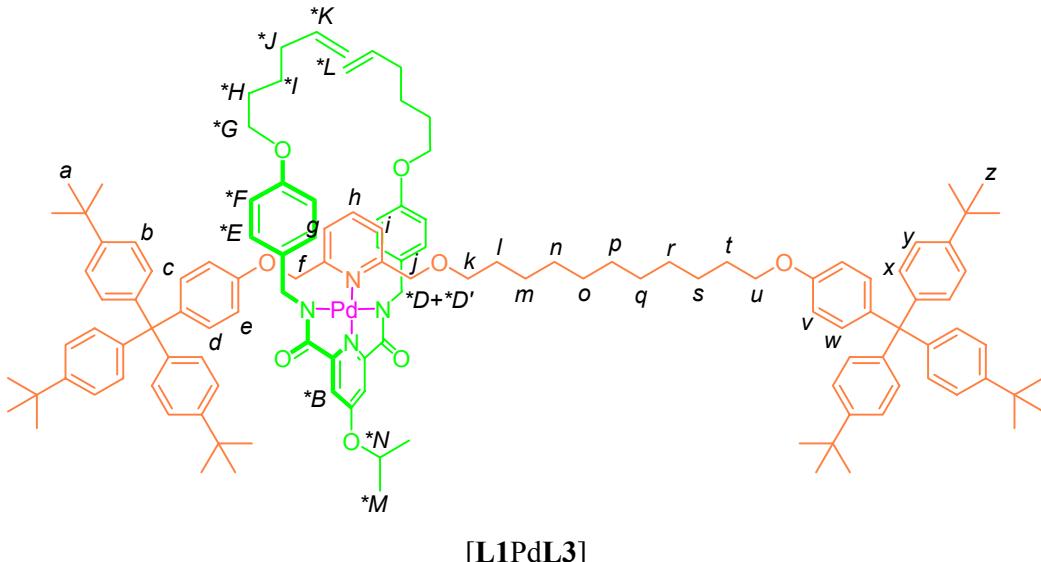
To a solution of **2** (1.7 g, 3.0 mmol) and iodopropane (0.4 mL, 4.0 mmol) in butan-2-one (75 mL), was added potassium carbonate (2.1 g, 15 mmol). The suspension was then heated at 70°C, for 18 h, under an atmosphere of nitrogen. Upon cooling, the potassium carbonate was removed by filtration and the filtrate concentrated under reduced pressure. The resultant oil was re-dissolved in dichloromethane (100 mL) and washed with water (2 x 50 mL), followed by a saturated aqueous solution of sodium

chloride (50 mL). The water layers were combined and re-extracted with dichloromethane (50 mL). The combined organic layers were dried over anhydrous magnesium sulfate, concentrated under reduced pressure and the crude product purified by flash chromatography (dichloromethane) to yield **L1** as a colorless gummy solid (1.7 g, 95%). ^1H NMR (400 MHz, CDCl_3): δ = 1.38 (d, 6H, J = 6.0 Hz, H_{*M}), 1.50-1.66 (m, 4H, H_{*I}), 1.72-1.84 (m, 4H, H_{*H}), 2.07-2.17 (m, 4H, H_{*J}), 3.93 (t, 4H, J = 6.4 Hz, H_{*G}), 4.57 (d, 4H, J = 6.0 Hz, H_{*D}), 4.72-4.84 (m, 1H, H_{*N}), 4.92-5.08 (m, 4H, H_{*L}), 5.75-5.89 (m, 2H, H_{*K}), 6.83 (d, 4H, J = 8.5 Hz, H_{*F}), 7.22 (d, 4H, J = 8.5 Hz, H_{*E}), 7.82 (s, 2H, H_{*B}), 7.99 (t, 2H, J = 5.7 Hz, H_{*C}); ^{13}C NMR (100 MHz, CDCl_3): δ = 21.7, 25.3, 28.7, 33.4, 42.9, 67.8, 71.2, 112.1, 114.6, 114.8, 129.1, 130.0, 138.5, 150.7, 158.5, 163.5, 166.9; LRMS (FAB, NOBA): m/z = 600 [MH] $^+$; HRMS (FAB, NOBA): m/z = 600.34331 [MH] $^+$ (calc. for $\text{C}_{36}\text{H}_{46}\text{N}_3\text{O}_5$, 600.34375).

[L1Pd(CH₃CN)]

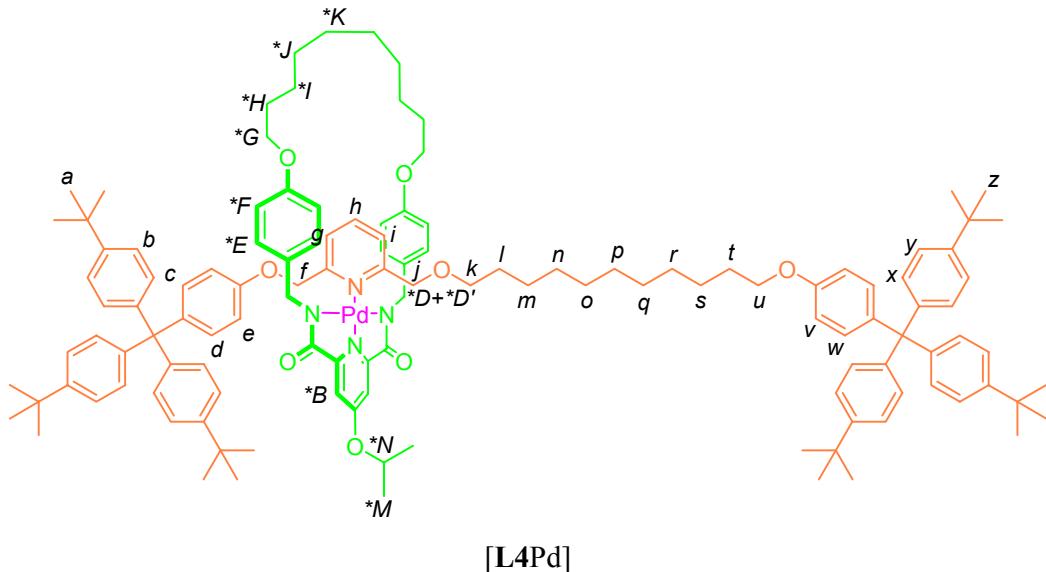
To a solution of **L1** (1.5 g, 2.5 mmol) in anhydrous acetonitrile (50 mL) was added palladium(II) acetate (0.56 g, 2.5 mmol) and the reaction was stirred at room temperature for 6 h under an atmosphere of nitrogen during which time the solution turned a dark green colour. The resultant black precipitate was filtered off, the filtrate concentrated to ~10 mL and triturated with ether. The resultant yellow solid was filtered under suction to afford [L1Pd(CH₃CN)] (1.3 g, 70%). Mp. 132 °C (decomp); ^1H NMR (400 MHz, $\text{CDCl}_3/\text{CD}_3\text{CN}$: 9/1): δ = 1.49 (d, 6H, J = 6.0 Hz, H_{*M}), 1.59-1.70 (m, 4H, H_{*I}), 1.80-1.96 (m, 4H, H_{*H}), 2.10 (s, 3H, H_{MeCN}), 2.16-2.25 (m, 4H, H_{*J}), 4.02 (t, 4H, J = 6.5 Hz, H_{*G}), 4.54 (s, 4H, H_{*D}), 4.81-4.91 (m, 1H, H_{*N}), 5.01-5.16 (m, 4H, H_{*L}), 5.85-5.98 (m, 2H, H_{*K}), 6.90 (d, 4H, J = 8.6 Hz, H_{*F}), 7.30 (d, 4H,

$J = 8.6$ Hz, H_{*E}), 7.39 (s, 2H, H_{*B}); ¹³C NMR (100 MHz, CD₂Cl₂/CD₃CN: 9/1): $\delta = 1.9, 21.6, 25.6, 29.0, 33.8, 49.6, 68.0, 72.8, 111.5, 114.3, 114.6, 117.0, 128.5, 134.0, 139.0, 154.7, 158.0, 168.9, 170.6$; LRMS (FAB, NOBA): $m/z = 704$ [M-CH₃CN]⁺ (calc. for C₃₈H₄₆N₄O₅Pd, 745).



A solution of **L3** (1.0 g, 0.78 mmol) and [L1Pd(CH₃CN)] (0.58 g, 0.78 mmol) in anhydrous dichloromethane (25 mL) under an atmosphere of nitrogen, was stirred for 5 h at room temperature. The solution was then concentrated under reduced pressure and the crude residue purified by column chromatography (ethyl acetate: 40-60 petroleum ether; 2: 3) to yield [L1PdL3] as a yellow solid (1.5 g, 97%). Mp. 158 °C (decomp); ¹H NMR (400 MHz, CD₂Cl₂): $\delta = 1.24\text{-}1.53$ (m, 78H, H_{a+z+s+r+q+p+o+n+m+*I+*M}), 1.56-1.71 (m, 6H, H_{l+*H}), 1.72-1.83 (m, 2H, H_t), 2.04-2.12 (m, 4H, H_{*j}), 3.37 (t, 2H, $J = 6.6$ Hz, H_k) 3.62-3.79 (m, 4H, H_{*G+*G'}), 3.83-3.96 (m, 4H, H_{*D'+u}), 4.01 (d, 2H, $J = 14.2$ Hz, H_{*D}), 4.56 (s, 2H, H_j), 4.82-5.05 (m, 7H, H_{*N+f+*L}), 5.75-5.88 (m, 2H, H_K), 6.40-6.52 (m, 8H, H_{*E+*F}), 6.77 (m, 4H, H_{e+v}), 7.12-7.21 (m, 16H, H_{c+d+w+x}), 7.24-32 (m, 14H, H_{b+y+*B}), 7.52 (d, 1H, $J = 7.8$ Hz, H_i), 7.59 (d, 1H, $J = 7.8$ Hz, H_g), 7.98 (t, 1H, $J = 7.8$ Hz, H_h); ¹³C NMR (100 MHz, CD₂Cl₂): $\delta = 21.8, 25.7$ (x2), 26.4, 26.6, 29.1, 29.7 (x2), 29.8, 30.0 (x2), 30.1, 31.5 (x2), 33.9, 34.5 (x2), 48.9, 63.4 (x2), 67.8, 68.2, 69.3, 72.1, 72.4, 72.7, 111.6, 113.4, 114.0, 114.3, 114.8, 121.9, 122.0, 124.6 (x2), 128.5, 130.7, 130.8, 132.2, 132.3, 133.4, 139.0, 139.7, 141.0 (x2), 144.7, 144.9, 148.6, 148.8, 154.5, 155.6, 157.3, 158.2, 159.1, 161.4, 168.9, 171.3; LRMS (FAB, NOBA): $m/z = 1988$ [MH₂]⁺; HRMS

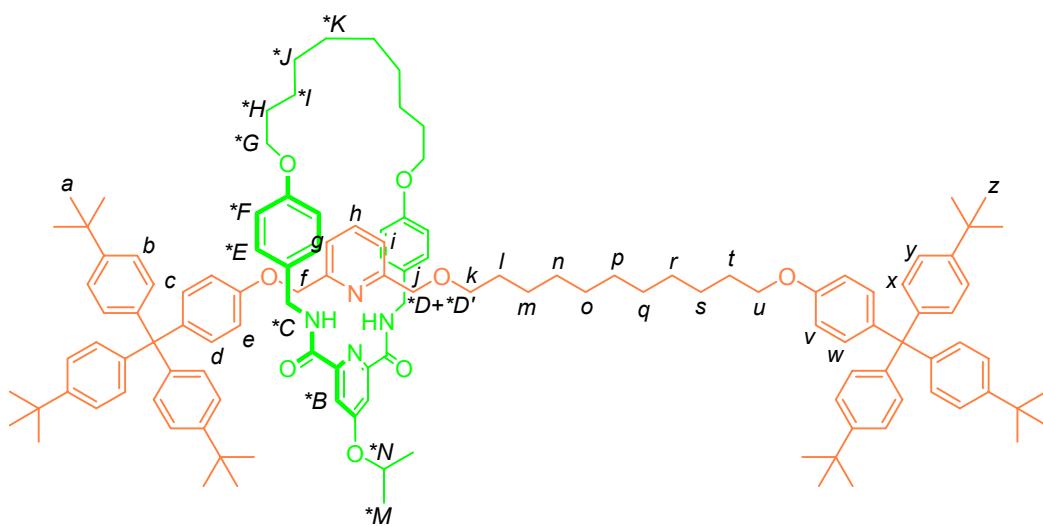
(FAB, NOBA): $m/z = 1987.12805$ [MH]⁺ (calc. for $^{12}\text{C}_{127}^{13}\text{CH}_{159}\text{N}_4\text{O}_8\text{Pd}$, 1987.12235).



(i) To a solution of first generation Grubbs' catalyst (70 mg, 0.08 mmol) in anhydrous dichloromethane (400 mL) under an atmosphere of nitrogen, **[L1PdL3]** (1.3 g, 0.65 mmol) in anhydrous dichloromethane (250 mL) was added. The solution was stirred at room temperature for 18 h, concentrated under reduced pressure and the crude residue purified by column chromatography (ethyl acetate: 40-60 petroleum ether; 1: 2) to yield a yellow solid (1.1 g).

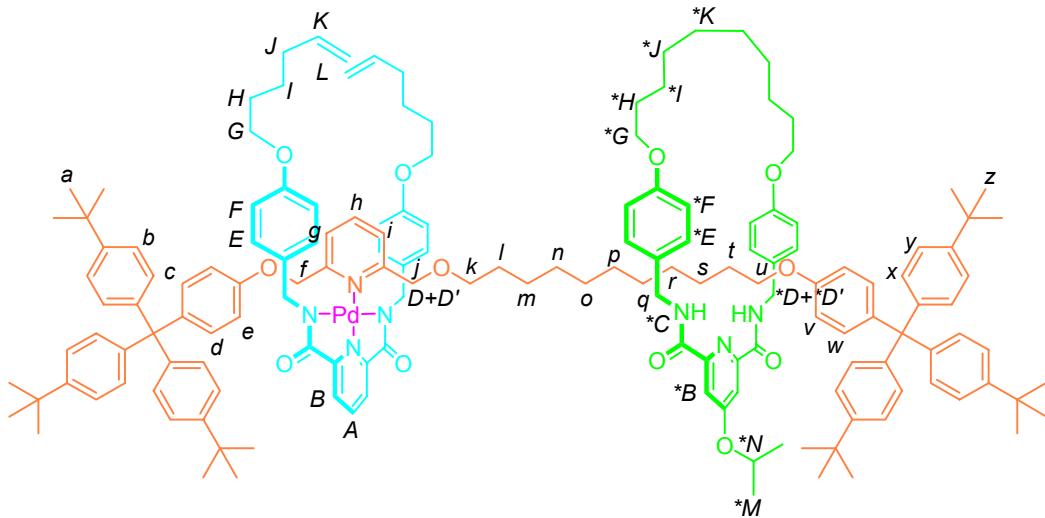
(ii) To a solution of the product obtained in step (i) in anhydrous dichloromethane (7 mL), under an atmosphere of nitrogen, *o*-nitrobenzenesulfonyl-hydrazide (NBSH) (1.2 g, 5.5 mmol) and triethylamine (1.0 mL, 7.2 mmol) were added and the suspension stirred overnight. The resultant orange/brown solution was then washed with sodium bicarbonate (3 X 75 mL). The combined organic layers were then dried over anhydrous magnesium sulfate, concentrated under reduced pressure and the crude product purified by column chromatography (ethyl acetate: 40-60 petroleum ether; 1: 2) to yield **[L4Pd]** as a yellow solid (0.89 g, 70% over 2 steps). Mp. 150 °C (decomp); ¹H NMR (400 MHz, CD₂Cl₂): $\delta = 1.13-1.49$ (m, 86H, H_{a+z+m+n+o+p+q+r+s+*I+*J+*K+*M}), 1.54-1.80 (m, 8H, H_{*H+l+t}), 3.50 (d, 2H, $J = 14.3$ Hz, H_{*D}), 3.59-3.85 (m, 6H, H_{k+*G+*G'}), 3.92 (t, 2H, $J = 6.6$ Hz, H_u), 4.66 (d, 2H, $J = 14.3$ Hz, H_{*D}), 4.79 (s, 2H, H_j), 4.81-4.90 (m, 1H, H_{*N}), 5.04 (s, 2H, H_j), 6.33 (s, 8H, H_{*E+*F}), 6.70-6.79 (m, 4H, H_{e+v}), 7.11-7.31(m, 31H, H_{b+c+d+g+w+*B}), 7.48 (d, 1H, $J =$

7.8 Hz, H_i), 7.83 (t, 1H, *J* = 7.8 Hz, H_h); ¹³C NMR (100 MHz, CD₂Cl₂): δ = 21.8, 25.8, 26.4, 26.5, 28.8, 28.9, 29.7 (x2), 29.8, 29.9 (x2), 30.0 (x3), 31.4 (x2), 34.5 (x2), 50.0, 63.4, 63.5, 67.4, 68.2, 70.0, 72.4, 72.7, 73.2, 111.6, 113.4, 114.9, 115.3, 121.3, 122.0, 124.6, 124.7, 128.4, 130.7 (x2), 132.0, 132.2, 133.3, 139.3, 139.7, 141.4, 144.8, 144.9, 148.7 (x2), 154.5, 155.5, 157.3, 157.9, 159.9, 160.0, 168.8, 171.6; LRMS (FAB, NOBA): *m/z* = 1959 [M-H]⁺; HRMS (FAB, NOBA): *m/z* = 1960.10257 [M]⁺ (calc. for ¹¹²C₁₂₅¹³CH₁₅₆N₄O₈Pd, 1960.09876).

**H₂L4**

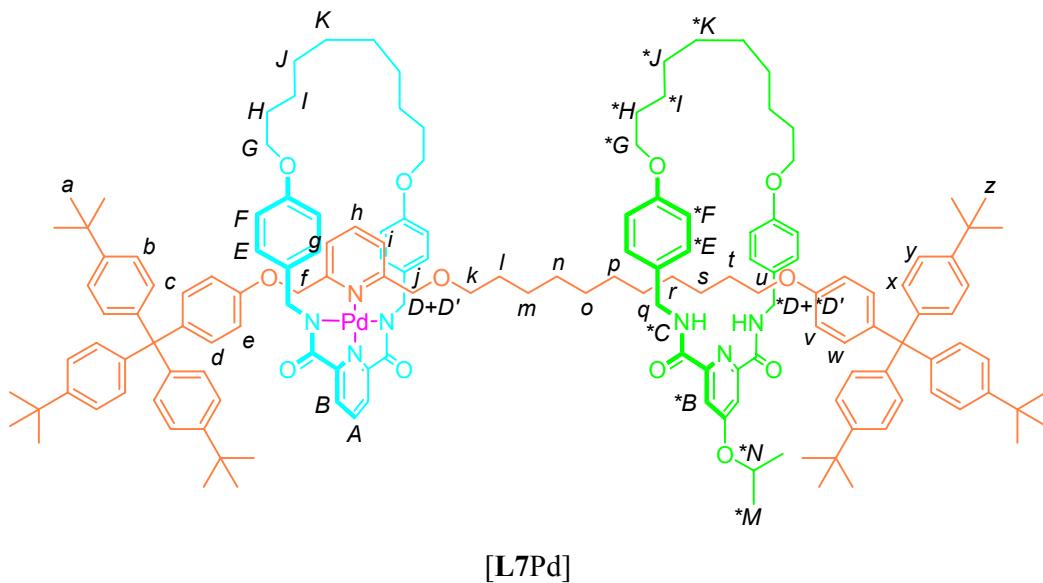
To a solution of potassium cyanide (0.35 g, 5.4 mmol) in methanol (20 mL) [**L4Pd**] (0.71 g, 0.36 mmol) in dichloromethane (20 mL) was added. The solution was heated gently until it went colorless, and then the overall volume was allowed to reduce to less than 5 mL. The resultant mixture was dispersed in water (100 mL) and extracted with dichloromethane (3 x 50 mL). The combined organic extracts were washed with a further portion of water (50 mL) and dried over anhydrous magnesium sulfate. After filtration, the solution was concentrated under reduced pressure to yield **H₂L4** as a colorless solid (0.64 g, 98%). Mp. 144-146 °C; ¹H NMR (400 MHz, CD₂Cl₂): δ = 1.13-1.48 (m, 88H, H_{a+z++l+m+n+o+p+q+r+s+*I+*J+*K+*M}), 1.56-1.70 (m, 6H, H_{*H+i}), 3.25 (t, 2H, *J* = 6.8 Hz, H_k), 3.68 (t, 2H, *J* = 6.7 Hz, H_u), 3.72-3.82 (m, 4H, H_{*G}), 3.85-3.94 (dd, 2H, *J* = 4.9, 14.5 Hz, H_{*D}), 4.23 (s, 2H, H_f), 4.30 (s, 2H, H_j), 4.51-4.60 (dd, 2H, *J* = 7.5, 14.5 Hz, H_{*D}), 4.81-4.91 (m, 1H, H_{*N}), 6.35 (d, 4H, *J* = 8.6, H_{*F}), 6.45 (d, 2H, *J* = 8.9, H_e), 6.64 (d, 4H, *J* = 8.6, H_{*E}), 6.71 (d, 2H, *J* = 8.9, H_v), 7.00 (d, 1H, *J* = 7.8, H_g), 7.06 (d, 2H, *J* = 8.9, H_d), 7.11-7.21 (m, 15H, H_{c+x+i+w}), 7.24-7.32 (m, 12H, H_{b+y}),

7.58 (t, 1H, $J = 7.8$ Hz, H_h), 7.85 (s, 2H, H_{*B}), 9.20-9.28 (m, 2H, H_{*C}); ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 21.9, 25.8, 26.3, 26.4, 28.7, 28.8$ (x2), 29.6, 29.7, 29.8, 29.9 (x4), 31.4 (x2), 34.5 (x2), 42.7, 63.4 (x2), 67.3, 68.2, 69.2, 71.4, 71.8, 73.1, 112.1, 113.4, 113.6, 114.4, 120.1, 120.2, 124.6, 124.7, 129.0, 130.4, 130.7 (x2), 132.0, 132.2, 137.4, 139.8, 140.3, 144.9 (x2), 148.6, 148.7, 151.6, 156.2, 156.6, 157.1, 158.2, 158.5, 163.9, 167.1; LRMS (FAB, NOBA): $m/z = 1859$ [MH_3^+]; HRMS (FAB, NOBA): $m/z = 1857.21925$ [MH^+] (calc. for $^{12}\text{C}_{125}\text{CH}_{159}\text{N}_4\text{O}_8$, 1857.21915).

[L2PdH₂L4]

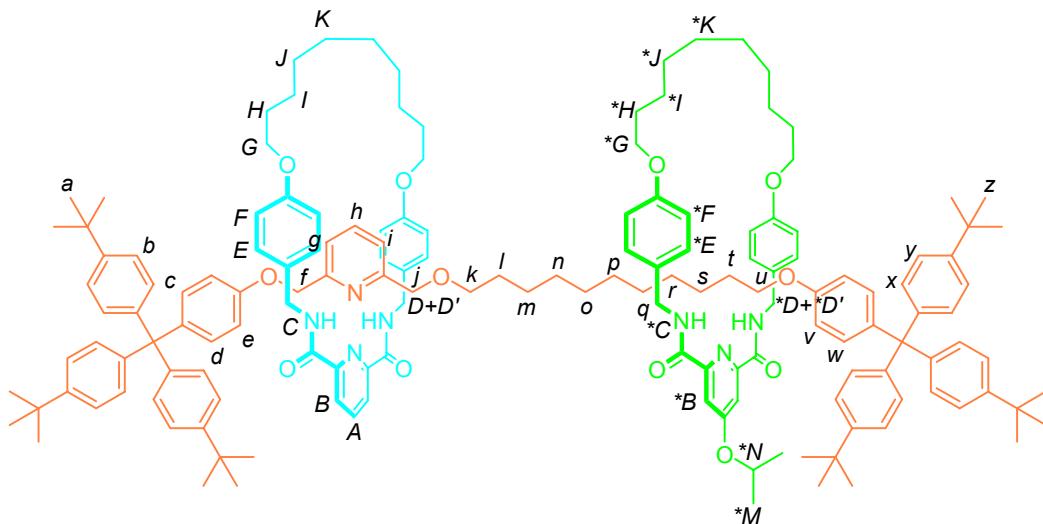
The synthesis was carried out as for the procedure for [L1PdL3] but using H₂L4 (0.56 g, 0.30 mmol) and L2Pd(CH₃CN)² (0.21 g, 0.30 mmol). The resultant crude residue was purified by column chromatography (ethyl acetate: 40-60 petroleum ether; 1: 1) to yield [L2H₂PdL4] as a yellow solid (0.73 g, 97%). Mp. 151 °C (decomp); ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 0.56\text{-}0.68$ (m, 2H, H_s), 0.76-1.74 (m, 100H, $H_{a+z+l+m+n+o+p+q+r+t+*H+H+*I+I+*J+*K+*M}$), 2.00-2.10 (m, 4H, H_J), 2.46 (t, 2H, $J = 7.6$ Hz, H_u), 3.37 (t, 2H, $J = 6.6$ Hz, H_k), 3.59-3.90 (m, 12H, $H_{G+G'+*D'+D'+*G}$), 4.08 (d, 2H, $J = 14.3$ Hz, H_D), 4.60 (s, 2H, H_f), 4.77-5.03 (m, 9H, $H_{j+*D+*N+L}$), 5.73-5.85 (m, 2H, H_K), 6.39-6.55 (m, 14H, $H_{F+E+v+*F}$), 6.70-6.82 (m, 6H, H_{e+*E}), 7.10-7.20 (m, 10H, H_{c+d+w}), 7.22-7.36 (m, 18H, H_{b+y+x}), 7.51-7.60 (m, 2H, H_{g+i}), 7.80 (d, 2H, $J = 7.8$ Hz, H_B), 7.87 (s, 2H, H_{*B}), 7.98 (t, 1H, $J = 7.9$ Hz, H_h), 8.12 (t, 1H, $J = 7.8$ Hz, H_A), 8.48-8.56 (m, 2H, H_{*C}); ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 21.9, 25.7$ (x2), 25.8, 26.6, 28.7 (x2), 28.8, 29.1, 29.7, 29.9 (x2), 30.0 (x2), 30.1 (x2), 31.4 (x2), 33.8, 34.5, 34.6, 43.1, 48.8, 63.5, 63.6, 67.3, 67.8, 67.9, 69.3, 71.4, 72.2, 72.6, 112.3, 113.1, 113.9, 114.4, 114.6, 114.8, 122.0, 122.2, 124.6, 124.8, 124.9, 128.5, 129.6, 130.3,

130.7, 130.8, 132.1, 132.3, 133.3, 139.0, 139.9, 140.3, 141.0, 141.1, 144.7, 145.0, 148.8 (x2), 151.7, 153.2, 155.6, 155.9, 158.3, 158.5, 159.2, 161.2, 163.8, 167.0, 171.3; LRMS (FAB, NOBA): m/z = 2500 [M-H]⁺; HRMS (FAB, NOBA): m/z = 2502.40106 [MH]⁺ (calc. for ¹¹²C₁₅₈¹³CH₁₉₆N₇O₁₂Pd, 2502.40076).



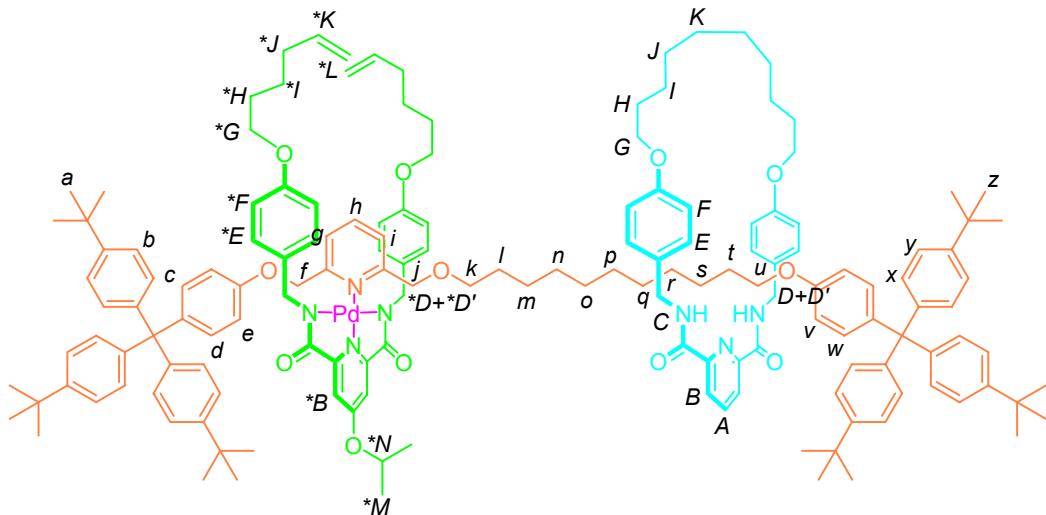
- (i) The synthesis was carried out as for the procedure for [L4Pd] using Grubbs' catalyst (23 mg, 0.028 mmol) and [L2PdH₂L4] (0.58 g, 0.23 mmol). The crude residue was purified by column chromatography using a gradient system (ethyl acetate: 40-60 petroleum ether; 1: 1 to 5: 2) to yield a yellow solid (0.49 g).
- (ii) The synthesis was carried out as for [L4Pd] using the product obtained in step (i) (0.49 g), NBSH (0.44 g, 2.0 mmol) and Et₃N (0.35 mL, 2.5 mmol). The crude residue was purified by column chromatography using a gradient system (ethyl acetate: dichloromethane; 0:1 to 1:1) to yield [L7Pd] as a yellow solid (0.41 g, 72% over two steps). Mp. 249 °C (decomp); ¹H NMR (400 MHz, CD₂Cl₂): δ = 0.59-0.71 (m, 2H, H_s), 0.80-1.50 (m, 98H, H_{a+z+m+n+o+p+q+r+t+*I+I+*J+J+*K+K+*M}), 1.54-1.76 (m, 10H, H_{*H+H+l}), 2.54 (t, 2H, J = 7.4 Hz, H_u), 3.49 (d, 2H, J = 14.3 Hz, H_{D'}), 3.58-3.92 (m, 12H, H_{k+G+G'+*D'+*G}), 4.70-4.92 (m, 7H, H_{D+f+*D+*N}), 5.09 (s, 2H, H_j), 6.35 (s, 8H, H_{F+E}), 6.47-6.58 (m, 6H, H_{v+*F}), 6.73 (d, 2H, J = 8.9 Hz, H_e), 6.82 (d, 4H, J = 8.5 Hz, H_{*E}), 7.11-7.36 (m, 29H, H_{b+c+d+g+w+x+y}), 7.53 (d, 1H, J = 7.7 Hz, H_i), 7.76-7.92 (m, 5H, H_{B+h+*B}), 8.08 (t, 1H, J = 7.8 Hz, H_A), 8.49-8.57 (m, 2H, H_C); ¹³C NMR (100 MHz, CD₂Cl₂): δ = 21.9, 25.7, 25.8 (x2), 26.6, 28.8 (x3), 28.9, 29.7, 29.7, 29.8 (x2), 29.9, 30.0 (x4), 31.5 (x2), 34.6 (x2), 43.1, 49.9, 63.5, 63.6, 67.3, 67.5, 67.9, 70.0,

71.5, 72.5, 73.3, 112.4, 113.2, 114.6, 115.0, 115.3, 121.4, 122.1, 124.8 (x2), 125.0, 128.4, 129.7, 130.3, 130.7 (x2), 132.1, 132.2, 133.4, 139.5, 140.3, 141.1 (x2), 144.8, 145.0, 148.7, 148.8, 151.7, 153.2, 155.5, 156.0, 158.0, 158.5, 159.8, 160.0, 163.8, 167.1, 171.6; HRMS (FAB, NOBA): LRMS (FAB, NOBA): $m/z = 2478$ $[\text{MH}_2]^+$; HRMS (FAB, NOBA): $m/z = 2476.38402$ $[\text{MH}]^+$ (calc. for $^{12}\text{C}_{156}^{13}\text{CH}_{194}\text{N}_7\text{O}_{12}\text{Pd}$, 2476.38511).

**H₂L7**

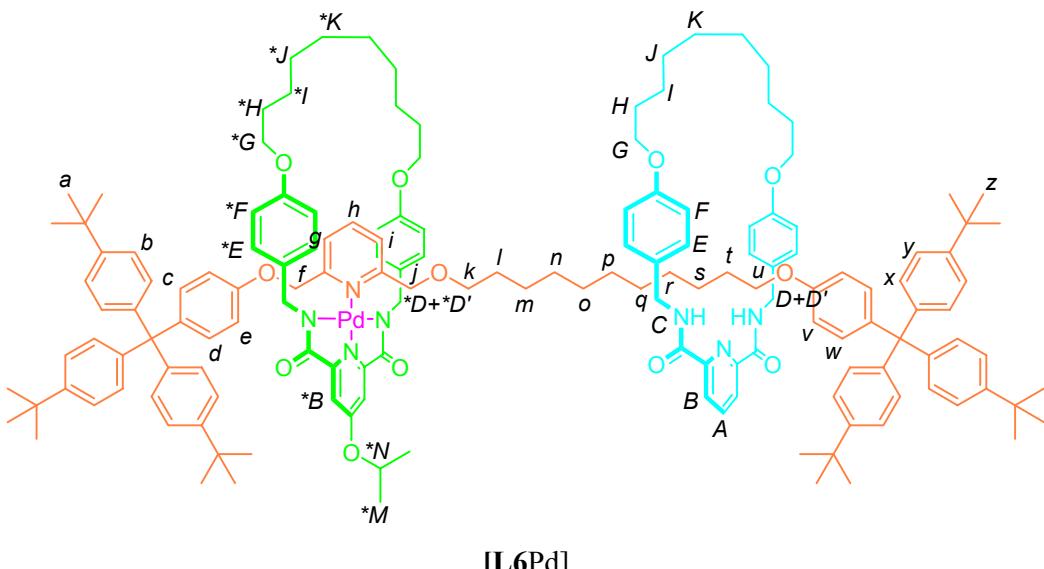
The synthesis was carried out as for H₂L4 using [L7Pd] (0.30 g, 0.12 mmol) and potassium cyanide (0.12 g, 1.8 mmol) to yield H₂L7 as a colorless solid (0.28 g, 98%). Mp. 132-136 °C; ¹H NMR (400 MHz, CD₂Cl₂): $\delta = 0.58\text{-}0.69$ (m, 2H, H_s), 0.80-1.51 (m, 100H, H_{a+z+l+m+n+o+p+q+r+t+*I+I+*J+J+*K+K+*M}), 1.59-1.72 (m, 8H, H_{*H+H}), 2.51 (t, 2H, J = 7.5 Hz, H_u), 3.16 (t, 2H, J = 6.9 Hz, H_k), 3.69-3.95 (m, 12H, H_{D'+*D'+G+*G}), 4.02 (s, 2H, H_f), 4.27 (s, 2H, H_j), 4.53-4.62 (dd, 2H, J = 7.7, 14.5 Hz, H_D), 4.75-4.90 (m, 3H, H_{*D+*N}), 6.28-6.35 (m, 6H, H_{F+e}), 6.46-6.55 (m, 6H, H_{v+*F}), 6.63 (d, 4H, J = 8.6 Hz, H_E), 6.79 (d, 4H, J = 8.5 Hz, H_{*E}), 6.91 (d, 1H, J = 7.7 Hz, H_g), 7.02 (d, 2H, J = 8.8 Hz, H_d), 7.12-7.21 (m, 9H, H_{i+w+c}), 7.23-7.35 (m, 18H, H_{b+y+x}), 7.57 (d, 1H, J = 7.7 Hz, H_h), 7.87 (s, 2H, H_{*B}), 8.01 (t, 1H, J = 7.8 Hz, H_A), 8.37 (d, 2H, J = 7.8 Hz, H_B), 8.47-8.54 (m, 2H, H_{*C}), 9.38-9.45 (m, 2H, H_C); ¹³C NMR (100 MHz, CD₂Cl₂): $\delta = 21.8, 25.7, 25.8$ (x3), 26.4, 28.7 (x3), 28.8, 29.7 (x3), 29.9 (x3), 30.0 (x2), 31.4 (x2), 34.5, 34.6, 42.6, 43.0, 63.4, 63.6, 67.2, 67.3, 67.8, 68.8, 71.5, 71.9, 73.0, 112.3, 113.1, 113.5, 114.4, 114.6, 120.1, 120.2, 124.7, 124.8, 125.2, 128.9, 129.6, 130.3, 130.4, 130.7 (x2), 131.9, 132.1, 137.5, 138.9, 140.3 (x2), 144.9, 145.0, 148.6, 148.7, 149.7, 151.7, 156.0, 156.4, 158.1, 158.3 (x2), 158.5, 163.8

(x2), 167.0; LRMS (FAB, NOBA): $m/z = 2370$ $[\text{M}-\text{H}]^+$; 1858(50%) $[\text{M}-\text{unsubstitutedmacrocycle}]^+$; 1800(30%) $[\text{M}-\text{iPrOmacrocyclic}]^+$; HRMS (FAB, NOBA): $m/z = 2372.49443$ $[\text{MH}]^+$ (calc. for $^{12}\text{C}_{156}^{13}\text{CH}_{196}\text{N}_7\text{O}_{12}$, 2372.49756).



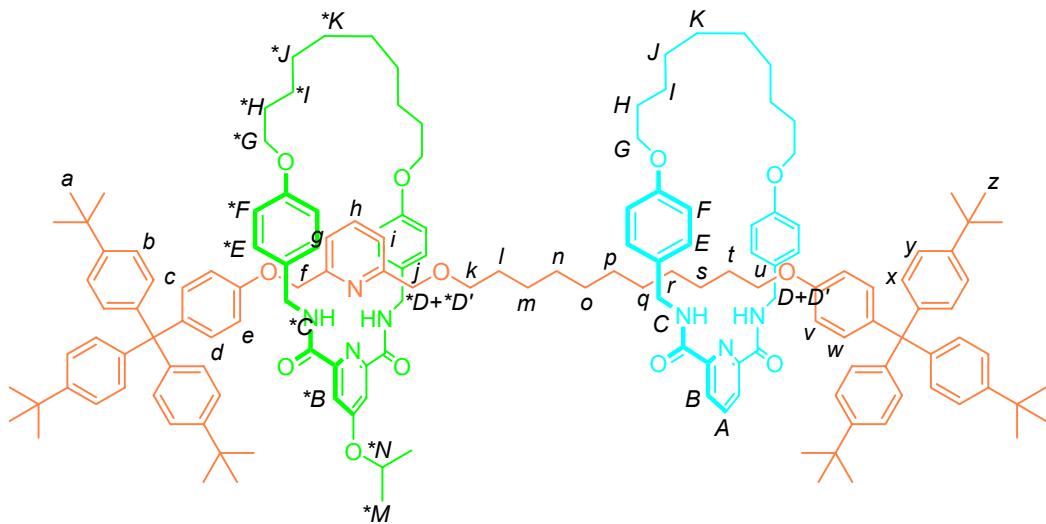
[L1PdH₂L5]

The synthesis was carried out as for [L1PdL3] using H₂L5 (0.63 g, 0.35 mmol) and [L1Pd(CH₃CN)] (0.26 g, 0.35 mmol). The resultant crude residue was purified by column chromatography (ethyl acetate: 40-60 petroleum ether; 1:1) to yield [L1PdH₂L5] as a yellow solid (0.83 g, 95%). Mp. 152 °C (decomp); ¹H NMR (400 MHz, CD₂Cl₂): $\delta = 0.55\text{-}0.67$ (m, 2H, H_s), 0.77-1.78 (m, 100H, H_{a+z+l+m+n+o+p+q+r+t+*H+H+*I+I+J+K+*M}), 2.02-2.11 (m, 4H, H_{*j}), 2.46 (t, 2H, $J = 7.6$ Hz, H_u), 3.37 (t, 2H, $J = 6.6$ Hz, H_k), 3.59-3.90 (m, 12H, H_{G+G'+*D'+D'+*G}), 4.08 (d, 2H, $J = 14.3$ Hz, H_D), 4.60 (s, 2H, H_f), 4.80-5.04 (m, 9H, H_{j+*D+*N+*L}), 5.73-5.85 (m, 2H, H_{*k}), 6.39-6.56 (m, 14H, H_{*F+*E+v+F}), 6.71-6.83 (m, 6H, H_{e+E}), 7.10-7.37 (m, 30H, H_{b+c+d+w+x+y+*B}), 7.50-7.59 (m, 2H, H_{g+i}), 7.96 (t, 1H, $J = 7.9$ Hz, H_h), 8.06 (t, 2H, $J = 7.8$ Hz, H_B), 8.41 (d, 1H, $J = 7.8$ Hz, H_A), 8.51-8.58 (m, 2H, H_C); ¹³C NMR (100 MHz, CD₂Cl₂): $\delta = 21.7, 25.6, 25.7(\text{x2}), 25.8, 26.6, 28.7(\text{x3}), 29.1, 29.7, 29.8, 30.0(\text{x3}), 30.1, 31.4(\text{x2}), 33.8, 34.5, 34.6, 43.0, 48.9, 63.4, 63.6, 67.3, 67.9(\text{x2}), 69.3, 72.1, 72.6, 72.7, 111.6, 113.1, 113.9, 114.4, 114.6, 114.7, 121.9, 122.0, 124.6, 124.8, 125.5, 128.5, 129.7, 130.2, 130.7, 130.8, 132.2, 132.3, 133.4, 139.0, 139.1, 139.7, 140.4, 141.0, 144.7, 145.0, 148.8(x2), 148.8, 149.7, 154.51, 155.6, 155.8, 158.3, 158.5, 159.2, 161.3, 163.7, 168.9, 171.3; LRMS (FAB, NOBA): $m/z = 2503$ $[\text{MH}_2]^+$; HRMS (FAB, NOBA): $m/z = 2502.4037$ $[\text{MH}]^+$ (calc. for $^{12}\text{C}_{158}^{13}\text{CH}_{196}\text{N}_7\text{O}_{12}\text{Pd}$, 2502.40076).$



- (i) The synthesis was carried out as for the procedure for **[L4Pd]** using Grubbs' catalyst (0.026 g, 0.032 mmol) and **[L1PdH₂L5]** (0.66 g, 0.26 mmol). The crude residue was purified by column chromatography using a gradient system (ethyl acetate: 40-60 petroleum ether; 1:1 to 5:2) to yield a yellow solid (0.58 g).
- (ii) The synthesis was carried out as for the procedure for **[L4Pd]** using the product obtained in step (i) (0.58 g), NBSH (0.50 g, 2.3 mmol) and Et₃N (0.40 mL, 2.9 mmol). The crude residue was purified by column chromatography using a gradient system (ethyl acetate: dichloromethane; 0:1 to 1:1) to yield **[L6Pd]** as a yellow solid (0.53 g, 82% over two steps). Mp. 153 °C (decomp); ¹H NMR (400 MHz, CD₂Cl₂): δ = 0.58-0.70 (m, 2H, H_s), 0.80-1.50 (m, 108H, H_{a+z+m+n+o+p+q+r+t+*I+I+*J+J+*K+K+*M}), 1.55-1.76 (m, 10H, H_{*H+H+l}), 2.54 (t, 2H, J = 7.6 Hz, H_u), 3.47 (d, 2H, J = 14.3 Hz, H_{*D'}), 3.60-3.93 (m, 12H, H_{k+*G+*G'+D'+G}), 4.70-4.95 (m, 7H, H_{*D+f+D+*N}), 5.10 (s, 2H, H_j), 6.35 (s, 8H, H_{*F+*E}), 6.49-6.59 (m, 6H, H_{v+F}), 6.74 (d, 2H, J = 8.8 Hz, H_e), 6.82 (d, 4H, J = 8.5 Hz, H_E), 7.12-7.37 (m, 31H, H_{b+c+d+g+w+x+y+*B}), 7.52 (d, 1H, J = 7.7 Hz, H_i), 7.84 (t, 1H, J = 7.9 Hz, H_h), 8.06 (t, 1H, J = 7.8 Hz, H_A), 8.43 (d, 2H, J = 7.8 Hz, H_B), 8.51-8.58 (m, 2H, H_C); ¹³C NMR (100 MHz, CD₂Cl₂): δ = 21.8, 25.6, 25.8 (x3), 26.5, 28.7, 28.8 (x3), 28.9, 29.7 (x2), 29.8 (x2), 29.9, 30.0 (x2), 31.5 (x2), 34.6 (x2), 43.0, 50.0, 63.5, 63.6, 67.3, 67.5, 67.9, 70.0, 72.4, 72.7, 73.2, 111.7, 113.1, 114.6, 114.9, 115.3, 121.3, 122.0, 124.7, 124.8, 125.6, 128.4, 129.7, 130.3, 130.7, 130.8, 132.0, 132.2, 133.3, 139.1, 139.3, 140.4, 141.4, 144.8, 144.9, 148.7, 148.8, 149.7, 154.5, 155.5, 155.9, 157.9, 158.5, 159.8, 160.0, 163.7, 168.8, 171.6; LRMS (FAB, NOBA):

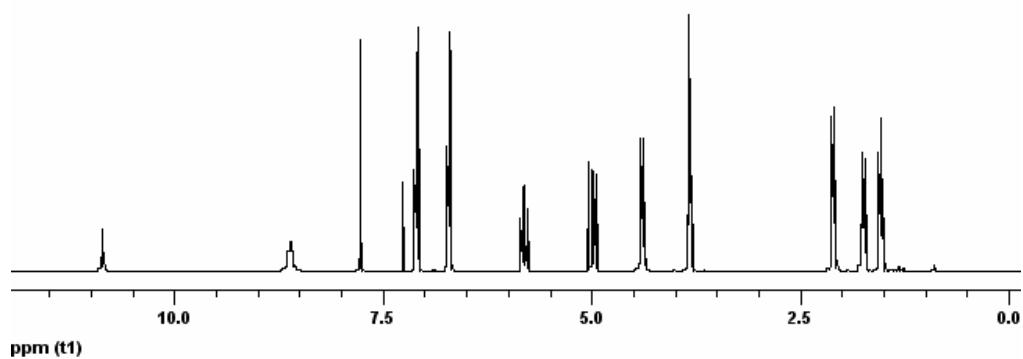
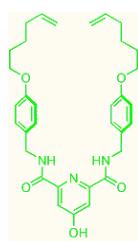
$m/z = 2479$ [MH₄]⁺; HRMS (FAB, NOBA): $m/z = 2476.38570$ [MH]⁺ (calc. for ¹²C₁₅₆¹³CH₁₉₄N₇O₁₂Pd, 2476.38511).



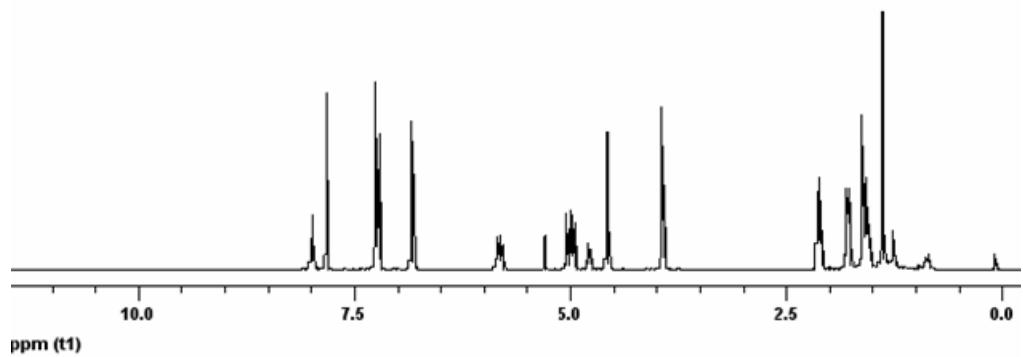
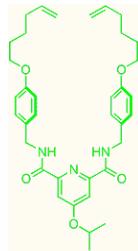
H₂L6

The synthesis was carried out as for H₂L4 using [L6Pd] (0.30 g, 0.12 mmol) and potassium cyanide (0.12 g, 1.8 mmol) to yield H₂L6 as a colorless solid (0.28 g, 98%). Mp. 129-131 °C (decomp); ¹H NMR (400 MHz, CD₂Cl₂): $\delta = 0.57\text{-}0.70$ (m, 2H, H_s), 0.79-1.51 (m, 100H, H_{a+z+l+m+n+o+p+q+r+t+*I+I+*J+J+*K+K+*M}), 1.61-1.72 (m, 8H, H_{*H+H}), 2.53 (t, 2H, $J = 7.6$ Hz, H_u), 3.20 (t, 2H, $J = 6.8$ Hz, H_k), 3.70-3.93 (m, 12H, H_{D+*D'+G+*G}), 4.01 (s, 2H, H_f), 4.30 (s, 2H, H_j), 4.54-4.63 (dd, 2H, $J = 7.7, 14.6$ Hz, H_{*D}), 4.79-4.92 (m, 3H, H_{D+*N}), 6.28-6.38 (m, 6H, H_{*F+e}), 6.48-6.56 (m, 6H, H_{v+F}), 6.62 (d, 4H, $J = 8.5$ Hz, H_{*E}), 6.80 (d, 4H, $J = 8.5$ Hz, H_E), 6.92 (d, 1H, $J = 7.8$ Hz, H_g), 7.05 (d, 2H, $J = 8.8$ Hz, H_d), 7.13-7.22 (m, 9H, H_{i+w+c}), 7.25-7.36 (m, 18H, H_{b+x+y}), 7.57 (d, 1H, $J = 7.8$ Hz, H_h), 7.86 (s, 2H, H_{*B}), 8.05 (t, 1H, $J = 7.8$ Hz, H_A), 8.41 (d, 2H, $J = 7.8$ Hz, H_B), 8.51-8.58 (m, 2H, H_C), 9.35-9.43 (m, 2H, H_{*C}); ¹³C NMR (100 MHz, CD₂Cl₂): $\delta = 21.9, 25.6, 25.8$ (x3), 26.4, 28.7 (x3), 28.8, 29.7 (x3), 29.8 (x2), 29.9, 30.0 (x2), 31.5 (x2), 34.5, 34.6, 42.6, 43.0, 63.5, 63.6, 67.2, 67.3, 67.9, 68.7, 71.4, 71.9, 73.0, 112.1, 113.1, 113.6, 114.4, 114.6, 120.0, 120.1, 124.7, 124.8, 125.6, 128.9, 129.7, 130.3, 130.4, 130.7 (x2), 131.9, 132.2, 137.5, 139.1, 140.2, 140.4, 144.9 (x2), 148.6, 148.8, 149.7, 151.6, 155.9, 156.1, 156.5, 158.1, 158.4, 158.5, 163.7, 163.9, 167.1; LRMS (FAB, NOBA): $m/z = 2371$ [M]⁺; 1858(50%) [M-unsubstitutedmacrocycle]⁺; 1800(87%) [M-iPrOmacrocycle]⁺; HRMS (FAB, NOBA): $m/z = 2372.49202$ [MH]⁺ (calc. for ¹²C₁₅₆¹³CH₁₉₄N₇O₁₂, 2372.49756).

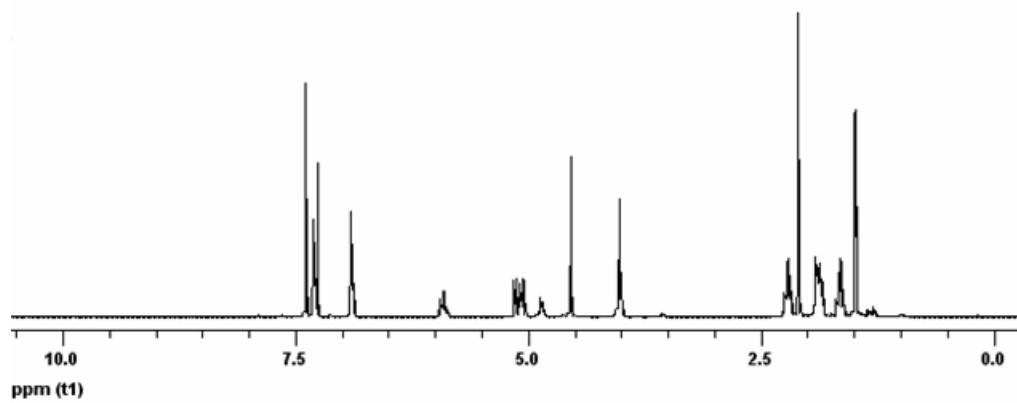
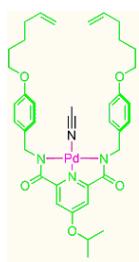
400 MHz, 300K, CDCl₃



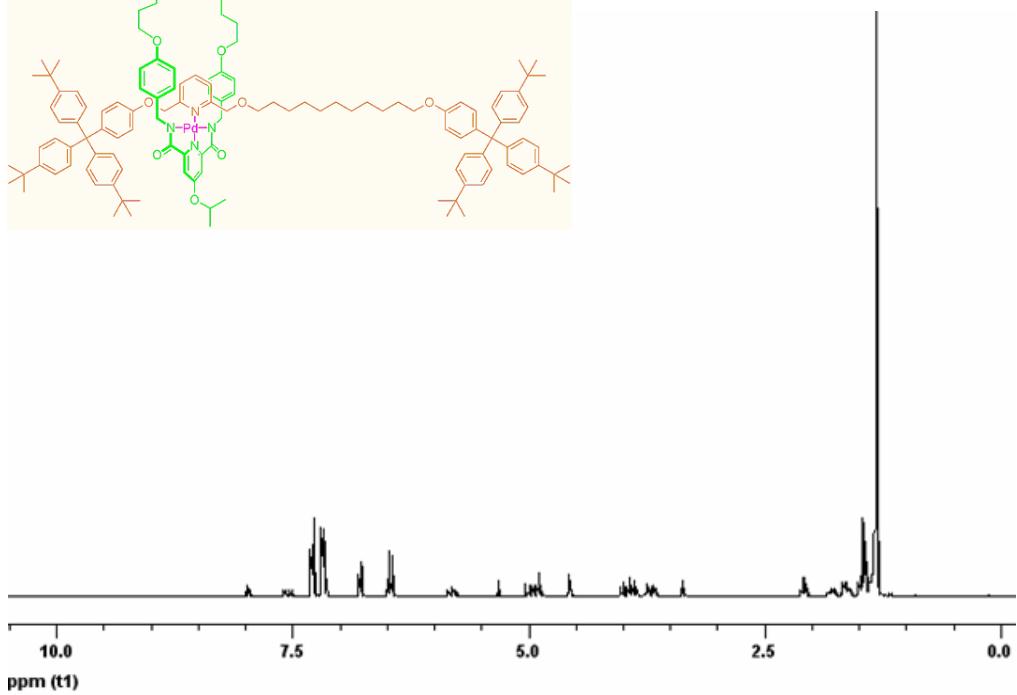
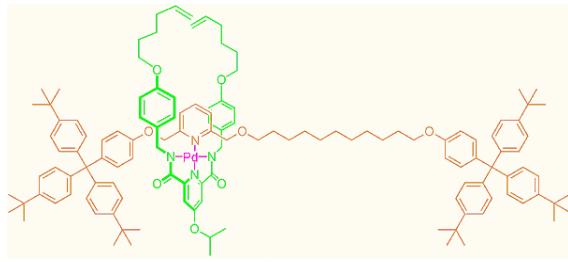
400 MHz, 300K, CDCl₃



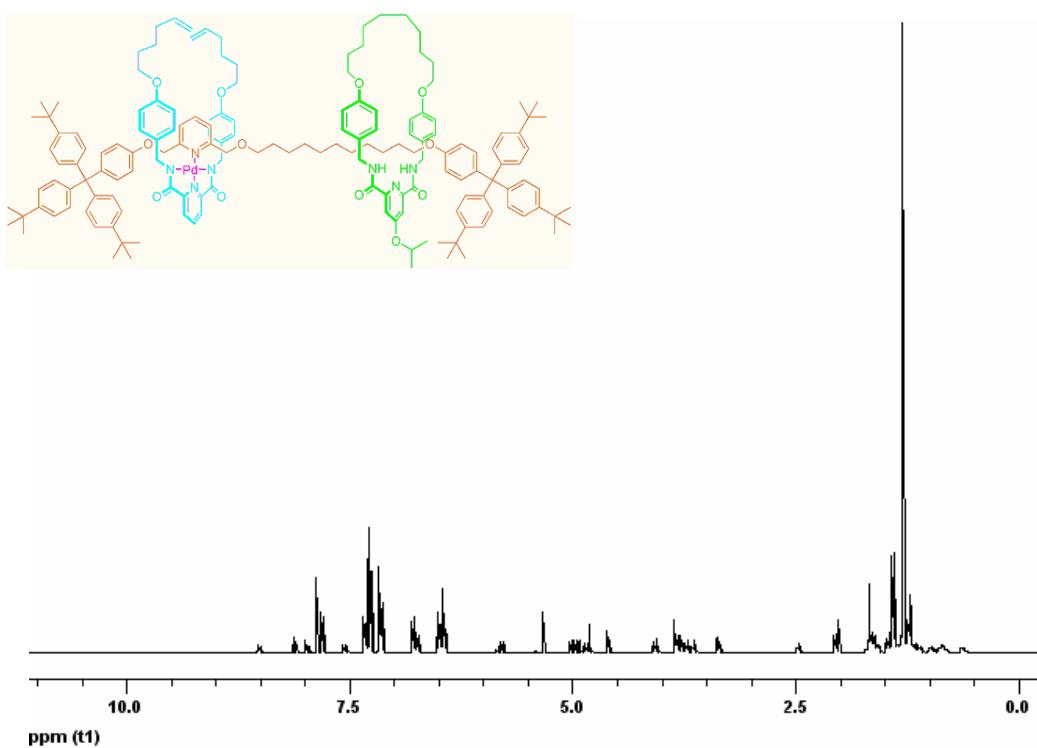
400 MHz, 300K, CDCl₃/CD₃CN: 9/1



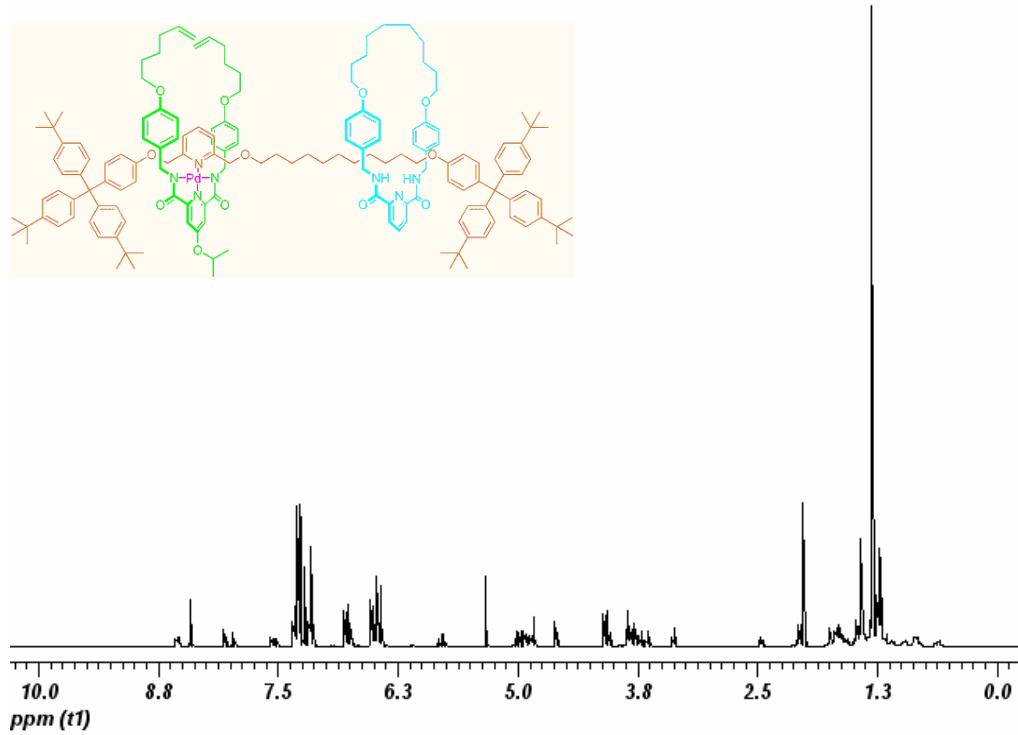
400 MHz, 300K, CD₂Cl₂



400 MHz, 300K, CD₂Cl₂



400 MHz, 300K, CD₂Cl₂



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