Supporting Information:

Synthesis, structure and dynamics of NHC-based palladium macrocycles

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Contents:

1. Preparation of bis-imidazoles

To a stirred solution of imidazole (2.00 g, 29.3 mmol) in THF (100 mL) at 0°C, NaH (60% wt suspension in mineral oil, 1.29 g, 32.3 mmol) was added portion-wise over 5 minutes followed by dibromoalkane (14.7 mmol; neat or in 50 mL THF). The resulting mixture was refluxed for 5 hours to give an off-white suspension. The reaction mixture was cooled to room temperature, removed from inert atmosphere, quenched with H_2O and extracted with EtOAc (3 x 50 mL). The combined organic extracts were washed with H_2O, dried over Na_2SO_4 and concentrated *in vacuo* to give the crude product. Sonication in Et_2O (**1a**, **1c**) or EtOAc/Et_2O (**1b**) and cooling to -10°C afforded the pure products as white crystalline solids.

1a: Yield: 2.85 g (79%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (s, 2H), 7.00 (s, 2H), 6.84 (s, 2H), 3.86 (t, $^3J_{HH}$ = 7.2, 4H), 1.70 (app. pentet, *J* = 7, 4H), 1.23 (br, 8H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 137.0, 129.4, 118.8, 46.9, 31.0, 28.9, 26.4. **ESI-MS** (CH_3CN, 180°C, 3 kV) positive ion: 247.1914 *m/z*, $[M]H^+$ (*calc.* 247.1917).

1b: Yield: 2.15 g (54%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 2H), 7.05 (s, 2H), 6.90 (s, 2H), 3.92 (t, $^3J_{HH}$ = 7.0, 4H), 1.76 (app. pentet, *J* = 7, 4H), 1.21 – 1.32 (m, 12H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 137.2, 129.5, 118.9, 47.2, 31.2, 29.4, 29.2, 26.7. **ESI-MS** (CH_3CN, 180°C, 3 kV) positive ion: 275.2225 *m/z*, $[M]H^+$ (*calc.* 275.2230).

1c: Yield: 3.60 g (81%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 2H), 7.01 (s, 2H), 6.86 (s, 2H), 3.88 (t, $^3J_{HH}$ = 7.1, 4H), 1.74 (app. pentet, *J* = 7, 4H), 1.16 – 1.31 (m, 16H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 137.1, 129.3, 118.8, 47.1, 31.1, 29.5, 29.4, 29.1, 26.6. **ESI-MS** (CH_3CN, 180°C, 3 kV) positive ion: 303.2547 *m/z*, $[M]H^+$ (*calc.* 303.2543).

2. Selected NMR data and spectra

1.1 Bis-imidazoles **1**

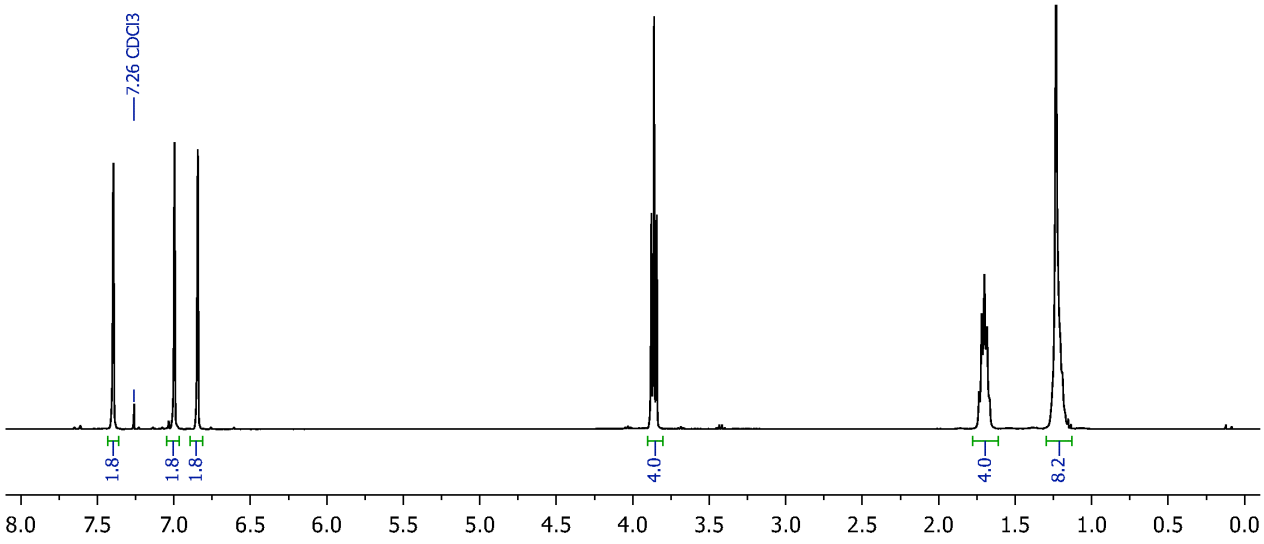


Figure S-1: ^{1}H NMR spectrum of **1a** ($CDCl_3$, 400 MHz).

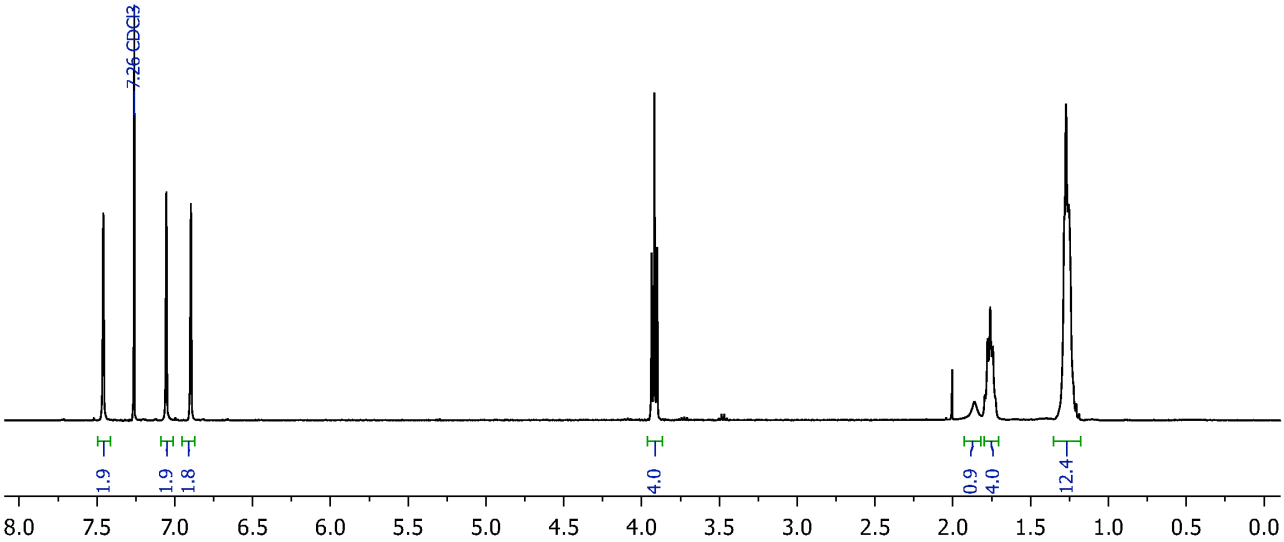


Figure S-2: ^{1}H NMR spectrum of **1b** ($CDCl_3$, 400 MHz).

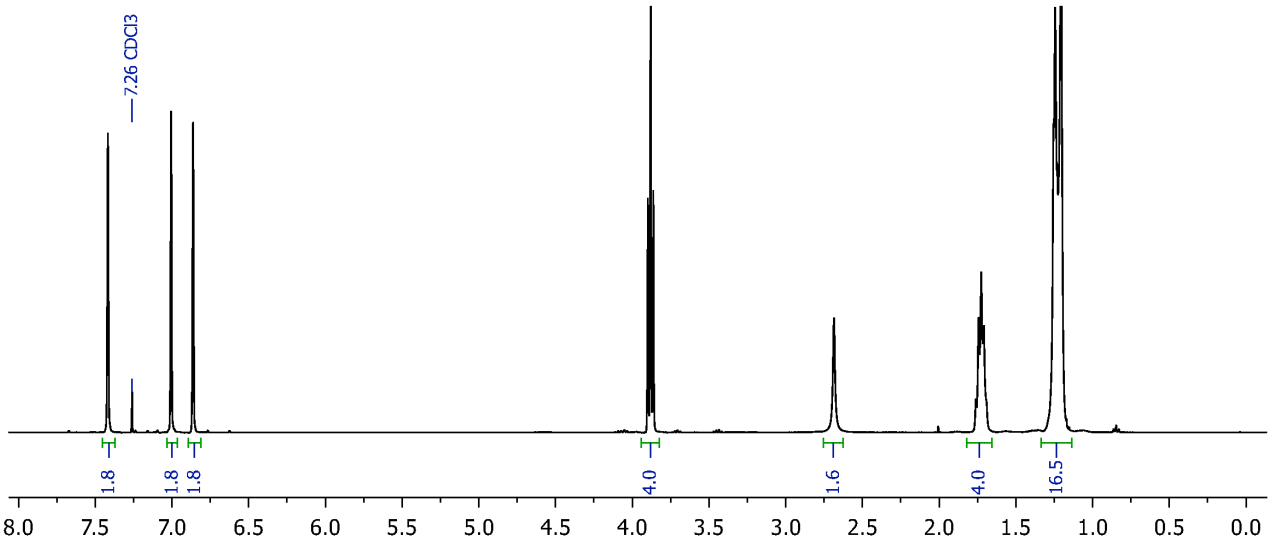


Figure S-3: ^{1}H NMR spectrum of **1c** ($CDCl_3$, 400 MHz).

1.2 Macrocyclic pro-ligands **2**

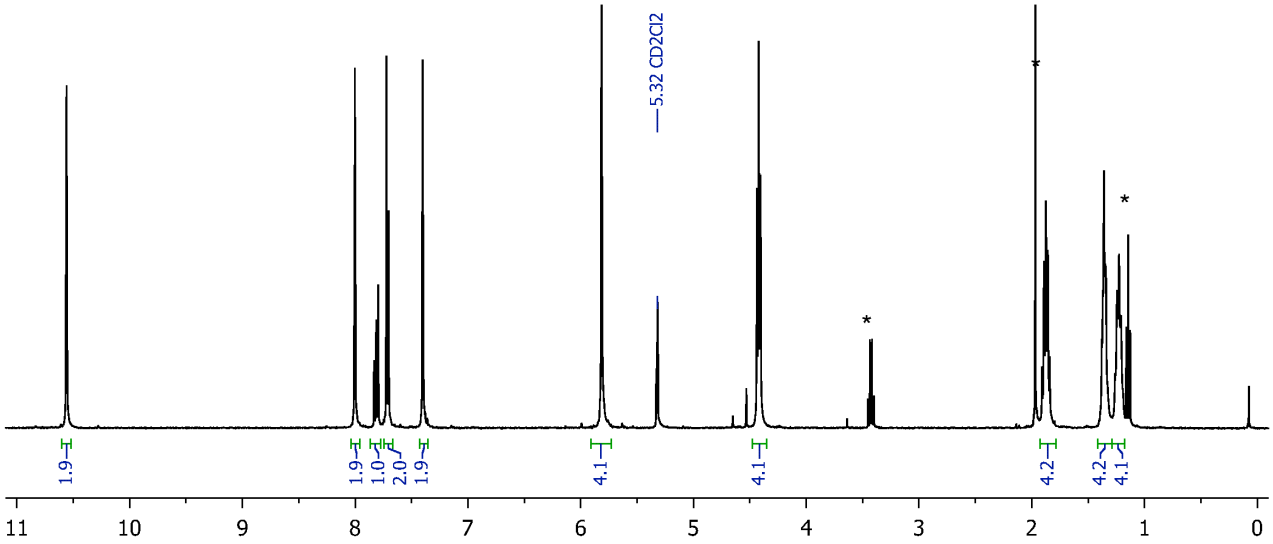


Figure S-4: ^{1}H NMR spectrum of **2a** (CD_2Cl_2, 400 MHz). * Et_2O.

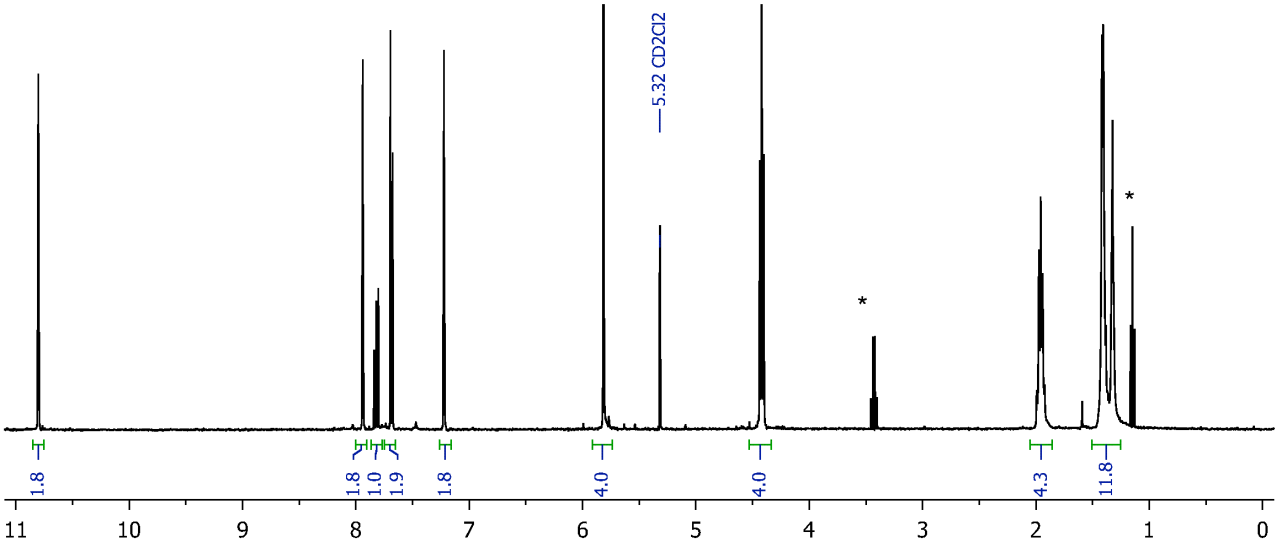


Figure S-5: ^{1}H NMR spectrum of **2b** (CD_2Cl_2, 400 MHz). * Et_2O.

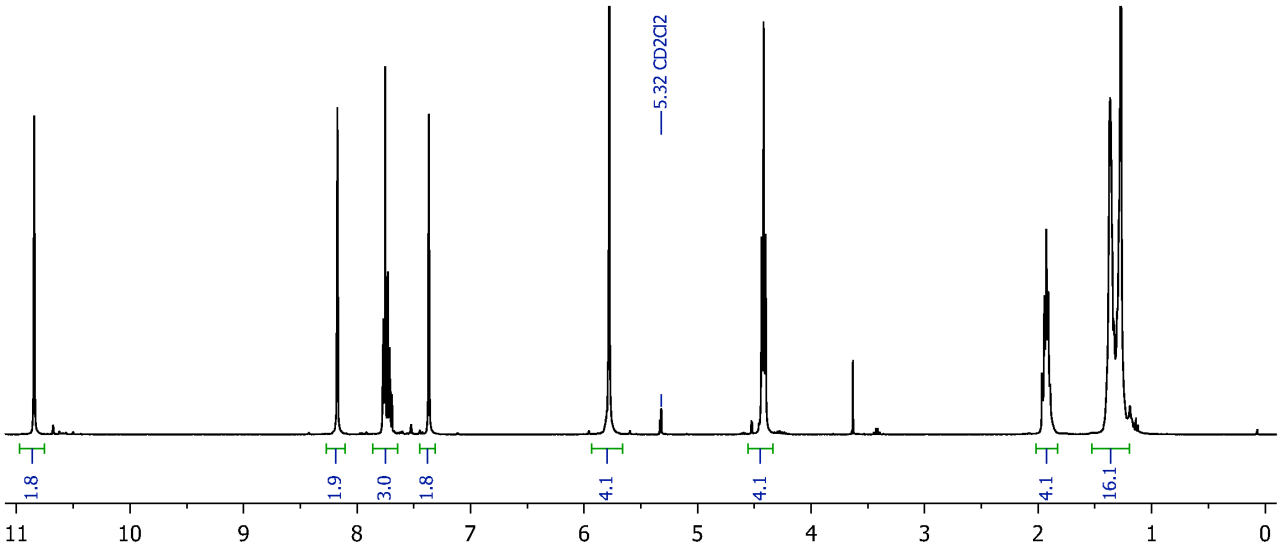


Figure S-6: ^{1}H NMR spectrum of **2c** (CD_2Cl_2, 400 MHz).

1.3 Palladium complexes **3**

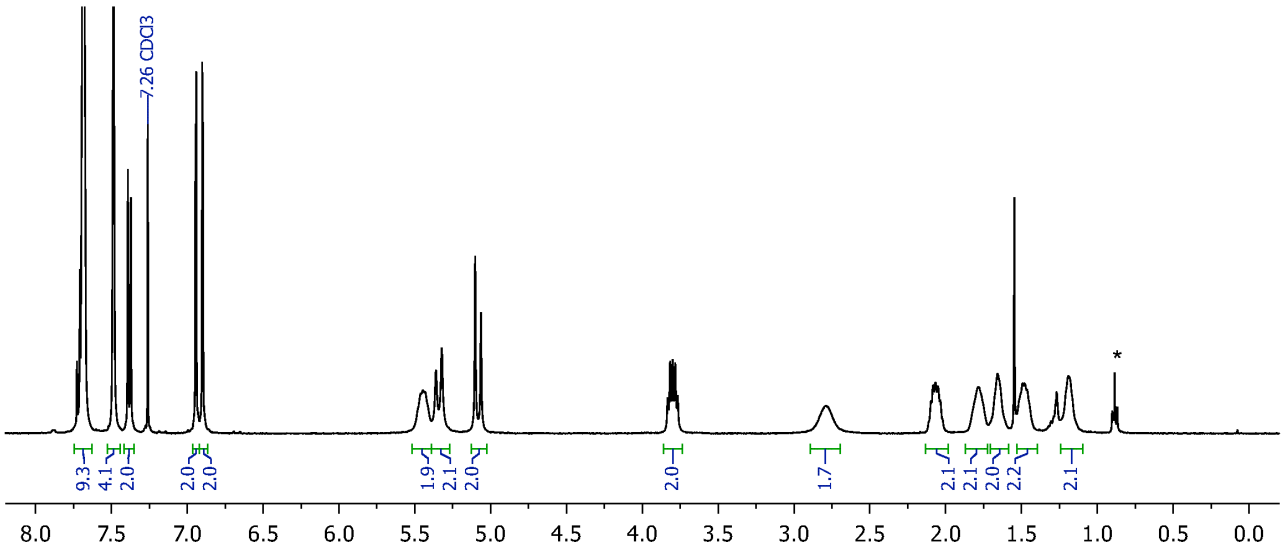


Figure S-7: ^{1}H NMR spectrum of **3a** ($CDCl_3$, 400 MHz). * Pentane.

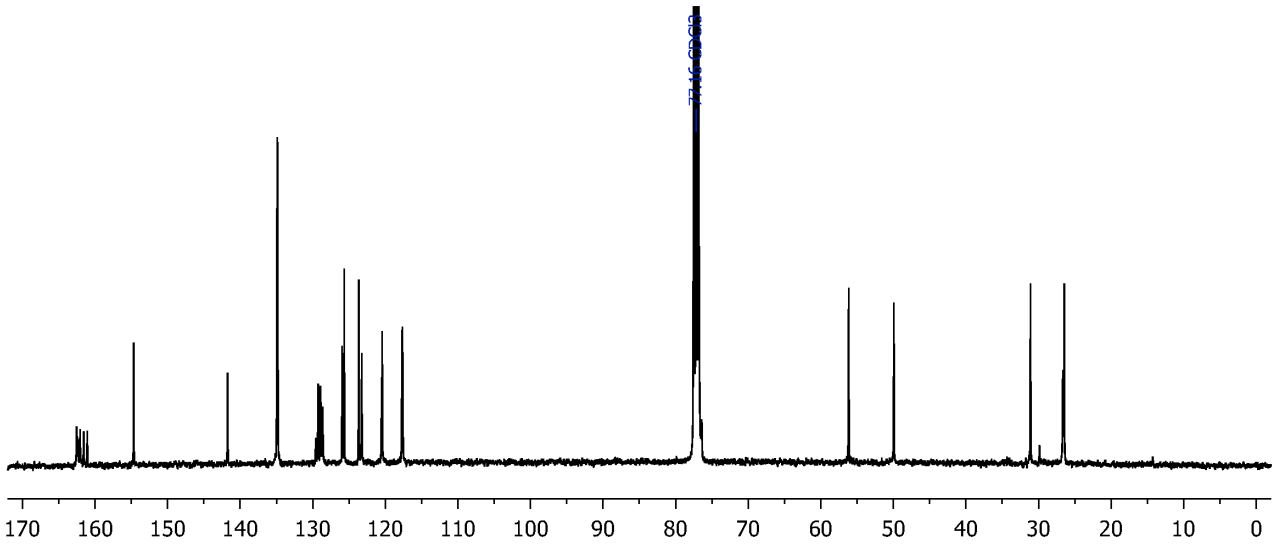


Figure S-8: $^{13}C\{^{1}H\}$ NMR spectrum of **3a** ($CDCl_3$, 400 MHz).

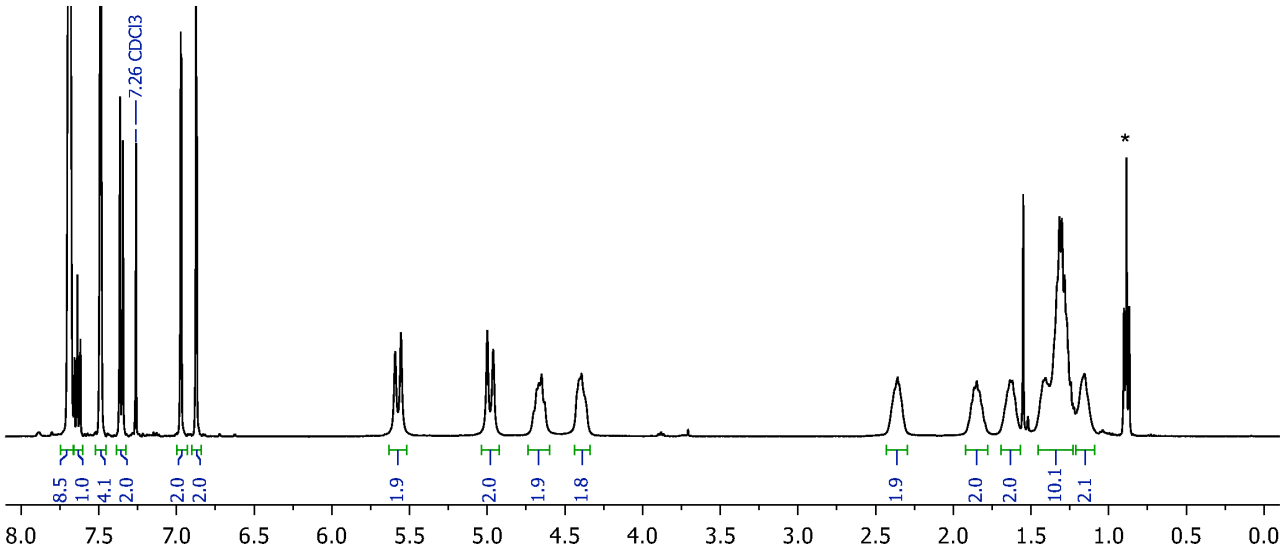


Figure S-9: ^{1}H NMR spectrum of **3b** ($CDCl_3$, 400 MHz). * Pentane.

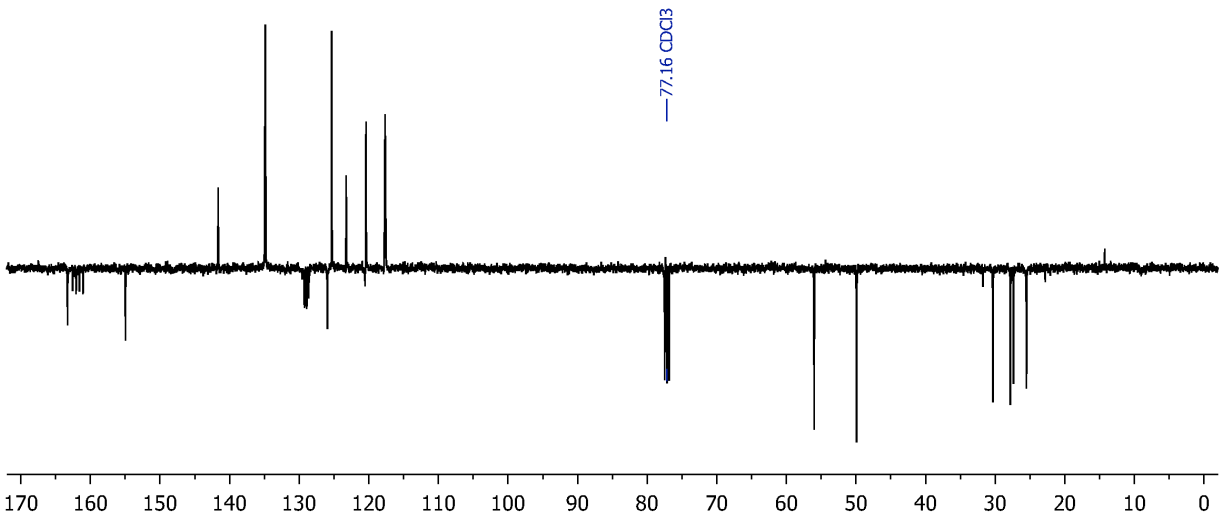


Figure S-10: $^{13}C\{^{1}H\}$(APT) NMR spectrum of **3b** ($CDCl_3$, 400 MHz).

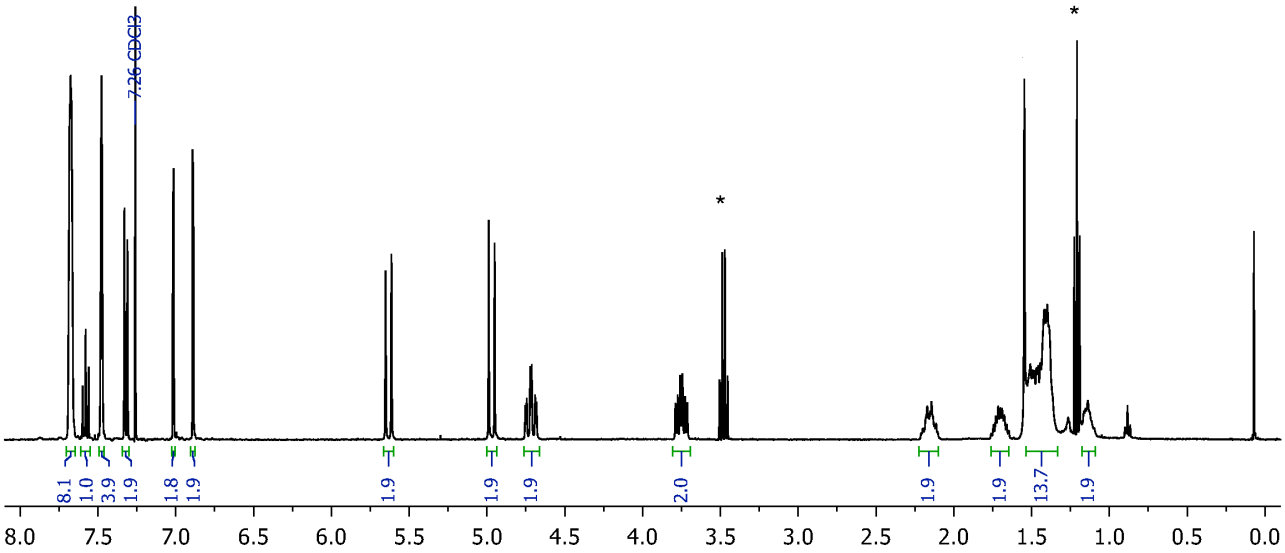


Figure S-11: ^{1}H NMR spectrum of **3c** ($CDCl_3$, 400 MHz). * Et_2O.

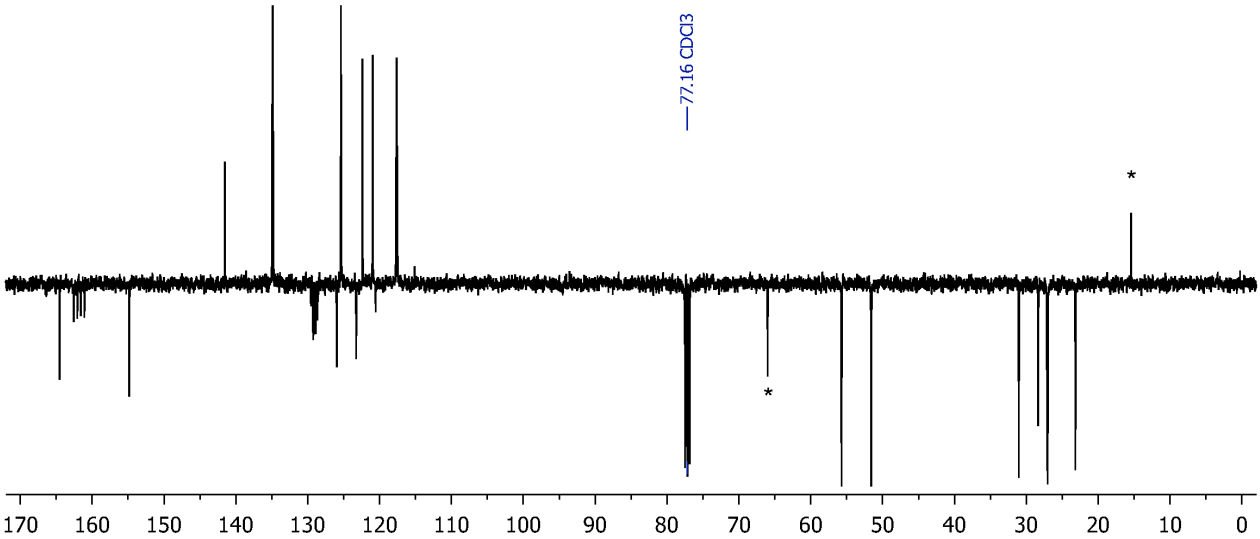


Figure S-12: $^{13}C\{^{1}H\}$(APT) NMR spectrum of **3c** ($CDCl_3$, 400 MHz). * Et_2O

1.4 Palladium complexes **4**

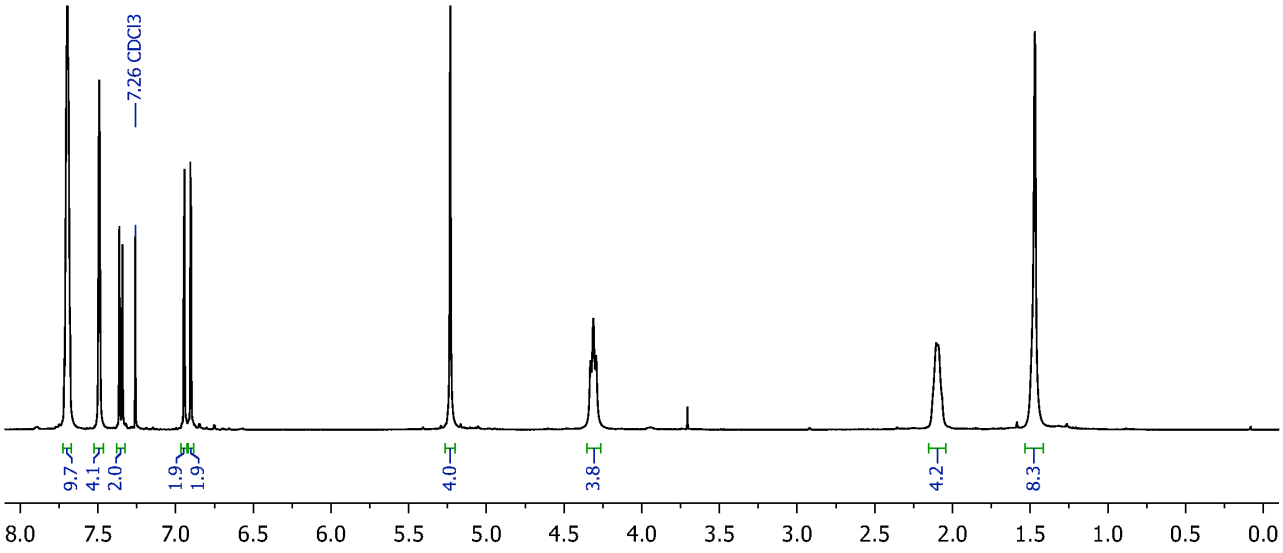


Figure S-13: ^{1}H NMR spectrum of **4a** ($CDCl_3$, 400 MHz).

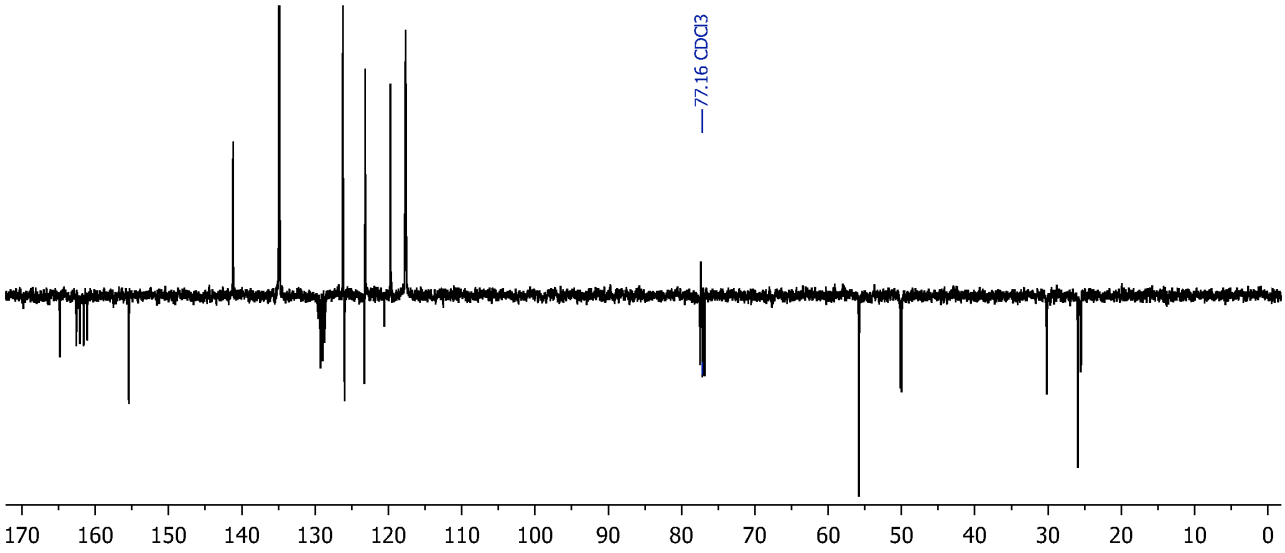


Figure S-14: $^{13}C\{^{1}H\}$(APT) NMR spectrum of **4a** ($CDCl_3$, 400 MHz).

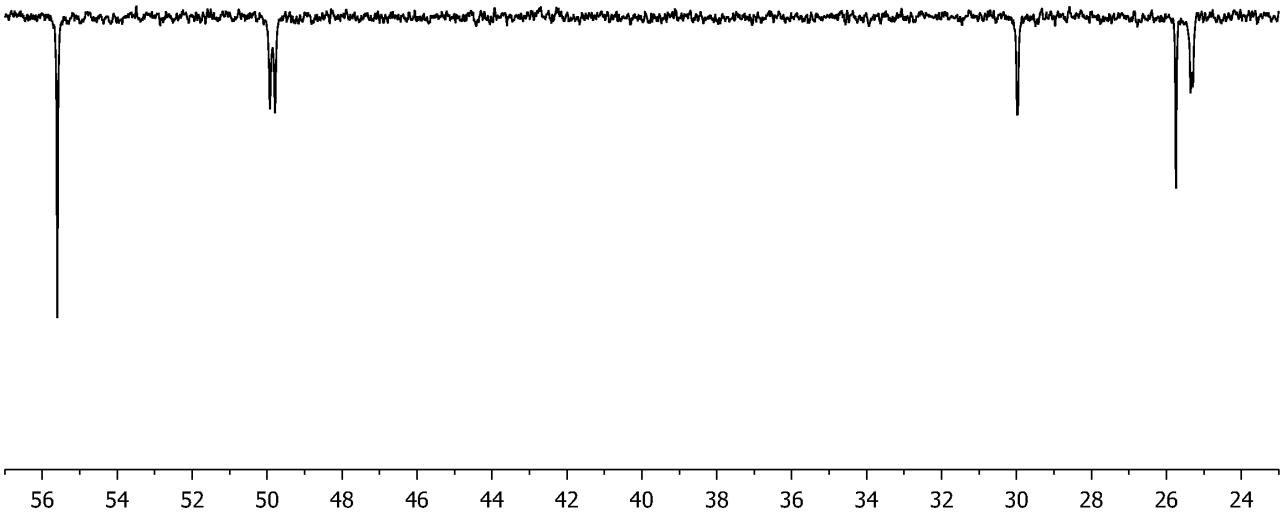


Figure S-15: Expansion of $^{13}C\{^{1}H\}$(APT) NMR spectrum of **4a** ($CDCl_3$, 400 MHz).

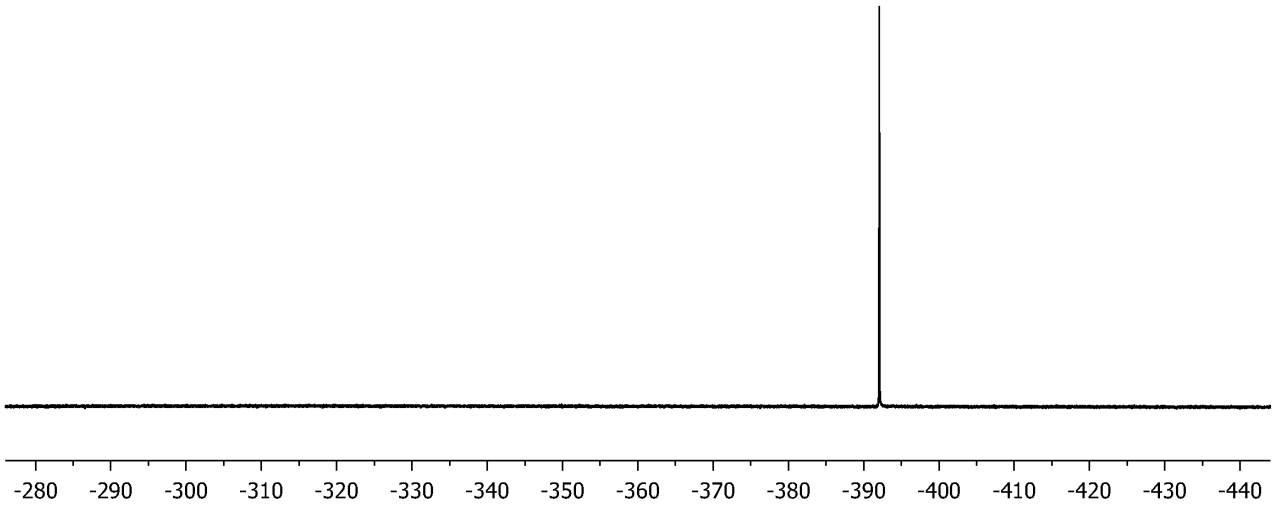


Figure S-16: ^{19}F NMR spectrum of **4a** ($CDCl_3$, 400 MHz).

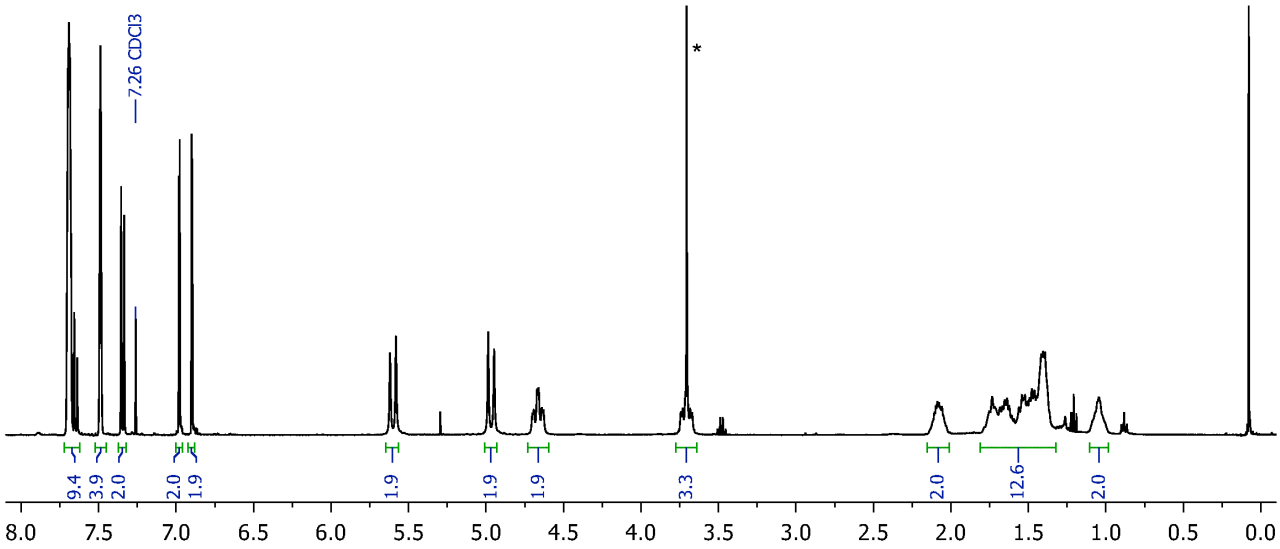


Figure S-17: ^{1}H NMR spectrum of **4b** ($CDCl_3$, 400 MHz), * 1,4-dioxane

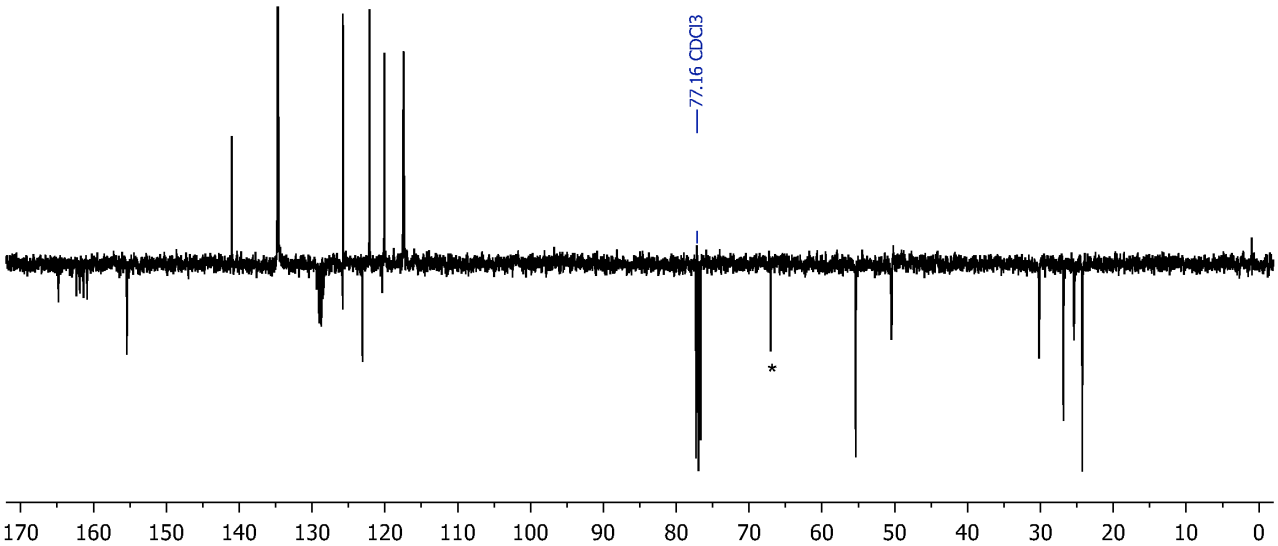


Figure S-18: $^{13}C\{^{1}H\}$(APT) NMR spectrum of **4b** ($CDCl_3$, 400 MHz), * 1,4-dioxane

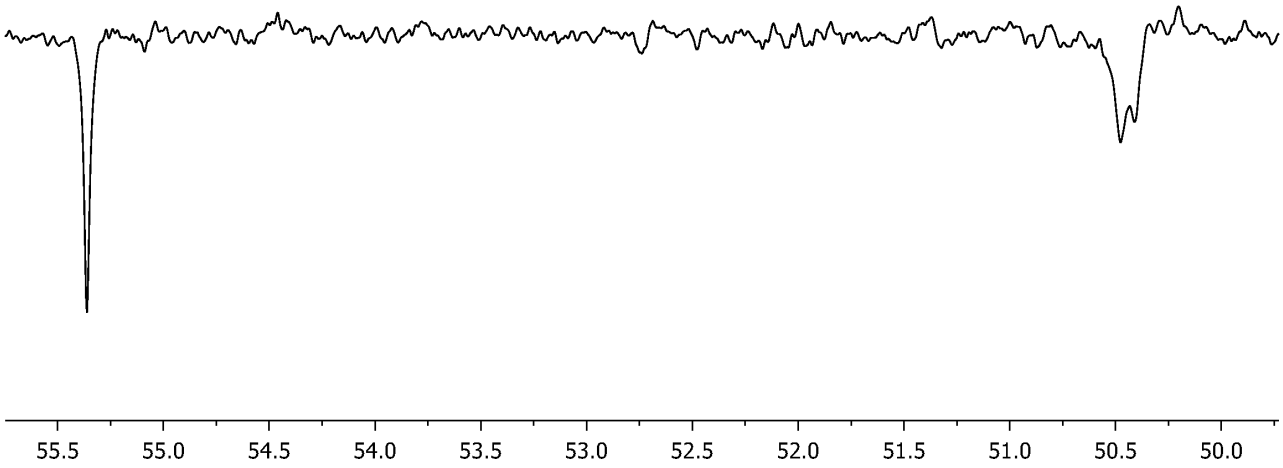


Figure S-19: Expansion of $^{13}C\{^{1}H\}$(APT) NMR spectrum of **4b** ($CDCl_3$, 400 MHz).

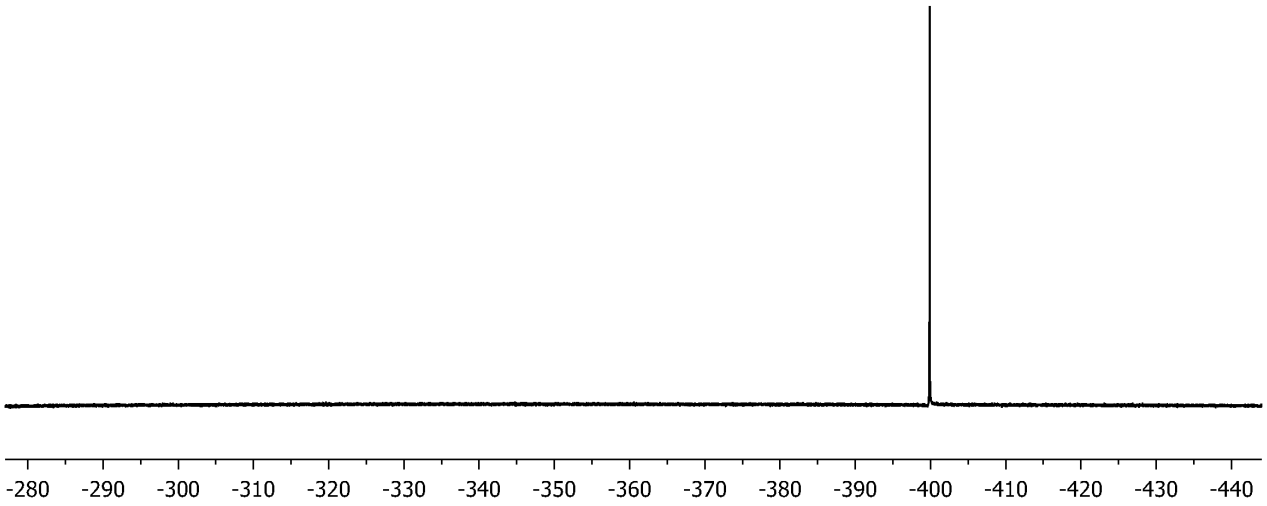


Figure S-20: ^{19}F NMR spectrum of **4b** ($CDCl_3$, 400 MHz).

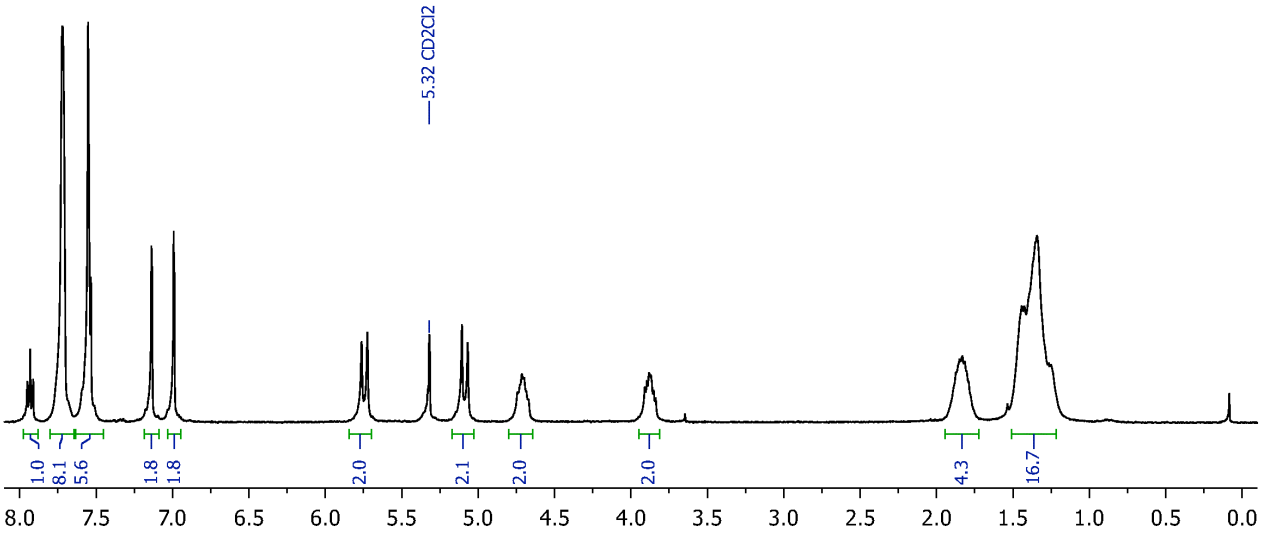


Figure S-21: ^{1}H NMR spectrum of **4c** (CD_2Cl_2, 400 MHz). **4c** slowly reforms starting material in $CDCl_3$.

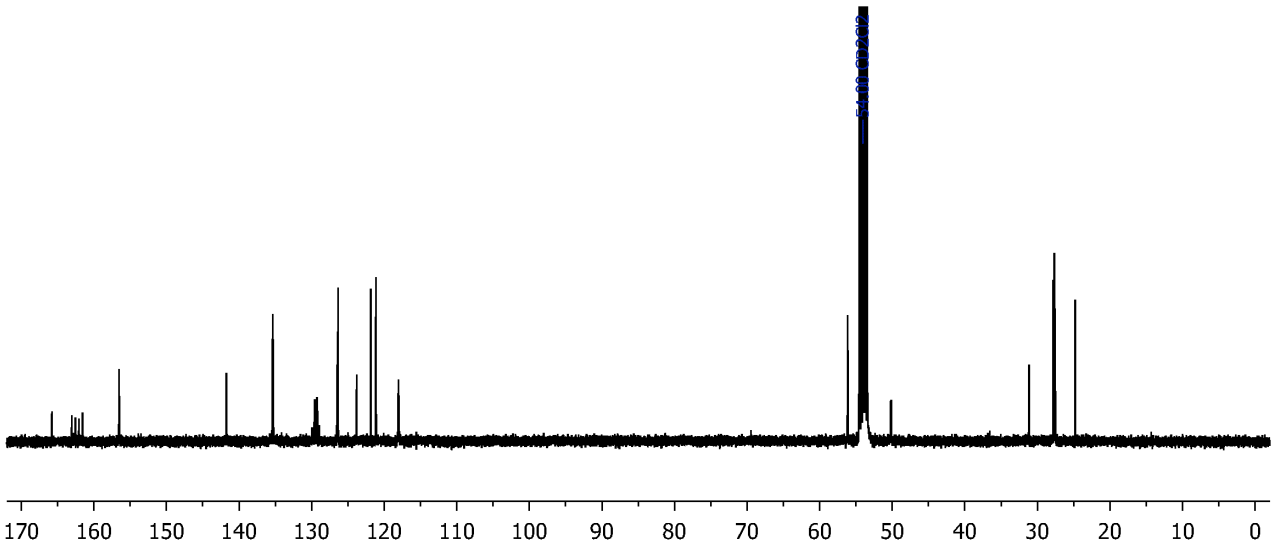


Figure S-22: $^{13}C\{^{1}H\}$ NMR spectrum of **4c** (CD_2Cl_2, 400 MHz). **4c** slowly reforms starting material in $CDCl_3$.

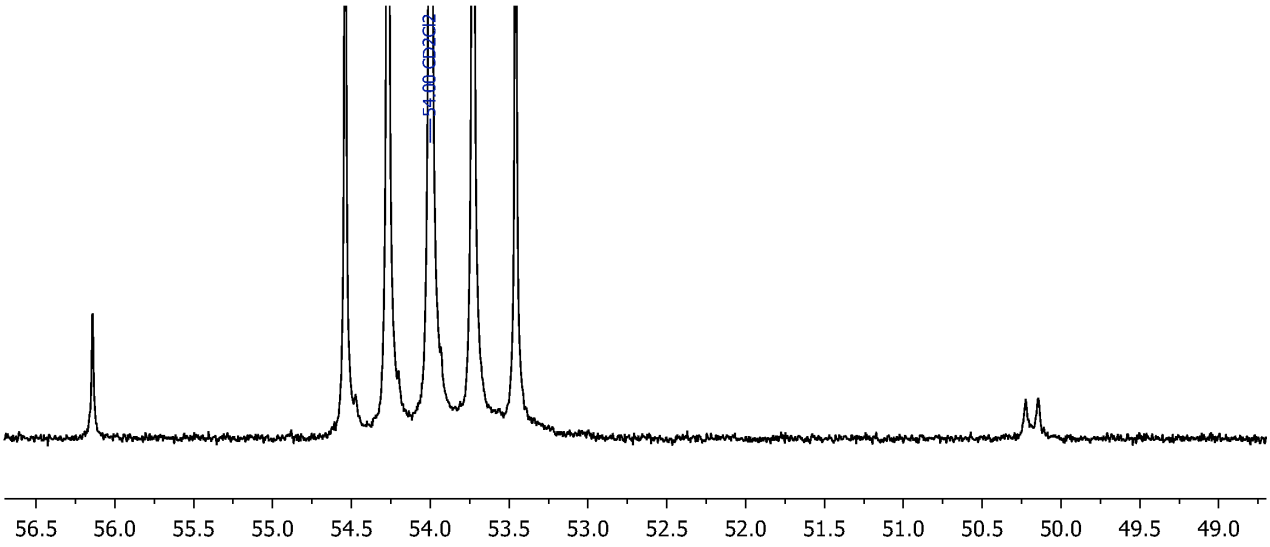


Figure S-23: Expansion of $^{13}C\{^{1}H\}$ NMR spectrum of **4c** (CD_2Cl_2, 400 MHz)

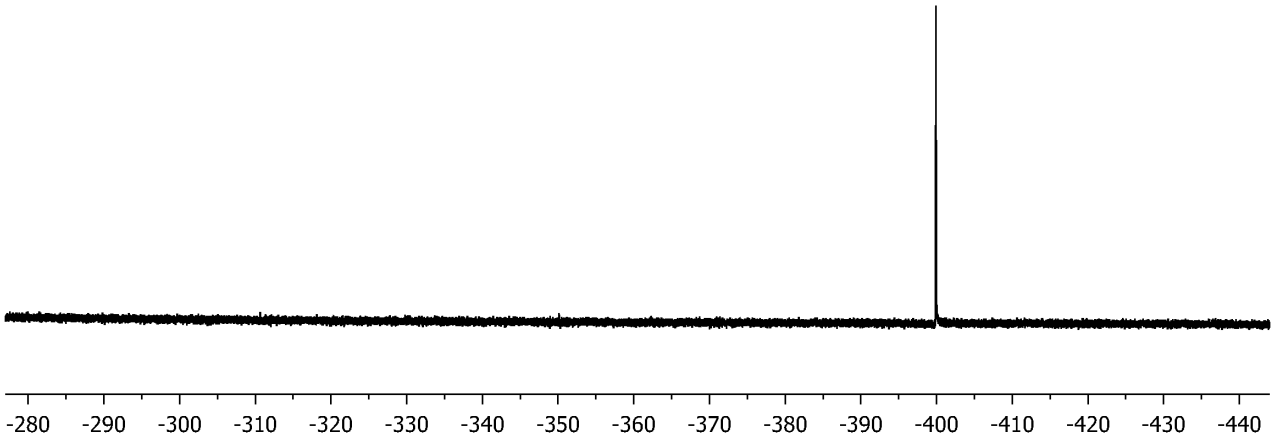


Figure S-24: ^{19}F NMR spectrum of **4c** ($CDCl_3$, 400 MHz).

1.5 ^{1}H NMR data for **3** and **4** in CD_2Cl_2 at 298 K

3a: **^{1}H NMR** (500 MHz, CD_2Cl_2) δ 8.03 (t, $^{3}J_{HH}$ = 7.7, 1H, py), 7.70 – 7.74 (m, 8H, Ar^F), 7.63 (d, $^{3}J_{HH}$ = 7.7, 2H, py), 7.55 (br, 4H, Ar^F), 7.10 (d, $^{3}J_{HH}$ = 1.8, 2H, imid), 7.00 (d, $^{3}J_{HH}$ = 1.8, 2H, imid), 5.46 (d, $^{2}J_{HH}$ = 15.3, 2H, pyC$\underline{H}_2$), 5.39 – 5.50 (m, 2H, *N*-CH_2), 5.19 (d, $^{2}J_{HH}$ = 15.3, 2H, pyC$\underline{H}_2$), 3.83 (dt, $^{2}J_{HH}$ = 13.4, $^{3}J_{HH}$ = 6.7, 2H, *N*-CH_2), 2.82 (br, 2H, CH_2), 2.02 – 2.12 (m, 2H, CH_2), 1.73 – 1.84 (m, 2H, CH_2), 1.64 – 1.72 (m, 2H, CH_2), 1.44 – 1.53 (m, 2H, CH_2), 1.16 – 1.24 (m, 2H, CH_2).

3b: **^{1}H NMR** (500 MHz, CD_2Cl_2) δ 7.98 (t, $^{3}J_{HH}$ = 7.7, 1H, py), 7.70 – 7.74 (m, 8H, Ar^F), 7.60 (d, $^{3}J_{HH}$ = 7.8, 2H, py), 7.55 (br, 4H, Ar^F), 7.12 (d, $^{3}J_{HH}$ = 1.8, 2H, imid), 6.97 (d, $^{3}J_{HH}$ = 1.8, 2H, imid), 5.63 (d, $^{2}J_{HH}$ = 15.1, 2H, pyC$\underline{H}_2$), 5.12 (d, $^{2}J_{HH}$ = 15.1, 2H, pyC$\underline{H}_2$), 4.63 – 4.73 (m, 2H, *N*-CH_2), 4.36 – 4.46 (m, 2H, *N*-CH_2), 2.32 – 2.44 (m, 2H, CH_2), 1.81 – 1.93 (m, 2H, CH_2), 1.59 – 1.70 (m, 2H, CH_2), 1.24 – 1.47 (m, 8H, CH_2), 1.11 – 1.23 (m, 2H, CH_2).

3c: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.96 (t, $^{3}J_{HH}$ = 7.8, 1H, py), 7.70 – 7.74 (m, 8H, Ar^F), 7.59 (d, $^{3}J_{HH}$ = 7.8, 2H, py), 7.55 (br, 4H, Ar^F), 7.14 (d, $^{3}J_{HH}$ = 1.8, 2H, imid), 6.96 (d, $^{3}J_{HH}$ = 1.8, 2H, imid), 5.71 (d, $^{2}J_{HH}$ = 15.1, 2H, pyC$\underline{H}_2$), 5.11 (d, $^{2}J_{HH}$ = 15.1, 2H, pyC$\underline{H}_2$), 4.73 (td, J_{HH} = 12.3, $^{3}J_{HH}$ = 3.9, 2H, *N*-CH_2), 3.79 (td, J_{HH} = 12.3, $^{3}J_{HH}$ = 5.7, 2H, *N*-CH_2), 2.07 – 2.18 (m, 2H, CH_2), 1.67 – 1.78 (m, 2H, CH_2), 1.32 – 1.55 (m, 14H, CH_2), 1.08 – 1.19 (m, 2H, CH_2).

4a: **^{1}H NMR** (500 MHz, CD_2Cl_2) δ 7.99 (t, $^{3}J_{HH}$ = 7.7, 1H, py), 7.70 – 7.74 (m, 8H, Ar^F), 7.57 (d, $^{3}J_{HH}$ = 7.7, 2H, py), 7.55 (br, 4H, Ar^F), 7.10 (d, $^{3}J_{HH}$ = 1.8, 2H, imid), 7.00 (d, $^{3}J_{HH}$ = 1.8, 2H, imid), 5.34 (s, 4H, pyC$\underline{H}_2$), 4.33 (app. t, *J* = 7, 4H, *N*-CH_2), 2.05 – 2.13 (m, 4H, CH_2), 1.44 – 1.51 (s, 8H, CH_2).

4b: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.96 (t, $^{3}J_{HH}$ = 7.8, 1H, py), 7.70 – 7.74 (m, 8H, Ar^F), 7.53 – 7.58 (m, 6H, py + Ar^F), 7.12 (d, $^{3}J_{HH}$ = 1.8, 2H, imid), 6.99 (d, $^{3}J_{HH}$ = 1.9, 2H, imid), 5.68 (d, $^{2}J_{HH}$ = 15.3, 2H, pyC$\underline{H}_2$), 5.10 (d, $^{2}J_{HH}$ = 15.3, 2H, pyC$\underline{H}_2$), 4.60 – 4.70 (m, 2H, *N*-CH_2), 3.73 (td, J_{HH} = 12.2, $^{3}J_{HH}$ = 5.2, 2H, *N*-CH_2), 2.01 – 2.12 (m, 2H, CH_2), 1.59 – 1.77 (m, 4H, CH_2), 1.33 – 1.57 (m, 8H, CH_2), 0.97 – 1.09 (m, 2H, CH_2).

4c: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.93 (t, $^{3}J_{HH}$ = 7.7, 1H, py), 7.69 – 7.75 (m, 8H, Ar^F), 7.53 – 7.57 (m, 6H, Ar^F + py), 7.14 (s, 2H, imid), 6.99 (s, 2H, imid), 5.75 (d, $^{2}J_{HH}$ = 15.2, 2H, pyC$\underline{H}_2$), 5.09 (d, $^{2}J_{HH}$ = 15.2, 2H, pyC$\underline{H}_2$), 4.66 – 4.75 (m, 2H, *N*-CH_2), 3.83 – 3.92 (m, 2H, *N*-CH_2), 1.74 – 1.93 (m, 4H, CH_2), 1.17 – 1.52 (m, 16H, CH_2).

1.6 Variable temperature NMR spectra of **3** and **4**.

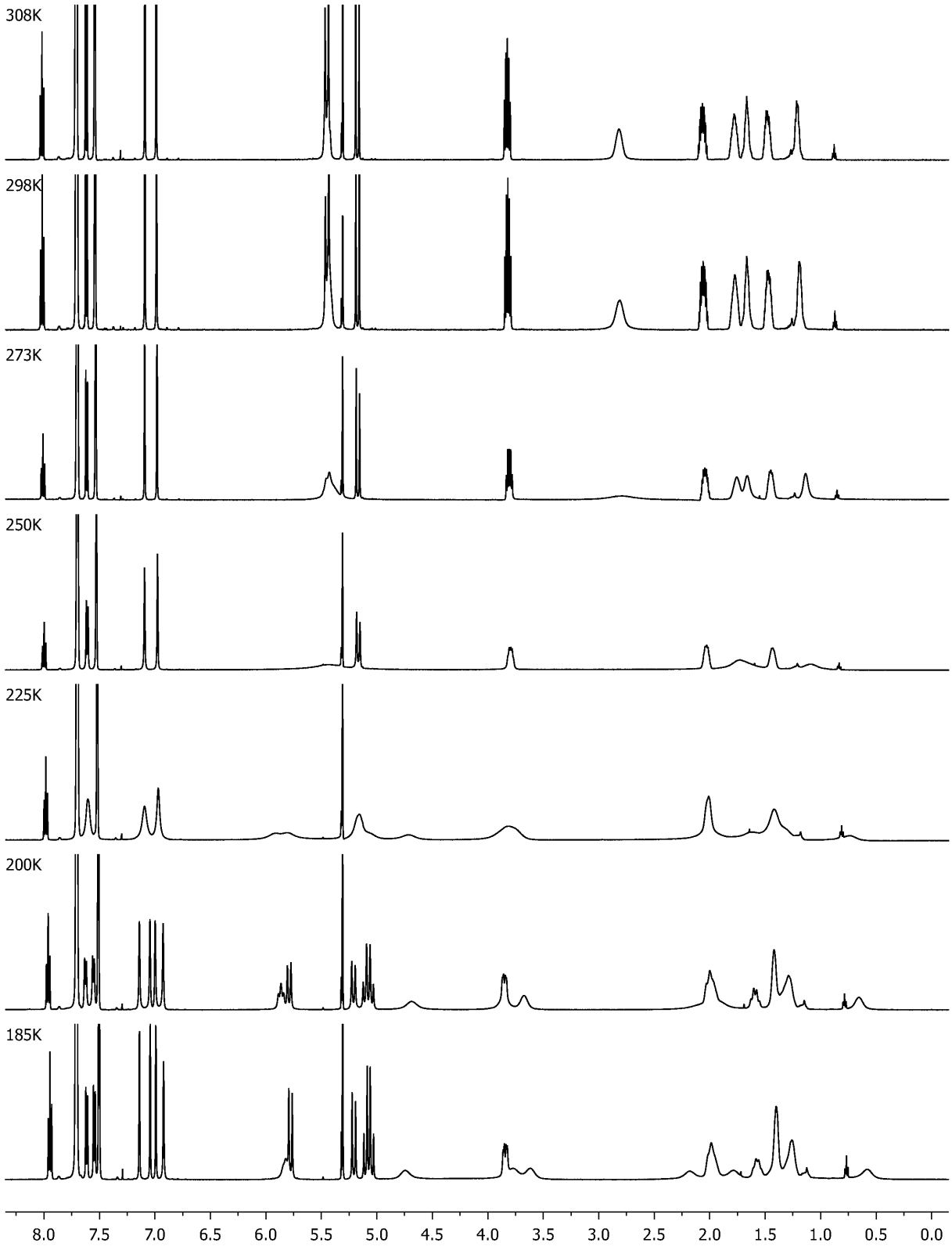


Figure S-25: ^{1}H VT NMR spectra of **3a** (CD_2Cl_2, 500 MHz).

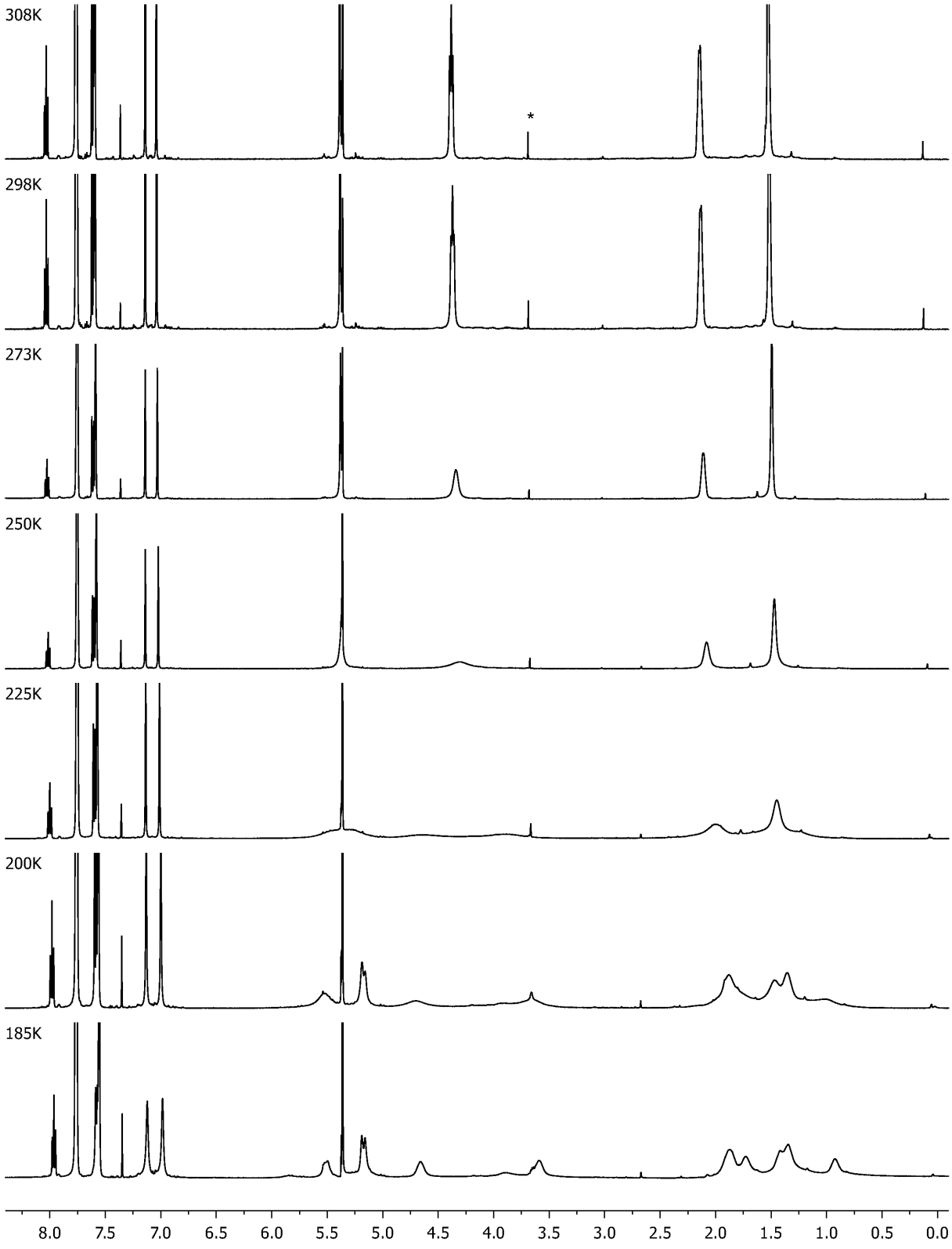


Figure S-26: ^{1}H VT NMR spectra of **4a** (CD_2Cl_2, 500 MHz), * 1,4-dioxane.

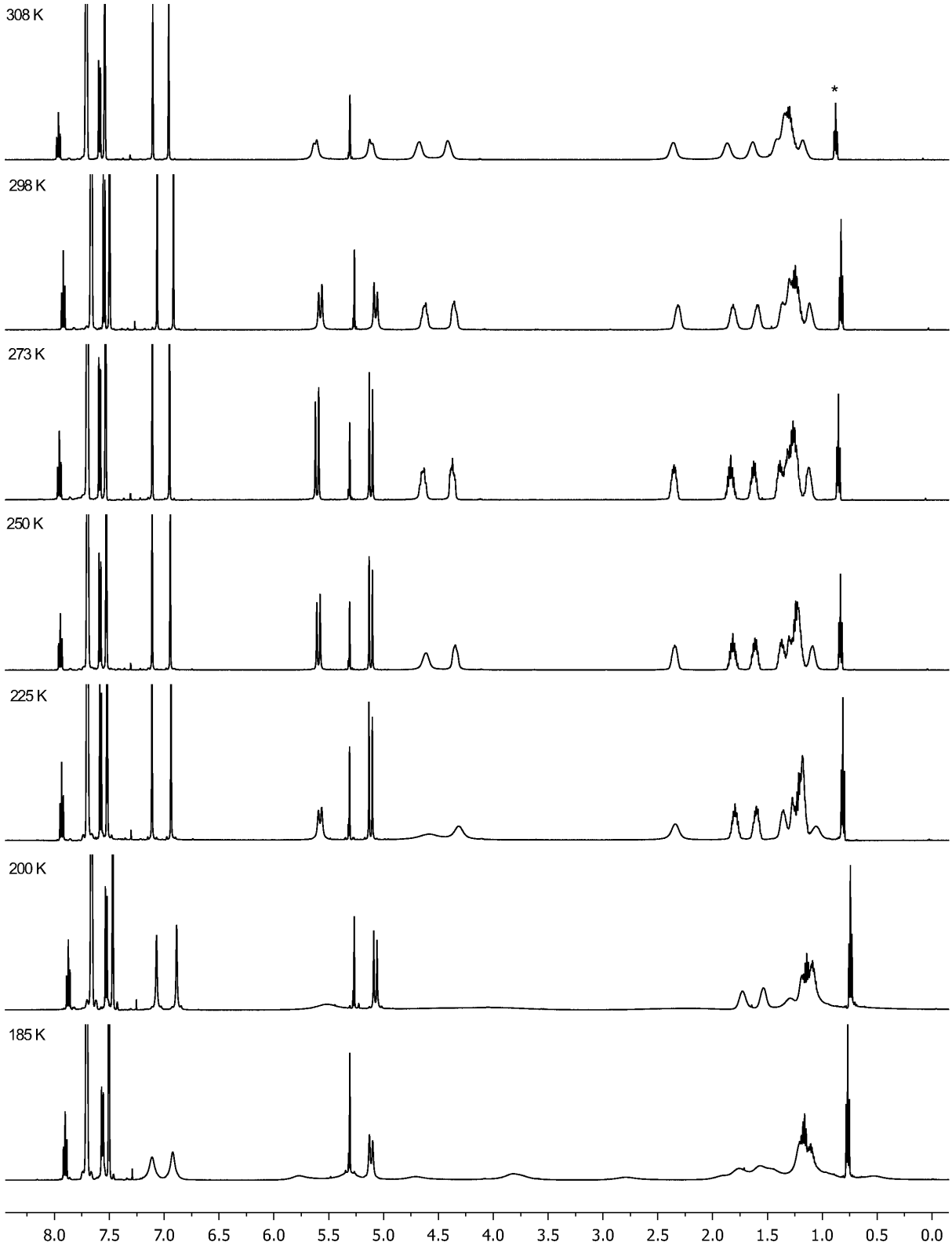


Figure S-27: ^{1}H VT NMR spectra of **3b** (CD_2Cl_2, 500 MHz). * Pentane.

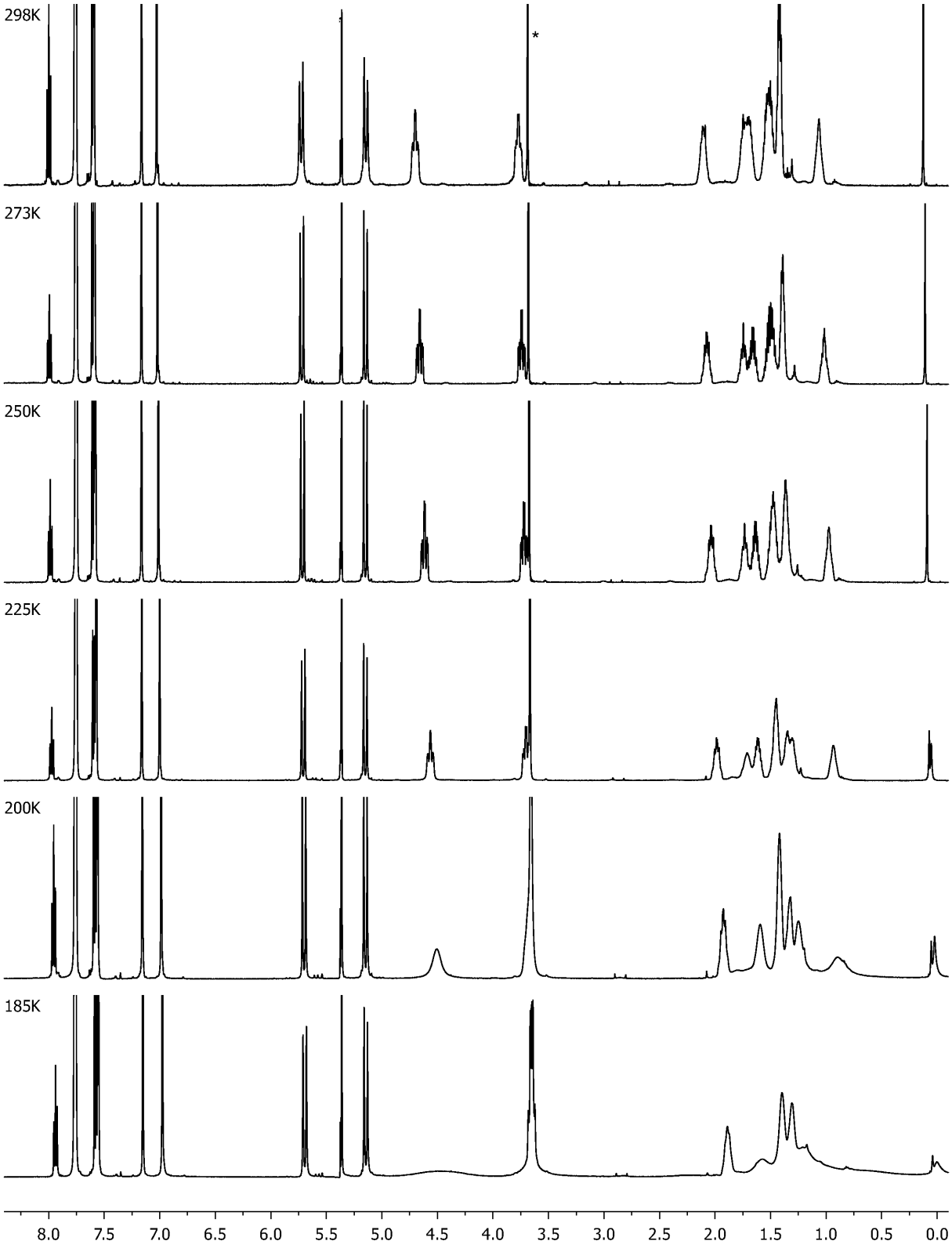


Figure S-28: ^{1}H VT NMR spectra of **4b** (CD_2Cl_2, 500 MHz), * 1,4-dioxane.

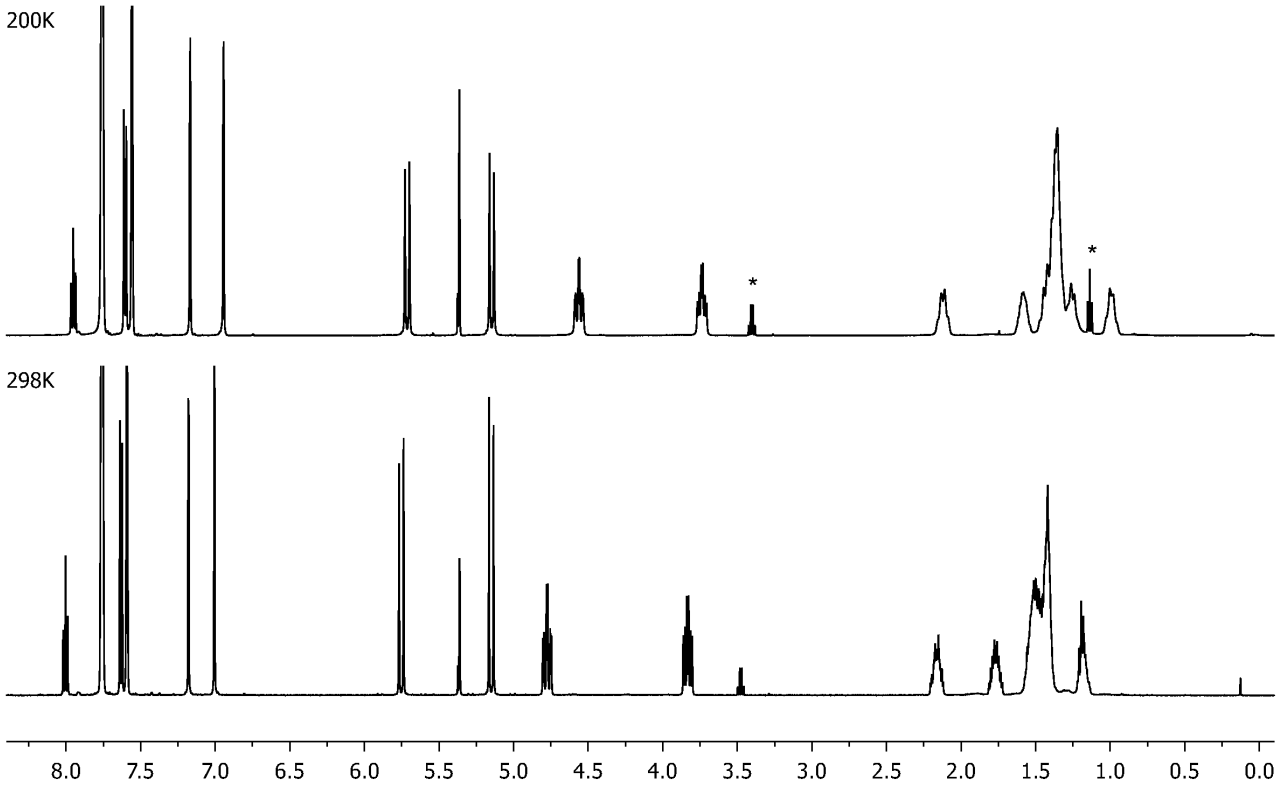


Figure S-29: ^{1}H VT NMR spectra of **3c** (CD_2Cl_2, 500 MHz), * Et_2O.

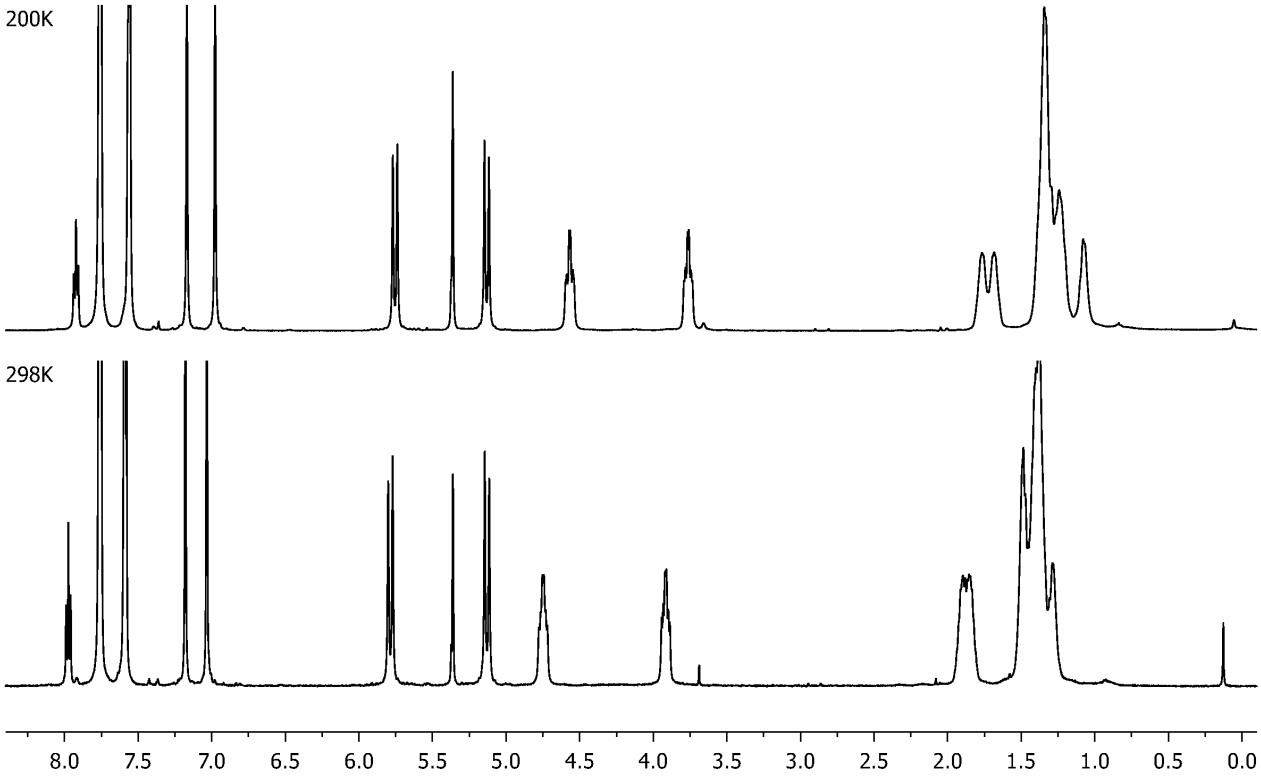


Figure S-30: ^{1}H VT NMR spectra of **4c** (CD_2Cl_2, 500 MHz).

3. Solid-state structure of 2b

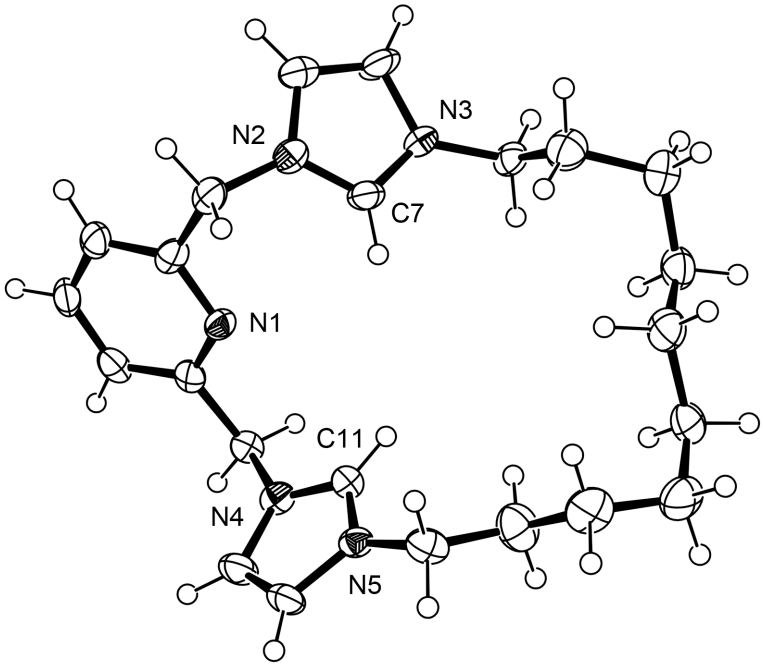


Figure S-31: Solid-state structure of **2b** (one of the two independent molecules; Z' = 2). Thermal ellipsoids drawn at 50%; anions and solvent molecule omitted for clarity.

4. Solid-state structure disorder modelling of 3b and 4a

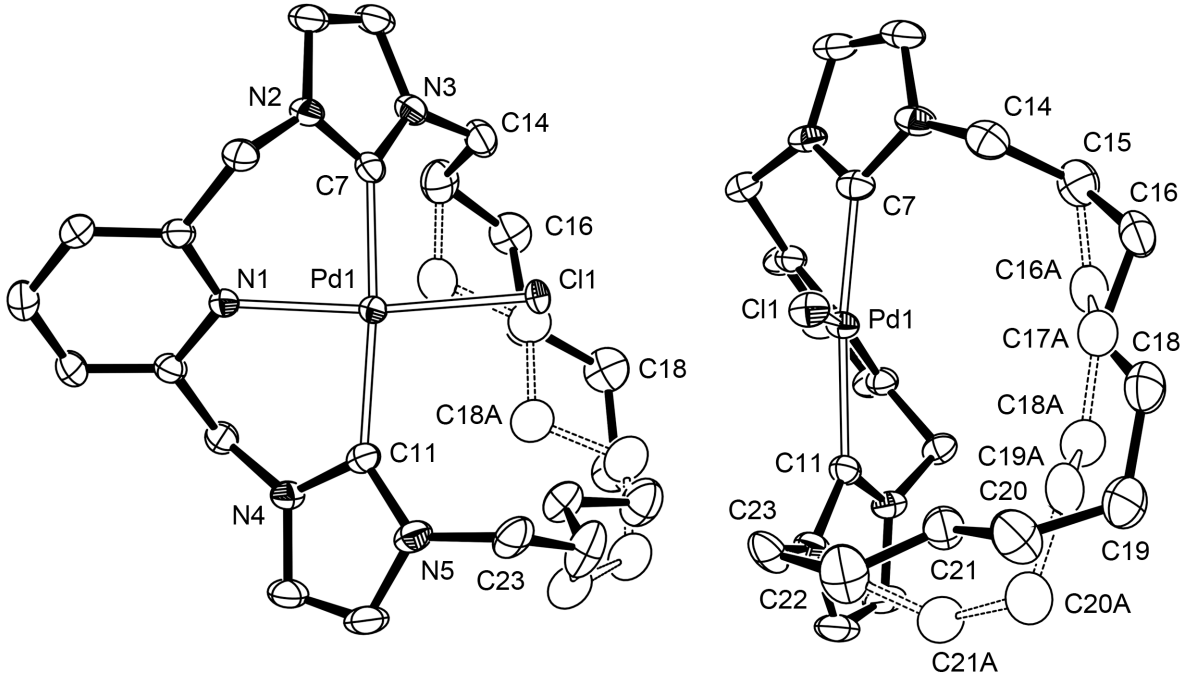


Figure S-32: Solid-state structure of **3b** – showing disorder of the alkyl chain (dashed bonds and open ellipsoids). Thermal ellipsoids drawn at 50%; hydrogen atoms, anion and solvent molecule omitted for clarity.

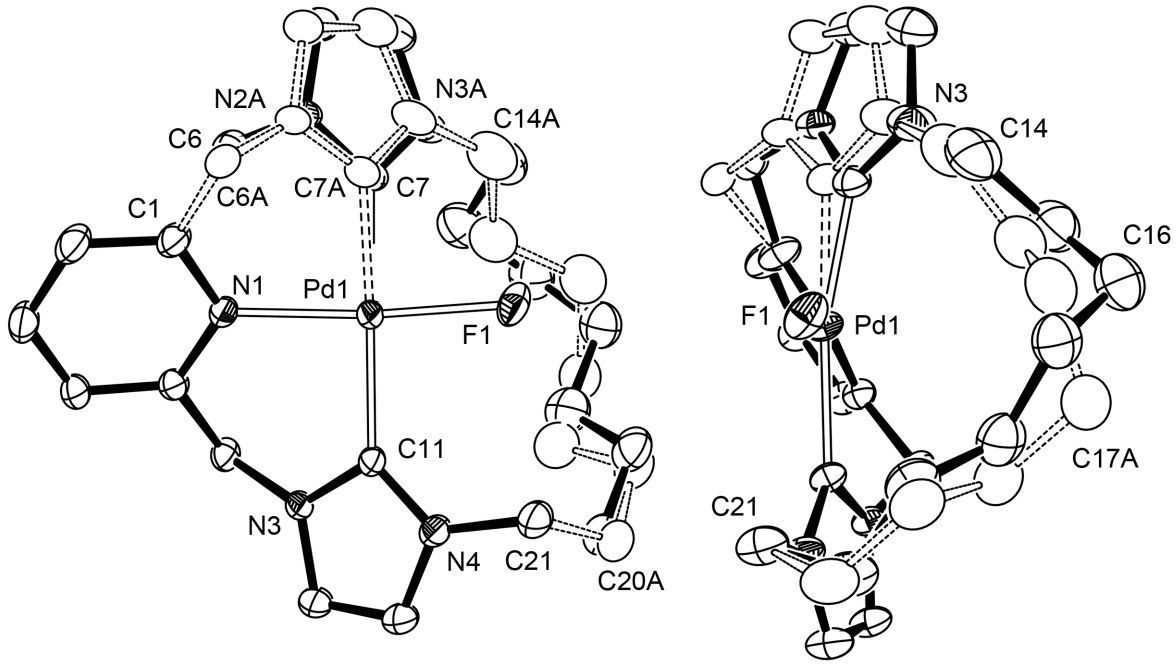


Figure S-33: Solid-state structure of **4a** – showing disorder of macrocyclic ligand (dashed bonds and open ellipsoids) in one of the unique molecules (Z' = 2). Thermal ellipsoids drawn at 30%; hydrogen atoms and anion omitted for clarity.

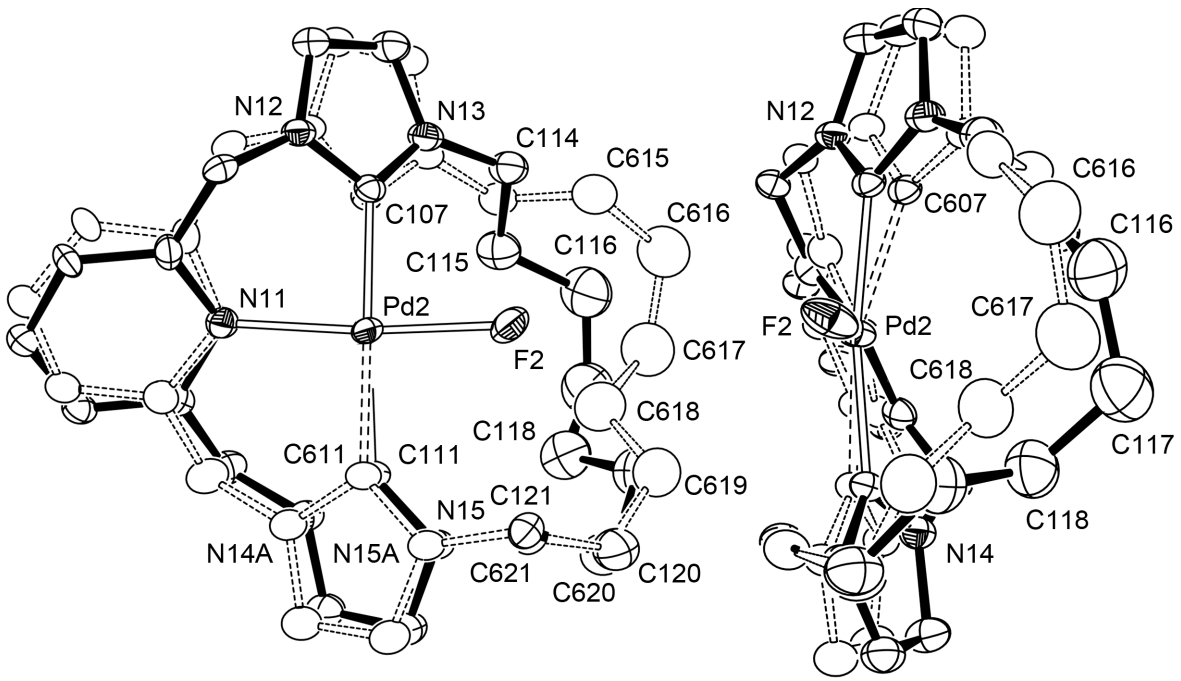


Figure S-34: Solid-state structure of **4a** – showing disorder of macrocyclic ligand (dashed bonds and open ellipsoids) in one of the unique molecules (Z' = 2). Thermal ellipsoids drawn at 30%; hydrogen atoms and anion omitted for clarity.

5. Variable temperature NMR simulation for 3a

Simulation of the fluxional process was carried out by line shape analysis of the imidazolylidene resonances using gNMR (v4.1.2). The $^{3}J_{HH}$ coupling constants and the line width parameters were fixed at 1.4 and 1.8 Hz following analysis of the 185 K and 298 K ^{1}H NMR spectra. Due to chemical shift changes of the signals with temperature Δδ of the interchanging resonances were fixed using the 185 K data. Selected simulated data are shown in Figure S-35. Eyring analysis of the rate data gave $\Delta H^{\ddagger}$ = 43 ± 4 kJ·mol^{-1}, $\Delta S^{\ddagger}$ = -7 ± 17 J·mol^{-1}K^{-1} and $\Delta G^{\ddagger}$(298 K) = 45 ± 9 kJ·mol^{-1} (Figure S-36). As an independent check of the simulation, $\Delta G^{\ddagger}$ was estimated using equation (1) for three separate resonance pairs giving 43.7, 45.1 and 46.4 kJ·mol^{-1}.

$$\Delta G^{\ddagger} = aT_c[9.972 + \log(T_c / \Delta v)] \qquad (1)$$

Where T_c is the coalescene temperature, Δv is the maximum peak separation in the low-temperature limit in Hz and a = 1.914 x 10^{-2} kJ·mol^{-1}K^{-1}

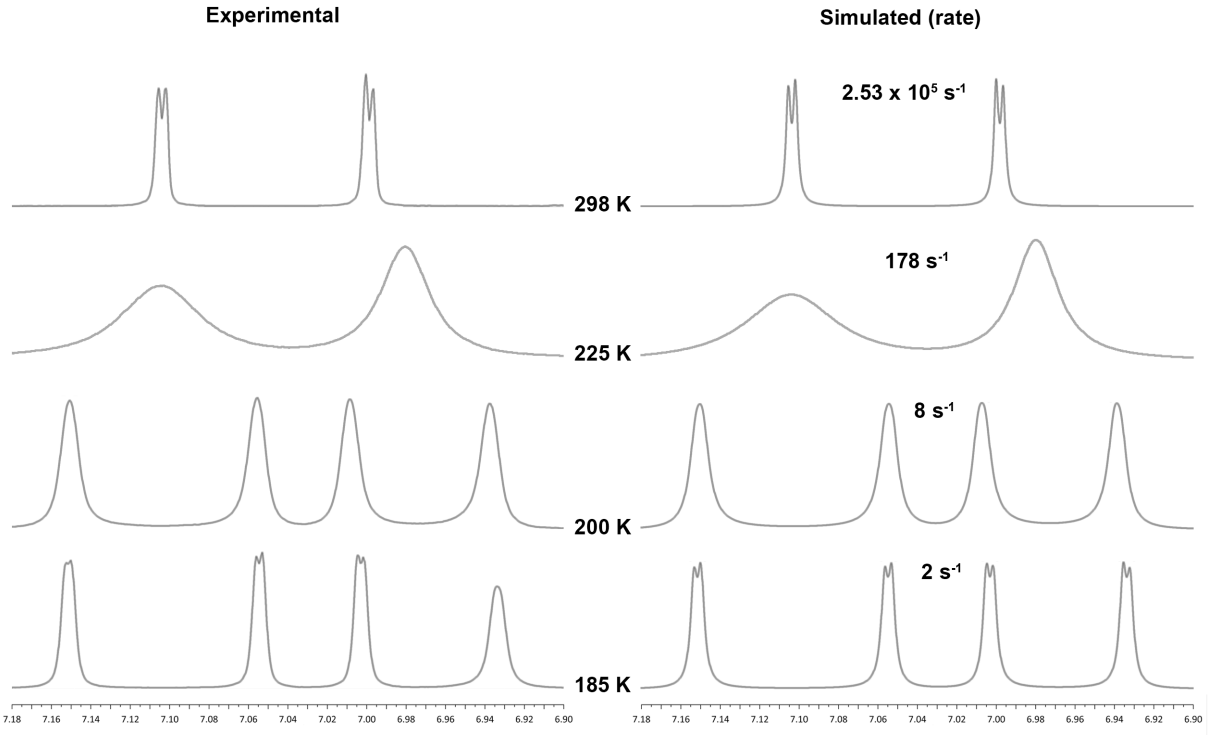


Figure S-35: Selected experimental and simulated ^{1}H NMR spectra featuring the imidazolylidene protons of **3a** (CD_2Cl_2, 500 MHz).

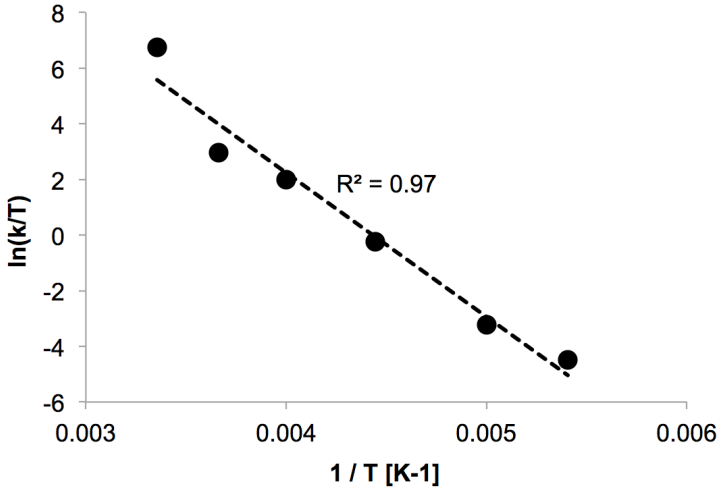
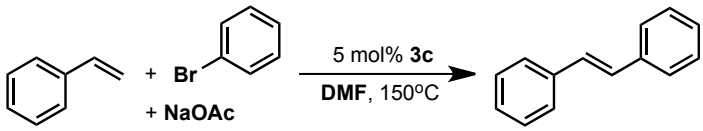


Figure S-36: Eyring plot for the fluxional behaviour observed for **3a**.

6. Preliminary catalytic screening of 3c

For a preliminary indication of the catalytic activity for the macrocyclic complexes, **3c** was evaluated as a pre-catalyst (5 mol%) for the Heck reaction between bromobenzene and styrene (Scheme S-1). Heating at 150ºC in DMF for 20 hours with excess NaOAc resulted in the selective formation of *trans*-stilbene – 50% conversion as determined by NMR spectroscopy. Significantly however, repeating this reaction in the presence of mercury, as a selective poison for heterogeneous catalysis,[1] lead to no catalytic turnover. This catalytic inhibition strongly suggests that the active species in the system is heterogeneous and discouraged us from further exploring the catalytic activity of **3** and **4**.

Scheme S-1: Preliminary catalytic screening.[a]



[a] 1.0 eqv. PhBr, 1.4 eqv. $PhCH{=}CH_2$, 1.10 eqv. NaOAc, 20h.

Experimental details

To a Schlenk flask charged with NaOAc (0.056 g, 0.684 mmol), **3c** (0.043 g, 0.031 mmol), bromobenzene (0.066 mL, 0.621 mmol) and styrene (0.100 mL, 0.870 mmol), DMF (anhydrous, 5 mL) was added (with or without 0.1 mL Hg). The flask was sealed and heated at 150°C for 20 hours. The reaction mixture was then cooled rapidly to room temperature, water added and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic fraction was washed with water (8 x 10

mL), dried over Na_2SO_4 and concentrated in vacuo and analysed by ^1H NMR spectroscopy ($CDCl_3$), using the catalyst (Ar^F signals) as an internal reference.

7. References

[1] (a) K. Yu, W. Sommer, J. M. Richardson, M. Weck, and C. W. Jones, *Adv. Synth. Catal.*, 2005, **347**, 161–171. (b) J. A. Widegren and R. G. Finke, *J. Mol. Catal. A: Chem.*, 2003, **198**, 317–341. (c) D. R. Anton and R. H. Crabtree, *Organometallics*, 1983, **2**, 855–859.