Supporting Information

Self-Assembled Squares and Triangles by Simultaneous Hydrogen Bonding and Metal Coordination

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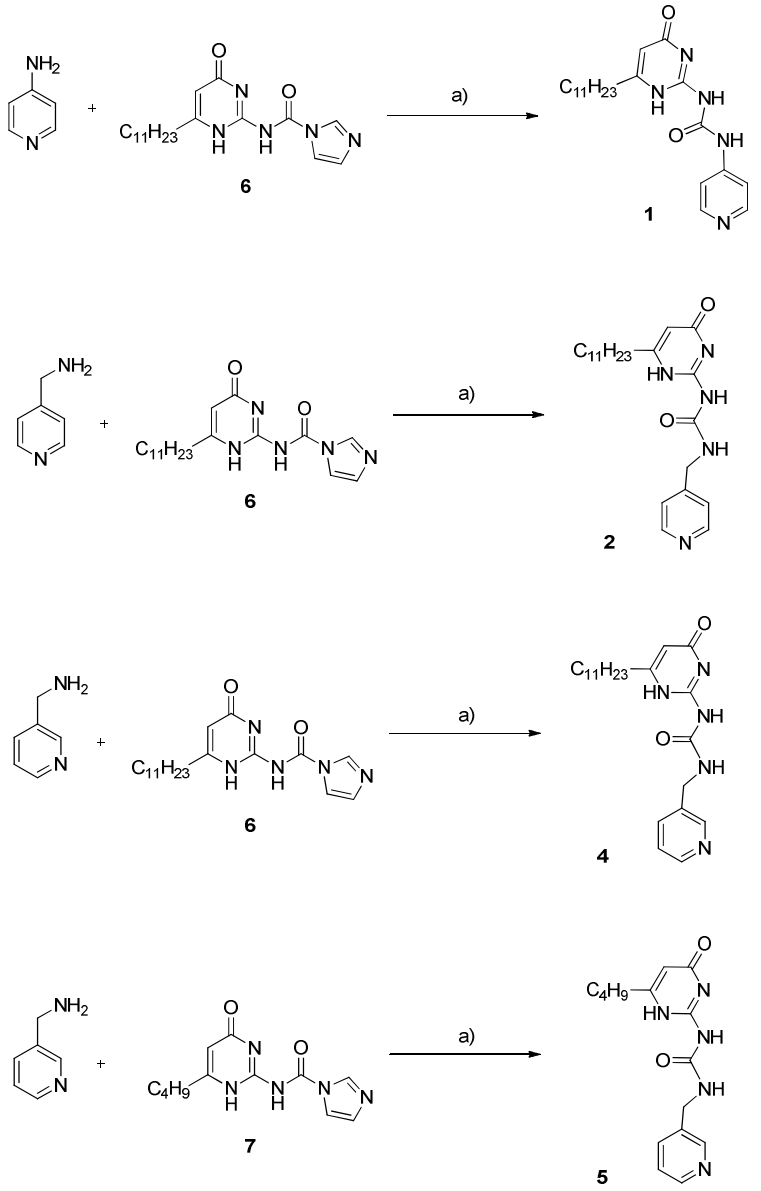
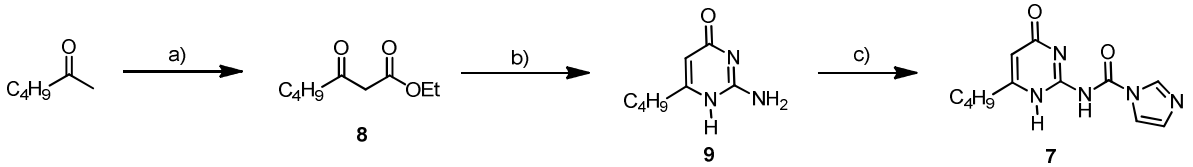
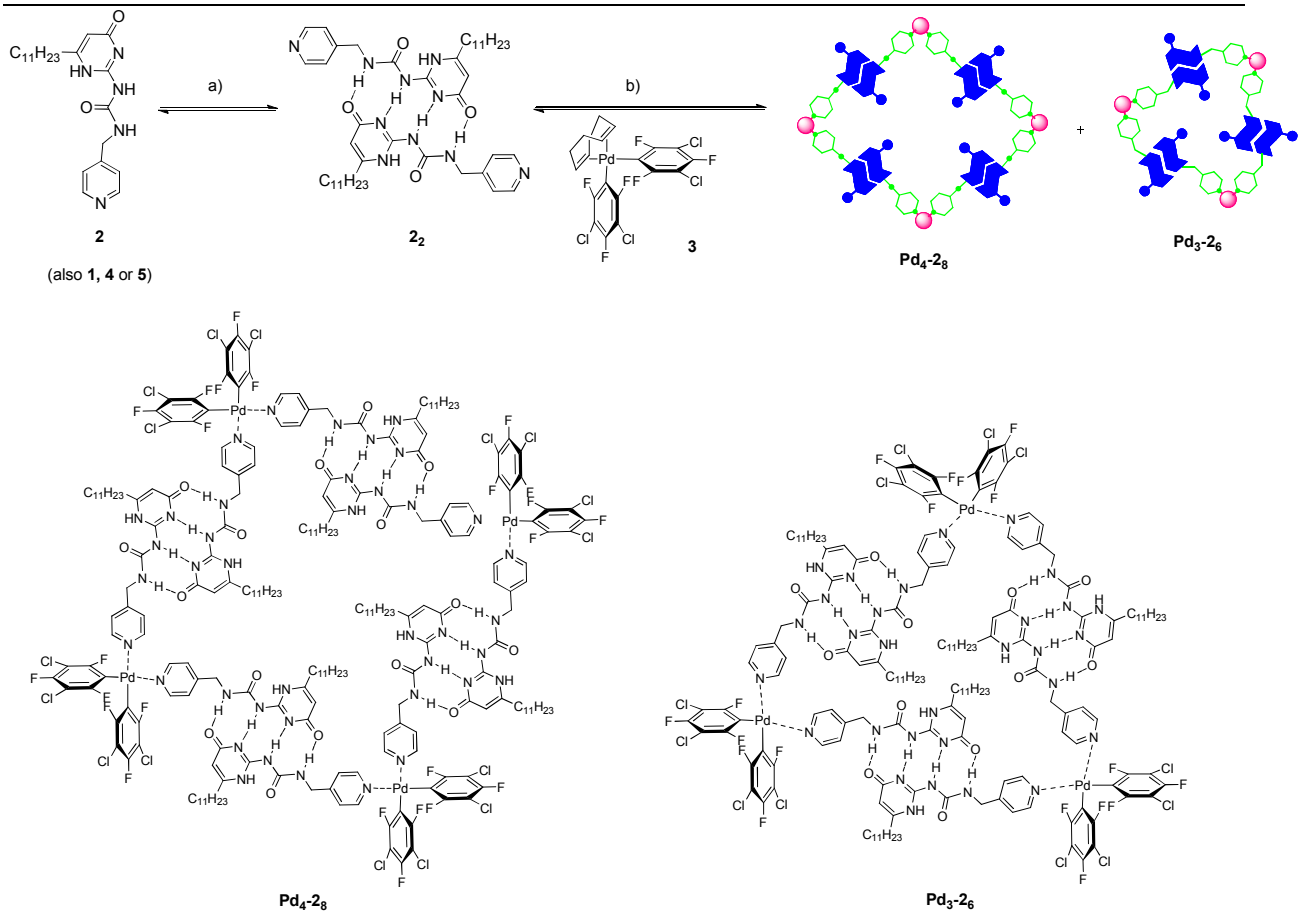
SECTION SS1: Synthetic Routes and Reaction Conditions



Scheme SS1: Synthetic route for preparation of the UPy-pyridine monomers; Reagents and conditions: a) Triethylamine, DMF, 70 °C, overnight, sealed tube (**1** 43%, **2** 40%, **4** 59%, **5** 77%).



Scheme SS2 – Preparation of the isocytosine derivative 7: Reagents and conditions: a) i) NaH, THF, reflux, 30 min, ii) Diethyl carbonate, THF, reflux O/N (38%); b) Guanidinium carbonate, EtOH, reflux, O/N (quant.); c) CDI, THF, rt, O/N (quant.).

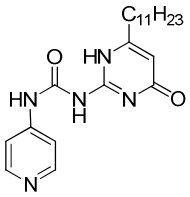


Scheme SS3: Synthetic route for preparation of the molecular architectures; Reagents and conditions: a) **1**, **2**, **4** or **5**, $CDCl_3$, 25 °C, 5 min; b) **3**, $CDCl_3$, 25 °C, 1 h – 2 weeks.

Compounds **6**[SS1] and **3**[SS2] were prepared according to literature procedures.

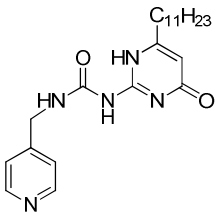
SECTION SS2: Preparation of the Building Blocks

1-(4-Oxo-6-undecyl-1,4-dihydropyrimidin-2-yl)-3-(pyridine-4-yl)urea (1)



Pyridin-4-amine (0.136 g, 1.445 mmol) and isocytosine derivative **6** (0.571 g, 1.590 mmol) were placed in a sealed tube and dissolved in DMF (8 mL). Triethylamine (2.44 mL) was added and the mixture warmed to 70 °C overnight. After this time, the solvent was removed at reduced pressure and the residue triturated with methanol and stored in the fridge for 1 h. The resulting white solid was filtered, washed with methanol, and purified by column chromatography (silica gel, $CHCl_3$-$CHCl_3$/EtOAc) to give the desired product **1** as a white solid (0.177 g, 43%). Mp >250 °C. The sample was not soluble in $CDCl_3$ and aggregation could not be studied. For characterisation purposes, TFA was added to the ^{1}H NMR samples. ^{1}H NMR ($CDCl_3$+TFA, 400 MHz) δ 0.90 (3H, t, *J* 6.8 Hz, CH_3), 1.22-1.49 (16H, m, CH_2), 1.72-1.82 (2H, m, CH_2), 2.75 (2H, t, *J* 7.8 Hz, CH_2), 6.31 (1H, s, CH), 8.24 (2H, d, *J* 7.1 Hz, CH_{pyr}) and 8.66 (2H, d, *J* 7.1 Hz, CH_{pyr}); ^{13}C NMR ($CDCl_3$+TFA, 100 MHz) δ 14.0 (CH_3), 22.6 (CH_2), 26.8 (CH_2), 28.7 (CH_2), 29.0 (CH_2), 29.1 (CH_2), 29.3 (CH_2), 31.8 (CH_2), 32.9 (CH_2), 105.7 (CH), 115.4 (CH_{pyr}), 141.8 (CH_{pyr}), 153.4 (C_q), 156.7 (C_q) and 191.7 (C_q); LRMS (ES^+) *m/z* 386.2 $[M+H]^+$; HRMS (ES^-) calculated for $C_{21}H_{30}N_5O_2$: 384.2400, found: 384.2404.

1-(4-Oxo-6-undecyl-1,4-dihydropyrimidin-2-yl)-3-(pyridine-4-ylmethyl)urea (2)

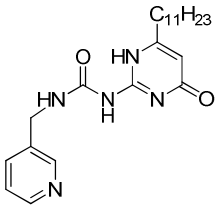


Pyridin-4-ylmethanamine (0.109 g, 1.012 mmol) and blocked isocytosine **6** (0.4 g, 1.113 mmol) were placed in a sealed tube and dissolved in DMF (8 mL). Triethylamine (1.706 mL) was added and the mixture warmed to 70 °C overnight. After this time, the solvent was removed at reduced pressure and the residue triturated with methanol and stored in the fridge for 1 h. The resulting white solid was filtered, washed with methanol, and purified by column chromatography (silica gel, $CHCl_3$-$CHCl_3$/EtOAc) to give the desired product **2** as a white solid (0.408 g, 40%). Mp >250 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) (dimer) δ 0.90 (6H, t, *J* 7.0 Hz, CH_3), 1.22-1.41 (32H, m, CH_2), 1.65 (4H, quint., *J* 7.5 Hz, CH_2), 2.48 (4H, t, *J* 7.5 Hz, CH_2), 4.49 (4H, d, *J* 5.8 Hz, CH_2), 5.86 (2H, s, CH), 7.30 (4H, d, *J* 6.0 Hz, CH_{pyr}), 8.57 (4H, d, *J* 6.0 Hz, CH_{pyr}), 11.04 (2H, s, NH), 12.17 (2H, s, NH) and 12.97 (2H, s, NH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.1 (CH_3), 22.6 (CH_2), 27.0 (CH_2), 28.8 (CH_2), 29.1 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 31.9 (CH_2), 32.7 (CH_2), 42.5 (CH_2), 106.1 (CH), 122.1 (CH_{pyr}), 147.8 (C_q), 149.9

(CH_{pyr}), 152.8 (C_q), 154.5 (C_q), 157.0 (C_q) and 173.2 (C_q); LRMS (ES^+) *m/z* 400.3 $[M+H]^+$; HRMS (ES^-) calculated for $C_{22}H_{34}N_5O_2$: 400.2713, found: 400.2699.

Data for the monomeric species (after addition of TFA): ^{1}H NMR ($CDCl_3$+TFA, 500 MHz) δ 0.90 (3H, t, *J* 6.8 Hz, CH_3), 1.21-1.43 (16H, m, CH_2), 1.67 (2H, quint., *J* 7.6 Hz, CH_2), 2.55 (2H, t, *J* 7.6 Hz, CH_2), 4.72 (2H, d, *J* 5.6 Hz, CH_2), 5.99 (1H, s, CH), 7.87 (2H, d, *J* 6.4 Hz, CH_{pyr}) and 8.88 (2H, d, *J* 6.4 Hz, CH_{pyr}); ^{13}C NMR ($CDCl_3$+TFA, 100 MHz) δ 14.0 (CH_3), 22.6 (CH_2), 26.8 (CH_2), 28.3 (CH_2), 28.7 (CH_2), 28.8 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 31.8 (CH_2), 32.7 (CH_2), 42.8 (CH_2), 105.7 (CH), 125.0 (CH_{pyr}), 142.2 (CH_{pyr}), 154.1 (C_q), 157.5 (C_q) and 158.2 (C_q).

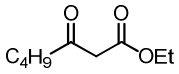
1-(4-Oxo-6-undecyl-1,4-dihydropyrimidin-2-yl)-3-(pyridine-3-ylmethyl)urea (4)



Pyridin-3-ylmethanamine (0.068 g, 0.632 mmol) and blocked isocytosine **6** (0.25 g, 0.695 mmol) were placed in a sealed tube and dissolved in DMF (8 mL). Triethylamine (1.01 mL) was added and the mixture warmed to 70 °C overnight. After this time, the solvent was removed at reduced pressure and the residue triturated with methanol and stored in the fridge for 1 h. The resulting white solid was filtered, washed with methanol, and purified by column chromatography (silica gel, $CHCl_3$-$CHCl_3$/EtOAc) to give the desired product **4** as a white solid (0.150 g, 59%). Mp >250 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) (dimer) δ 0.90 (6H, t, *J* 7.1 Hz, CH_3), 1.22-42 (32H, m, CH_2), 1.58-1.69 (4H, m, CH_2), 2.48 (4H, t, *J* 7.6 Hz, CH_2), 4.49 (4H, d, *J* 5.7 Hz, CH_2), 5.84 (2H, s, CH), 7.27 (2H, ddd, *J* 7.9, 4.8, 0.8 Hz, CH_{Ar5}), 7.73 (2H, dt, *J* 7.9, 2.0 Hz, CH_{Ar4}), 8.53 (2H, dd, *J* 4.8, 1.6 Hz, CH_{Ar6}), 8.66 (2H, d, *J* 2.0 Hz, CH_{Ar2}), 10.99 (2H, s, NH), 12.09 (2H, s, NH) and 12.99 (2H, s, NH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.1 (CH_3), 22.7 (CH_2), 22.8 (CH_2), 27.0 (CH_2), 28.8 (CH_2), 29.1 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.6 (CH_2), 31.9 (CH_2), 32.7 (CH_2), 41.1 (CH_2), 106.0 (CH), 123.4 (CH_{Ar5}), 134.3 (C_q), 135.2 (CH_{Ar4}), 148.6 (CH_{Ar6}), 149.3 (CH_{Ar2}), 152.7 (C_q), 154.5 (C_q) and 156.8 (C=O); LRMS (ES^+) *m/z* 400.5 $[M+H]^+$; HRMS (ES^-) calculated for $C_{22}H_{34}N_5O_2$: 400.2713, found: 400.2733.

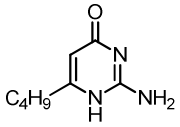
Data for the monomeric species (after addition of TFA): ^{1}H NMR ($CDCl_3$+TFA, 500 MHz) δ 0.90 (3H, t, *J* 6.9 Hz, CH_3), 1.22-43 (16H, m, CH_2), 1.67 (2H, quin, *J* 7.4 Hz, CH_2), 2.54 (2H, t, *J* 7.5 Hz, CH_2), 4.63 (2H, d, *J* 5.5 Hz, CH_2), 5.93 (1H, s, CH), 7.80 (1H, dd, *J* 7.9, 5.5 Hz, CH_{Ar}), 8.33 (1H, d, *J* 7.6 Hz, CH_{Ar}), 8.81 (1H, d, *J* 4.5 Hz, CH_{Ar}), 8.88 (1H, s, CH_{Ar}), 11.06 (1H, s, NH) and 12.87 (1H, s, NH); ^{13}C NMR ($CDCl_3$+TFA, 100 MHz) δ 14.0 (CH_3), 22.6 (CH_2), 26.9 (CH_2), 27.1 (CH_2), 28.8 (CH_2), 29.1 (CH_2), 29.2 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 31.9 (CH_2), 32.7 (CH_2), 40.7 (CH_2), 105.9 (CH), 126.2 (CH_{Ar}), 138.6 (C_q), 141.6 (CH_{Ar}), 142.2 (CH_{Ar}), 143.0 (CH_{Ar}), 153.7 (C_q), 156.6 (C=O) and 162.0 (C_q).

Ethyl 3-oxoheptanoate (8)



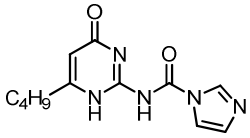
NaH (60% dispersion in mineral oil, 1.148 g, 49.9 mmol) was suspended in dry THF (25 mL) and the mixture heated to reflux. A solution of hexan-2-one (5 g, 49.9 mmol) in dry THF (20 mL) was added dropwise and the mixture heated under reflux for 30 min. A solution of diethyl carbonate (8.84 g, 74.9 mmol) in dry THF (20 mL) was the added and the reaction heated under reflux overnight. The mixture was then cooled to room temperature, saturated ammonium chloride solution (50 mL) added, and the aqueous phase extracted with diethyl ether (2 x 50 mL). The organic phase was dried ($MgSO_4$) and the solvents removed at reduced pressure. The resulting oil was used crude without further purification.

2-Amino-6-butylpyrimidin-4(*1H*)-one (9)



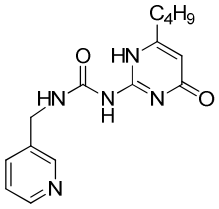
A suspension of the keto ester **8** (1 g, 5.81 mmol) and guanidinium carbonate (0.531 g, 2.9 mmol) in absolute ethanol (100 mL) was heated under reflux overnight. Solvent was then removed at reduced pressure and the reaction mixture cooled to 4 °C. The resulting residue was triturated with acetone and cooled in the fridge for 15 min. The precipitate was filtered off and washed with cold acetone, yielding the pyrimidinone **9** as a white solid (490 mg, quant.). Mp 191-193 °C. ^{1}H (DMSO-d_6, 400 MHz) 0.88 (3H, t, *J* 7.3 Hz, CH_3), 1.29 (2H, sex, *J* 7.4 Hz, CH_2), 1.51 (2H, quint, *J* 7.5 Hz, CH_2), 2.21 (2H, t, *J* 7.4 Hz, CH_2), 5.31 (1H, s, CH) and 6.67 (3H, brs, NH_2); ^{13}C (DMSO-d_6, 100 MHz) 14.3 (CH_3), 22.1 (CH_2), 30.1 (CH_2), 37.0 (CH_2), 99.8 (CH), 166.2 (C_q) and 169.4 (C=O).

***N*-(4-Oxo-6-butyl-1,4-dihydropyrimidin-2-yl)-*1H*-imidazole-1-carboxamide (7)**



Using a modified procedure to that previously reported.[SS3] A suspension of the pyrimidinone **9** (485 mg, 2.9 mmol) and CDI (941 mg, 5.8 mmol) in dry THF (150 mL) was stirred overnight under reflux in an argon atmosphere. The solvent was then removed under reduced pressure and the residue triturated with acetone. The solid was filtered off, washed with cold acetone and dried under air, affording the desired isocytosine derivative **7** as a white solid (910 mg, quant.). Data agree with literature values.[SS3] Mp 163-164 °C. ^{1}H ($CDCl_3$, 400 MHz) 1.01 (3H, t, *J* 7.3 Hz, CH_3), 1.51 (2H, sex, *J* 7.6 Hz, CH_2), 1.77 (2H, quint, *J* 7.6 Hz, CH_2), 2.68 (2H, t, *J* 7.7 Hz, CH_2), 5.83 (1H, s, CH), 7.03-7.04 (1H, m, CH), 7.66 (1H, t, *J* 1.4 Hz, CH) and 8.87 (1H, t, *J* 1.0 Hz, CH); ^{13}C ($CDCl_3$, 100 MHz) 13.8 (CH_3), 22.1 (CH_2), 29.4 (CH_2), 32.4 (CH_2), 103.9 (CH), 117.8 (CH), 127.8 (CH), 137.9 (CH), 156.9 (C_q), 159.6 (C=O) and 160.7 (C=O).

1-(4-Oxo-6-butyl-1,4-dihydropyrimidin-2-yl)-3-(pyridine-3-ylmethyl)urea (5)

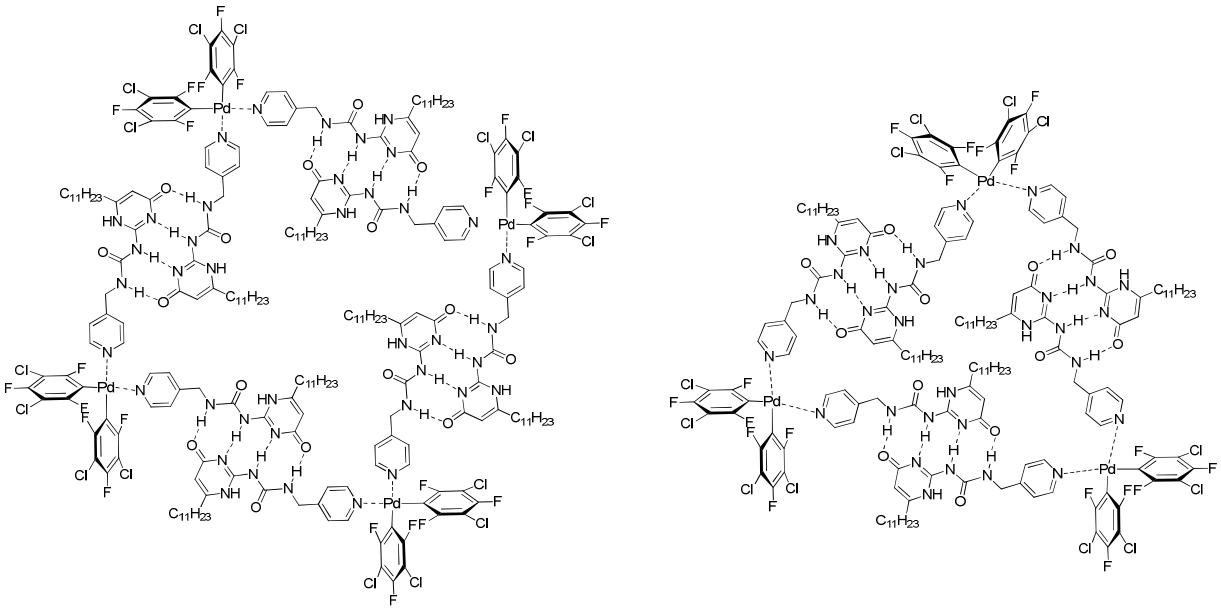


Pyridin-3-ylmethanamine (0.075 g, 0.696 mmol) and isocytosine derivative **7** (0.2 g, 0.765 mmol) were placed in a sealed tube and dissolved in DMF (10 mL). Triethylamine (1.174 mL) was added and the mixture warmed overnight at 70 °C. After this time, the solvent was removed at reduced pressure and the residue triturated with methanol and stored in the fridge for 1 h. The resulting white solid was filtered, washed with methanol, and purified by column chromatography (silica gel, $CHCl_3$-$CHCl_3$/EtOAc) to give the desired product **5** as a white solid (0.161 g, 77%). Mp >250 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) (dimer) δ 0.97 (6H, t, *J* 7.3 Hz, CH_3), 1.42 (4H, sex, *J* 7.4 Hz, CH_2), 1.65 (4H, quint, *J* 7.5 Hz, CH_2), 2.49 (4H, t, *J* 7.5 Hz, CH_2), 4.49 (4H, d, *J* 5.8 Hz, CH_2), 5.85 (2H, s, CH), 7.27 (2H, d, *J* 4.7 Hz, CH_{Ar5}), 7.73 (2H, d, *J* 7.9 Hz, CH_{Ar4}), 8.53 (2H, d, *J* 4.7 Hz, CH_{Ar6}), 8.66 (2H, d, *J* 1.7 Hz, CH_{Ar2}), 10.99 (2H, s, NH), 12.09 (2H, s, NH) and 12.99 (2H, s, NH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.6 (CH_3), 21.9 (CH_2), 28.9 (CH_2), 32.4 (CH_2), 41.1 (CH_2), 106.1 (CH), 123.4 (CH_{Ar5}), 134.7 (C_q), 135.3 (CH_{Ar4}), 148.6 (C_{Ar6}), 149.3 (CH_{Ar2}), 152.6 (C_q) and 156.9 (C=O); LRMS (ES^+) *m/z* 302.3 $[M+H]^+$; HRMS (ES^-) calculated for $C_{15}H_{19}N_5O_2$: 301.1539, found: 301.1556.

Data for the monomeric species (after addition of TFA): ^{1}H NMR ($CDCl_3$+TFA, 500 MHz) δ 0.98 (3H, t, *J* 7.4 Hz, CH_3), 1.44 (2H, sex, *J* 7.5 Hz, CH_2), 1.68 (2H, quint, *J* 7.8 Hz, CH_2), 2.63 (2H, t, *J* 7.6 Hz, CH_2), 4.74 (2H, d, *J* 5.9 Hz, CH_2), 6.14 (1H, s, CH), 8.01 (1H, dd, *J* 8.0, 5.9 Hz, CH_{Ar}), 8.53 (1H, dt, *J* 8.0, 1.6 Hz, CH_{Ar}), 8.89 (1H, d, *J* 5.9 Hz, CH_{Ar}) and 9.12 (1H, d, *J* 1.6 Hz, CH_{Ar}); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.5 (CH_3), 21.6 (CH_2), 28.8 (CH_2), 32.4 (CH_2), 40.9 (CH_2), 106.1 (CH), 126.8 (CH_{Ar}), 138.7 (C_q), 140.8 (CH_{Ar}), 141.8 (C_{Ar}), 145.8 (CH_{Ar}), 154.2 (C_q) and 157.1 (C=O)

SECTION SS3: Preparation of the Molecular Architectures

Preparation of Molecular Square and Triangle (Pd_4-2_8 and Pd_3-2_6)



A solution of dimer $\mathbf{2_2}$ (2 eq., 0.125 mmol) in $CDCl_3$ (2 mL) was stirred at room temperature for 10 minutes. After this time, the palladium complex (COD)Pd($C_6F_3Cl_2$)$_2$ **3** (1 eq., 0.0625 mmol) was added and the resulting mixture stirred at room temperature for two days. ^{1}H, ^{18}F and ^{13}C NMR spectra were recorded both with and without the addition of TFA. Elemental analysis for solid sample: for both square $C_{224}H_{264}Cl_{16}F_{24}N_{40}O_{16}Pd_4$ and triangle $C_{168}H_{198}Cl_{12}F_{18}N_{30}O_{12}Pd_3$, exp. C 51.15%, H 5.13%, N 10.30%, calc. C 51.5%, H 5.10% and N 10.73%. Using ^{1}H DOSY NMR the two different species could be identified in the ^{1}H NMR spectrum.

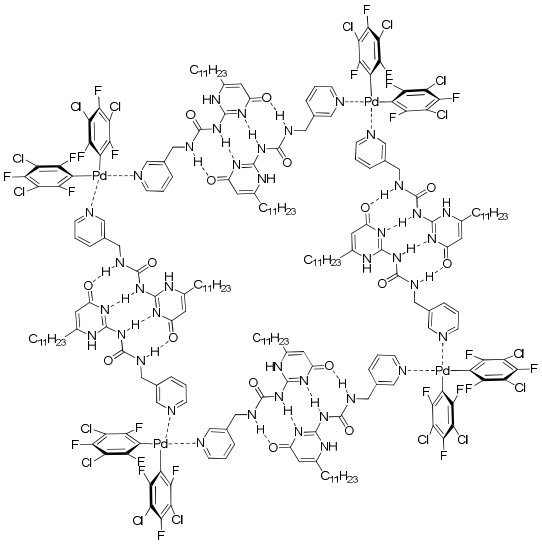
Data for the triangle $\mathbf{Pd_3}$-$\mathbf{2_6}$: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.91 (3H, t, *J* 6.7 Hz, CH_3), 1.20-1.42 (16H, m, CH_2), 1.63 (2H, brquint., CH_2), 2.45 (2H, t, *J* 7.4 Hz, CH_2), 4.39 (2H, d, *J* 5.6 Hz, CH_2), 5.80 (1H, s, CH), 7.35 (2H, d, *J* 6.0 Hz, CH_{pyr}), 8.45 (2H, d, *J* 6.0 Hz, CH_{pyr}), 10.96 (1H, t, *J* 5.6 Hz, NH), 12.08 (1H, s, NH) and 12.87 (1H, s, NH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.2 (CH_3), 22.7 (CH_2), 26.9 (CH_2), 28.8 (CH_2), 29.1 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 31.9 (CH_2), 32.7 (CH_2), 42.3 (CH_2), 106.1 (CH), 124.4 (CH_{pyr}), 150.3 (C_q), 150.9 (CH_{pyr}), 152.8 (C_q), 154.3 (C_q), 156.8 (C_q) and 173.0 (C_q); ^{19}F NMR ($CDCl_3$, 376 MHz) δ -119.4 (F_{para}) and -90.8 (F_{ortho}).

Data for the square $\mathbf{Pd_4}$-$\mathbf{2_8}$: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.91 (3H, t, *J* 6.7 Hz, CH_3), 1.20-1.42 (16H, m, CH_2), 1.63 (2H, brquint., CH_2), 2.45 (2H, t, *J* 7.4 Hz, CH_2), 4.43 (2H, d, *J* 4.9 Hz, CH_2), 5.81 (1H, s, CH), 7.29 (2H, d, *J* 6.0 Hz, CH_{pyr}), 8.45 (2H, d, *J* 6.0 Hz, CH_{pyr}), 11.12 (1H, t, *J* 5.6 Hz, NH), 12.16 (1H, s, NH) and 12.84 (1H, s, NH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.2 (CH_3), 22.7 (CH_2), 26.9 (CH_2), 28.8 (CH_2), 29.1 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 31.9 (CH_2), 32.7 (CH_2), 42.1 (CH_2), 117.2 (CH), 123.8 (CH_{pyr}), 150.3 (C_q), 150.7

(CH_{pyr}), 153.0 (C_q), 154.3 (C_q), 156.9 (C_q) and 173.0 (C_q); ^{19}F NMR ($CDCl_3$, 376 MHz) δ -119.6 (F_{para}), and -90.9 to -90.8 (m, F_{ortho}).

After the addition of TFA, these molecular architectures are no longer observed: ^{1}H NMR ($CDCl_3$+TFA, 500 MHz) δ 0.91 (3H, t, *J* 6.7 Hz, CH_3), 1.20-1.42 (16H, m, CH_2), 1.70 (2H, quint., *J* 7.4 Hz, CH_2), 2.65 (2H, t, *J* 7.8 Hz, CH_2), 4.78 (2H, d, *J* 6.0 Hz, CH_2), 5.67 (1H, s, CH), 7.99 (2H, d, *J* 6.0 Hz, CH_{pyr}) and 8.98 (2H, d, *J* 6.0 Hz, CH_{pyr}); ^{19}F NMR ($CDCl_3$+TFA, 376 MHz) δ -111.7, -110.3 and -96.3.

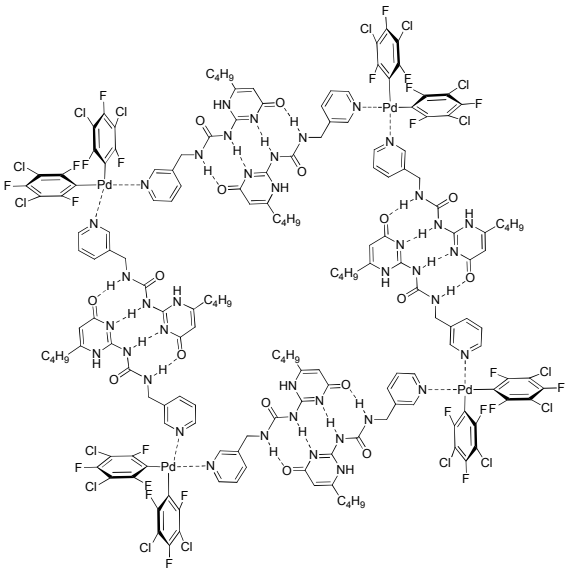
Attempted Preparation of Molecular Square and Triangle (Pd_4-4_8 and Pd_3-4_6)



A solution of dimer $\mathbf{4_2}$ (2 eq., 0.250 mmol) in $CDCl_3$ (4 mL) was stirred at room temperature for 10 minutes. After this time, the palladium complex (COD)Pd($C_6F_3Cl_2$)$_2$ **3** (1 eq., 0.125 mmol) was added and the resulting mixture stirred at room temperature for two days. ^{1}H and ^{18}F NMR spectra were recorded. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.89 (3H, t, *J* 6.7 Hz, CH_3), 1.20-1.45 (16H, m, CH_2), 1.67 (2H, quint., *J* 7.5 Hz, CH_2), 2.50 (2H, t, *J* 7.7 Hz, CH_2), 4.38 (2H, s, CH_2), 6.00 (1H, s, CH), 7.22 (1H, dd, *J* 7.9, 5.5 Hz, CH_{Ar5}), 7.63 (1H, d, *J* 8.0 Hz, CH_{Ar4}), 8.52 (1H, dd, *J* 5.5, 1.3 Hz, CH_{Ar6}), 9.03 (1H, d, *J* 1.3 Hz, CH_{Ar2}), 11.11 (1H, t, *J* 5.3 Hz, NH), 12.11 (1H, s, NH) and 12.89 (1H, s, NH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.1 (CH_3), 22.6 (CH_2), 26.9 (CH_2), 28.0 (CH_2), 29.0 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 29.6 (CH_2), 31.9 (CH_2), 32.7 (CH_2), 40.9 (CH_2), 106.2 (CH), 124.9 (CH_{Ar5}), 136.2 (C_q), 137.1 (CH_{Ar4}), 149.8 (CH_{Ar6}), 150.3 (CH_{Ar2}), 152.6 (C_q), 154.4 (C_q), 156.7 (C=O) and 173.1 (C=O); ^{18}F NMR ($CDCl_3$, 376 MHz) δ -119.770 (F_{para}) and -90.801 (F_{ortho}).

After the addition of TFA, the molecular architecture is no longer observed: ^{1}H NMR ($CDCl_3$+TFA, 500 MHz) δ 0.89 (3H, t, *J* 6.7 Hz, CH_3), 1.19-1.46 (16H, m, CH_2), 1.68 (2H, quint., *J* 7.1 Hz, CH_2), 2.52-2.66 (2H, m, CH_2), 4.47 (2H, d, *J* 5.5 Hz, CH_2), 6.06 (1H, s, CH), 6.93 (1H, dt, *J* 8.6, 2.3 Hz, CH_{Ar}), 7.33 (1H, d, *J* 6.7 Hz, CH_{Ar}), 7.80 (1H, d, *J* 7.9 Hz, CH_{Ar}) and 9.02 (1H, s, CH_{Ar}); ^{18}F NMR ($CDCl_3$+TFA, 376 MHz) δ -117.0155, -111.6967, -110.3932 and -90.7952.

Attempted Preparation of Molecular Square and Triangle (Pd_4-5_8 and Pd_3-5_6)



A solution of dimer $\mathbf{5_2}$ (2 eq., 0.332 mmol) in $CDCl_3$ (4 mL) was stirred at room temperature for 10 minutes. After this time, the palladium complex (COD)Pd($C_6F_3Cl_2$)$_2$ **3** (1 eq., 0.166 mmol) was added and the resulting mixture stirred at room temperature for two days. The resulting mixture was poorly soluble without the addition of TFA to the $CDCl_3$ solution, and therefore well-resolved NMR signals could not be obtained for the sample. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.96 (3H, t, *J* 7.1 Hz, CH_3), 1.43 (2H, sex, *J* 7.6 Hz, CH_2), 1.67 (2H, quint, *J* 7.6 Hz, CH_2), 2.51 (2H, t, *J* 7.6 Hz, CH_2), 4.38 (2H, d, *J* 6.3 Hz, CH_2), 6.00 (1H, s, CH), 7.21-7.23 (1H, m, CH_{Ar}), 7.64 (1H, d, *J* 7.8 Hz, CH_{Ar}), 8.53 (1H, dd, *J* 5.5, 1.5 Hz, CH_{Ar}), 9.02 (1H, d, *J* 1.5 Hz, CH_{Ar}), 11.10 (1H, t, *J* 5.5 Hz, NH), 12.11 (1H, s, NH) and 12.89 (1H, s, NH).

Data for the monomeric species (after addition of TFA): ^{1}H NMR ($CDCl_3$+TFA, 500 MHz) δ 0.97 (3H, t, *J* 7.3 Hz, CH_3), 1.43 (2H, sex, *J* 7.5 Hz, CH_2), 1.67 (2H, quint, *J* 7.6 Hz, CH_2), 2.56 (2H, t, *J* 7.6 Hz, CH_2), 4.40 (2H, brs, CH_2), 5.96 (1H, s, CH), 6.93 (1H, dt, *J* 8.6, 2.3 Hz, CH_{Ar}), 7.28-7.34 (1H, brs, CH_{Ar}), 7.80 (1H, d, *J* 7.9 Hz, CH_{Ar}), 7.87 (1H, brs, CH_{Ar}), 10.56 (1H, brs, NH) and 13.04 (1H, s, NH).

SECTION SS4: References

(SS1) Huerta, E.; Metselaar, G. A.; Fragoso, A.; Santos, E.; Bo, C.; de Mendoza, J. *Angew. Chem. Int. Ed.* **2007**, *46*, 202.

(SS2) Espinet, P.; Martínez-Ilarduya, J. M.; Pérez-Briso, C.; Casado, A. L.; Alonso, M. A. *J. Organomet. Chem.* **1998**, *551*, 9-20.

(SS3) Keizer, H. M.; Sijbesma, R. P.; Meijer, E. W. *Eur. J. Org. Chem.* **2004**, 2553-2555.

SECTION SS5: Spectra for Dimers 1, 2, 4 and 5

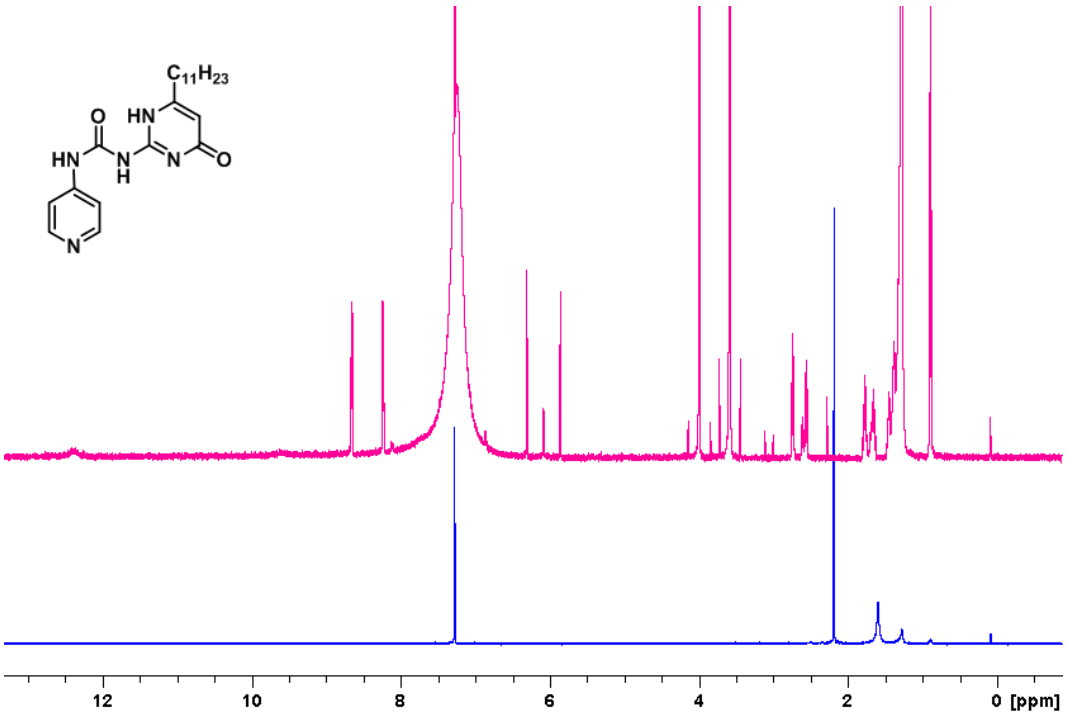


*Figure SS1 – ^{1}H NMR Spectrum of **1** (blue spectrum, 298K, $CDCl_3$, 400 MHz) and monomer **1** (pink spectrum, 298K, $CDCl_3$+TFA, 400 MHz).*

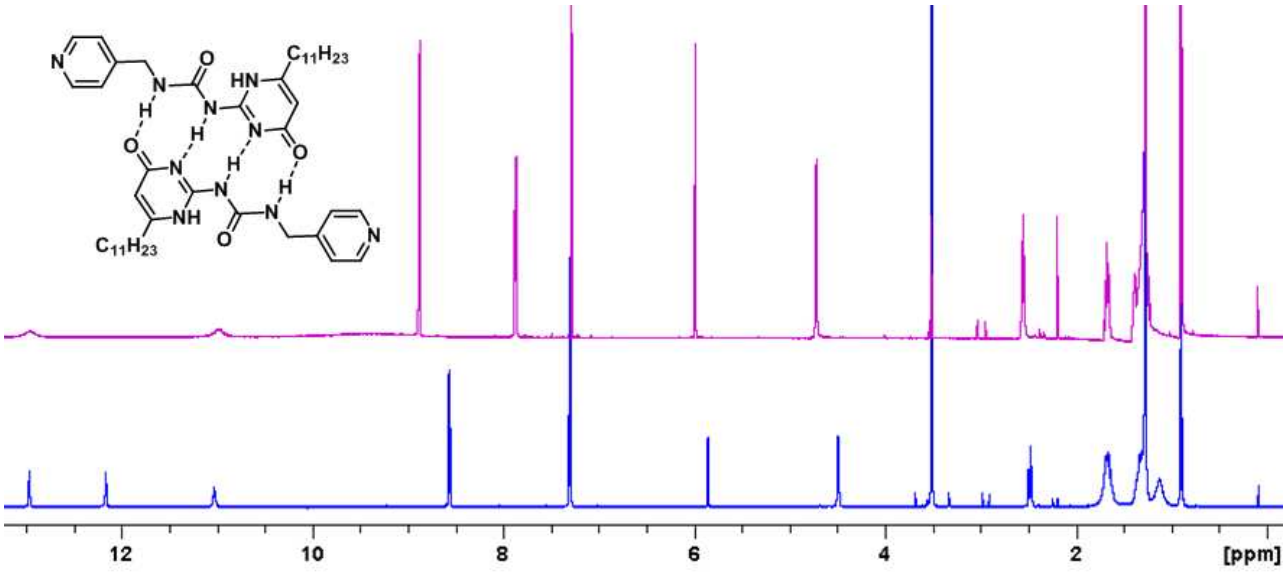


*Figure SS2 – ^{1}H NMR Spectrum of dimer **2_2** (blue spectrum, 298K, $CDCl_3$, 500 MHz) and monomer **2** (pink spectrum, 298K, $CDCl_3$+TFA, 500 MHz).*

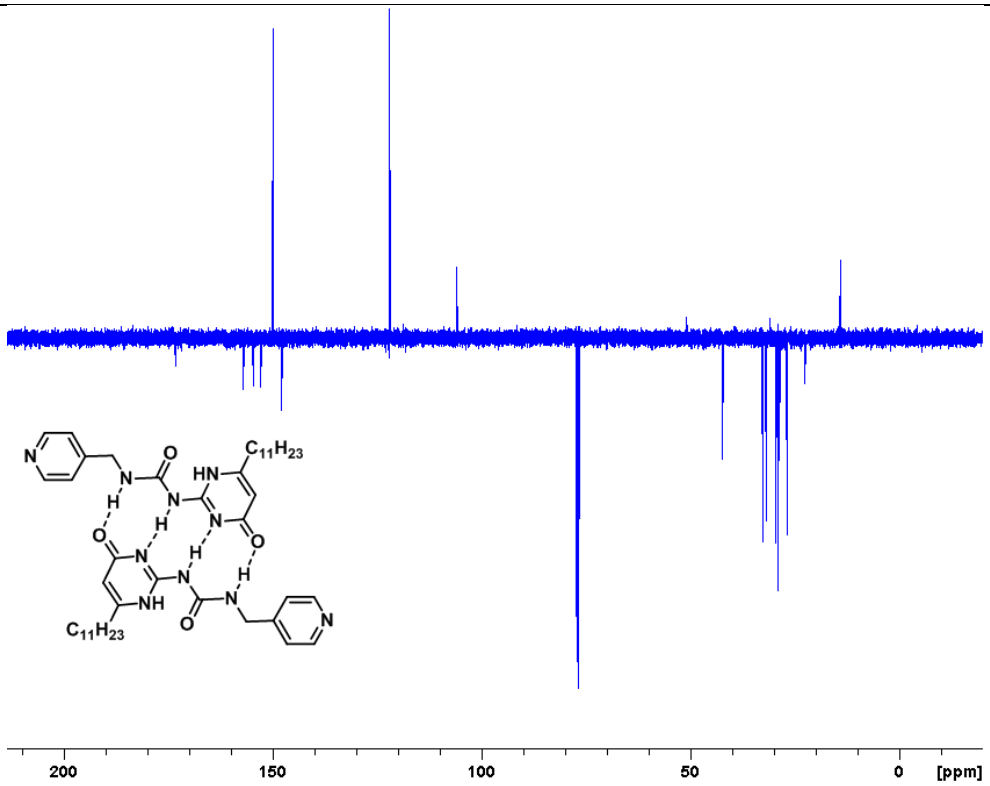


*Figure SS3 – ^{13}C NMR Spectrum of dimer **2**$_2$ (298K, $CDCl_3$, 100 MHz).*

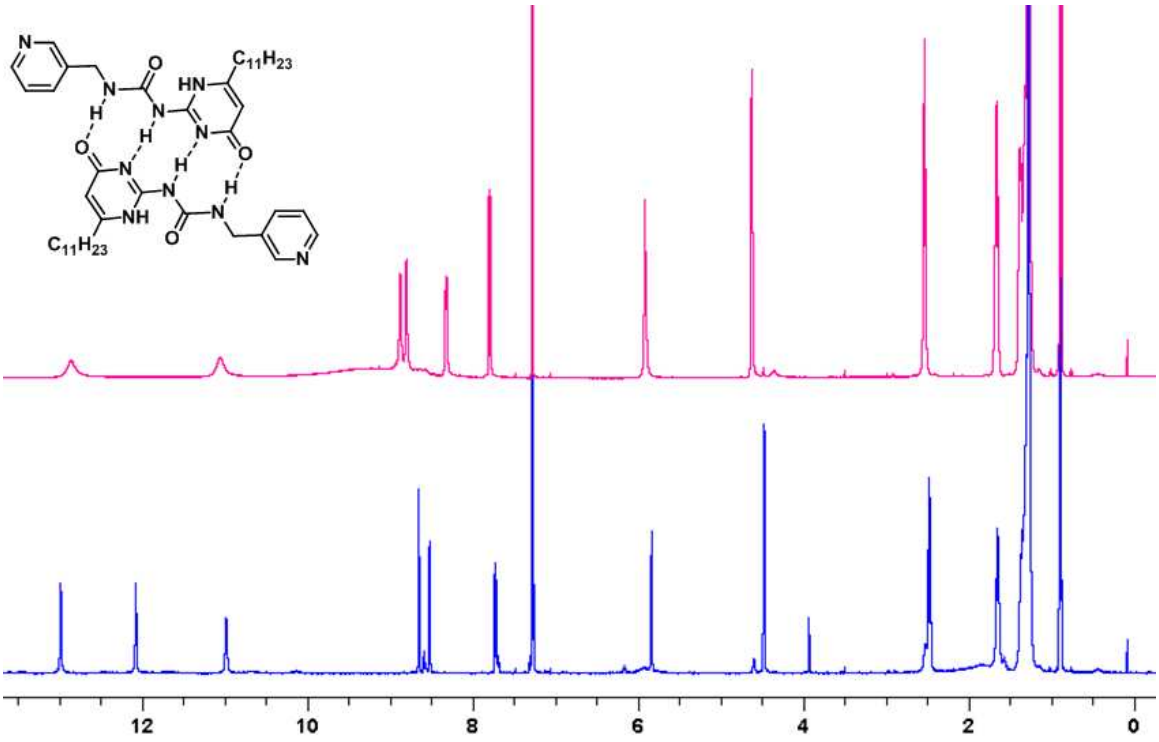


*Figure SS4 – ^{1}H NMR Spectrum of dimer **4**$_X$ (blue spectrum, 298K, $CDCl_3$, 500 MHz) and monomer **4** (pink spectrum, 298K, $CDCl_3$+TFA, 500 MHz).*

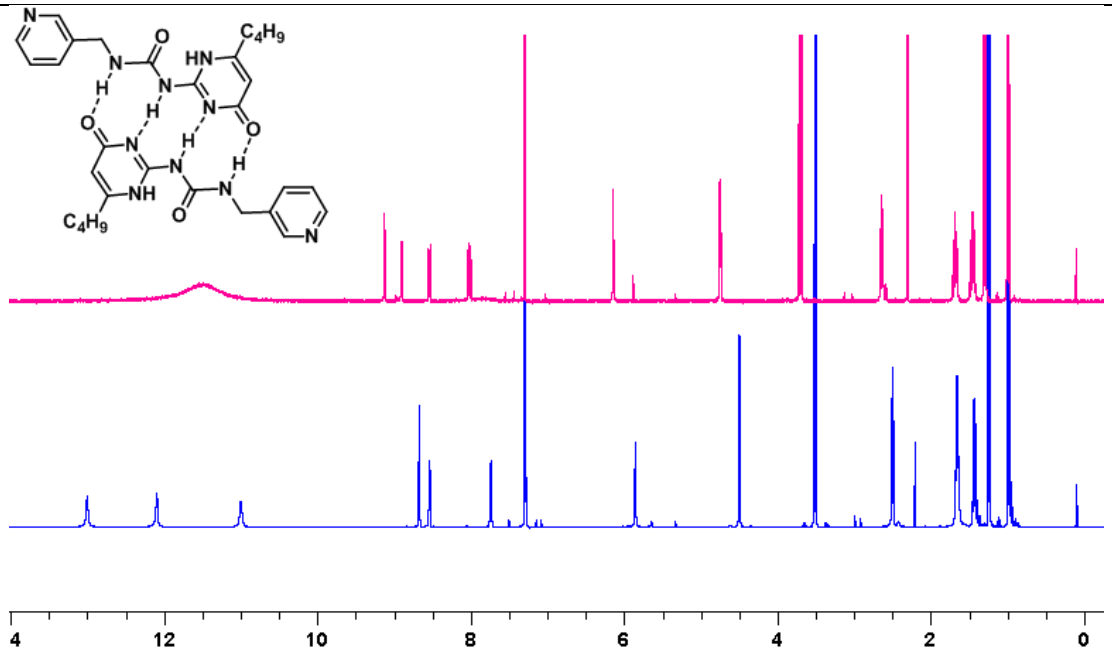


*Figure SS5 – ^{1}H NMR Spectrum of dimer **5**$_2$ (blue spectrum, 298K, $CDCl_3$, 500 MHz) and monomer **5** (pink spectrum, 298K, $CDCl_3$+TFA, 500 MHz).*

SECTION SS6: Spectra for Molecular Architectures Pd_4-2_8 and Pd_3-2_6

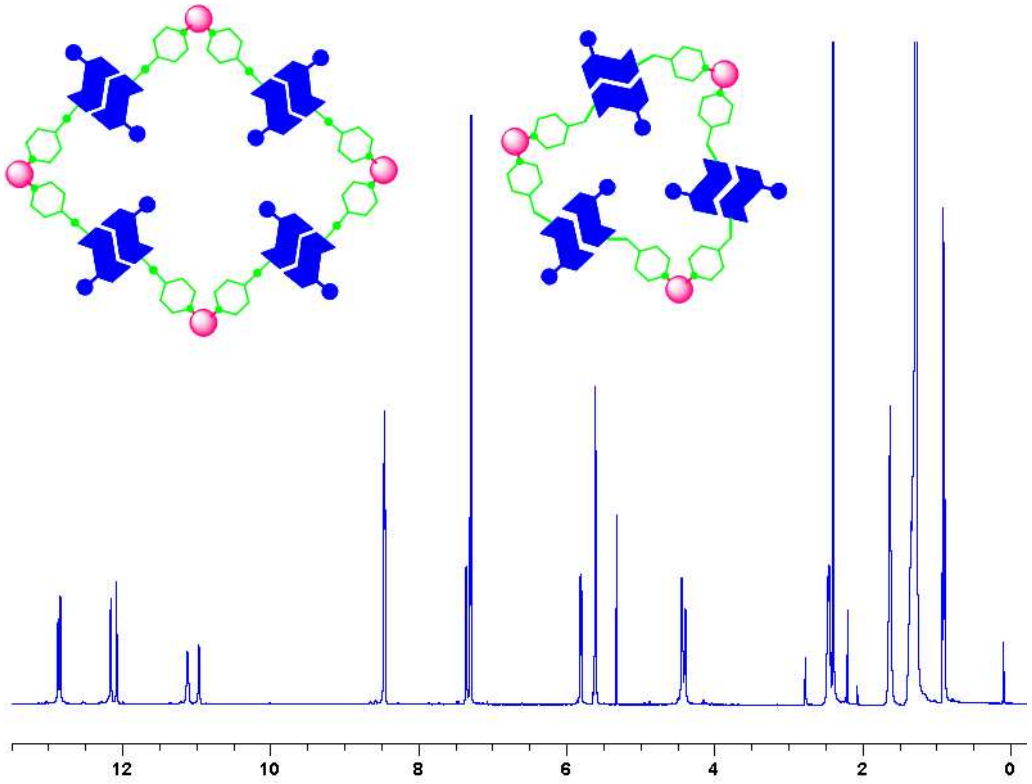


*Figure SS6 – ^{1}H NMR Spectrum of the equilibrium mixture of **Pd_4-2_8** and **Pd_3-2_6** (298K, $CDCl_3$, 500 MHz).*

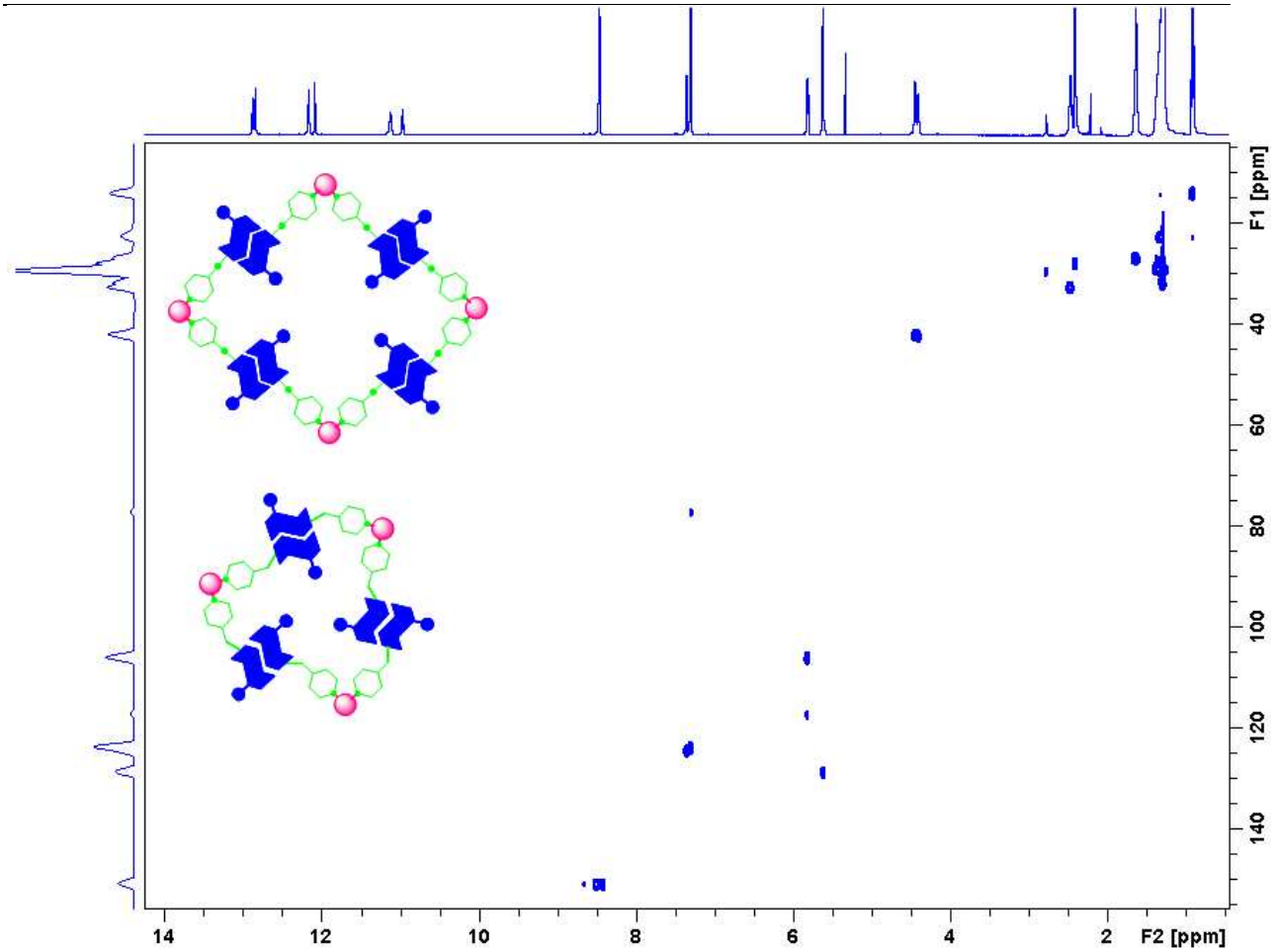


Figure SS7 – ^{1}H-^{13}C HSQC NMR Spectrum of the equilibrium mixture of ***Pd_4-2_8*** *and* ***Pd_3-2_6*** *(298K, $CDCl_3$, 500 MHz).*

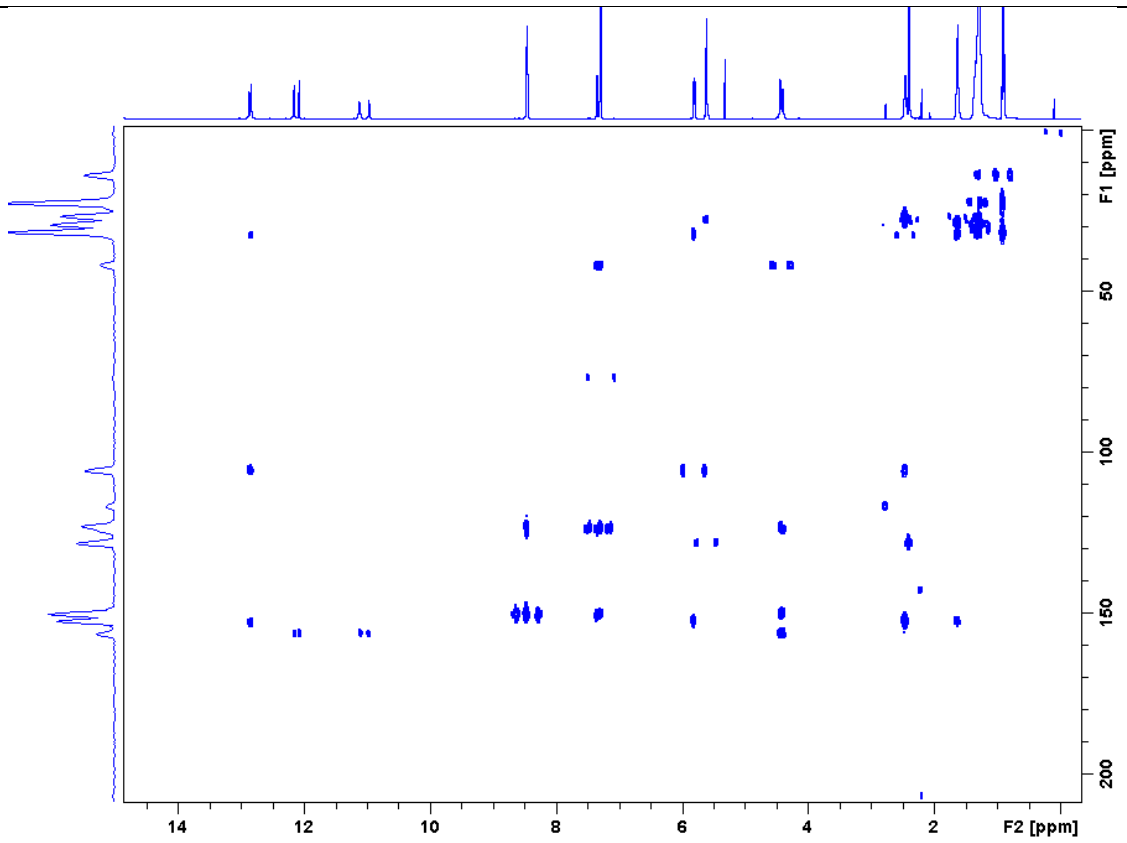


Figure SS8 – ^{1}H-^{13}C HMBC NMR Spectrum of the equilibrium mixture of ***Pd_4-2_8*** *and* ***Pd_3-2_6*** *(298K, $CDCl_3$, 500 MHz).*

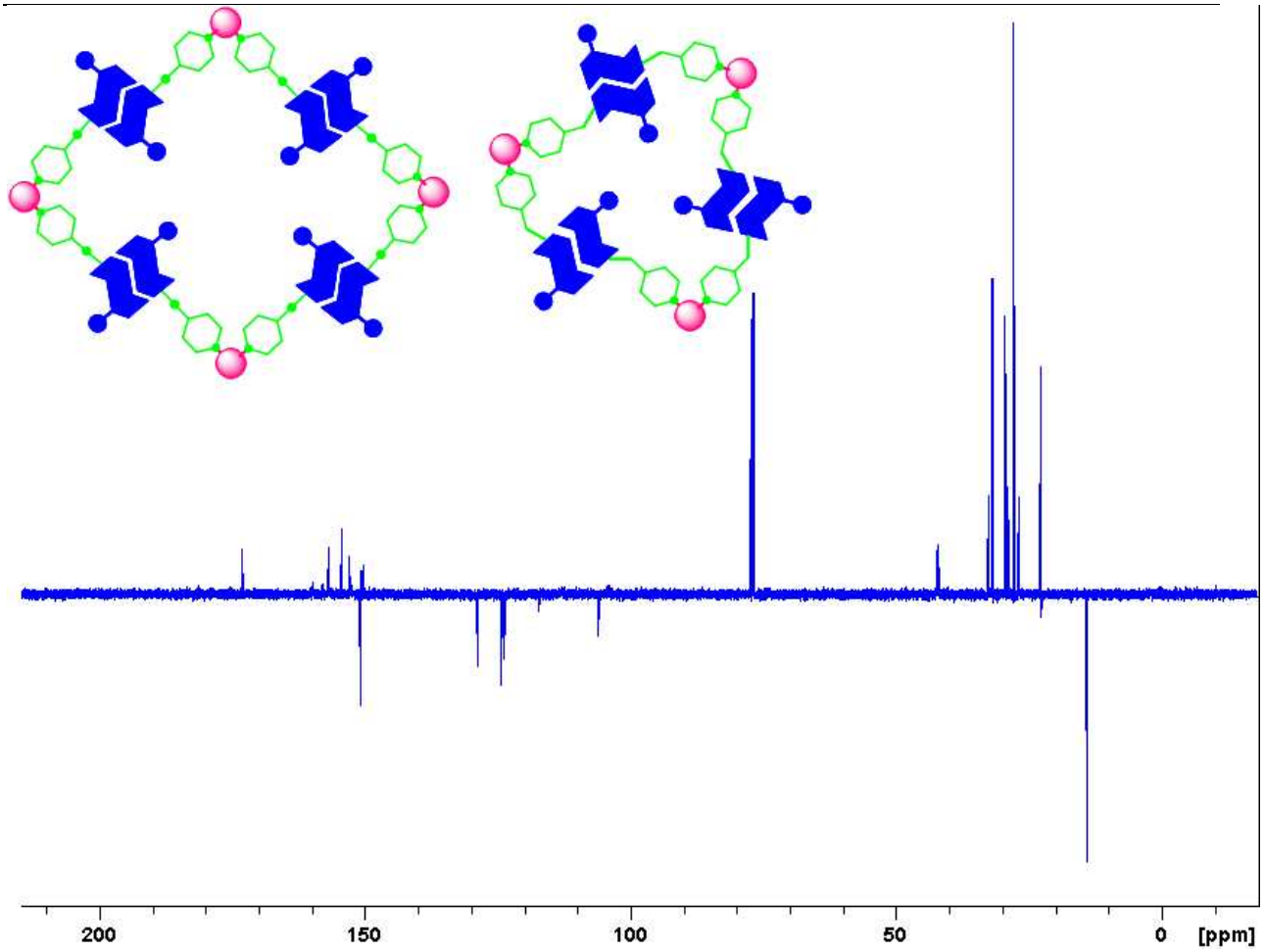


*Figure SS9 – ^{13}C NMR Spectrum of the equilibrium mixture of **Pd_4-2_8** and **Pd_3-2_6** (298K, $CDCl_3$, 100 MHz).*

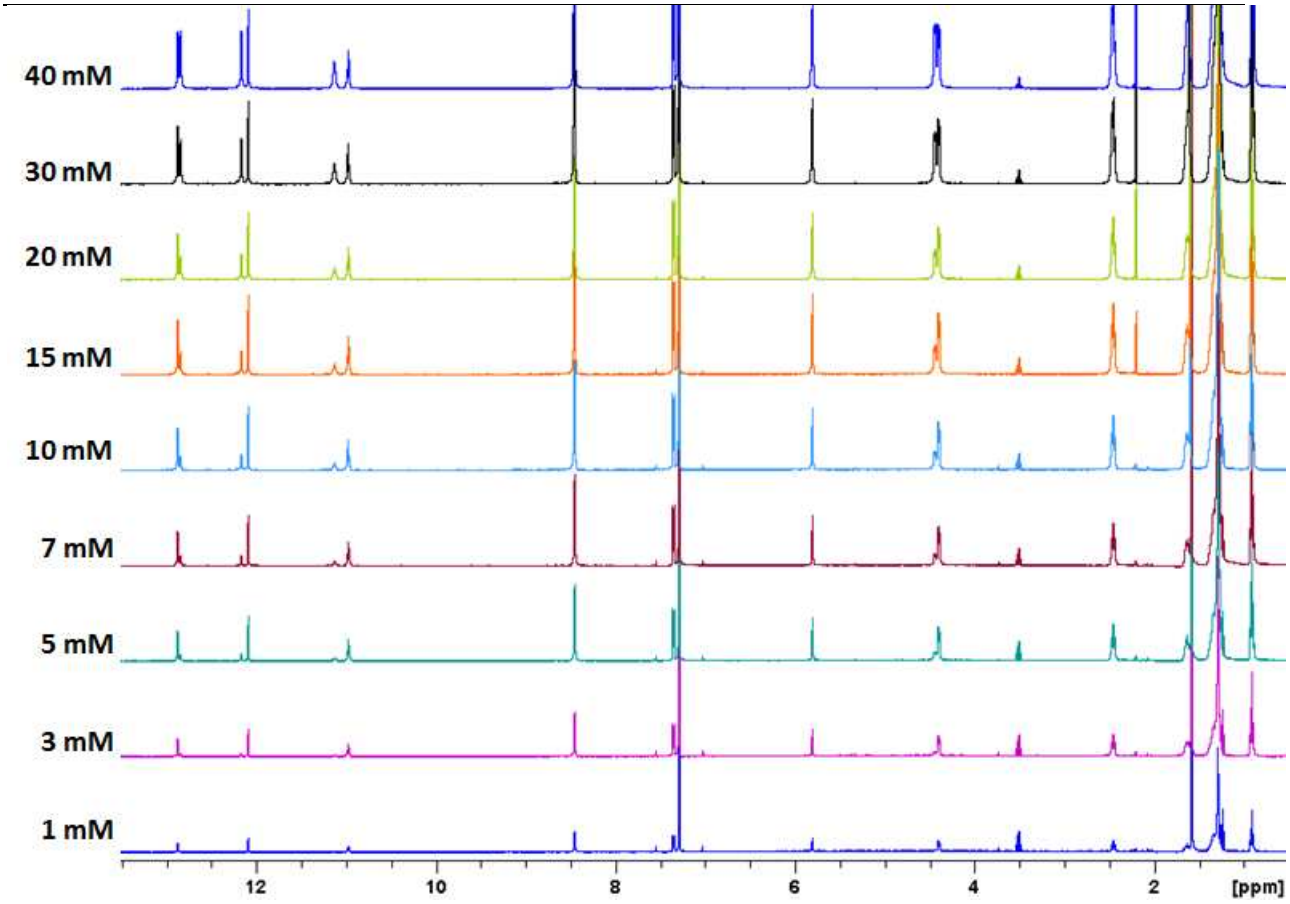


*Figure SS10 – ^{1}H NMR Concentration studies (1-40 mM) of the equilibrium mixture of **Pd_4-2_8** and **Pd_3-2_6** (298K, $CDCl_3$, 400 MHz).*

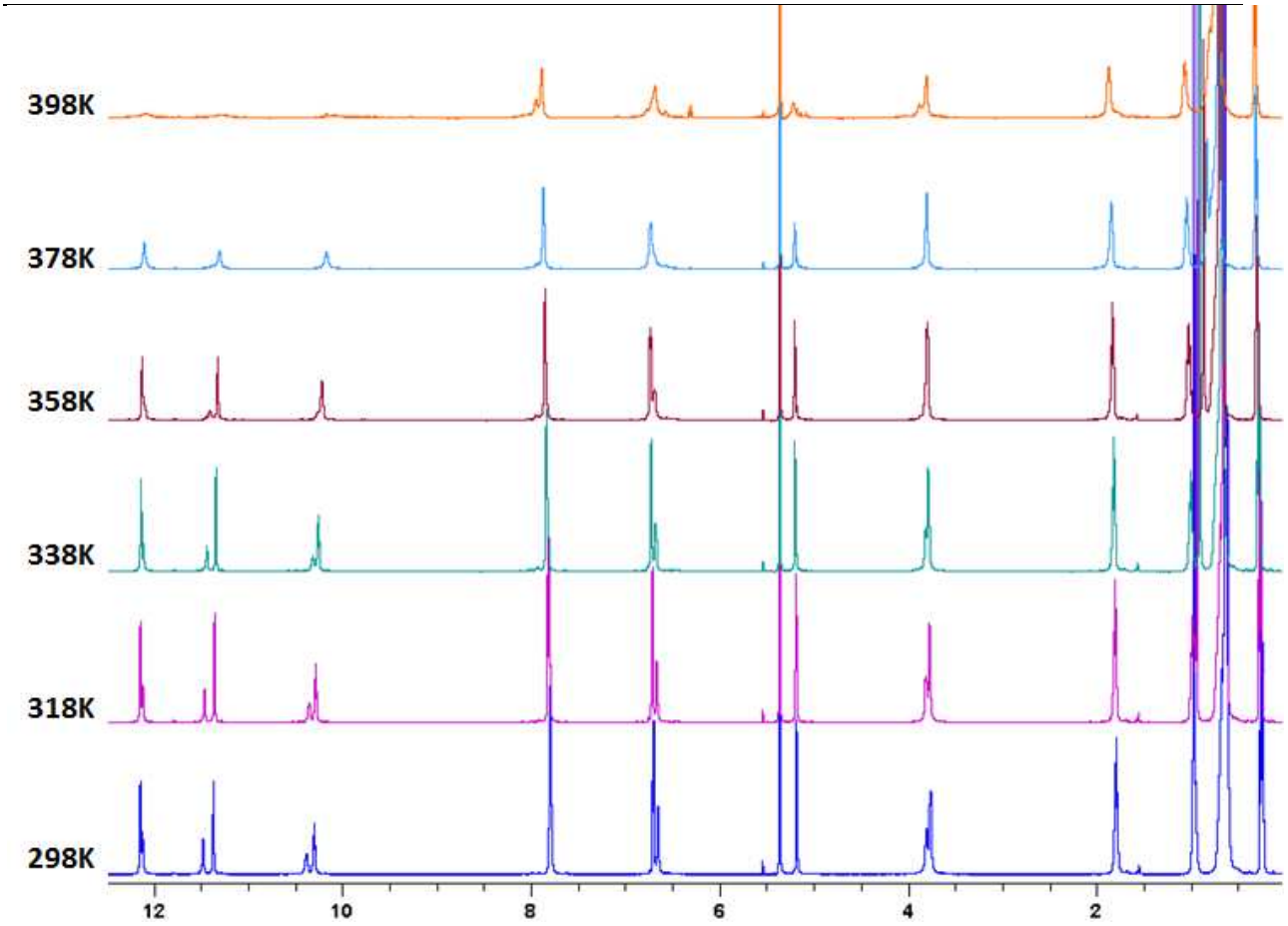


Figure SS11 – Variable temperature ^{1}H NMR spectra of the equilibrium mixture of ***Pd_4-2$_8$*** *and* ***Pd_3-2$_6$****, 298-398K (TCE, 500 MHz).*

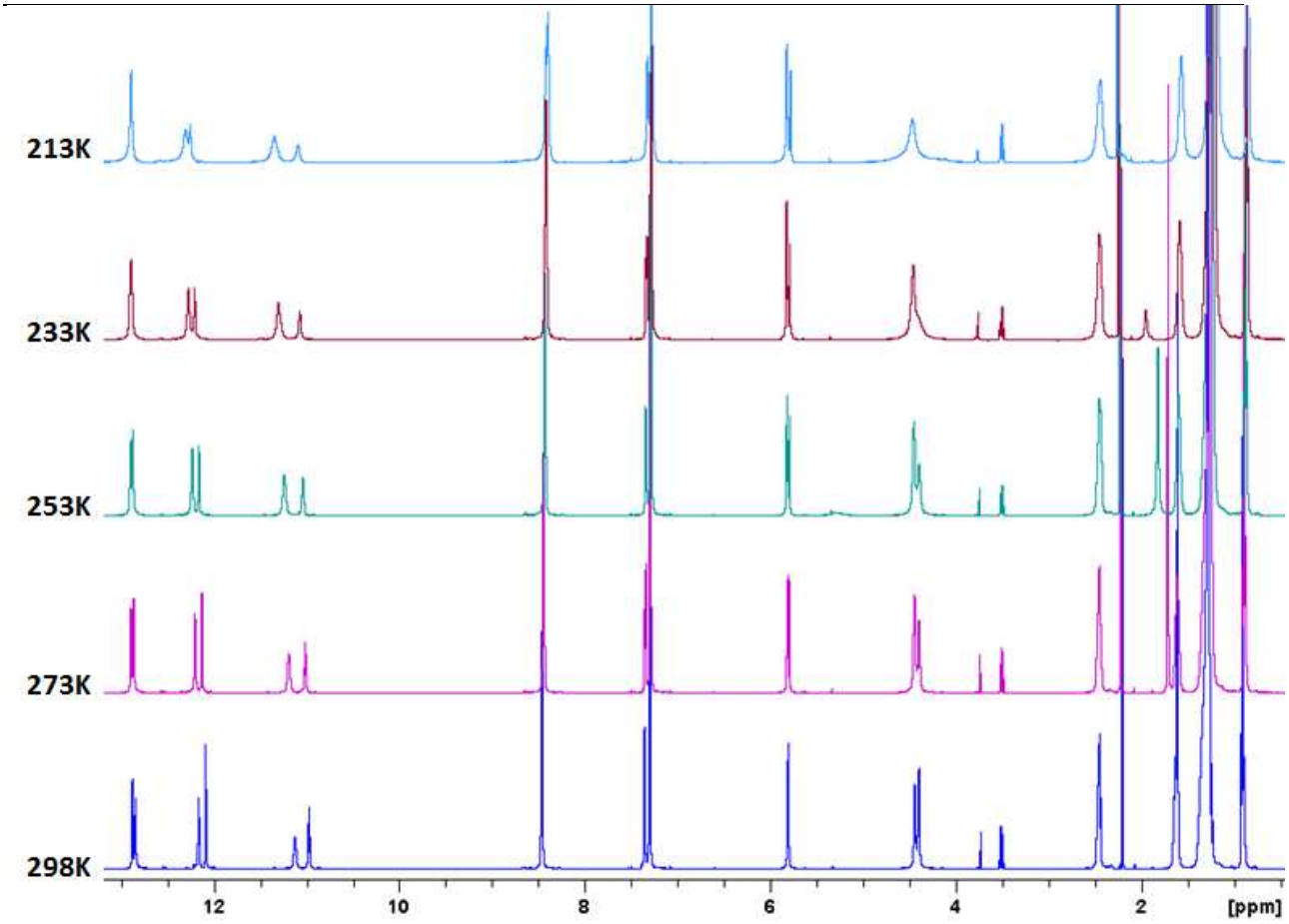


Figure SS12 – Variable temperature ^{1}H NMR spectra of the equilibrium mixture of ***Pd_4-2$_8$*** *and* ***Pd_3-2$_6$****, 298-213K ($CDCl_3$, 500 MHz).*

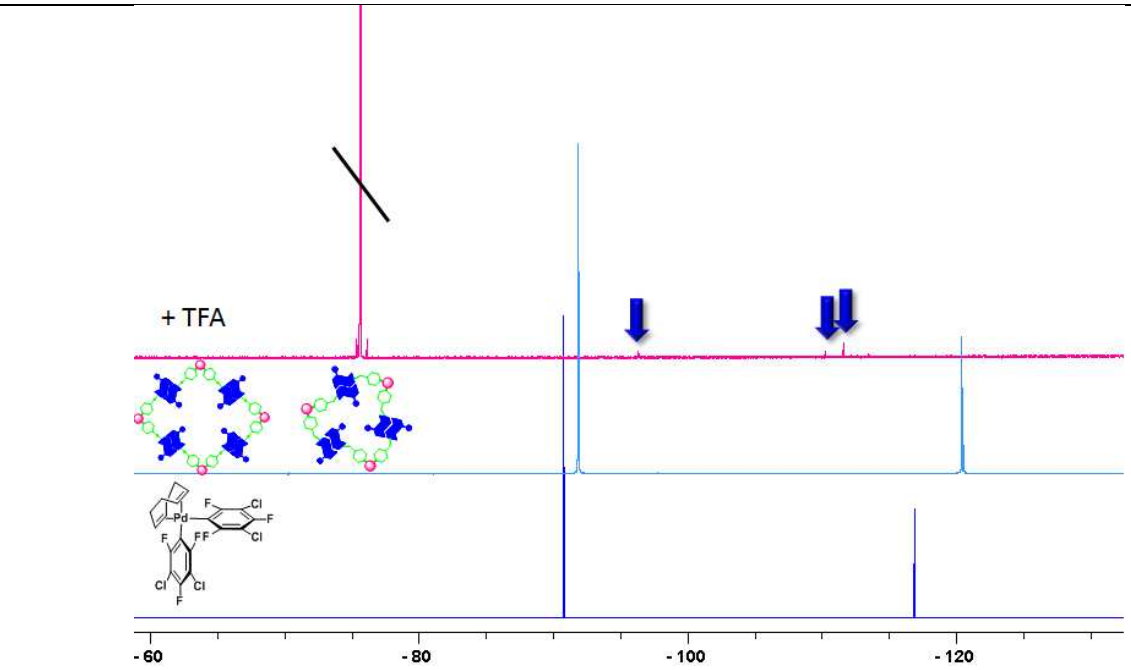


*Figure SS13 – ^{19}F NMR Spectrum of palladium complex **3** (dark blue), equilibrium mixture of **Pd_4-2_8** and **Pd_3-2_6** (light blue), and after the addition of TFA (pink), (298K, $CDCl_3$, 376 MHz).*

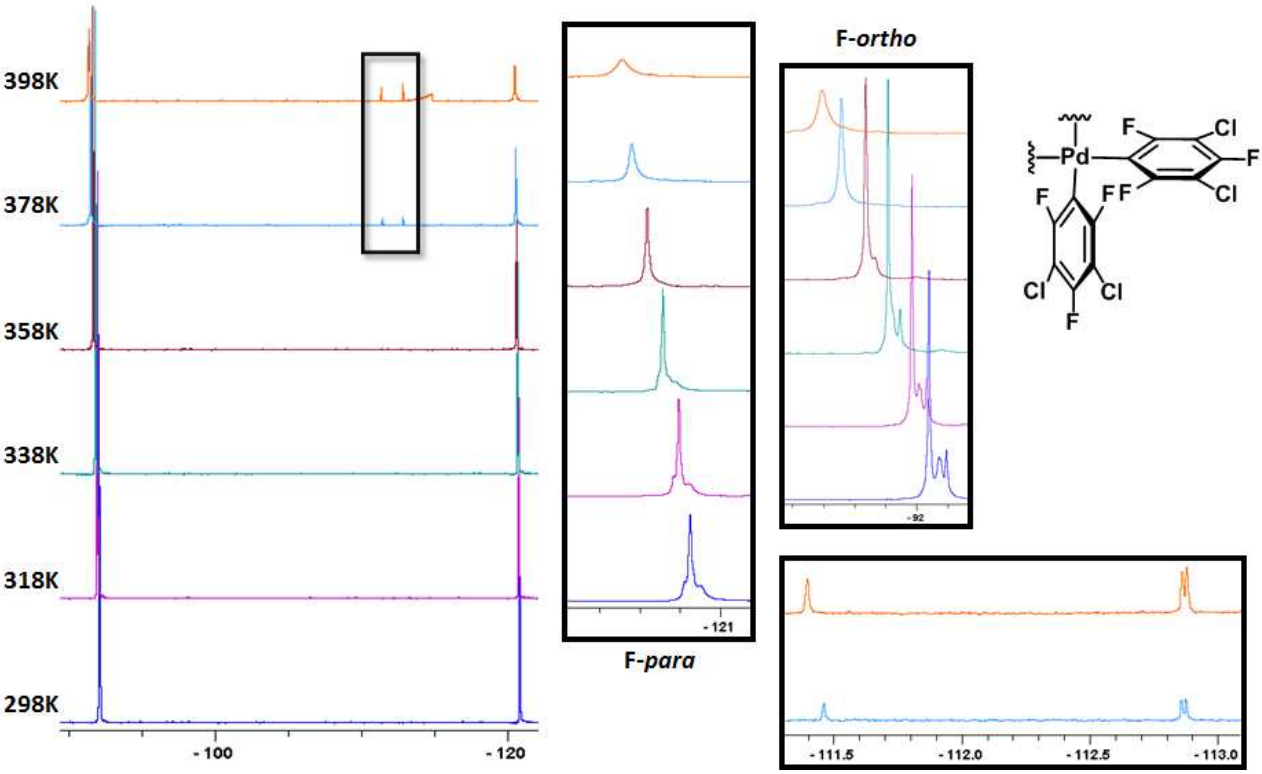


*Figure SS14 – Variable temperature ^{19}F NMR spectra of the equilibrium mixture of **Pd_4-2_8** and **Pd_3-2_6** , 298-398K (TCE, 376 MHz).*

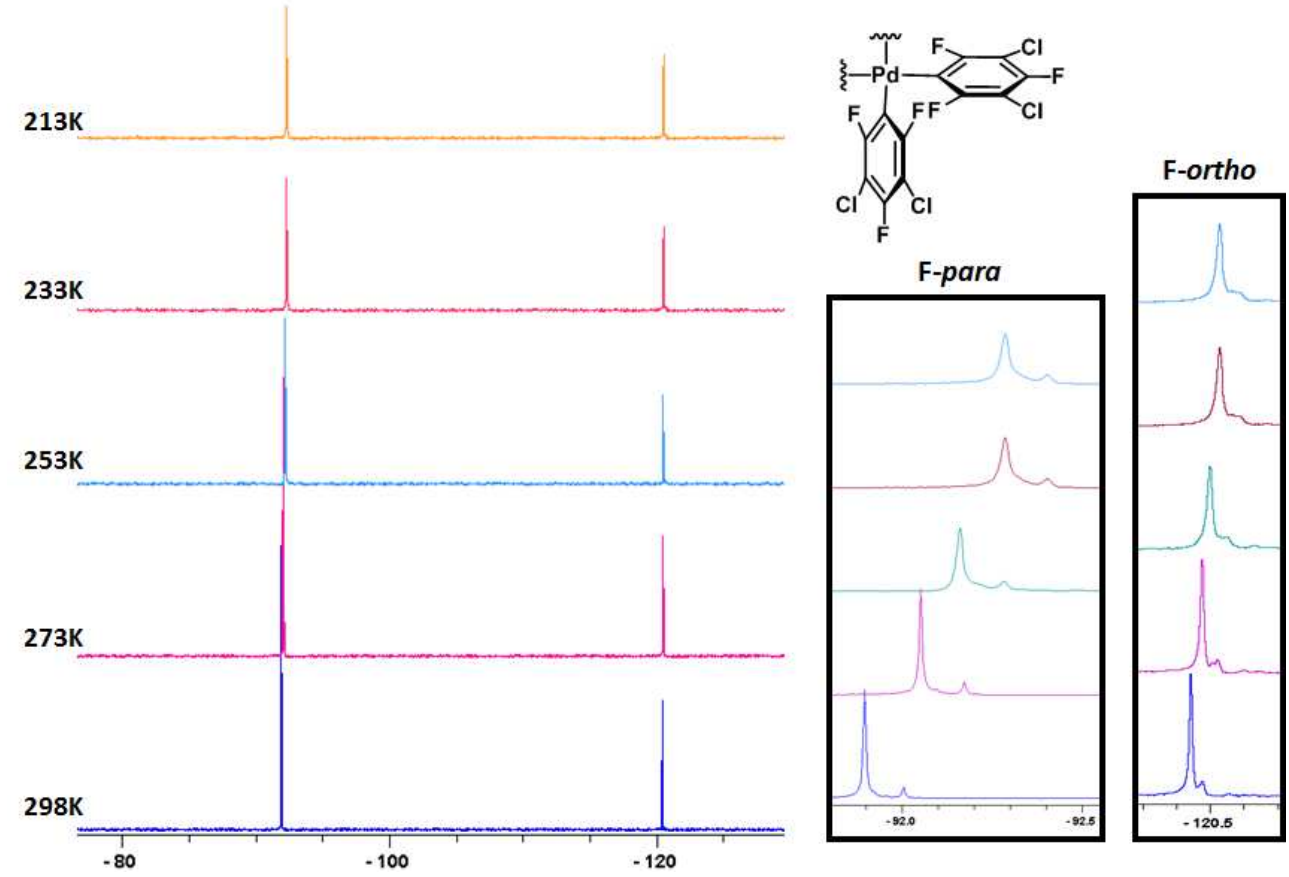


Figure SS15 – Variable temperature ^{19}F NMR spectra of the equilibrium mixture of ***Pd$_4$-2$_8$*** *and* ***Pd$_3$-2$_6$*** *, 298-213K ($CDCl_3$, 376 MHz).*

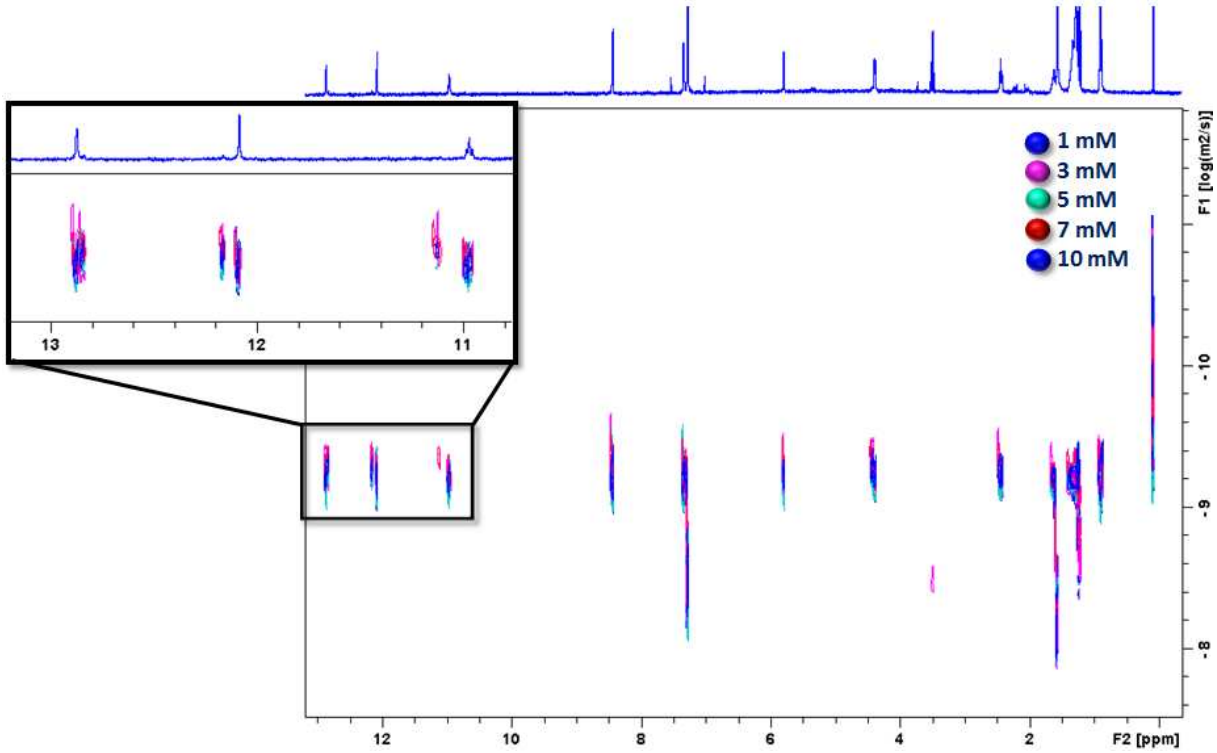


*Figure SS16 – ^{1}H DOSY NMR Spectrum of the equilibrium mixture of **Pd_4-2$_8$** and **Pd_3-2$_6$** 1-10 mM (298K, $CDCl_3$, 500 MHz).*

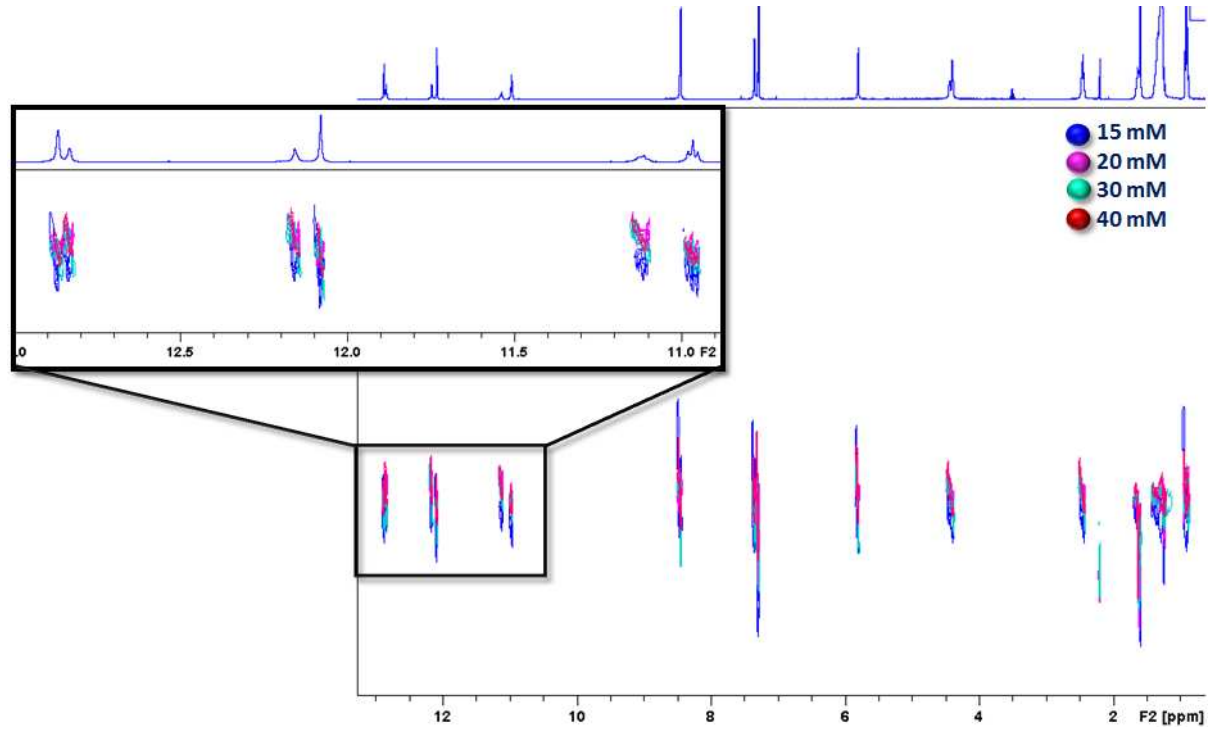


*Figure SS17 – ^{1}H DOSY NMR Spectrum of the equilibrium mixture of **Pd_4-2$_8$** and **Pd_3-2$_6$** 15-40 mM (298K, $CDCl_3$, 500 MHz).*

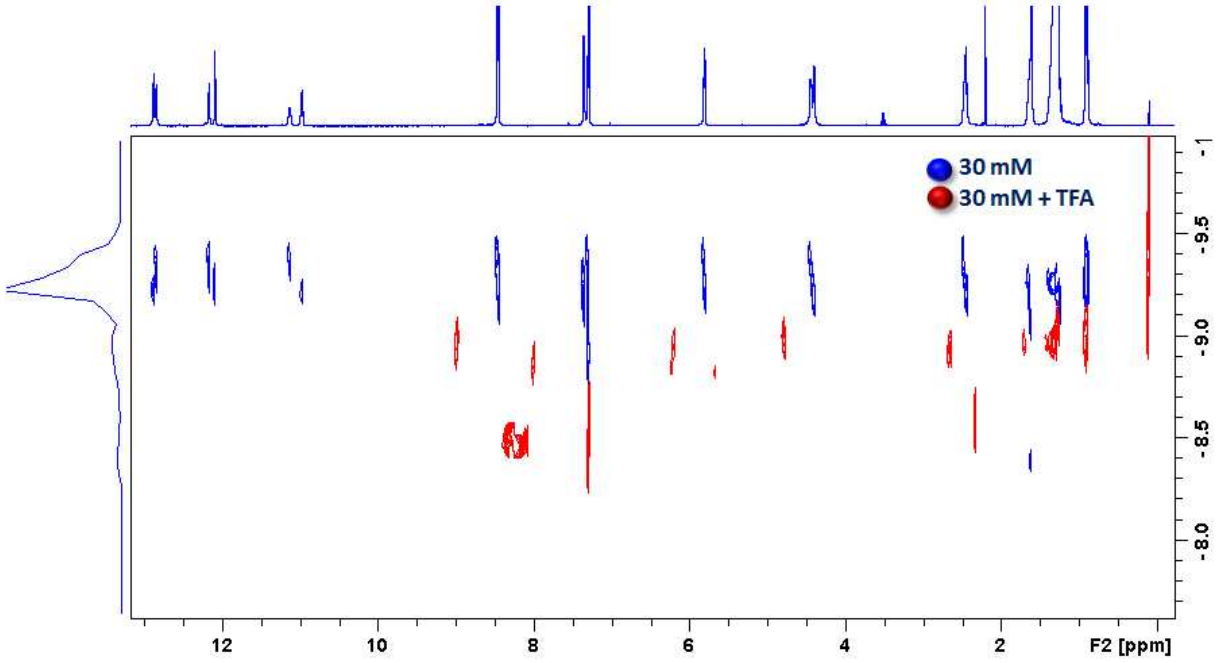


*Figure SS18 – ^{1}H DOSY NMR Spectrum of the equilibrium mixture of **Pd_4-2_8** and **Pd_3-2_6** 30 mM with and without TFA (298K, $CDCl_3$, 500 MHz).*

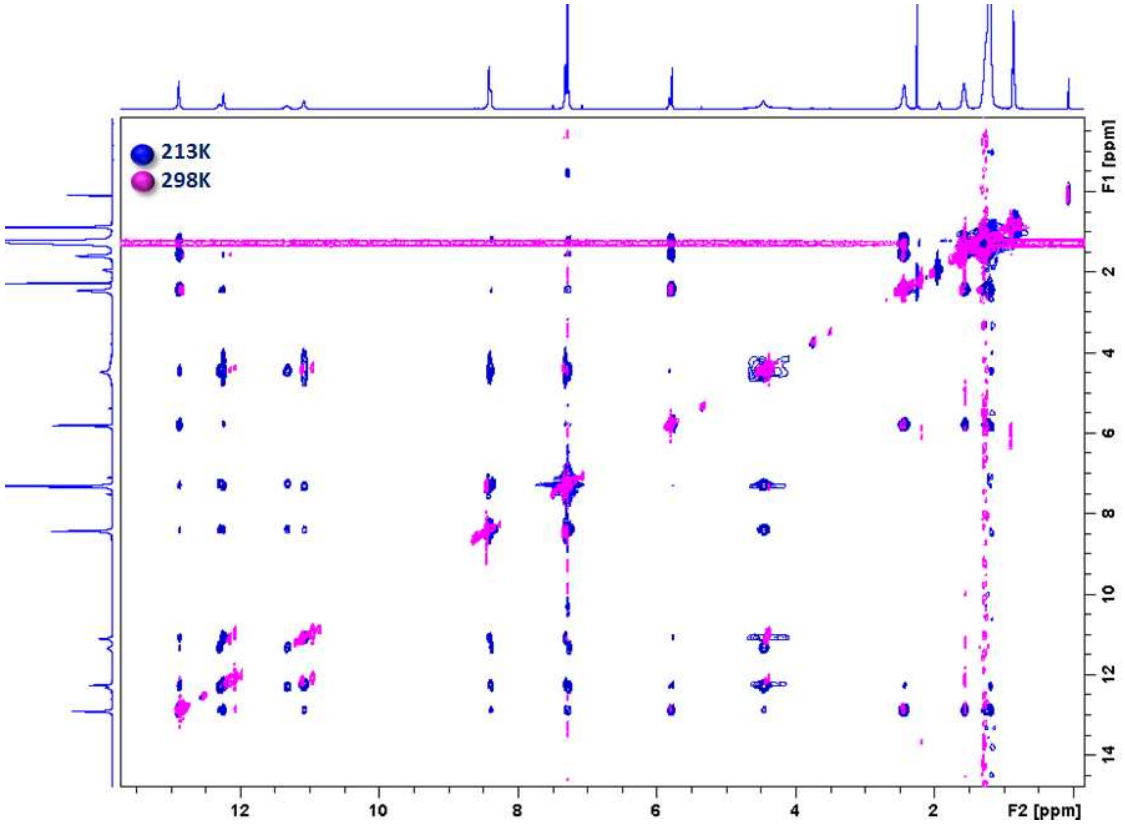


*Figure SS19 – ^{1}H NOESY spectrum of the equilibrium mixture of **Pd_4-2_8** and **Pd_3-2_6** (20 mM, 298K and 213K, $CDCl_3$, 500 MHz).*

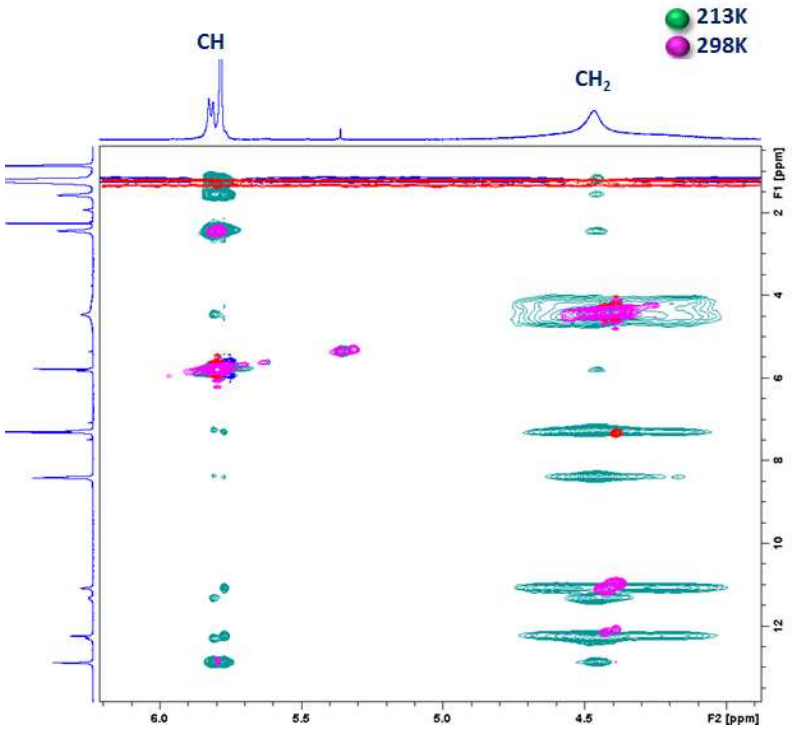


Figure SS20 – Zoom 1 of ^{1}H NOESY spectrum of the equilibrium mixture of ***Pd$_4$-2$_8$*** *and* ***Pd$_3$-2$_6$*** *(20 mM, 298 K and 213K, $CDCl_3$, 500 MHz).*

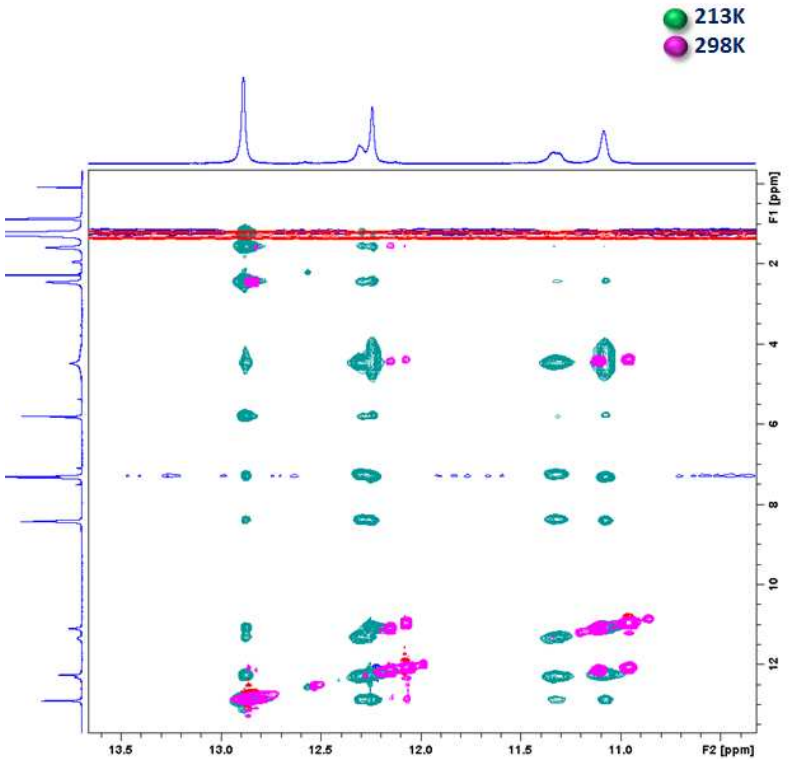


Figure SS21 – Zoom 1 of ^{1}H NOESY spectrum of the equilibrium mixture of ***Pd$_4$-2$_8$*** *and* ***Pd$_3$-2$_6$*** *(20 mM, 298 K and 213K, $CDCl_3$, 500 MHz).*

SECTION SS7: Spectra for Molecular Architectures based on 4

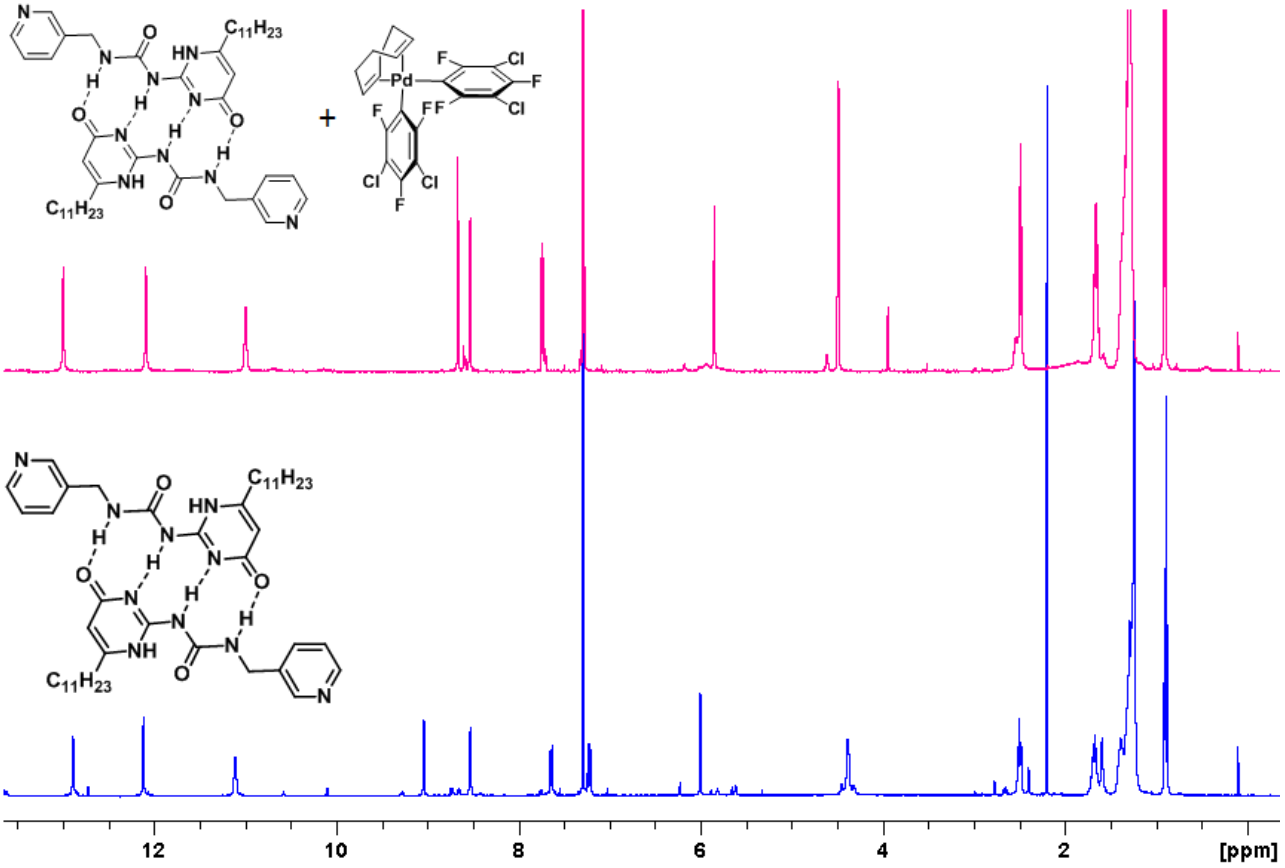


*Figure SS22 – ^{1}H NMR Spectrum of the mixture of dimer **4**$_2$ and Pd complex **3** (298K, $CDCl_3$, 500 MHz).*

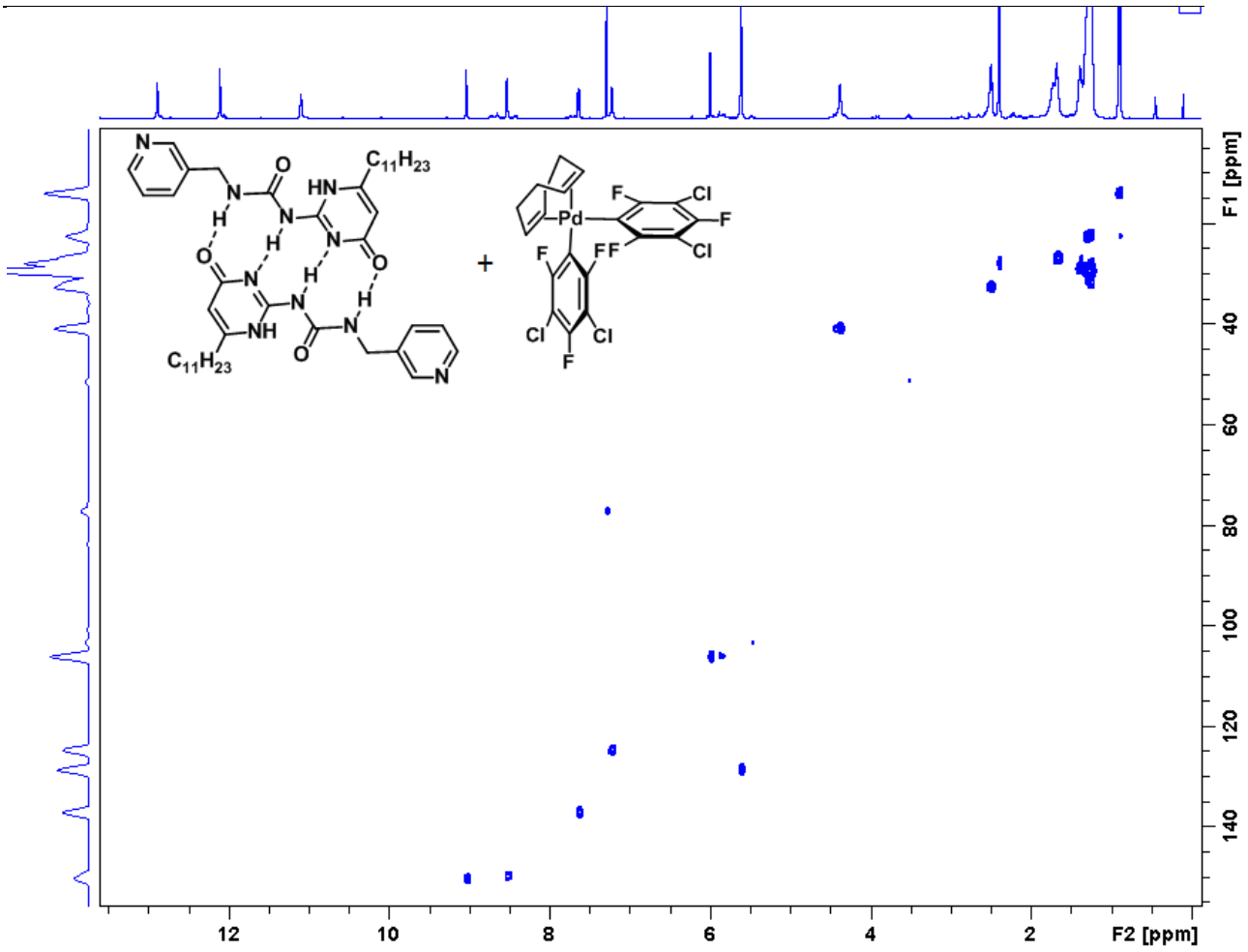


*Figure SS23 – ^{1}H-^{13}C HSQC NMR Spectrum of the mixture of dimer **4**$_2$ and Pd complex **3** (298K, $CDCl_3$, 500 MHz).*

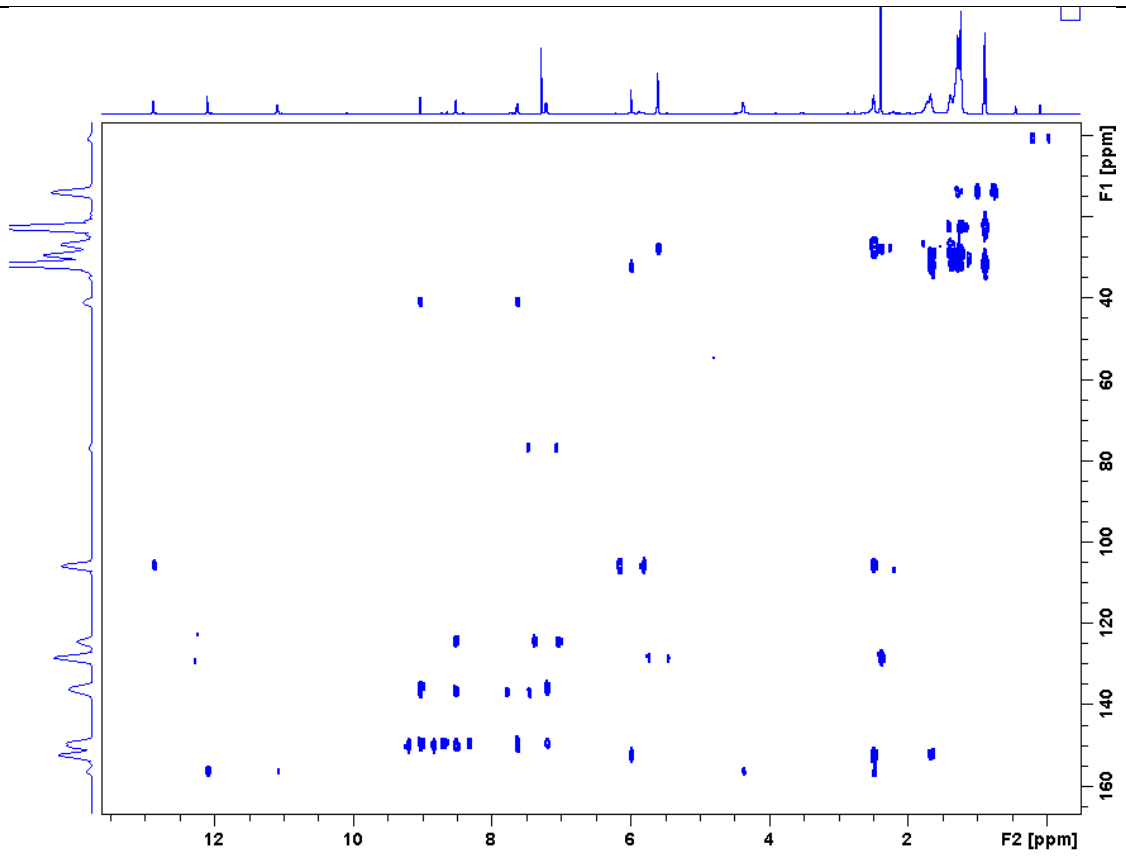


*Figure SS24 – ^{1}H-^{13}C HMBC NMR Spectrum of the mixture of dimer **4**$_2$ and Pd complex **3** (298K, $CDCl_3$, 500 MHz).*

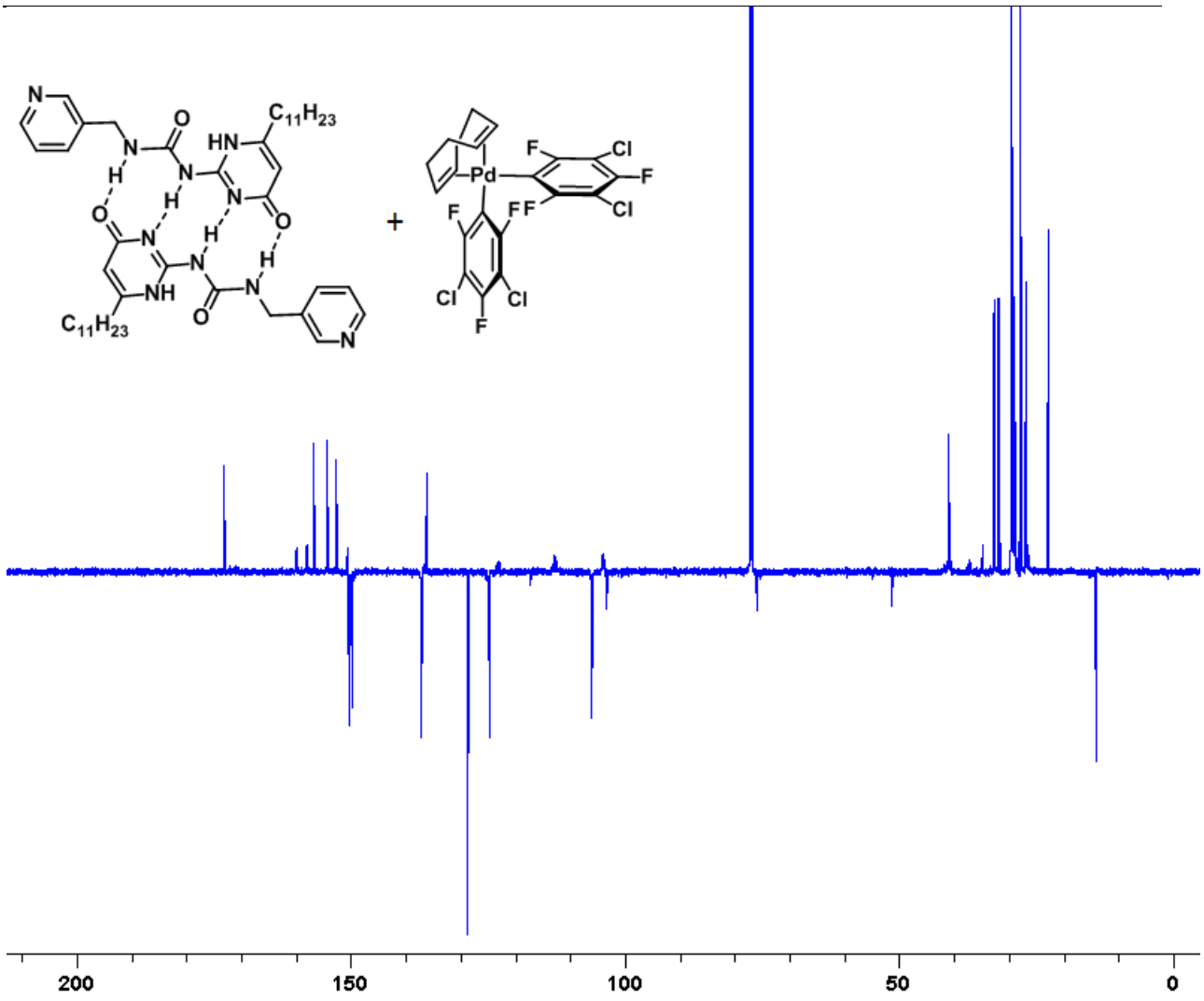


*Figure SS25 – ^{13}C NMR Spectrum of the mixture of dimer **4**$_2$ and Pd complex **3** (298K, $CDCl_3$, 100 MHz).*

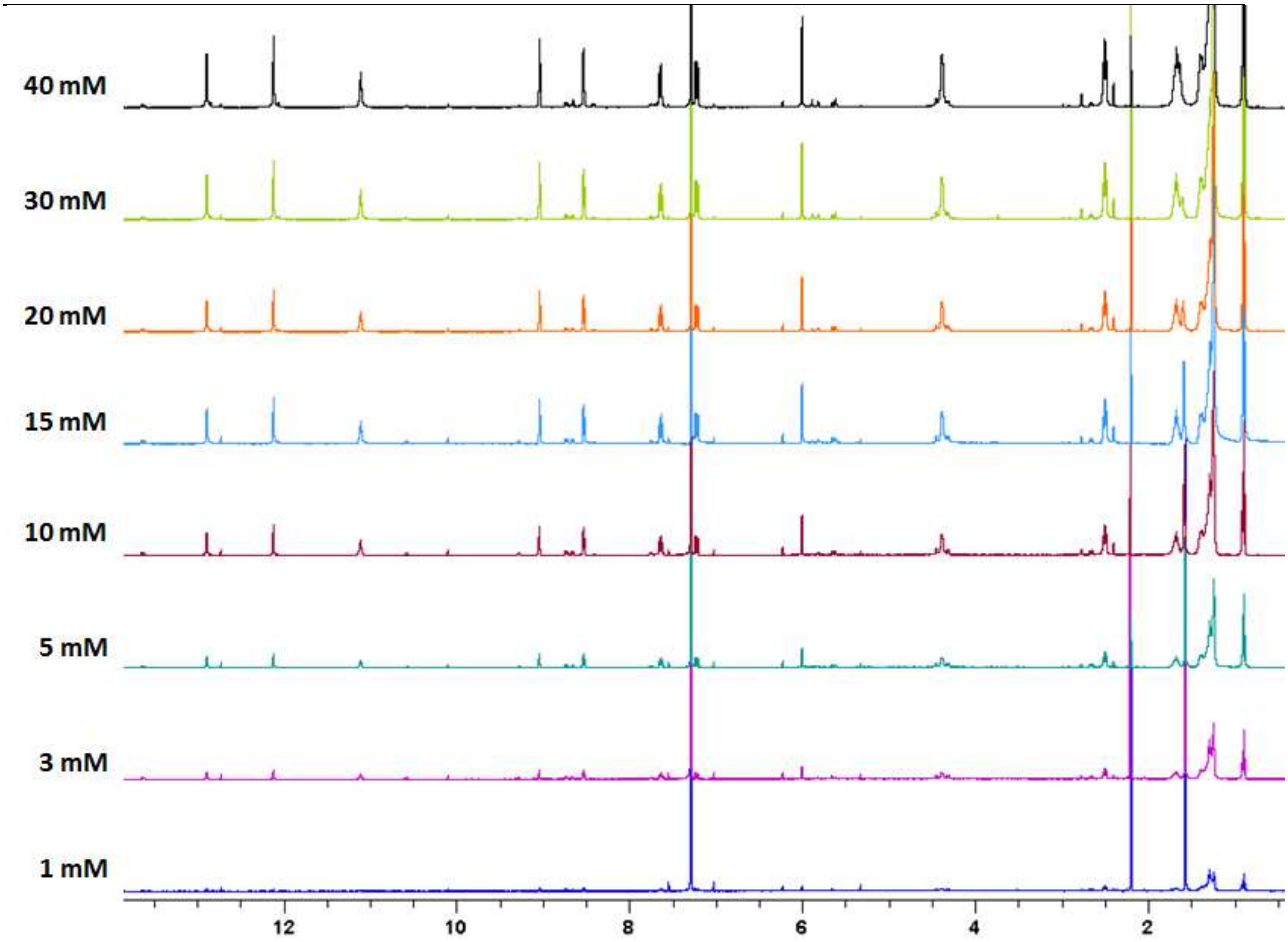


*Figure SS26 – ^{1}H NMR Concentration studies (1-40 mM) of the mixture of dimer **4**$_2$ and Pd complex **3** (298K, $CDCl_3$, 400 MHz).*

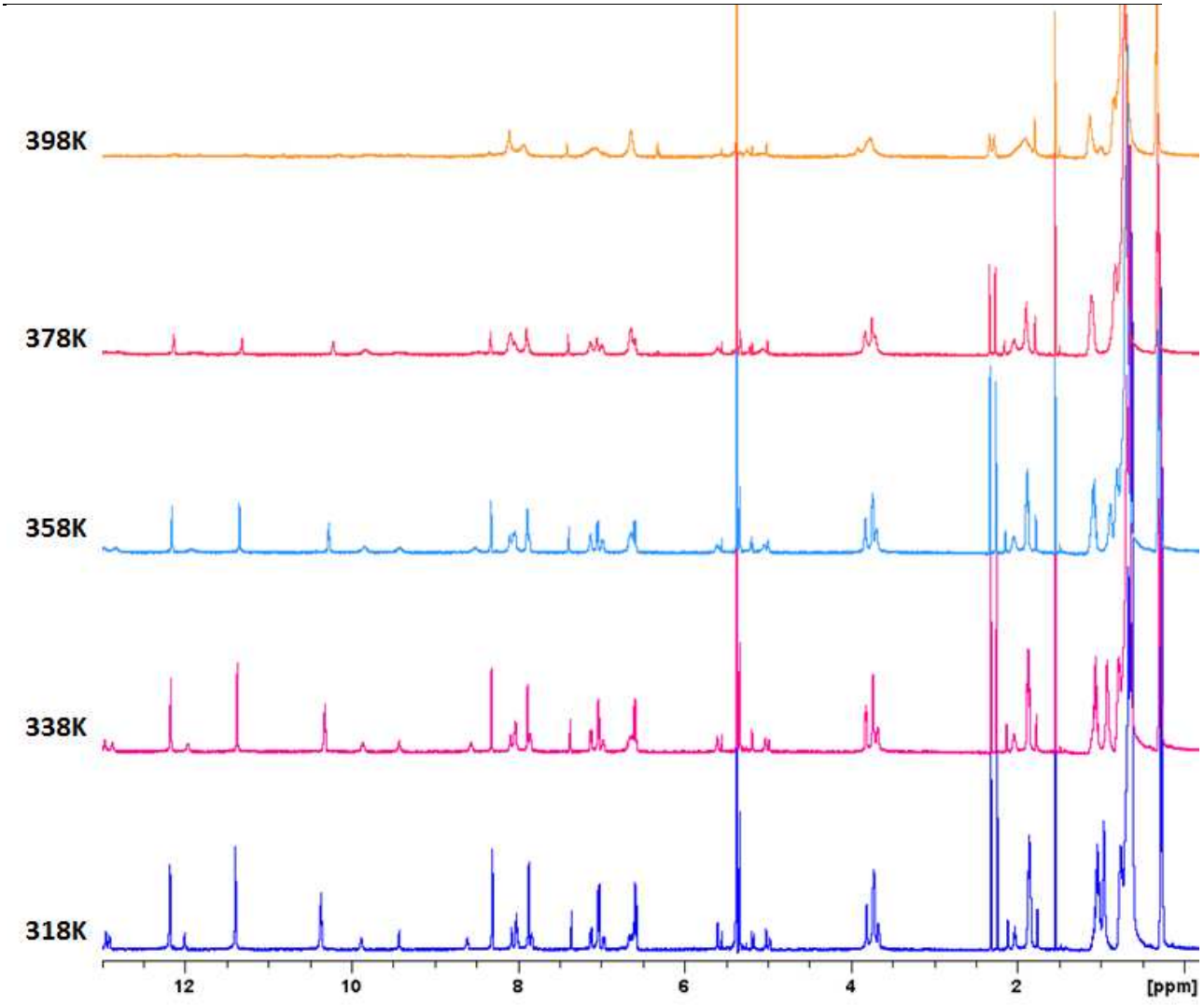


*Figure SS27 – Variable temperature ^{1}H NMR spectra of the mixture of dimer **4**$_2$ and Pd complex **3**, 318-398K (TCE, 500 MHz).*

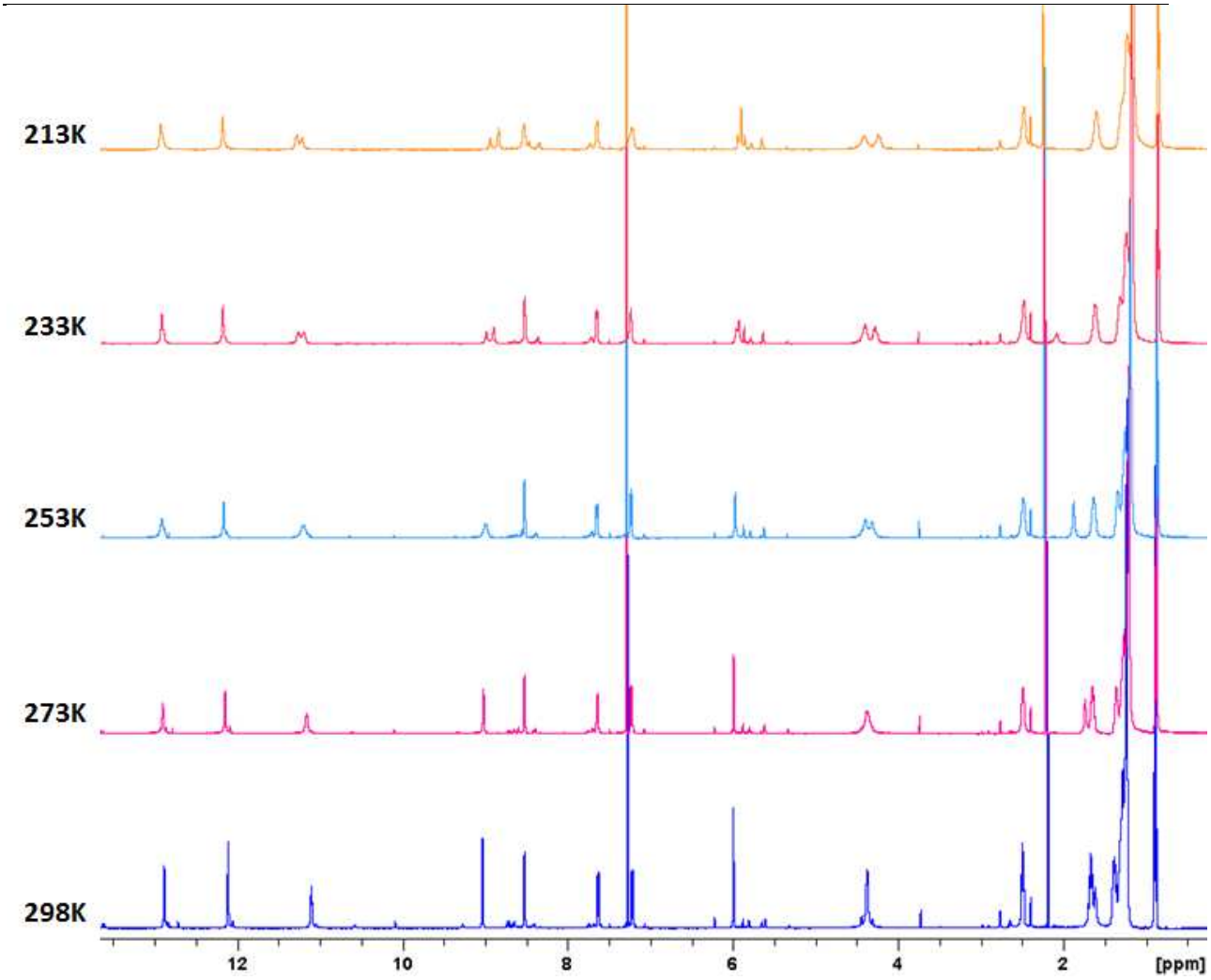


*Figure SS28 – Variable temperature ^{1}H NMR spectra of the mixture of dimer **4**$_2$ and Pd complex **3**, 298-213K ($CDCl_3$, 500 MHz).*

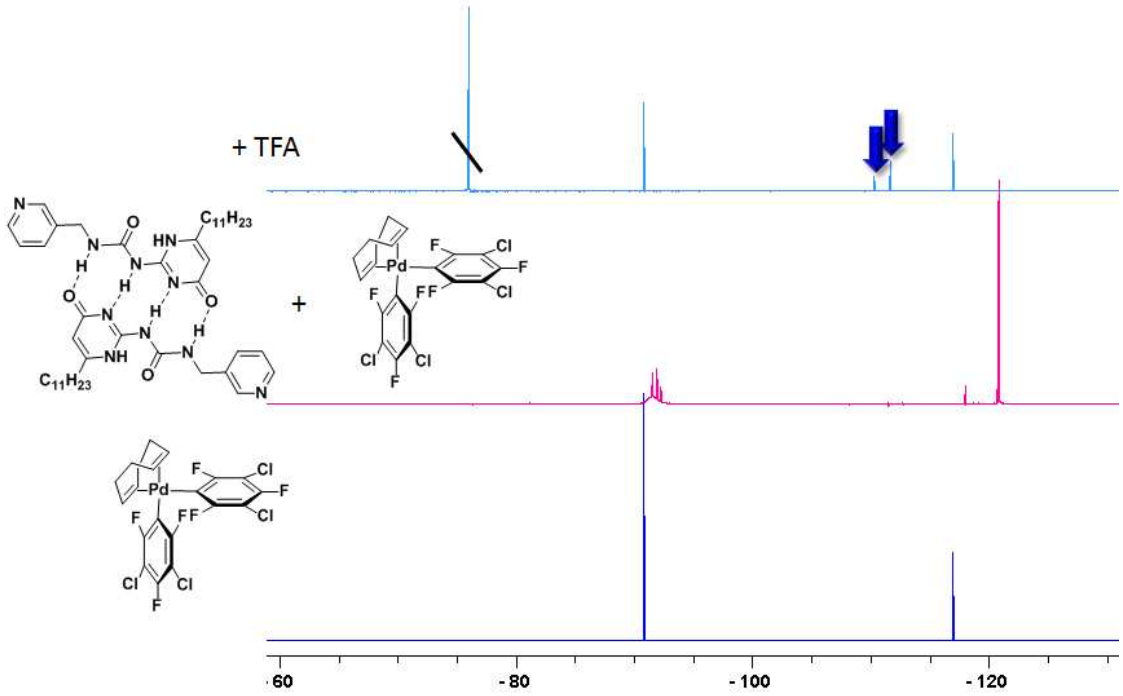


*Figure SS29 – ^{19}F NMR Spectrum of palladium complex **3** (dark blue), mixture of dimer **4**$_2$ and Pd complex **3** (light blue), and after the addition of TFA (pink), (298K, $CDCl_3$, 376 MHz).*

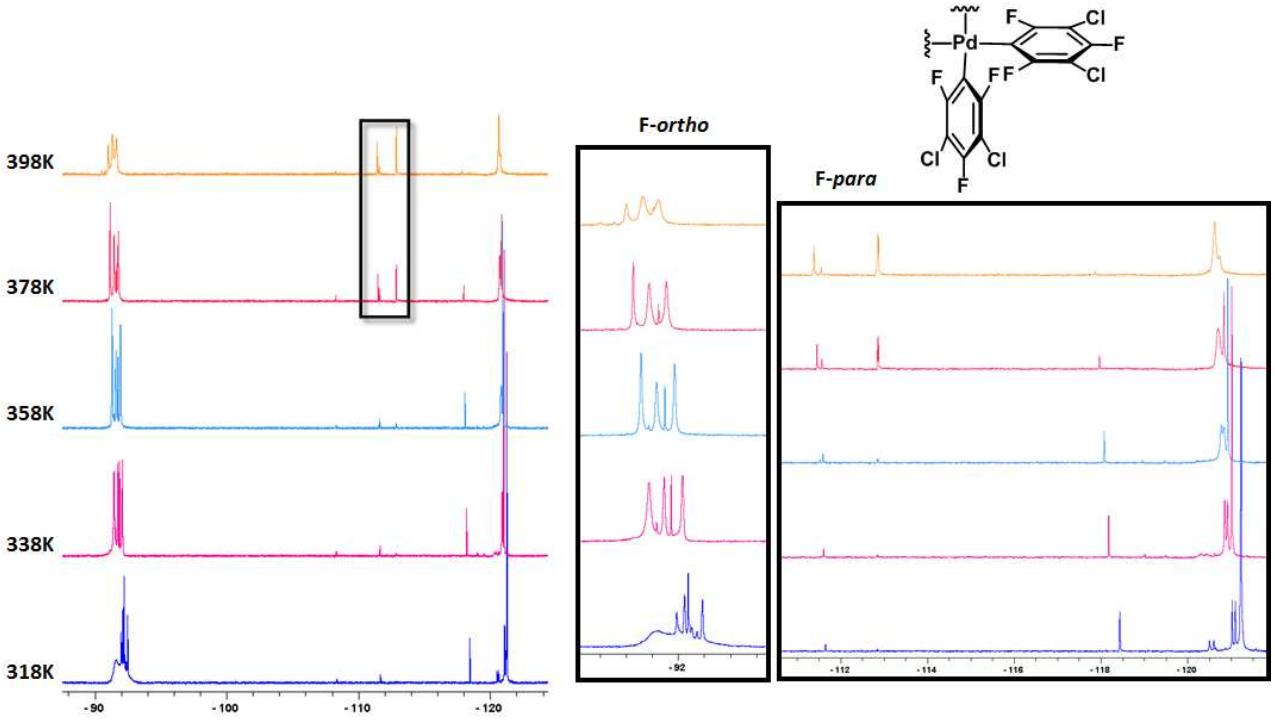


*Figure SS30 – Variable temperature ^{19}F NMR spectra of the mixture of dimer **4**$_2$ and Pd complex **3**, 318-398K (TCE, 376 MHz).*

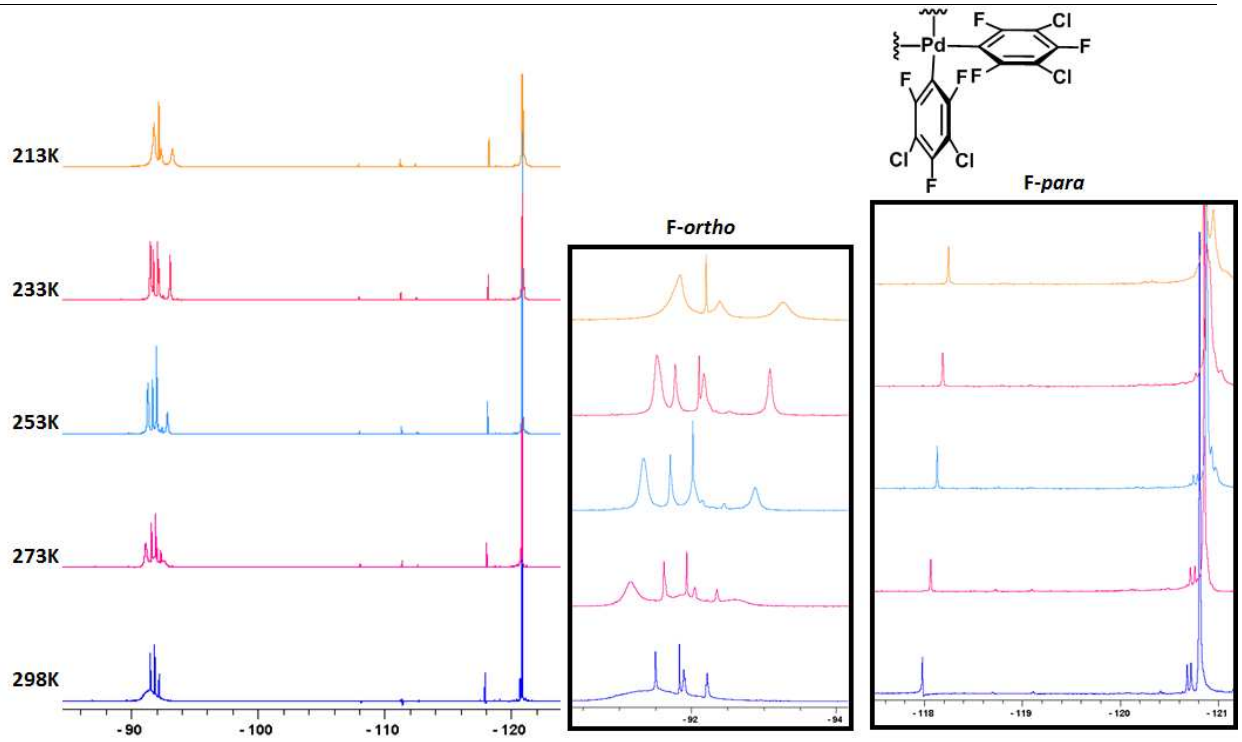


*Figure SS31 – Variable temperature ^{19}F NMR spectra of the mixture of dimer **4**$_2$ and Pd complex **3**, 298-213K ($CDCl_3$, 376 MHz).*

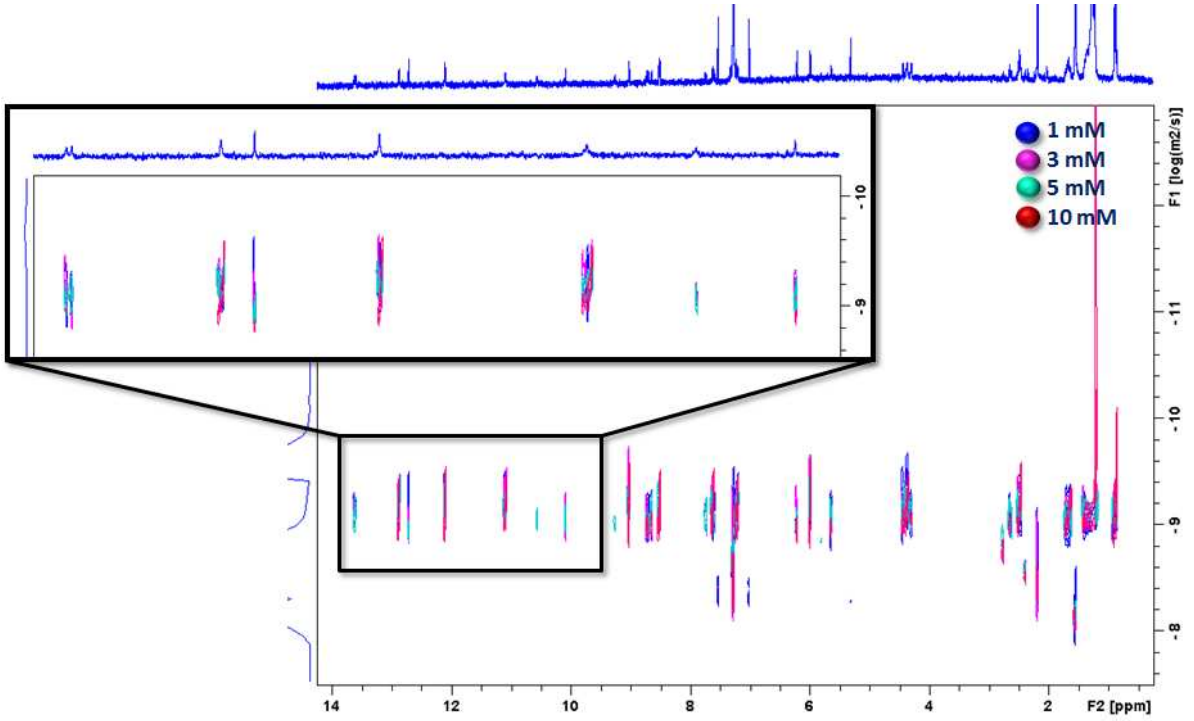


*Figure SS32 – ^{1}H DOSY NMR Spectrum of the mixture of dimer **4**$_2$ and Pd complex **3** 1-10 mM (298K, $CDCl_3$, 500 MHz).*

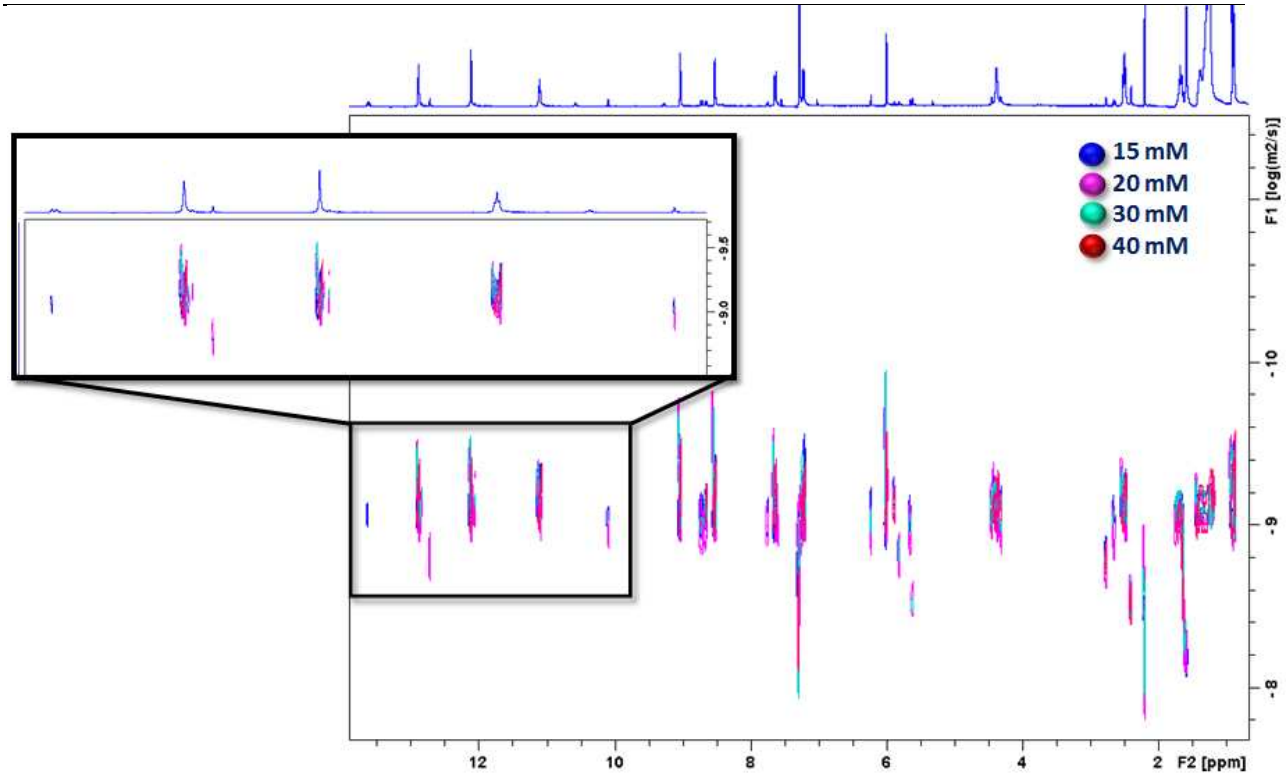


*Figure SS33 – ^{1}H DOSY NMR Spectrum of the mixture of dimer **4**$_2$ and Pd complex **3** 15-40 mM (298K, $CDCl_3$, 500 MHz).*

SECTION SS8: Spectra for Attempted Molecular Architectures based on 5

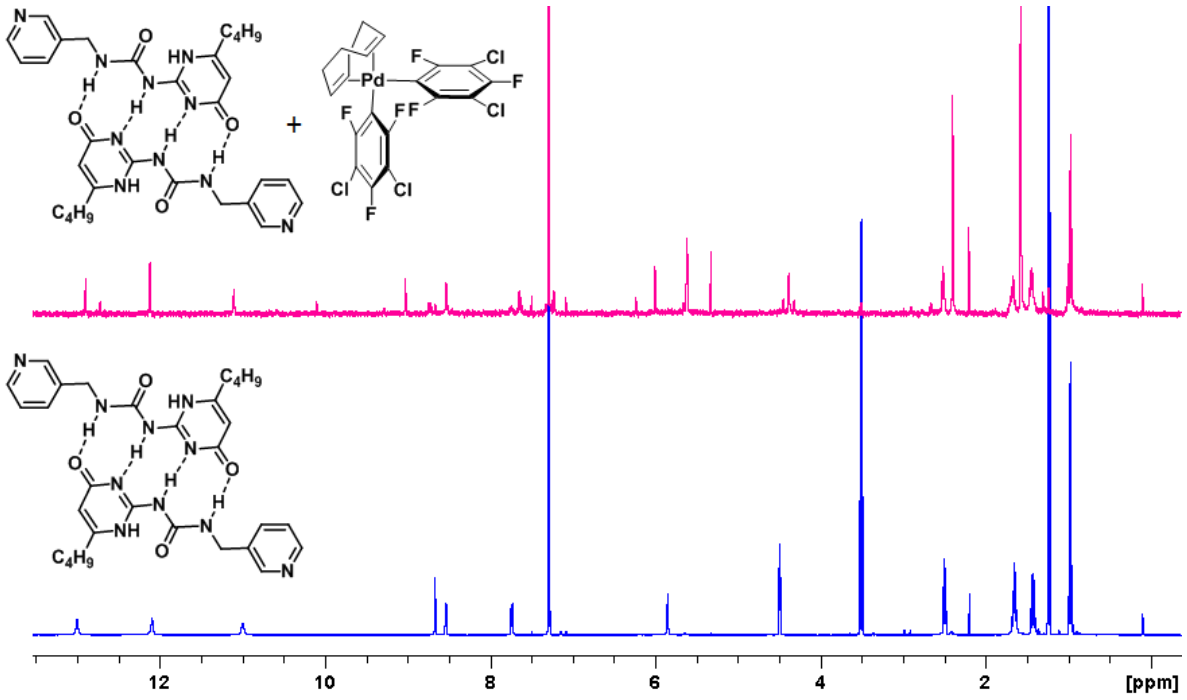


*Figure SS34 – ^{1}H NMR Spectrum of the mixture of dimer **5**$_2$ and Pd complex **3** (298K, $CDCl_3$, 500 MHz).*

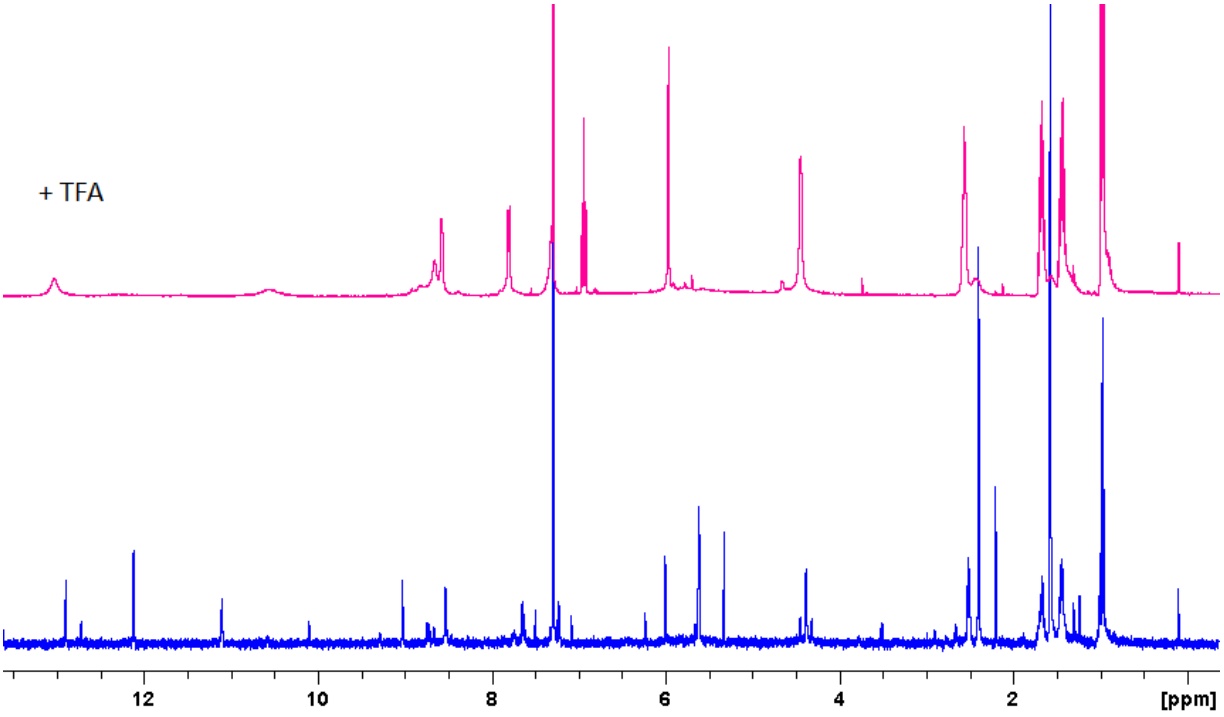


*Figure SS35 – ^{1}H NMR Spectrum of the mixture of dimer **5**$_2$ and Pd complex **3** (blue spectrum) and after the addition of TFA (pink spectrum), (298K, $CDCl_3$, 500 MHz).*

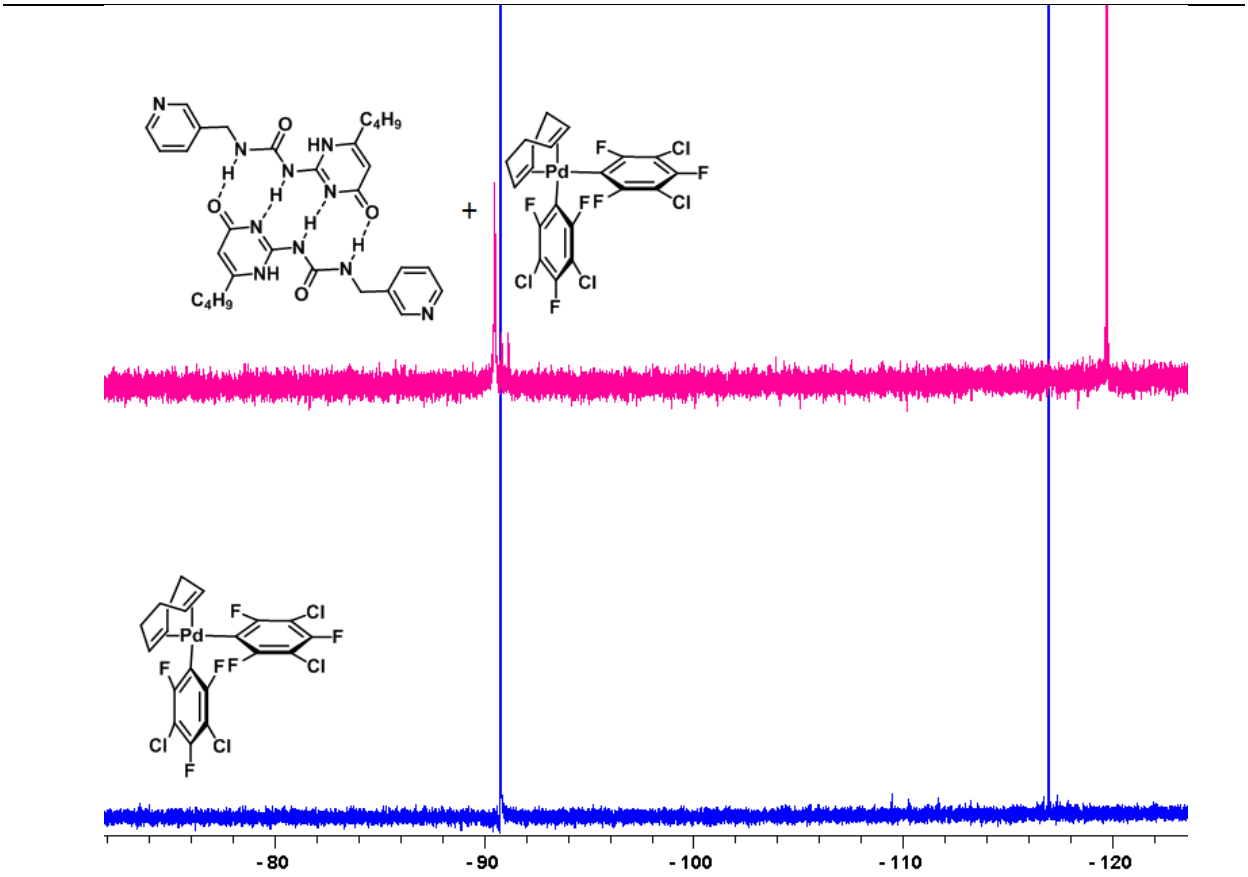


*Figure SS36 – ^{19}F NMR Spectrum of palladium complex **3** (dark blue), and the mixture of dimer **4**$_2$ and Pd complex **3** (pink), (298K, $CDCl_3$, 376 MHz).*