Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information for

Ligand-Modulated Ring-Expansion

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Table of Contents

Materials and Equipment

Solvents and starting materials were used as received from suppliers. $CDCl_3$ and THF-d_8 were purchased from Cambridge Isotope Laboratories. All reactions were performed under N_2 using dry solvents obtained from an INERT solvent purification system. Single crystal X-ray diffraction data (SCXRD) data were collected on Bruker APEX DUO and Bruker APEX X8 diffractometers. Nuclear magnetic resonance (NMR) spectra were recorded on Bruker AV-400 and AV-300 spectrometers. ^1H DOSY NMR spectra were collected on a Bruker AV-400 inverse probe spectrometer and were calibrated to the residual protonated solvent at δ 7.27 for $CDCl_3$. The concentration of the solutions was 5 mM. Low resolution mass spectra were obtained on a Waters ZQ equipped with ESCI ion source. Waters 2695 HPLC is used to deliver the samples. High resolution electrospray ionization mass spectra (HRMS) were obtained on a Micromass LCT time-of-flight (TOF) mass spectrometer equipped with an electrospray ion source. Fourier transform infrared (FT-IR) spectra were collected on a Thermo Scientific Nicolet 6700 FT-IR spectrometer equipped with a diamond Attenuated Total Reflectance (ATR) tip. Ultraviolet-visible (UV-Vis) spectra were obtained on a Cary 5000 spectrometer using a 1 cm path length quartz cuvette.

Experimental

Precursors **1**, **2** and **2-lut** were synthesized following the reported methodologies.[1] The obtained spectroscopic data matched with that previously reported.

Ring-expansion reaction attempted on compound 1. Compound **1** (80 mg, 0.19 mmol) and second generation Grubbs catalyst (7.6 mg, 0.0095 mmol) were stirred in 16 mL of dry THF at 55 °C for 2 h under a N_2 atmosphere. The reaction mixture was cooled to room temperature, quenched with ethyl vinyl ether and concentrated under vacuum. The resulting solid was washed with hexanes (3 × 10 mL) to give 83 mg of a brown powder (0.19 mmol), 100% yield assuming cis/trans **1**. Characterization of the material showed a 2:1 mixture of compound **1** in cis:trans forms.

Ring-expansion reaction attempted on compound 2. Compound **2** (79 mg, 0.14 mmol) and second generation Grubbs catalyst (5.8 mg, 0.007 mmol) were stirred in 12 mL of dry THF at 55 °C for 2 h under a N_2 atmosphere. The reaction was cooled to room temperature and quenched with ethyl vinyl ether. The precipitate formed was filtered and washed with THF (3 × 10 mL) and hexanes (3 × 10 mL) to give compound **2** as a yellow solid. Yield: 43 mg (0.07 mmol, 54%). The filtrate was concentrated under vacuum and washed with hexanes.

Ring-expansion reaction on compound 2-lut. Compound **2-lut** (125 mg, 0.19 mmol) and second generation Grubbs catalyst (8.1 mg, 0.0095 mmol) were stirred in 16 mL of dry THF at 55 °C for 2 h under a N_2 atmosphere. The reaction was cooled to room temperature and quenched with ethyl vinyl ether. The precipitate formed (**2-lut-prec**) was filtered and washed with THF (3 × 10 mL) and hexanes (3 × 10 mL) to give 48 mg of a grey solid. The filtrate was concentrated under vacuum and purified by column chromatography with an alumina column (eluent, gradient 0-10% MeOH in DCM; R_f = 0.38 (3% MeOH in DCM)) to give **3** as a yellow solid that was recrystallized by slow evaporation of a 1:1 solution of DCM and THF. Yield: 25 mg (0.02 mmol, 20%). A single crystal suitable for X-ray analysis was grown by vapour diffusion of THF into a DCM solution of **3**.

Data for 3. ^1H NMR (400 MHz, $CDCl_3$): δ 8.12 (t, 1H, J = 7.9 Hz), 7.87 (d, 2H, J = 7.9 Hz), 7.65 (m, 1H,), 6.97 (d, 1H, J = 7.6 Hz), 6.57 (m, 4H), 6.50 (m, 4H), 6.11 (m, 2H), 4.45 (s, 4H), 4.04 (s, 4H), 2.46 (s, 1H), 2.39 (s, 1H), 2.38 (s, 1H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 160.8, 157.5, 153.0, 140.6, 138.7, 134.0, 128.9, 128.2, 124.9, 122.9, 114.2, 68.0, 49.5, 25.69, 25.67, 25.6. HRMS (ESI/TOF). Calc for $C_{64}H_{61}N_8O_8{}^{104}Pd^{105}Pd$ [**3** + H^+]: 1278.2703 *m/z*. Found: 1278.2686 *m/z*. UV-Vis (CH_2Cl_2): λmax (ε_{max} (M^{-1} cm^{-1})) = 276 (6.3×10^4), 339 (2.2×10^4, 1 shoulder). FT-IR (ATR) ν = 3409, 2923, 1585, 1507, 1379, 1259, 1224, 1173, 1094, 1013, 793, 763, 676 cm^{-1}.

Data for 2-lut-prec. ^1H NMR (400 MHz, $CDCl_3$): δ 8.09 (br, 1H), 7.85 (br, 2H), 7.65 (br, 1H), 6.99 (d, 2H, J = 7.0 Hz), 6.57 (d, 4H, J = 7.7 Hz), 6.49 (d, 4H, J = 7.7 Hz), 6.03 (br, 2H), 4.49 (br, 4H), 4.00 (br, 4H), 2.47 (br, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.2, 160.4, 157.3, 153.0, 140.7, 139.0, 133.8, 128.7, 128.5, 124.9, 122.9, 114.4, 67.9, 48.9, 29.8, 25.7. UV-Vis (CH_2Cl_2): λmax (ε_{max} (M^{-1} cm^{-1})) = 276 (3.0×10^4), 332 (8.9×10^2, 1 shoulder). FT-IR (ATR) ν = 3472, 2920, 1582, 1506, 1380, 1216, 1172, 998, 823, 760, 726, 674 cm^{-1}.

NMR spectroscopic characterization of new compounds

Ring-expansion reaction attempted on compound 1

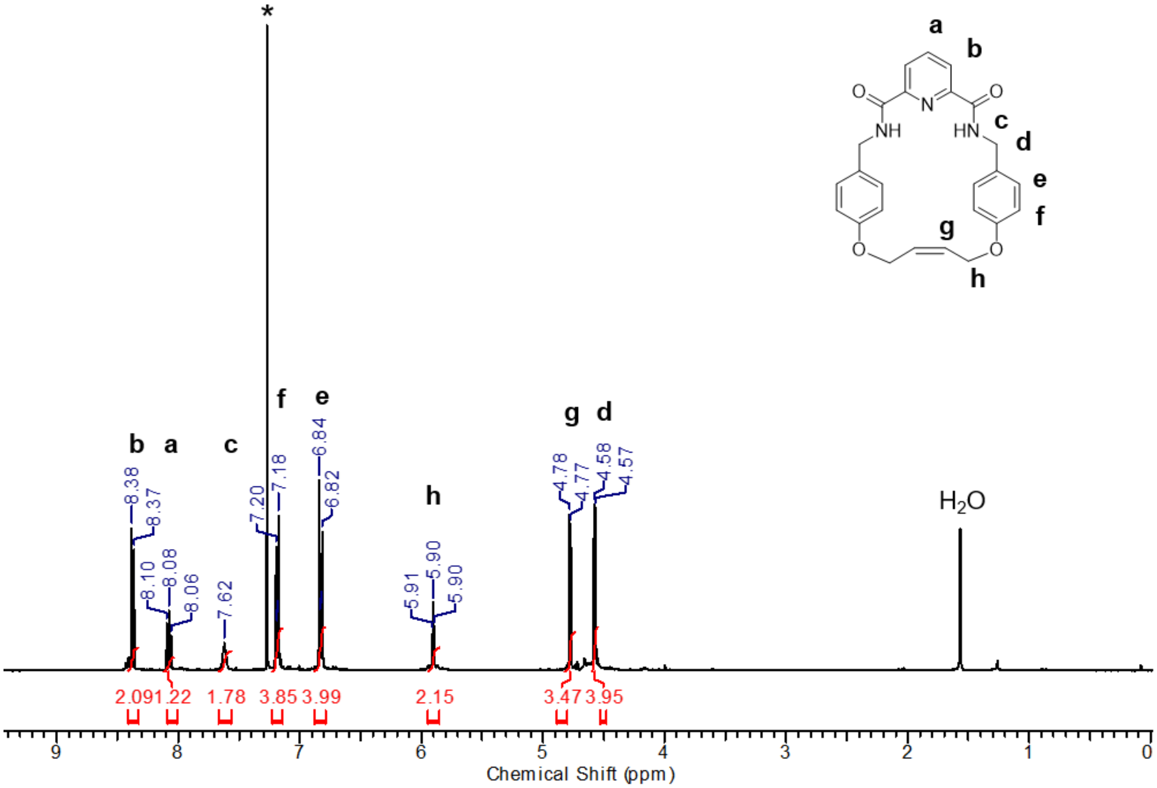

Figure S1 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1**. Residual solvent peaks are indicated with *.

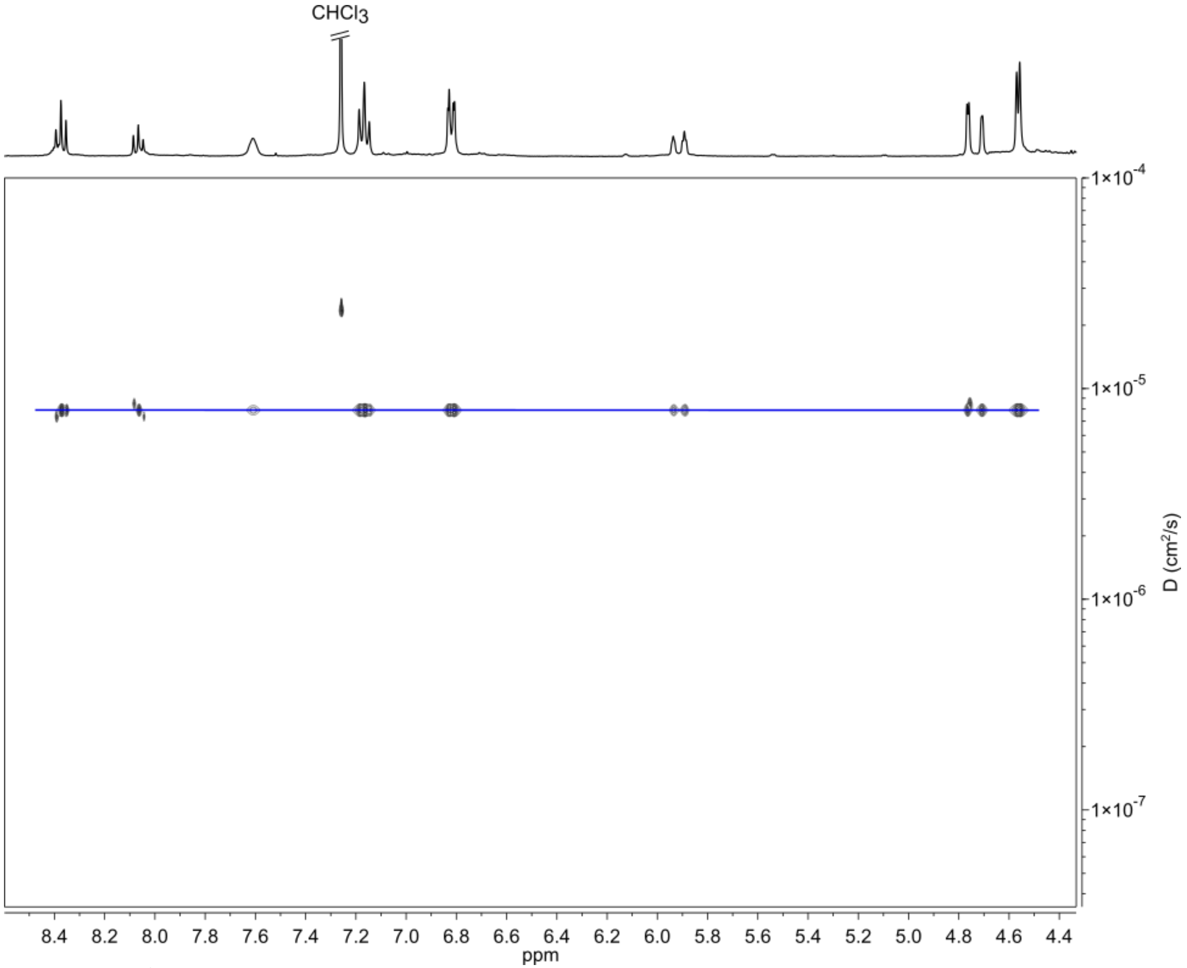

Figure S2 ^{1}H DOSY NMR (400 MHz, $CDCl_3$) experiment on compound **1**.

Ring-expansion reaction attempted on compound 2

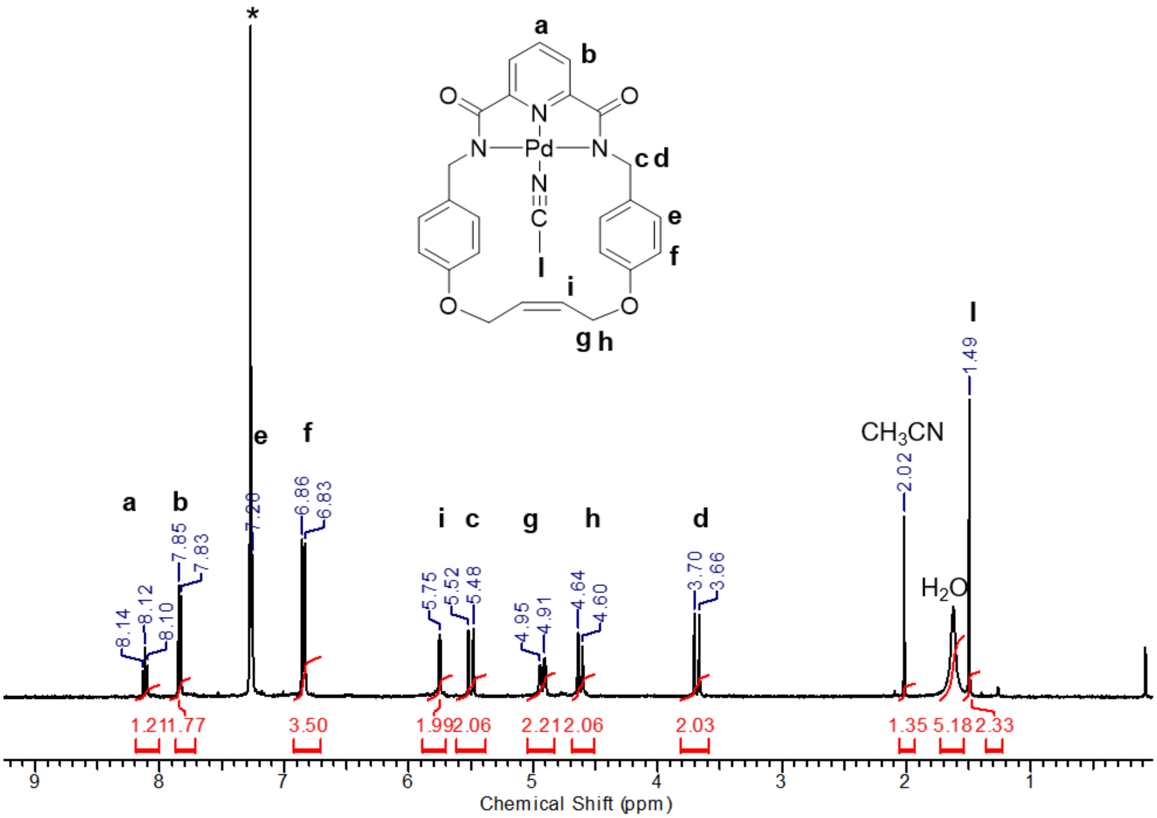

Figure S3 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **2**. Residual solvent peaks are indicated with *.

Figure S4 shows that the spectrum of the precipitate completely overlaps with the starting material **2**. The crude filtrate is mostly compound **2**, but some other side product (blue circles) is present.

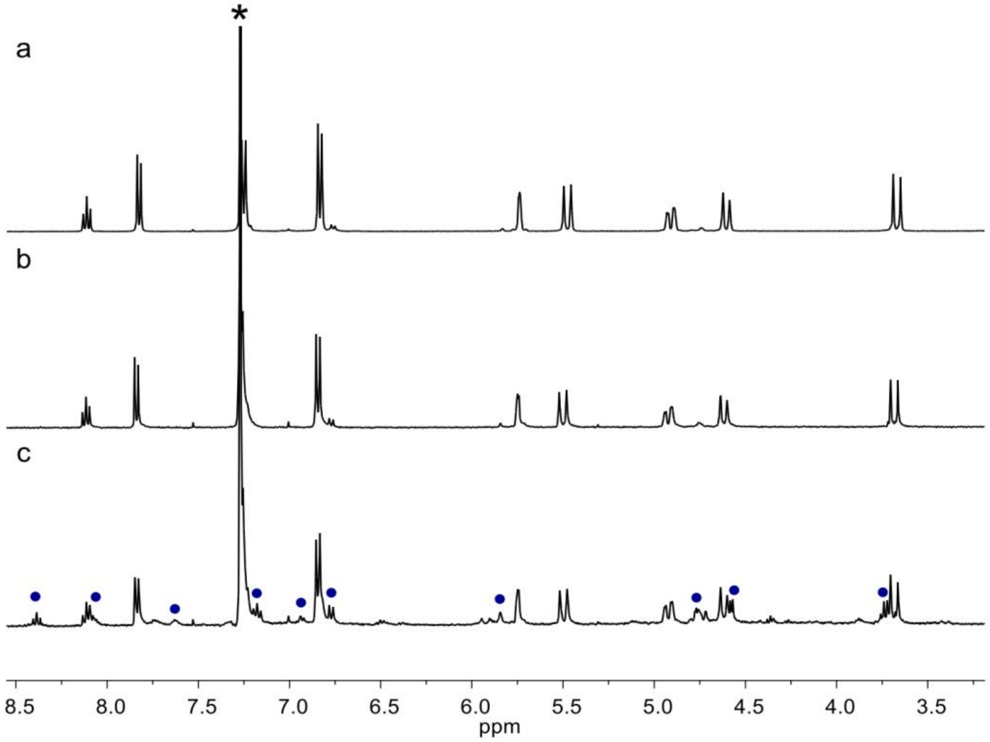

Figure S4 ^{1}H NMR (400 MHz, CDCl$_3$) spectra of: (a) pure compound **2**; (b) precipitate obtained from the ring-expansion reaction performed on compound **2**; (c) crude filtrate. Residual solvents peaks are indicated with *.

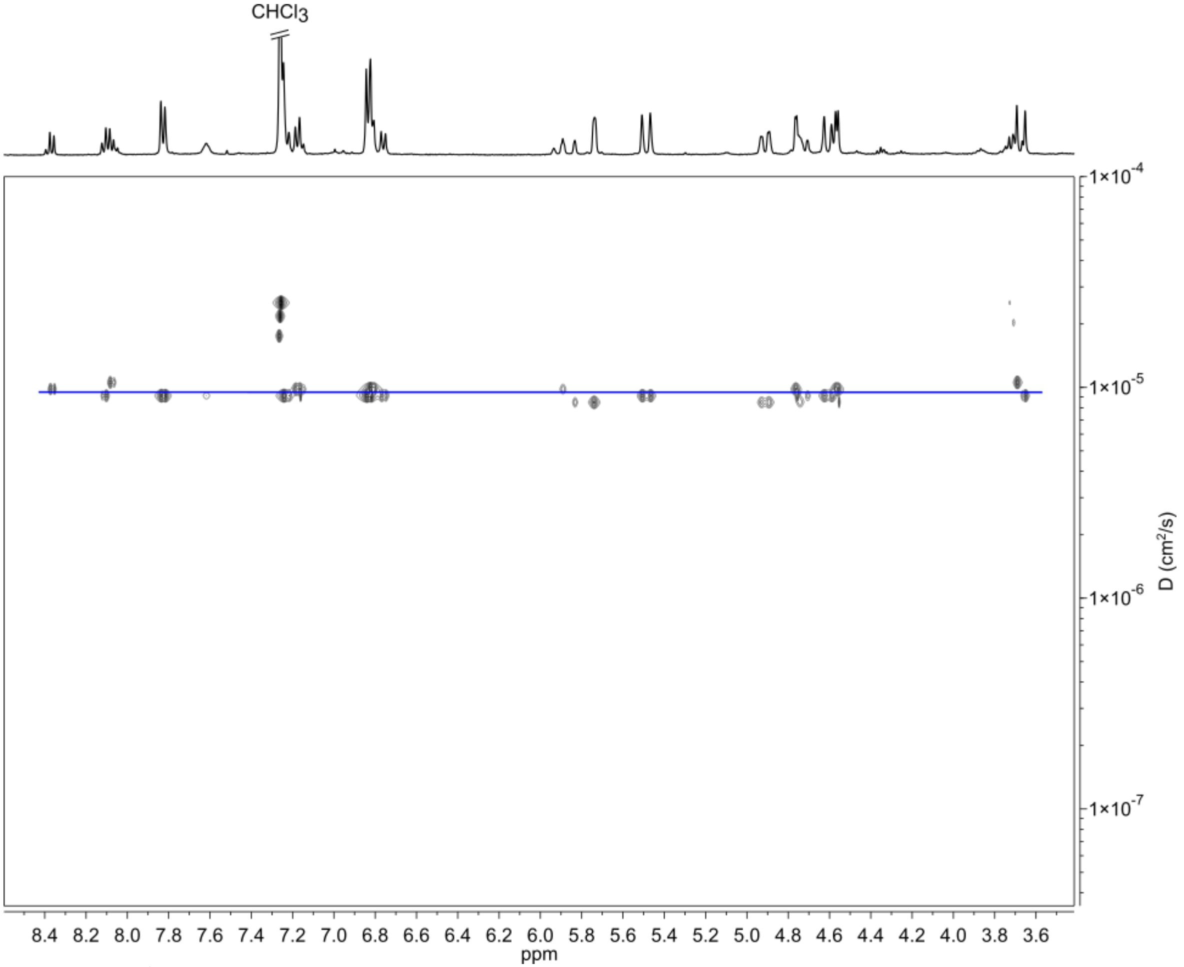

Figure S5 ^{1}H DOSY NMR (400 MHz, $CDCl_3$) experiment on compound **2**.

Ring-expansion on 2-lut monitored by ^{1}H NMR spectroscopy

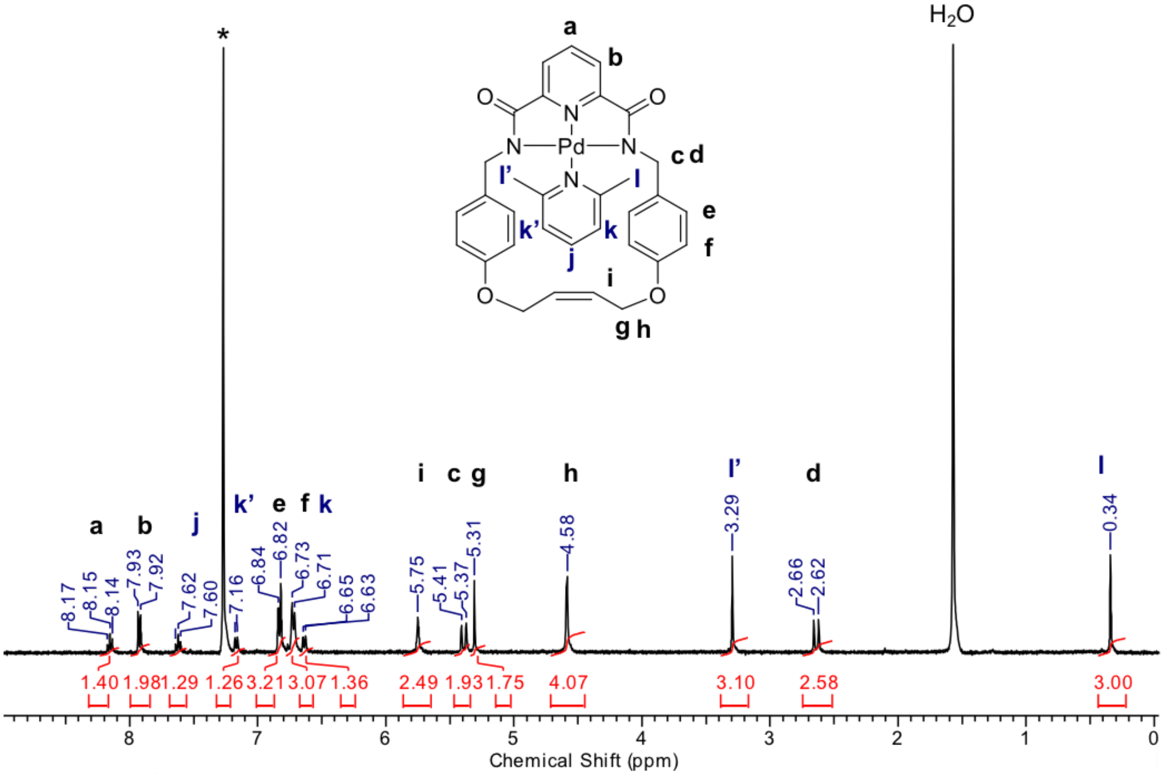

Figure S6 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **2-lut**. Residual solvent peaks are indicated with *.

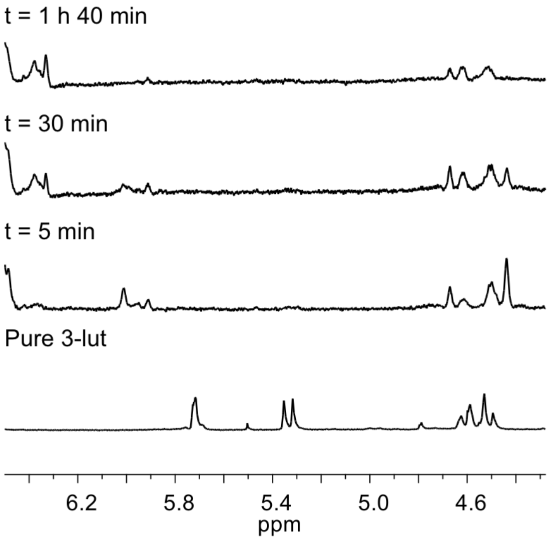

Figure S7 Reaction of Grubbs catalyst with **2-lut** monitored by ^{1}H NMR spectroscopy (400 MHz, THF-d_8, 50 °C) in the spectral region from 4.30 to 6.50 ppm.

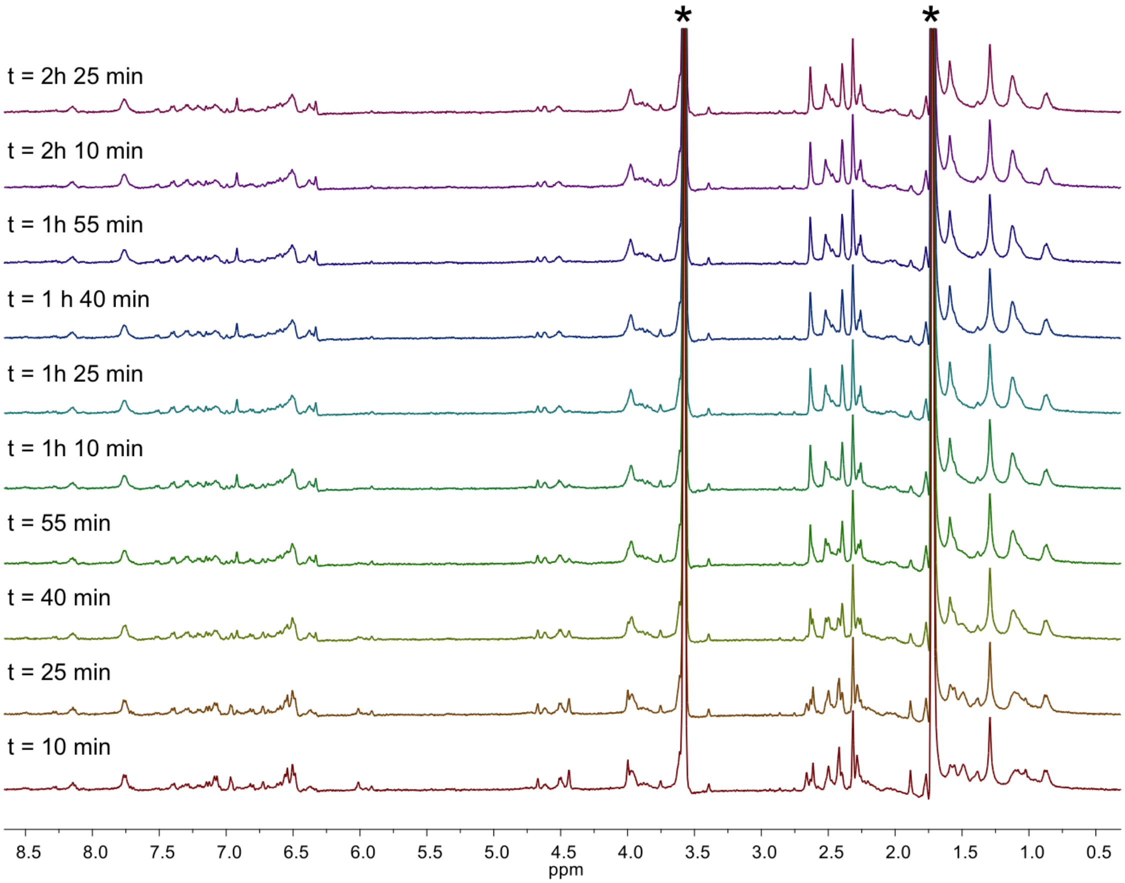

Figure S8 Reaction of Grubbs catalyst with **2-lut** monitored by ^{1}H NMR spectroscopy (400 MHz, THF-d_8, 50 °C). Residual solvent peaks are indicated with *.

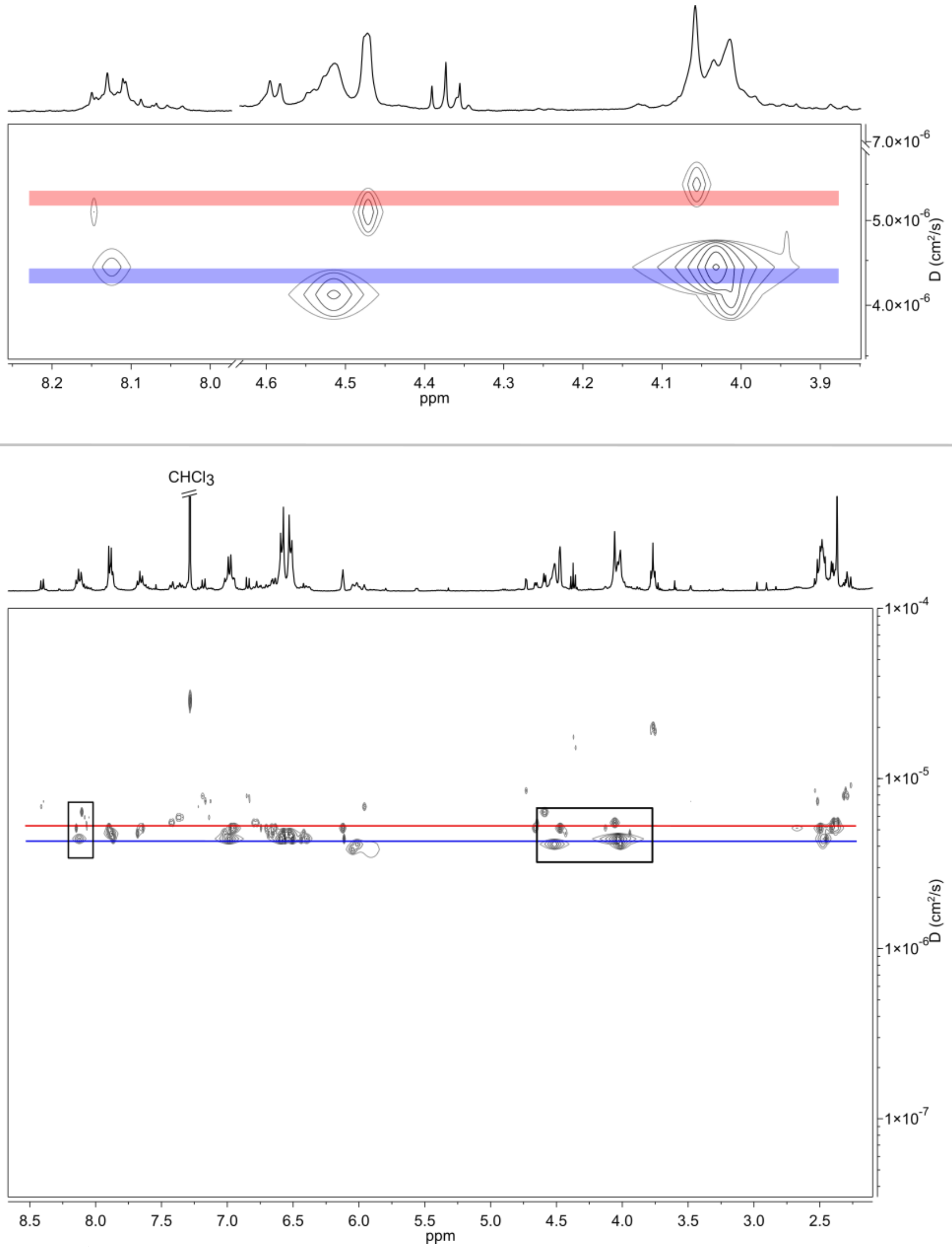

Figure S9 ^{1}H DOSY NMR (400 MHz, $CDCl_3$) experiment on the ring-expansion crude reaction mixture when the reaction was performed on compound **2-lut**. The red line corresponds to **3** and the blue line to **2-lut-prec**. Some regions of the spectrum (black box in the full 2D spectrum) are magnified and reported in the top image to show more clearly the difference between the two species.

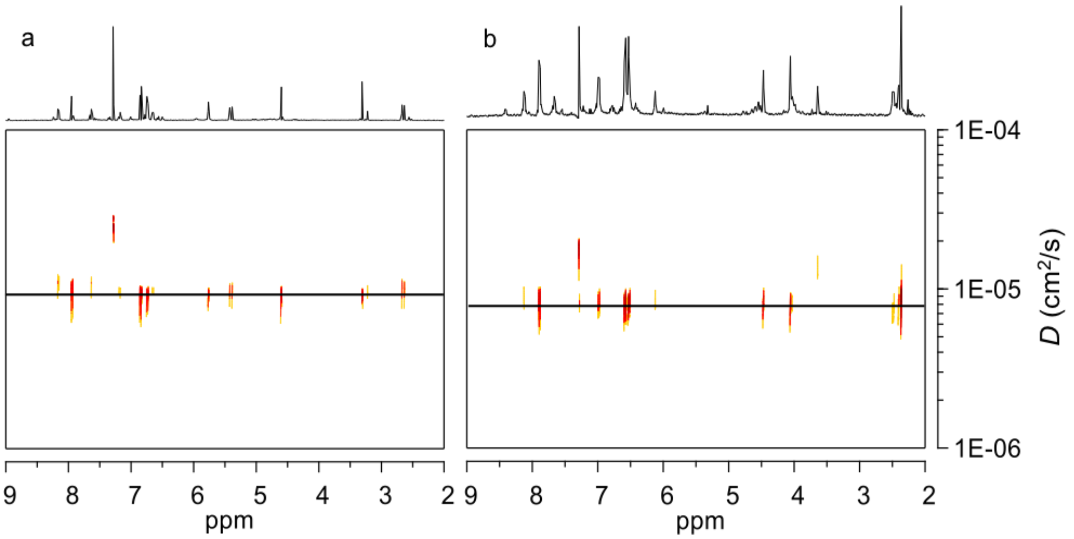

Figure S10 ^{1}H DOSY NMR (400 MHz, $CDCl_3$) of compounds (a) **2-lut** and (b) **3**. Residual solvent peaks are indicated with *.

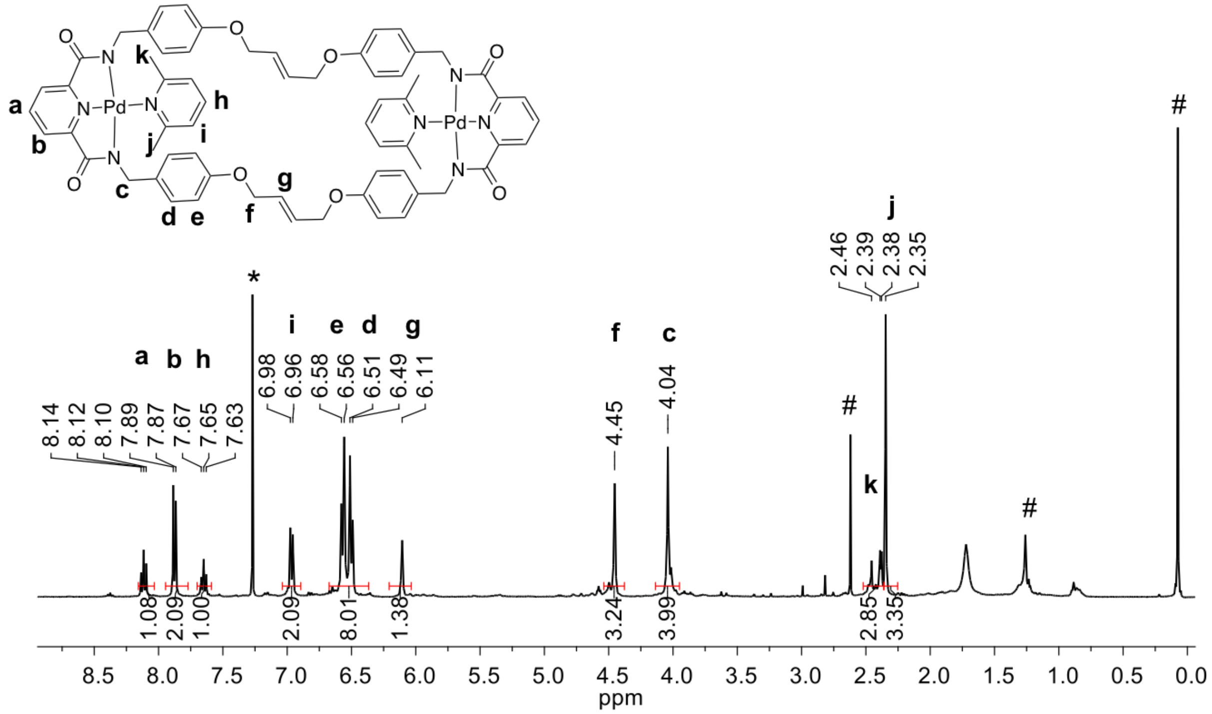

Figure S11 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3**. Residual solvent peaks are indicated with *. Impurities indicated with #.

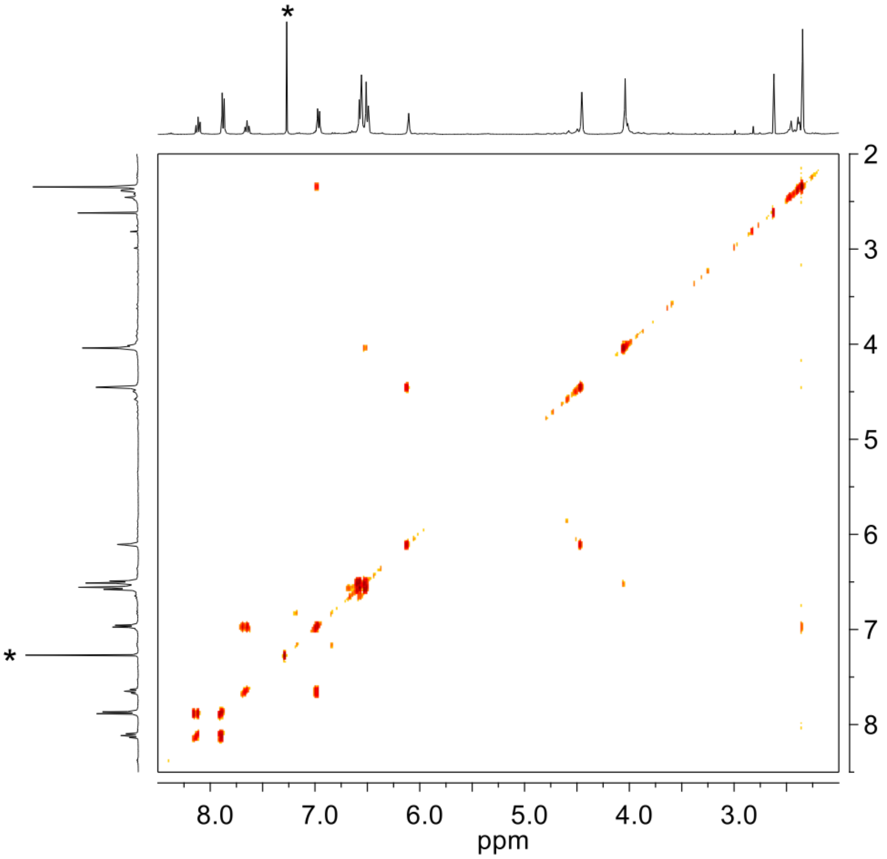

Figure S12 ^{1}H COSY NMR (400 MHz, CDCl$_3$) of compound **3**. Residual solvent peaks are indicated with *.

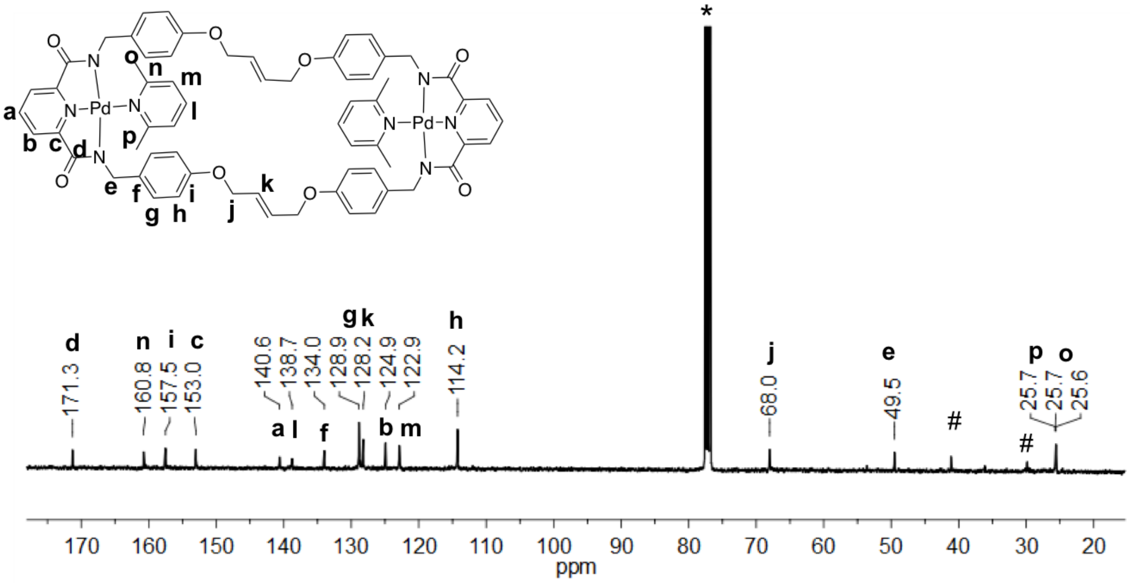

Figure S13 ^{13}C NMR (100 MHz, CDCl$_3$) spectrum of compound **3**. Residual solvent peaks are indicated with *. Impurities indicated with #.

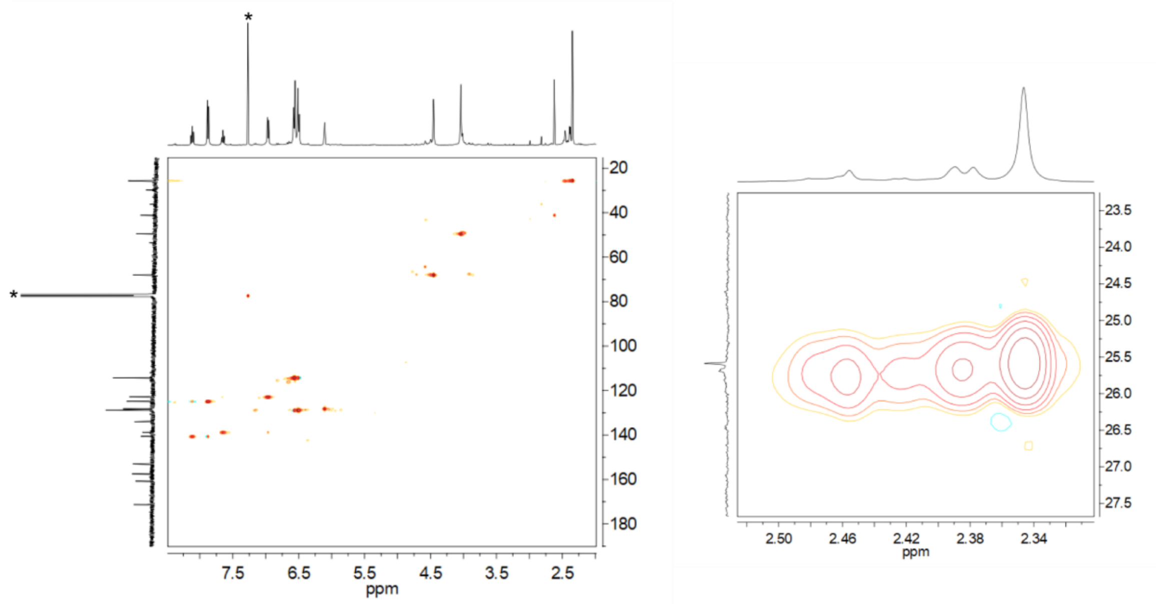

Figure S14 HSQC NMR spectroscopy experiment of compound **3** (400 MHz, $CDCl_3$). Residual solvent peaks are indicated with *.

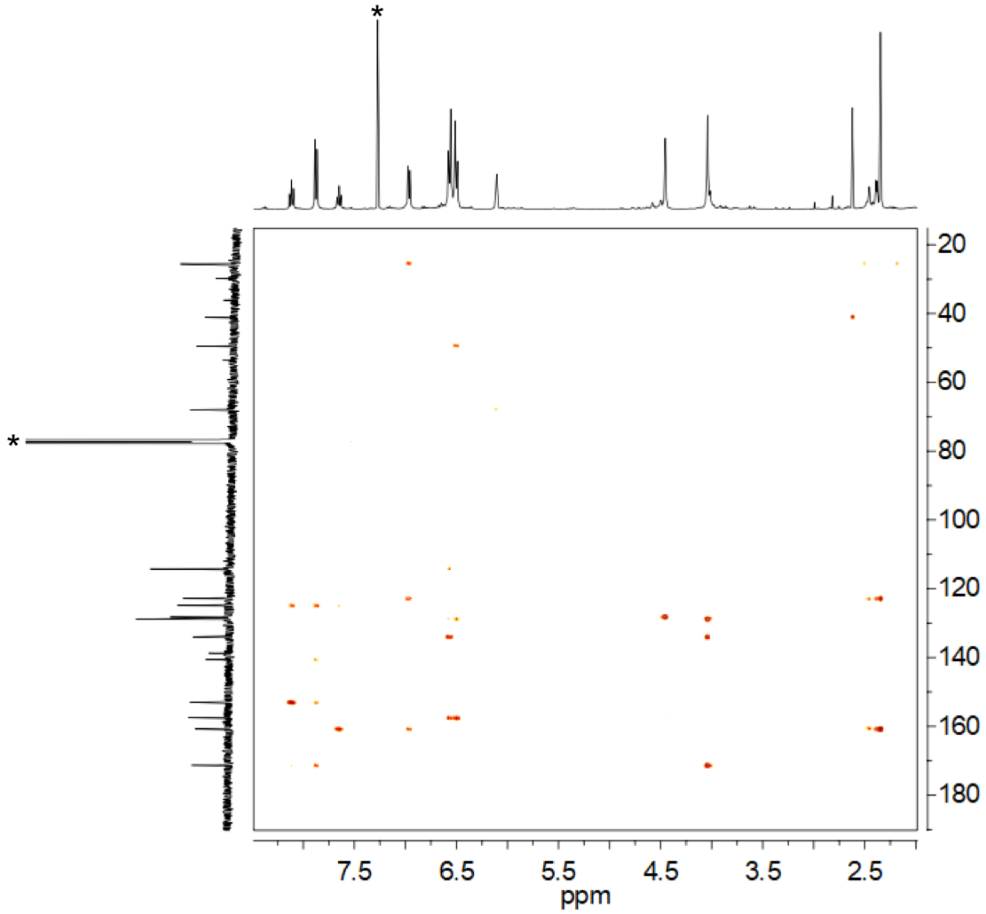

Figure S15 HMBC NMR (400 MHz, $CDCl_3$) of compound **3**. Residual solvent peaks are indicated with *.

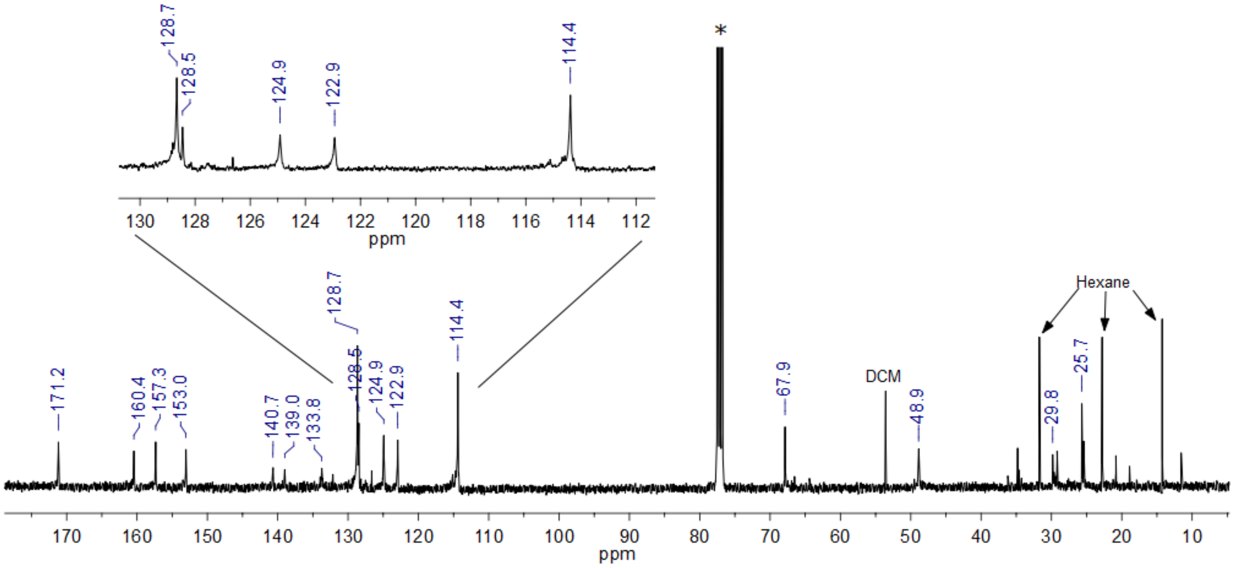

Figure S16 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **2-lut-prec**. Residual solvent peaks are indicated with *.

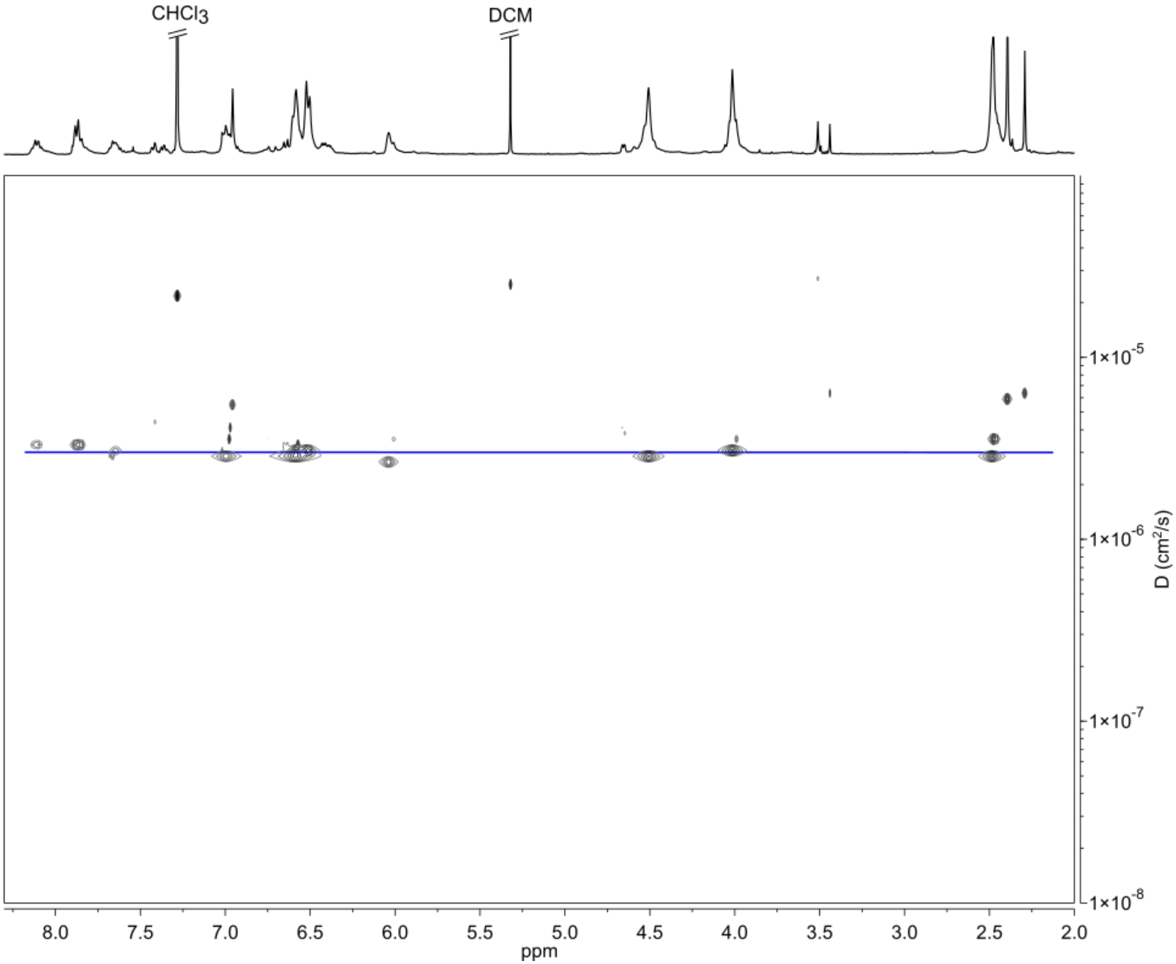

Figure S17 ^{1}H DOSY NMR (400 MHz, $CDCl_3$,) experiment on compound **2-lut-prec**.

Mass Spectrometry on Crude Mixture from Polymerization Reaction

Figure S18 shows the low resolution mass spectra of the crude product for the reaction of **1** with Grubbs catalyst (shown are three different slices of the total ion chromatogram). In all of them there is a peak corresponding to compound **1** (m/z = 464). In spectra (a) and (b) there is a peak corresponding to two times compound **1** (m/z = 893). However, this higher mass peak does not appear at 2.333 s. What is clear is that the dominant peak by far is the one with m/z = 464, corresponding to the monomer and consistent with NMR results.

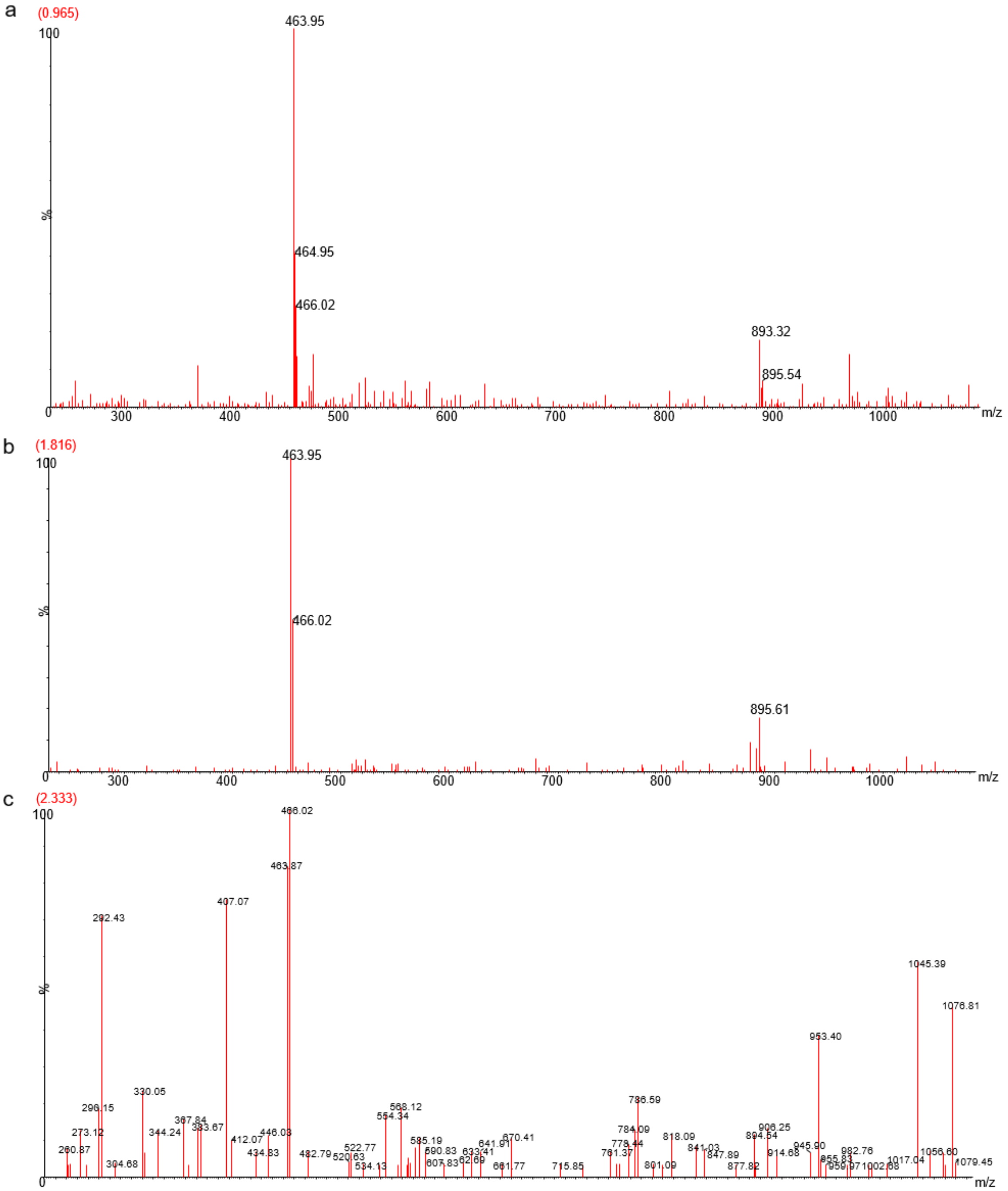

Figure S18 Low Resolution ESI of the crude reaction mixture of the polymerization reaction performed on compound **1**. The mass spectra reported are slices of the total ion chromatogram at three different times: (a) 0.965 s; (b) 1.816 s; (c) 2.333 s.

Figure S19 shows the low resolution mass spectra (three different slices of the total ion chromatogram). No dimer was detected.

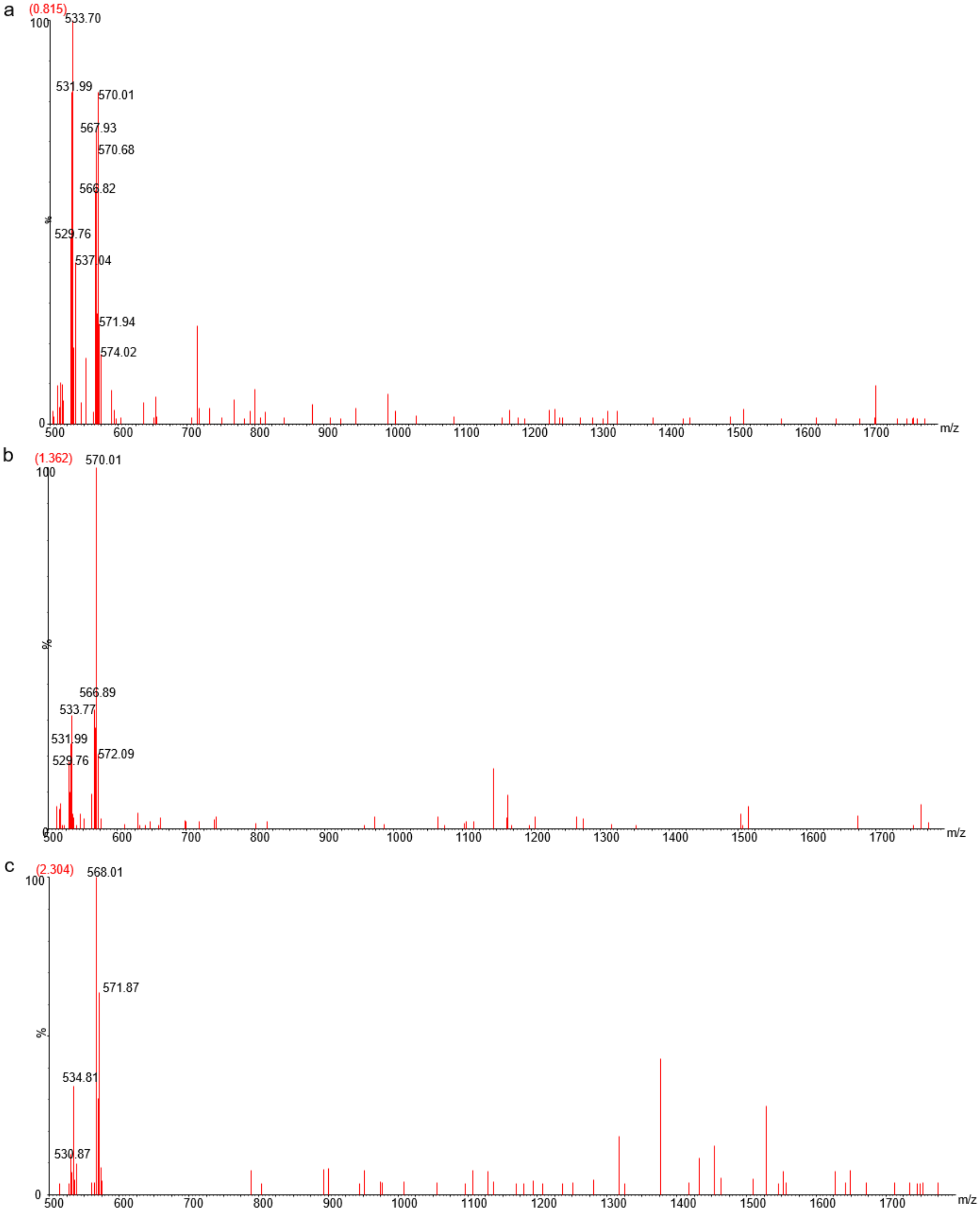

Figure S19 Low Resolution ESI of the crude reaction mixture of the polymerization reaction performed on compound **2.** The mass spectra reported are slices of the total ion chromatogram collected at three different times: (a) 0.815 s; (b) 1.362 s; (c) 2.304 s.

Figure S20 shows the low resolution spectra (three different slices of the total ion chromatogram). In all of spectra the peak corresponding to the dimer (m/z = 1211) is prominent and the dimer is the only species detected at 2.303 s.

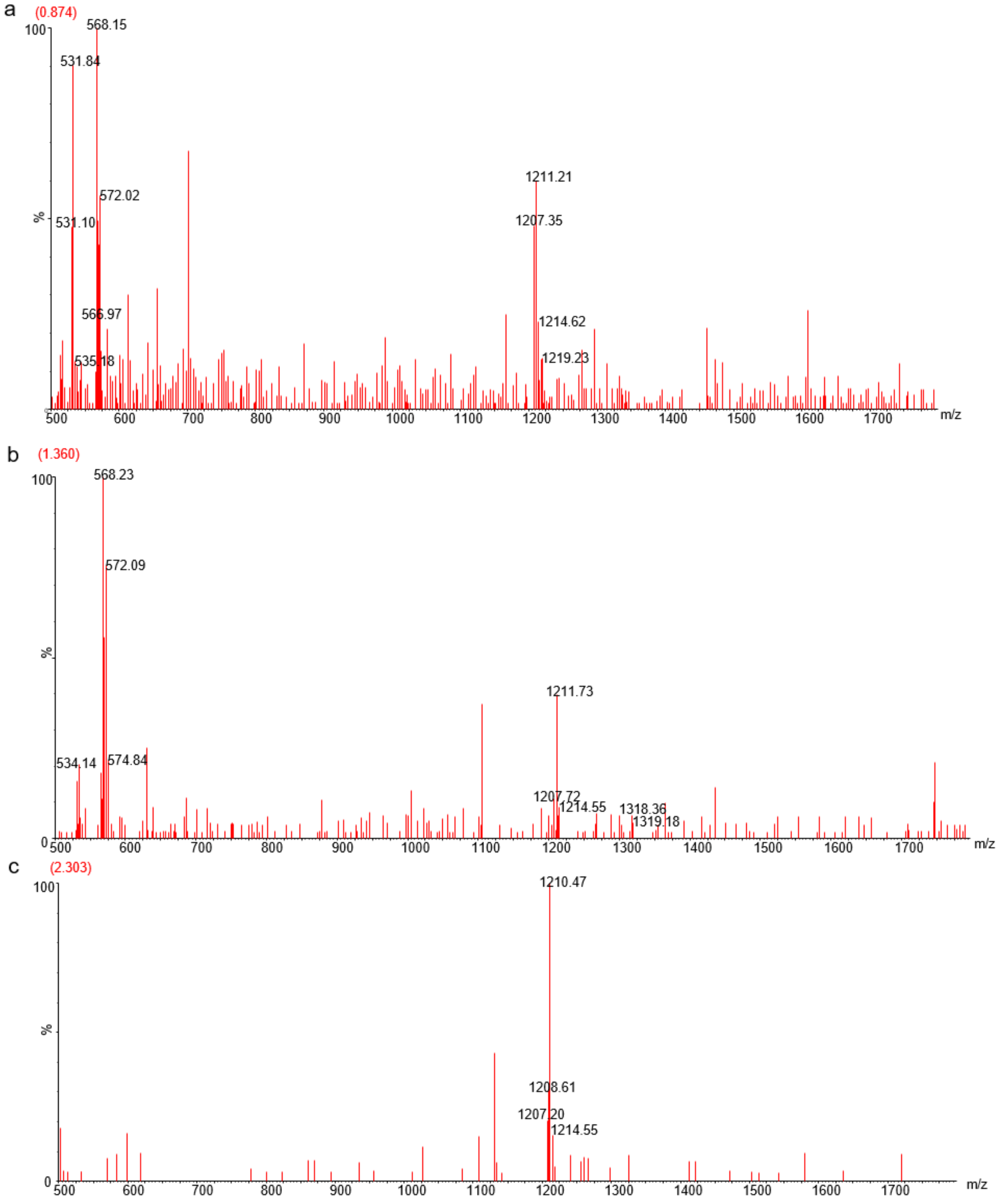

Figure S20 Low Resolution ESI of the crude reaction mixture of the polymerization reaction performed on compound **2-lut**. The mass spectra reported are slices of the total ion chromatogram collected at three different times: (a) 0.874 s; (b) 1.360 s; (c) 2.303 s.

Single-Crystal X-ray Diffraction

SCXRD raw data were collected on a Bruker APEX DUO diffractometer at 90 K for **2-lut** and on a Bruker APEX X8 diffractometer at 100 K for **3**. Graphite monochromated MoKα radiation (λ = 0.71073) was used and data were collected to a resolution of 0.77 Å. The data elaboration was performed with the software APEX2[2] for **2-lut** and APEX3[3] for **3**. Structures were solved using SUPERFLIP[4] and refined using full-matrix least-squares on F^2 within the CRYSTALS[5] suite. Hydrogen atoms were initially refined with restraints on bond lengths and angles, after which the positions were used as the basis for a riding model.[6] All non-hydrogen atoms were refined anisotropically. A summary of the crystallographic data is reported in Table S1.

Table S1 Summary of crystallographic data for compounds **2-lut** and **3**.

Compound	**2-lut**	**3**
Chemical formula	$C_{32}H_{30}N_4O_4Pd$, C_4H_8O	$C_{32}H_{30}N_4O_4Pd$, 1.72($CHCl_3$), 1.28(C_4H_8O)
Formula weight	713.12	938.19
a (Å)	16.706(4)	11.9782(10)
b (Å)	10.745(2)	15.6397(12)
c (Å)	17.859(4)	21.9976(17)
α (deg)	90	90
β (deg)	102.827(5)	94.145(4)
γ (deg)	90	90
Unit cell volume (Å^3)	3125.8(12)	4110.2(6)
Temperature (K)	90	100
Crystal system	monoclinic	monoclinic
Space group	$P\ 2_1/c$	$P\ 2_1/c$
Z	4	4
Absorption coefficient (μ/mm^{-1})	0.645	0.835
Total number of reflections	30358	87723
Unique reflections	7166	9433
Final R_1 values ($I > 2\sigma(I)$)	0.0290	0.0416
Final $wR(F^2)$ values (all data)	0.0742	0.1001

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