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Supplementary material for manuscript:

A $[Pd_2L_4]^{4+}$ cage complex for *n*-octyl-β-D-glycoside recognition

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Section S1. Materials and methods

All solvents and chemical were purchased from commercial suppliers and used without further purification. Solvents, when needed, were dried by standard distillation techniques or for larger amounts (>10 mL), the solvent was tapped from a Solvent Purification System (SPS) from mbraun (MB SPS-800, with standard mbraun drying columns). Reactions were carried out under a Nitrogen atmosphere using standard Schlenk techniques, where dry solvents are specified. 1,3,5-benzenetricarboxylic acid tris-pentafluorophenyl ester (TMA-PFP) was prepared according to a literature procedure (H. Destecroix, T. J. Mooibroek and A. P. Davis, *Angew. Chem. Int. Ed.*, 2015, *54* (7), 2057-2061). 3,3-dimethyl-1-bromobutane was prepared according to a literature procedure, when this compound was not commercially available (H. Hamano, K. Nagata, N. Fukada, H. Shimotahira, X.-L. Ju, Y. Ozoe, *Bioorg. Med. Chem.* 2000, *8* (3), 665-674).

Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker DRX 500 (125.72 MHz for ^{13}C), Bruker AMX 400 (100.62 MHz for ^{13}C, 128.38 MHz for ^{11}B or 376.50 MHz for ^{19}F), Bruker DRX 300 (75.48 MHz for ^{13}C) or on a Varian Mercury 300 (75.48 MHz for ^{13}C or 282.32 MHz for ^{19}F) spectrometer at room temperature. The residual solvent peaks were used as internal standards (^{1}H: δ 7.26 p.p.m., $^{13}C\{^{1}H\}$: δ 77.16 p.p.m. for $CDCl_3$; ^{1}H: δ 5.32 p.p.m., $^{13}C\{^{1}H\}$: δ 53.84 p.p.m. for CD_2Cl_2; ^{1}H: δ 2.50 p.p.m., $^{13}C\{^{1}H\}$: δ 39.52 p.p.m. for DMSO-d_6), while ^{11}B spectra were externally referenced to 15% $BF_3{\cdot}OEt_2$ in $CDCl_3$ (0.00 p.p.m.) and ^{19}F NMR spectra were externally referenced to CF_3COOH (–76.55 p.p.m.). Chemical shifts (δ) are given in parts per million (p.p.m.) and coupling constants (J) are quoted in hertz (Hz). Resonances are described as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), a combination thereof, broad singlet (br s) or multiplet (m). **NB:** The Log(D) values measured by DOSY-NMR were always calibrated on the Log(D) value of the solvent. This value could not be found for CD_2Cl_2. Hence, the diffusion coefficient (D) of CD_2Cl_2 was measured in $CDCl_3$ (with d20 = 0.05 s and p30 = 500 μs) using 50, 75 and 95% CD_2Cl_2 in $CDCl_3$ solution resulting in the used log(D) of –8.604 ± 0.001 $m^2{\cdot}s^{-1}$.

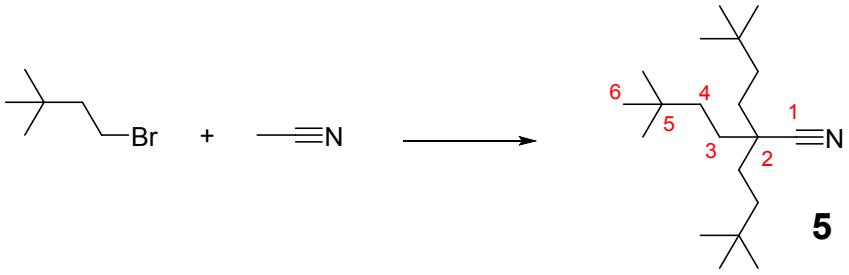
Low resolution mass spectra were recorded on an Advion (T)LC-MS expression^{L} CMS mass spectrometer (with a TLC plate express and isocratic pump), using the Electron Spray Ionization (ESI) method. High Resolution Mass Spectra (HRMS) were recorded on a JEOL AccuTOFC-plus JMS-T100LP mass spectrometer, with the indicated ionization method. Flash chromatography was performed on Silicycle Siliaflash P60 Silica Gel (particle size 40-63 µm, pore diameter 60Å) using the indicated eluent. Thin Layer Chromatography (TLC) was performed using TLC plates from Merck (SiO_2, Kieselgel 60 F254 neutral, on aluminium with fluorescence indicator).

CryoSpray Ionization High Resolution Mass Spectrometry (CSI HRMS) was conducted on a HR-ToF Bruker Daltonik GmbH (Bremen, Germany) Impact II, an ESI-ToF MS capable of resolution of at least 40000 FWHM, which was coupled to a Bruker cryo-spray unit. Detection was in positive-ion mode and the source voltage was between 4 and 6 kV. The sample was introduced with a syringe pump at a flow rate of 18 ul/hr. The drying gas (N2) was held at -35 °C and the spray gas was held at -40 °C. The machine was calibrated prior to every experiment via direct infusion of a TFA-Na solution, which provided a m/z range of singly charged peaks up to 3500 Da in both ion modes. Software acquisition with Compass 2.0 for Otof series and software processing with Compass DataAnalysis 4.0 sri (x64) (both Bruker Daltonik GmbH (Bremen, Germany)). The peak with the highest intensity of an isotope distribution was used to report and calculate the difference between measured and calculated values (Δ, expressed in p.p.m.). These reported values were obtained from Bruker DataAnalysis 4.4 software, wherein the positive ionization is taken into account by subtracting the mass of the missing electrons (0.0005486 Da per electron). **NB:** the isotope distributions were simulated with mMass software, which *does not* take into account the mass of the missing electrons in positive ions. This leads to apparent mass differences as large as 0.0021944 Da (4 x 0.0005486) in a 4+ species.

^{1}H NMR titrations were performed using a Bruker DRX 500 spectrometer operating at 298 K. A 3.33 mM solution of [**3'**][BF_4]$_4$ was prepared, sonicated for 15 minutes and then used to make 0.25 M stock solutions of *n*-oct-β-D-Glc **10** or *n*-oct-β-D-Gal **11** (all in in CD_2Cl_2/DMSO-d_6 (9:1)). During the titration, known aliquots of the 0.25 M stock solution was added to an NMR tube containing 600 µL of a 3.33 mM solution of [**3'**][BF_4]$_4$ and a ^{1}H NMR spectra was recorded.

Association constants (K_a) were determined by monitoring the change in chemical shift (Δδ) for a selected proton resonance of **3'** and fitting these shifts to a 1:1 binding model using a non-linear least squares fitting protocol implemented within Microsoft Excel. An estimated error for K_a was calculated from individual data points by assuming the fitted K_a and the measured Δδ values.

Section S2. Syntheses and characterizations



tris(3,3-dimethylbutyl)acetonitrile) (5). 2.5 M *n*BuLi in hexanes (34 mL, 85 mmol, 1 eq.) was added slowly to a solution of *i*Pr_2NH (15 mL, 10.83 g, 107 mmol, 1.26 eq.) in dry THF (51 mL) at 0 °C. 22 mL (22 mmol, 1.15 eq.) of this freshly prepared 1M lithium diisopropylamide (LDA) solution in dry THF at 0 °C was added to a solution of acetonitrile (1 mL, 786 mg, 19.1 mmol, 1 eq.) in dry THF (80 mL) at -78 °C. After stirring for 15 min. at -78 °C, 3,3-dimethyl-1-bromobutane **4** (3.4 mL, 3.93 g, 23.8 mmol, 1.25 eq.) was added to the solution. After stirring for an additional 1 h at -78 °C, another 26 mL of 1M LDA (26 mmol, 1.36 eq.) was added at -78 °C. After stirring for 30 min at -78 °C, another portion of 3,3-dimethyl-1-bromobutane (4 mL, 4.62 g, 28.0 mmol, 1.47 eq.) was added at -78 °C to the solution. Subsequently, the reaction mixture was allowed to warm to room temperature for 1 h, before it was cooled again to -78 °C. A final 30 mL 1M LDA solution (30 mmol, 1.57 eq.) was added to the solution and after stirring for 30 min at -78 °C, the last portion of 3,3-dimethyl-1-bromobutane (4.6 mL, 5.32 g, 32.2 mmol, 1.69 eq.) was added. The resulting solution was allowed to warm to room temperature and stirred for 2.5 h. The reaction mixture was quenched with MeOH (10 mL) and the solvent was evaporated *in vacuo*. The residue was taken up in petroleum ether / water and the organic layer was extracted thrice with water. The organic layer was dried over Na_2SO_4, filtrated and evaporated *in vacuo*, affording **5** without further purification as a white solid. Yield: 92%, 18.4 mmol, 5.41 g.

See Figure S1 – Figure S4 for NMR spectra: ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.55–1.48 (m, 6H, H3), 1.29–1.22 (m, 6H, H4), 0.91 (s, 27H, H6). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 124.66 (C1), 40.50 (C2), 37.82 (C4), 30.66 (C3), 30.25 (C5), 29.41 (C6). {^{1}H-^{13}C}-HSQC (500, 126 MHz, $CDCl_3$): δ 37.82-1.26 (C4-H4), 30.66-1.52 (C3-H3), 29.41-0.91 (C6-H6). {^{1}H-^{13}C}-HMBC (500, 126 MHz, $CDCl_3$): δ 124.66-1.52 (C1-H3), 40.50-1.52 (C2-H3), 37.82-1.52/0.91 (C4-H3/H6), 30.66-1.52/1.26 (C3-H3/H4), 30.25-1.52/1.26/0.91 (C5-H3/H4/H6), 29.41-1.26/0.91 (C6-H6/H4).

HRMS (FD+): *m/z* calculated for $C_{20}H_{40}N$ $[M+H]^+$ 294.3161, found 294.3161.

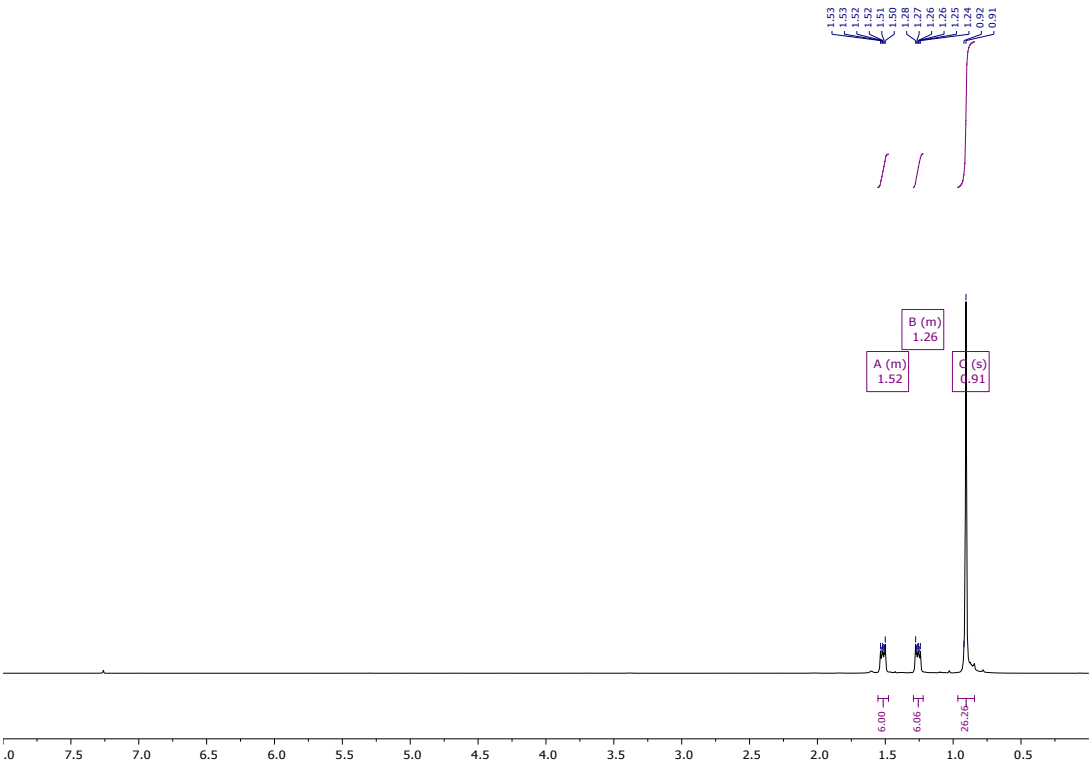


Figure S1. ^{1}H NMR spectrum of **5** in $CDCl_3$.

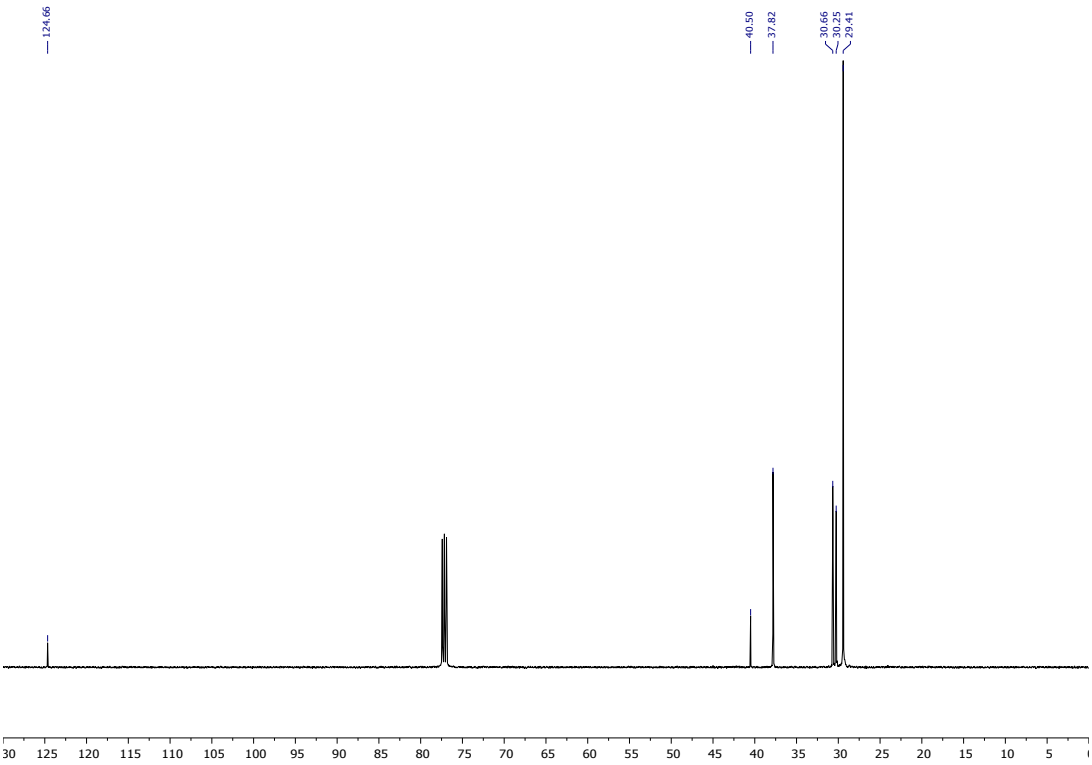


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **5** in $CDCl_3$.

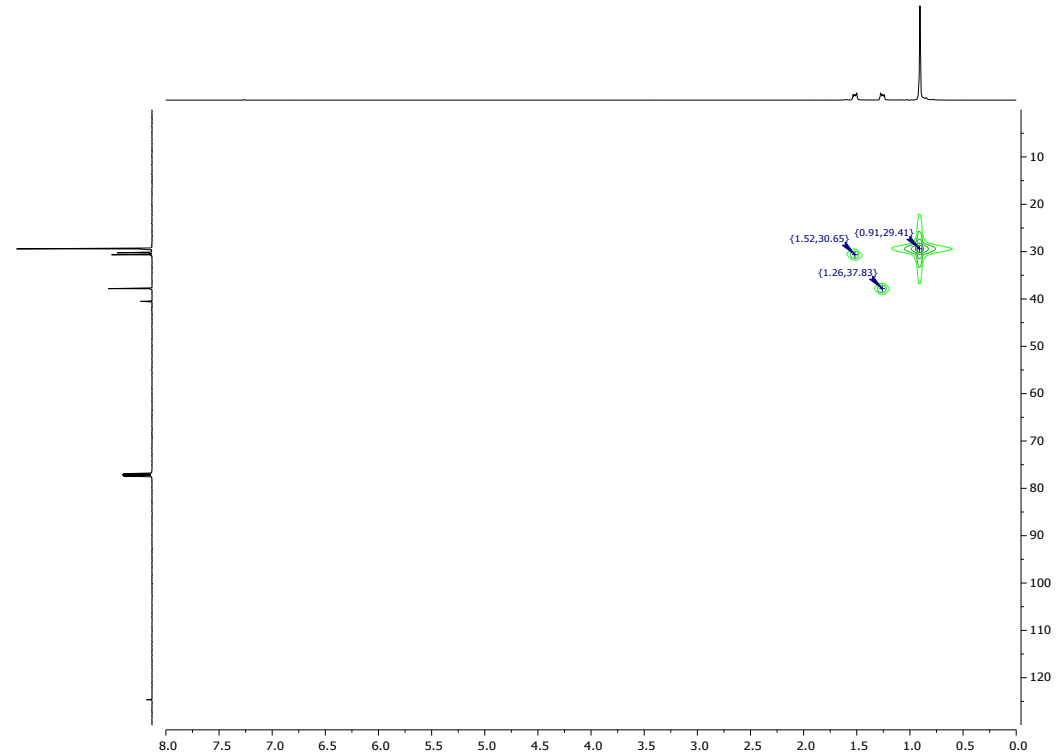


Figure S3. {^{1}H-^{13}C}-HSQC spectrum of **5** in $CDCl_3$.

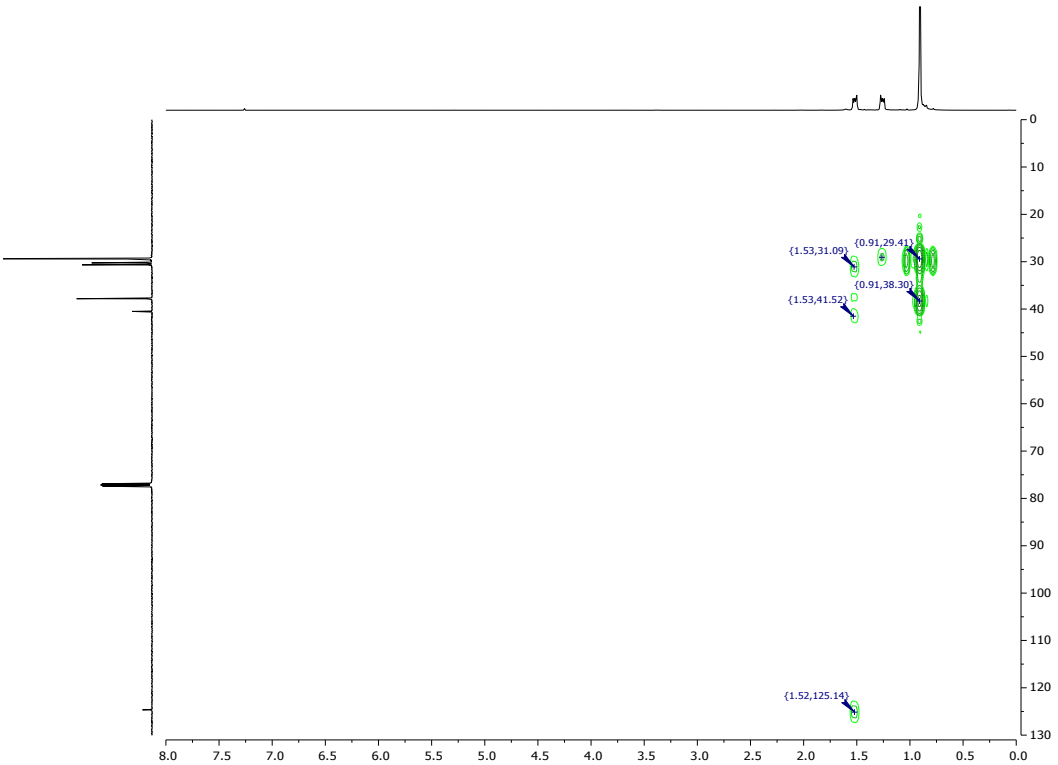
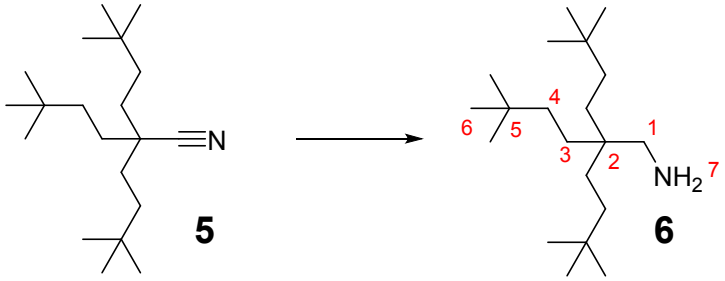


Figure S4. {^{1}H-^{13}C}-HMBC spectrum **5** in $CDCl_3$.



2,2,2-tris(3,3-dimethylbutyl)ethylamine (6). To an ice cold solution of **5** (1.18 g, 4.0 mmol, 1 eq.) in dry Et_2O (8 mL) was added dropwise a 2.4 M $LiAlH_4$ solution in THF (3.4 mL, 8.16 mmol, 2 eq.). After addition, the reaction mixture was stirred at room temperature for 21 h. The resulting grey suspension was quenched with water and basified with aqueous NaOH (5M). The suspension was filtrated and the residue was washed thoroughly with Et_2O and aqueous NaOH (5M). The organic layer of the combined filtrates was separated from the aqueous layer, dried over Na_2SO_4, filtered and evaporated to dryness *in vacuo* to afford pure **6** as a white solid. Yield: 89%, 3.6 mmol, 1.06 g.

See Figure S5 – Figure S8 for NMR spectra: ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 2H, H1), 1.12 – 0.99 (m, 12H, H3 & H4), 0.88 (s, 27H, H6). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 46.84 (C1), 38.20 (C2), 36.62 (C4), 30.32 (C5), 29.61 (C6), 28.23 (C3). {^{1}H-^{13}C}-HSQC (400, 101 MHz, $CDCl_3$): δ 46.84-2.41 (C1-H1), 36.62-1.07 (C4-H4), 29.61-0.88 (C6-H6), 28.23-1.07 (C3-H3). {^{1}H-^{13}C}-HMBC (400, 101 MHz, $CDCl_3$): δ 38.20-2.41 (C2-H1), 36.62-1.07/0.88 (C4-H3/H6), 30.32-1.07/0.88 (C5-H4/H6), 29.61-1.07 (C6-H4), 28.23-2.41/1.07 (C3-H1/H4).

HRMS (ESI+): *m/z* calculated for $C_{20}H_{44}N$ $[M+H]^+$ 298.3474, found 298.3478.

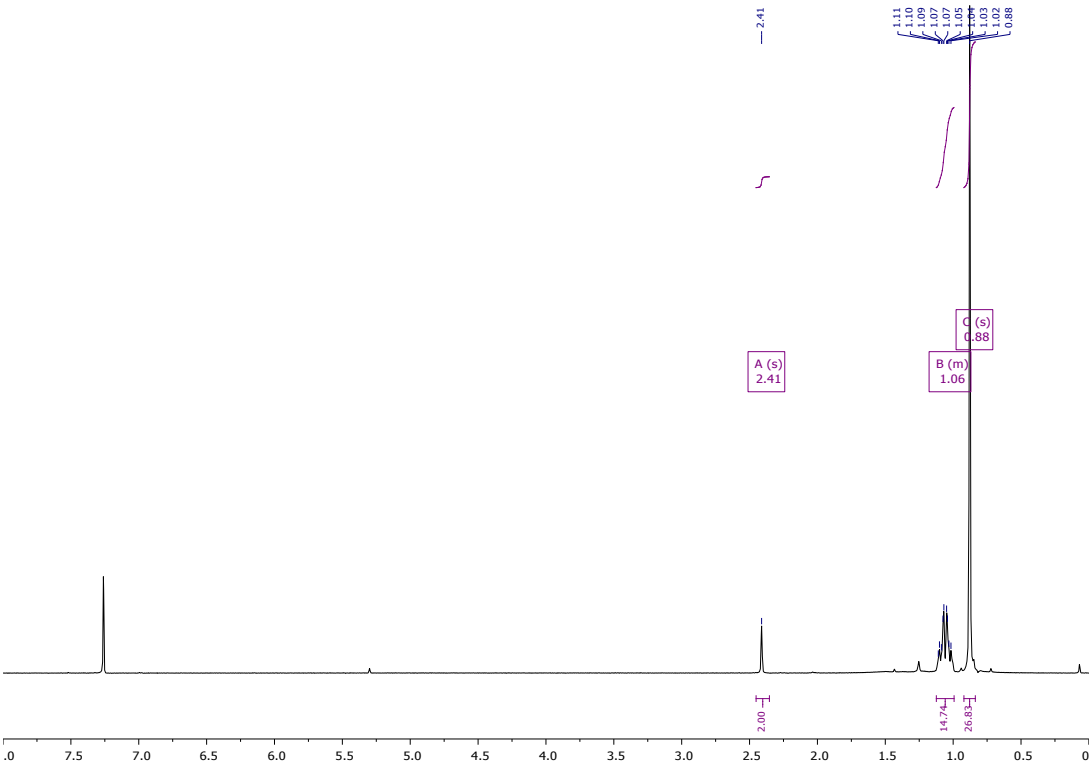


Figure S5. ^{1}H NMR spectrum of **6** in $CDCl_3$.

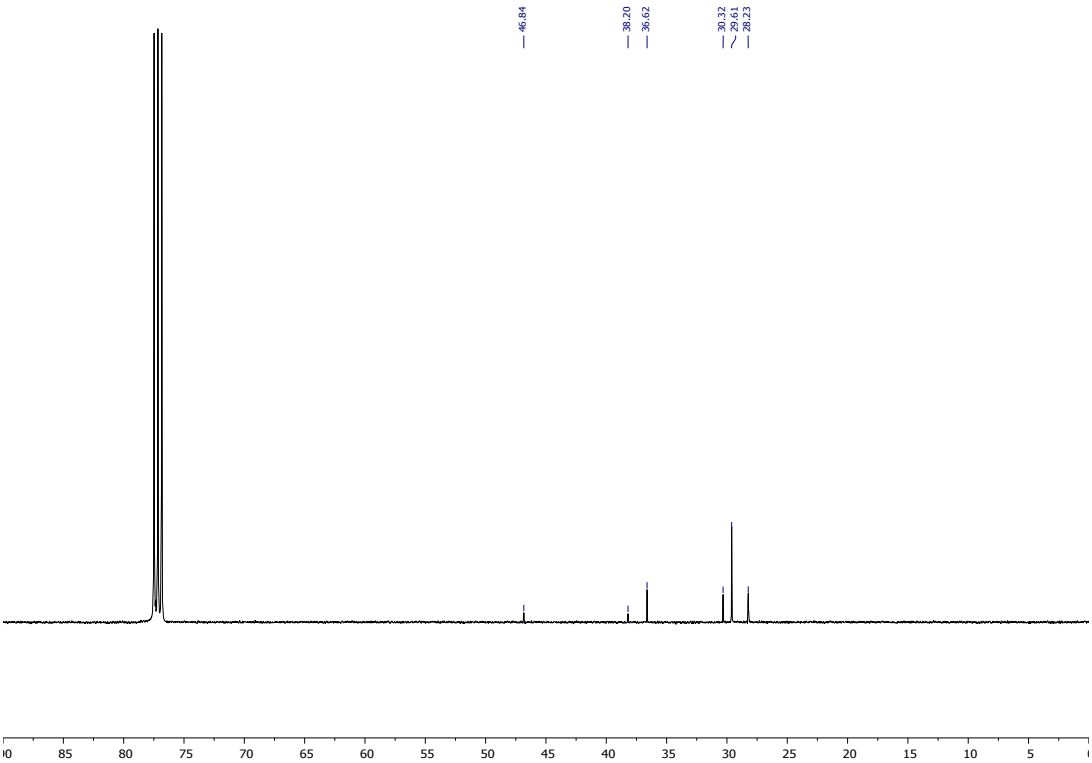


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of **6** in $CDCl_3$.

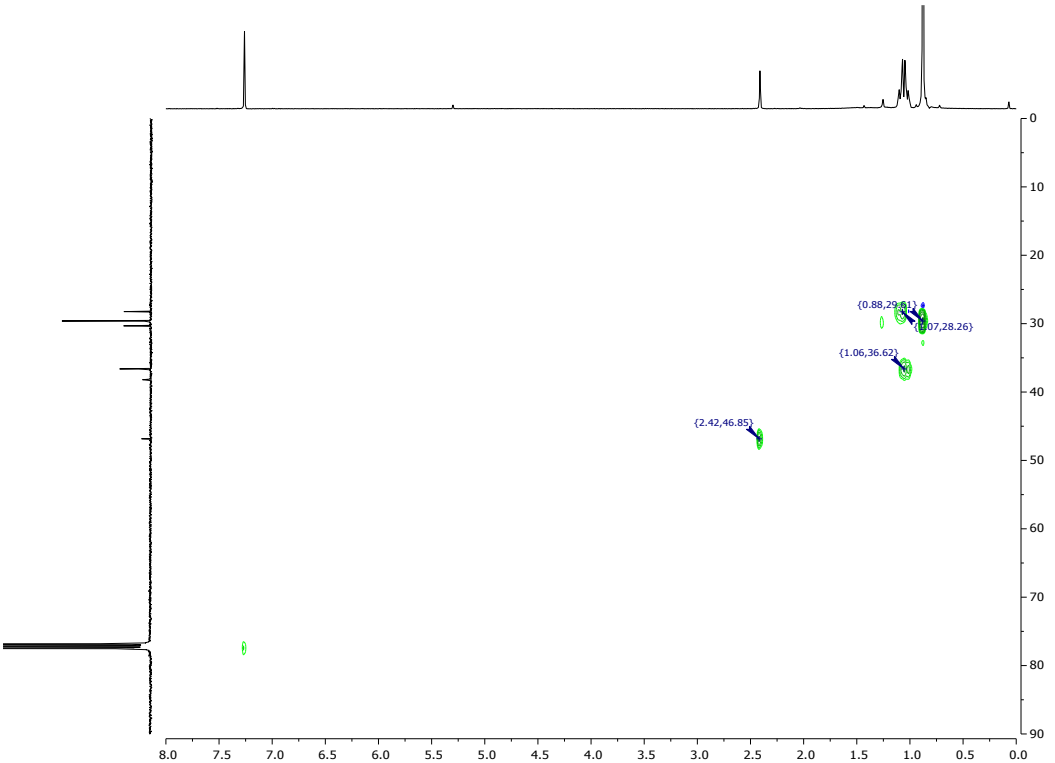


Figure S7. {^{1}H-^{13}C}-HSQC spectrum of **6** in $CDCl_3$.

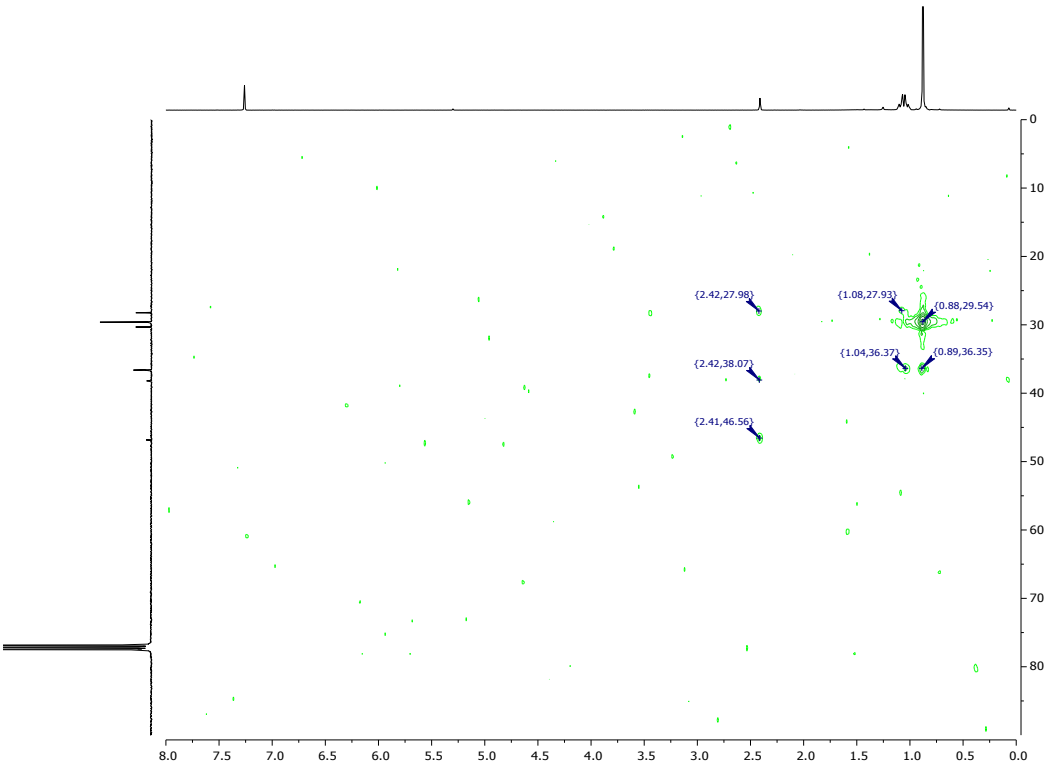
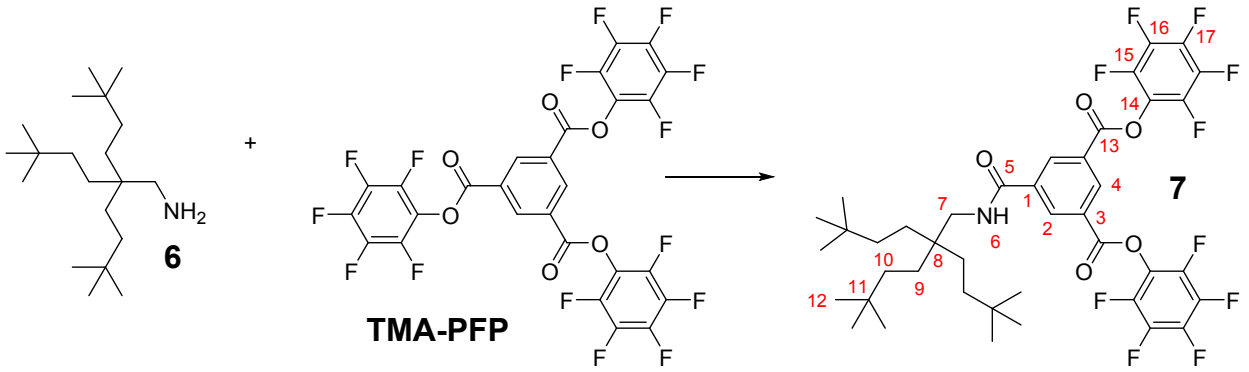


Figure S8. {^{1}H-^{13}C}-HMBC spectrum of **6** in $CDCl_3$.



Bis(pentafluorophenyl) ester 7. Compound **7** was prepared according to a literature procedure[2] with slight modifications. 1,3,5-benzene triscarboxylic acid tris(pentafluorophenyl) ester (**TMA-PFP**, 5.7 g, 8.0 mmol, 2.2 eq.) was suspended in dry THF (29 mL) and DIPEA (2.7 mL, 2.0 g, 15.5 mmol, 4.3 eq.). To this suspension was added dropwise a solution of **6** (1.1 g, 3.6 mmol, 1 eq.) in dry THF (8 mL) and DIPEA (1.2 mL, 890 mg, 6.9 mmol, 1.9 eq.) over a period of 20.5 h. The resulting solution was stirred at room temperature for another 25 h and the solvent was evaporated *in vacuo*. The residue was purified by column chromatography on silica gel (DCM/petroleum ether 1:1), affording **7** as a white solid. Yield: 59%, 2.1 mmol, 1.8 g.

See Figure S9 – Figure S17 for NMR spectra: ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.10 (s, 1H, H4), 8.83 (s, 2H, H2), 6.06 (t, J = 8 Hz, 1H, NH, H6), 3.38 (d, J = 8 Hz, 2H, H7), 1.34–1.07 (m, 12H, H9/H10), 0.90 (s, 27H, H12). ^{19}F NMR (282 MHz, $CDCl_3$): δ -152.20 (d, J = 24.0 Hz, 4F, F15), -156.62 (t, J = 30.0 Hz, 2F, F17), -161.51 (t, J = 28.0 Hz, 4F, F16). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 164.32 (C5), 160.97 (C13), 141.40 (ddd, J = 1004, 52, 16 Hz, C16), 140.17 (dt, J = 1012, 52 Hz, C17), 138.18 (dt, J = 1016, 52 Hz, C15), 137.39 (C3), 134.96 (C4), 134.29 (C2), 128.99 (C1), 124.94 (t, J = 60 Hz, C14), 44.79 (C7), 38.16 (C8), 36.60 (C10), 30.31 (C11), 29.52 (C12), 29.19 (C9). {^{1}H-^{1}H}-COSY (400, 400 MHz, $CDCl_3$): δ 9.10-8.83 (H4-H2), 8.83-9.10 (H2-H4), 6.06-3.38 (H6-H7), 3.38-6.06(H7-H6). {^{1}H-^{13}C}-HSQC (400, 101 MHz, $CDCl_3$): δ 134.96-9.10 (C4-H4), 134.29-8.83 (C2-H2), 44.79-3.38 (C7-H7), 36.60-1.16 (C10-H10), 29.52-0.90 (C12-H12), 29.19-1.25 (C9-H9). {^{1}H-^{13}C}-HMBC (400, 101 MHz, $CDCl_3$): δ 164.32-8.83/6.06/3.38 (C5-H2/H6/H7), 160.97-9.10/8.83 (C13-H4/H2), 134.96-8.83 (C4-H2), 134.29-9.10 (C2-H4), 128.99-9.10/8.83 (C1-H4/H2), 44.79-1.25 (C7-H10), 38.16-3.38/1.25 (C8-H7/H10), 36.60-1.25/0.90 (C10-H9/H12), 30.31-0.90 (C11-H12) 29.52-1.16 (C12-H10), 29.19-3.38 (C9-H7).

HRMS (FD+): *m/z* calculated for $C_{41}H_{46}F_{10}NO_5$ $[M+H]^+$ 822.3216, found 822.3223.

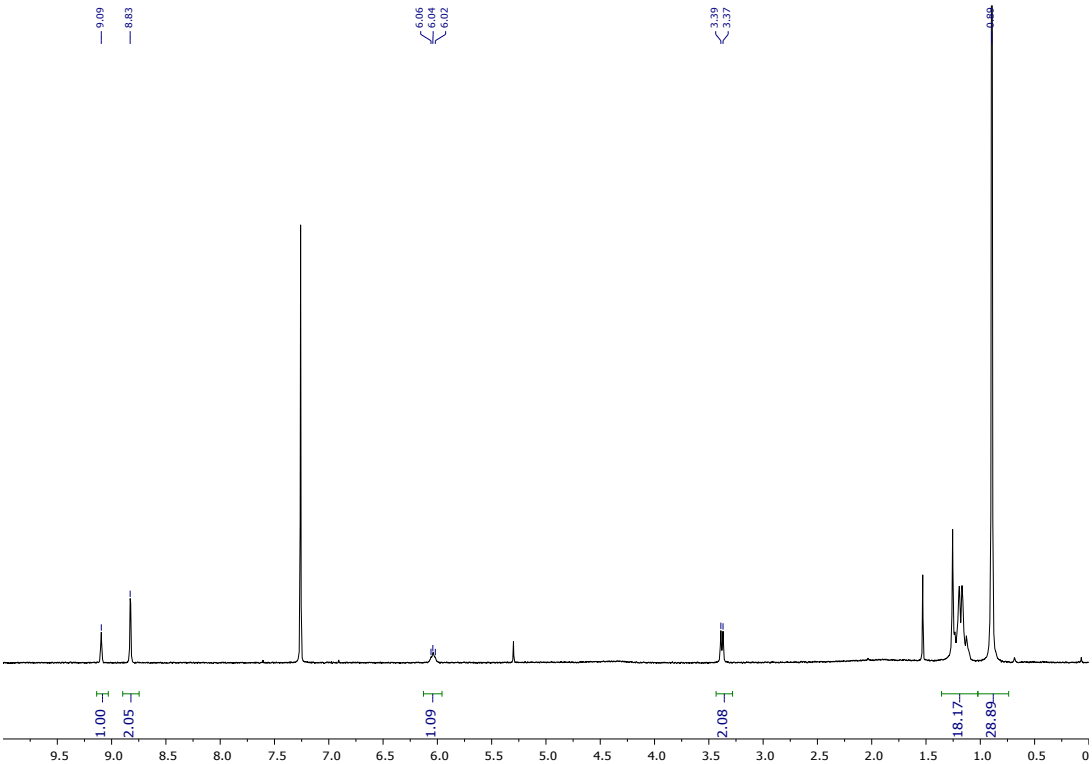


Figure S9. ^{1}H NMR spectrum of **7** in $CDCl_3$.

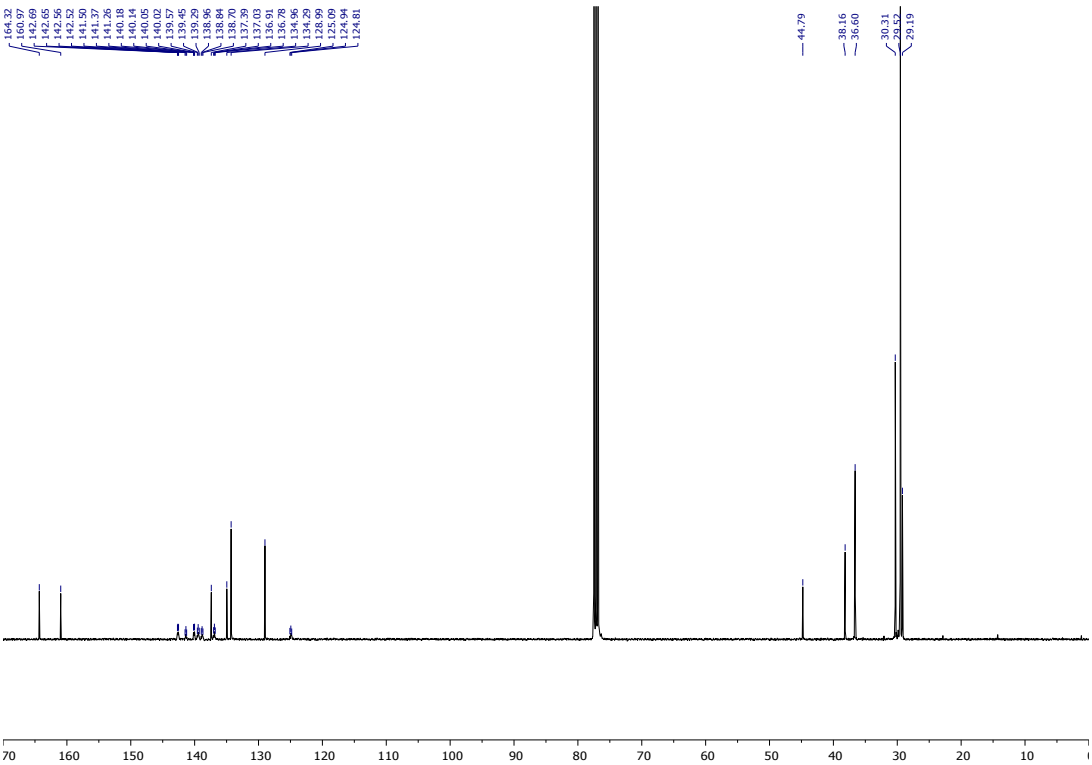


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of **7** in $CDCl_3$.

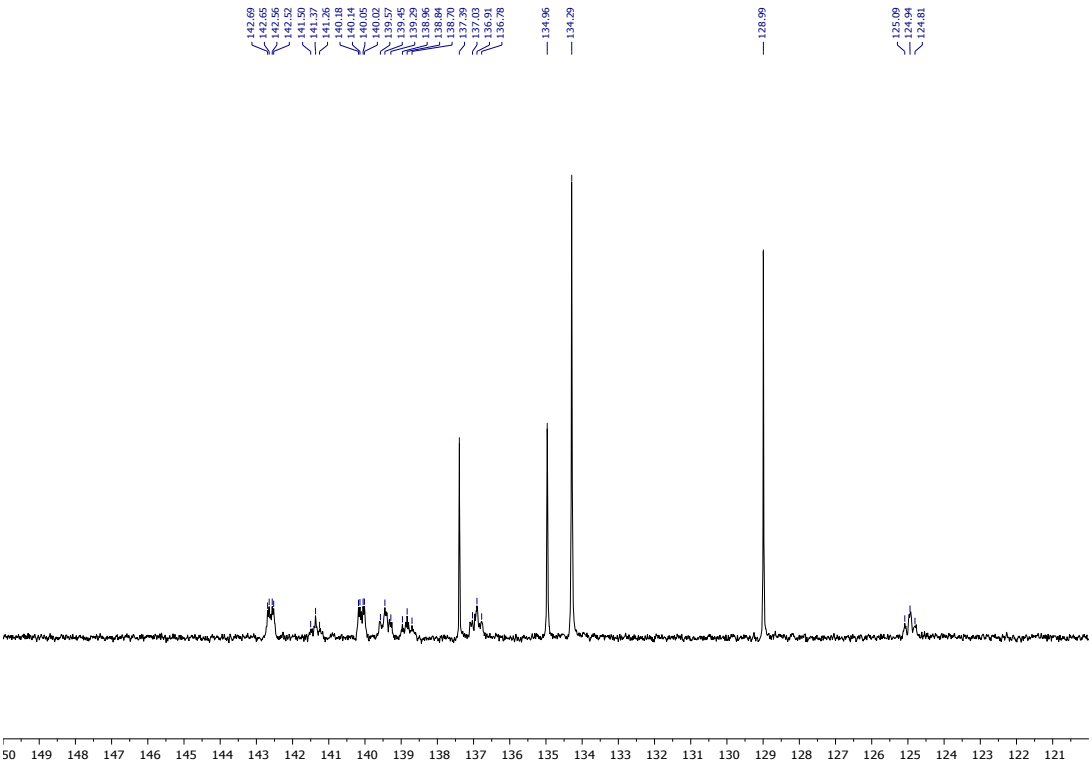


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of **7** in $CDCl_3$, zoomed 150-120 p.p.m..

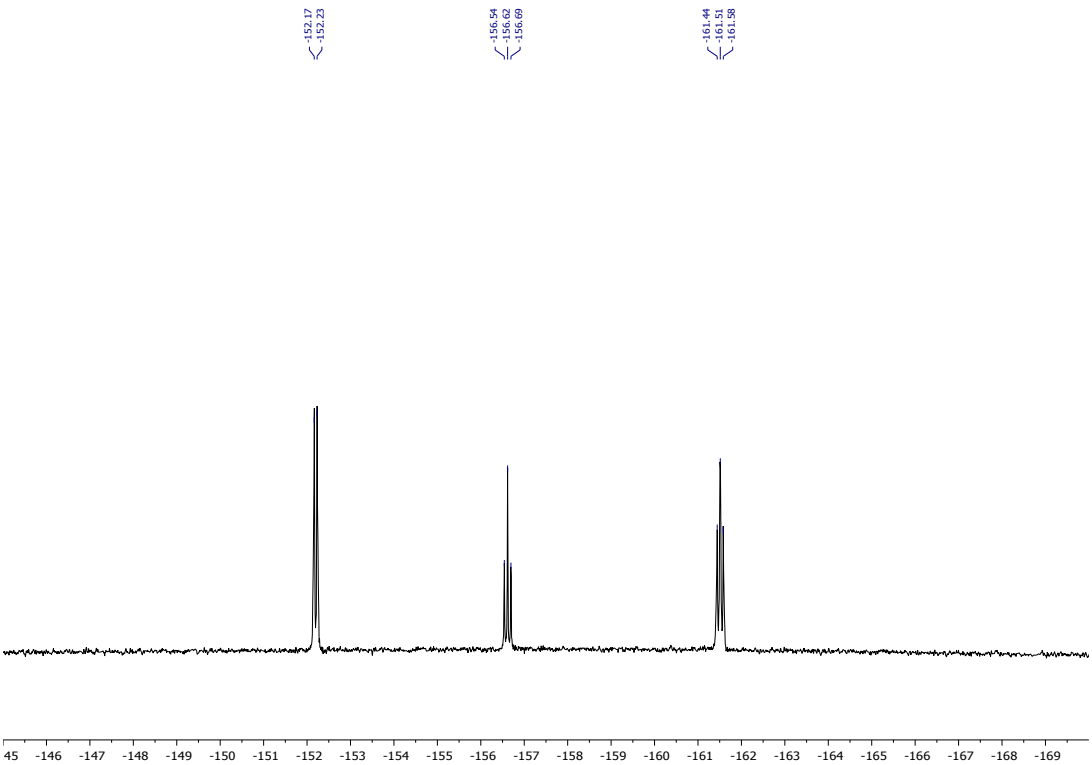


Figure S12. ^{19}F NMR spectrum of **7** in $CDCl_3$.

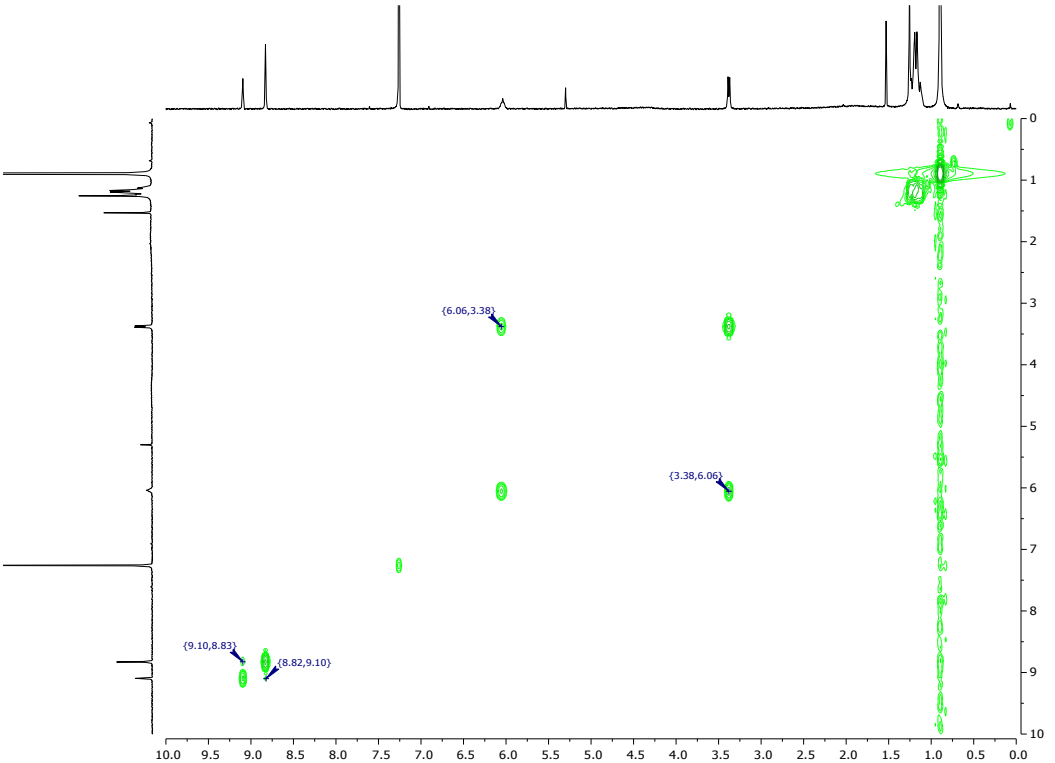


Figure S13. {^{1}H-^{1}H}-COSY spectrum of **7** in $CDCl_3$.

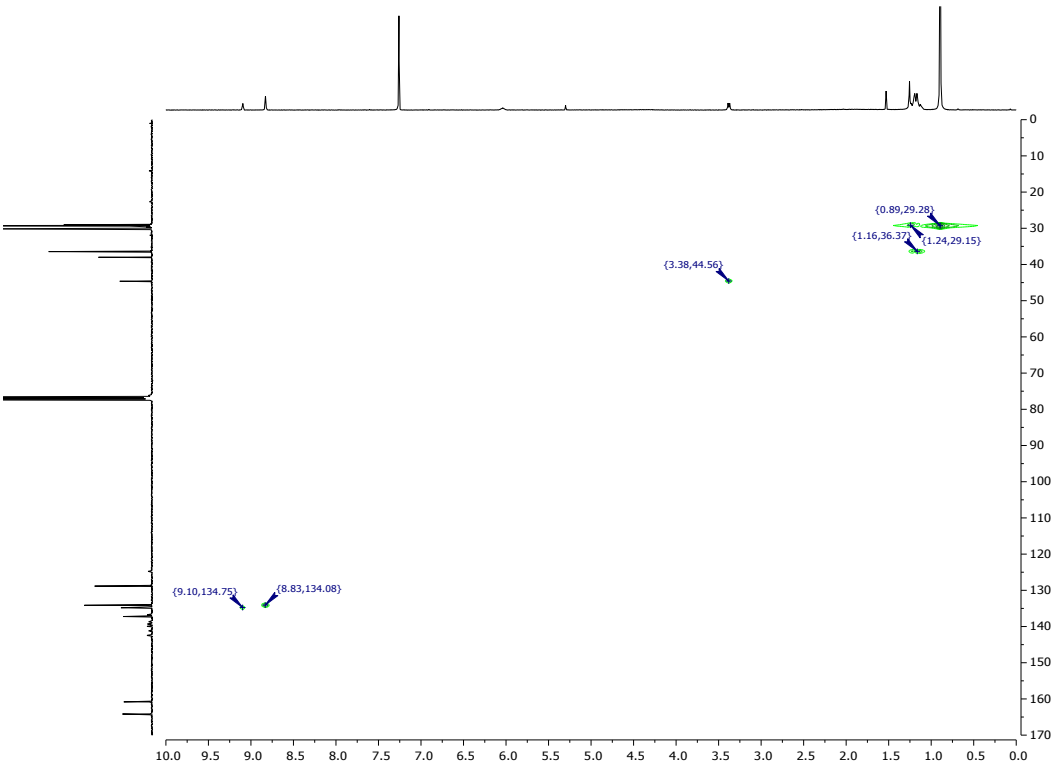


Figure S14. {^{1}H-^{13}C}-HSQC spectrum of **7** in $CDCl_3$.

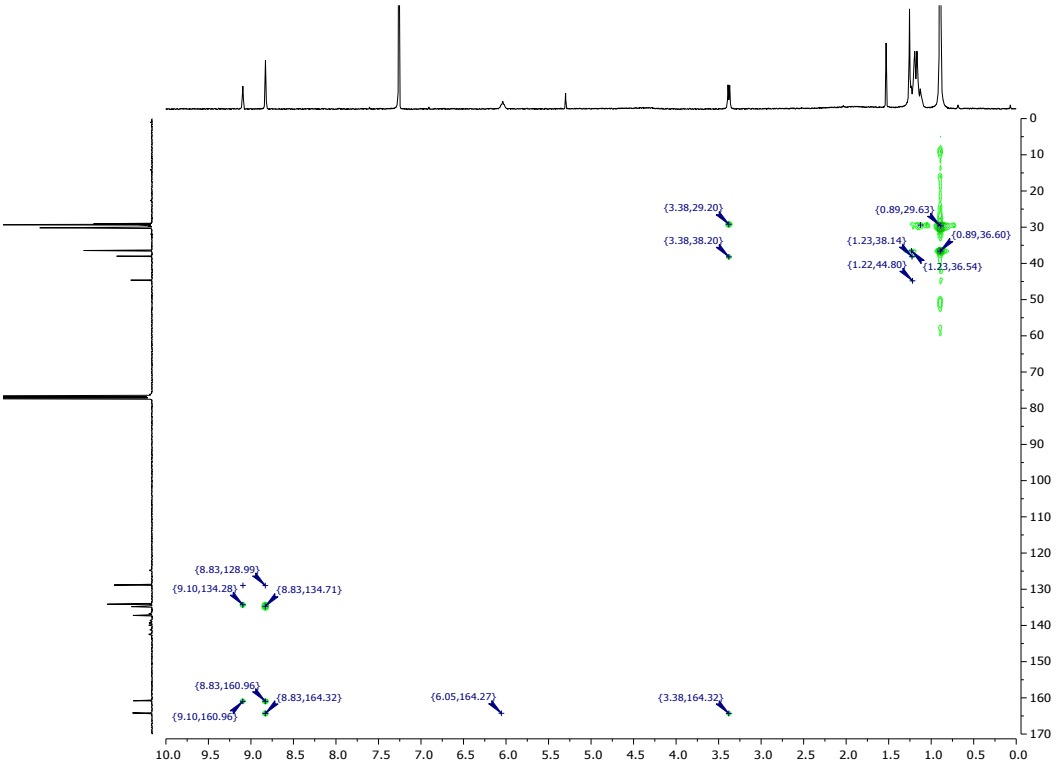


Figure S15. {^{1}H-^{13}C}-HMBC spectrum of **7** in $CDCl_3$.

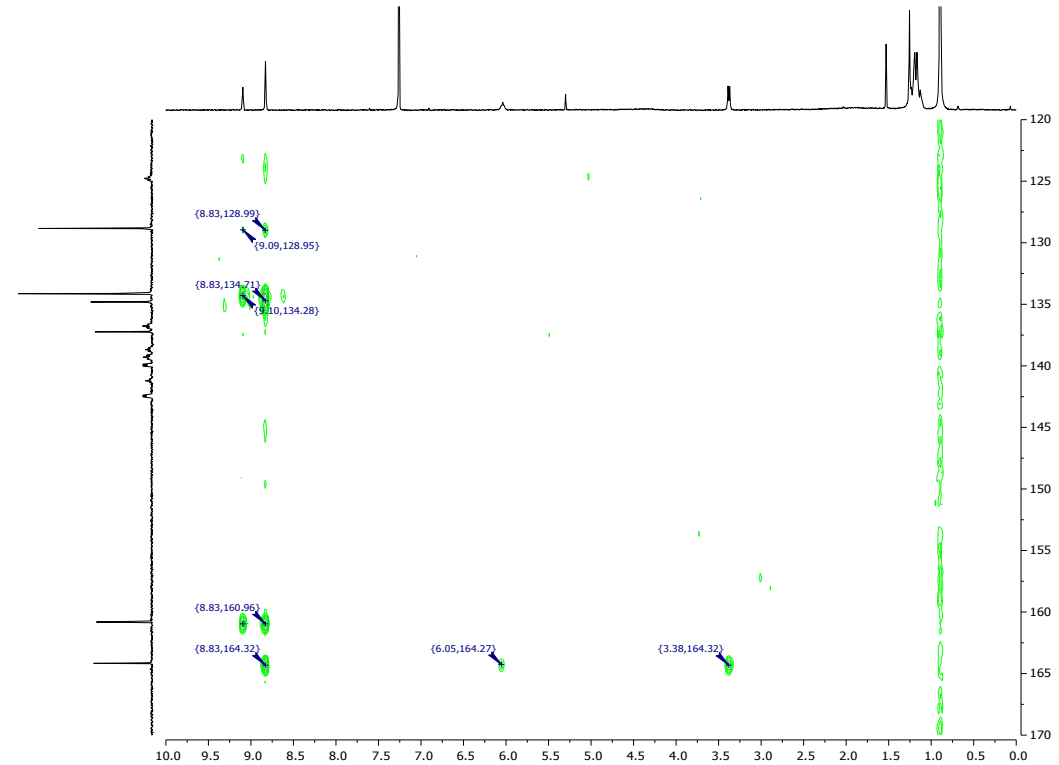


Figure S16. {^{1}H-^{13}C}-HMBC spectrum of **7** in $CDCl_3$, zoomed 170-120 p.p.m..

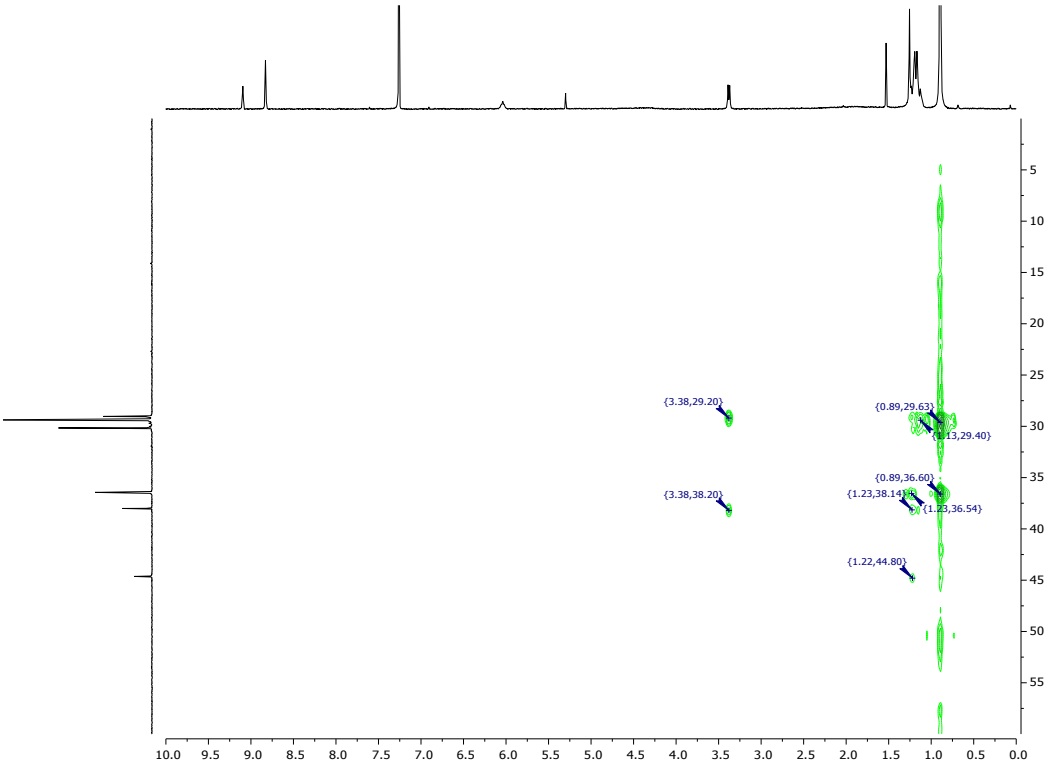
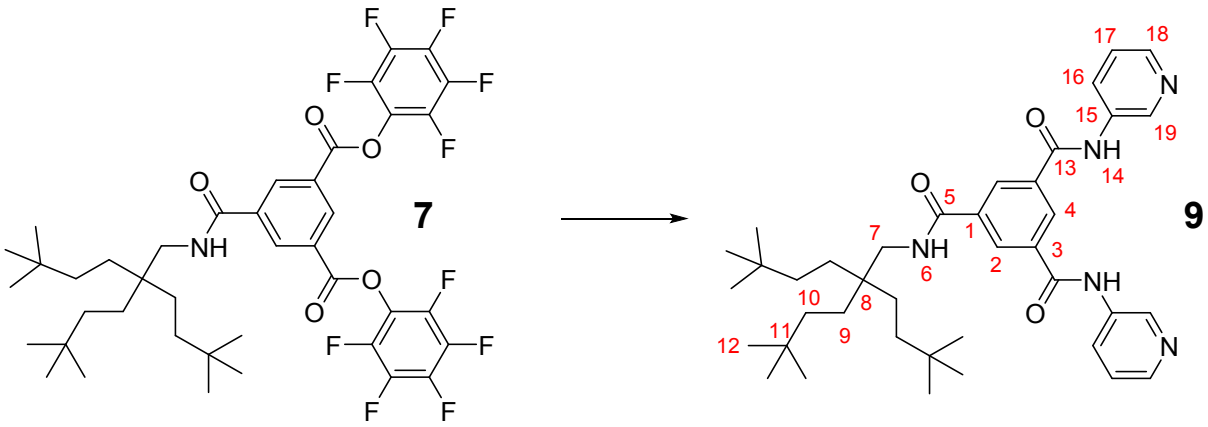


Figure S17. {^{1}H-^{13}C}-HMBC spectrum of **7** in $CDCl_3$, zoomed 60-0 p.p.m..



Bis(3-pyridyl) 9. A suspension of **7** (821 mg, 1.0 mmol, 1 eq.) and 3-aminopyridine (589 mg, 6.26 mmol, 6.3 eq.) in pyridine (20 mL) was heated at 100 °C for 42.5 h. The solvent was evaporated *in vacuo* of the resulting red solution with a solid was co-evaporated thrice with toluene. The residue was then partitioned between DCM and water. The organic layer was extracted thrice with water and then thrice with a mixture of 1:1 conc. ammonia / water. When an unclear separation was observed, some brine was added. The organic layer was then dried over Na_2SO_4, filtrated and evaporated *in vacuo*. Pure product **9** was isolated as an off white/beige solid. Yield: 75%, 0.75 mmol, 483 mg.

See Figure S18 – Figure S26 for NMR spectra: ^{1}H NMR (300 MHz, DMSO-d_6): δ 10.77 (s, 2H, NH, H14), 8.95 (s, 2H, H19), 8.72 – 8.64 (m, 1H, H4), 8.60-8.44 (m, 2H. H2), 8.35 (d, J = 4.6 Hz, 2H, H18), 8.29 – 8.03 (m, 3H, H16/NH, H6), 7.43 (dd, J = 8.4, 4.6 Hz, 2H, H17), 3.18 (d, J = 5.7 Hz, 2H, H7), 1.31 – 0.99 (m, 12H, H9/H10), 0.86 (s, 27H, H12). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ 166.17 (C5), 164.99 (C13), 144.86 (C18), 141.96 (C19), 136.09 (C15), 135.59 (C3), 134.71 (C1), 129.96 (C2), 129,12 (C4), 127.35 (C16), 123.63 (C17), 44.39 (C7), 37.95 (C8), 35.78 (C10), 29.91 (C11), 29.32 (C12), 28.57 (C9). {^{1}H-^{1}H}-COSY (300, 300 MHz, DMSO-d_6): δ 8.95-8.22 (H19-H16), 8.68-8.50 (H4-H2), 8.35-7.43 (H18-H17), 8.22-8.95/7.43/3.18 (H16-H19/H17, NH, H6-H7), 7.43-8.35/8.22 (H17-H18/H16), 3.18-8.22 (NH, H6-H7). {^{1}H-^{13}C}-HSQC (300, 75 MHz, DMSO-d_6): δ 144.86-8.35 (C18-H18), 141.96-8.95 (C19-H19), 129.96-8.50 (C2-H2), 129.12-8.68 (C4-H4), 127.35-8.22 (C16-H16), 123.63-7.43 (C17-H17), 44.39-3.18 (C7-H7), 35.78-1.24 (C10-H10), 29.32-0.86 (C12-H12), 28.57-1.05 (C9-H9). {^{1}H-^{13}C}-HMBC (300, 75 MHz, DMSO-d_6): δ 166.17-8.50 (C5-H2), 164.99-10.77/8.67/8.50 (C13-NH, H14, H4/H2), 37.95-1.18 (C8-H9), 35.78-0.86 (C10-H12), 29.91-0.86 (C11-H12). ^{1}H 2D-DOSY (500 MHz, DMSO-d_6): log (D) = -9.03 m^2/s, with d20 = 0.08 sec and p30 = 500 µsec.

HRMS (FD+): *m/z* calculated for $C_{39}H_{55}N_5O_3$ $[M]^+$ 641.4305, found 641.4325, calculated for $C_{39}H_{56}N_5O_3$ $[M+H]^+$ 642.4383, found 642.4359.

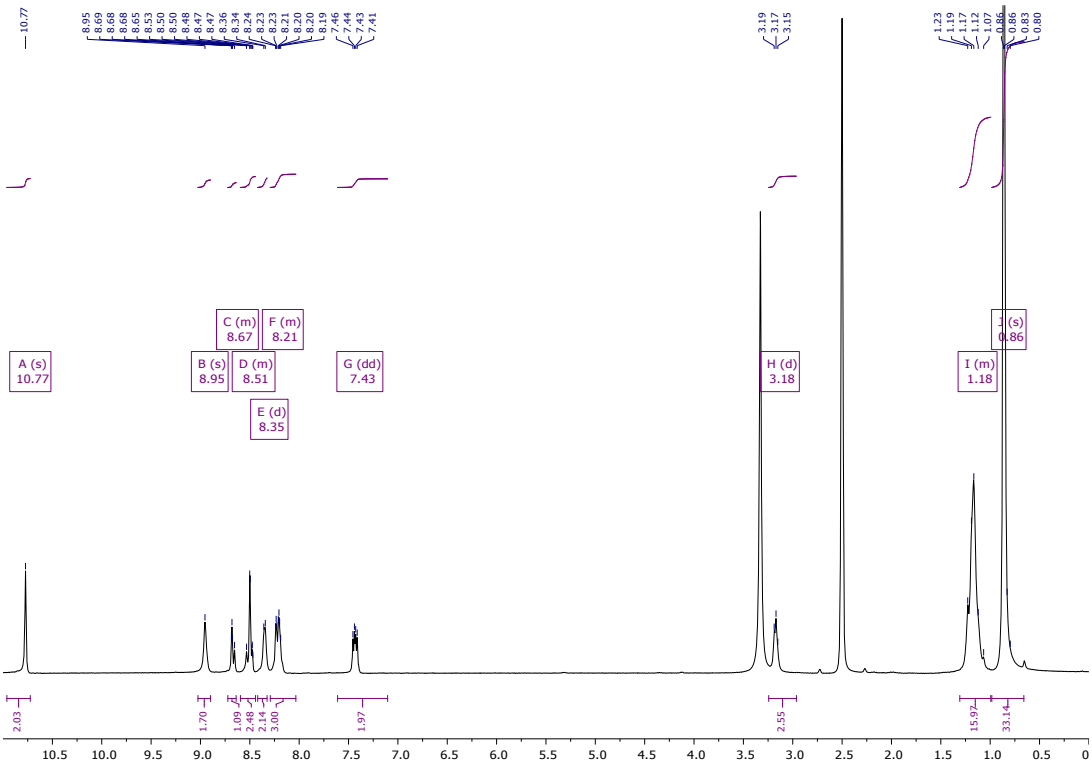


Figure S18. ^{1}H NMR spectrum of **9** in DMSO-d_6.

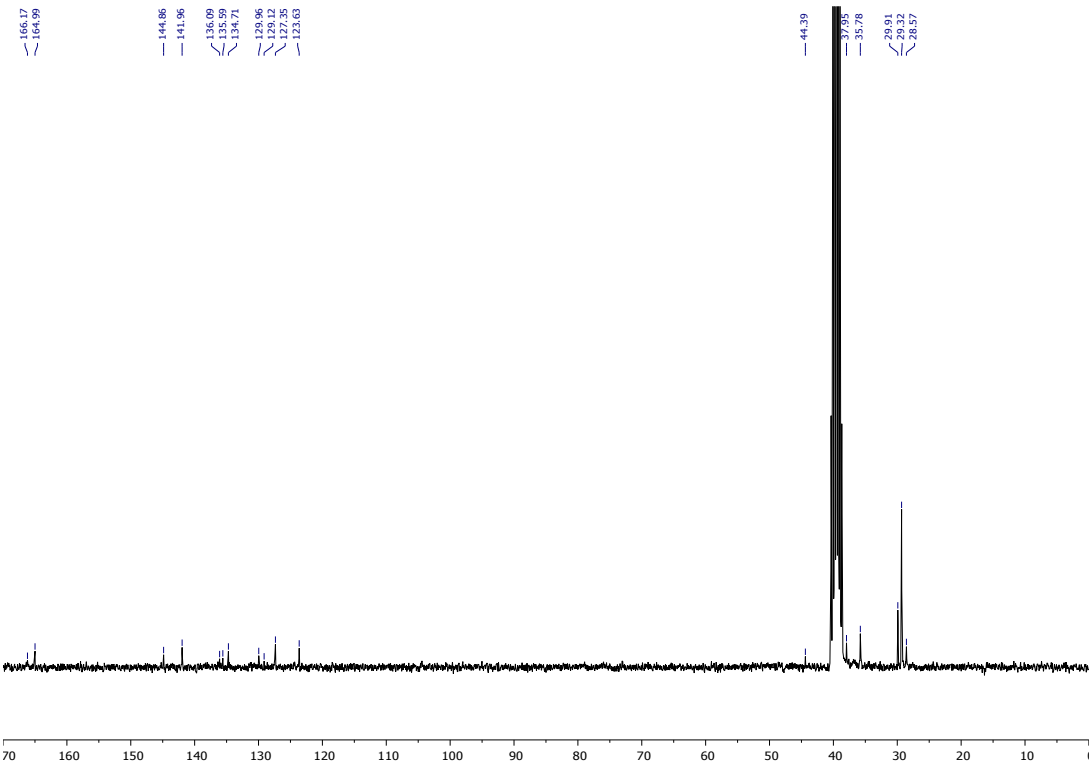


Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum of **9** in DMSO-d_6.

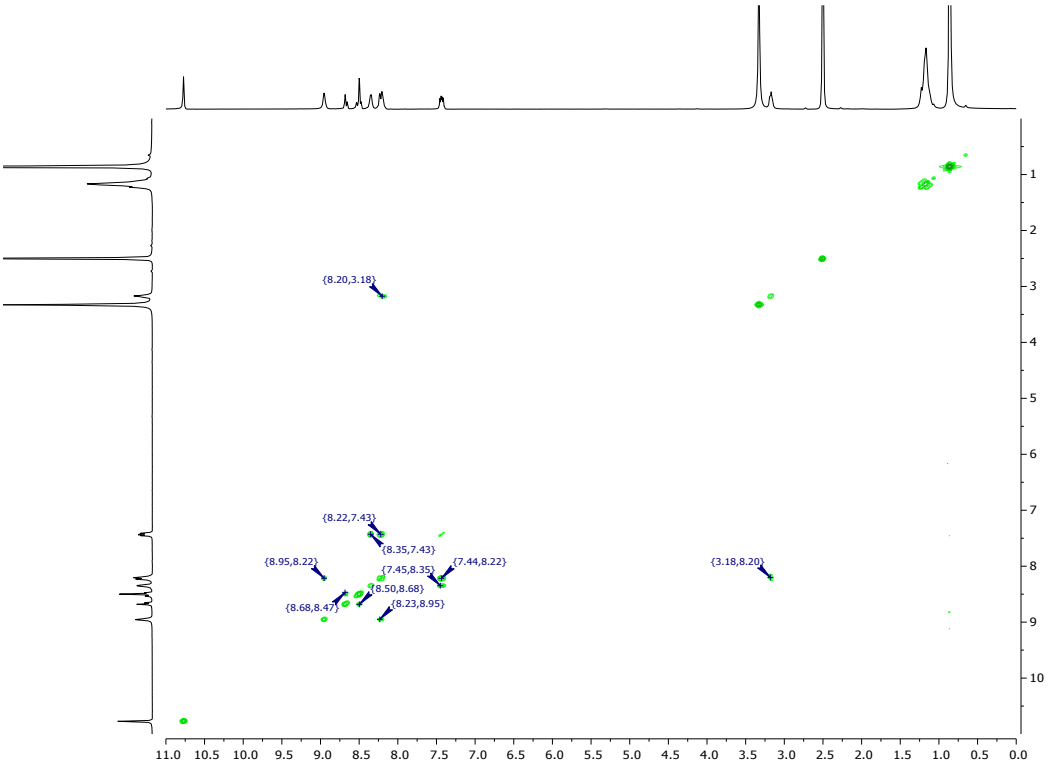


Figure S20. {^{1}H-^{1}H}-COSY spectrum of **9** in DMSO-d_6.

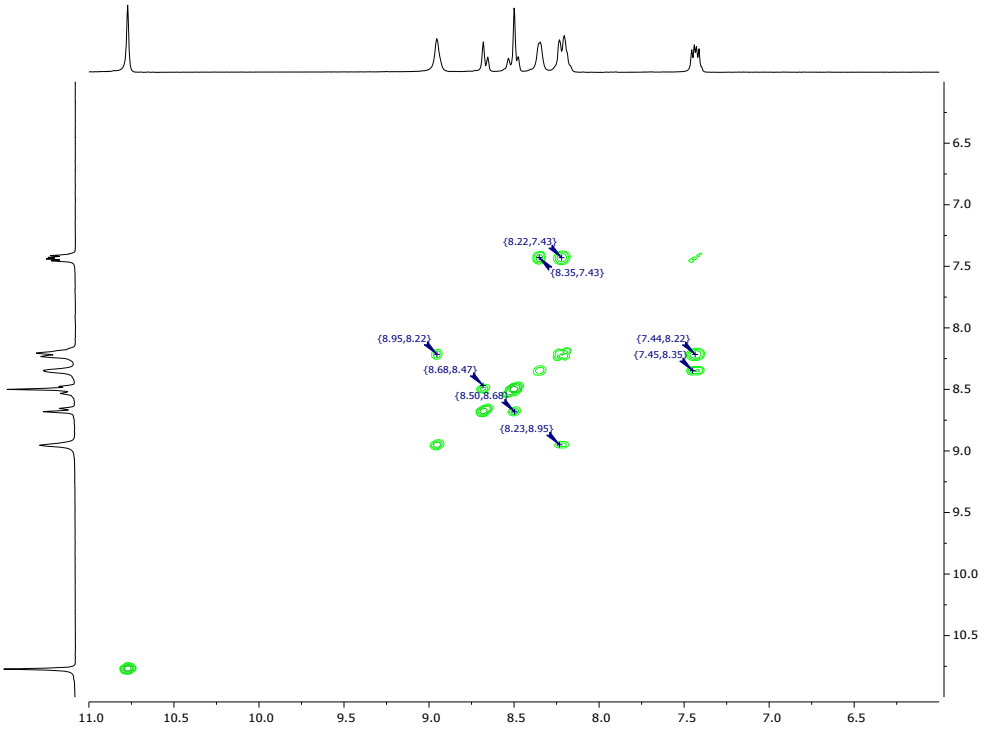


Figure S21. {^{1}H-^{1}H}-COSY spectrum of **9** in DMSO-d_6, zoomed 11-6 p.p.m..

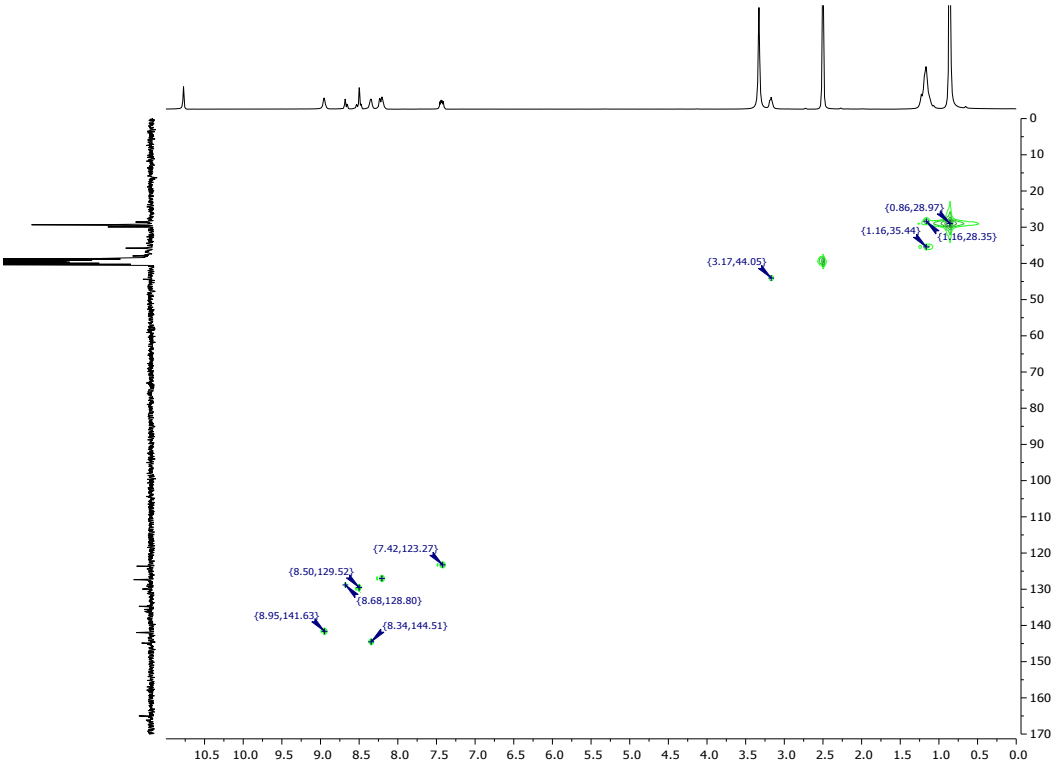


Figure S22. {^{1}H-^{13}C}-HSQC spectrum of **9** in DMSO-d_6.

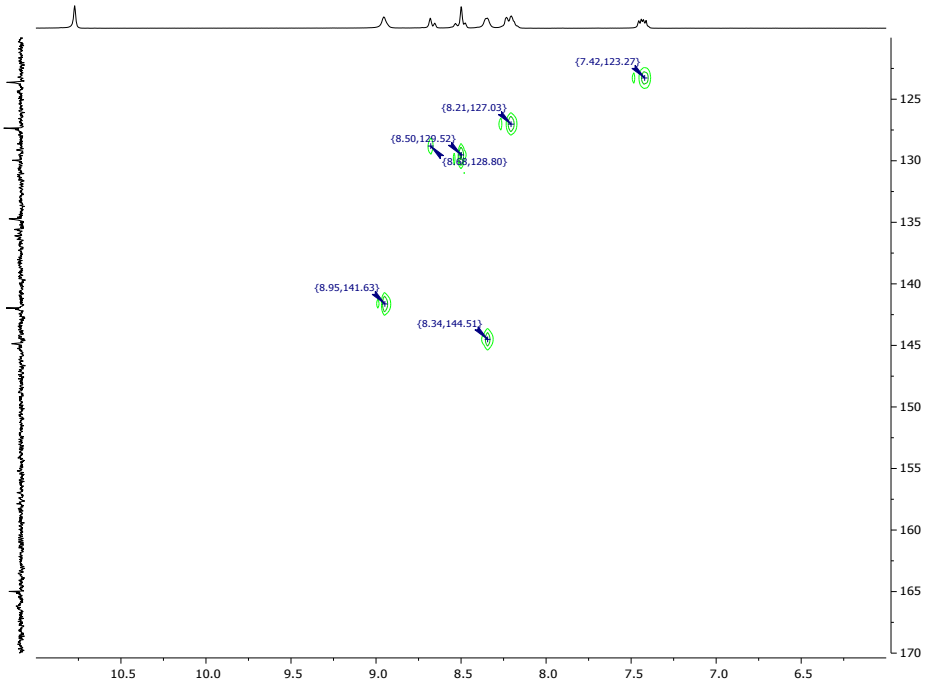


Figure S23. {^{1}H-^{13}C}-HSQC spectrum of **9** in DMSO-d_6, zoomed 170-120 11-6 p.p.m..

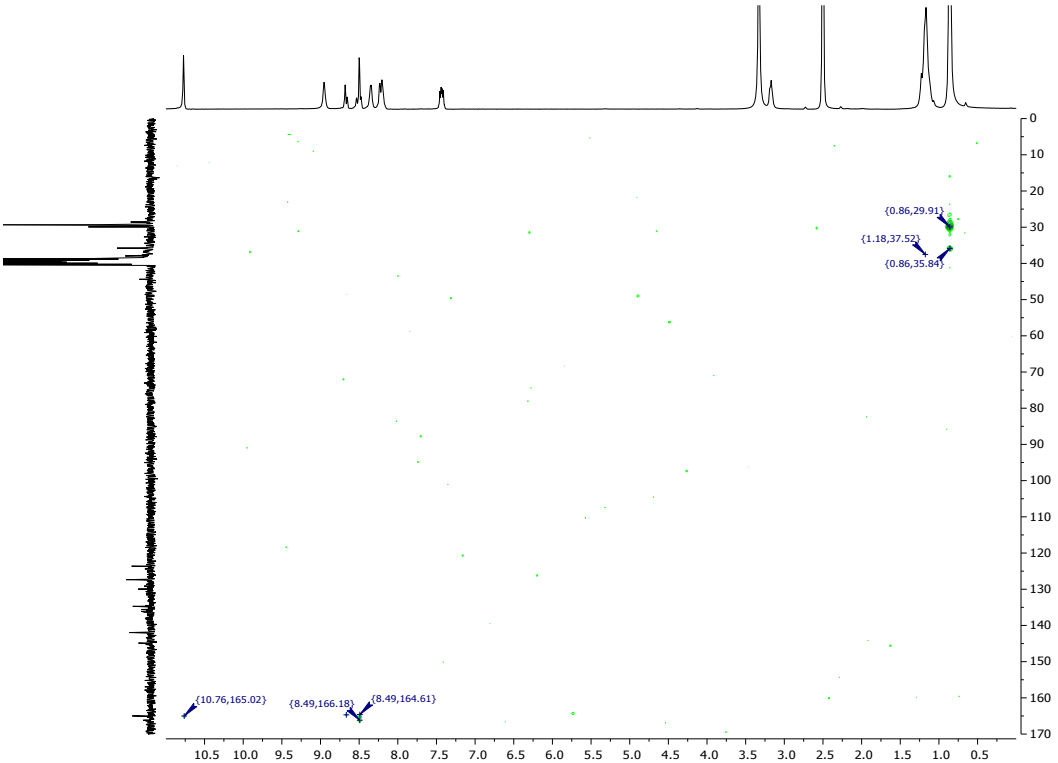


Figure S24. {^{1}H-^{13}C}-HMBC spectrum of **9** in DMSO-d_6.

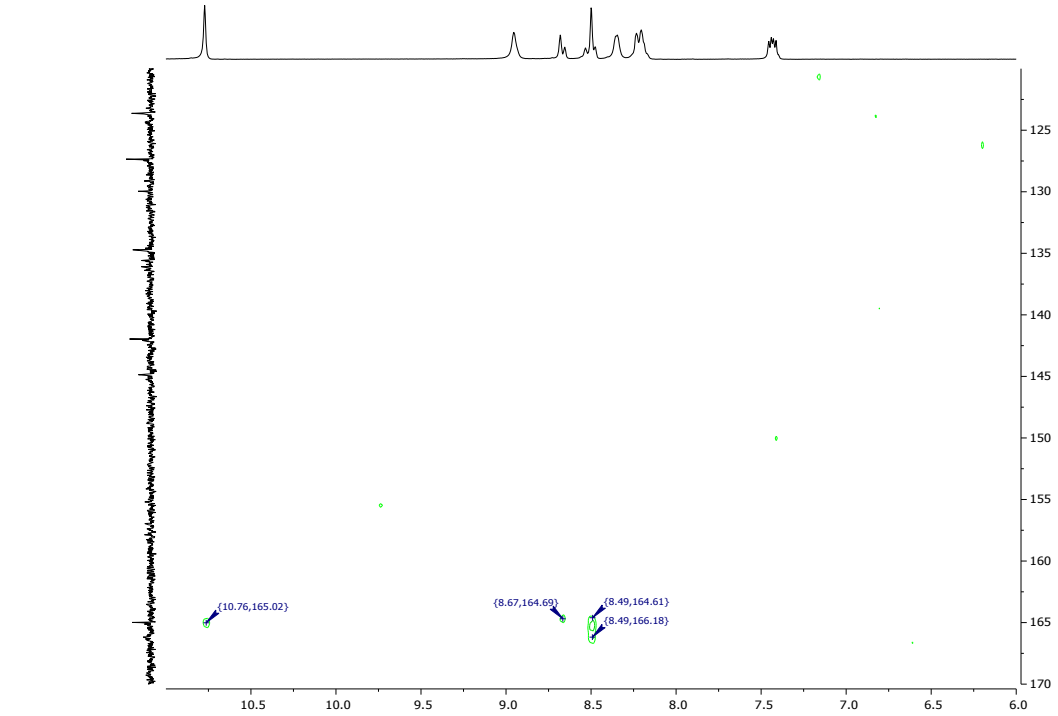


Figure S25. {^{1}H-^{13}C}-HMBC spectrum of **9** in DMSO-d_6, zoomed 170-120 11-6 p.p.m..

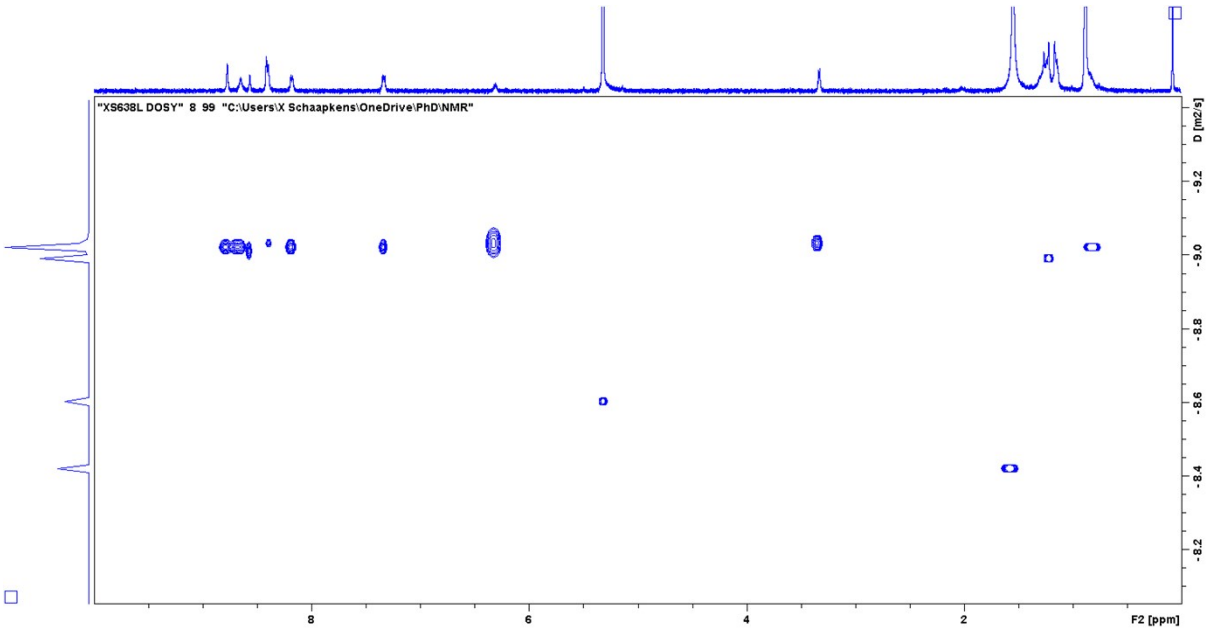
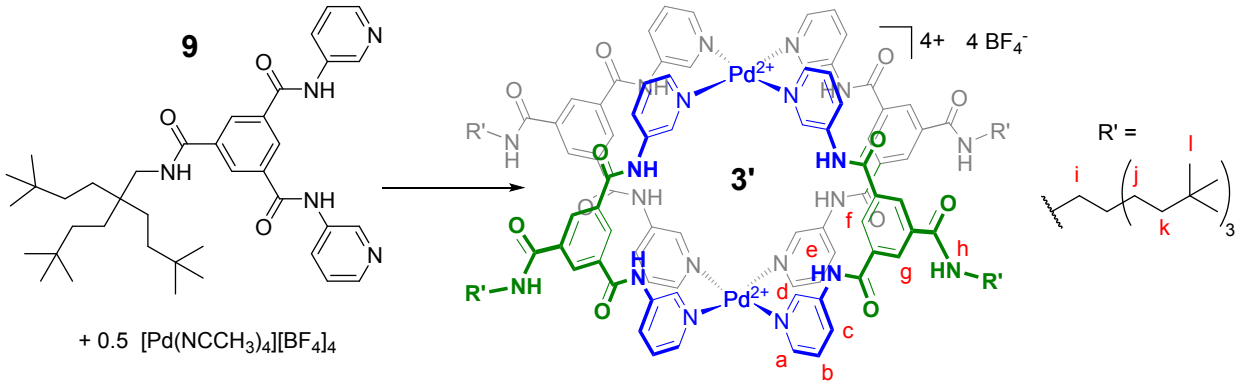


Figure S26. ^{1}H 2D DOSY spectrum of **9** in DMSO-d_6.



[Pd$_2$9$_4$][BF$_4$]$_4$ (3'[BF$_4$]$_4$) in DMSO-d$_6$. To 0.6 mL of a 13.25 µM solution of ligand **9** (7.95 µmol) in DMSO-d$_6$ was added 45 µL of a 98.5 mM solution of [Pd(MeCN)$_4$](BF$_4$)$_2$ in DMSO-d$_6$ in a stepwise fashion (4x10 and 1x5 µL, 4.43 µmol). After each addition a ^{1}H NMR spectrum was recorded (see Figure S27). This study revealed formation of one major species, consistent with **3'** already after addition of 40 µL (3.94 µmol Pd^{2+}, 0.5 eq. on **9**). The major species became even more pronounced when heated to 80 °C and **3'** could be characterized at this temperature with various NMR measurements (see also Figure S29 for a VT study).

See Figure S27 and Figure S28 for NMR spectra at room temperature: ^{1}H NMR (500 MHz, 298 K, DMSO-d$_6$): δ 11.23 (s, 8H, H$_e$), 9.69 (s, 8H, H$_d$), 8.90 (d, J = 5.5 Hz, 8H, H$_a$), 8.70 (s, 4H, H$_f$), 8.57 (s, 8H, H$_g$), 8.54 (d, J = 8.9 Hz, 8H, H$_c$), 8.18 (s, 4H, H$_h$), 7.79 (dd, J = 8.6, 5.6 Hz, 8H, H$_b$), 3.22-3.04 (m, 8H, H$_i$), 1.35-0.94 (m, 48H, H$_j$/H$_k$), 0.90-0.75 (m, 108H, H$_l$). ^{1}H 2D-DOSY (500 MHz, 298 K, DMSO-d$_6$): log (*D*) = -9.88 m^2/s, with d20 = 0.20 sec and p30 = 1000 µsec.

See Figure S29 – Figure S37 for NMR spectra at 80 °C: ^{1}H NMR (500 MHz, 353 K, DMSO-d$_6$): δ 11.07 (s, 8H, H$_e$), 9.70 (s, 8H, H$_d$), 8.91 (d, J = 5.6 Hz, 8H, H$_a$), 8.73 (s, 4H, H$_f$), 8.56 (s, 8H, H$_g$), 8.52 (d, J = 8.6 Hz, 8H, H$_c$), 7.90 (t, J = 5.5 Hz, 4H, H$_h$), 7.78 (dd, J = 8.5, 5.7 Hz, 8H, H$_b$), 3.27-3.16 (m, 8H, H$_i$), 1.29-1.03 (m, 48H, H$_j$/H$_k$), 0.93-0.73 (m, 108H, H$_l$). ^{13}C{^{1}H} NMR (125 MHz, 353 K, DMSO-d$_6$): δ 164.55 (C13), 146.06 (C$_a$), 141.49 (C$_d$), 137.83 (C15), 130.68 (C$_c$), 129.92 (C$_f$, C$_g$), 127.06 (C$_b$), 44.64 (C$_i$), 37.54 (C8), 35.62 (C$_k$), 29.43 (C11), 28.86 (C$_l$), 28.54 (C$_j$). {^{1}H-^{1}H}-COSY (500, 500 MHz, 353 K, DMSO-d$_6$): δ 9.70-11.07/8.52 (H$_d$-H$_e$/H$_c$), 8.91-8.52/7.78 (H$_a$-H$_c$/H$_b$), 8.73-11.07/8.56 (H$_f$-H$_e$/H$_g$), 8.56-11.07/8.73 (H$_g$-H$_e$/H$_f$), 8.52-9.70/8.91/7.78 (H$_c$-H$_d$/H$_a$H$_b$), 7.90-3.18 (H$_h$-H$_i$), 7.78-8.91/8.52 (H$_b$-H$_a$/H$_c$), 3.18-7.90 (H$_i$-H$_h$). {^{1}H-^{13}C}-HSQC (500, 125 MHz, 353 K, DMSO-d$_6$): δ 146.06-8.91 (C$_a$-H$_a$), 141.49-9.70 (C$_d$-H$_d$), 130.68-8.52 (C$_c$-H$_c$), 129.92-8.73/8.56 (C$_f$-H$_f$, C$_g$-H$_g$), 127.06-7.78 (C$_b$-H$_b$), 44.64-3.18 (C$_i$-H$_i$), 35.62-1.18 (C$_k$-H$_k$), 28.86-0.84 (C$_l$-H$_l$), 28.54-1.13 (C$_j$-H$_j$). {^{1}H-^{13}C}-HMBC (500, 125 MHz, 353 K, DMSO-d$_6$): δ 165.12-8.56/7.90/3.18 (C5-H$_g$/H$_h$/H$_i$), 164.55-11.07/8.73/8.56 (C13-H$_e$/H$_f$/H$_g$), 146.06-9.70/8.52/7.90 (C$_a$-H$_d$/H$_c$/H$_b$), 145.99-8.73/8.56 (C1/C3-H$_f$/H$_g$), 141.49-11.07/8.91/8.52 (C$_d$-H$_e$/H$_a$/H$_c$), 137.83-9.70/8.52/7.78 (C15-H$_d$/H$_c$/H$_a$), 130.68-11.07/9.70/8.91 (C$_c$-H$_e$/H$_d$/H$_a$), 129.92-8.73/8.56 (C$_f$/C$_g$-H$_f$/H$_g$), 127.06-8.91 (C$_b$-H$_a$), 44.64-1.19 (C$_i$-H$_j$), 37.54-3.18/1.19 (C8-H$_i$/H$_k$), 35.62-1.19/0.84 (C$_k$-H$_j$/H$_l$), 29.43-0.84 (C11-H$_l$), 28.54-3.18/1.14 (C$_j$-H$_i$/H$_k$). ^{1}H 2D-DOSY (500 MHz, 353 K, DMSO-d$_6$): log (*D*) = -8.90 m^2/s, with d20 = 0.15 sec and p30 = 500 µsec.

CSI HRMS (see Figure S39 – Figure S42 for full isotope distributions): m/z calculated for [(C$_{39}$H$_{55}$N$_5$O$_3$)$_4$Pd$_2$]$^{4+}$ [M]$^{4+}$ 694.8832, found 694.8949 (Δ = 16.84); calculated for [(C$_{39}$H$_{55}$N$_5$O$_3$)$_4$Pd$_2$(C$_2$H$_6$SO)]$^{4+}$ [M+C$_2$H$_6$SO]$^{4+}$ 714.3867, found 714.3987 (Δ = 16.80); calculated for [(C$_{39}$H$_{55}$N$_5$O$_3$)$_4$Pd$_2$(C$_2$H$_6$SO)$_2$]$^{4+}$ [M+(C$_2$H$_6$SO)$_2$]$^{4+}$ 733.8902, found 733.9025 (Δ = 16.76); calculated for [(C$_{39}$H$_{55}$N$_5$O$_3$)$_4$Pd$_2$(BF$_4$)]$^{3+}$ [M]$^{3+}$ 955.5124, found 955.5281 (Δ = 16.43).

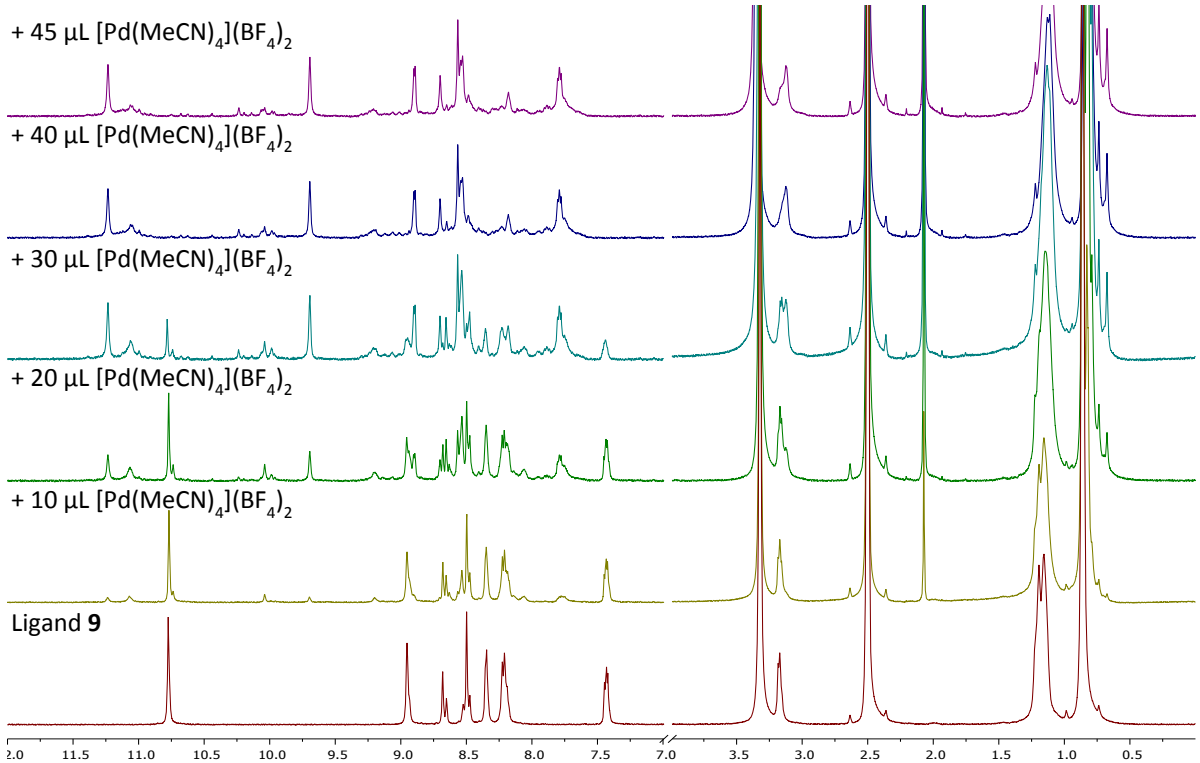


Figure S27. ^{1}H NMR of stepwise formation of the **3'**$[BF_4]_4$ in DMSO-d_6. See Figure S29 for a VT study.

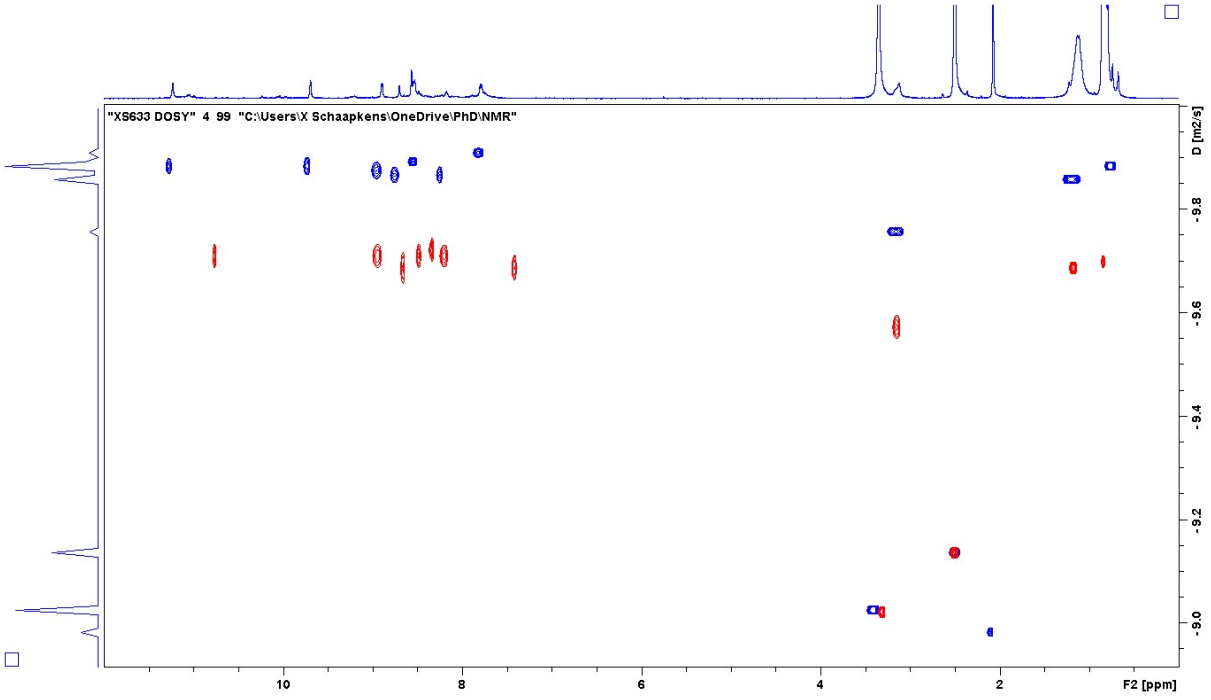


Figure S28. ^{1}H 2D DOSY spectrum of **3'**$[BF_4]_4$ (blue) and ligand **9** (red) in DMSO-d_6.

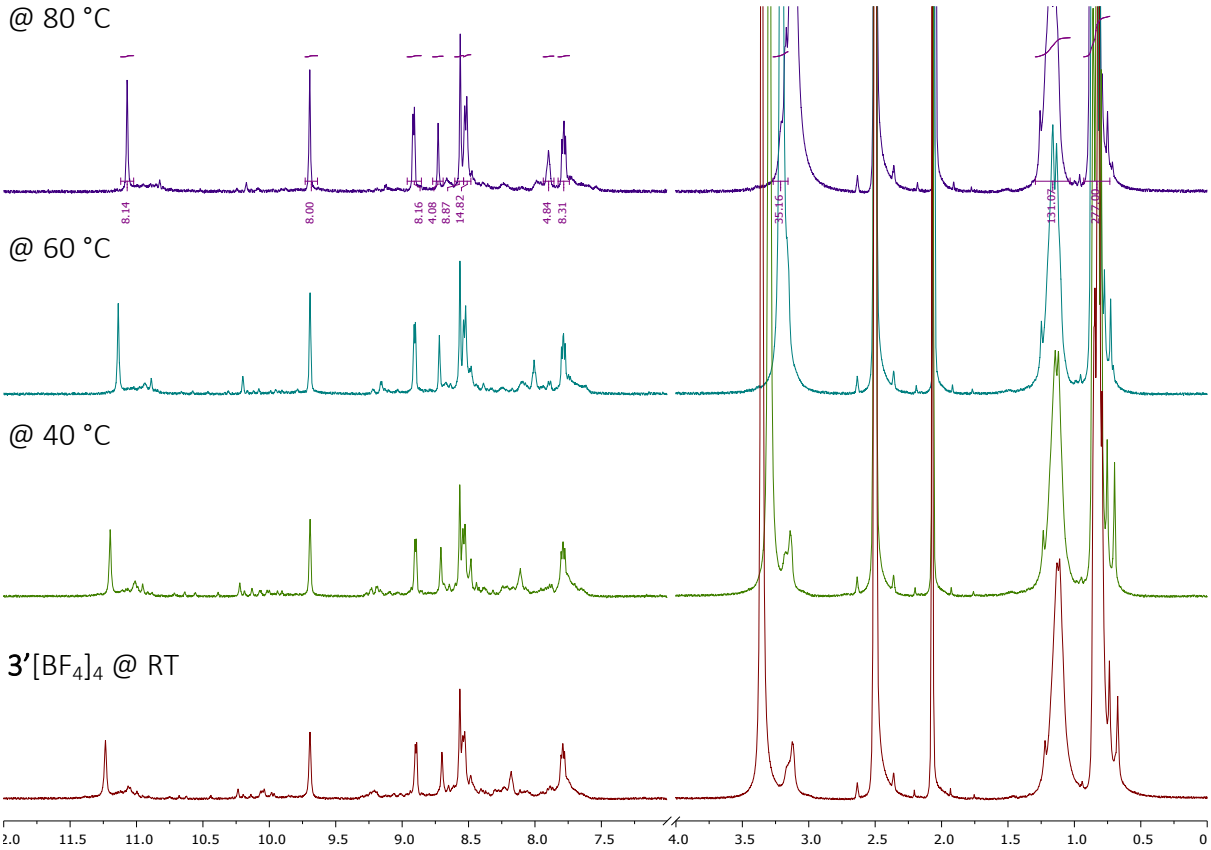


Figure S29. ^{1}H NMR of stepwise heating of **3'**$[BF_4]_4$ in DMSO-d_6 (see Figure S27 for complex formation).

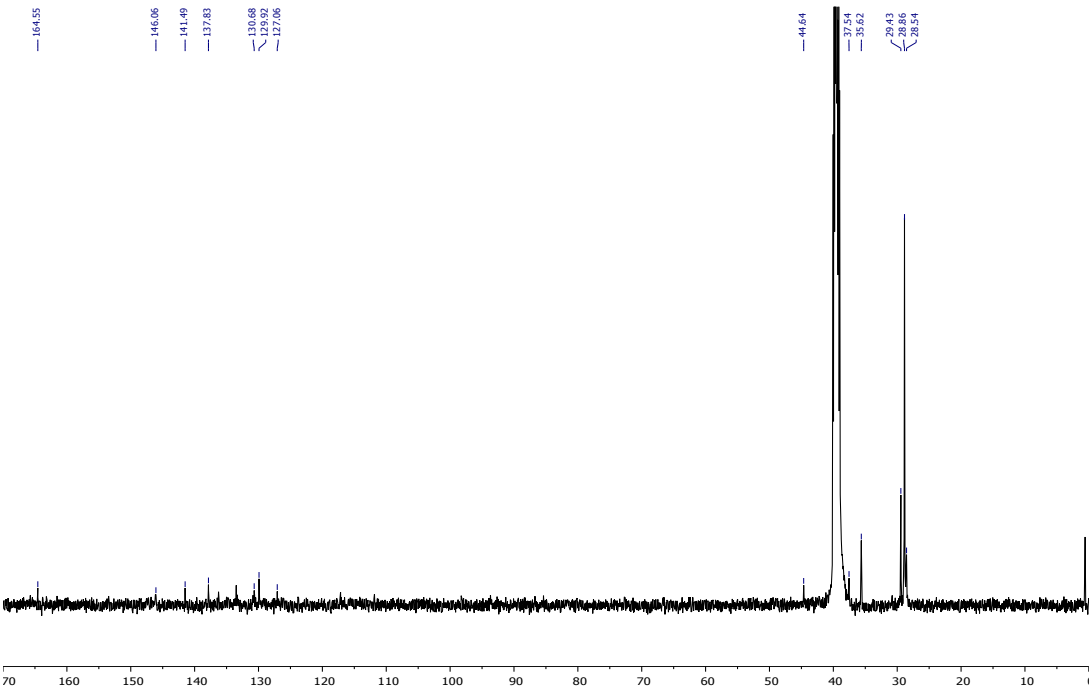


Figure S30. $^{13}C\{^{1}H\}$ NMR spectrum of **3'**$[BF_4]_4$ complex in DMSO-d_6 at 80 °C.

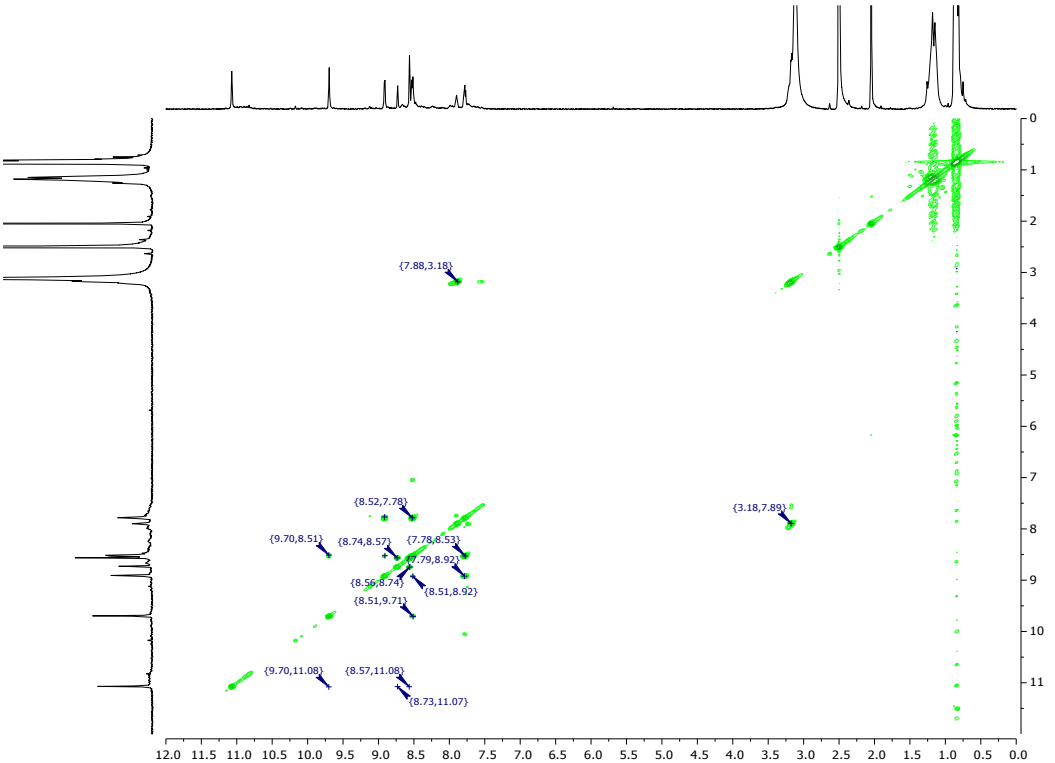


Figure S31. {^{1}H-^{1}H}-COSY s spectrum of **3'**$[BF_4]_4$ complex in DMSO-d_6 at 80 °C.

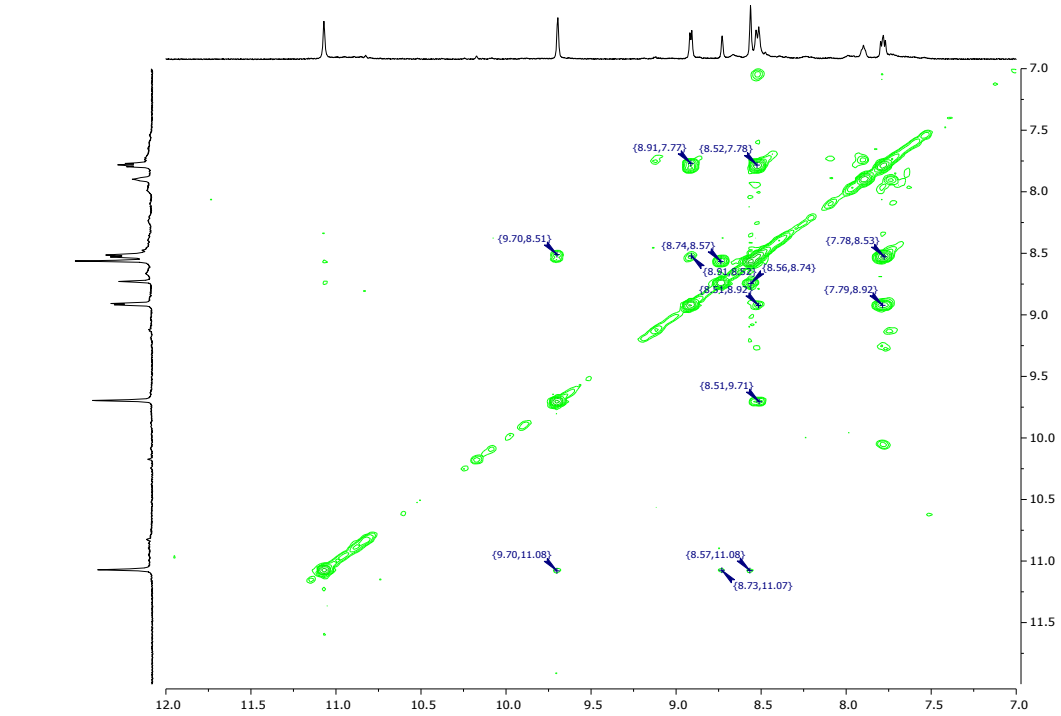


Figure S32. Partial {^{1}H-^{1}H}-COSY spectrum of **3'**$[BF_4]_4$ complex in DMSO-d_6 at 80 °C.

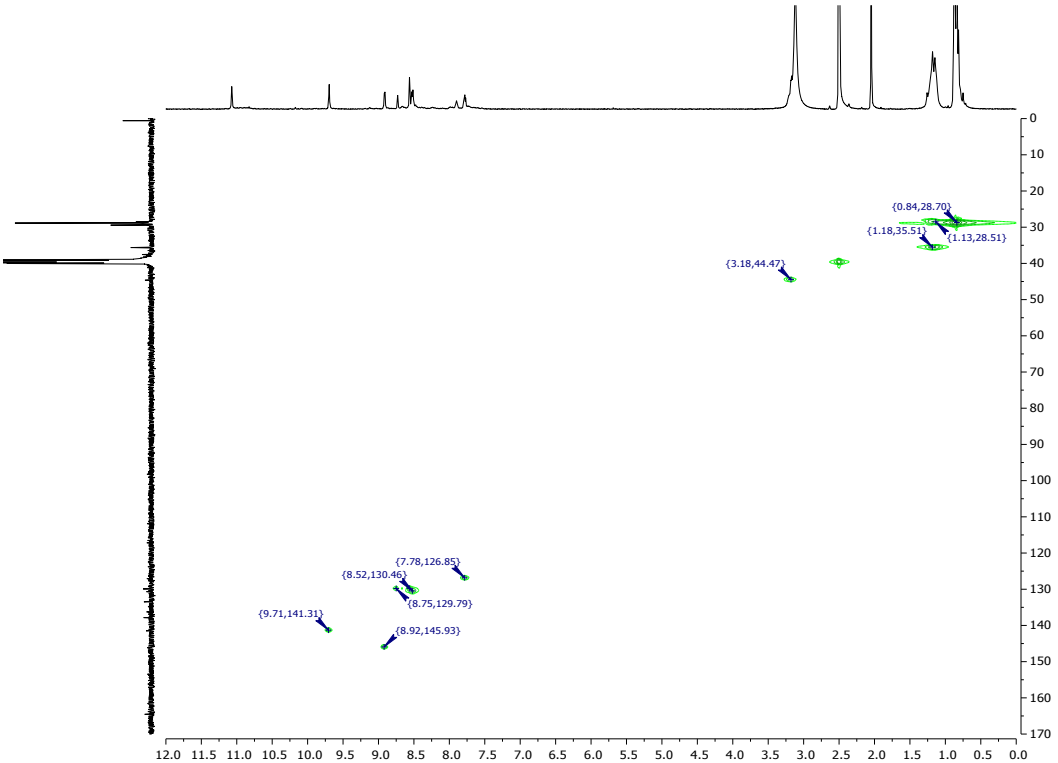


Figure S33. {^{1}H-^{13}C}-HSQC spectrum of **3'**$[BF_4]_4$ complex in DMSO-d_6 at 80 °C.

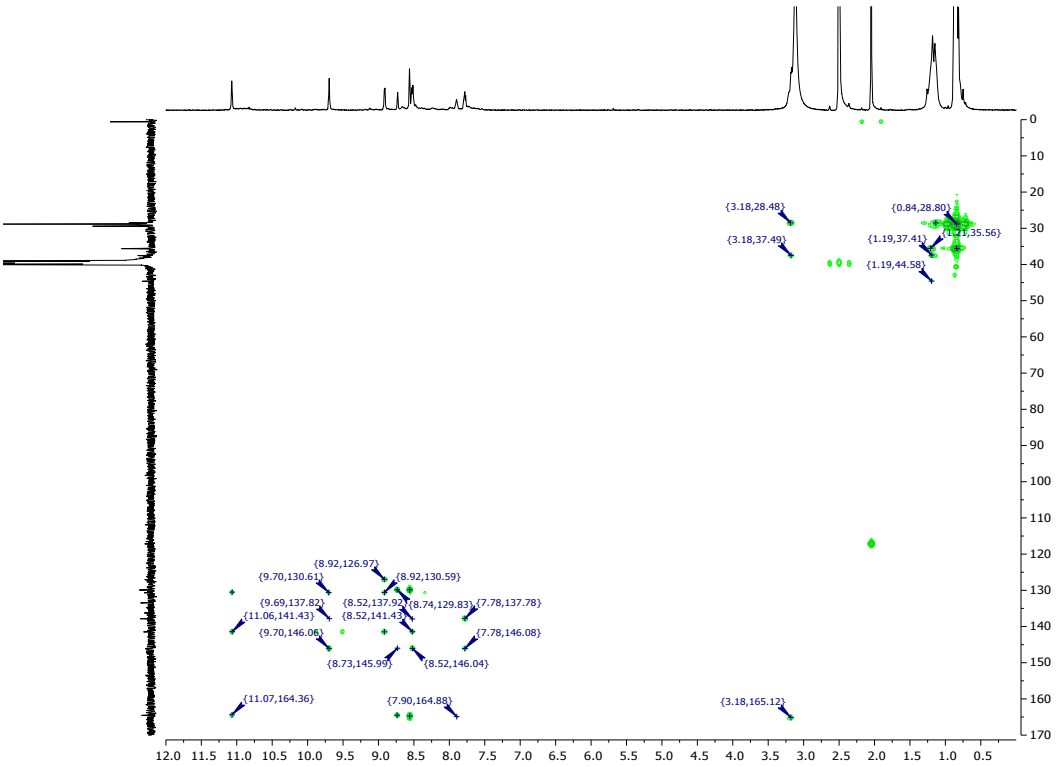


Figure S34. {^{1}H-^{13}C}-HMBC s spectrum of **3'**$[BF_4]_4$ complex in DMSO-d_6 at 80 °C.

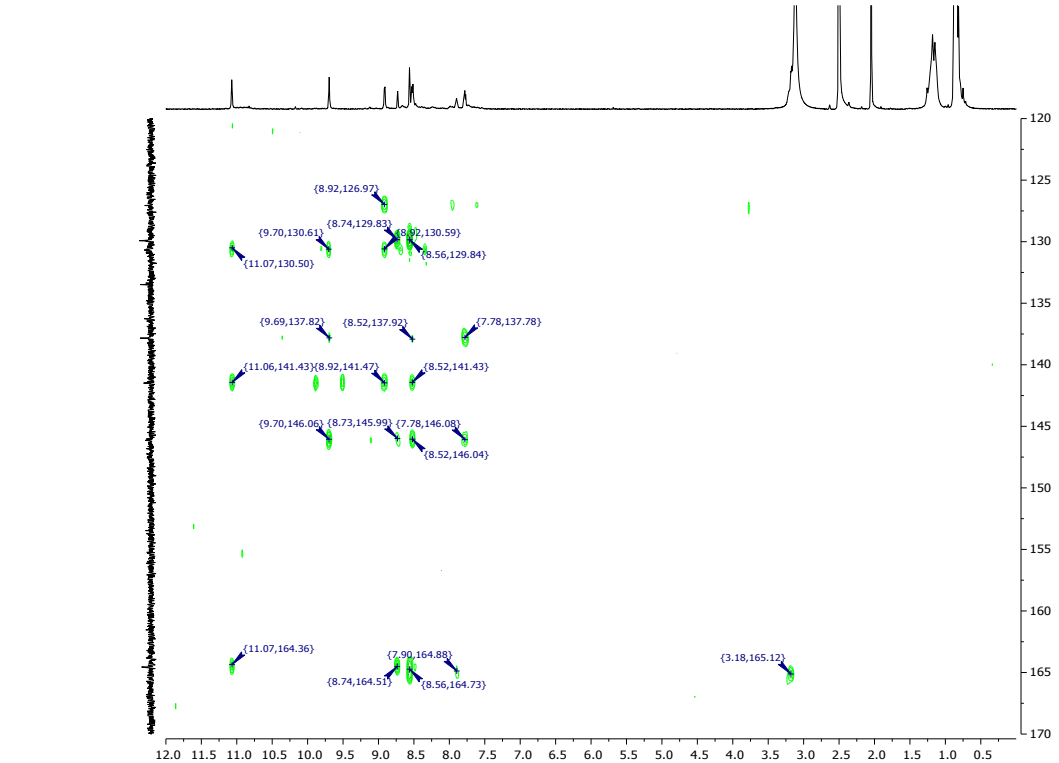


Figure S35. Partial {^{1}H-^{13}C}-HMBC s spectrum of **3'**$[BF_4]_4$ complex in DMSO-d_6 at 80 °C.

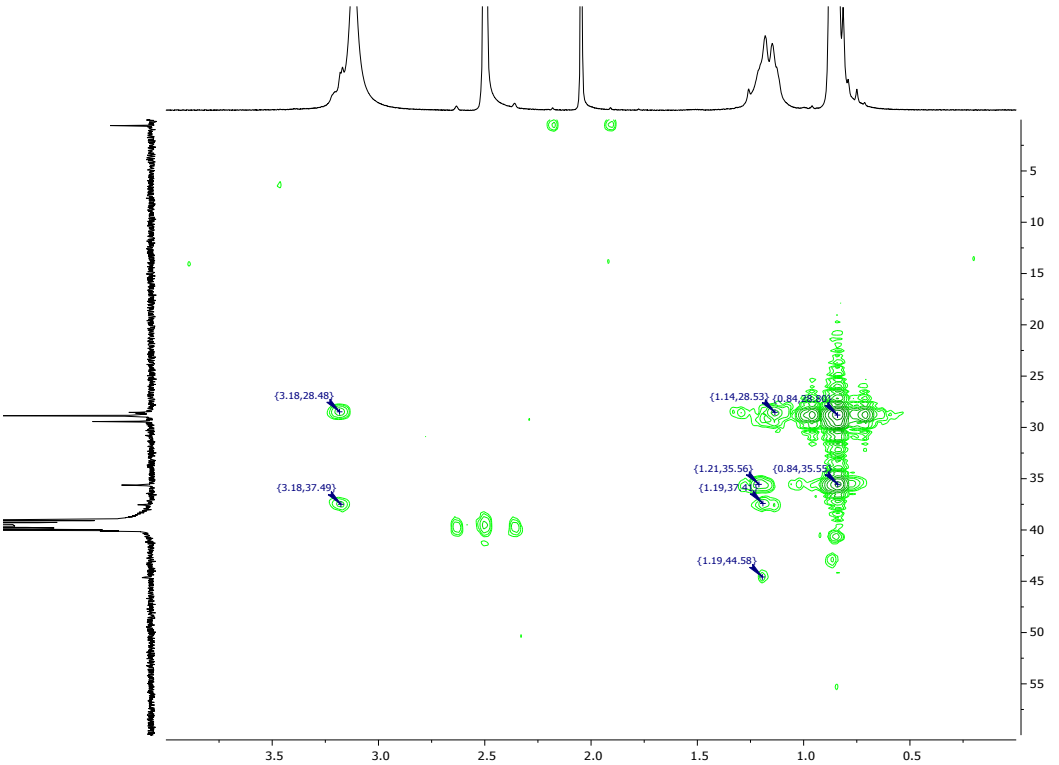


Figure S36. Partial {^{1}H-^{13}C}-HMBC spectrum of **3'**$[BF_4]_4$ complex in DMSO-d_6 at 80 °C.

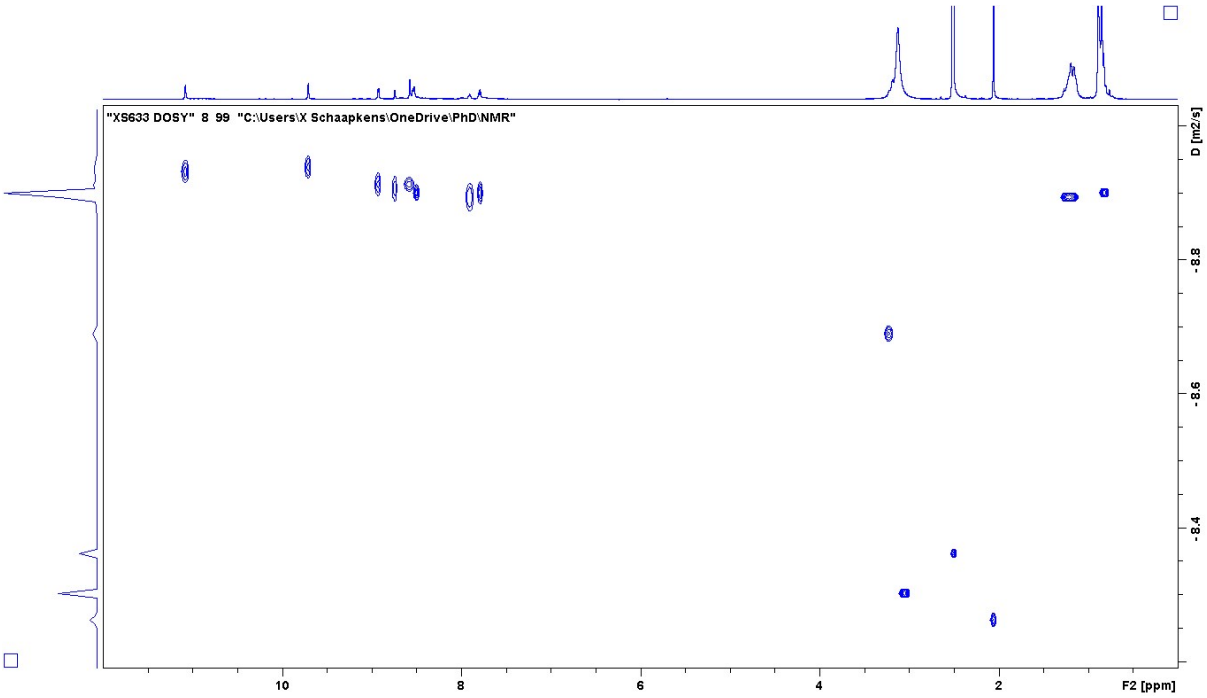


Figure S37. ^{1}H 2D DOSY s spectrum of **3'**$[BF_4]_4$ complex in DMSO-d_6 at 80 °C.

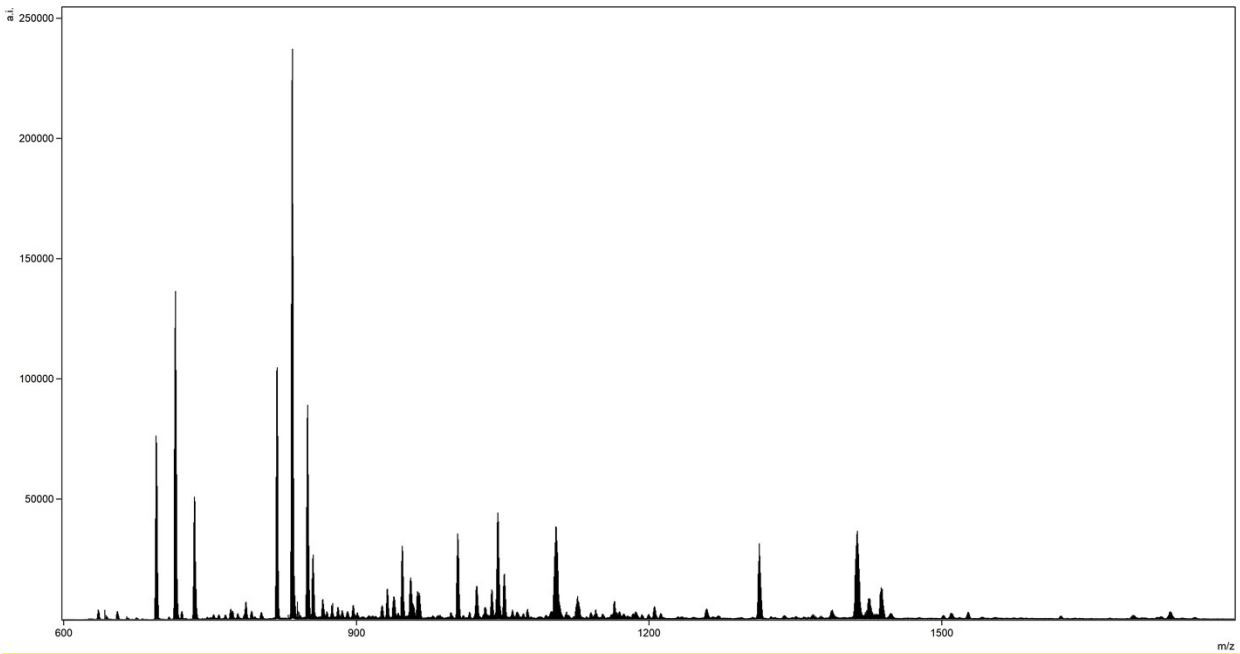


Figure S38. Full CSI HRMS of $[(C_{39}H_{55}N_5O_3)_4Pd_2](BF_4)_4$ form DMSO. See Figure S39–Figure S42 for representative fits to specific atomic stoichiometries.

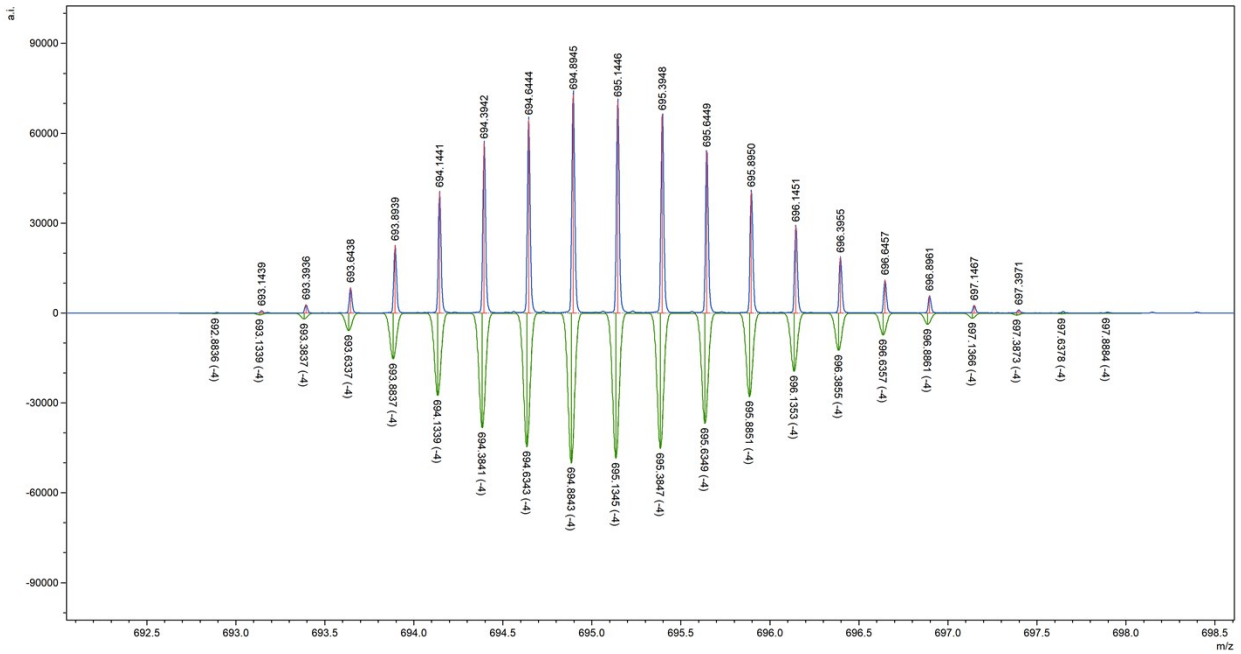


Figure S39. CSI HRMS of $[(C_{39}H_{55}N_5O_3)_4Pd_2]^{4+}$ (top) and calculated spectrum (bottom) around 695 *m*/*z*.

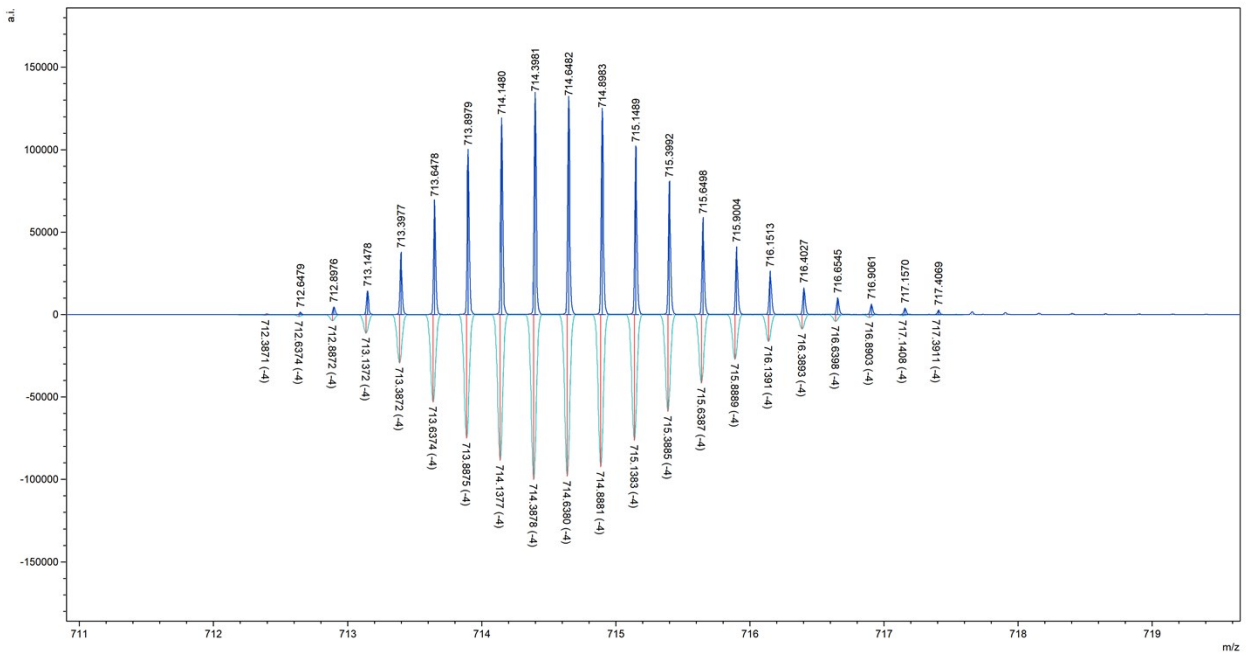


Figure S40. CSI HRMS of $[(C_{39}H_{55}N_5O_3)_4Pd_2(C_2H_6SO)]^{4+}$ (top) and calculated spectrum (bottom) around 714 *m*/*z*.

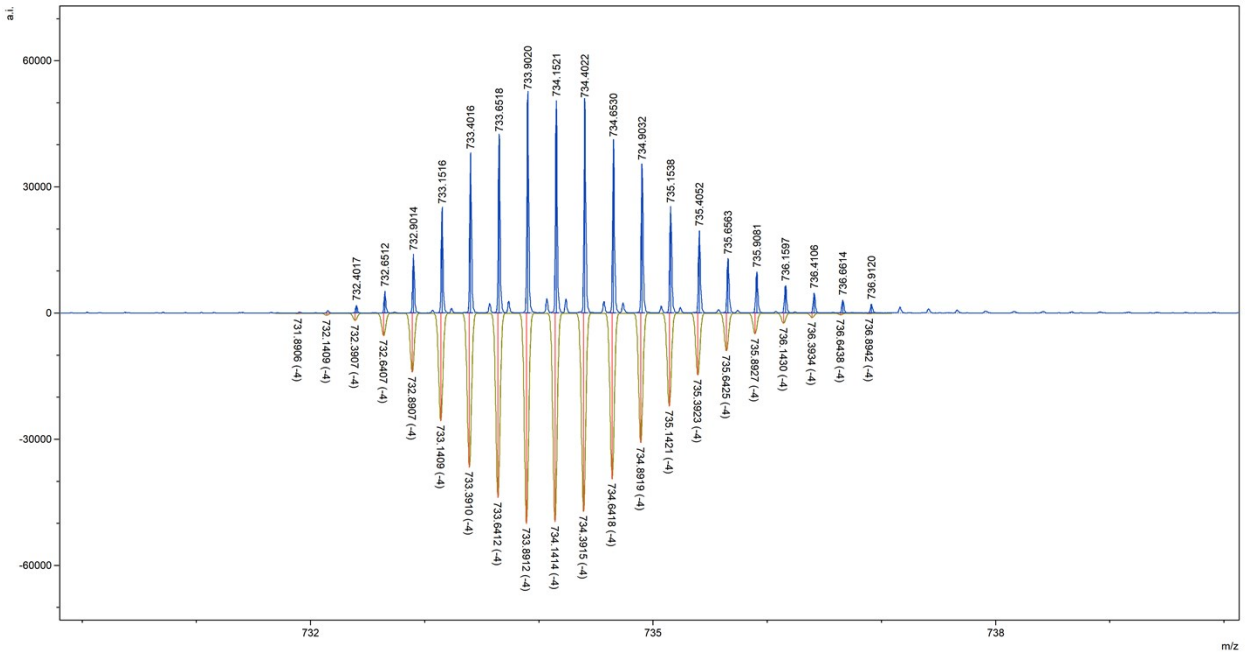


Figure S41. CSI HRMS of $[(C_{39}H_{55}N_5O_3)_4Pd_2(C_2H_6SO)_2]^{4+}$ (top) and calculated spectrum (bottom) around 734 *m*/*z*.

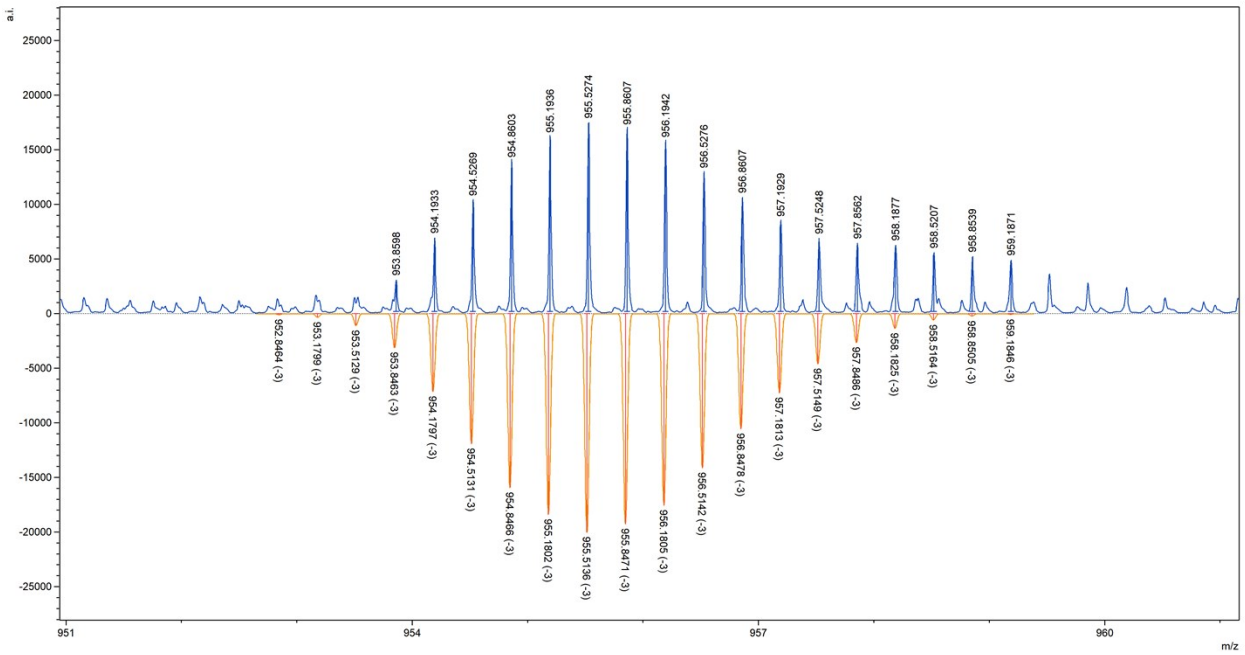
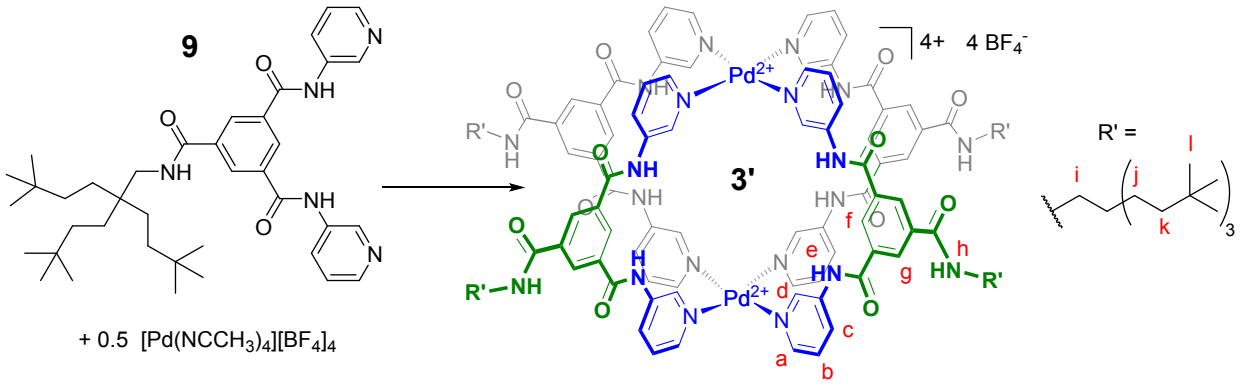


Figure S42. CSI HRMS of $[(C_{39}H_{55}N_5O_3)_4Pd_2(BF_4)]^{3+}$ (top) and calculated spectrum (bottom) at 956 *m*/*z*.



[$Pd_2$9$_4$][BF_4]$_4$ (3'[BF_4]$_4$) in CD_2Cl_2/DMSO-d_6 (9:1). To 0.6 mL of a 13.33 µM solution of ligand **9** (8.0 µmol) in CD_2Cl_2/DMSO-d_6 (9:1) was added a 44 µL of a 100 mM solution of $[Pd(MeCN)_4](BF_4)_2$ in DMSO-d_6 in a stepwise fashion (4x10 and 1x4 µL, 4.4 µmol). After each addition a ^{1}H NMR spectrum was recorded (see Figure S43 and also Figure 2). This study revealed formation of one major species, consistent with **3'** already after addition of 40 µL (4.0 µmol Pd^{2+}, 0.5 eq. on **9**). The major species became even more pronounced after 30 minutes of sonication (used for titration experiments, see

).

See Figure S43 – Figure S48 for NMR spectra: ^{1}H NMR (500 MHz, CD_2Cl_2/DMSO-d_6 (9:1)): δ 10.61 (s, 8H, H_e), 9.87 (s, 8H, H_d), 9.09 (d, J = 5.6 Hz, 8H, H_a), 8.99 (s, 4H, H_f), 8.57 (s, 8H, H_g), 8.52 (d, J = 8.7 Hz, 8H, H_c), 7.53 (dd, J = 8.5, 5.6 Hz, 8H, H_d), 6.79 (t, J = 5.9 Hz, 4H, H_h), 3.22 (d, J = 6.0 Hz, 8H, H_i), 1.27 – 0.99 (m, 48H, H_j/H_k), 0.90 – 0.67 (m, 108H, H_l). ^{11}B NMR (128 MHz, CD_2Cl_2/DMSO-d_6 (9:1)): δ -0.76 (s). ^{19}F NMR (376 MHz, CD_2Cl_2/DMSO-d_6 (9:1)): δ -149.19 (d, J = 20.0 Hz). ^{1}H 2D-DOSY (500 MHz, CD_2Cl_2/DMSO-d_6 (9:1)): log (D) = -9.42 m^2/s, with d20 = 0.12 sec and p30 = 750 µsec. {^{1}H-^{19}F}-HOESY (300, 282 MHz, CD_2Cl_2/DMSO-d_6 (9:1)): δ -149.19-10.61/9.87/9.09/8.99 (F-H_e/H_d/H_a/H_f), with t_m = 500 ms.

CSI HRMS (see Figure S50 – Figure S52 for full isotope distributions): m/z calculated for $[(C_{39}H_{55}N_5O_3)_4Pd_2]^{4+}$ $[M]^{4+}$ 694.8832, found 694.8864 (Δ = 4.61); calculated for $[(C_{39}H_{55}N_5O_3)_4Pd_2(BF_4)]^{3+}$ $[M]^{3+}$ 955.5179, found 955.5179 (Δ = 5.76); calculated for $[(C_{39}H_{55}N_5O_3)_4Pd_2(BF_4)(CH_2Cl_2)_2]^{3+}$ $[M+(CH_2Cl_2)_2]^{3+}$ 983.8299, found 983.8544 (Δ = 24.90); calculated for $[(C_{39}H_{55}N_5O_3)_4Pd_2(BF_4)_2(CH_2Cl_2)(CH_3CN)(H_2O)]^{2+}$ $[M+ (CH_2Cl_2) + (CH_3CN) + (H_2O)]^{2+}$ 1549.7718, found 1549.7619 (Δ = 6.39).

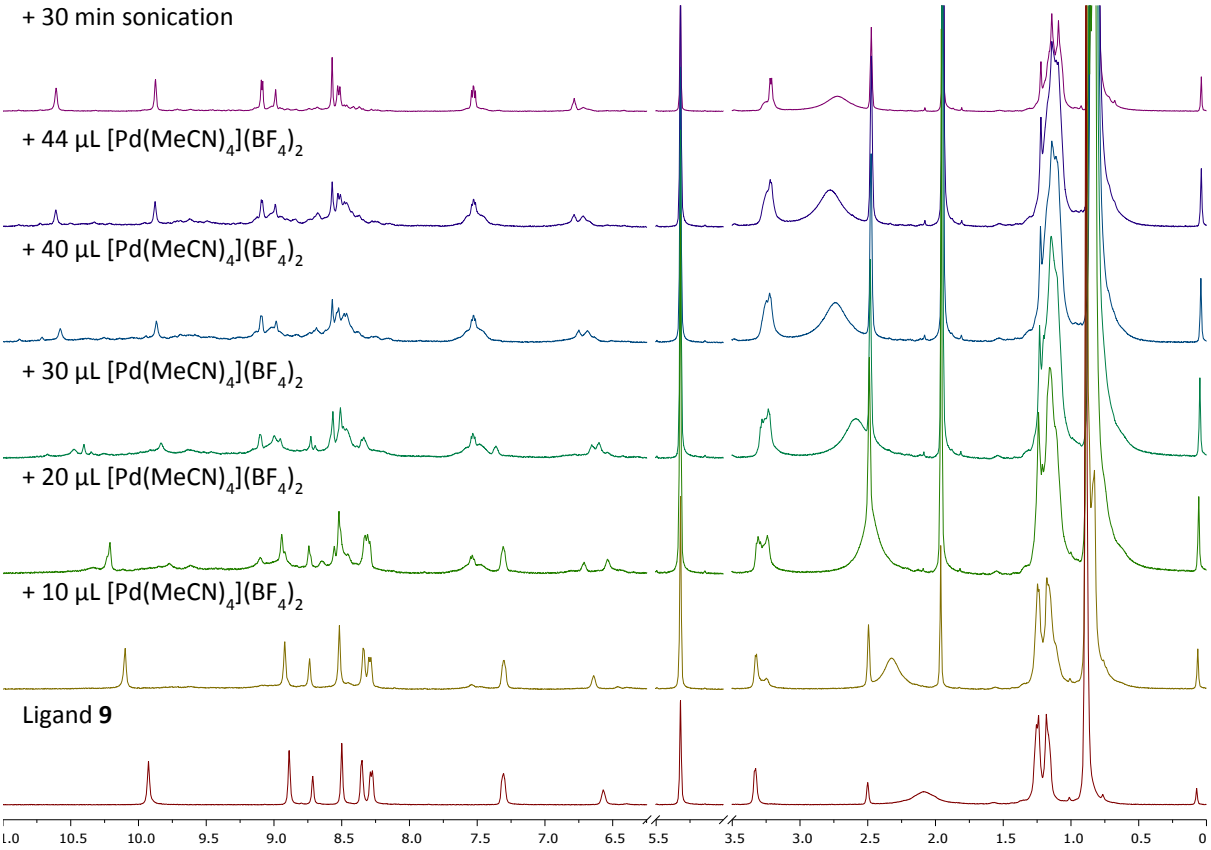


Figure S43. ^{1}H NMR of the stepwise formation of **3'**$[BF_4]_4$ in CD_2Cl_2/DMSO-d_6 (9:1).

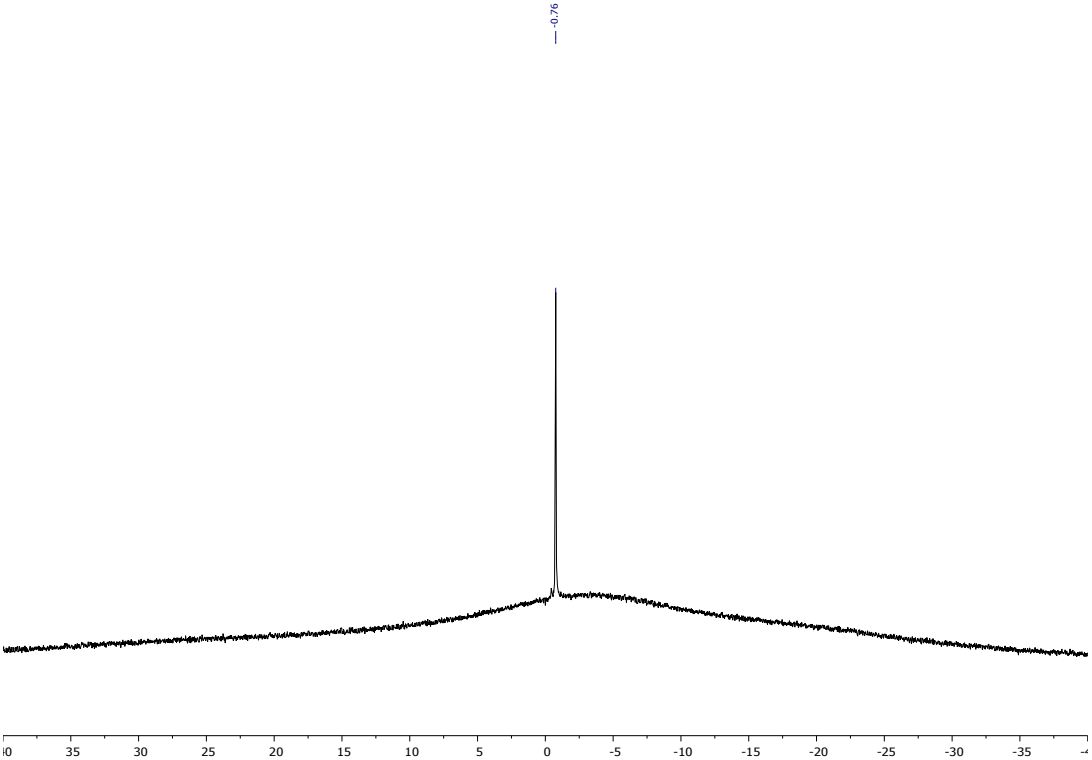


Figure S44. ^{11}B NMR spectrum of **3'**$[BF_4]_4$ complex in CD_2Cl_2/DMSO-d_6 (9:1).

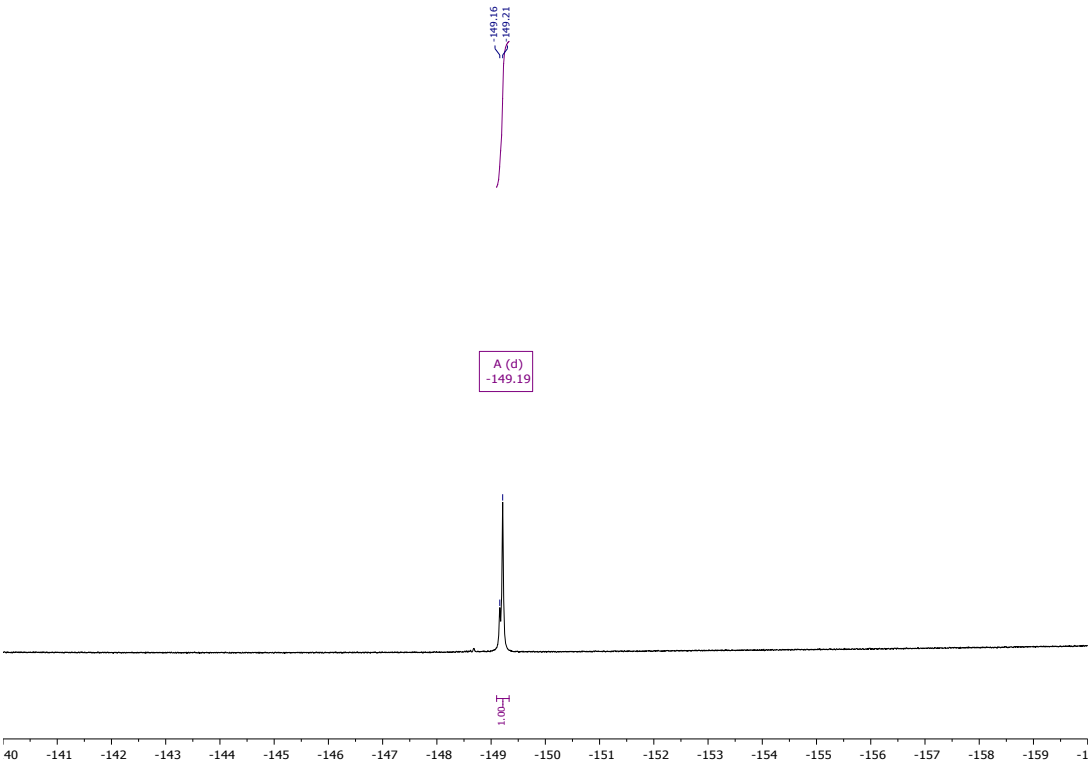


Figure S45. ^{19}F NMR s spectrum of **3'**$[BF_4]_4$ complex in CD_2Cl_2/DMSO-d_6 (9:1).

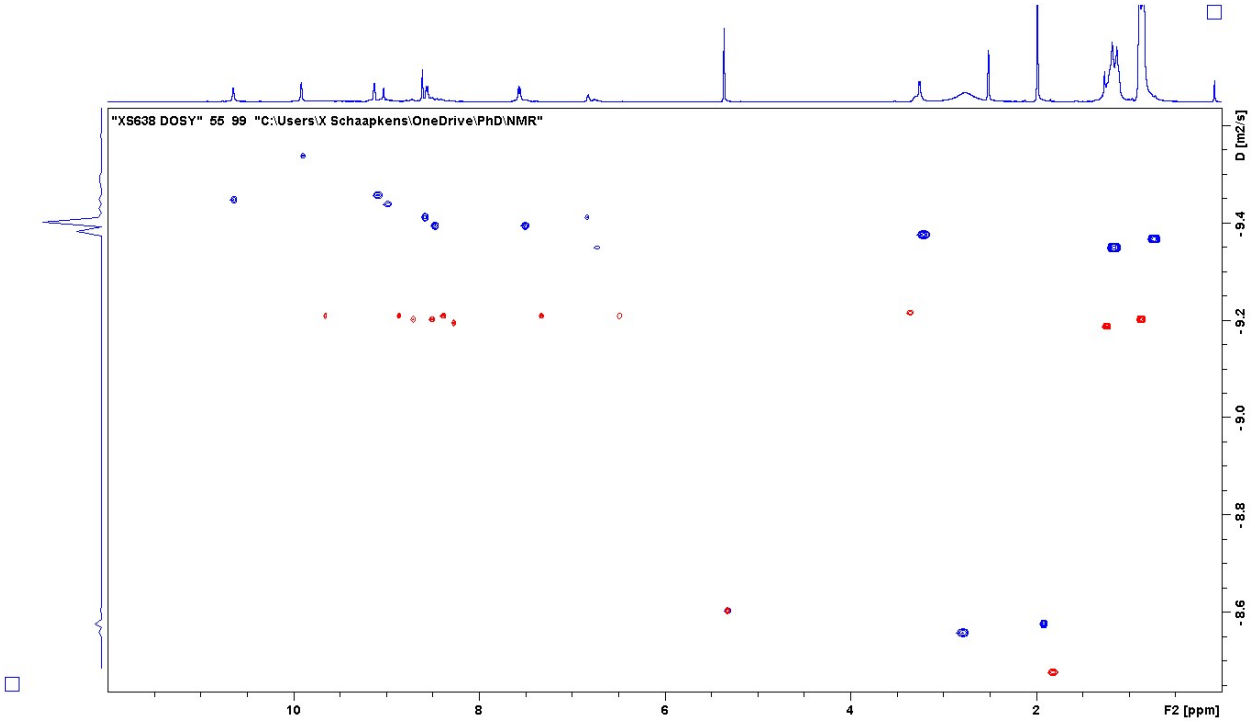


Figure S46. ^{1}H 2D DOSY spectrum of **3'**$[BF_4]_4$ (blue, top) and ligand **9** (red, bottom) in CD_2Cl_2/DMSO-d_6 (9:1).

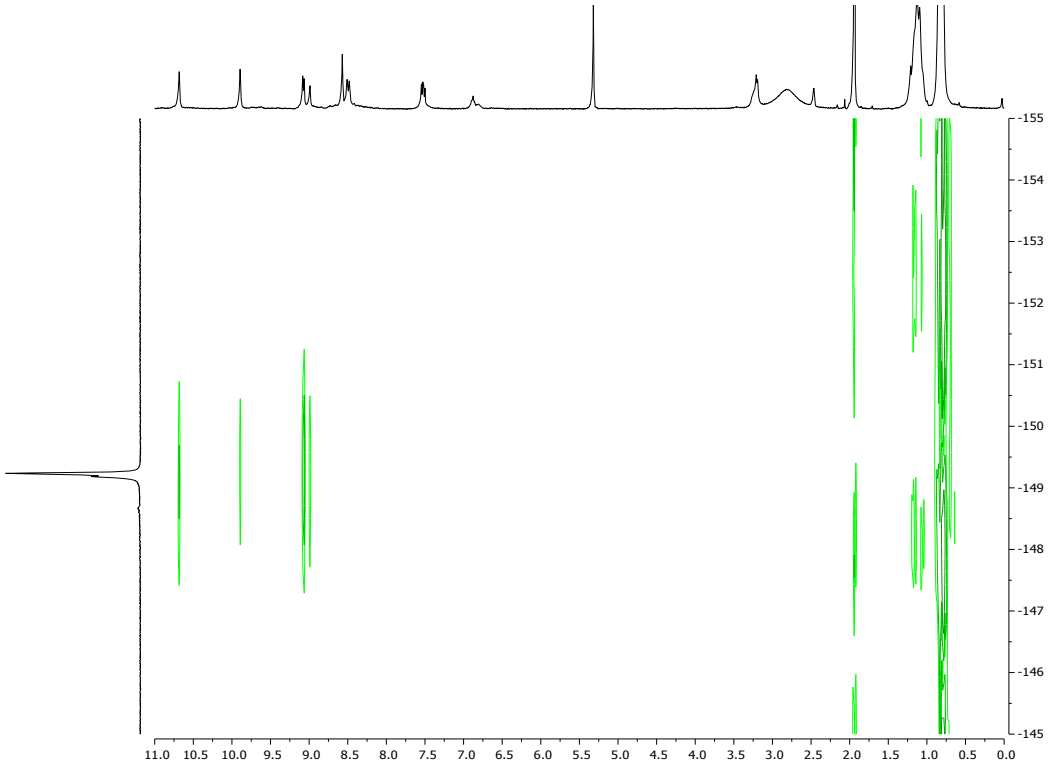


Figure S47. {^{1}H-^{19}F}-HOESY spectrum of **3'**$[BF_4]_4$ complex in CD_2Cl_2/DMSO-d_6 (9:1).

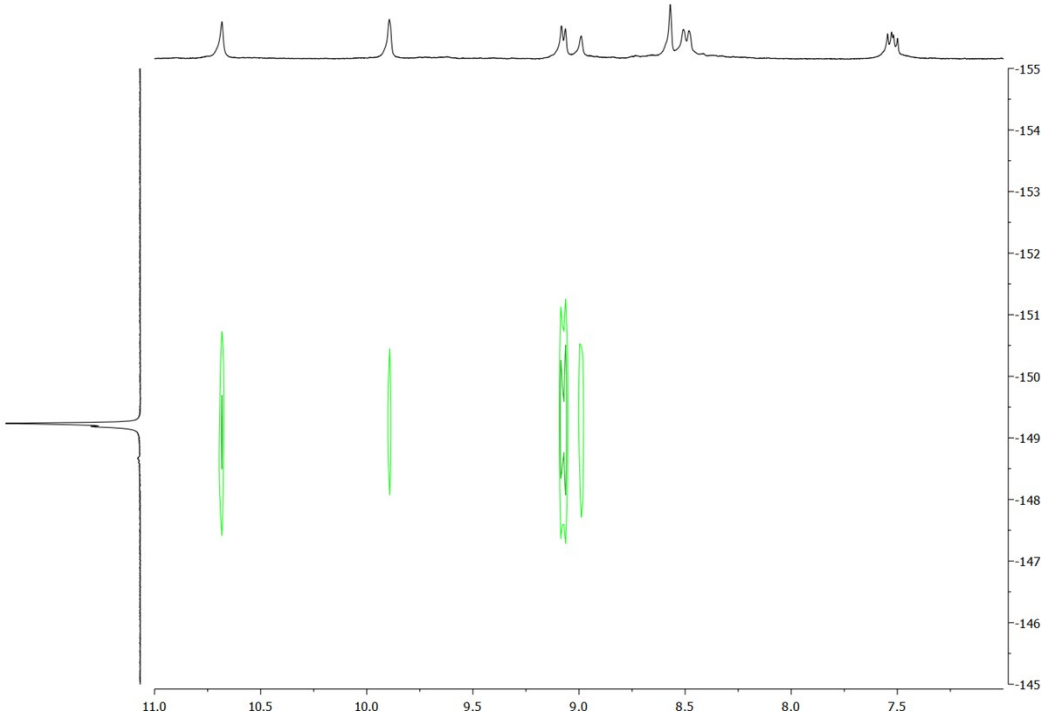


Figure S48. Partial {^{1}H-^{19}F}-HOESY spectrum of spectrum of **3'**$[BF_4]_4$ complex in CD_2Cl_2/DMSO-d_6 (9:1).

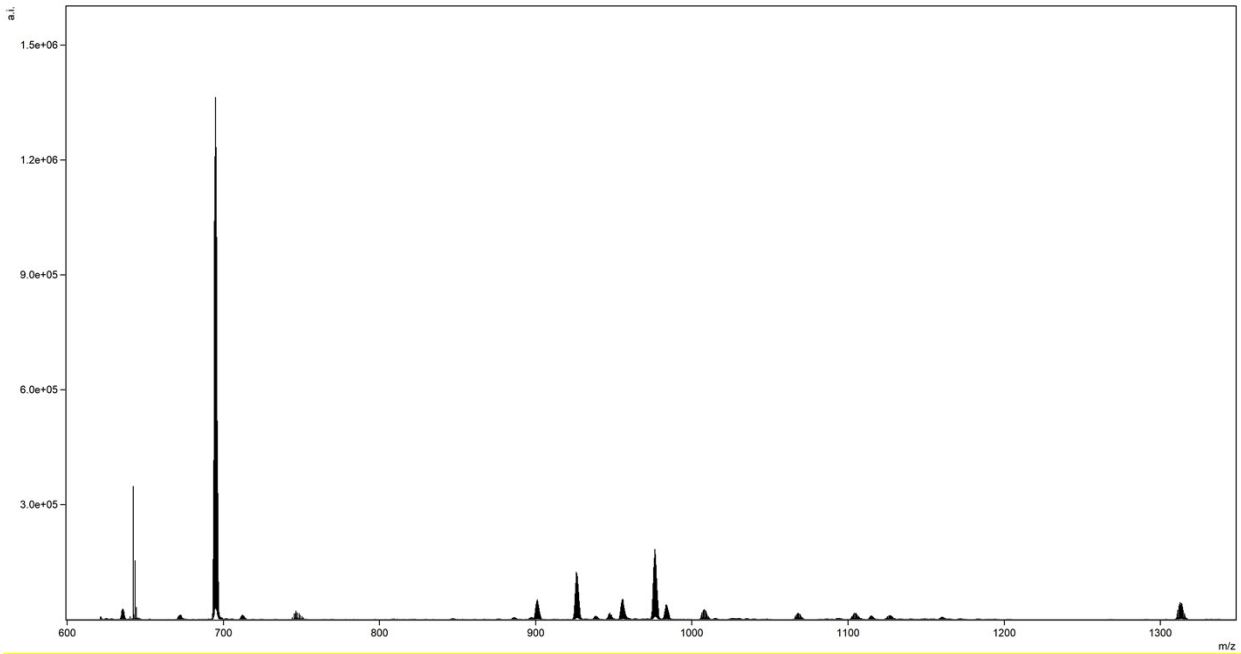


Figure S49. Full CSI HRMS of $[(C_{39}H_{55}N_5O_3)_4Pd_2](BF_4)_4$ from DMC/DMSO (9:1). See Figure S50–Figure S52 for representative fits to specific atomic stoichiometries.

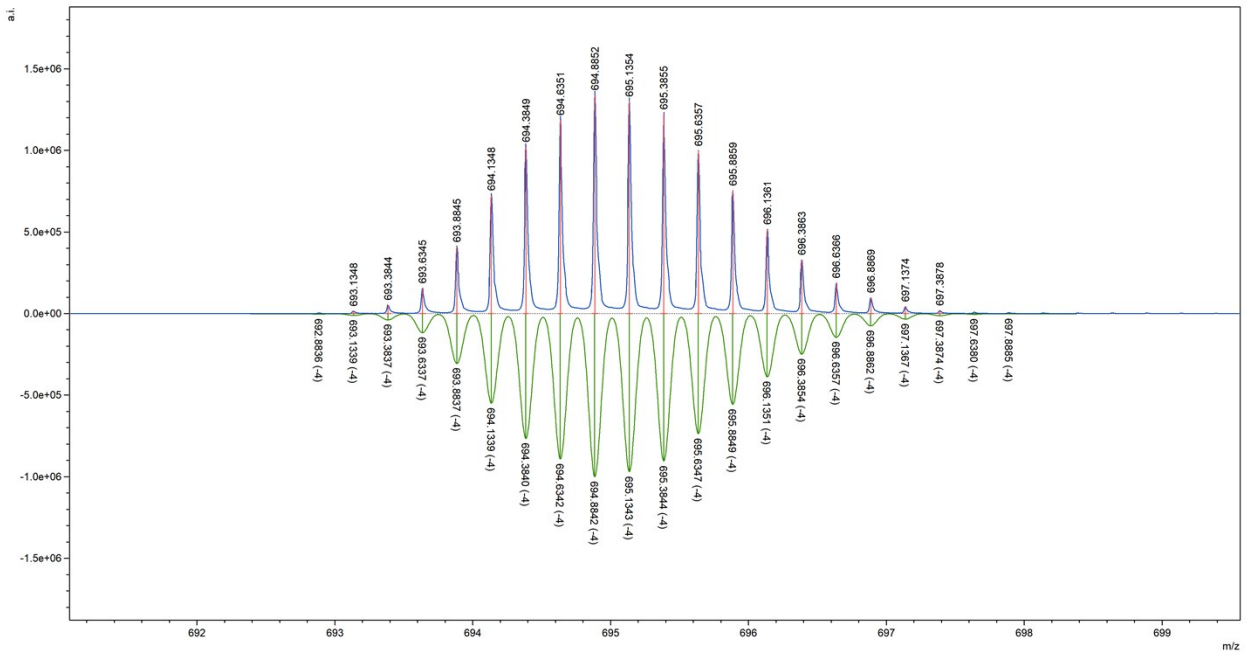


Figure S50. CSI HRMS of $[(C_{39}H_{55}N_5O_3)_4Pd_2]^{4+}$ (top) and calculated spectrum (bottom) around 695 *m*/*z*.

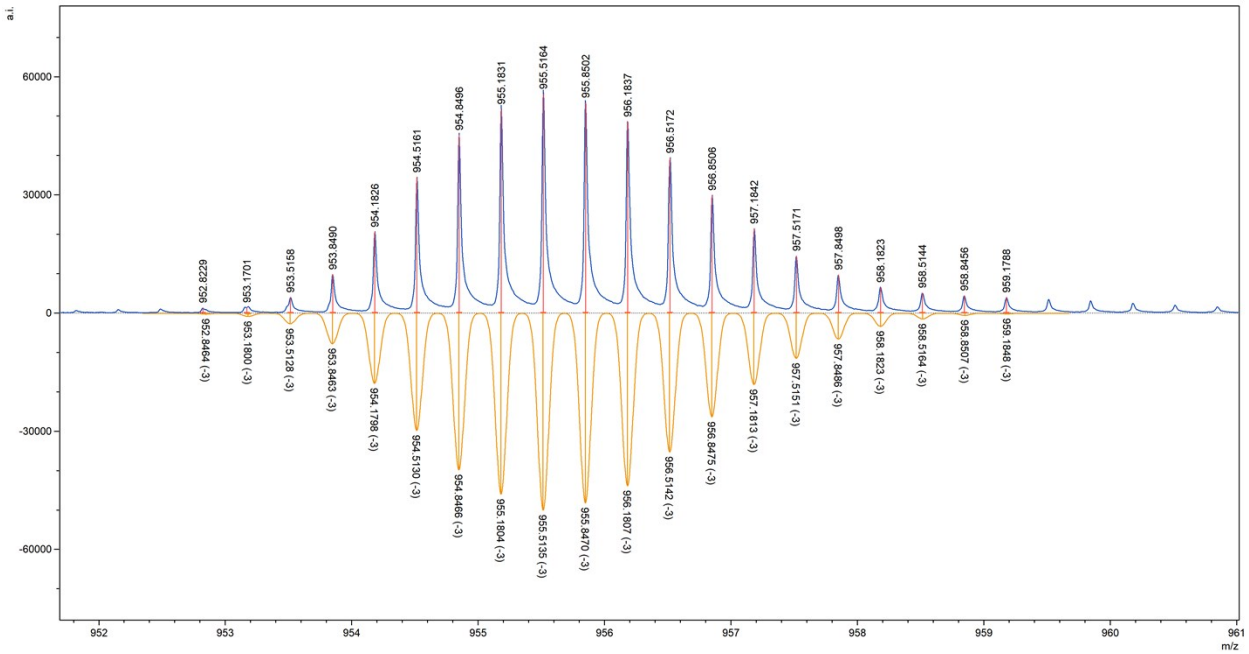


Figure S51. CSI HRMS of $[(C_{39}H_{55}N_5O_3)_4Pd_2(BF_4)]^{3+}$ (top) and calculated spectrum (bottom) around 955 *m/z*.

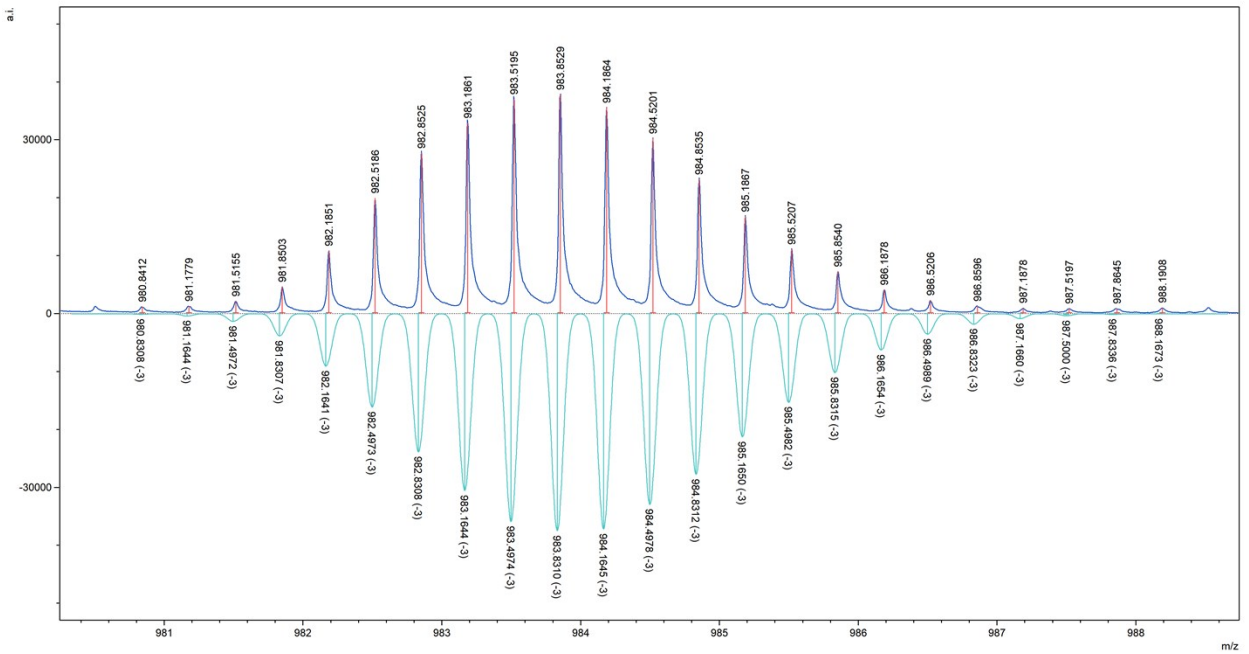


Figure S52. CSI HRMS of $[(C_{39}H_{55}N_5O_3)_4Pd_2(BF_4)]^{3+}\cdot CD_2Cl_2$ (top) and calculated spectrum (bottom) around 984 *m/z*.

Section S3. Studies of the binding of 3' with *n*-octyl glycosides

Titrations were performed in a CD_2Cl_2/DMSO-d_6 (9:1) matrix and the resulting solutions were subjected to CSI HRMS (both described in the materials and methods section, Section S1, page 2).

^{1}H NMR spectra of the titration with *n*-oct-β-D-Glucoside **10** are shown in Figure S53 and Figure S54; the fit of these data to a 1:1 binding model is shown in Figure S55. NMR data of the final solution containing [**3'**⊂**10**]$^{4+}$ are shown in Figure S56 (DOSY), Figure S57 (HOESY) and
Figure **S58** and Figure S59 (NOESY). CSI HRMS data of this solution are given in Figure S60 and Table S1.

^{1}H NMR spectra of the titration with *n*-oct-β-D-Galactoside **11** are shown in Figure S61 and Figure S62; the fit of these data to a 1:1 binding model is shown in Figure S63. CSI HRMS data of the final solution containing [**3'**⊂**11**]$^{4+}$ are given in Figure S64 and Table S2.

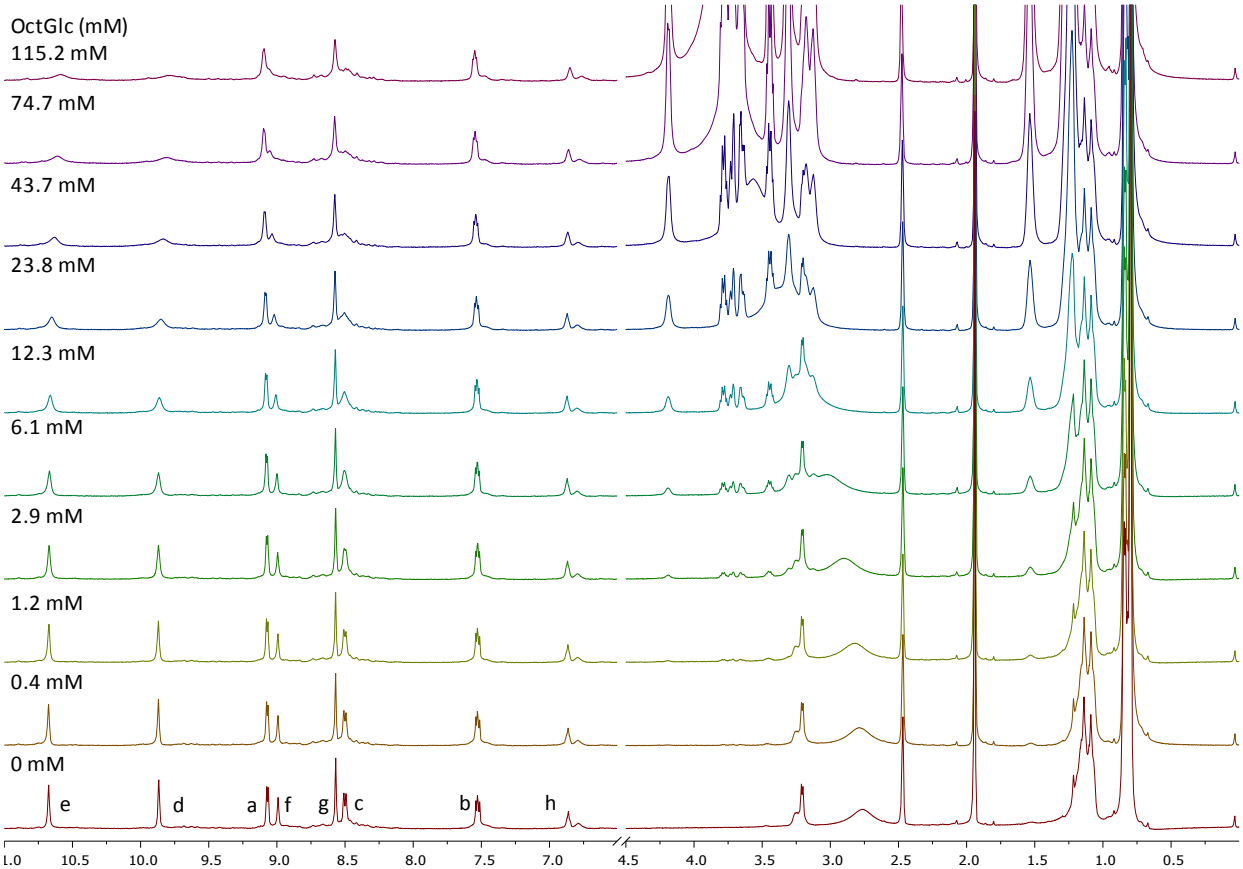


Figure S53. ^{1}H NMR spectra of the titration of **3'**$[BF_4]_4$ with *n*-oct-β-D-Glc **10** in CD_2Cl_2/DMSO-d_6 (9:1). See Figure S54 for a zoom-in from 7.9 – 9.6 p.p.m., Figure S55 for the fit to a 1:1 binding model and see also Figure 3.

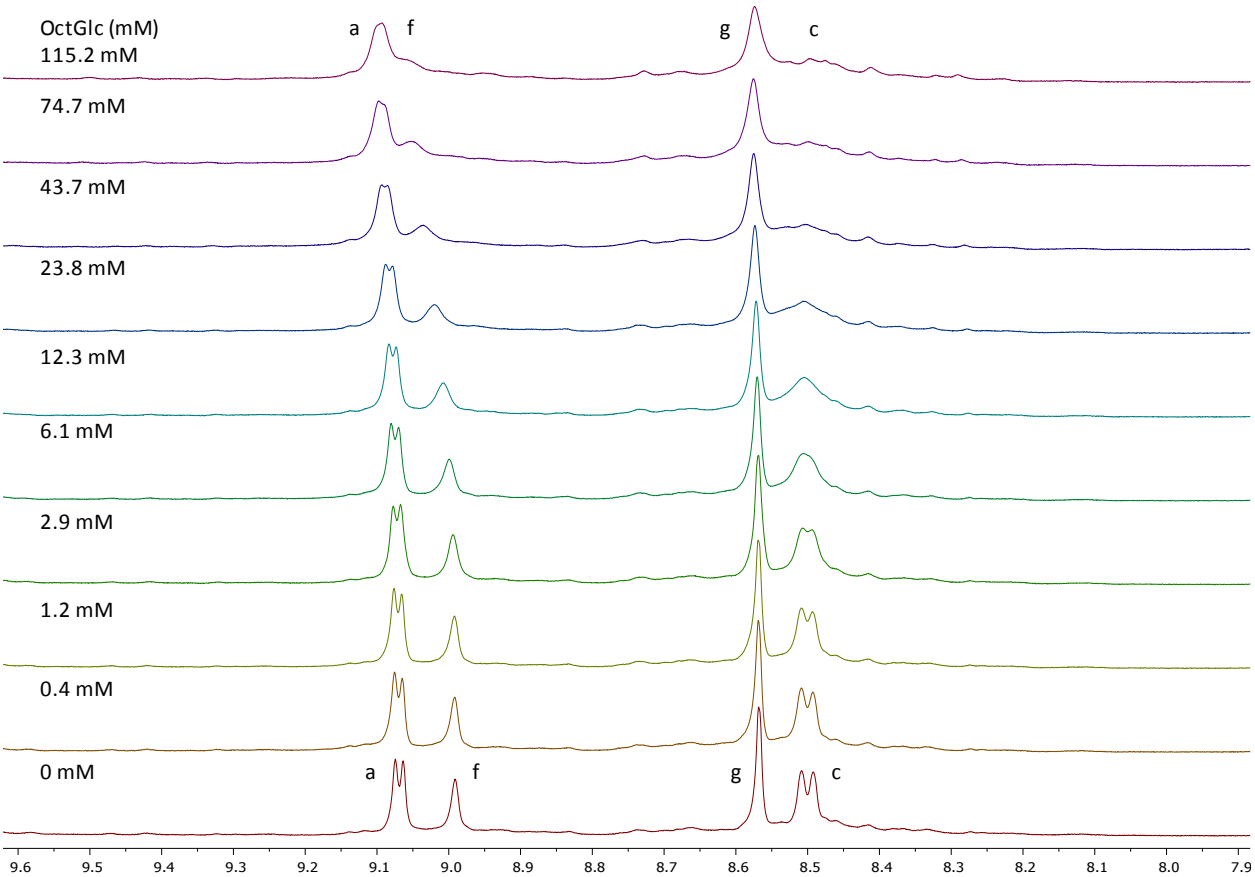


Figure S54. Zoom-in on resonances assigned to protons a, f, g and c of the titration shown in Figure S53. See Figure S55 for the fit to a 1:1 binding model and see also Figure 3.

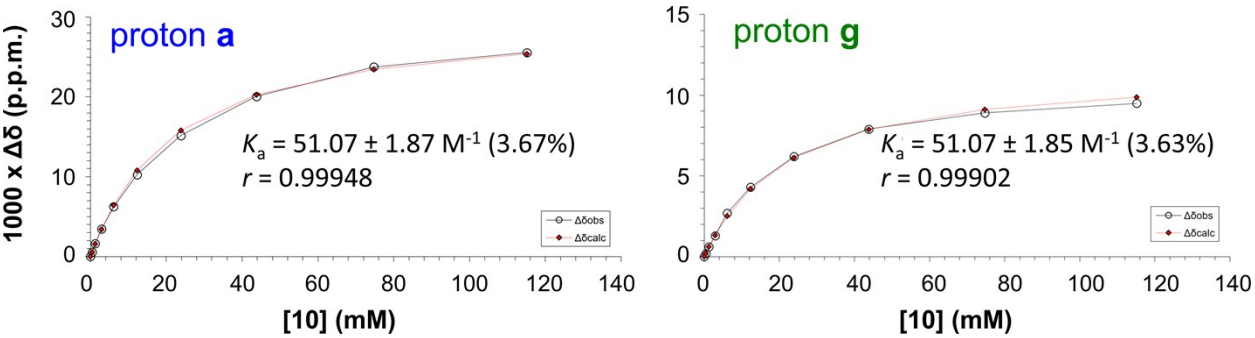


Figure S55. 1:1 Binding isotherm for the titration of **3'**$[BF_4]_4$ with *n*-oct-β-D-Glucoside **10** by analyzing shifts of protons assigned a (left) and g (right). The fit using both resonances gave K_a = 51.07 ± 2.75 M^{-1} (5.38%) with r = 0.99587. See Figure S53 and Figure S54 for spectra, and see also Figure 3.

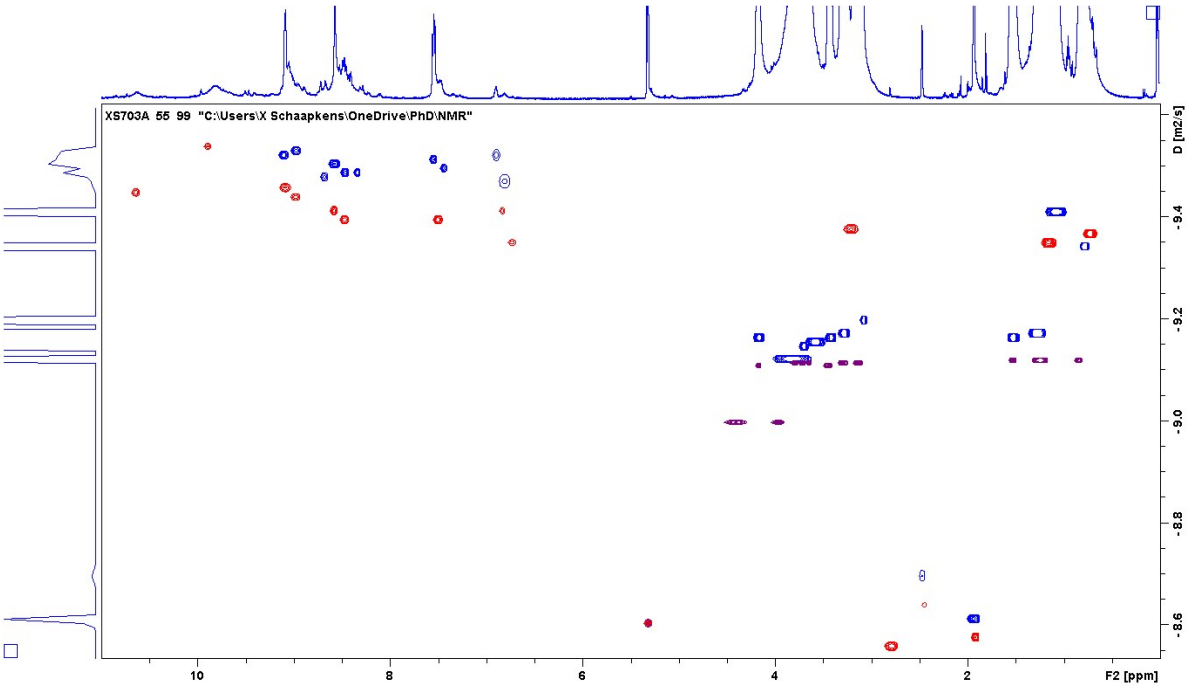


Figure S56. ^{1}H 2D-DOSY spectrum of the **3'**$[BF_4]_4$ before (red) and after (blue) the titration with **10**. The DOSY of **10** is also shown (purple).

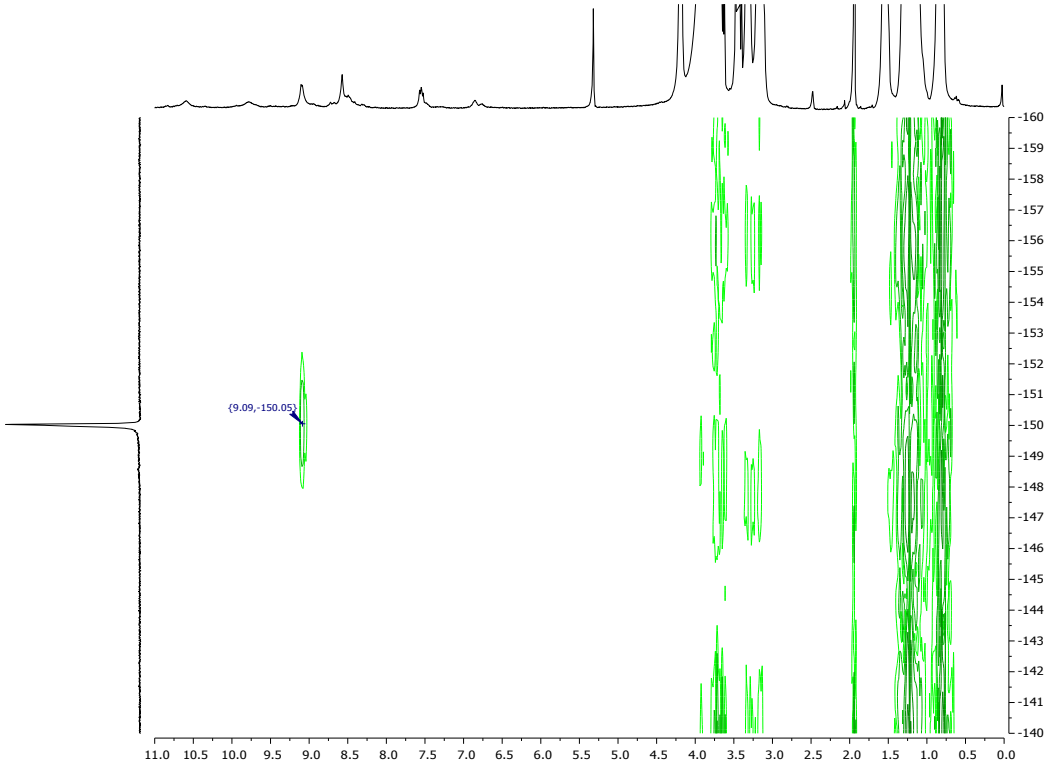


Figure S57. {^{1}H-^{19}F}-HOESY spectrum taken after the titration of **3'**$[BF_4]_4$ with **10** (see Figure S53 and Figure S54).

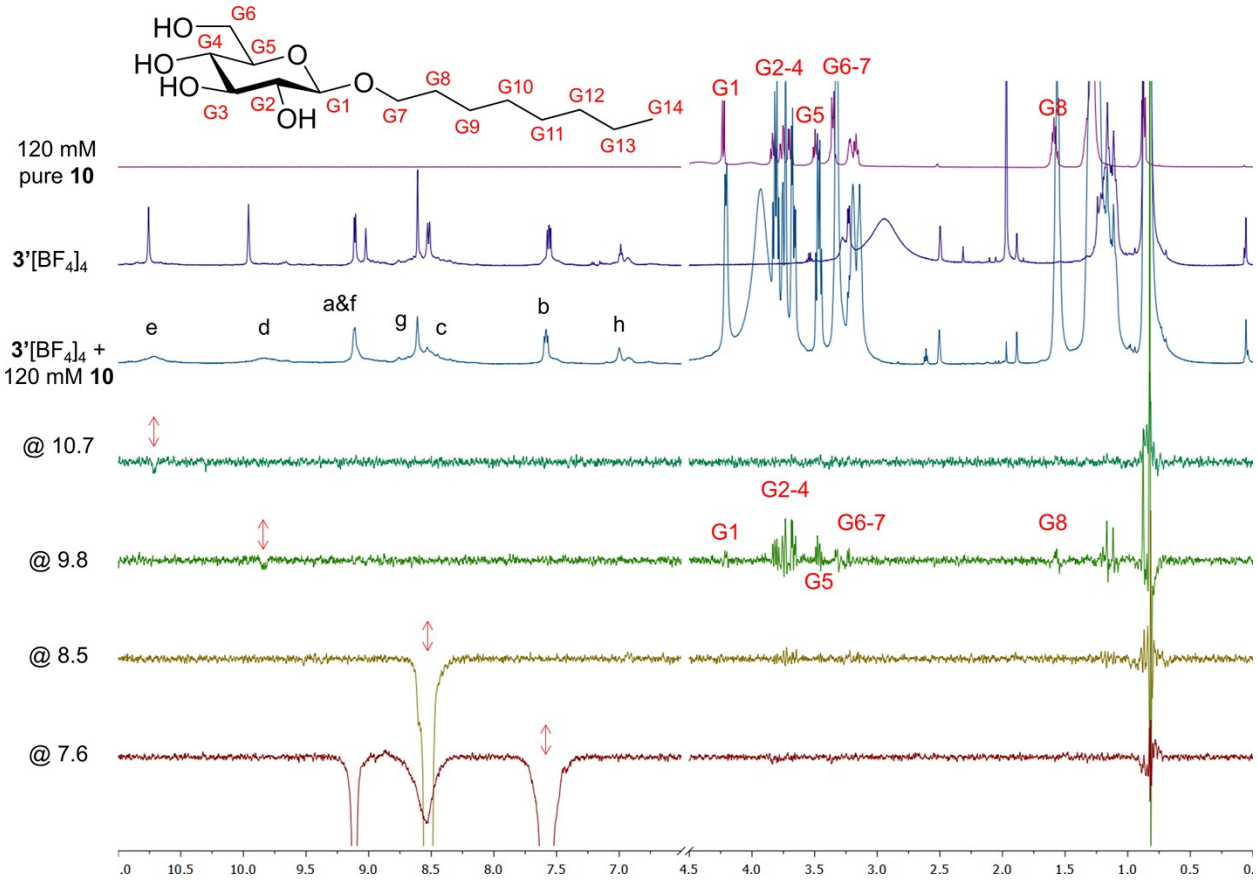


Figure S58. Top three spectra are ^{1}H NMR spectra of pure **10** (120 mM), pure **3'**$[BF_4]_4$ (3.33 mM) and a mixture of both obtained after a titration together (with a partial assignment, see Figure S53 and Figure S54 for data) in CD_2Cl_2/DMSO-d_6 (9:1). Bottom four spectra are selective nOe spectra of the **3'**/**10** mixture collected with a mixing time (t_m) of 500 ms after irradiation at 5355.2 Hz (10.7 p.p.m.), 4915.17 Hz (9.8 p.p.m.), 4263.95 Hz (8.5 p.p.m.), and 3790.88 Hz (7.6 p.p.m.). An assignment of the CH-resonances of the glucoside (G… in red) is also shown for pure **10** (top) and for the nOe spectrum used in the paper (middle, excited at 9.8 p.p.m. (H_d), see also Figure 4). All data was recorded at 500 MHz.

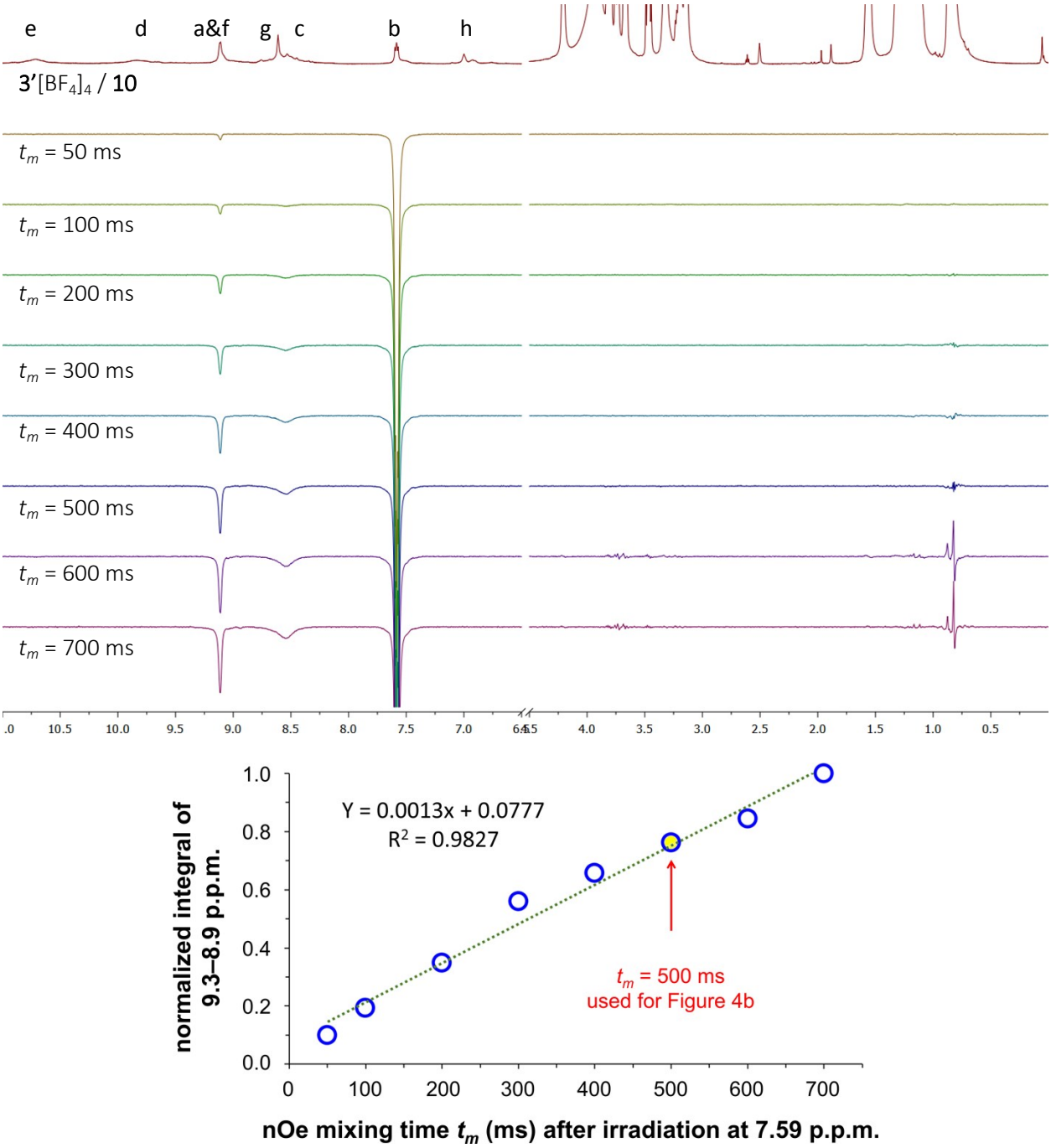


Figure S59. Top: ^{1}H NMR stack of Selective nOe experiments of the solution of **3'**$[BF_4]_4$ after titration with **10** (see Figure S53 and Figure S54 for titration) irradiated on H_b (7.59 p.p.m, 3790.88 Hz) with a variable mixing times (t_m = 50 – 700 ms). Bottom: normalized integral of the selective 1D nOe peak at 9.3 – 8.9 p.p.m. as a function of the {^{1}H-^{1}H}-nOe mixing time (t_m in ms) when irradiating the resonance at 7.59 p.p.m. (blue open spheres). The green dotted line represents a trend line of the data, indicating a linear relationship in the region t_m = 50 – 700 ms (i.e.: no significant spin-diffusion occurs). Based on these measurements, a mixing time of 500 ms was judged to give reliable data and used in the paper (Figure 4b). All data was recorded at 500 MHz.

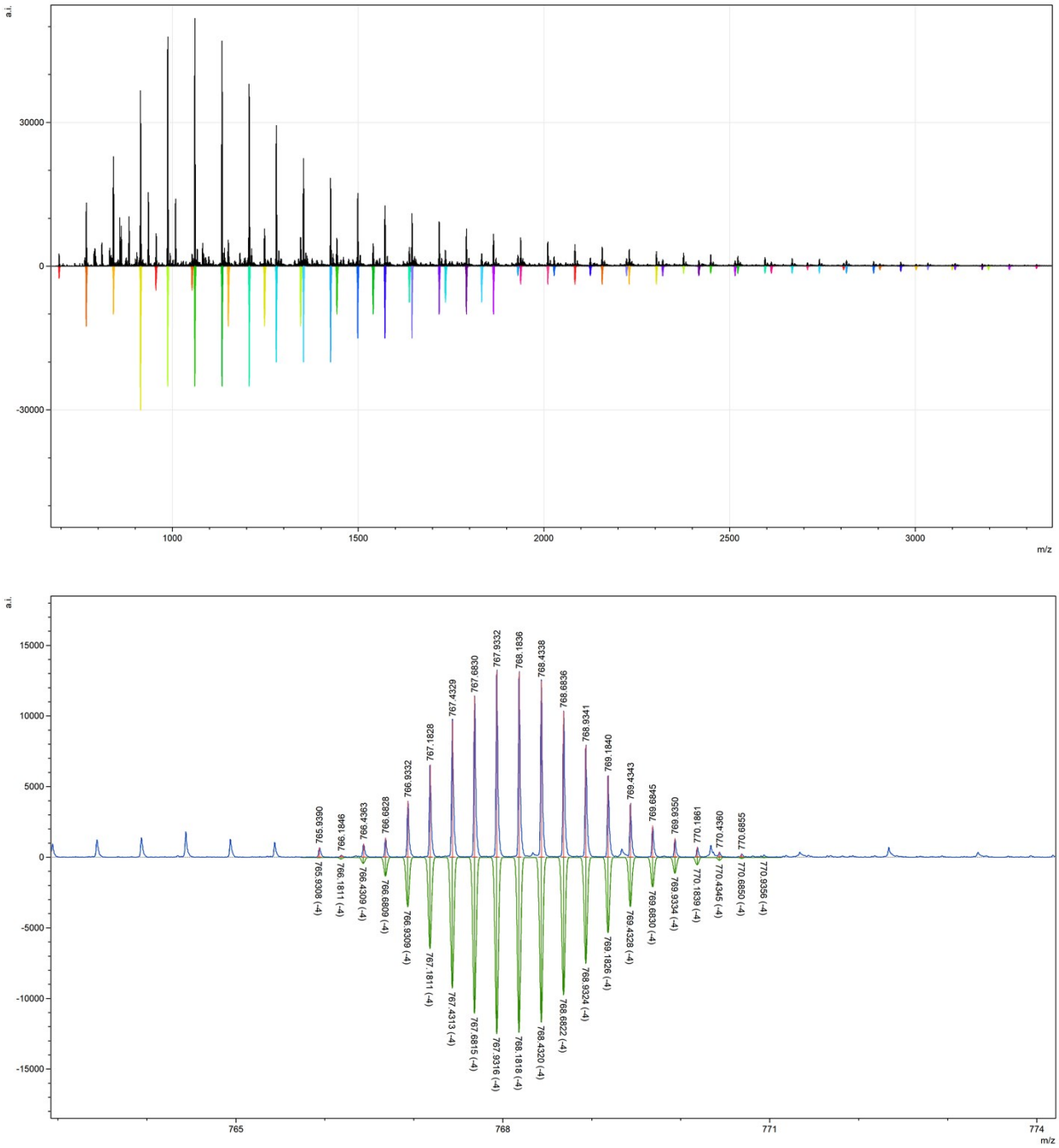


Figure S60. CSI HRMS of the solution taken after the titration of **3'**$[BF_4]_4$ with *n*-oct-β-D-Glucoside **10** (see Figure S53 and Figure S54 for titration data). Top: full spectrum that could be analyzed as adducts of [**3'**]$^{4+}$ with up to 35 equivalents of 10 (see Table S1 for details). **NB:** This result can be rationalised by the formation of a sort of reversed micelle structure, wherein multiple carbohydrates cluster around the cage. Whether this happens solely in the near vacuum of the mass spectrometer is unknown. Bottom: zoom-in of the isotope distribution with an *m/z* ratio consistent with [**3'**⊂**10**]$^{4+}$ (see also Figure 4a).

Table S1. Observed (Obs.) and calculated (Calc.) *m/z* ratio's with deviations (Δ, in p.p.m.) of mass peaks observed in the CSI HRMS spectrum of the solution after the titration of **3'**$[BF_4]_4$ with *n*-oct-β-D-Glucoside **10** (see Figure S60 (top) for full mass spectrum).

	m/z for $[(C_{39}H_{55}N_5O_3)_4Pd_2]^{4+}$			*m/z* for$[(C_{39}H_{55}N_5O_3)_4Pd_2 \cdot BF_4]^{3+}$		
eq. **10**	Obs.	Calc.	Δ	Obs.	Calc.	Δ
0	694.8871	694.8832	5.61	955.18370	955.17910	4.82
1	767.9344	767.9305	5.08	1052.9127	1052.9088	3.70
2	841.2319	841.2280	4.64	1150.3096	1150.3052	3.83
3	914.2795	914.2752	4.70	1248.0396	1248.0351	3.61
4	987.3269	987.3225	4.46	1345.4360	1345.4314	3.42
5	1060.3742	1060.3697	4.24	1442.8325	1442.8278	3.26
6	1133.6718	1133.6672	4.06	1540.2291	1540.2241	3.25
7	1206.7190	1206.7144	3.81	1637.6255	1637.6204	3.11
8	1279.7659	1279.7617	3.28	1735.3551	1735.3504	2.71
9	1352.8137	1352.8089	3.55	1832.7521	1832.7467	2.95
10	1425.8610	1425.8562	3.37	1930.1483	1930.1430	2.75
11	1498.9082	1498.9034	3.20	2027.5440	2027.5394	2.27
12	1572.2060	1572.2009	3.24	2124.9423	2124.9357	3.11
13	1645.2535	1645.2482	3.22	2222.6721	2222.6657	2.88
14	1718.3003	1718.2954	2.85	2320.0677	2320.0620	2.46
15	1791.3479	1791.3427	2.90	2417.4640	2417.4583	2.36
16	1864.3952	1864.3899	2.84	2514.8611	2514.8547	2.54
17	1937.4424	1937.4371	2.74	2612.2559	2612.2510	1.88
18	2010.7395	2010.7347	2.39	2709.6514	2709.6473	1.51
19	2083.7864	2083.7819	2.16	2807.3826	2807.3773	1.89
20	2156.8344	2156.8291	2.46	2904.7782	2904.7737	1.55
21	2229.8806	2229.8764	1.88	3002.1760	3002.1700	2.00
22	2302.9283	2302.9236	2.04	3099.5735	3099.5663	2.32
23	2375.9753	2375.9708	1.89	3196.9675	3196.9626	1.53
24	2449.2732	2449.2684	1.96			
25	2522.3201	2522.3156	1.78			
26	2595.3670	2595.3629	1.58			
27	2668.4144	2668.4101	1.61			
28	2741.4608	2741.4573	1.28			
29	2814.7551	2814.7549	0.07			
30	2887.8043	2887.8021	0.76			
31	2960.8520	2960.8493	0.91			
32	3033.8982	3033.8966	0.53			
33	3106.9444	3106.9438	0.19			
34	3179.9920	3179.9910	0.31			
35	3253.2914	3253.2886	0.86			

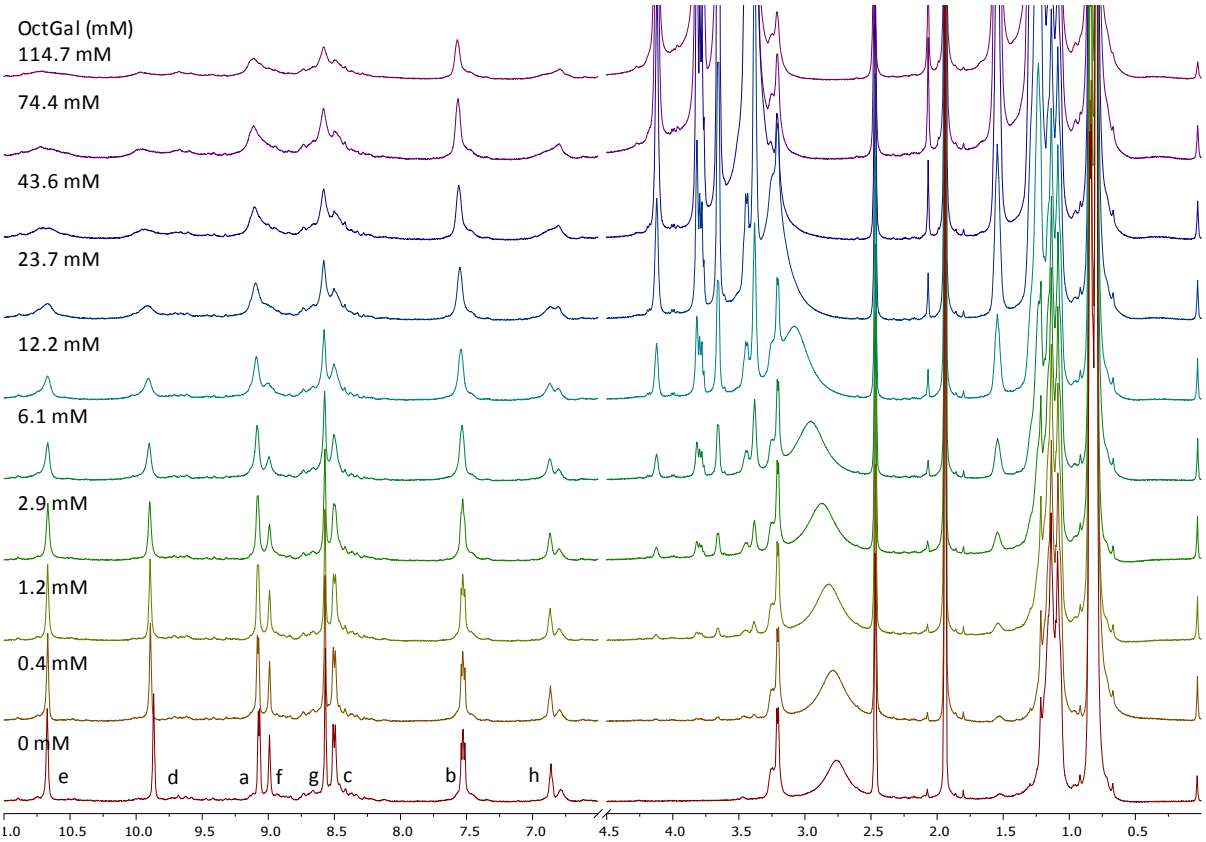


Figure S61. ^{1}H NMR spectra of the titration of **3'**$[BF_4]_4$ with *n*-oct-β-D-Gal **11** in CD_2Cl_2/DMSO-d_6 (9:1). See Figure S62 for a zoom-in from 7.2 – 9.4 p.p.m. and Figure S63 for the fit to a 1:1 binding model.

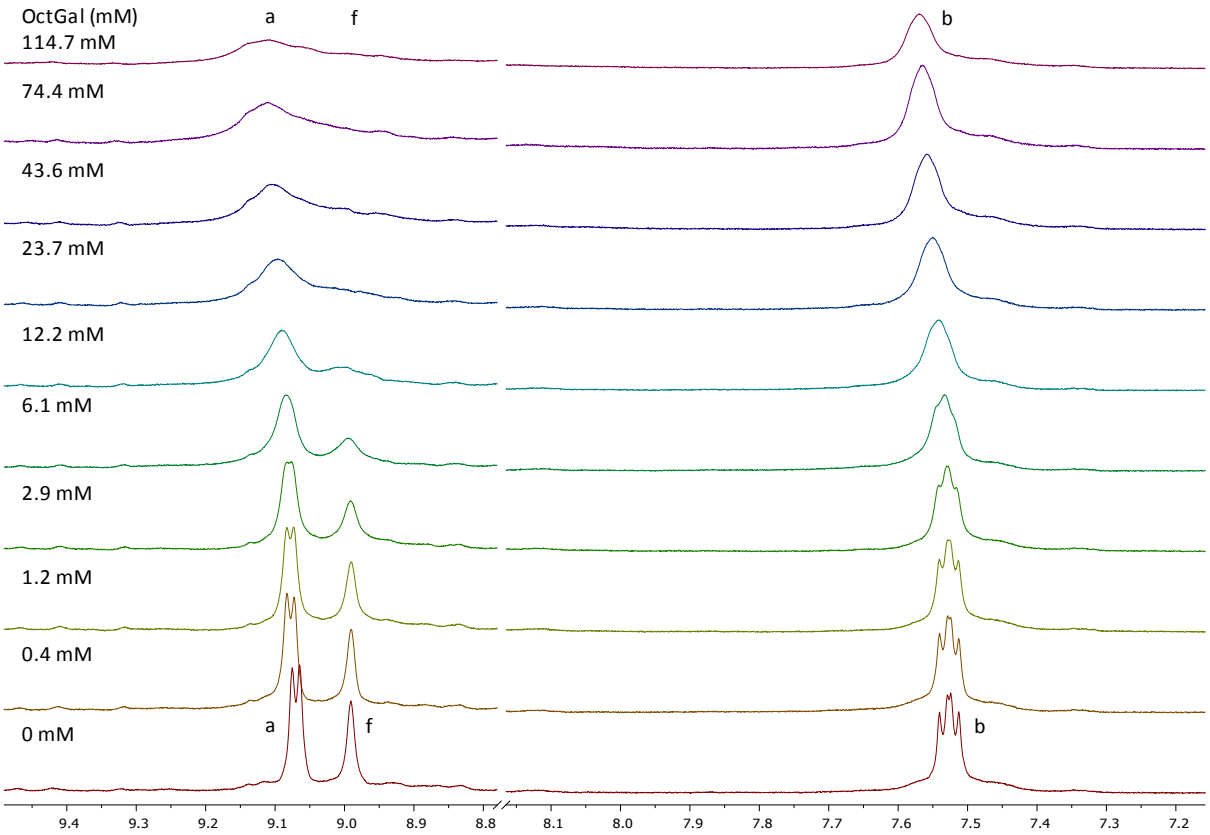


Figure S62. Zoom-in on resonances assigned to protons a, f, and b of the titration shown in Figure S61. See Figure S63 for the fit to a 1:1 binding model.

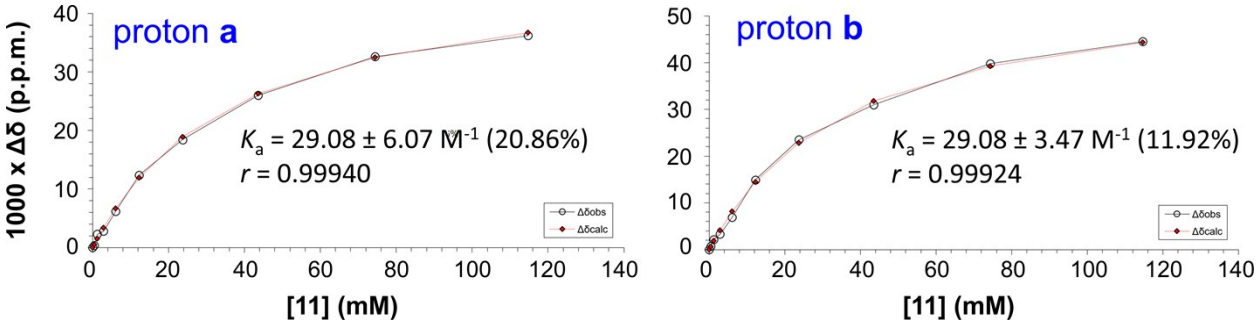


Figure S63. 1:1 Binding isotherms for the titration of **3'**$[BF_4]_4$ with *n*-oct-β-D-Galactoside **11** based on the shifts of resonances assigned a (left) and b (right). The fit using both resonances gave K_a = 29.08 ± 4.79 M^{-1} (16.48%) with r = 0.99930. See Figure S61 and Figure S62 for spectra.

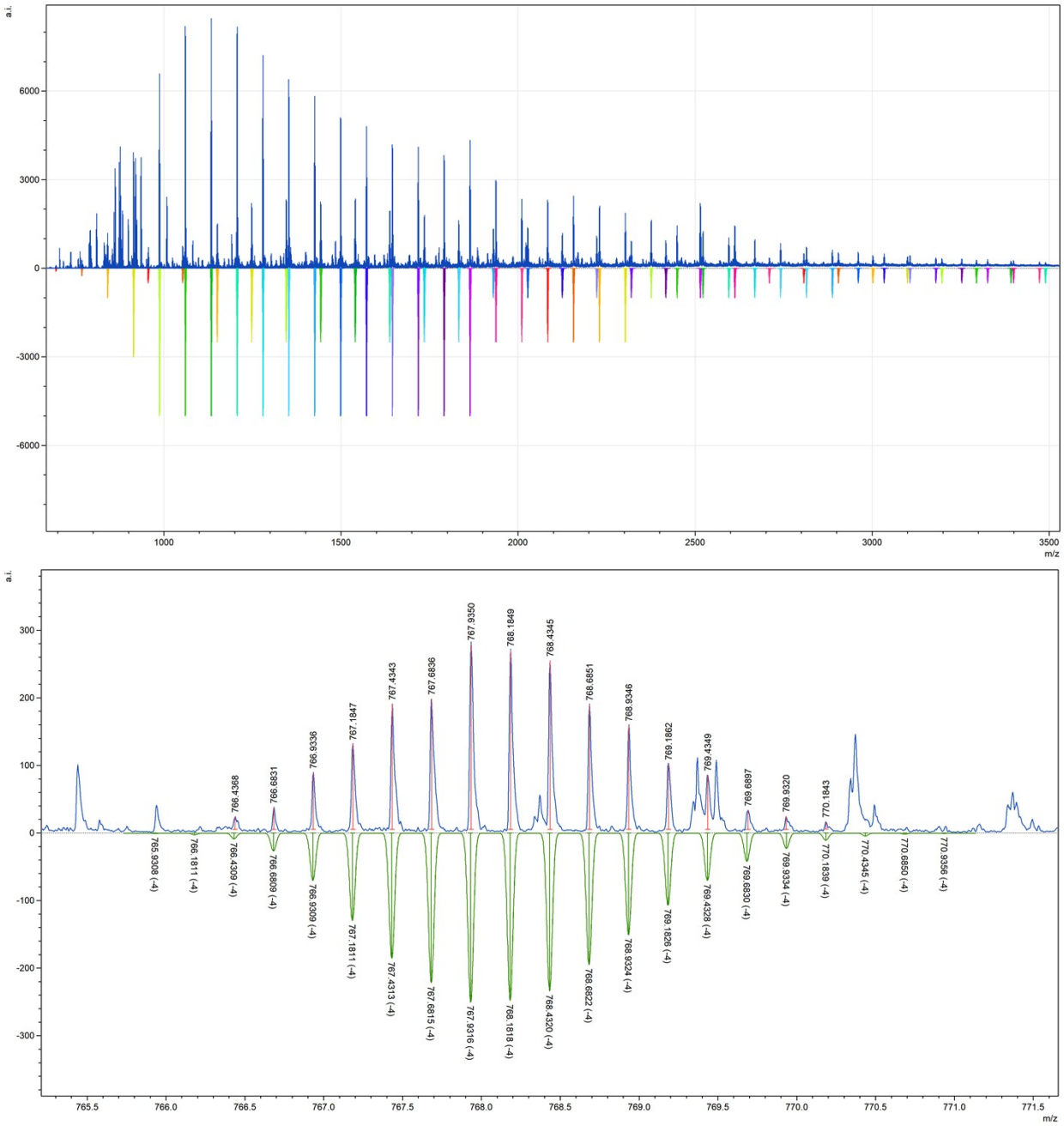
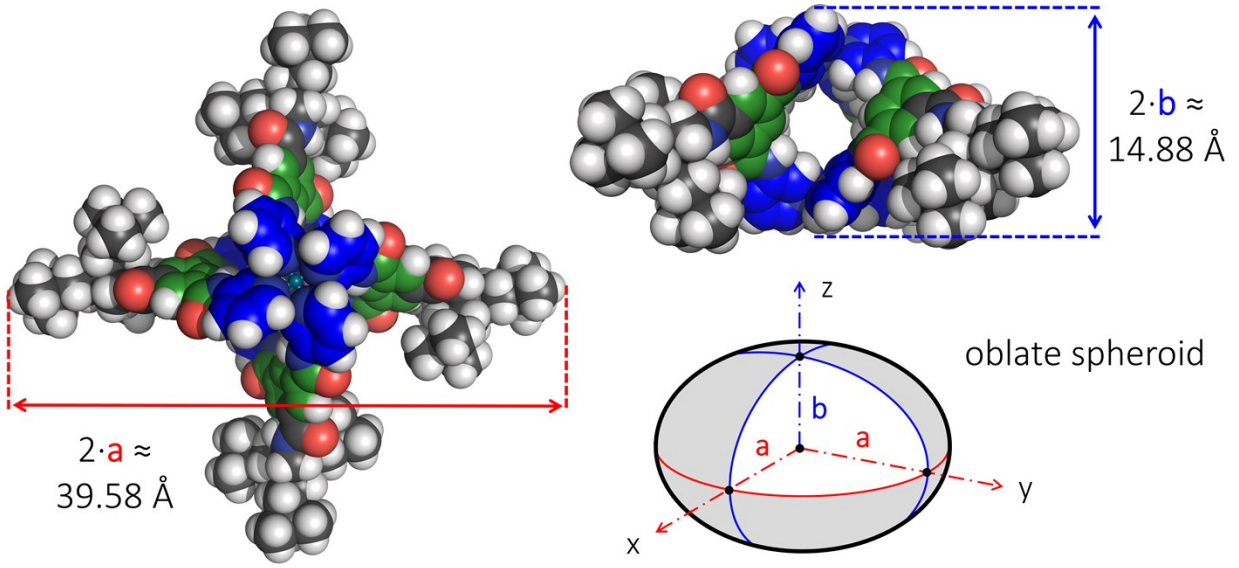


Figure S64. CSI HRMS of the solution taken after the titration of **3'**$[BF_4]_4$ with *n*-oct-β-D-Galactoside **11** (see Figure S53 and Figure S54 for titration data). Top: full spectrum that could be analyzed as adducts of [**3'**]$^{4+}$ with up to 38 equivalents of 10 (see Table S1 for details). **NB:** This result can be rationalised by the formation of a sort of reversed micelle structure, wherein multiple carbohydrates cluster around the cage. Whether this happens solely in the near vacuum of the mass spectrometer is unknown. Bottom: zoom-in of the isotope distribution with an *m*/*z* ratio consistent with [**3'**⊂**11**]$^{4+}$.

Table S2. Observed (Obs.) and calculated (Calc.) *m/z* ratio's with deviations (Δ, in p.p.m.) of mass peaks observed in the CSI HRMS spectrum of the solution after the titration of **3'**$[BF_4]_4$ with *n*-oct-β-D-Galactoside **11** (see Figure S64 (top) for full mass spectrum).

	m/z for $[(C_{39}H_{55}N_5O_3)_4Pd_2]^{4+}$			*m/z* for$[(C_{39}H_{55}N_5O_3)_4Pd_2 \cdot BF_4]^{3+}$		
eq. **11**	Obs.	Calc.	Δ	Obs.	Calc.	Δ
0	694.8841	694.8832	1.30	955.5145	955.5124	2.20
1	767.9366	767.9305	7.94	1052.9151	1052.9088	5.98
2	841.2346	841.2280	7.85	1150.3124	1150.3052	6.26
3	914.2819	914.2752	7.33	1248.0424	1248.0351	5.85
4	987.3294	987.3225	6.99	1345.4391	1345.4314	5.72
5	1060.3771	1060.3697	6.98	1442.8355	1442.8278	5.34
6	1133.6746	1133.6672	6.53	1540.2322	1540.2241	5.26
7	1206.7220	1206.7144	6.30	1637.6287	1637.6204	5.07
8	1279.7698	1279.7617	6.33	1735.3590	1735.3504	4.96
9	1352.8171	1352.8089	6.06	1832.7554	1832.7467	4.75
10	1425.8643	1425.8562	5.68	1930.1539	1930.1430	5.65
11	1498.9115	1498.9034	5.40	2027.5483	2027.5394	4.39
12	1572.2094	1572.2009	5.41	2124.9454	2124.9357	4.56
13	1645.2571	1645.2482	5.41	2222.6734	2222.6657	3.46
14	1718.3043	1718.2954	5.18	2320.0714	2320.0620	4.05
15	1791.3518	1791.3427	5.08	2417.4682	2417.4583	4.10
16	1864.3989	1864.3899	4.83	2514.8632	2514.8547	3.38
17	1937.4464	1937.4371	4.80	2612.2605	2612.2510	3.64
18	2010.7437	2010.7347	4.48	2709.6565	2709.6473	3.40
19	2083.7908	2083.7819	4.27	2807.3861	2807.3773	3.13
20	2156.8385	2156.8291	4.36	2904.7816	2904.7737	2.72
21	2229.8855	2229.8764	4.08	3002.1804	3002.1700	3.46
22	2302.9325	2302.9236	3.86	3099.5756	3099.5663	3.00
23	2375.9805	2375.9708	4.08	3196.9727	3196.9626	3.16
24	2449.2777	2449.2684	3.80	3294.3678	3294.3589	2.70
25	2522.3250	2522.3156	3.73	3392.0981	3392.0890	2.68
26	2595.3714	2595.3629	3.28	3489.4911	3489.4853	1.66
27	2668.4185	2668.4101	3.15			
28	2741.4662	2741.4573	3.25			
29	2814.7615	2814.7549	2.34			
30	2887.8086	2887.8021	2.25			
31	2960.8551	2960.8493	1.96			
32	3033.9039	3033.8966	2.41			
33	3106.9485	3106.9438	1.51			
34	3179.9950	3179.9910	1.26			
35	3253.3003	3253.2886	3.60			
36	3326.3449	3326.3358	2.74			
37	3399.3931	3399.3831	2.94			
38	3472.4380	3472.4303	2.22			

Section S4. Additional figures referred to in main text



Ellipsoidal quadratic mean radius (Q_r) for an oblate spheroid =

$$Q_r = \frac{1}{2}\sqrt{3a^2 + b^2} \quad = \frac{1}{2}\sqrt{3(19.79)^2+(7.44)^2} \; = \; 17.5 \text{ Å}$$

measured with DOSY ≈ 13.9 Å

Figure S65. Estimation of mean radius of **3'**, assuming an overall oblate pheroid shape. The molecular model was obtained by a conformational search using the MMFF forcefield implemented in Spartan 2016. The dimensions for a and b were estimated based on the average of four interatomic H···H distances, plus twice the van der Waals radius of H (1.09 Å). **NB:** the overestimation of the modelled radius (17.5 Å) compared to the measured radius (13.9 Å, with DOSY, see also Figure S46) is likely due to a solvation phere of the tetracationic complex.

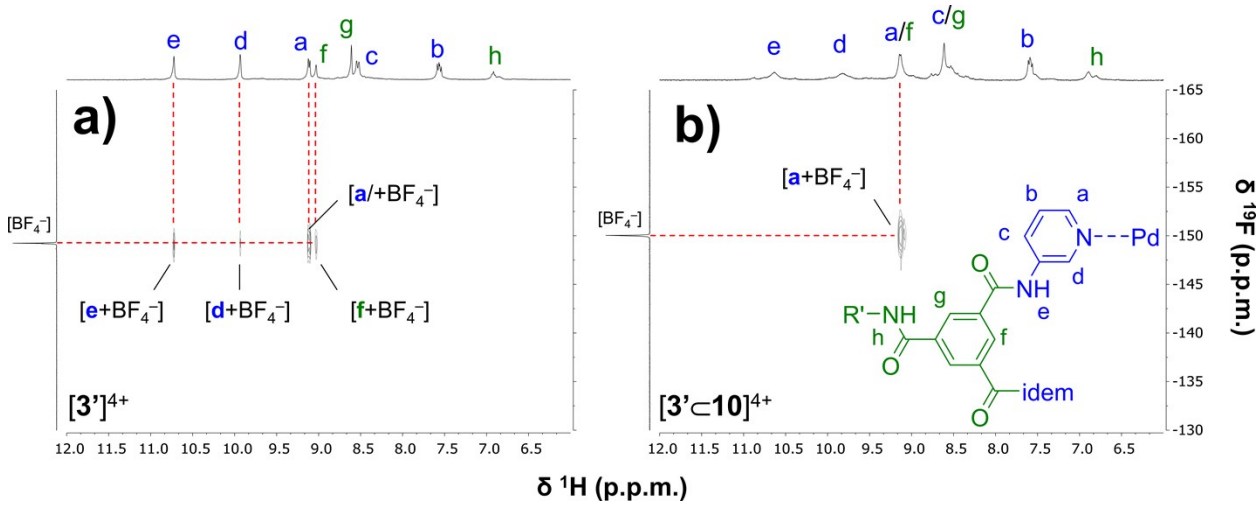


Figure S66. {^{1}H-^{19}F}-HOESY NMR spectra of a solution of **3'**$(BF_4)_4$ in 9:1 CH_2Cl_2:DMSO-d_6: a) without addition of *n*-octyl-β-D-glucoside **10**, and b) after addition of 115 mM of **10**. The mixing time (t_m) was set to 500 ms in both cases. See also Figure S47 and Figure S57.

Table S3. Atomic coordinates of the energy minimum model for [**3'⊂10**]$^{4+}$ used for Figure 5 obtained by a conformational search with the Merck Molecular Force Field implemented in Spartan 2016.

Atom	x	y	z
N1	3.799	0.185	-4.761
N2	3.071	-5.220	-0.237
N3	-3.512	-5.507	-1.751
N4	-2.984	-0.361	-6.020
N5	-0.699	3.439	1.151
N6	-1.753	0.198	3.583
N7	-3.211	1.979	1.750
N8	0.769	1.635	3.025
N9	3.144	-1.067	3.115
N10	1.702	3.922	-1.489
N11	-4.814	1.923	-1.479
N12	-3.320	-2.974	2.941
N13	7.797	-4.896	5.182
N14	-6.717	-8.369	3.940
N15	-8.666	4.131	-5.988
N16	6.251	6.969	-4.815
N17	1.303	-5.404	-3.368
N18	-0.230	-2.669	-6.151
N19	-1.341	-4.884	-4.549
N20	2.462	-3.157	-4.969
C1	-3.623	0.741	-6.556
C2	4.912	0.986	-4.572
C3	-4.761	-5.873	-1.283
C4	3.549	-5.868	0.888
C5	-4.915	-5.901	0.203
C6	-5.297	-6.037	2.972
C7	-5.826	-6.816	0.748
C8	-4.203	-5.035	1.049
C9	-4.402	-5.100	2.436
C10	-6.003	-6.902	2.132
C11	4.653	2.428	-4.278
C12	4.373	5.133	-3.605
C13	3.512	2.862	-3.586
C14	5.650	3.352	-4.622
C15	5.504	4.707	-4.307
C16	3.383	4.212	-3.234
C17	-1.344	4.536	1.201
C18	-1.063	5.582	0.330
C19	-0.052	5.429	-0.602
C20	0.643	4.235	-0.604
C21	0.263	3.266	0.331
C22	-2.331	-0.780	3.003
C23	-2.669	-1.958	3.678
C24	-2.355	-2.041	5.020
C25	-1.756	-0.941	5.608
C26	-1.481	0.176	4.827
C27	-3.420	1.970	0.492
C28	-4.702	1.961	-0.065
C29	-5.771	1.989	0.809

C30	-5.495	2.043	2.165
C31	-4.171	2.041	2.585
C32	1.431	2.655	3.403
C33	2.783	2.568	3.714
C34	3.416	1.342	3.624
C35	2.652	0.253	3.255
C36	1.298	0.475	2.983
C37	-3.666	-4.231	3.398
C38	4.468	-1.461	3.198
C39	-5.994	1.865	-2.199
C40	2.212	4.739	-2.481
C41	-5.876	1.860	-3.686
C42	-5.800	1.914	-6.483
C43	-6.922	2.449	-4.413
C44	-4.804	1.267	-4.365
C45	-4.765	1.293	-5.769
C46	-6.878	2.494	-5.809
C47	4.741	-2.907	2.958
C48	5.436	-5.578	2.472
C49	3.963	-3.686	2.092
C50	5.873	-3.466	3.568
C51	6.209	-4.806	3.345
C52	4.325	-5.016	1.833
C53	-7.969	3.116	-6.607
C54	-6.973	-7.894	2.671
C55	7.415	-5.419	3.966
C56	6.602	5.645	-4.670
C57	8.952	-5.382	5.912
C58	-9.750	4.844	-6.635
C59	7.226	8.005	-5.111
C60	-7.563	-9.355	4.585
C61	1.566	0.038	-1.480
C62	-0.395	-1.493	-1.238
C63	-0.350	0.432	-2.866
C64	-1.245	-0.449	-1.974
C65	0.736	-0.792	-0.488
C66	-1.120	1.592	-3.515
C67	1.099	-6.650	-3.540
C68	1.496	-7.590	-2.596
C69	2.145	-7.161	-1.453
C70	2.382	-5.807	-1.323
C71	1.925	-4.964	-2.344
C72	-1.267	-2.026	-5.780
C73	-1.855	-1.024	-6.555
C74	-1.284	-0.749	-7.782
C75	-0.183	-1.500	-8.159
C76	0.306	-2.469	-7.289
C77	-1.813	-4.966	-3.366
C78	-3.100	-5.447	-3.101
C79	-3.872	-5.840	-4.176
C80	-3.304	-5.759	-5.435
C81	-2.007	-5.274	-5.562
C82	3.487	-3.899	-5.122

C83	4.770	-3.367	-5.151
C84	4.935	-2.000	-5.024
C85	3.798	-1.225	-4.905
C86	2.565	-1.887	-4.901
C87	9.939	-4.261	6.366
C88	10.821	-3.792	5.154
C89	9.189	-3.029	6.978
C90	10.887	-4.860	7.468
C91	8.344	-3.308	8.234
C92	11.823	-5.995	7.012
C93	10.166	-2.838	4.140
C94	12.705	-6.625	8.127
C95	11.843	-7.289	9.214
C96	13.591	-7.709	7.481
C97	13.620	-5.573	8.777
C98	7.411	-2.147	8.681
C99	6.312	-1.882	7.637
C100	6.733	-2.560	10.002
C101	8.205	-0.853	8.922
C102	10.973	-2.580	2.837
C103	10.207	-1.535	2.001
C104	11.102	-3.864	2.001
C105	12.374	-2.028	3.145
C106	7.195	9.184	-4.086
C107	5.823	9.931	-4.248
C108	7.299	8.648	-2.614
C109	8.410	10.128	-4.371
C110	8.561	7.832	-2.276
C111	8.387	10.854	-5.729
C112	5.649	11.214	-3.415
C113	9.571	11.829	-5.987
C114	10.922	11.098	-5.934
C115	9.396	12.430	-7.397
C116	9.575	12.980	-4.967
C117	8.555	7.138	-0.885
C118	7.486	6.033	-0.819
C119	9.936	6.486	-0.668
C120	8.310	8.149	0.247
C121	4.323	11.991	-3.653
C122	4.303	13.205	-2.702
C123	3.097	11.115	-3.350
C124	4.233	12.508	-5.099
C125	-11.090	4.838	-5.834
C126	-10.865	5.121	-4.309
C127	-12.013	5.969	-6.417
C128	-11.821	3.460	-6.014
C129	-12.468	5.786	-7.877
C130	-11.307	2.279	-5.171
C131	-10.234	6.482	-3.961
C132	-11.882	0.885	-5.547
C133	-11.420	0.456	-6.951
C134	-11.346	-0.142	-4.529
C135	-13.417	0.876	-5.490

C136	-13.328	6.942	-8.462
C137	-12.540	8.263	-8.496
C138	-13.711	6.569	-9.908
C139	-14.619	7.143	-7.653
C140	-9.789	6.651	-2.481
C141	-9.284	8.095	-2.295
C142	-8.639	5.689	-2.131
C143	-10.960	6.414	-1.514
C144	-8.225	-8.871	5.913
C145	-8.964	-7.503	5.722
C146	-9.279	-9.955	6.350
C147	-7.151	-8.745	7.054
C148	-8.713	-11.340	6.719
C149	-6.344	-7.435	7.124
C150	-10.166	-7.507	4.760
C151	-5.142	-7.439	8.109
C152	-4.050	-8.417	7.643
C153	-4.539	-6.019	8.134
C154	-5.582	-7.808	9.534
C155	-9.767	-12.408	7.125
C156	-10.743	-12.698	5.973
C157	-9.018	-13.712	7.468
C158	-10.563	-11.964	8.364
C159	-10.743	-6.107	4.406
C160	-12.000	-6.313	3.537
C161	-9.732	-5.274	3.598
C162	-11.144	-5.331	5.671
C163	3.886	0.274	-0.938
C164	4.841	1.223	-0.227
C165	6.299	0.863	-0.496
C166	7.245	1.812	0.240
C167	8.705	1.523	-0.112
C168	9.654	2.434	0.667
C169	11.111	2.177	0.286
C170	12.058	3.071	1.071
O1	3.404	-7.049	1.175
O2	6.078	0.612	-4.578
O3	-3.323	1.312	-7.598
O4	-5.732	-6.173	-1.964
O5	1.811	5.856	-2.788
O6	5.428	-0.736	3.428
O7	-3.426	-4.695	4.507
O8	-7.129	1.839	-1.732
O9	7.738	5.216	-4.822
O10	-8.192	2.723	-7.745
O11	-7.917	-8.252	1.979
O12	7.996	-6.330	3.391
O13	-2.259	-1.101	-2.743
O14	0.740	1.003	-2.126
O15	-1.224	-2.232	-0.322
O16	1.544	-1.753	0.209
O17	-1.921	2.303	-2.569
O18	2.558	0.767	-0.754

Pd1	-1.239	1.876	2.447
Pd2	0.572	-4.078	-4.825
H1	2.894	0.633	-4.816
H2	3.293	-4.241	-0.352
H3	-2.780	-5.335	-1.076
H4	-3.338	-0.747	-5.152
H5	-6.397	-7.474	0.090
H6	-3.507	-4.316	0.632
H7	-5.457	-6.058	4.048
H8	2.740	2.161	-3.296
H9	6.554	3.013	-5.130
H10	4.266	6.171	-3.299
H11	-2.147	4.631	1.930
H12	0.166	6.244	-1.281
H13	0.791	2.320	0.385
H14	-2.556	-0.667	1.946
H15	-2.581	-2.908	5.629
H16	-1.002	1.048	5.267
H17	-2.546	1.966	-0.148
H18	-6.804	1.988	0.485
H19	-3.933	2.062	3.646
H20	0.921	3.616	3.448
H21	4.471	1.276	3.861
H22	0.653	-0.351	2.699
H23	-6.301	2.078	2.891
H24	-1.505	-0.946	6.664
H25	3.333	3.455	4.014
H26	-1.634	6.504	0.380
H27	2.436	-1.785	3.018
H28	2.147	3.022	-1.322
H29	-3.935	2.015	-1.987
H30	-3.619	-2.700	2.014
H31	-7.779	2.849	-3.874
H32	-4.011	0.792	-3.800
H33	-5.767	1.945	-7.573
H34	3.089	-3.270	1.606
H35	6.506	-2.835	4.189
H36	5.711	-6.615	2.277
H37	7.150	-4.306	5.685
H38	-5.804	-8.211	4.344
H39	-8.301	4.527	-5.134
H40	5.274	7.219	-4.886
H41	8.550	-5.913	6.782
H42	9.476	-6.129	5.306
H43	-9.390	5.871	-6.766
H44	-9.904	4.439	-7.640
H45	6.983	8.363	-6.117
H46	8.229	7.569	-5.168
H47	-8.330	-9.693	3.880
H48	-6.914	-10.217	4.772
H49	0.002	-2.234	-1.940
H50	-1.760	0.158	-1.224
H51	0.302	-0.144	0.278

H52	2.036	-0.604	-2.234
H53	-0.596	-2.700	0.266
H54	-1.321	2.940	-2.128
H55	2.204	-1.198	0.678
H56	0.074	-0.166	-3.679
H57	-0.434	2.307	-3.983
H58	-1.787	1.216	-4.287
H59	-2.691	-1.730	-2.128
H60	0.575	-6.971	-4.438
H61	2.463	-7.893	-0.721
H62	2.089	-3.892	-2.292
H63	-1.694	-2.288	-4.818
H64	-1.672	0.001	-8.460
H65	1.176	-3.064	-7.561
H66	-4.879	-6.225	-4.074
H67	-1.550	-5.190	-6.546
H68	3.342	-4.974	-5.208
H69	5.936	-1.588	-5.049
H70	1.641	-1.326	-4.829
H71	-3.862	-6.068	-6.314
H72	0.292	-1.337	-9.121
H73	5.630	-4.019	-5.268
H74	1.296	-8.644	-2.756
H75	-1.170	-4.641	-2.554
H76	11.709	-3.286	5.556
H77	11.184	-4.681	4.627
H78	8.545	-2.585	6.214
H79	9.935	-2.263	7.225
H80	10.270	-5.233	8.292
H81	11.495	-4.043	7.876
H82	9.022	-3.544	9.064
H83	7.728	-4.201	8.076
H84	12.488	-5.616	6.228
H85	11.227	-6.793	6.555
H86	9.998	-1.872	4.633
H87	9.180	-3.213	3.855
H88	12.467	-7.834	9.932
H89	11.138	-8.004	8.777
H90	11.268	-6.552	9.785
H91	14.236	-8.191	8.224
H92	14.238	-7.282	6.706
H93	12.981	-8.491	7.013
H94	14.319	-6.041	9.480
H95	13.047	-4.829	9.340
H96	14.212	-5.044	8.022
H97	5.586	-1.149	8.007
H98	5.764	-2.800	7.399
H99	6.720	-1.483	6.703
H100	7.474	-2.745	10.788
H101	6.144	-3.476	9.875
H102	6.055	-1.777	10.364
H103	9.025	-1.019	9.630
H104	7.562	-0.068	9.336

H105	8.635	-0.463	7.994
H106	10.107	-0.588	2.543
H107	9.198	-1.887	1.755
H108	10.724	-1.326	1.058
H109	11.724	-4.615	2.497
H110	11.565	-3.656	1.029
H111	10.120	-4.312	1.811
H112	12.995	-2.767	3.663
H113	12.316	-1.134	3.776
H114	12.900	-1.752	2.224
H115	5.672	10.161	-5.307
H116	5.018	9.238	-3.975
H117	6.406	8.054	-2.394
H118	7.270	9.502	-1.929
H119	9.329	9.534	-4.322
H120	8.482	10.863	-3.563
H121	9.428	8.503	-2.321
H122	8.729	7.065	-3.039
H123	7.455	11.422	-5.826
H124	8.377	10.105	-6.531
H125	6.482	11.897	-3.612
H126	5.706	10.957	-2.350
H127	11.741	11.764	-6.231
H128	10.932	10.237	-6.611
H129	11.150	10.738	-4.926
H130	10.203	13.132	-7.634
H131	8.448	12.975	-7.480
H132	9.400	11.648	-8.164
H133	10.335	13.728	-5.221
H134	9.798	12.627	-3.955
H135	8.604	13.488	-4.941
H136	7.544	5.487	0.130
H137	7.619	5.305	-1.627
H138	6.472	6.438	-0.895
H139	10.736	7.233	-0.700
H140	10.145	5.736	-1.440
H141	9.990	5.985	0.305
H142	9.026	8.976	0.198
H143	8.417	7.674	1.229
H144	7.301	8.571	0.201
H145	5.155	13.868	-2.889
H146	4.350	12.888	-1.654
H147	3.389	13.795	-2.829
H148	3.001	10.289	-4.063
H149	2.171	11.699	-3.407
H150	3.157	10.686	-2.343
H151	4.140	11.690	-5.820
H152	5.121	13.092	-5.365
H153	3.358	13.154	-5.232
H154	-11.835	5.049	-3.801
H155	-10.243	4.329	-3.885
H156	-11.485	6.925	-6.339
H157	-12.901	6.048	-5.777

H158	-11.789	3.187	-7.073
H159	-12.881	3.604	-5.763
H160	-13.048	4.859	-7.957
H161	-11.587	5.656	-8.516
H162	-11.551	2.476	-4.119
H163	-10.218	2.222	-5.228
H164	-10.959	7.272	-4.194
H165	-9.364	6.664	-4.603
H166	-11.730	-0.573	-7.169
H167	-10.329	0.499	-7.038
H168	-11.846	1.091	-7.734
H169	-11.712	-1.151	-4.751
H170	-11.661	0.108	-3.510
H171	-10.250	-0.176	-4.541
H172	-13.812	-0.133	-5.655
H173	-13.854	1.523	-6.258
H174	-13.778	1.219	-4.514
H175	-13.104	9.044	-9.018
H176	-11.584	8.139	-9.017
H177	-12.329	8.638	-7.489
H178	-14.290	5.638	-9.937
H179	-12.820	6.427	-10.530
H180	-14.319	7.352	-10.374
H181	-15.180	6.206	-7.565
H182	-15.275	7.879	-8.133
H183	-14.413	7.509	-6.642
H184	-10.073	8.823	-2.516
H185	-8.438	8.307	-2.959
H186	-8.950	8.271	-1.265
H187	-8.962	4.643	-2.139
H188	-8.246	5.895	-1.129
H189	-7.809	5.791	-2.840
H190	-11.301	5.373	-1.538
H191	-11.813	7.055	-1.763
H192	-10.670	6.635	-0.481
H193	-9.318	-7.169	6.706
H194	-8.243	-6.754	5.383
H195	-10.001	-10.088	5.538
H196	-9.838	-9.559	7.206
H197	-6.464	-9.594	6.979
H198	-7.668	-8.851	8.017
H199	-8.004	-11.230	7.548
H200	-8.139	-11.730	5.870
H201	-7.026	-6.628	7.421
H202	-5.970	-7.167	6.134
H203	-10.970	-8.101	5.212
H204	-9.895	-8.016	3.829
H205	-3.155	-8.336	8.271
H206	-3.749	-8.210	6.609
H207	-4.384	-9.458	7.694
H208	-3.677	-5.964	8.808
H209	-5.275	-5.283	8.475
H210	-4.201	-5.716	7.137

H211	-4.752	-7.708	10.242
H212	-5.934	-8.844	9.593
H213	-6.393	-7.156	9.878
H214	-11.407	-13.535	6.221
H215	-10.204	-12.963	5.056
H216	-11.382	-11.837	5.753
H217	-8.319	-13.560	8.298
H218	-8.445	-14.076	6.609
H219	-9.715	-14.505	7.763
H220	-9.894	-11.698	9.189
H221	-11.222	-12.767	8.716
H222	-11.198	-11.098	8.151
H223	-12.764	-6.887	4.076
H224	-11.760	-6.858	2.617
H225	-12.447	-5.355	3.250
H226	-8.844	-5.021	4.186
H227	-10.178	-4.329	3.268
H228	-9.402	-5.813	2.703
H229	-10.272	-5.073	6.281
H230	-11.830	-5.917	6.292
H231	-11.648	-4.392	5.414
H232	4.119	0.238	-2.003
H233	3.972	-0.736	-0.527
H234	4.636	1.204	0.849
H235	4.642	2.253	-0.551
H236	6.493	0.911	-1.574
H237	6.491	-0.169	-0.178
H238	7.096	1.710	1.322
H239	7.006	2.849	-0.023
H240	8.856	1.669	-1.189
H241	8.937	0.475	0.107
H242	9.520	2.267	1.743
H243	9.403	3.482	0.469
H244	11.252	2.358	-0.786
H245	11.368	1.129	0.475
H246	13.095	2.870	0.782
H247	11.964	2.892	2.147
H248	11.851	4.128	0.878