Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Supporting Information

Active Template Synthesis of Rotaxanes and Molecular Shuttles with Switchable Dynamics via Four-Component Pd(II)-Promoted Michael Additions

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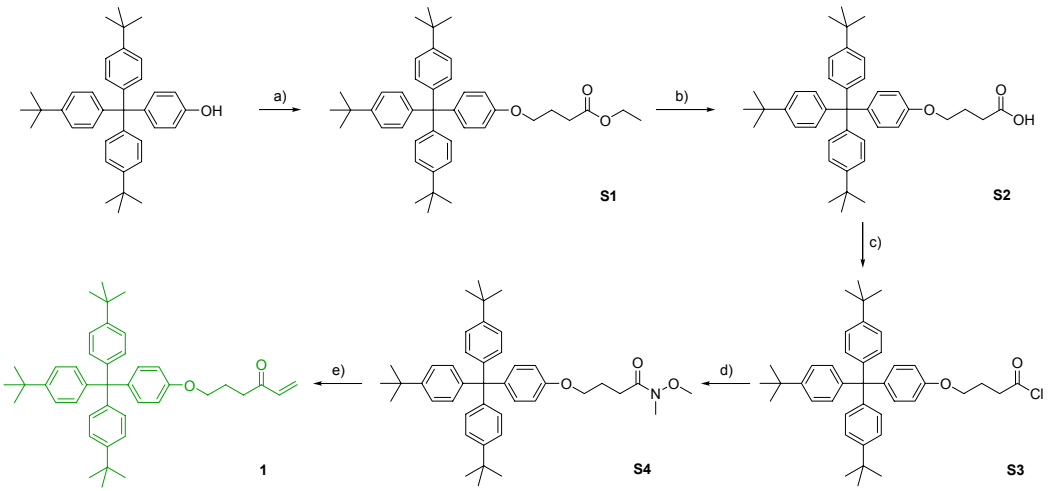
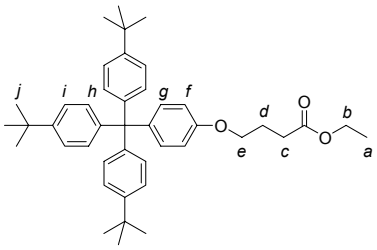
General Experimental Section

Unless stated otherwise, all reagents and solvents were purchased from Aldrich Chemicals and used without further purification, tetrahydrofuran, dichloromethane, chloroform, acetonitrile and *N*,*N*-dimethylformamide were dried using a solvent purification system manufactured by Innovative Technology, Newburyport, MA, USA. 4-[Tris(4-*tert*-butylphenyl)methyl]-phenol[1] was prepared according to literature procedures. Unless stated otherwise, all reactions were carried out under an atmosphere of nitrogen. Column chromatography was carried out using Silica 60A (particle size 35-70 μm, Fisher, UK) as the stationary phase, and TLC was performed on precoated silica gel plates (0.25 mm thick, 60 F_{254}, Merck, Germany) and observed under UV light. By petrol is meant the fraction of petroleum ether boiling between 40 ºC - 60 ºC. ^{1}H spectra were recorded on Bruker AV 400, Bruker DMX 500 and Bruker AVA 600 instruments whilst all ^{13}C NMR spectra were recorded on a Bruker AV 400 instrument. Chemical shifts are reported in parts per million (ppm) from low to high frequency and referenced to the residual solvent resonance. Coupling constants (*J*) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s = singlet, d = doublet, t = triplet, dd = double doublet, q = quartet, m = multiplet, b = broad, ddd = doublet of double doublets. Melting points (m.p.) were determined using a Sanyo Gallenkamp apparatus and are reported uncorrected. FAB mass spectrometry was carried out by the services at the University of Edinburgh and the EPSRC National Mass Spectrometry Service Centre, Swansea, UK.

Synthesis and Experimental Section



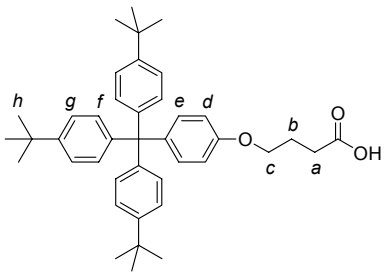
Scheme S1: a) ethyl 4-bromobutyrate, K_2CO_3, butanone, reflux, 94%; b) LiOH, THF, H_2O, RT, 85%; c) $(COCl)_2$, CH_2Cl_2, DMF (cat.), RT, 96%; d) *N*,*O*-dimethylhydroxylamine hydrochloride, Et_3N, THF, 0 °C, 95%; e) vinyl magnesium bromide, THF, -78 °C, 92%.



Ethyl 4-(4-(tris(4-*tert*-butylphenyl)methyl)phenoxy)butanoate, S1

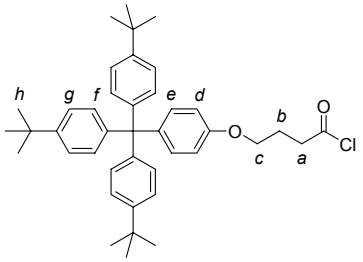
To a stirred solution of 4-[tris(4-*tert*-butylphenyl)methyl]-phenol (2.10 g, 4.1 mmol) and ethyl 4-bromobutyrate (0.90 ml, 6.2 mmol) in butanone (50 ml) was added K_2CO_3 (5.70 g, 41 mmol). The suspension was heated at reflux for 18 h. The solvent was removed under reduced pressure and the residue was redissolved in CH_2Cl_2 (200 ml), washed with H_2O (3 × 100 ml), dried ($MgSO_4$) and concentrated under reduced pressure. The crude residue was purified by column chromatography (CH_2Cl_2:petroleum ether 1:1) to yield the title compound as a colorless powder (2.40 g, 94%). m.p. 212 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 1.26 (t, J = 7.1 Hz, 3H, H_a), 1.30 (s, 27H, H_j), 2.09 (m, 2H, H_d), 2.51 (t, J = 7.3 Hz, 2H, H_c), 3.98 (t, J = 6.1 Hz, 2H, H_e), 4.14 (q, J = 7.1 Hz, 2H, H_b), 6.75 (d, J = 8.9 Hz, 2H, H_f), 7.08 (d, J = 8.6

Hz, 8H, H_{g+h}), 7.23 (d, J = 8.6 Hz, 6H, H_i); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ = 14.2, 24.7, 30.9, 31.4, 34.3, 60.4, 63.0, 66.5, 112.9, 124.0, 130.7, 132.2, 139.6, 144.1, 148.3, 156.6, 173.3; LRFAB-MS (3-NOBA matrix): *m/z* = 618 [M]; HRFAB-MS (Glycerol matrix): *m/z* = 618.4096 (calcd. for $C_{43}H_{54}O_3$, 618.4073).



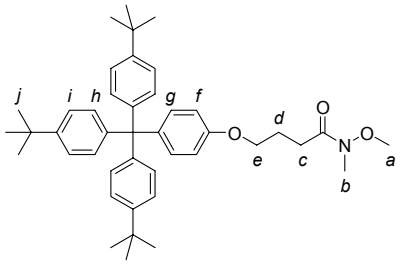
4-(4-(Tris(4-*tert*-butylphenyl)methyl)phenoxy)butanoic acid, S2

A solution of ester **S1** (3.75 g, 6.06 mmol) and LiOH (1.02 g, 24.2 mmol) in THF (45 ml) and H_2O (15 ml) was stirred at RT until **S1** had been consumed, as evidenced by TLC (EtOAc). The reaction mixture was diluted with CH_2Cl_2 (100 ml), washed with 1 M HCl (50 ml), a saturated aqueous solution of $NaHCO_3$ (50 ml) and brine (50 ml). The organic layer was dried ($MgSO_4$), and concentrated under reduced pressure to yield the title compound as a colorless solid (3.03 g, 85%). The product was used without further purification. m.p. 272 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 1.30 (s, 27H, H_h), 2.11 (m, 2H, H_b), 2.58 (t, J = 7.3 Hz, 2H, H_a), 4.00 (t, J = 6.0 Hz, 2H, H_c), 6.75 (d, J = 8.75 Hz, 2H, H_d), 7.08 (d, J = 8.7 Hz, 8H, H_{e+f}), 7.23 (d, J = 8.7 Hz, 6H, H_g); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ = 24.4, 30.3, 31.4, 34.3, 63.0, 66.3, 112.9, 124.0, 130.7, 132.3, 139.7, 144.1, 148.3, 156.5, 177.8; LRFAB-MS (3-NOBA matrix): *m/z* = 590 [M]; HRFAB-MS (3-NOBA matrix): *m/z* = 590.3752 (calcd. for $C_{41}H_{50}O_3$, 590.3760).



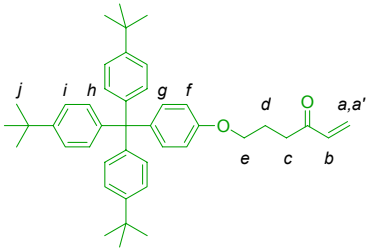
4-(4-(Tris(4-*tert*-butylphenyl)methyl)phenoxy)butanoyl chloride, S3

To a solution of acid **S2** (3.4 g, 5.7 mmol) in CH_2Cl_2 (60 ml) was added dropwise $(COCl)_2$ (2.9 ml, 29 mmol) and DMF (0.1 ml). The solution was stirred at RT for 5 h at which time the solvent was removed under reduced pressure. The crude residue was redissolved in boiling hexane and filtered whilst hot. The filtrate was concentrated under reduced pressure to yield the title compound as a colorless solid (3.30 g, 96%). m.p. 254 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 1.30 (s, 27H, H_h), 2.16 (m, 2H, H_b), 3.14 (t, J = 7.1 Hz, 2H, H_a), 3.98 (t, J = 5.8 Hz, 2H, H_c), 6.74 (d, J = 8.9 Hz, 2H, H_d), 7.07 (d, J = 8.6 Hz, 6H, H_f), 7.09 (d, J = 8.9 Hz, 2H, H_e), 7.23 (d, J = 8.6 Hz, 6H, H_g); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ = 24.5, 30.3, 31.4, 34.3, 63.0, 66.3, 112.9, 124.0, 130.7, 132.2, 139.8, 144.1, 148.3, 156.5, 177.6; LRFAB-MS (3-NOBA matrix): *m/z* = 608 [M]; HRFAB-MS (3-NOBA matrix): *m/z* = 608.3420 (calcd. for $C_{41}H_{49}{}^{35}ClO_2$, 608. 3421).



***N*-Methoxy-*N*-methyl-4-(4-(tris(4-*tert*-butylphenyl)methyl)phenoxy)butanamide, S4**

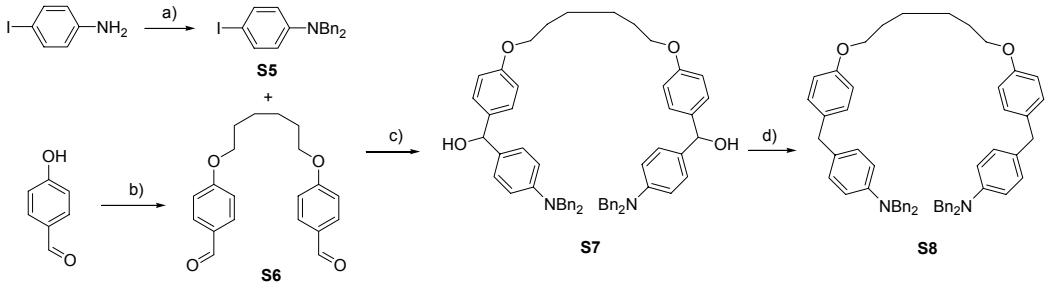
To a solution of *N*,*O*-dimethyl hydroxylamine (0.58 g, 5.9 mmol) and Et_3N (1.7 ml, 12 mmol) in CH_2Cl_2 (60 ml) at 0 °C was added dropwise a solution of acid chloride **S3** (3.3 g, 5.4 mmol) in CH_2Cl_2 (10 ml). The solution was allowed to warm to RT and stirred for 18 h. The reaction mixture was diluted with CH_2Cl_2 (200 ml) and washed with 1M HCl (100 ml), saturated aqueous $NaHCO_3$ (100 ml) and brine (100 ml). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by column chromatography (CH_2Cl_2) to yield the title compound as a colorless solid (3.27 g, 95%). m.p. 218 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 1.30 (s, 27H, H_j), 2.11 (m, 2H, H_d), 2.65 (t, J = 7.0 Hz, 2H, H_c), 3.19 (s, 3H, H_b), 3.67 (s, 3H, H_a), 4.01 (t, J = 6.0 Hz, 2H, H_e), 6.77 (d, J = 8.9 Hz, 2H, H_f), 7.09 (d, J = 8.6 Hz, 8H, H_{g+h}), 7.23 (d, J = 8.6 Hz, 6H, H_i); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ = 24.2, 28.3, 31.4, 32.2, 34.3, 61.2, 63.0, 66.8, 112.9, 124.0, 130.7, 132.2, 139.5, 144.2, 148.3, 156.7, 174.0; LREI-MS: *m/z* = 634 $[MH]^+$; HRFAB-MS (3-NOBA matrix): *m/z* = 634.4260 (calcd. for $C_{43}H_{56}NO_3$, 634.4260).



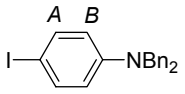
6-(4-(Tris(4-*tert*-butylphenyl)methyl)phenoxy)hex-1-en-3-one, 1

To a solution of Weinreb amide **S4** (1.33 g, 2.1 mmol) in THF (20 ml) at -78 ˚C was added dropwise vinyl magnesium bromide (1 M in THF, 5.2 mmol, 5.2 ml). The solution was stirred at -78 °C for 30 min, and then allowed to warm to 0 °C for 2 h. The reaction was quenched with a cold solution of saturated aqueous NH_4Cl (50 ml), extracted with CH_2Cl_2 (4 × 50 ml), the combined organic layers were washed with

brine (50 ml), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by column chromatography (CH_2Cl_2:petrol 1:1) to yield the title compound as colorless solid (1.13 g, 92%) which was stored under an atmosphere of N_2 in a freezer. m.p. 208 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 1.30 (s, 27H, H_j), 2.10 (m, 2H, H_d), 2.82 (t, J = 7.1 Hz, 2H, H_c), 3.98 (t, J = 5.9 Hz, 2H, H_e), 5.84 (d, J = 10.5 Hz, 1H, H_b), 6.25 (d, J = 17.3 Hz, 1H, $H_{a'}$), 6.37 (dd, J = 10.5 Hz, 17.3 Hz, 1H, H_a), 6.75 (d, J = 8.8 Hz, 2H, H_f), 7.08 (d, J = 8.6 Hz, 8H, H_{g+h}), 7.23 (d, J = 8.6 Hz, 6H, H_i); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): 23.5, 31.4, 34.3, 35.9, 63.0, 66.6, 112.9, 124.0, 128.2, 130.7, 132.3, 136.6, 139.6, 144.1, 148.3, 156.6, 200.2; LRFAB-MS (3-NOBA matrix): *m/z* = 600 [M]; HRFAB-MS (3-NOBA matrix): *m/z* = 600.3966 (calcd. for $C_{43}H_{52}O_2$, 600.3967).



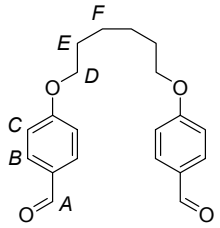
Scheme S2: a) BnBr, K_2CO_3, KI, DMF, RT, 97%; b) 1,6-dibromohexane, K_2CO_3, butanone, reflux, 66%; c) i) **S5**, *n*-BuLi, THF, -78 °C, ii) **S6**, THF, -78 °C; d) $NaBH_4$, TFA, CH_2Cl_2, RT, 46% (over 2 steps).



_N,N_-Dibenzyl-4-iodoaniline, S5

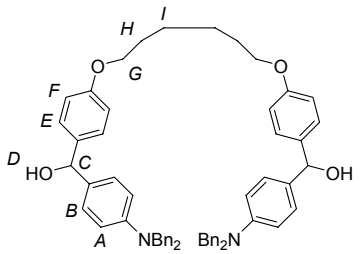
To a vigorously stirred solution of 4-iodoaniline (16.1 g, 73.4 mmol), BnBr (18.3 ml, 154 mmol) and KI (2.40 g, 14.7 mmol) in DMF (75 ml) was added K_2CO_3 (24.4 g, 176 mmol). The reaction was stirred for 18 h at RT. CH_2Cl_2 (200 ml) was added and the reaction mixture was washed with H_2O (100 ml), the organic layer was dried

($MgSO_4$) and concentrated under reduced pressure. The crude residue was recrystallized from EtOH (1 L) to yield the title compound as colorless needles (25.5 g, 97%). m.p. 122 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 4.54 (s, 4H, $H_{benzylic}$), 6.41 (d, J = 9.1 Hz, 2H, H_A), 7.21 (m, 12H, $H_{B+phenyl}$); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ = 54.2, 77.6, 114.7, 126.4, 127.1, 128.8, 137.7, 137.9, 148.6; LRFAB-MS (3-NOBA matrix): *m/z* = 399 [M]; HRFAB-MS (3-NOBA matrix): *m/z* = 399.0502 (calcd. for $C_{20}H_{18}IN$, 399.0484).



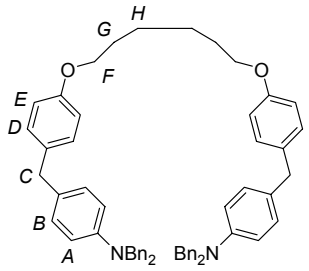
4,4'-Hexanediyldioxy dibenzaldehyde, S6

To a solution of 1,6-dibromohexane (4.4 ml, 29 mmol) and 4-hydroxybenzaldehyde (10.5 g, 85.9 mmol) in butanone (300 ml) was added K_2CO_3 (39.5 g, 286 mmol). The suspension was heated at reflux for 18 h. The solvent was removed under reduced pressure and the crude residue was redissolved in CH_2Cl_2 (500 ml) and washed with H_2O (200 ml). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure. The crude residue was dissolved in hot MeOH and allowed to cool to RT, the resultant precipitate was collected by suction filtration to yield the title compound as a colorless powder (6.11 g, 66%). m.p. 81-83 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 1.57 (m, 4H, H_F), 1.87 (m, 4H, H_E), 4.06 (t, J = 6.4 Hz, 4H, H_D), 6.99 (d, J = 8.8 Hz, 4H, H_C), 7.83 (d, J = 8.8 Hz, 4H, H_B), 9.88 (s, 2H, H_A); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ = 25.8. 29.0, 68.0, 114.7, 129.8, 132.0, 164.1, 190.8; LRFAB-MS (3-NOBA matrix): *m/z* = 327 $[MH]^+$; HRFAB-MS (3-NOBA matrix): *m/z* = 327.1593 (calcd. for $C_{20}H_{23}O_4$, 327.1596).



S7

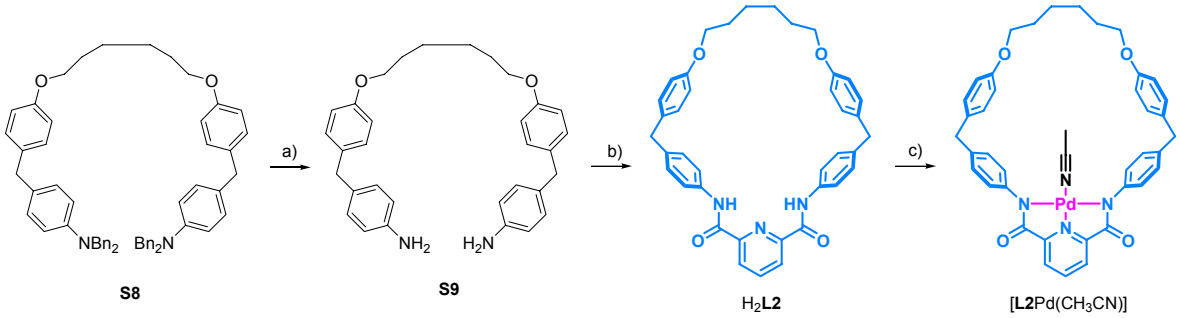
To a solution of aldehyde **S6** (6.55 g, 20.1 mmol) in THF (200 ml) at -78 °C was added *n*-BuLi (1.6 M in hexane, 36.4 ml, 58.2 mmol) dropwise. The temperature was maintained at -78 °C for 30 min. A solution of iodide **S5** (24.1 g, 60.3 mmol) in THF (100 ml) was added dropwise whilst maintaining the temperature at -78 °C. The reaction was allowed to warm to RT over 2 h. The reaction mixture was diluted with CH_2Cl_2 (500 ml) and washed with saturated aqueous NH_4Cl (300 ml) and brine (300 ml). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure. The product was used without further purification. LRFAB-MS (3-NOBA matrix): *m/z* = 872; HRFAB-MS (3-NOBA matrix): *m/z* = 872.4553 (calcd. for $C_{60}H_{60}N_2O_4$, 872.4553).



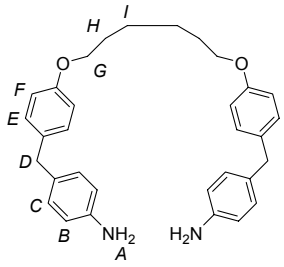
4-(4-(6-(4-(4-(Dibenzylamino)benzyl)phenoxy)hexyloxy)benzyl)-*N*,*N*-dibenzylaniline, S8[2]

To a solution of diol **S7**, obtained from the previous reaction, and TFA (90 ml) in CH_2Cl_2 (120 ml) at 0 ºC was added $NaBH_4$ (7.53 g, 199 mmol) portion-wise. The reaction was stirred for 18 h. The reaction was diluted with CH_2Cl_2 (1 L) and neutralized with 1 M NaOH (1.5 L). The organic layer was washed with brine (500

ml), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by column chromatography (petrol:CH_2Cl_2 3:2) to yield the title compound as a colorless solid (7.82 g, 46% from **S6**). m.p. 105 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 1.56 (m, 4H, H_H), 1.83 (m, 4H, H_G), 3.84 (s, 4H, H_C), 3.97 (t, J = 6.5 Hz, 4H, H_F), 4.66 (s, 8H, H_{benzyl}), 6.70 (d, J = 8.7 Hz, 4H, H_A), 6.84 (d, J = 8.6 Hz, 4H, H_E), 7.01 (d, J = 8.7 Hz, 4H, H_B), 7.13 (d, J = 8.6 Hz, 4H, H_D), 7.33 (m, 20H, H_{phenyl}); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ = 25.9, 29.3, 40.0, 54.3, 67.8, 112.5, 114.5, 126.8, 127.0, 128.3, 129.2, 129.8, 131.3, 138.8, 133.9, 147.5, 157.3; LRFAB-MS (3-NOBA matrix): m/z = 841 $[MH]^+$; HRFAB-MS (3-NOBA matrix): m/z = 841.4710 (calcd. for $C_{60}H_{61}N_2O_2$, 841.4733).



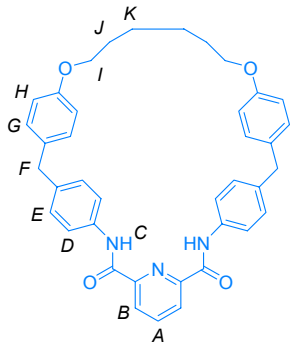
Scheme S3: a) Pd/C (10% w/w), H_2, THF, EtOH, RT, 78%; b) pyridine-2,6-dicarbonyl dichloride, Et_3N, THF, RT, 30%; b) $Pd(OAc)_2$, CH_3CN, reflux then RT, 88%.



4-(4-(6-(4-(4-Aminobenzyl)phenoxy)hexyloxy)benzyl)aniline, S9

To a solution of benzyl aniline **S8** (7.82 g, 9.30 mmol) in THF (80 ml) and EtOH (20 ml) was added 10% w/w Pd/C (1.56 g). The reaction mixture was initially purged

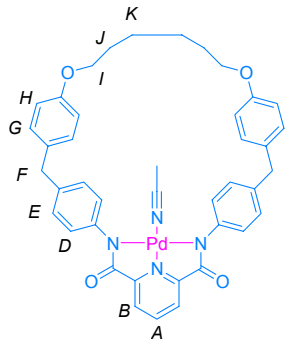
with an atmosphere of N_2 and then purged with H_2 before being stirred for 18 h under an atmosphere of H_2. The reaction mixture was filtered through celite, concentrated under reduced pressure and purified by column chromatography (CH_2Cl_2:MeOH 99.5:0.5) to give the title compound as a colorless solid (3.48 g, 78%). m.p. 120 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 1.53 (m, 4H, H_I), 1.80 (m, 4H, H_J), 3.56 (br, 4H, H_A), 3.82 (s, 4H, H_D), 3.94 (t, J = 6.4 Hz, 4H, H_G), 6.63 (d, J = 8.3 Hz, 4H, H_B), 6.82 (d, J = 8.5 Hz, 4H, H_F), 6.98 (d, J = 8.3 Hz, 4H, H_C), 7.08 (d, J = 8.5 Hz, 4H, H_E); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ = 25.9, 29.3, 40.2, 67.8, 114.4, 115.3, 129.6, 129.7, 131.7, 133.9, 144.4, 157.3; LRFAB-MS (3-NOBA matrix): *m/z* = 480 [M]; HRFAB-MS (3-NOBA matrix): *m/z* = 480.2765 (calcd. for $C_{32}H_{36}N_2O_2$, 480.2777).



H_2L2

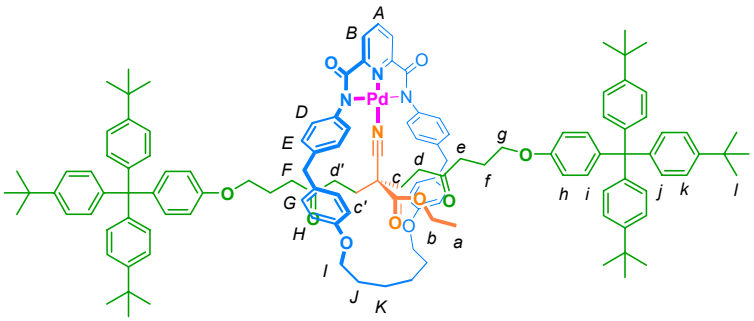
To a solution of aniline **S9** (3.363 g, 7.00 mmol) and Et_3N (2.9 ml, 21.0 mmol) in THF (4 L) was added, in one portion, pyridine-2,6-dicarbonyl dichloride (1.429 g, 7.00 mmol), the reaction was stirred for 18 h. The reaction mixture was filtered, concentrated under reduced pressure, and purified first by column chromatography (CH_2Cl_2:MeOH; 99.5:0.5) then recrystallized from acetonitrile (50 ml) to yield the title compound as colorless powder (1.28 g, 30%). m.p. 325 °C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 1.52 (m, 4H, H_K), 1.82 (m, 4H, H_J), 3.94 (s, 4H, H_F), 3.97 (t, J = 6.3 Hz, 4H, H_I), 6.83 (d, J = 8.6 Hz, 4H, H_H), 7.07 (d, J = 8.5 Hz, 4H, H_E), 7.08

(d, J = 8.6 Hz, 4H, H_G), 7.55 (d, J = 8.5 Hz, 4H, H_D), 8.15 (t, J = 7.8 Hz, 1H, H_A), 8.44 (d, J = 7.8 Hz, 2H, H_B), 9.52 (s, 2H, H_C); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ = 25.4, 29.1, 40.0, 67.8, 114.7, 119.5, 125.1, 129.3, 130.4, 132.7, 134.8, 139.2, 140.0, 148.7, 157.7, 160.5; LRFAB-MS (3-NOBA matrix): m/z = 612 $[MH]^+$; HRFAB-MS (3-NOBA matrix): m/z = 612.2864 (calcd. for $C_{39}H_{38}N_3O_4$, 612.2862).



[**L2**Pd(CH_3CN)]

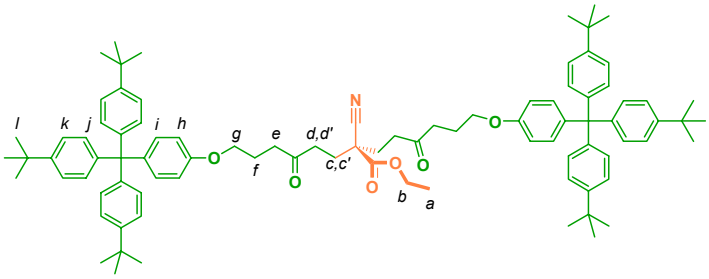
A stirred suspension of amide H_2**L2** (1.163 g, 1.90 mmol) and $Pd(OAc)_2$ (0.470 g, 2.094 mmol) in CH_3CN (50 ml) was heated at reflux for 10 mins then stirred at RT for 18 h. The resulting suspension was filtered and the precipitate was redissolved in CH_2Cl_2 (50 ml) and filtered through celite. The filtrate was concentrated under reduced pressure to yield the title compound as a yellow solid (1.27 g, 88%). m.p. 310 °C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$:CD_3CN 95:5, 300 K): δ = 1.46 (m, 4H, H_K), 1.75 (m, 4H, H_J), 3.79 (s, 4H, H_F), 3.84 (t, J = 6.2 Hz, 4H, H_I), 6.66 (d, J = 8.6 Hz, 4H, H_H), 6.98 (d, J = 8.6 Hz, 4H, H_G), 7.05 (d, J = 8.3 Hz, 4H, H_E), 7.11 (d, J = 8.3 Hz, 4H, H_D), 7.85 (d, J = 7.8 Hz, 2H, H_B), 8.10 (t, J = 7.8 Hz, 1H, H_A); ^{13}C NMR (100 MHz, $CDCl_3$:CD_3CN 95:5, 300 K): 23.6, 26.8, 38.9, 65.9, 112.3, 123.8, 124.5, 126.7, 127.4, 132.8, 136.5, 139.1, 142.9, 151.1, 155.5, 166.4; LRFAB-MS (3-NOBA matrix): m/z = 756 [M]; HRFAB-MS (3-NOBA matrix): m/z = 756.1922 (calcd. for $C_{41}H_{38}N_4O_4{}^{106}$Pd, 756.1928).



[**L3**Pd]

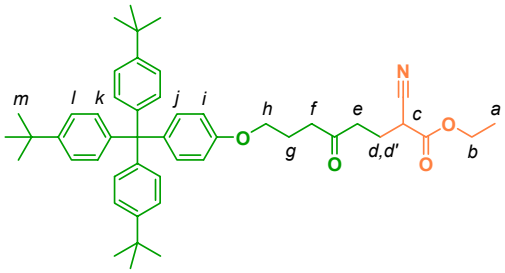
Representative Synthesis of Rotaxane [**L3**Pd]

To a solution of complex [**L2**Pd(CH_3CN)] (0.0304 g, 0.0402mmol), ketone **1** (0.1208 g, 0.201 mmol) and ethyl cyano acetate **L1** (10.7 µl, 0.1005 mmol) in CH_2Cl_2 (0.4 ml) was added DIPEA (0.698 µl, 0.004 mmol). The solution was stirred for 7 d at 40˚C. The solvent was removed under reduced pressure and the crude residue was purified by column chromatography (CH_2Cl_2 then CH_2Cl_2:MeOH 99:1) to yield rotaxane [**L3**Pd] as a yellow solid (0.081 g, >99%). m.p. 213 °C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$, 323 K): δ = 0.32 (br, 2H, $H_{c'}$), 0.90 (br, 2H, H_c), 1.17 (t, J = 7.1 Hz, 3H, H_a), 1.25 (br, 2H, $H_{d'}$), 1.31 (s, 54H, H_l), 1.44 (br, 4H, H_K), 1.49 (br, 2H, $H_{d'}$), 1.73 (br, 4H, H_J), 2.02 (br, 4H, H_f), 2.36 (br, 4H, H_e), 3.75 (s, 4H, H_F), 3.87 (m, J = 7.1 Hz, 2H, H_b), 3.89 (br, 4H, H_I), 4.00 (t, J = 4.0 Hz, 4H, H_g), 6.71 (dd, J = 8.5 Hz, 16.5 Hz, 4H, H_H), 6.81 (d, J = 8.3 Hz, 4H, H_h), 6.99 (dd, J = 8.5 Hz, 22.7 Hz, 4H, H_G), 7.10 (m, 20H, H_{E+i+j}), 7.19 (d, J = 8.2 Hz, 4H, H_D), 7.23 (d, J = 8.6 Hz, 12H, H_k), 7.83 (dd, J = 3.6 Hz, 7.8 Hz, 2H, H_B), 8.05 (t, J = 7.8 Hz, 1H, H_A); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ = 13.8, 25.3, 25.7, 28.9, 29.4, 31.4, 34.3, 40.9, 48.8, 63.0, 63.5, 66.3, 67.9, 68.1, 112.8, 114.7, 121.5, 124.1, 125.8, 126.3, 128.4, 129.4, 130.7, 132.4, 134.3, 138.7, 139.1, 139.9, 141.1, 144.1, 144.6, 148.3, 152.9, 156.5, 157.5, 165.1, 168.6, 206.3; LRFAB-MS (3-NOBA matrix): m/z = 2030 $[MH]^+$; HRFAB-MS (3-NOBA matrix): m/z = 2030.015 (calcd. for $C_{130}H_{147}N_4O_{10}Pd^{106}$, 2030.015).



Thread, S10

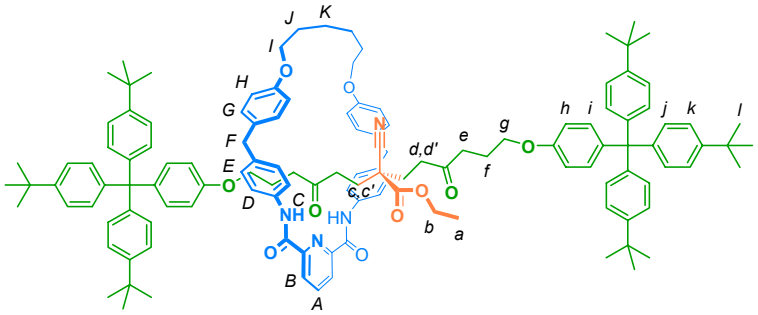
m.p. 202 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 1.32 (s, 57H, H_{a+l}), 2.07 (m, 4H, H_f), 2.13 (ddd, J = 5.1 Hz, 10.3 Hz, 15.8 Hz, 2H, $H_{c'}$), 2.28 (ddd, J = 5.4 Hz, 10.3 Hz, 15.8, 2H, H_c), 2.58 (ddd, J = 5.4 Hz, 10.3 Hz, 17.7 Hz, 2H, $H_{d'}$), 2.66 (t, J = 7.1 Hz, 4H, H_e), 2.74 (ddd, J = 5.1 Hz, 10.3 Hz, 17.7 Hz, 2H, H_d), 3.95 (t, J = 5.9 Hz, 4H, H_g), 4.25 (q, J = 7.1 Hz, 2H, H_b), 6.75 (d, J = 8.9 Hz, 4H, H_h), 7.10 (d, J = 8.7 Hz, 16H, H_{i+j}), 7.24 (d, J = 8.6 Hz, 12H, H_k); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ = 14.1, 22.6, 29.7, 31.4, 34.5, 38.3, 39.3, 48.1, 63.1, 63.2, 66.5, 112.9, 118.5, 124.3, 131.1, 132.6, 139.7, 144.2, 148.3, 156.5, 168.5, 207.3; LRFAB-MS (3-NOBA matrix): m/z = 1314 [M]; HRFAB-MS (3-NOBA matrix): m/z = 1313.846 (calcd. for $C_{91}H_{111}O_6N$, 1313.841).



Half thread, S11

m.p. 194 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 1.22 (s, 30H, H_{a+m}), 1.98 (m, 2H, H_g), 2.17 (m, 1H, $H_{d'}$), 2.28 (m, 1H, H_d), 2.58 (t, J = 7.1 Hz, 2H, H_f), 2.64 (t, 7.0 Hz, 2H, H_e), 3.62 (dd, J = 6.1 Hz, 8.3 Hz, 1H, H_c), 3.87 (d, J = 5.9 Hz, 2H, H_h), 4.18 (q, J = 7.1 Hz, 2H, H_b), 6.74 (d, J = 8.9 Hz, 2H, H_i), 7.08 (d, J = 8.6 Hz, 8H, H_{j+k}),

7.23 (d, J = 8.6 Hz, 6H, H_l); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ = 14.0, 23.4, 23.5, 31.4, 34.3, 36.4, 38.6, 39.3, 63.0, 63.0, 66.4, 112.9, 116.2, 124.1, 130.7, 132.3, 139.7, 144.1, 148.3, 156.5, 165.7, 208.1; LRFAB-MS (3-NOBA matrix): m/z = 713; HRFAB-MS (3-NOBA matrix): m/z = 713.4442 (calcd. for $C_{48}H_{59}NO_4$, 713.4444).

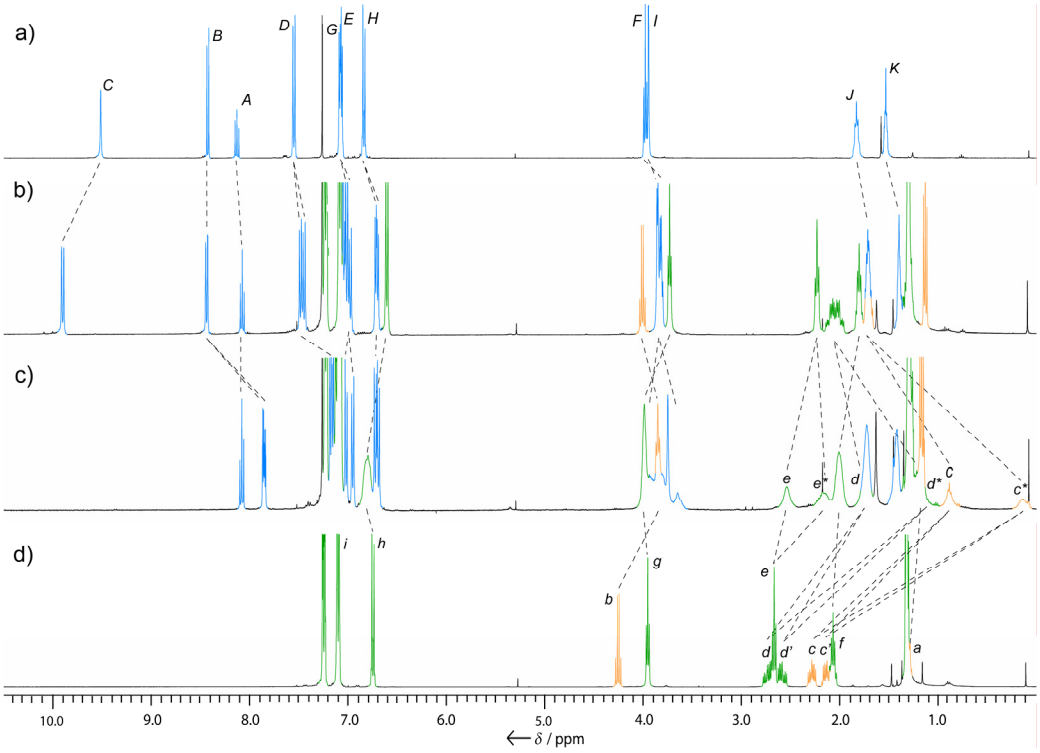


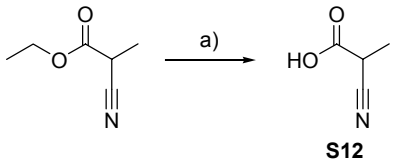
H_2**L3**

A solution of [**L3**Pd] (0.222 g, 0.109 mmol) in CH_2Cl_2 (0.5 ml) and 1M HCl (0.5 ml) was heated at reflux for 18 h. The solution was diluted with CH_2Cl_2 (50 ml) and washed with saturated $NaHCO_3$ (20 ml), brine (20 ml), dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude residue was purified by column chromatography (CH_2Cl_2:MeOH 99:1) to yield the title compound as a colorless solid (0.194 g, 92%). m.p. 141 ˚C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 1.13 (t, J = 7.1 Hz, 3H, H_a), 1.30 (s, 56H, $H_{c'+l}$), 1.39 (m, 4H, H_K), 1.71 (m, 6H, H_{J+c}), 1.80 (m, 4H, H_f), 2.00 (m, 2H, $H_{d'}$), 2.06 (m, 2H, H_d), 2.22 (t, J = 7.1 Hz, 4H, H_e), 3.72 (t, J = 5.9 Hz, 4H, H_g), 3.81 (q, J = 4.3 Hz, 6.4 Hz, 4H, H_I), 3.85 (d, J = 4.1 Hz, 4H, H_F), 4.00 (q, J = 7.1 Hz, 2H, H_b), 6.60 (d, J = 8.9 Hz, 4H, H_h), 6.70 (dd, J = 5.3 Hz, 8.5 Hz, 4H, H_H), 7.00 (m, 8H, H_{G+E}), 7.08 (d, J = 8.6 Hz, 16H, H_{i+j}), 7.22 (d, J = 8.6 Hz, 12H, H_k), 7.46 (dd, J = 8.4 Hz, 15.0 Hz, 4H, H_D), 8.07 (t, J = 7.8 Hz, 1H, H_A), 8.43 (d, J = 7.8 Hz, 2H, H_B), 9.89 (d, J = 9.0 Hz, 2H, H_C); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ = 13.9, 23.1, 25.4, 29.1, 30.1, 31.4, 34.3, 37.9, 40.2, 40.4, 47.7, 63.0, 66.3, 67.8, 112.8,

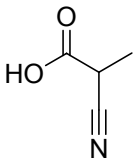
114.7, 118.7, 121.4, 124.1, 125.1, 129.0, 130.1, 130.7, 131.1, 132.3, 133.5, 134.9, 139.3, 139.6, 139.7, 144.1, 148.3, 149.0, 156.4, 157.7, 161.1, 167.7, 207.3; LRFAB-MS (3-NOBA matrix): *m/z* = 1926 $[MH]^+$; HRFAB-MS (3-NOBA matrix): *m/z* = 1926.121 (calcd. for $C_{130}H_{149}N_4O_{10}$, 1926.127).

Figure S1: ^{1}H NMR (400 MHz, $CDCl_3$, 300 K) spectra of (a) H_2**L2** (b) H_2**L3** (c) [**L3**Pd] and (d) **S10**.



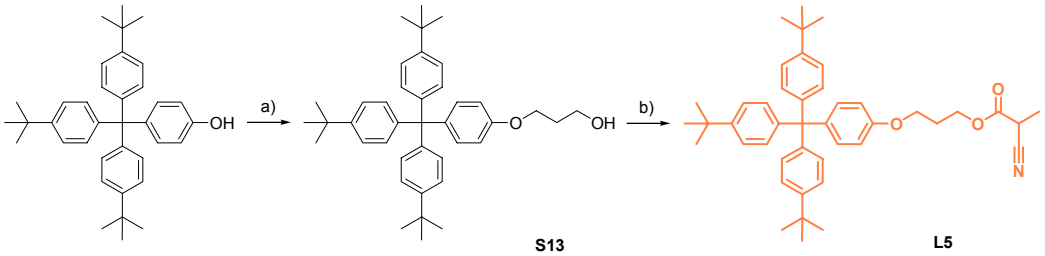


Scheme S4: a) LiOH, MeOH, H_2O, RT, 89%.

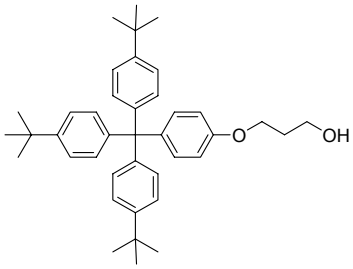


2-Cyanopropanoic acid, S12

To a solution of ethyl 2-cyanopropionate (0.749 g, 5.89 mmol) in MeOH (10 ml) and water (10 ml) was added LiOH (1.24 g, 29.5 mmol). The suspension was stirred at RT for 36 h. The reaction mixture was acidified with 1M HCl (100 ml), saturated with NaCl, the crude product was then extracted with Et_2O (3 x 100 ml), dried ($MgSO_4$) and concentrated under reduced pressure to yield acid **S12** as a colorless liquid (0.521 g, 89%). ^{1}H NMR and ^{13}C NMR data were consistent with the published data.[3]

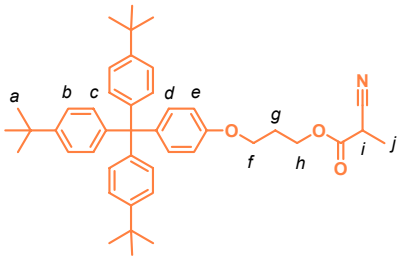


Scheme S5: a) 3-bromopropan-1-ol, K_2CO_3, butanone, reflux, 87%; b) **S12**, EDCI, DMAP, CH_2Cl_2, 0 °C → RT, 79%.



3-(4-(Tris(4-*tert*-butylphenyl)methyl)phenoxy)propan-1-ol, S13

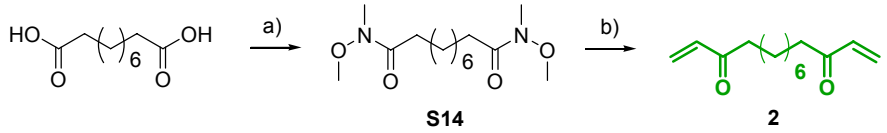
To a solution of 4-[tris(4-*tert*-butylphenyl)methyl]-phenol (2.06 g, 4.08 mmol) and 3-bromopropan-1-ol (0.540 ml, 6.12 mmol) in butanone (40 ml) was added K_2CO_3 (2.82 g, 20.4 mmol), the suspension was heated at reflux for 36 h. The suspension was diluted with CH_2Cl_2 (100 ml) and washed with H_2O (100 ml), the aqueous layer was further extracted with CH_2Cl_2 (100 ml), the combined organic layers were dried ($MgSO_4$), and concentrated under reduced pressure. The crude residue was purified by column chromatography (CH_2Cl_2) to yield the title compound as a colorless powder (2.00 g, 87%). ^{1}H NMR and ^{13}C NMR data were consistent with the published data.[4]



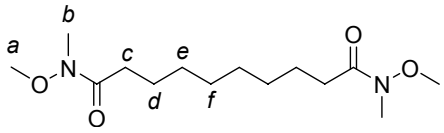
3-(4-(Tris(4-*tert*-butylphenyl)methyl)phenoxy)propyl 2-cyanopropanoate, L5

To a 0 ˚C solution of alcohol **S13** (0.938 g, 1.67 mmol) and 2-cyanopropanoic acid **S12** (0.206 g, 2.08 mmol) in CH_2Cl_2 (20 ml) was added DMAP (0.102 g, 0.835 mmol) and EDCI (0.640 g, 3.34 mmol). The solution was stirred for 18 h. The reaction was diluted with CH_2Cl_2 (100 ml) and washed with 1M HCl (50 ml), $NaHCO_3$ (50 ml) and brine (50 ml). The organic layer was dried ($MgSO_4$), filtered, concentrated under reduced pressure and purified by column chromatography (CH_2Cl_2) to yield the title compound as colorless solid (0.855 g, 79%). m.p. 224 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 1.30 (s, 27H, H_a), 1.59 (d, J = 7.4 Hz, 3H, H_j), 2.16 (m, 2H, H_g), 3.55 (q, J = 7.4 Hz, 1H, H_i), 4.04 (t, J = 5.9 Hz, 2H, H_f), 4.41 (t, J = 6.3 Hz, 2H, H_h), 6.76 (d, J = 8.9 Hz, 2H, H_e), 7.08 (d, J = 8.9 Hz, 12H, H_c), 7.09 (d, J = 8.6 Hz, 2H, H_d), 7.23 (d, J = 8.6 Hz, 12H, H_b); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ = 15.3, 28.4, 31.4, 31.5,

34.3, 63.0, 63.6, 63.8, 112.9, 117.5, 124.1, 130.7, 132.3, 139.9, 144.1, 148.3, 156.4, 166.5; LRFAB-MS (3-NOBA matrix): *m/z* = 643 [M]; HRFAB-MS (3-NOBA matrix): *m/z* = 643.4070 (calcd. for $C_{44}H_{53}NO_3$, 643.4025).



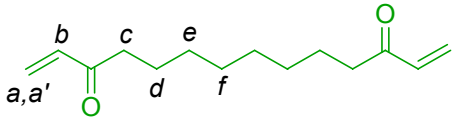
Scheme S6: a) i) $(COCl)_2$, CH_2Cl_2, DMF (cat.), ii) *N,O*-dimethyl hydroxylamine hydrochloride, Et_3N, CH_2Cl_2, 0 ˚C, 95%; b) vinyl magnesium bromide, THF, -78 ˚C, 75%.



_N_-Methoxy-11-(methoxy(methyl)amino)-_N_-methyl-10-oxoundecanamide, S14

To a suspension of sebacic acid (5.20 g, 25.7 mmol) in CH_2Cl_2 (250 ml) and DMF (0.1 ml) was added dropwise $(COCl)_2$ (22.1 ml, 257 mmol). The suspension was stirred for 16 h. The resulting solution was concentrated under reduced pressure and the residue was redissolved in CH_2Cl_2 (20 ml) and added slowly to a 0 ˚C solution of *N,O*-dimethyl hydroxylamine hydrochloride (5.52 g, 56.54 mmol) and Et_3N (14.4 ml, 102 mmol) in CH_2Cl_2 (250 ml). After the addition was complete the reaction was allowed to warm to RT and stirred for 2 h. The reaction was diluted with Et_2O (1 L) and washed with 1M HCl (500 ml), saturated aqueous $NaHCO_3$ (500 ml) and brine (500 ml) before being dried ($MgSO_4$) and concentrated under reduced pressure to give the title compound as a pale oil (7.08 g, 95%). The product was used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): 1.30 (br, 8H, H_{e+f}), 1.60 (m, 4H, H_d), 2.38 (t, J = 7.5 Hz, 4H, H_c), 3.16 (s, 6H, H_b), 3.66 (s, 6H, H_a); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): 24.6, 24.8, 29.2, 29.4, 32.1, 61.2, 174.8; LRFAB-MS (3-NOBA

matrix): *m/z* = 289 $[MH]^+$; HREI-MS (perfluorotributylamine): *m/z* = 288.2043 (calcd. for $C_{14}H_{28}N_2O_4$, 288.2044).



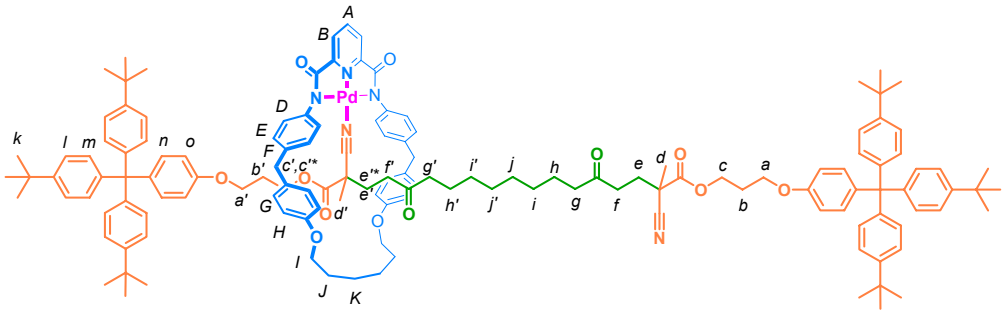
Tetradeca-1,13-diene-3,12-dione, 2

To a solution of Weinreb amide **S14** (6.87 g, 23.8 mmol) in THF (200 ml) at -78 ˚C was added dropwise a 1M solution of vinyl magnesium bromide in THF (119 ml, 119 mmol). The reaction was stirred at -78 ˚C for 30 min, then allowed to warm to 0 ˚C and stirred for 1 h. The reaction was poured into cold saturated NH_4Cl (500 ml) and extracted with Et_2O (2 x 1 L). The combined organic extracts were washed with brine (500 ml), dried ($MgSO_4$) and concentrated under reduced pressure. The crude residue was purified by column chromatography (Et_2O:petrol 1:1) to yield the title compound as a waxy pale solid (3.99 g, 75%). m.p. 60 ˚C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): 1.30 (br, 8H, H_{e+f}), 1.60 (m, 4H, H_d), 2.57 (t, *J* = 7.4 Hz, 4H, H_c), 5.81 (dd, *J* = 1.2, 10.5 Hz, 2H, H_b), 6.21 (dd, *J* = 1.2, 17.7 Hz, 2H, H_a), 6.35 (dd, *J* = 10.5, 17.7 Hz, 2H, $H_{a'}$); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): 23.9, 29.2, 29.2, 39.6, 127.9, 136.6, 201.2; LRFAB-MS (3-NOBA matrix): *m/z* = 223 $[MH]^+$; HREI-MS (perfluorotributylamine): *m/z* = 222.1617 (calcd. for $C_{14}H_{22}O_2$, 222.1614).

Synthesis of Molecular Shuttle [**L4**Pd]

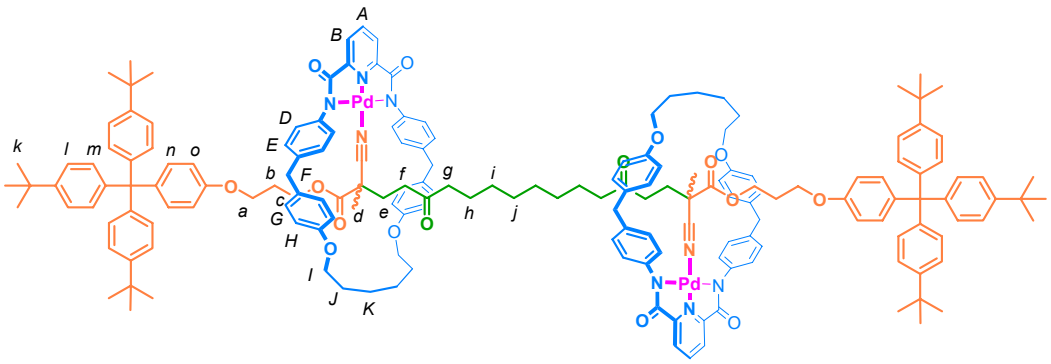
To a solution of complex [**L2**Pd(CH_3CN)] (0.0305 g, 0.040 mmol), nitrile **L5** (0.0519 g, 0.081 mmol) and vinyl ketone **2** (0.0089 g, 0.040 mmol) in CH_2Cl_2 (0.4 ml) was added DIPEA (0.7 µl, 0.004 mmol). The reaction was stirred at 40 °C for 7 days. The solvent was removed under reduced pressure and the crude residue was purified by

column chromatography (CH_2Cl_2 then CH_2Cl_2:MeOH 99:1) to yield rotaxane [**L4**Pd] as a yellow solid (0.024 g, 27 %) and [3]rotaxane [**L5**Pd] as a yellows solid (0.018 g, 32%).



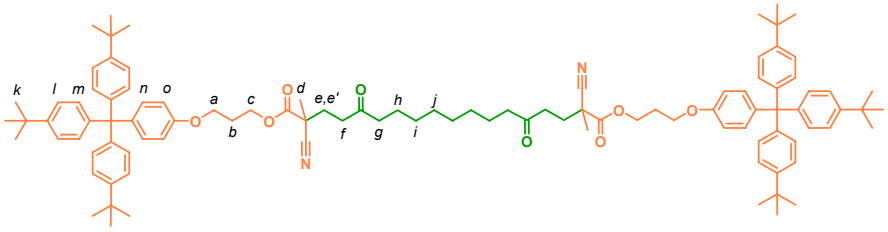
[**L4**Pd]

^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 0.00 (s, 3H, $H_{d'}$), 0.94 (m, 1H, $H_{e'*}$), 1.07 (m, 1H, $H_{e'}$), 1.30 (br, 64H, $H_{f+i+i'+j+j'+k}$), 1.45 (br, 4H, H_K), 1.52 (m, 4H, H_h), 1.59 (s, 3H, H_d), 1.74 (br, 4H, H_J), 2.01 (m, 2H, $H_{b'}$), 2.12 (m, 2H, $H_{b'}$), 2.17 (m, 2H, H_b), 2.19 (m, 2H, H_e), 2.40 (t, J = 7.4 Hz, 2H, H_g), 2.59 (m, 2H, H_f), 3.72 (m, 4H, H_F), 3.85 (m, 4H, H_I), 3.98 (m, 3H, $H_{a'+c'*}$), 4.04 (t, J = 5.9 Hz, 2H, H_a), 4.15 (m, 1H, $H_{c'}$), 4.40 (m, 2H, H_c), 6.64 (m, 4H, H_H), 6.76 (d, J = 8.9 Hz, 2H, $H_{o'}$), 6.82 (d, J = 8.9 Hz, 2H, H_o), 7.00 (m, 6H, $H_{n, G'}$), 7.07 (m, 18H, H_{m+E+G}), 7.14 (dd, J = 2.2, 8.6 Hz, 4H, H_D), 7.22 (dd, J = 2.5, 8.6 Hz, 12H, H_l), 7.84 (d, J = 7.8 Hz, 2H, H_B), 8.07 (t, J = 7.8 Hz, 1H, H_A); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ = 21.5, 23.5, 23.6, 23.7, 25.2, 25.4, 28.5, 28.9, 29.2, 29.3, 29.4, 29.7, 31.6, 34.3, 36.8, 38.3, 41.3, 42.7, 42.9, 43.2, 43.6, 63.0, 63.3, 63.6, 63.9, 64.1, 67.7, 68.1, 112.8, 112.9, 114.6, 114.8, 119.5, 121.9, 124.1, 124.1, 125.8, 126.2, 126.4, 128.2, 128.4, 128.8, 129.3, 130.7, 130.7, 132.3, 132.4, 134.0, 134.3, 138.8, 138.9, 139.9, 140.3, 141.1, 144.0, 144.1, 144.6, 144.7, 148.3, 148.4, 152.8, 152.9, 156.2, 156.4, 157.7, 157.7, 166.1, 168.6, 168.9, 207.0, 208.2; LRFAB-MS (3-NOBA matrix): *m/z* = 2224 [M]; HRFAB-MS (3-NOBA matrix): *m/z* = 2224.148 (calcd. for $C_{141}H_{164}O_{12}N_5{}^{105}Pd$, 2224.142).



[**L6**Pd]

m.p. 219 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 0.00 (s, 6H, H_d), 1.04 (m, 4H, H_e), 1.29 (s, 54H, H_k), 1.38 (m, 10H, $H_{half\ of\ f+i+j}$), 1.46 (m, 8H, H_K), 1.53 (m, 4H, H_h), 1.74 (m, 10H, $H_{half\ of\ f+J}$), 2.01 (m, 4H, H_b), 2.14 (t, J = 7.4 Hz, 4H, H_g), 3.73 (m, 8H, H_F), 3.84 (m, 8H, H_I), 3.99 (m, 6H, $H_{half\ of\ c+a}$), 4.16 (m, 2H, $H_{half\ of\ c}$), 6.65 (m, 8H, H_H), 6.82 (d, J = 8.9 Hz, 4H, H_o), 7.07 (m, 32H, $H_{m+n+E+G}$), 7.14 (d, J = 8.2 Hz, 8H, H_D), 7.22 (d, J = 8.6 Hz, 12H, H_l), 7.83 (d, J = 7.8 Hz, 4H, H_B), 8.07 (t, J = 7.8 Hz, 2H, H_A); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ = 21.5, 23.5, 25.2, 25.2, 28.3, 28.9, 29.5, 31.0, 31.4, 34.3, 36.9, 41.3, 42.7, 43.6, 63.1, 63.3, 64.1, 67.8, 112.8, 114.8, 121.9, 124.1, 125.8, 126.2, 128.4, 129.3, 130.7, 132.4, 134.0, 138.8, 140.3, 141.2, 144.0, 144.6, 148.4, 152.8, 156.2, 157.7, 166.1, 168.6, 207.0; LRFAB-MS (3-NOBA matrix): m/z = 2940 $[MH]^+$; HRFAB-MS (3-NOBA matrix): m/z = 2944.326 (calcd. for $^{12}C_{176}{}^{13}C_4H_{199}O_{16}N_8{}^{102}Pd^{104}Pd$, 2944.326).



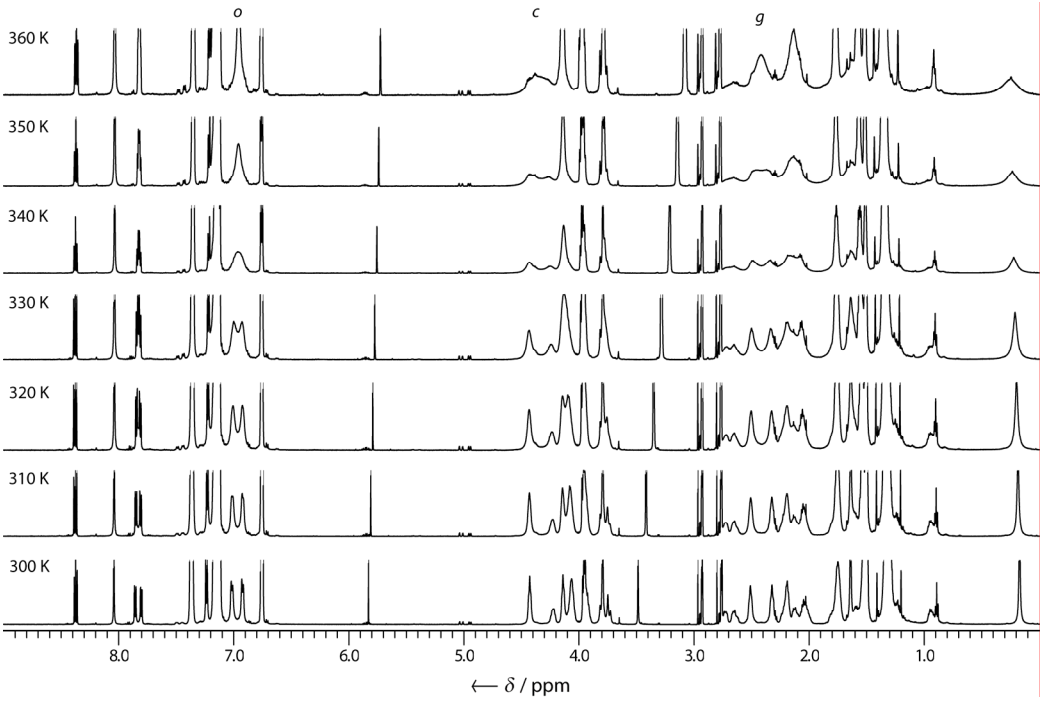
Thread, S15

To a solution of **L5** (0.0554 g, 0.086 mmol), **2** (0.0096 g, 0.043 mmol), benzylic amide Pd-macrocycle[5] (0.0296 g, 0.043 mmol) in CH_2Cl_2 (0.4 ml) was added DIPEA (7.5 µl, 0.043 mmol). The solution was heated at 40 ˚C for 7 d, the crude residue was concentrated under reduced pressure and purified by column chromatography (CH_2Cl_2) to yield the title compound as a colorless solid (0.048 g, 74%). ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 1.26 (br, 8H, H_{i+j}), 1.30 (s, 54H, H_k), 1.54 (m, 4H, H_h), 1.60 (s, 6H, H_d), 2.07 (m, 2H, H_e), 2.17 (m, 4H, H_b), 2.24 (m, 2H, $H_{e'}$), 2.39 (t, J = 7.4 Hz, 4H, H_g), 2.61 (m, 4H, H_f), 4.05 (t, J = 5.9 Hz, 4H, H_a), 4.40 (m, 4H, H_c), 6.76 (d, J = 8.9 Hz, 4H, H_o), 7.09 (m, 16H, H_{m+n}), 7.23 (d, J = 8.6 Hz, 12H, H_l); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ = 23.6, 23.7, 28.5, 29.1, 29.6, 31.2, 31.6, 34.3, 38.2, 42.9, 43.2, 63.0, 63.6, 63.9, 112.9, 119.5, 124.1, 130.7, 132.3, 139.9, 144.1, 148.3, 156.4, 168.9, 208.2. LRFAB-MS (3-NOBA matrix): *m/z* = 1510 $[MH]^+$; HRFAB-MS (3-NOBA matrix): *m/z* = 1509.971 (calcd. for $C_{102}H_{129}O_8N_2$ 1509.975).

Variable Temperature ^{1}H NMR investigation of Degenerate Shuttling Process in [L4Pd]

Variable temperature ^{1}H NMR experiments allow the estimation of the activation energy for the shuttling process in rotaxane [**L4**Pd]. Using a Bruker AVA 600 MHz spectrometer, ^{1}H NMR spectra were taken at 2 K increments from 298 K to 360 K, a stacked plot of ^{1}H NMR obtained at every 10 K from 300 K to 360 K is shown in Figure S2. Upon heating the spectra simplified as many of the peaks coalesced, although only a few resonances were usable for interpretation.

Figure S2: ^{1}H NMR (600 MHz, [D_7]DMF) of [**L4**Pd] at 10 K intervals from 300 K to 360 K:



Three proton resonances, H_o, H_c and H_g, are useful for interpretation. The coalescence temperature, T_c, for those protons along with the maximum peak separation, Δv_o, and an estimation of both the observed, k_{obs}, and bimolecular, k_{bi}, rates and activation free

energy, $\Delta G^{\ddagger}$, at the coalescence temperature are listed in Table S1. $\Delta G^{\ddagger}$ was estimated using a modified Eyring equation:

$$k_{obs} = \frac{\pi \Delta \nu_o}{\sqrt{2}}$$

$$k_{bi} = \frac{k_{obs}}{[Nu]}$$

$$\Delta G^{\ddagger} = -RT \ln \frac{k_{bi} h}{k_B T}$$

(R = 1.9872 *cal* K^{-1} *mol*$^{-1}$, k_B = 3.30 x 10^{-24} *cal* K^{-1}, h = 1.58 x 10^{-34} *cal s*)

	T_c (K)	$\Delta\nu_o$ (Hz)	k_{obs} (s^{-1})	k_{bi} (M^{-1} s^{-1})	$\Delta G^{\ddagger}$ (kcal mol^{-1})
H_o	338	55.38	123	9.54	18.4
H_g	353	112.69	250	19.4	18.7
H_c	357	123.42	274	21.3	18.9

Table S1: Estimation of kinetic parameters of [**L4**Pd] from VT ^{1}H NMR.

Exchange Spectroscopy (2D-EXSY) Investigation of Degenerate Shuttling Process in [L4Pd].[6]

2D-EXSY allows investigation of the shuttling process in the degenerate molecular shuttle [**L4**Pd]; all spectra were recorded on a Bruker 400 MHz NMR spectrometer at 300 K and the mixing time, τ_m, was 0.3 s. Using the equations shown below, where I_{AA} and I_{BB} are the diagonal peak intensities and I_{AB} and I_{BA} are the cross-peak intensities, we obtain a value for k which is the *sum* of the forward, k_1, and backward, k_{-1}, pseudo-first order rate constants for the shuttling process. As both stations are identical k_1 and k_{-1} are equal and thus the observed pseudo-first order rate constant, k_{obs}, can be determined. It is assumed that the shuttling is mediated by a nucleophile which displaces the palladium complex from the nitrile station in an associative fashion and that this is the rate determining step. If this is not an intramolecular process, the shuttling is a bimolecular process and, where the dominant nucleophile could be determined, k_{obs} was converted to k_{bi} which allows the value of $\Delta G^{\ddagger}$ to be determined using a modified Eyring equation.

$$A + Nu \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A' + Nu$$

$$r = \frac{\left(I_{AA} + I_{BB}\right)}{\left(I_{AB} + I_{AB}\right)}$$

$$k = \frac{1}{\tau_m} \times \ln \frac{r+1}{r-1}$$

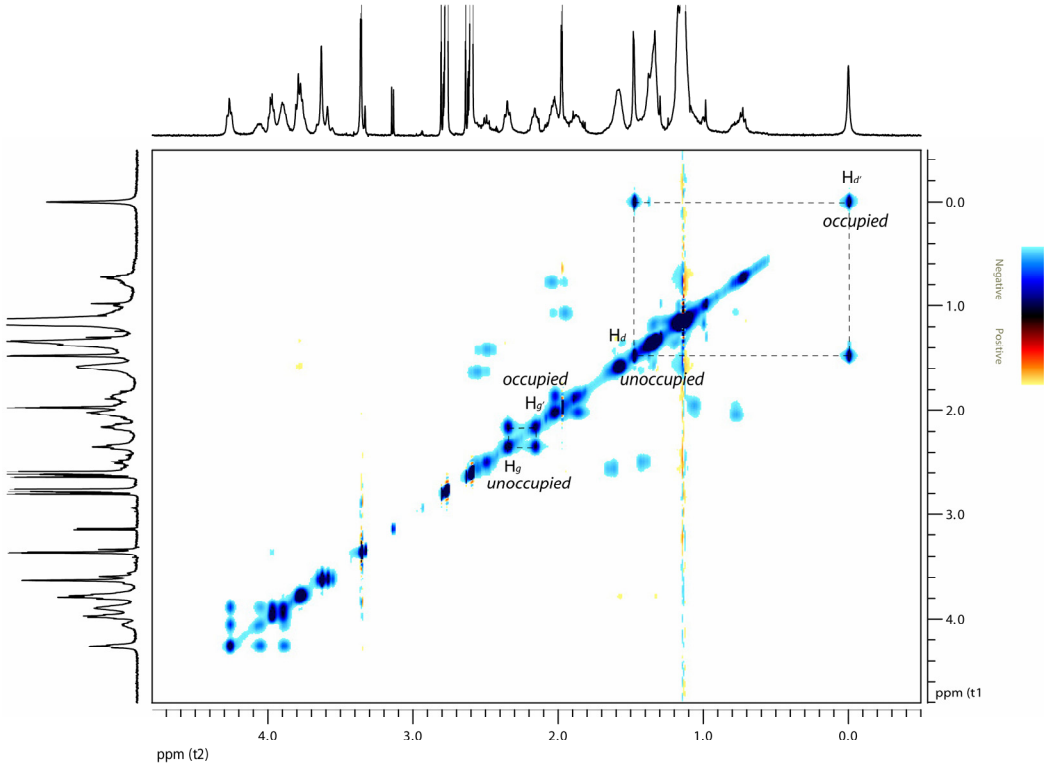
$$k = k_1 + k_{-1} \qquad (k_1 = k_{-1} = k_{obs})$$

$$k_{bi} = \frac{k_{obs}}{[Nu]}$$

$$\Delta G^{\ddagger} = -RT \ln \frac{k_{bi} h}{k_B T}$$

(R = 1.9872 *cal* K^{-1} *mol*$^{-1}$, k_B = 3.30 x 10^{-24} *cal* K^{-1}, h = 1.58 x 10^{-34} *cal s*)

Figure S3: Partial 2D-EXSY spectrum of [**L4**Pd] (400 MHz, [D_7]DMF, 300 K):



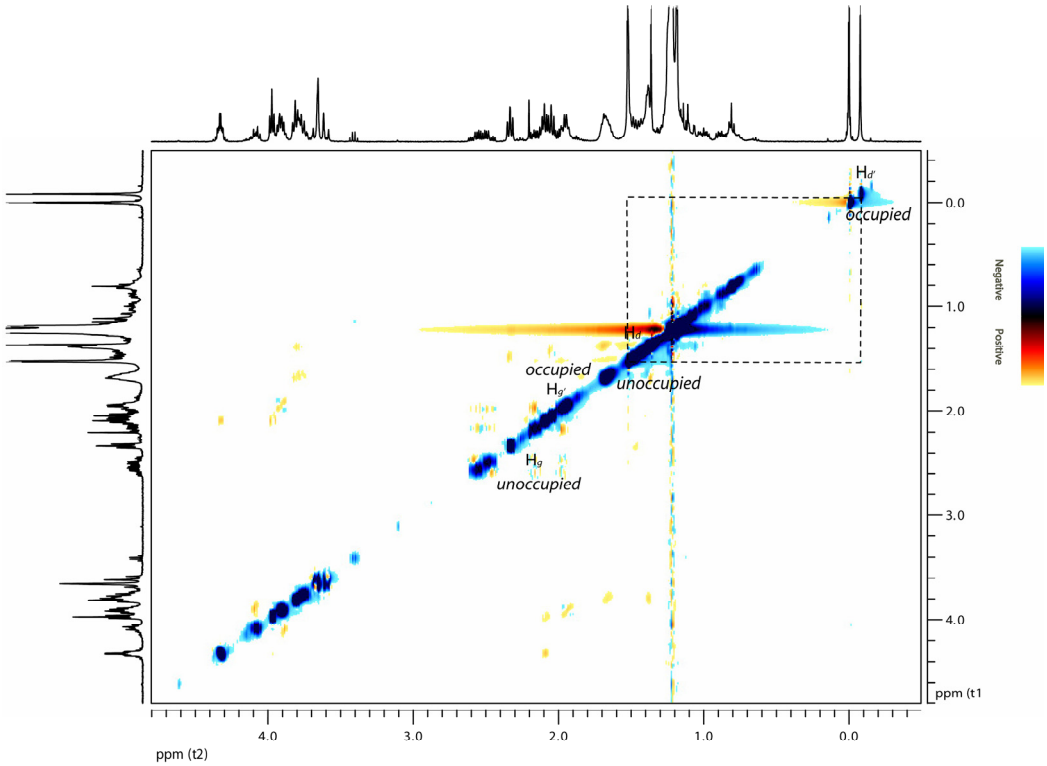
	I_{AA}	I_{AB}	I_{BB}	I_{BA}	k_{obs} (s^{-1})	k_{bi} (M^{-1} s^{-1})	$\Delta G^{‡}$ (kcal mol^{-1})
H_d	1.86	1.00	0.93	1.04	3	0.2	18
H_g	1.80	1.00	1.47	1.04	2	0.2	19

Table S2: Kinetic parameters of [**L4**Pd] in [D_7]DMF. Concentration of [D_7]DMF in [D_7]DMF is 12.9 mol dm^{-3}. Estimated error in k_{obs} ± 1 s^{-1}.

Controlling Shuttling Rates *via* the Addition and Removal of Pyridine

[**L4**Pd] (0.023 g, 0.0113 mmol) was dissolved in $CDCl_3$ (0.75 ml) and a 2D-EXSY spectra was obtained. Pyridine (0.92 µl, 0.0113 mmol) was added to the yellow solution and a 2D-EXSY was obtained. *p*-Toluenesulfonic acid (0.0022 g, 0.0113 mmol) was added to the yellow solution and a 2D-EXSY spectra was obtained which showed that the rates had returned to the background level.

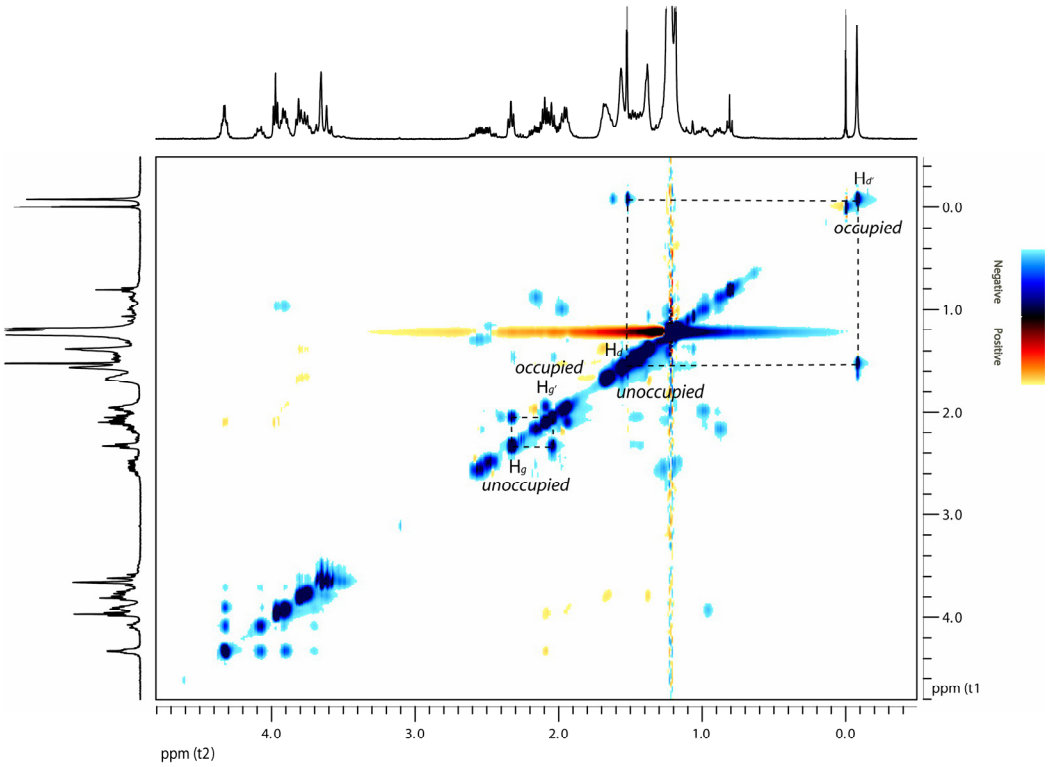
Figure S4: Partial 2D-EXSY spectrum of [**L4**Pd] (400 MHz, $CDCl_3$, 300 K):



	I_{AA}	I_{AB}	I_{BB}	I_{BA}	k_{obs} (s^{-1})
H_d	1402.72	1.00	436.63	1.10	5×10^{-3}

Table S3: Kinetic parameters of [**L4**Pd] in $CDCl_3$. Estimated error in $k_{obs} \pm 1 \times 10^{-3}$ s^{-1}.

Figure S5: Partial 2D-EXSY spectrum of [**L4**Pd] plus 1 equiv. of pyridine (400 MHz, $CDCl_3$, 300 K):



	I_{AA}	I_{AB}	I_{BB}	I_{BA}	k_{obs} (s^{-1})	k_{bi} (M^{-1} s^{-1})	$\Delta G^{\ddagger}$ (kcal mol^{-1})
H_d	4.16	1.00	1.93	1.00	1	96	15
H_g	4.07	1.00	3.01	1.26	1	93	15

Table S4: Kinetic parameters of [**L4**Pd] in $CDCl_3$ with 1 equiv. of pyridine. Concentration of pyridine present, 0.0119 mol dm^{-3}. Average k_{bi} = 95 M^{-1} s^{-1}. Estimated error in k_{obs} ± 0.1 s^{-1}.

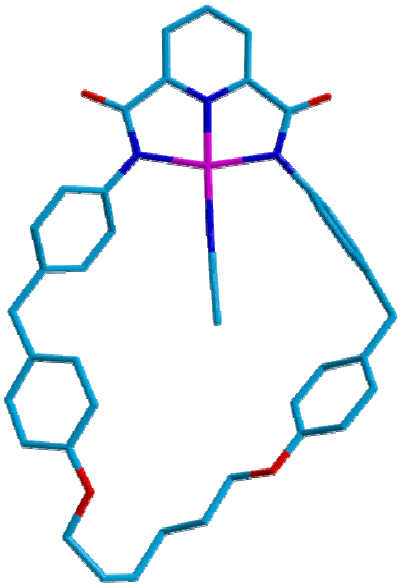


Figure S6: The X-ray crystal structure of [**L2**Pd(CH_3CN)].

Table S5**:** Crystal data and structure refinement for [**L2**Pd(CH_3CN)].

CCDC-670786		
Identification code	[**L2**Pd(CH_3CN)]	
Empirical formula	$C_{41}H_{38}N_4O_4Pd$	
Formula weight	757.15	
Temperature	93(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 13.774(3) Å	α = 90°.
	b = 15.345(3) Å	β = 94.23(3)°.
	c = 16.410(3) Å	γ = 90°.
Volume	3459.3(12) $Å^3$	
Z	4	
Density (calculated)	1.454 Mg/m^3	
Absorption coefficient	0.586 mm^{-1}	
F(000)	1560	
Crystal size	0.0800 x 0.0800 x 0.0800 mm^3	
Theta range for data collection	1.48 to 25.44°.	
Index ranges	-16<=h<=16, -18<=k<=18, -16<=l<=19	
Reflections collected	22408	

Independent reflections	6336 [R(int) = 0.0500]
Completeness to theta = 25.00°	99.7 %
Absorption correction	Multiscan
Max. and min. transmission	1.0000 and 0.7573
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6336 / 0 / 453
Goodness-of-fit on F^2	1.069
Final R indices [I>2sigma(I)]	R1 = 0.0437, wR2 = 0.0787
R indices (all data)	R1 = 0.0630, wR2 = 0.0864
Largest diff. peak and hole	0.966 and -0.866 e.Å^{-3}

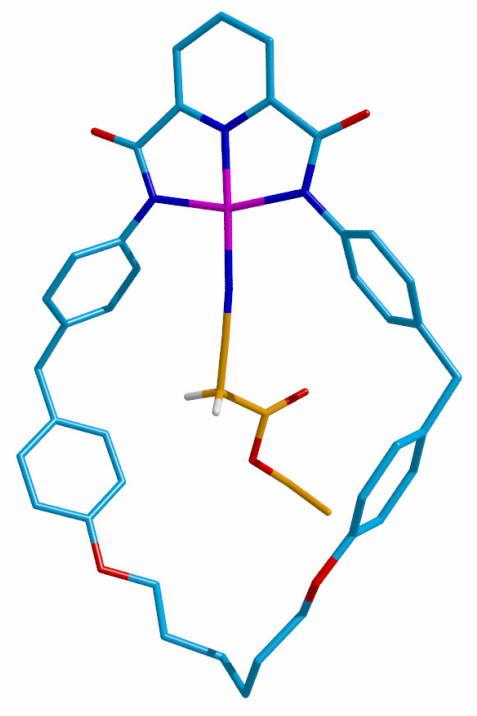


Figure S7: The X-ray crystal structure of [**L2**Pd**L1**].

Table S6: Crystal data and structure refinement for [**L2**Pd**L1**].

CCDC-670785	
Identification code	[**L2**Pd**L1**]
Empirical formula	$C_{45}H_{44}Cl_2N_4O_6Pd$
Formula weight	914.14
Temperature	93(2) K
Wavelength	0.71073 Å

Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 13.658(5) Å	α= 90°.
	b = 10.548(4) Å	β= 95.009(7)°.
	c = 14.508(6) Å	γ = 90°.
Volume	2082.1(14) $Å^3$	
Z	2	
Density (calculated)	1.458 Mg/m^3	
Absorption coefficient	0.628 mm^{-1}	
F(000)	940	
Crystal size	0.2000 x 0.1000 x 0.0500 mm^3	
Theta range for data collection	2.99 to 25.29°.	
Index ranges	-16<=h<=16, -12<=k<=12, -17<=l<=17	
Reflections collected	19257	
Independent reflections	7224 [R(int) = 0.0498]	
Completeness to theta = 25.00°	97.1 %	
Absorption correction	Multiscan	
Max. and min. transmission	1.0000 and 0.8801	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7224 / 1 / 524	
Goodness-of-fit on F^2	1.045	
Final R indices [I>2sigma(I)]	R1 = 0.0384, wR2 = 0.0979	
R indices (all data)	R1 = 0.0387, wR2 = 0.0985	
Absolute structure parameter	0.02(2)	
Largest diff. peak and hole	0.637 and -0.755 $e.Å^{-3}$	

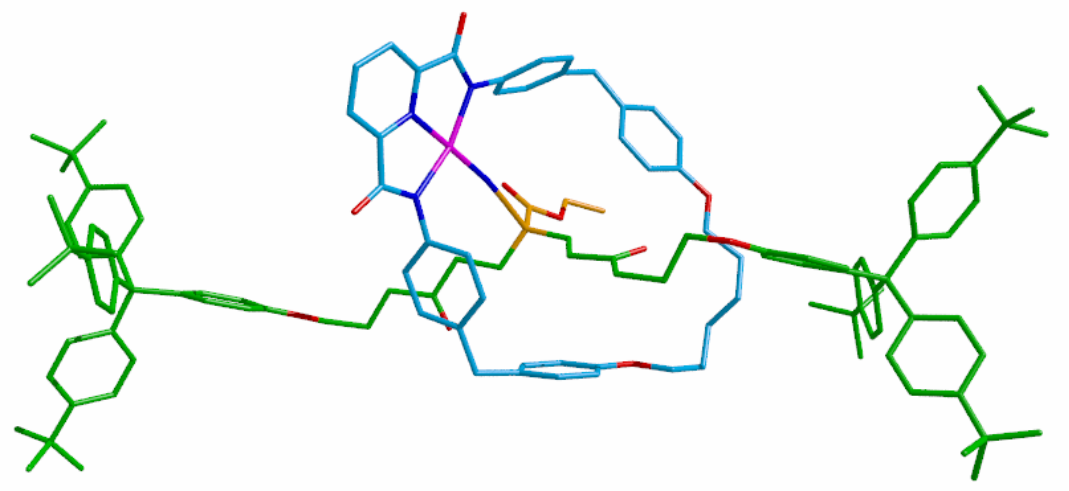


Figure S8: The X-ray crystal structure of [**L3**Pd].

Table S7: Crystal data and structure refinement for [**L3**Pd].

CCDC-670784		
Identification code	[**L3**Pd]	
Empirical formula	$C_{133.50}H_{155}ClN_4O_{11.50}Pd$	
Formula weight	2141.47	
Temperature	93(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.767(2) Å	α= 82.166(6)°.
	b = 21.409(5) Å	β= 79.665(8)°.
	c = 27.970(6) Å	γ = 86.688(10)°.
Volume	6280(2) $Å^3$	
Z	2	
Density (calculated)	1.132 Mg/m^3	
Absorption coefficient	0.227 mm^{-1}	
F(000)	2278	
Crystal size	0.2000 x 0.1000 x 0.0100 mm^3	
Theta range for data collection	2.09 to 25.36°.	
Index ranges	-12<=h<=12, -25<=k<=25, -33<=l<=30	
Reflections collected	63886	
Independent reflections	22787 [R(int) = 0.0988]	
Completeness to theta = 25.00°	99.4 %	
Absorption correction	Multiscan	

Max. and min. transmission	1.0000 and 0.9554
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	22787 / 6 / 1426
Goodness-of-fit on F^2	1.180
Final R indices [I>2sigma(I)]	R1 = 0.1256, wR2 = 0.3114
R indices (all data)	R1 = 0.1606, wR2 = 0.3348
Largest diff. peak and hole	1.011 and -0.656 e.Å^{-3}

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