Supporting information

Tuning the thermal properties of *L*-lactide /ε-caprolactone chain shuttled copolymers *via* catalyst selection

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1. Experimental part:

1.1 Materials and methods.

1.1.1 Chemicals.

All chemicals and solvent were purchase from commercial suppliers and used without further purification. Trimethylaluminium ($AlMe_3$) (2M in toluene), aqueous formaldehyde (37wt% in water), yttrium isopropoxide oxide $OY_5(OCH(CH_3)_2)_{13}$ and benzyl alcohol were purchased from Sigma Aldrich. Di-*tert*-butyl dicarbonate, 2,4-*tert*-butylphenol, *N,N*-diethylethylene-1,2-diamine and 4-(2-aminoethyl)morpholine were purchased from Fluorochem. Ethylene diamine, Aluminium triisopropoxide and benzylbromide were purchased from Acros organic chemicals. 2-Picolylamine was purchased from TCI. Magnesium sulfate ($MgSO_4$), acetonitrile (CH_3CN), hydrochloric acid (HCl), 2-propanol, dichloromethane (CH_2Cl_2), cyclohexane, petroleum ether and ethyl acetate were purchased from VWR. Chloroform ($CHCl_3$) and methanol (MeOH) were purchased from Fisher scientific. Toluene, tetrahydrofurane (THF) without stabiliser and pentane were purchased from Sigma Aldrich, purified through an alumina column (Mbraun SPS) and stored on 3Å molecular sieves. All operations were performed under dry argon using a glove box (Jacomex) or Schlenk techniques. ε-Caprolactone (ε-CL) was purchased from Sigma Aldrich and dried over calcium hydride, distilled under argon atmosphere, and stored on 3Å molecular sieves under argon. *L*-lactide (*L*-LA) was purchased from Corbion and used as received after being opened in a glove box. Analytical thin-layer chromatography (TLC) was performed on ALUGRAM® Xtra SIL G/UV_{254} (Layer: 0.20 mm silica gel 60 with fluorescent indicator UV_{254}), visualised by irradiation with UV light (254 nm). Column chromatography was performed using Macherey-Nagel silica gel 60 M (0.04 – 0.063 mm).

1.1.2 Characterisation.

Mass spectrometry was performed by the by the SALSA platform from ICOA laboratory of Orléans in France. High-resolution ESI mass spectra (HRMS) were performed on a Bruker maXis Q-TOF in the positive ion mode. The analytes were dissolved in a suitable solvent at a concentration of 1 mg/mL and diluted 500 times in methanol (≈ 2 mg/mL). The diluted solutions (0.2 µL) were delivered to the ESI source by a Dionex Ultimate 3000 RSLC chain used in FIA (Flow Injection Analysis) mode at a flow rate of 200 µL/min with a mixture of CH_3CN/H_2O+0.1% of HCO_2H (65/35). ESI conditions were as follows: capillary voltage was set at 4.5 kV; dry nitrogen was used as nebulizing gas at 0.6 bar and as drying gas set at 200°C and 7.0 L/min. ESI-MS spectra were recorded at 1 Hz in the range of 50-3000 m/z. Calibration was performed with ESI-TOF Tuning mix from Agilent and corrected using lock

masses at m/z 299.294457 (methyl stearate) and 1221.990638 (HP-1221). Data were processed using Bruker DataAnalysis 4.4 software. Melting points were measured with a Barnstead Electrothermal IA9300 Digital Melting Point Apparatus.

NMR data were recorded on a Bruker Avance III spectrometer (300 MHz for ^{1}H and 75 MHz for ^{13}C) using tetramethylsilane (TMS) as internal standard and $CDCl_3$ or C_6D_6 as solvent. Chemical shifts (δ) are given in parts per million (ppm), coupling constants (J) are given in hertz (Hz) and multiplicities were abbreviated as following: s (singlet), d (doublet), t (triplet), q (quadruplet), m (multiplet), dd (doublet of doublet), ddd (doublet of doublet of doublet), td (triplet of doublet), tt (triplet of triplet). DOSY spectra were recorded on Avance NEO 400 Bruker spectrometer (9.4 Tesla, 400 MHz) regulated at 298 K in toluene-d_8. DOSY experiments were realized using a TBI probe at 298 K. 1D DOSY pulse program was ledbpgp2s1d to calibrate the gradient strength in absolute value G= 5.35 G/mm with NS = 1 D1 = 10s TD= 16K points, sw = 12 ppm and O1P= 5ppm. SMSQ10.100 gradients were used with a GPZ6 from 2 to 95%, GPZ7 = -17.13% and GPZ8 = -13.17%. and a mix 80% Toluene and 20% Toluene-d_8. At the end, the signal must be between 5% to 10% of the residual signal. The value G have had adjusted to 4.95 G/mm for 2.27 10^{-9} m^2s^{-1} of self-diffusion coefficient D for Toluene. We have used ledbpgp2s DOSY 2D pulse program.

We used 50 mg of polymer for 0.6 mL of deutered toluene. Parameters values: pl1: - power level for pulse 90 degree: 10.773W; p1: 90-degree high power pulse 10 µsec; p19: gradient pulse 2 (spoil gradient) = 600 µsec; p30: gradient pulse (little DELTA * 0.5) = 2000-2500 µsec; d1: relaxation delay; 1-5 * T1 = 8 sec; d20: diffusion time (big DELTA) = 0.1000-0.1400 sec; NS: 2-16 scans; td1: number of experiments = 16-128; td2 size of fid = 4096-32768 points.

The conversion of both *L*-LA units and CL units were determined by ^{1}H NMR by integration of the peaks at 5.2 ppm and 4.3 ppm respectively using the crude medium of the reaction as follow:

Conversion LLA (%) = $I_a / (I_a + I_b)x100$

Conversion CL (%) = = $I_c / (I_c + I_d)x100$

The chemical composition of isolated copolymers was also assessed via ^{1}H NMR, using the integration of *L*-LA units methine proton (5.1 ppm) and ε-CL units methylene proton (4.1 ppm). A typical spectrum ^{1}H NMR spectrum of the crude of a statistical copolymerisation is provided in the manuscript as Figure 2.

The Differential Scanning Calorimetry (DSC) experiments were carried out on a DSC 25 TA instrument calibrated according to standard procedures using a high purity Indium sample. For the analyses,

samples (5 mg) were placed into aluminium pans, heated from -70°C to 190°C at a rate of 10°C/min under nitrogen atmosphere.

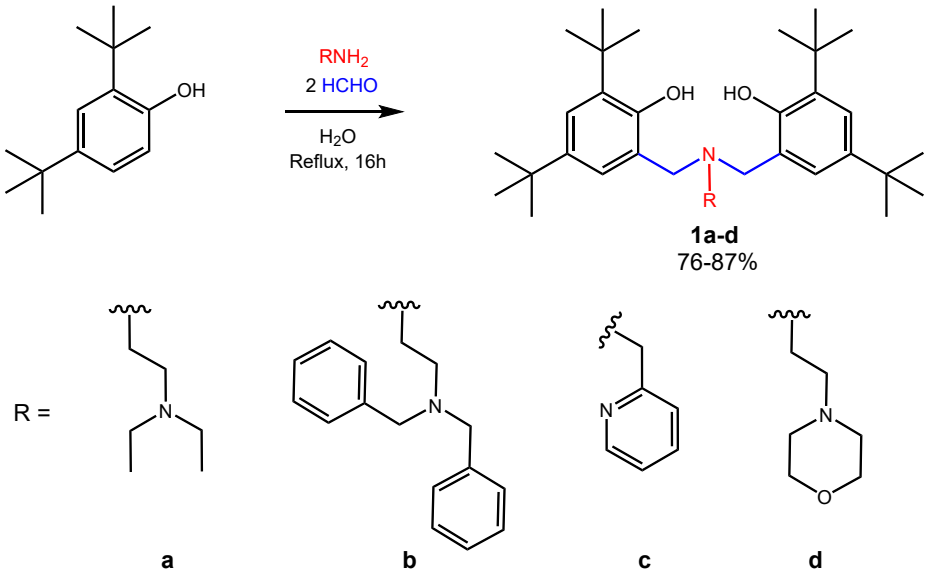
Size exclusion chromatography (SEC) was performed in THF as eluent at 40 °C (1 $mL.min^{-1}$) using a Waters SIS HPLC-pump, a Waters 410 refractometer and Waters Styragel column (HR2, HR3, HR4, HR5E) calibrated with polystyrene standards. The number-average molecular weight is corrected by the following formulae that combines the correction factors of 0.58 for poly(L-lactide), [1] and 0.56 for poly(ε-caprolactone) [2]: $M_{n\ corrected} = M_n$ raw × 0.56 × wt% PCL + M_n raw × 0.58 × wt%PLA.

Positive-ion Matrix assisted LASER Desorption/Ionization-Mass Spectrometry (MALDI-MS) experiments were performed using a Waters QToF Premier mass spectrometer equipped with a Nd:YAG laser operating at 355 nm (third harmonic) with a maximum output of 65 µJ delivered to the sample in 2.2 ns pulses at 50 Hz repeating rate. Time-of-flight mass analysis was performed in the reflectron mode at a resolution of about 10k (m/z 569). All samples were analyzed using trans-2-[3-(4-tert-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) as a matrix. Polymer samples were dissolved in THF to obtain 1$mg.mL^{-1}$ solution. Additionally, 40 µL of 2$mg.mL^{-1}$ NaI solution in acetonitrile was added to the polymer solution. Both, matrix solution and sample solution were applied following the dried droplet method.

Elemental analyses were performed on a Flash 2000, Organic Elemental Analyzer, Thermo Scientific by the London Metropolitan University Elemental Analysis Service.

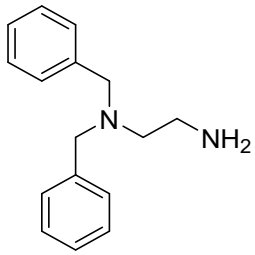
1.1.3 Ligand synthesis.

Four amino*(bis)*phenolate ligands were synthetised starting from substituted phenols as shown in Scheme S 1. A Mannich condensation reaction in water was adapted from the literature.[3] A washing with cold methanol afforded the efficient purification of the crude product over vacuum filtration, affording 50-87% yields. The appearance of a single peak corresponding to 4 protons between 4-5 ppm ^{1}H NMR proved the bridging between the tertiary amine and the two phenol groups. Synthesis details and analytics, including intermediates compounds, are provided below.



Scheme S 1. General synthesis of the amino*(bis)*phenolate ligands **1a-d**

***N*,*N*-Dibenzylethane-1,2-diamine**



Boc-protected ethyl diamine[4] (1 g, 6.25 mmol) was added to benzyl bromide (1.64 mL, 13.74 mmol), potassium carbonate (4 g, 29 mmol) and potassium iodide (0.5 g, 3 mmol) in CH_3CN (250 mL). After stirring under reflux for 16 h, the solution was filtered. The filtrate was concentrated under reduced pressure and directly used without further purification. To the protected amine solution dissolved in $CHCl_3$ (50 mL), a HCl solution (6M in isopropanol, 50 mL) was added gently. After stirring at 20°C for 16 hours, the solution was concentrated under reduced pressure, neutralised with a NaOH solution (1M) and extracted with CH_2Cl_2 (3x50 mL). The organic phases were combined, dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified on a silica gel column with a CH_2Cl_2/MeOH eluent (98.5/1.5) to give *N*,*N*-dibenzylethane-1,2-diamine as an orange oil (1.14 g, 76%).[4]

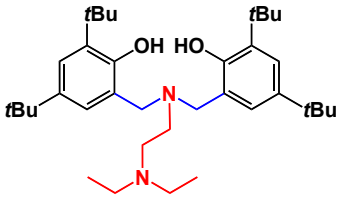
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38 – 7.17 (m, 10H, Ar); 3.59 (s, 4H, CH_2-Ar); 2.75 (t, 2H, *J* = 5.9 Hz, CH_2-NH_2); 2.51 (t, 2H, *J* = 5.9 Hz, CH_2-N); 1.27 (s, 2H, NH_2) ppm.

HRMS (CD) *m/z* calcd $C_{16}H_{21}N_2$ $[M + H]^+$ 241.1699, found 241.1697.

General procedure for the amino(*bis*)phenolate ligand synthesis:

Ligands **1a-d** were synthesised following the same procedure reported in the literature.[3,5] To a solution of the amine (1 equiv) dissolved in water were added aqueous formaldehyde (5.5 equiv) and a phenol derivative (2.2 equiv). The solution was heated under reflux in an oil bath for 16 hours. The solution was filtered through sintered glass and the residue obtained was washed with cold MeOH (0°C). The white solid obtained was oven dried for 48 hours to obtain a white powder.

6,6'-(((2-(Diethylamino)ethyl)azanediyl)bis(methylene))bis(2,4-di-*tert*-butylphenol) (1a)



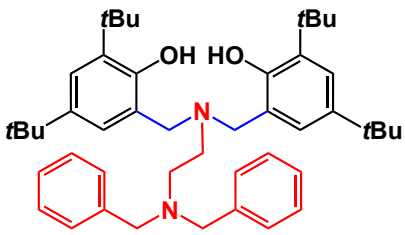
Starting from 2,4-di-*tert*-butylphenol (1.65 g, 8.01 mmol), *N,N*-diethylethyl-1,2-diamine (413 mg, 3.56 mmol), aqueous formaldehyde (0.75 mL, 19.9 mmol), the compound **1a** was obtained as a white powder (1,59 g, 81%).

Mp: 146-148 °C

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.62 (s, 2H, *OH*); 7.18 (d, 2H, *J* = 2.4 Hz, Ar); 6.86 (d, 2H, *J* = 2.4 Hz, Ar); 3.58 (s, 4H, C*H*$_2$-Ar); 2.71 – 2.57 (m, 8H, *CH*$_2$-N); 1.38 (s, 18H, *t*Bu); 1.26 (s, 18H, *t*Bu); 1.10 (t, 6H, *J* = 7.1 Hz, *CH*$_3$-CH$_2$) ppm.

^{13}C NMR (75 MHz, $CDCl_3$): δ 153.2; 140.0; 135.9; 124.7; 123.3; 121.3 (Ar); 57.0 (Ar*C*H$_2$N); 50.0; 45.4 (N*C*H$_2$CH$_2$N); 48.8 (N*C*H$_2$CH$_3$); 34.9; 34.0 (Ar*C*(CH$_3$)$_3$); 31.7; 29.9 (ArC(*C*H$_3$)$_3$); 9.7 (NCH$_2$*C*H$_3$) ppm.

6,6'-(((2-(Dibenzylamino)ethyl)azanediyl)bis(methylene))bis(2,4-di-*tert*-butylphenol) (1b)



Starting from 2,4-di-*tert*-butylphenol (1.65 g, 8.01 mmol), *N,N*-dibenzylethyl-1,2-diamine (0.84 g, 3.51 mmol), aqueous formaldehyde (0.75 mL, 19.9 mmol), the compound **1b** was obtained as a white powder (2.09 g, 87%).

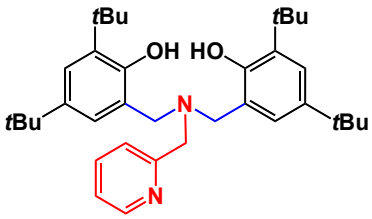
Mp: 186-188 °C

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.78 (s, 2H, *OH*); 7.38 (d, 2H, *J* = 2.0 Hz, Ar); 7.35 (d, 2H, *J* = 1.5 Hz, Ar); 7.29 – 7.21 (m, 6H, Ar); 7.20 (d, 2H, *J* = 2.4 Hz, Ar); 6.83 (d, 2H, *J* = 2.4 Hz, Ar); 3.63 (s, 4H, CH_2-Ar); 3.41 (s, 4H, CH_2-Ar); 2.64 (m, 4H, CH_2-N); 1.36 (s, 18H, *t*Bu); 1.27 (s, 18H, *t*Bu) ppm.

^{13}C NMR (75 MHz, $CDCl_3$): δ 152.4; 140.7; 136.7; 136.1; 130.4; 128.2; 127.3; 124.9; 123.4; 121.4 (Ar); 58.5; 56.5; 49.5 (ArCH_2N); 49.2 (NCH_2CH_2N); 34.9; 34.1 (Ar$C(CH_3)_3$); 31.7; 29.6 (ArC(CH_3)$_3$) ppm.

HRMS (CD) *m/z* calcd $C_{46}H_{65}N_2O_2$ $[M + H]^+$ 677.5041, found 677.5032.

6,6'-(((Pyridin-2-ylmethyl)azanediyl)bis(methylene))bis(2,4-di-*tert*-butylphenol) (1c)



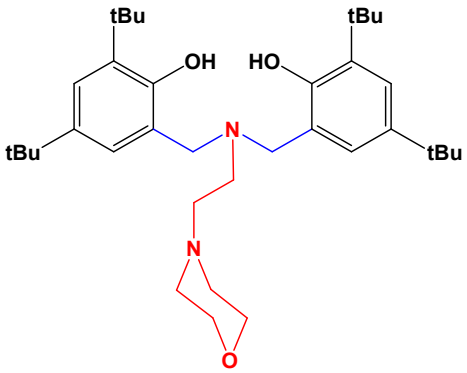
Starting from 2,4-di-*tert*-butylphenol (2.29 g, 11.14 mmol), 2-picolylamine (535 mg, 4.95 mmol), aqueous formaldehyde (1.03 mL, 27.22 mmol), the compound **1c** was obtained as a white powder (2.26 g, 84%);

Mp: 204-206 °C

^{1}H NMR (300 MHz, $CDCl_3$): δ 10.52 (s, 2H, *OH*); 8.72 – 8.67 (m, 1H, Ar); 7.69 (td, 1H, *J* = 7.7, 1.8 Hz, Ar); 7.31 – 7.24 (m, 1H, Ar); 7.22 (d, 2H, *J* = 2.5 Hz, Ar); 7.12 (d, 1H, *J* = 7.8 Hz, Ar); 6.93 (d, 2H, *J* = 2.5 Hz, Ar); 3.84 (s, 2H, CH_2-N); 3.80 (s, 4H, CH_2-N);1.40 (s, 18H, *t*Bu); 1.29 (s, 18H, *t*Bu) ppm.

^{13}C NMR (75 MHz, $CDCl_3$): δ 156.3; 153.8; 148.2; 140.4; 137.2; 136.3; 125.1; 123.7; 123.4; 122.4; 121.3 (Ar); 56.9; 55.4 (ArCH_2N); 35.1; 34.1 (Ar$C(CH_3)_3$); 31.7; 29.6 (ArC(CH_3)$_3$) ppm.

6,6'-(((2-Morpholinoéthyl)azanediyl)bis(méthyléne))bis(2,4-di-*tert*-butylphénol) (1d)



Starting from 2,4-di-*tert*-butylphenol (1.67 g, 8.13 mmol), 2-morpholinoethane-1-amine (469 mg, 3.6 mmol), aqueous formaldehyde (0.748 mL, 19.86 mmol), the compound **1d** was obtained as a white powder (1.53 g, 76%).

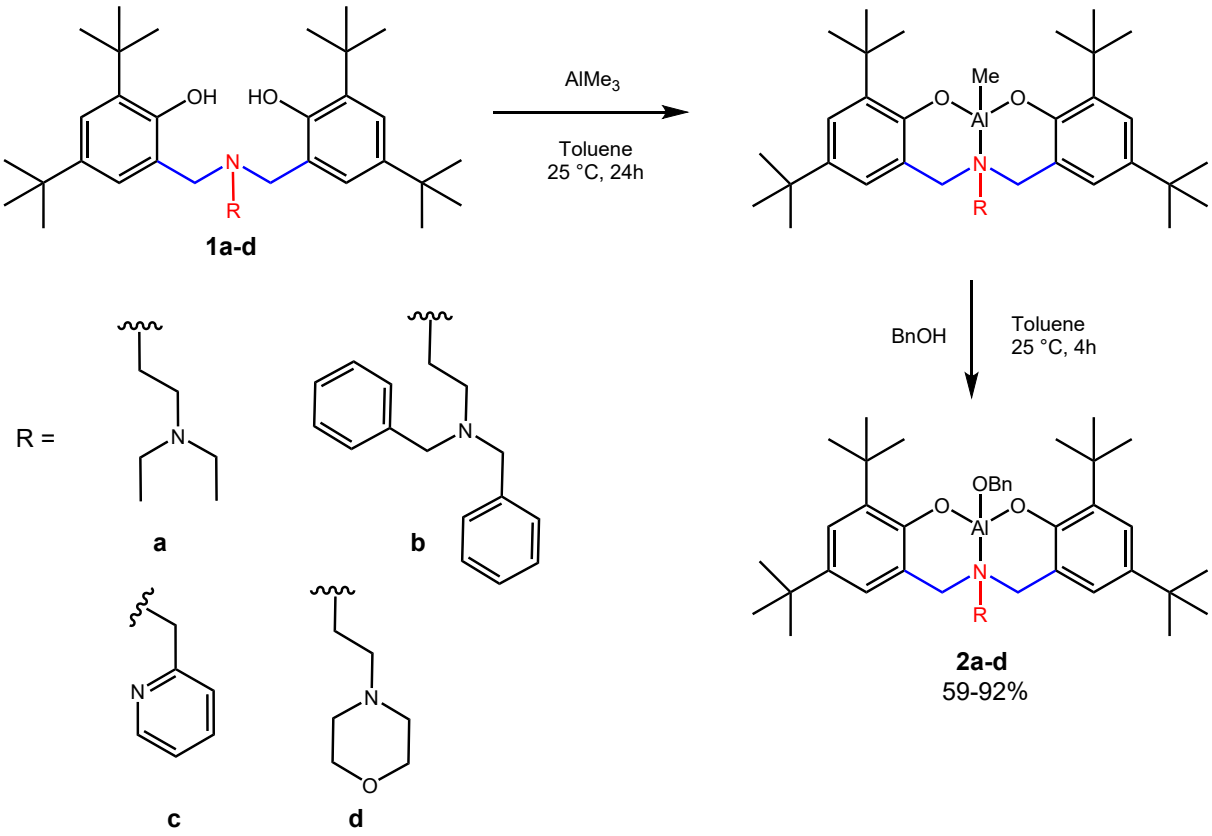
Mp: 182-184 °C

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.24 (s, 2H, *OH*); 7.20 (d, 2H, *J* = 2.4 Hz, Ar); 6.88 (d, 2H, *J* = 2.4 Hz, Ar); 3.96 – 3.83 (m, 4H, CH_2-O); 3.59 (s, 4H, CH_2-Ar); 2.65 (s, 4H, CH_2-N); 2.53 (s, 4H, CH_2-N); 1.38 (s, 18H, *t*Bu); 1.26 (s, 18H, *t*Bu) ppm.

^{13}C NMR (75 MHz, $CDCl_3$): δ 152.7; 140.6; 136.0; 124.9; 123.5; 121.2 (Ar); 67.0 (CH_2O); 56.2; 55.0; 53.6; 48.0 (CH_2N); 35.0; 34.1 (Ar$C(CH_3)_3$); 31.7; 29.6 (ArC($CH_3)_3$) ppm.

1.1.4 Complex synthesis.

Starting from the amino(*bis*)phenol ligands **1a-d** synthesis, the corresponding alkoxide aluminium complexes **2a-d** were synthesised (Scheme S 2). The reaction was conducted by reacting the protonated ligands in toluene with a slight excess of $AlMe_3$ (1.05 eq.), followed by the addition of 1.2 equivalent of BnOH to form *in situ* the corresponding alkoxide complex. The reaction product was dried under vacuum and washed with pentane giving rise to solids with yields ranging from 59 to 92% depending on the ligand. ^{1}H and ^{13}C NMR analysis of the resulting products were consistent with the formation of the corresponding **2a-d** complexes. The structures of **2a** and **2b** were confirmed by elemental analysis (**2c** and **2d** were previously published).[6] Synthesis details and analytics are provided below.



Scheme S 2. Synthesis of amino(*bis*)phenolate supported aluminium alkoxide. BnOH = benzyl alcohol.

The synthesis of the complexes was inspired from protocols reported in the literature.[6] All the protonated-ligands were dry by three azeotropic distillation in toluene (3×20 mL) and then stored under argon in a glove-box prior the reaction. Under argon atmosphere, the desired dry protonated-ligand (1 equiv) was dissolved in toluene at low concentration (between 0.04 M and 0.29 M), then a solution of $AlMe_3$ (2 M in toluene, 1.05 equiv) solubilised in toluene was slowly added dropwise at room temperature. The Schlenk flask was degassed every 30 min to remove CH_4 formed during the reaction. After the solution was left under stirring for 24 h, dry benzyl alcohol (1.2 equiv) diluted (below 0.58 M) in toluene was slowly added dropwise at room temperature. After 16 h the solution was dry under reduced pressure. The crude product was washed three times with pentane and dry under reduced pressure to obtain the desired product.

*Complex **2a** ($Al(O_2N^{NEt2})OBn$)*

Following the general procedure, ligand **1a** (4 g, 7.23 mmol, 0.29 M in toluene), $AlMe_3$ (2 M in toluene) (3.08 g, 7.6 mmol) dissolved in toluene (30 mL) and benzyl alcohol (939 mg, 8.68 mmol, 0.58 M in toluene) afforded the desired product as a white solid in good yield (3.51 g, 71 %).

^{1}H NMR (300 MHz, C_6D_6): δ 7.82 (d, *J* = 7.4 Hz, 2H), 7.60 (d, *J* = 2.3 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 6.82 (s, 2H), 5.75 (s, 2H), 2.72 (b, 6H), 1.75 (s, 18H), 1.43 (s, 18H), 0.63 (b, 6H) ppm.
^{13}C NMR (75 MHz, C_6D_6): δ 156.0, 138.5, 138.3, 126.5, 125.5, 124.0, 123.5, 121.1, 66.4, 64.7, 59.0, 48.8, 41.1, 35.3, 34.0, 31.9, 29.7 ppm.
Elemental analysis: found: C, 75.12; H, 9.86; N, 4.01. $C_{45}H_{63}AlN_2O_3$ calculated: C, 75.40; H, 9.57; N, 4.09%.

*Complex **2b** ($Al(O_2N^{NBn2})OBn$)*

Following the general procedure ligand **1a** (0.5 g, 0.739 mmol, 0.07 M in toluene), $AlMe_3$ (2 M in toluene) (0.314 g, 0.775 mmol) dissolved in toluene (10 mL) and benzyl alcohol (96 mg, 0.887 mmol, 0.07 M in toluene) afforded the desired product as a white solid in high yield (0.550 g, 92 %).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46 (d, *J* = 7.4 Hz, 2H), 7.40 – 7.21 (m, 15H), 6.62 (d, *J* = 2.5 Hz, 2H), 5.07 (s, 2H), 4.71 (d, *J* = 5.7 Hz, 4H), 3.68 (s, 4H), 2.77 (dt, *J* = 12.0, 5.6 Hz, 4H), 1.40 (s, 18H), 1.26 (s, 18H) ppm.
^{13}C NMR (75 MHz, $CDCl_3$): δ 155.36, 139.60, 138.09, 130.20, 128.65, 127.88, 124.35, 124.15, 120.70, 65.69, 58.92, 56.65, 48.90, 35.18, 34.23, 31.88, 29.71 ppm.
Elemental analysis: found: C, 78.68; H, 8.38; N, 3.59. $C_{53}H_{69}AlN_2O_3$. calculated: C, 78.68; H, 8.60; N, 3.46%.

*Complex **2c** ($Al(O_2N^{Py})OBn$)*[6]

Following the general procedure ligand **1c** (1.5 g, 2.75 mmol, 0.18 M in toluene, $AlMe_3$ (2 M in toluene) (1.17 g, 2.89 mmol) dissolved in toluene (20 mL) and benzyl alcohol (357 mg, 3.3 mmol, 0.33 M in toluene) afforded the desired product as a white solid in moderate yield (1.1 g, 59 %).

^{1}H NMR (300 MHz, C_6D_6): δ 9.8 (d, *J* = 5.4 Hz, 1H), 8.0 (d, *J* = 7.2 Hz, 2H), 7.6 (d, *J* = 2.5 Hz, 2H), 7.5 (t, *J* = 7.2 Hz, 2H), 7.3 (t, *J* = 6.3 Hz, 1H), 6.8 (s, 2H), 6.6 (t, *J* = 7.7 Hz, 1H), 6.3 (t, *J* = 6.6 Hz, 1H), 6.0 (s, 2H), 5.9 (d, *J* = 7.7 Hz, 1H), 3.3 (b, 6H), 1.8 (s, 18H), 1.4 (s, 18H) ppm.
^{13}C NMR (75 MHz, C_6D_6): δ 156.30, 153.05, 141.92, 138.64, 138.31, 127.82, 126.73, 124.39, 124.06, 123.72, 123.21, 120.73, 65.74, 56.90, 35.20, 34.17, 31.91, 29.62, 22.49, 14.22 ppm.

*Complex **2d** ($Al(O_2N^{Mor})OBn$)*[6]

Following the general procedure ligand **1d** (1 g, 1.76 mmol, 0.12 M in toluene), $AlMe_3$ (2 M in toluene) (750 mg, 1.85 mmol) dissolved in toluene (20 mL) and benzyl alcohol (229 mg, 2.12 mmol, 0.42 M in toluene) yielded to the desired product as a white solid in good yield (972 mg, 79 %).

^{1}H NMR (300 MHz, C_6D_6): δ 7.70 (d, *J* = 7.4 Hz, 2H), 7.60 (d, *J* = 2.5 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.11 (t, *J* = 5.7 Hz, 1H), 6.86 (d, *J* = 1.8 Hz, 2H), 5.42 (s, 2H), 3.62 (dd, *J* = 46.7, 11.9 Hz, 4H), 3.27 (t, *J* = 4.5 Hz, 4H), 2.50 (d, *J* = 82.3 Hz, 6H), 2.11 (t, *J* = 7.1 Hz, 2H), 1.72 (s, 18H), 1.45 (s, 18H) ppm.
^{13}C NMR (75 MHz, $CDCl_3$): δ 155.4, 139.9, 138.5, 128.3, 126.7, 124.8, 124.1, 120.5, 65.9, 65.0, 58.3, 53.6, 50.0, 35.3, 34.3, 31.9, 29.8 ppm.

1.1.5 Polymerisation.

***L*-lactide polymerisation:**

Under argon in a glove-box, the initiator (14 µmol), *L*-lactide (50 equiv, 101 mg) and toluene (1 M) were added in this order into an oven-dried Young-valve Schlenk flask charged with a magnetic stirring bar. Once closed, the flask was heated at 100 °C outside the glove-box with stirring for the desired amount of time, after which the reaction was quenched with few drops of acidified methanol. The resulting mixture was poured into cold methanol (100 mL). The white precipitate was filtered and dried under vacuum for 48 h.

***ε*-Caprolactone polymerisation:**

Under argon in a glove-box, the initiator (14 µmol), ε-caprolactone (500 equiv, 399 mg or 1000 equiv, 798 mg) and toluene (0.5 M) were added in this order into an oven-dried Young-valve Schlenk flask charged with a magnetic stirring bar. Once closed, the flask was heated at 50 °C or 30 °C outside the gloves-box with stirring for the desired amount of time, after which the reaction was quenched with few drops of acidified methanol, and then poured into cold methanol (200 mL). The resulting white precipitate was filtered and dried under vacuum for 48 h.

***L*-LA and *ε*-CL copolymerisation:**

Under argon in a glove-box, the initiator (14 µmol) *L*-lactide (50 equiv, 101 mg), ε-caprolactone (50 equiv, 80 mg) and toluene (1 M) were added in this order into an oven-dried Young-valve Schlenk flask charged with a magnetic stirring bar. Once closed, the flask was heated at 100 °C outside the glove-box with stirring for the desired amount of time, after which the reaction was quenched with few drops of acidified methanol, and then poured into cold methanol (100 mL). The resulting white precipitate was filtered and dried under vacuum for 48 h.

***L*-LA and ε-CL chain-shuttling copolymerisation:**

Under argon in a glove-box, the soft-block initiator (35 µmol), *L*-lactide (500 equiv, 504 mg), ε-caprolactone (500 equiv, 399 mg), toluene (5 mL) then the hard-block initiator (7 µmol) in toluene (2 mL) were added in this order into an oven-dried Young-valve Schlenk flask charged with a magnetic stirring bar. Once closed, the flask was heated at 100 °C outside the glove-box with stirring for the desired amount of time, after which the reaction was quenched with few drops of acidified methanol, and then poured into cold methanol (150 mL). The resulting white precipitate was filtered and dried under vacuum for 48 h.

2. MALDI ToF Analysis of polylactide

Entry	Cata	Cat/L-LA ratio	Time (h)	Conc.	Conv.[a] (%)	M_n SEC[b] (g/mol)	M_n MALDI (g/mol)	M_n calc[c] (g/mol)	$Đ^b$
SI1	**2a**	1/100	24	2M	62	8800	8600	8900	1.09
SI2	**2b**	1/100	24	2M	50	5000	4600	7200	1,09
SI3	**2c**	1/100	2	2M	98	14900	13100	14100	1.13
4	**2d**	1/50	24	1M	62	4200	3800	4500	1.08

[a] Conversion determined by ^1H NMR in $CDCl_3$. [b] Number-average molecular weight determined by size exclusion chromatography in THF with 0.58 as correction factor for PLA[1]and dispersity. [c] $M_{n\ calcd}$ = (50×144×conversion)/100 for PLA and ([ε-CL]/[Al]×114×conversion)/100 .

Table SI1. PLA samples used for the MALDI analysis. Reaction conducted at 100°C and 1M (mol/L).

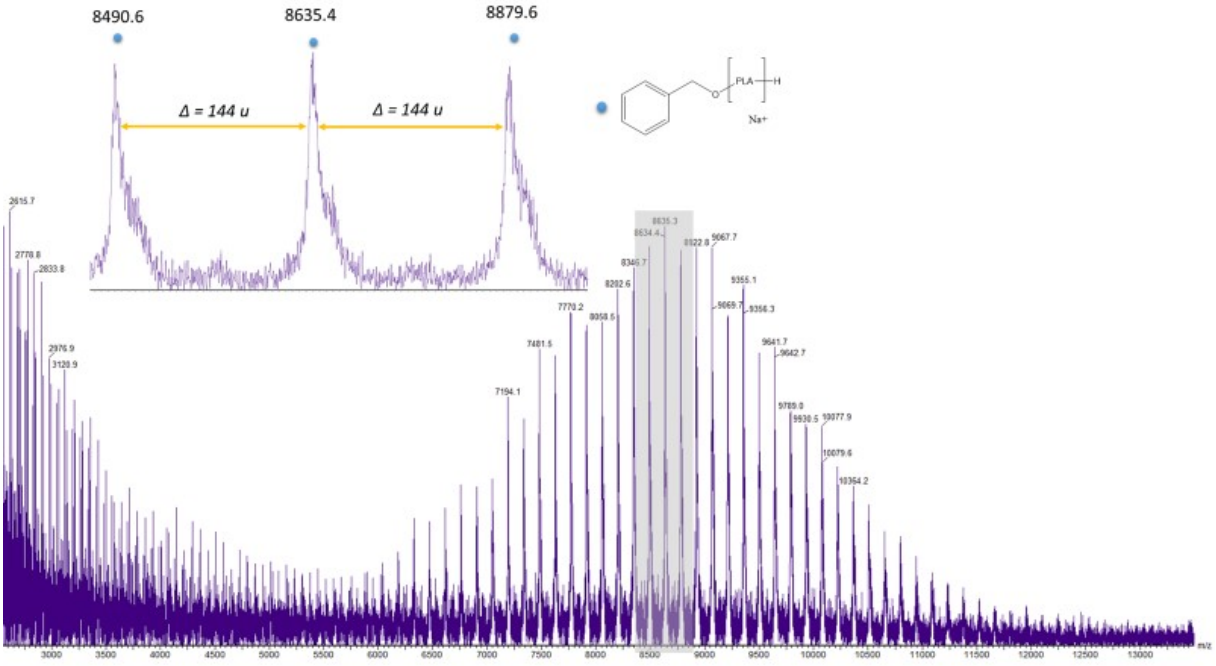


Figure SI1. MALDI ToF analysis of entry SI1 – complex **2a**

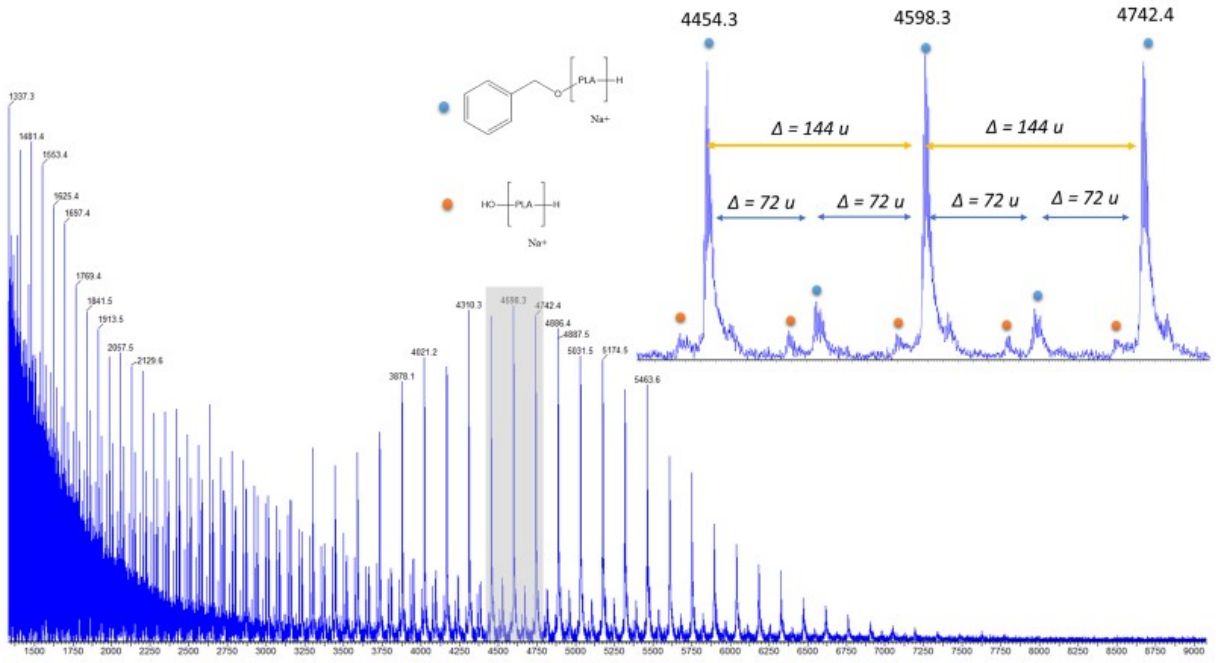


Figure SI2. MALDI ToF analysis of entry SI2 – complex **2b**

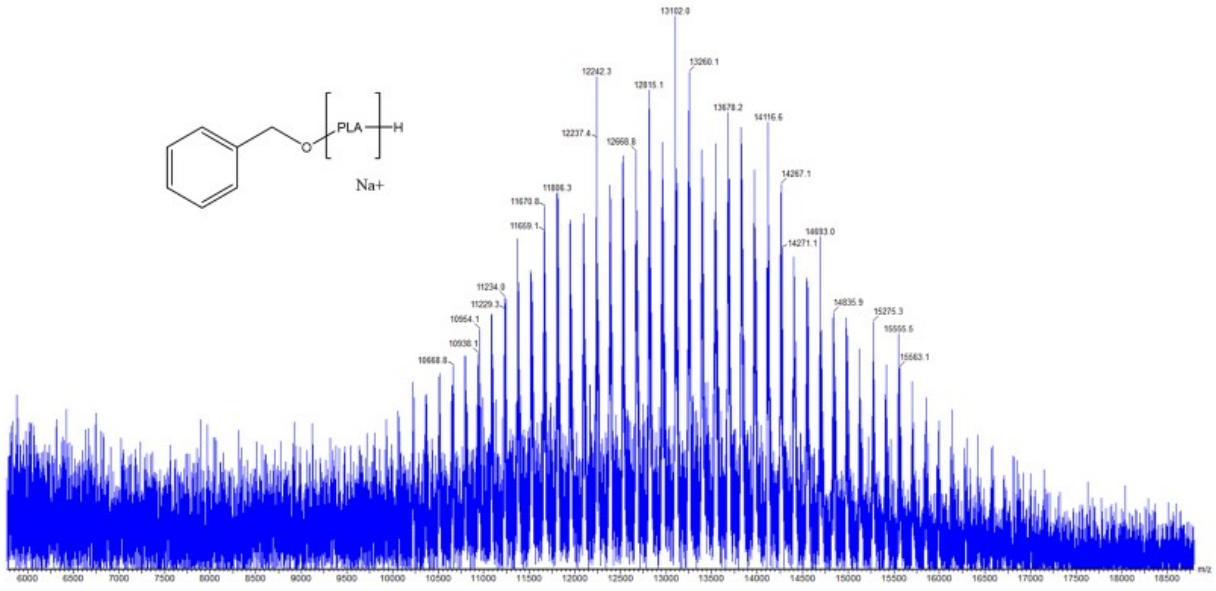


Figure SI3. MALDI ToF analysis of entry SI3 – complex **2c**

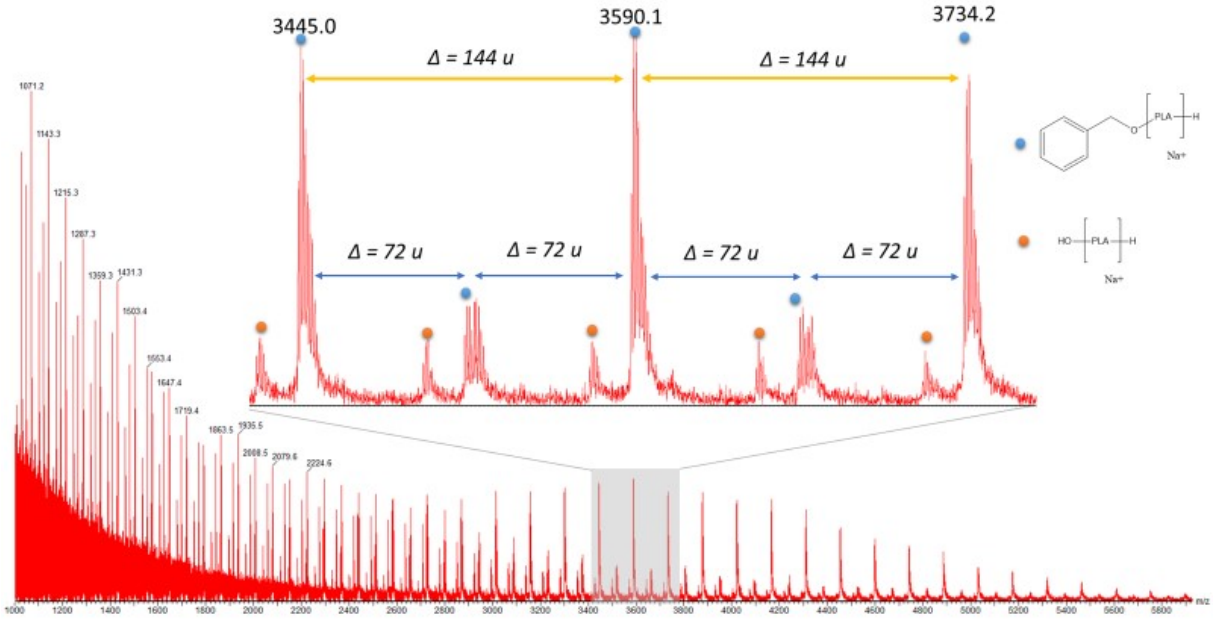


Figure SI4. MALDI ToF analysis of entry 4 – complex **2d**

3. Additional experiments

Entry [a]	Complex	Monomer	M/I[b]	t[c]	T (°C)	Conv.[d] (%)	$M_{n\ calcd}$[e] (g/mol)	$M_{n\ exp}$[f] (g/mol)	$Đ^f$
SI4	**2d**	*L*-LA	100	24h	100	66	4700	4800	1.07
SI5	**2a**	ε-CL	500	30 min	50	100	57100	42800	2.12
SI6	**2b**	ε-CL	500	10 min	50	100	57100	44000	1.37
SI7	**2c**	ε-CL	500	24h	70	2	1100	n.d.	n.d.
SI8	**2d**	ε-CL	1000	10 min	50	100	113000	89400	1.31

[a] Polymerisations conducted in toluene at 1M (mol/L). [b] Monomer / Initiator molar ratio. [c] Time. [d] Conversion determined by ^{1}H NMR in $CDCl_3$. [e] $M_{n\ calcd}$ = (50×144×conversion)/100 for PLA and ([ε-CL]/[Al]×114×conversion)/100. [f] Number-average molecular weight determined by size exclusion chromatography in THF with 0.58 as correction factor for PLA[1], 0.56 as correction coefficient factor for PCL[2] and dispersity.

Table SI2. Additional homopolymerizations experiments conducted at 1M (mol/L).

Entry [a]	Complex	Conv.[a] (ε-CL/*L*-LA %)	$M_{n\ exp}$[b] (g/mol)	$Đ^b$
SI9	$OY_5(OCH(CH_3)_2)_{13}$	3/89	10900	1.36
SI10	$Al(OiPr)_3$	5/87	9100	2.21
SI11	**2c**	4/61	23100	1.13

[a] Conversion determined by ^{1}H NMR in $CDCl_3$. [b] Number-average molecular weight determined by size exclusion chromatography in THF corrected by the following formulae that combines the correction factors of 0.58 for poly(L-lactide), [1] and 0.56 for poly(ε-caprolactone) [2]: $M_{n\ corrected} = M_n\ raw \times 0.56 \times wt\%\ PCL + M_n\ raw \times 0.58 \times wt\%PLA$.

Table SI3. Statistical copolymerization using the three hard block catalysts (*L*-LA / ε-CL / Initiator 250/250/1, 1M (mol/L) in toluene, 100°C, 16h).

4. ^{13}C NMR analysis of statistical copolymers in the carbonyl zone

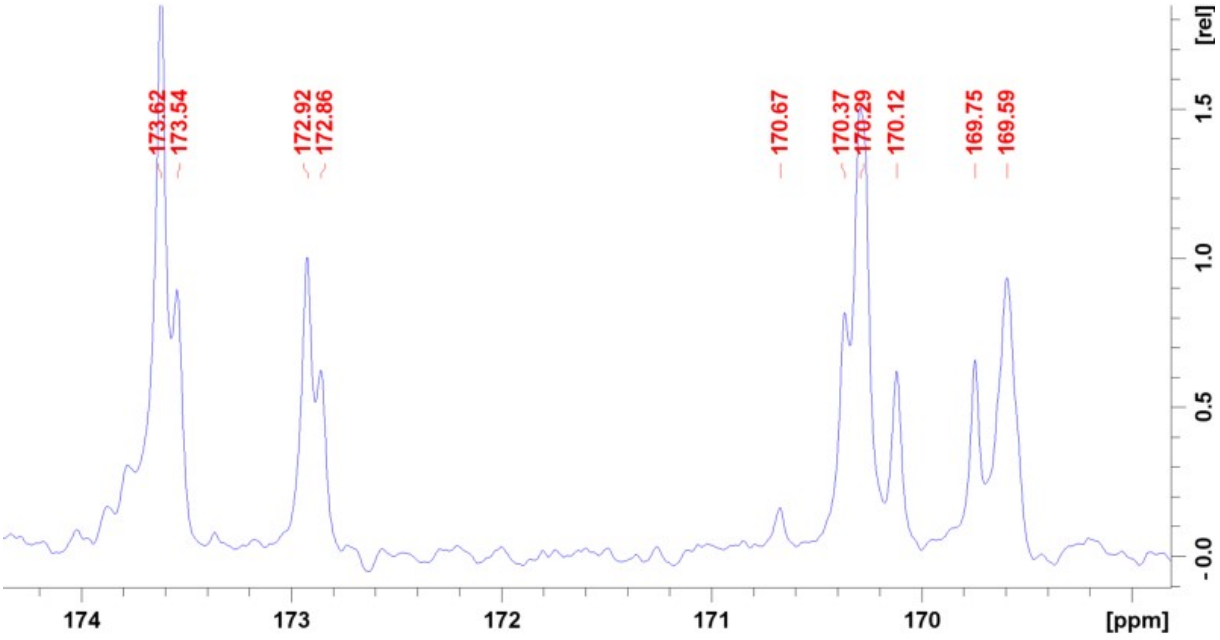


Figure SI5. ^{13}C NMR analysis of entry 9 in the carbonyl zone

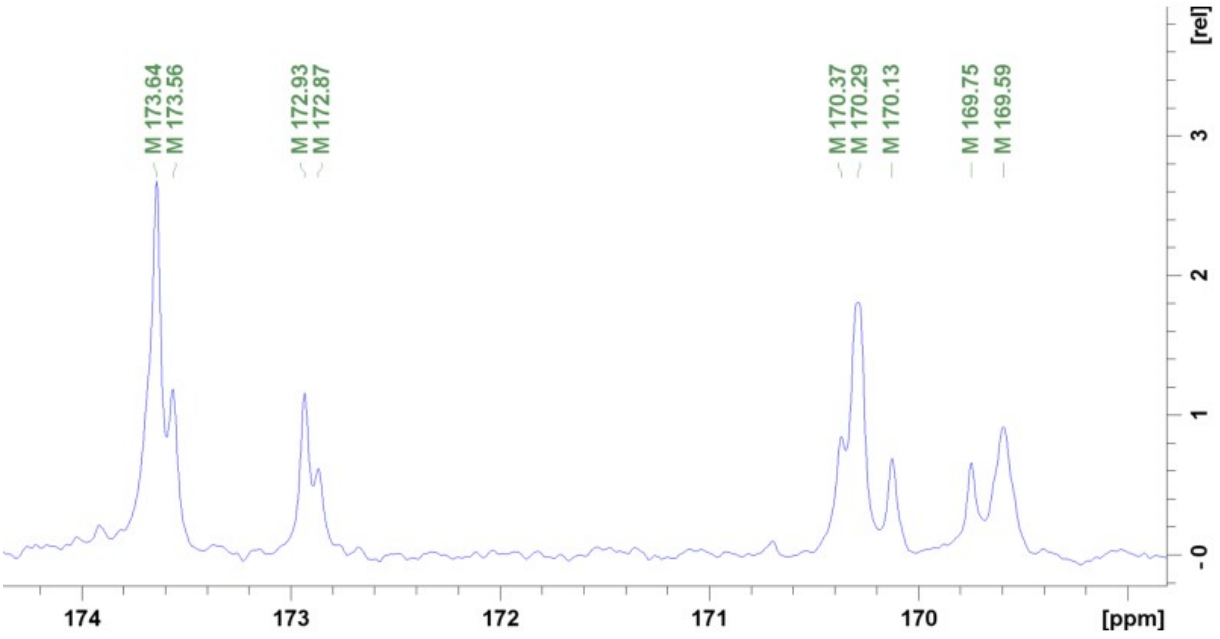


Figure SI6. ^{13}C NMR analysis of entry 10 in the carbonyl zone

Figure SI7. ^{13}C NMR analysis of entry 12 in the carbonyl zone

5. SEC of chain shuttled copolymers

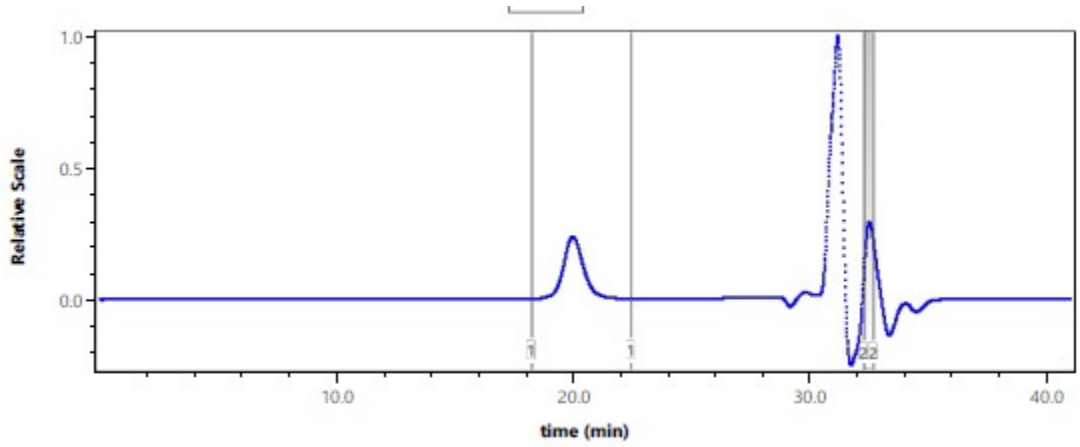


Figure SI8. SEC analysis of entry 13 – **2c** / **2a** combination

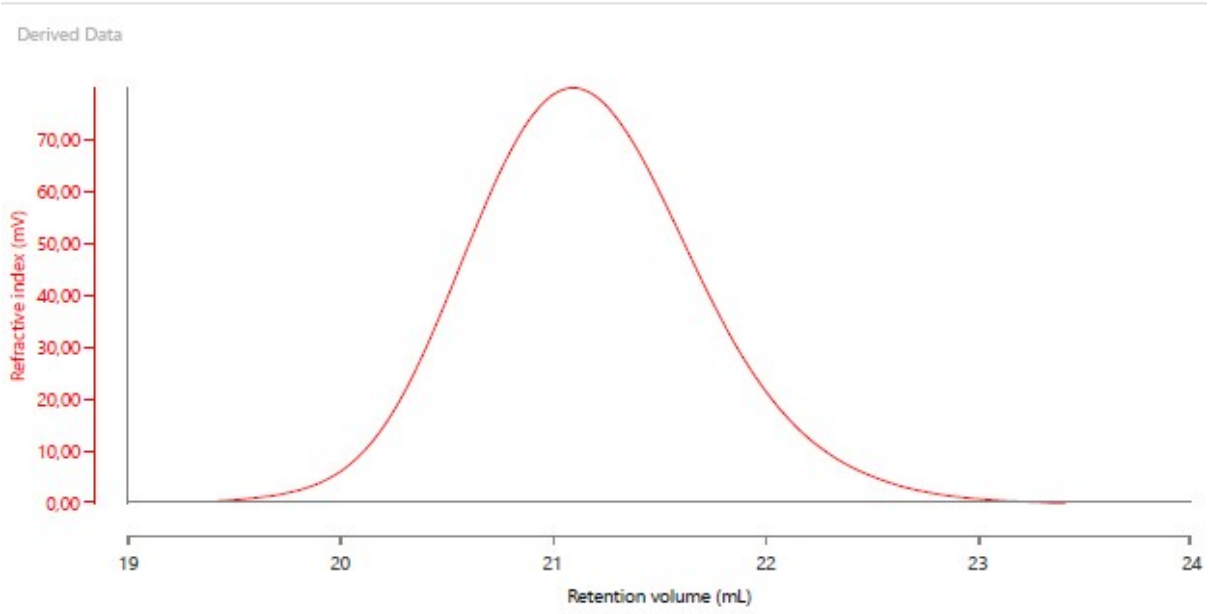


Figure SI9. SEC analysis of entry 15 – **2c** / **2b** combination

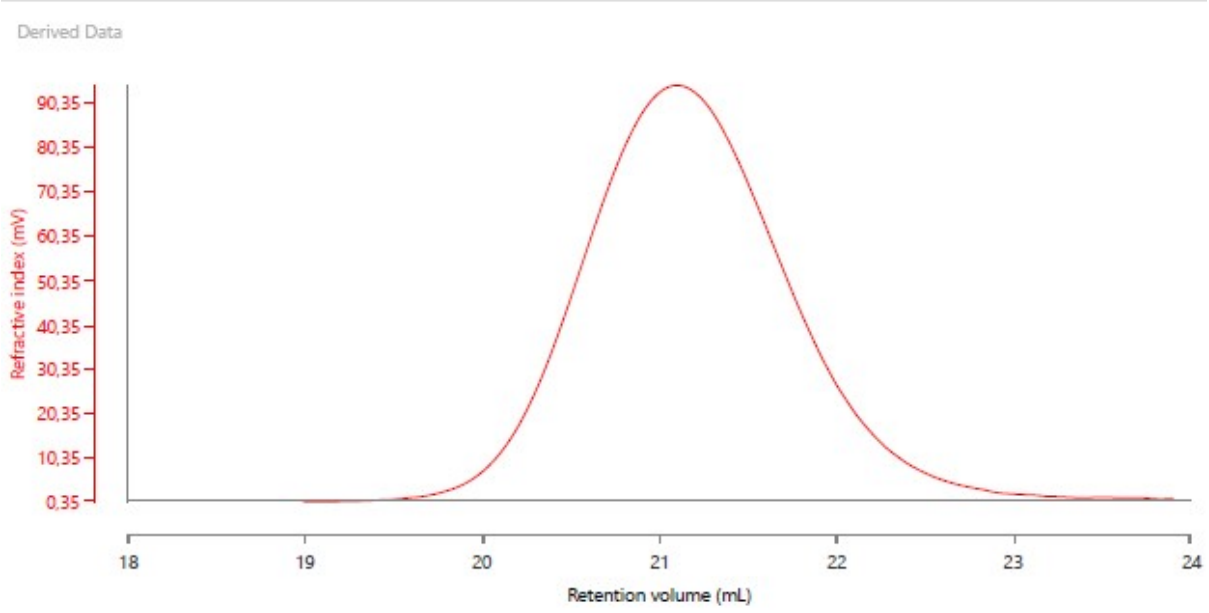


Figure SI10. SEC analysis of entry 16 – **2c** / **2d** combination

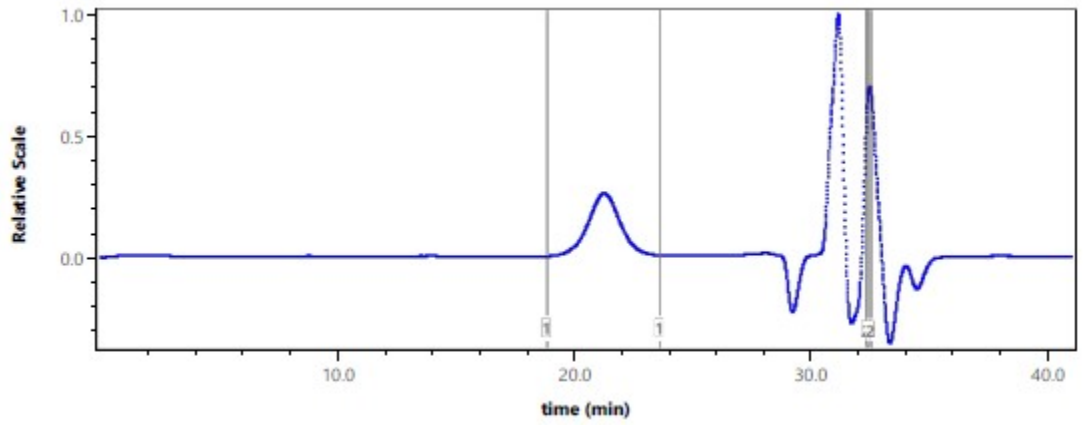


Figure SI11. SEC analysis of entry 18 – **$Al(OiPr)_3$** / **2a** combination

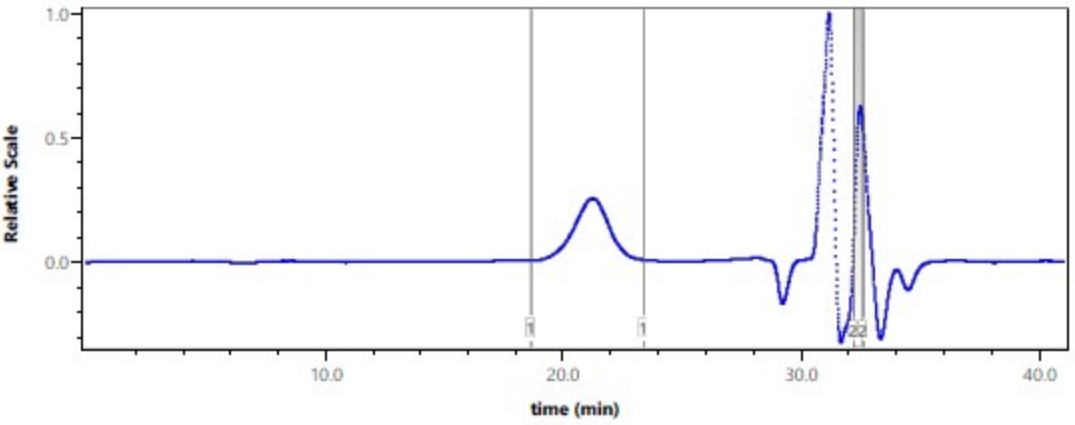


Figure SI12. SEC analysis of entry 19 – **$OY_5(OCH(CH_3)_2)_{13}$** / **2a** combination

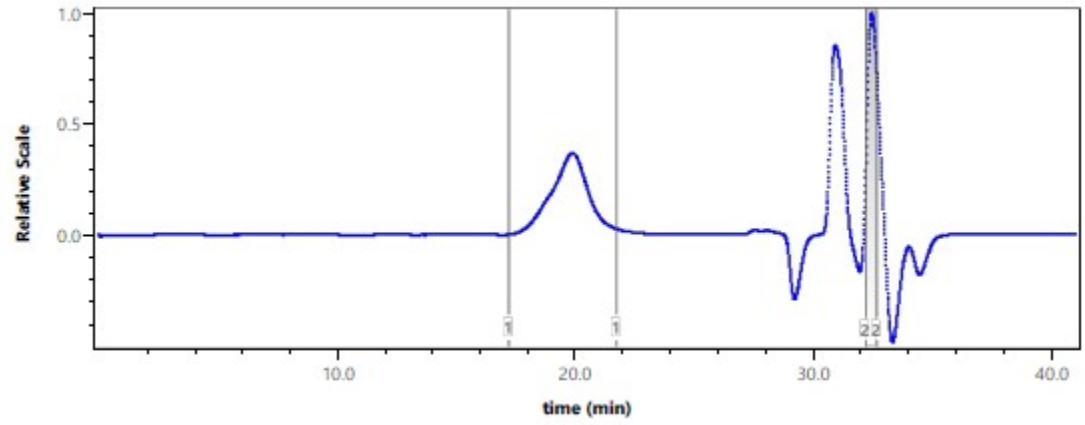


Figure SI13. SEC analysis of entry 21 – **$OY_5(OCH(CH_3)_2)_{13}$** / **2d** combination

6. DOSY analysis of chain shuttled copolymers

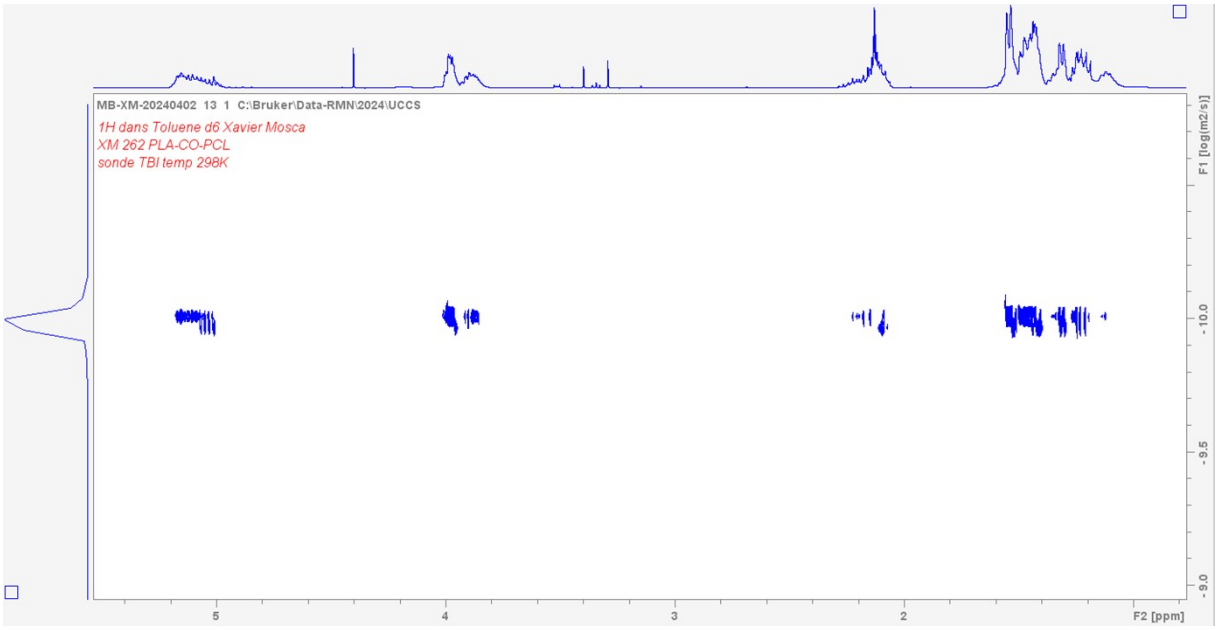


Figure SI14. DOSY analysis of entry 15 – **2c** / **2b** combination

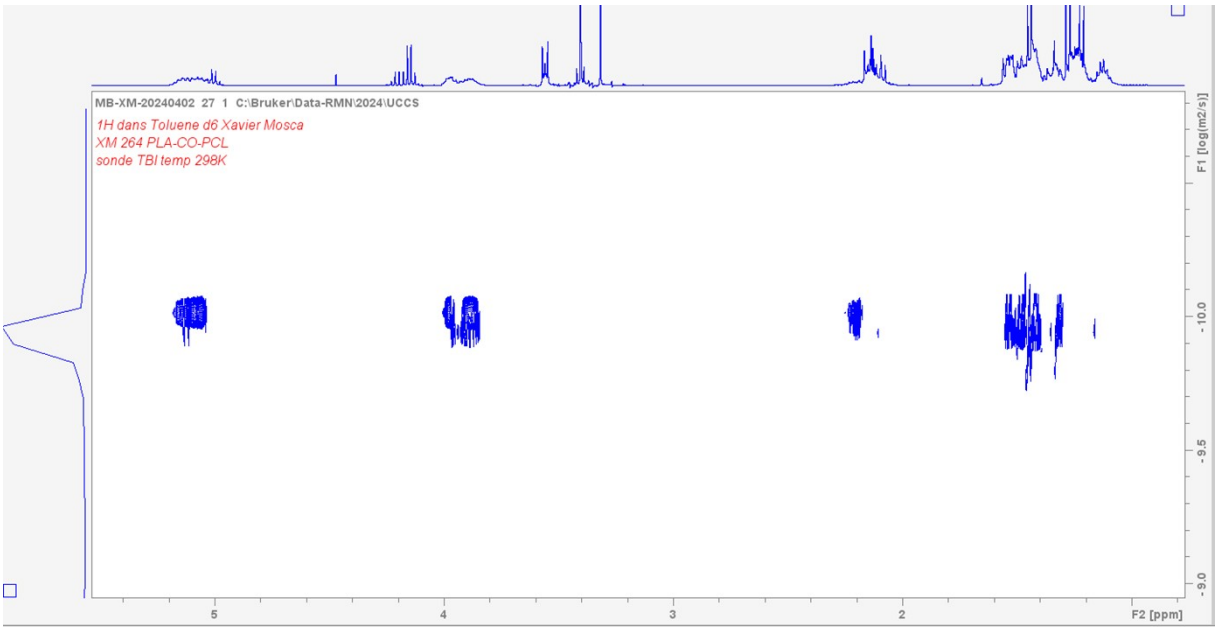


Figure SI15. DOSY analysis of entry 17 – **2c** / **2d** combination

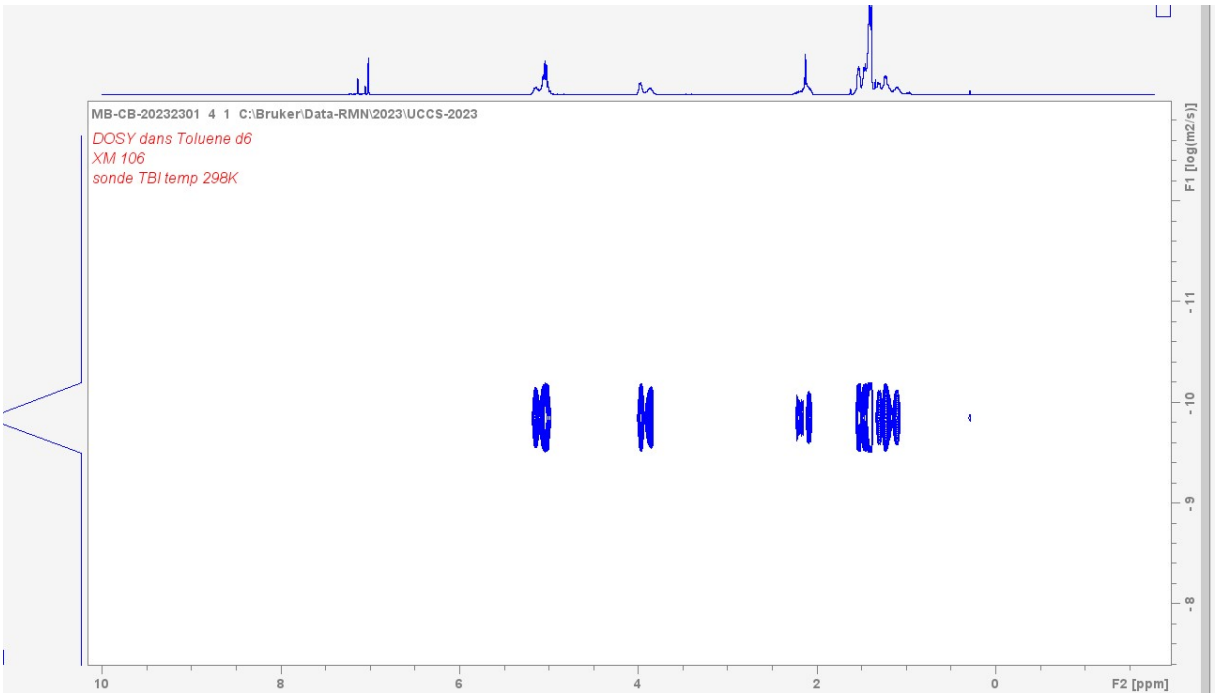


Figure SI16. DOSY analysis of entry 18 – **$Al(OiPr)_3$** / **2a** combination

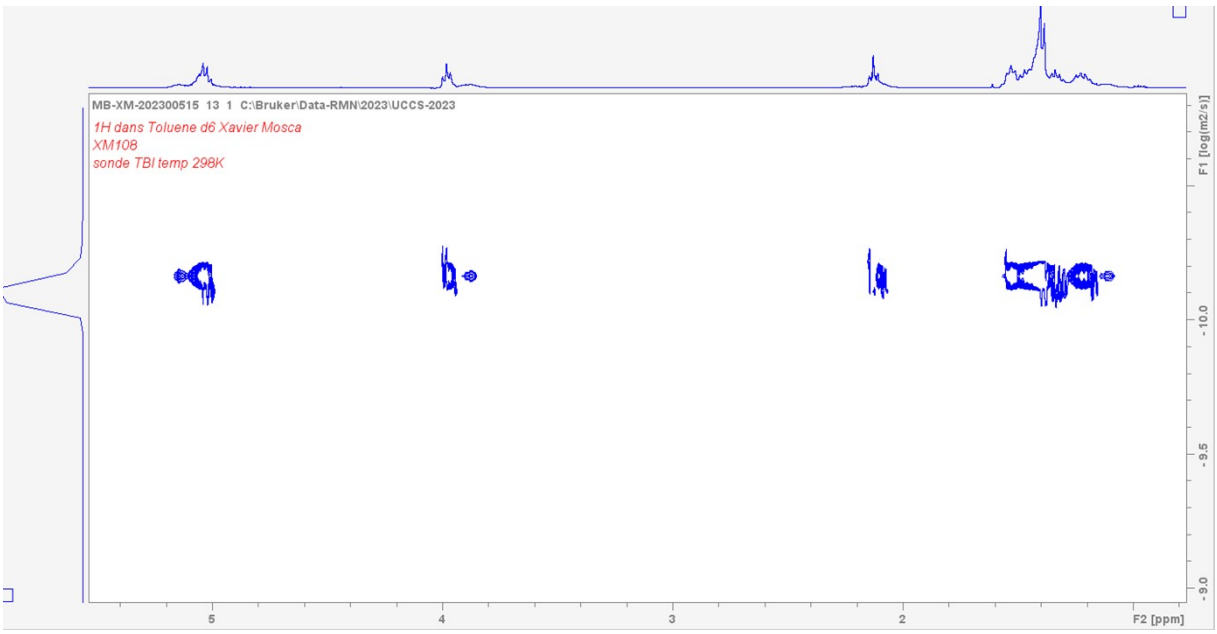


Figure SI17. DOSY analysis of entry 19 – **$OY_5(OCH(CH_3)_2)_{13}$** / **2a** combination

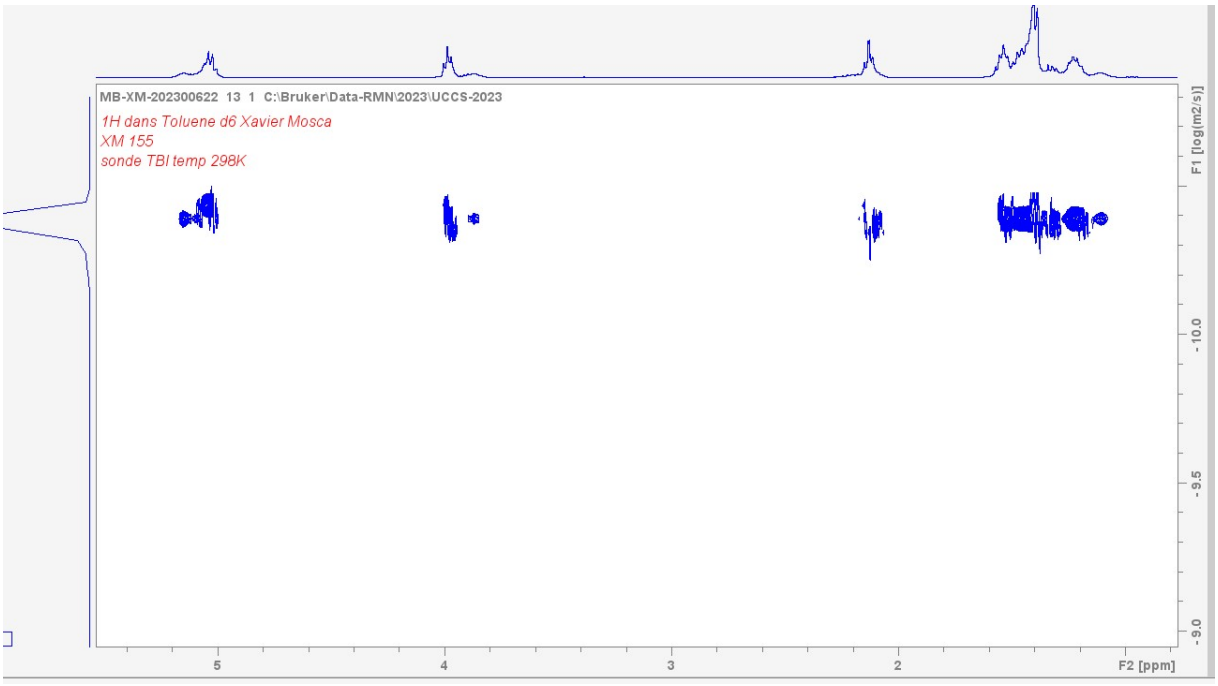


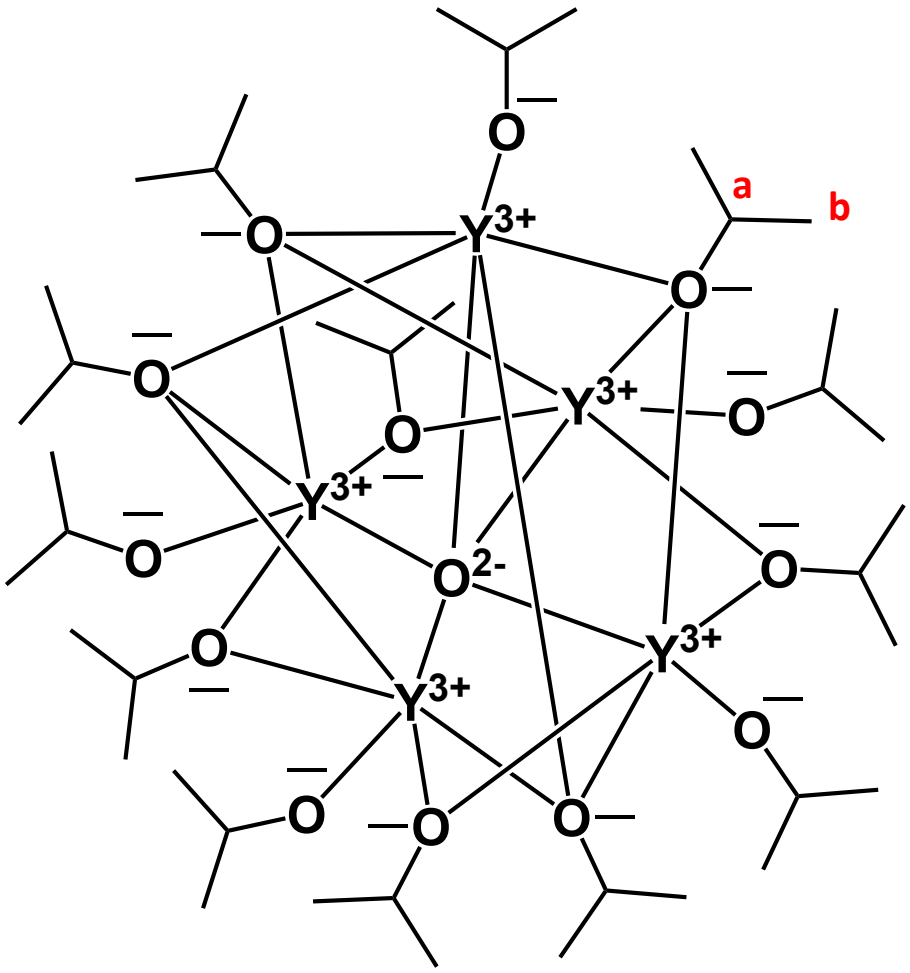
Figure SI18. DOSY analysis of entry 21 – **$OY_5(OCH(CH_3)_2)_{13}$** / **2d** combination

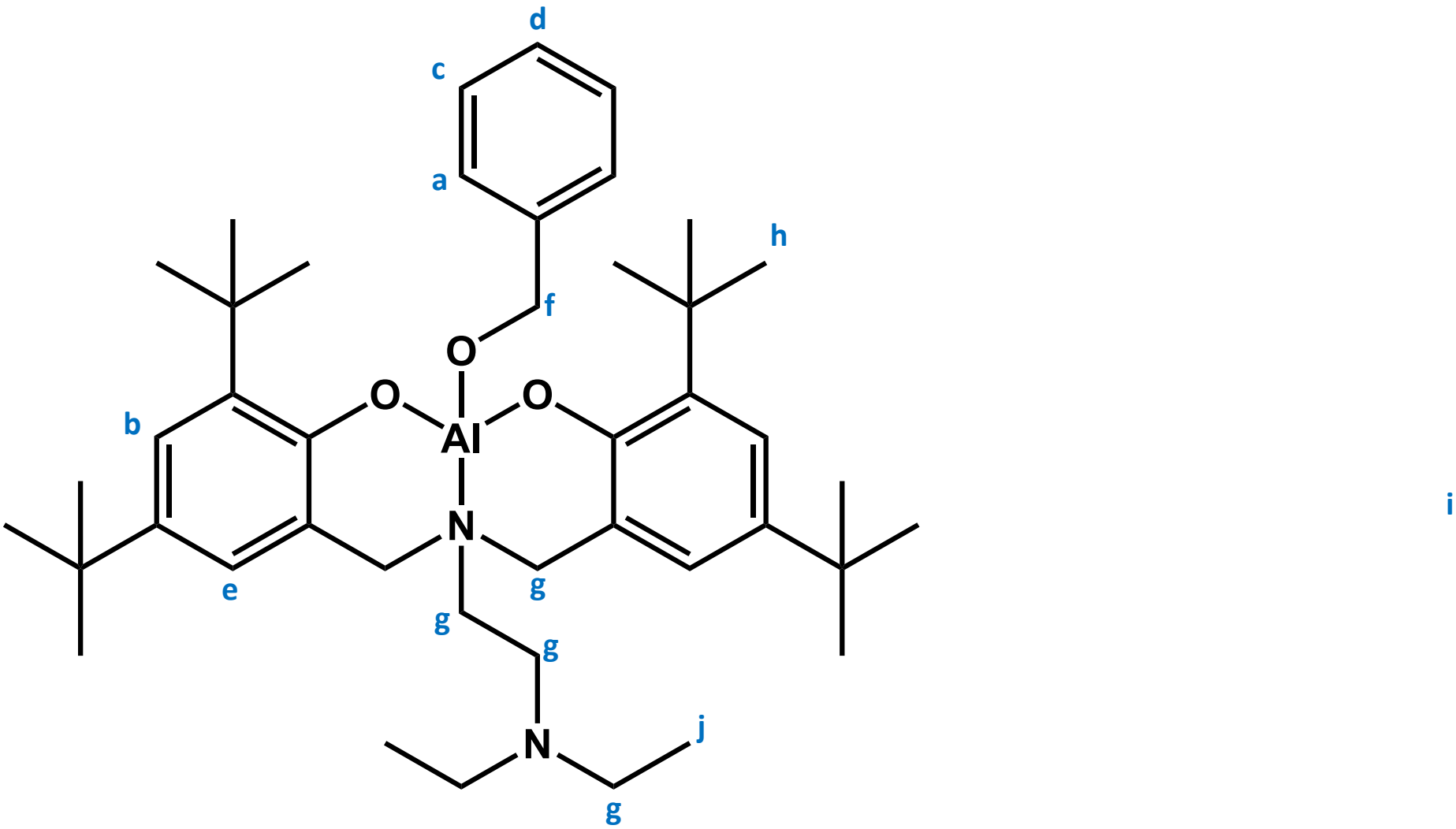
7. ^{1}H NMR study of the interaction between Y and Al catalysts

A ^{1}H NMR study was conducted to assess if the catalysts structures remain stable when combining Y and Al catalysts. This was conducted using **2a** as a case study. In a Young valve NMR tube, 3.5×10^{-6} mol of the complexes, in a 1:1 molar ratio per metal centre, were dissolved in 0.6 mL of deuterated benzene. The solution was then analysed by ^{1}H NMR spectroscopy after 1 hour at room temperature, and then after 6 hours at 80 °C. The resulting spectra were overlaid (Figures SI19 and SI20) with those of the isolated complexes to assess potential interactions.

Firstly, it was observed that the aluminum-based amino(*bis*)phenolate ligand remains stable under these conditions, with no evidence of transfer between the phenolate moieties associated with aluminum and yttrium metal centre. This stability was particularly evident in the aromatic proton region (Figure SI20), which remained unchanged even after heating. However, an exchange was observed between the alkoxide moieties bound to aluminum (OBn) and yttrium (OiPr), indicating efficient transfer between the two metal centres, even at room temperature within one hour. This exchange was notably visible in the 4-6 ppm region of the spectra, where two news species were evidenced, that may tentatively be attributed to the Al-O^{i}Pr and the Y-OBn species.

In conclusion, this experiment demonstrated that these two complexes are able of alcohol group transfer, facilitating chain transfer during chain-shuttling copolymerization by tranesterification, while remaining stable without exchange of the amino(*bis*)phenolate ligand.


O
Y3+
O
a
b
O
O
Y3+
O
O
Y3+
O
O2-
O
O
Y3+
O
Y3+
O
O
O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c
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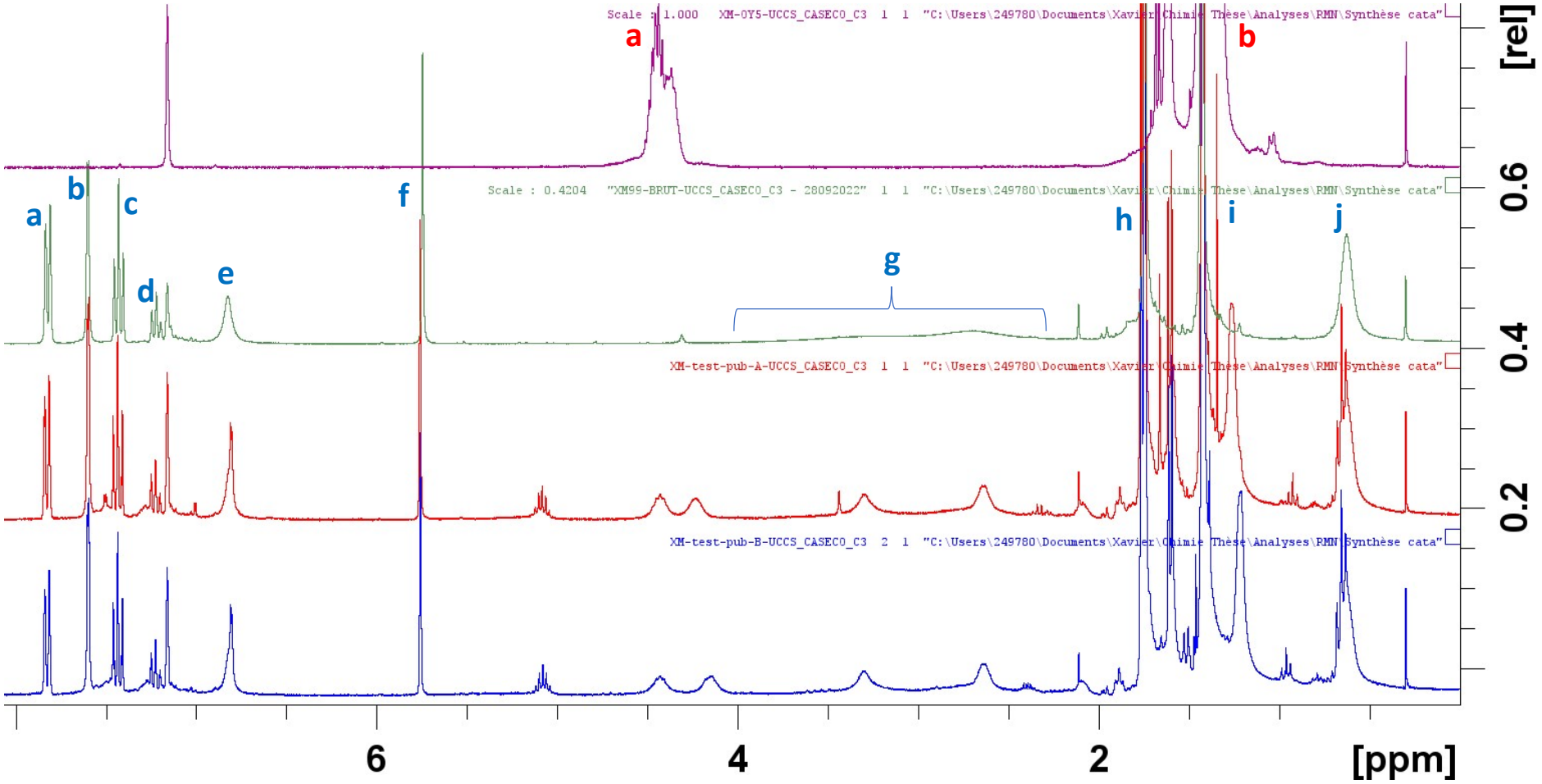

Figure SI 19: ^{1}H NMR spectra overlay between 0-8.5 ppm: from top to bottom isolated $(OY_5(OCH(CH_3)_2)_{13}$, isolated L_4AlOBn, Complexes mixture after 1h at room temperature, complexes mixture after 6h at 80 °C. (300MHz, C_6D_6)

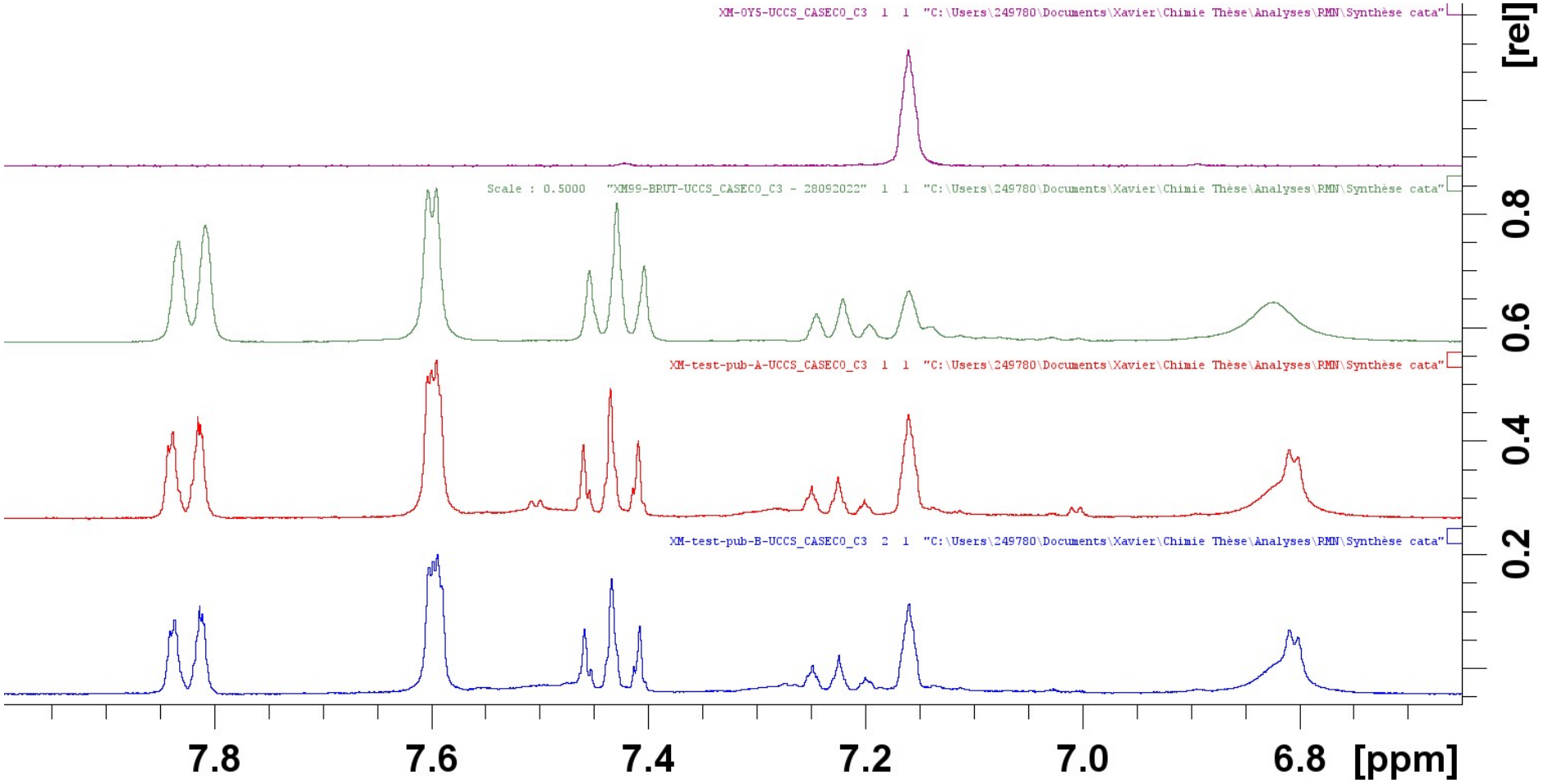

Figure SI 20: ^{1}H NMR spectra overlay between 6.5-8.0 ppm: from top to bottom isolated $(OY_5(OCH(CH_3)_2)_{13}$, isolated L_4AlOBn, Complexes mixture after 1h at room temperature, complexes mixture after 6h at 80 °C. (300MHz, C_6D_6)

6. Bibliography

1 A. Kowalski, A. Duda and S. Penczek, *Macromolecules*, 1998, **31**, 2114–2122.

2 J. E. Puskas, A. Michel and S. Barghi, Eds., *Ionic Polymerizations and Related Processes*, Springer Netherlands, Dordrecht, 1999.

3 F. M. Kerton, S. Holloway, A. Power, R. G. Soper, K. Sheridan, J. M. Lynam, A. C. Whitwood and C. E. Willans, *Can J Chem*, 2008, **86**, 435–443.

4 A. Morrell, M. S. Placzek, J. D. Steffen, S. Antony, K. Agama, Y. Pommier and M. Cushman, *J Med Chem*, 2007, **50**, 2040–2048.

5 R. K. Dean, S. L. Granville, L. N. Dawe, A. Decken, K. M. Hattenhauer and C. M. Kozak, *Dalton Trans*, 2010, **39**, 548–559.

6 E. D. Cross, G. K. Tennekone, A. Decken and M. P. Shaver, *Green Mater.*, 2013, **1**, 79–86.