

Supporting information for:

**Phenoxy-based aluminum complexes: Simple and efficient catalysts for the Ring-Opening
Co-Polymerization of epoxides and anhydrides.**

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Experimental Section.

General considerations. All manipulations of air- and/or water-sensitive compounds were carried out under a dry nitrogen atmosphere using a Braun Labmaster drybox or standard Schlenk line techniques. Glassware and vials used in the polymerization were dried in an oven at 120 °C overnight and exposed three times to vacuum–nitrogen cycles.

Benzene, hexane and toluene (Sigma-Aldrich) were distilled under nitrogen over sodium/benzophenone. The aluminum precursor AlMe_3 was purchased from Aldrich and was used as received. Deuterated solvents were dried over molecular sieves. Cyclohexene oxide and limonene oxide were purchased from Sigma-Aldrich and distilled over CaH_2 . All other chemicals were commercially available and used as received unless otherwise stated. The synthesis of complex **1** and **4** was performed according published procedure.[1,2]

NMR spectra were recorded on Bruker Advance 250, 300, 400 and 600 MHz spectrometers at 25 °C, unless otherwise stated. Chemical shifts (δ) are expressed as parts per million and coupling constants (J) in hertz. ^1H NMR spectra are referenced using the residual solvent peak at $\delta = 7.16$ for C_6D_6 and $\delta = 7.27$ for CDCl_3 . ^{13}C NMR spectra are referenced using the residual solvent peak at $\delta = 128.06$ for C_6D_6 and $\delta = 77.23$ for CDCl_3 . In the case of ^{19}F , resonances were automatically referenced versus $\text{CF}_3\text{C}_6\text{H}_5$ by the software.

Melting points (T_m) of the polymers were measured by differential scanning calorimetry (DSC) using a DSC 2920 apparatus manufactured by TA Instruments under a nitrogen flux of 50 mL min^{-1} with a heating and cooling rate of 10 °C min^{-1} in the range -10 to 120 °C. All calorimetric data were reported for the second heating cycle.

Mass spectra were acquired using a Bruker solariX XR Fourier transform ion cyclotron resonance mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a 7 T refrigerated actively-shielded superconducting magnet (Bruker Biospin, Wissembourg, France). The polymer samples were ionized in positive ion mode using the MALDI ion source. The mass range was set to m/z 200 – 5000. The laser power was 12 % and 18 laser shots were used for each scan. Mass spectra were calibrated externally using a mix of peptide clusters in MALDI ionization positive ion mode. A linear calibration was applied. The polymer samples were dissolved in THF at a concentration of 1 mg/mL. The cationization agent used was potassium trifluoroacetate (Fluka, >

99 %) dissolved in THF at a concentration of 5 mg/mL. The matrix used was trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) (Fluka) and was dissolved in THF at a concentration of 40 mg/mL. Solutions of matrix, salt and polymer were mixed in a volume ratio of 4:1:4, respectively. The mixed solution was hand-spotted on a stainless steel MALDI target and left to dry.

General procedure for the synthesis of complexes 2a-e.

To a stirred solution containing 46 mg (0.61 mmol) of AlMe_3 (97 % wt) in dry benzene (2 mL) was added dropwise a solution of the appropriate pro-ligand (0.61 mmol) in dry benzene (2 mL). The reaction mixture was stirred for 2 hours at room temperature. The solvent was removed under vacuum, forming a yellow solid in almost quantitative yield.

Complex phenoxy-imine phenyl (2a).

^1H NMR (300 MHz, C_6D_6 , 298 K): δ -0.17 (s, 6H, Al-CH_3), 1.31 (s, 9H, $\text{CH}(\text{CH}_3)_2$), 1.60 (s, 9H, $\text{CH}(\text{CH}_3)_2$), 6.73 (d, 1H, Ar-*H*), 6.94-6.96 (m, 5H, Ar-*H*), 7.42 (s, 1H, CH=N), 7.72 (d, 1H, Ar-*H*).

^{13}C NMR (75 MHz, C_6D_6 , 298 K): δ -8.6 (Al-CH_3), 29.6 ($\text{C}(\text{CH}_3)$), 31.5 ($\text{C}(\text{CH}_3)$), 34.2 ($\text{C}(\text{CH}_3)$), 35.6 ($\text{C}(\text{CH}_3)$), 119.4, 122.5, 129.8, 129.9, 132.9, 139.3, 141.2, 147.2 (all Ar-C, one peak obscured), 162.9 (C-O), 170.8 (CH=N).

Complex phenoxy-imine 2,6-diisopropylphenyl (2b).

^1H NMR (300 MHz, C_6D_6 , 298 K): δ -0.23 (s, 6H, Al-CH_3), 0.79 (d, 6H, $\text{CH}(\text{CH}_3)_2$), 1.18 (d, 6H, $\text{CH}(\text{CH}_3)_2$), 1.24 (s, 9H, $\text{C}(\text{CH}_3)$), 1.60 (s, 9H, $\text{C}(\text{CH}_3)$), 3.11 (m, 2H, $\text{CH}(\text{CH}_3)_2$), 6.83 (d, 1H, Ar-*H*), 6.96 (s, 1H, CH=N), 7.01 (1H, Ar-*H*), 7.08 (1H, Ar-*H*), 7.74 (d, 1H, Ar-*H*), 7.89 (s, 1H, Ar-*H*).

^{13}C NMR (101 MHz, C_6D_6 , 298 K): δ -8.9 (Al-CH_3), 22.9 ($\text{CH}(\text{CH}_3)_2$), 25.9 ($\text{CH}(\text{CH}_3)_2$), 28.5 ($\text{CH}(\text{CH}_3)_2$), 29.7 ($\text{C}(\text{CH}_3)_3$), 31.4 ($\text{C}(\text{CH}_3)_3$), 34.2 ($\text{C}(\text{CH}_3)_3$), 35.7 ($\text{C}(\text{CH}_3)_3$), 118.8, 124.5, 129.1, 133.4, 139.8, 141.6, 142.8, 142.9 (all Ar-C, one peak obscured), 163.2 (C-O), 174.5 (CH=N).

Complex phenoxy-imine 2,6-dimethylphenyl (2c).

^1H NMR (400 MHz, C_6D_6 , 298 K): δ -0.29 (s, 6H, Al-CH₃), 1.29 (s, 9H, C(CH₃)), 1.60 (s, 9H, C(CH₃)), 1.97 (s, 6H, Ar-CH₃), 6.71 (d, 1H, Ar-H), 6.82 (1H, Ar-H), 6.84 (1H, Ar-H), 6.88 (dd, 1H, Ar-H), 7.72 (d, 1H, Ar-H).

^{13}C NMR (101 MHz, C_6D_6 , 298 K): δ -8.4 (Al-CH₃), 18.5 (CH₃), 29.6 (C(CH₃)), 31.5 (C(CH₃)), 34.3 (C(CH₃)), 35.7 (C(CH₃)), 119.1, 127.4, 129.0, 129.5, 131.9, 133.1, 139.3, 141.4, 145.3, 163.1 (C-O), 174.9 (CH=N).

Complex phenoxy-imine 4-methoxyphenyl (2d).

^1H NMR (400 MHz, C_6D_6 , 298 K): δ -0.13 (s, 6H, Al-CH₃), 1.32 (s, 9H, C(CH₃)), 1.63 (s, 9H, C(CH₃)), 3.23 (s, 3H, OCH₃), 6.59 (d, 2H, Ar-H), 6.77 (d, 1H, Ar-H), 6.90 (d, 2H, Ar-H), 7.52 (s, 1H, CH=N), 7.72 (d, 1H, Ar-H).

^{13}C NMR (75 MHz, C_6D_6 , 298 K): δ -8.6 (Al-CH₃), 29.6 (C(CH₃)), 31.5 (C(CH₃)), 34.2 (C(CH₃)), 35.6 (C(CH₃)), 59.0 (OCH₃), 117.9, 119.4, 123.9, 129.9, 132.9, 139.4, 141.1, 142.3, 157.7, 162.8 (C-O), 170.2 (CH=N).

Complex phenoxy-imine pentafluorophenyl (2e).

^1H NMR (400 MHz, C_6D_6 , 298 K): δ -0.24 (s, 6H, Al-CH₃), 1.25 (s, 9H, C(CH₃)), 1.51 (s, 9H, C(CH₃)), 6.73 (d, 1H, Ar-H), 7.18 (s, 1H, CH=N), 7.73 (s, d, Ar-H).

^{13}C NMR (75 MHz, C_6D_6 , 298 K): δ -9.8 (Al-CH₃), 29.4 (C(CH₃)), 31.2 (C(CH₃)), 34.1 (C(CH₃)), 35.6 (C(CH₃)), 118.6, 121.8 (C-N), 129.9, 135.5, 136.4 (C-F), 140.0, 140.3 (C-F), 142.0, 143.6 (C-F), 164.8 (C-O), 177.1 (CH=N).

^{19}F NMR (377 MHz, C_6D_6 , 298 K): δ -160.72 (td, 2F, *o*-F), -154.52 (t, 1F, *p*-F), -148.35 (d, 2F, *m*-F).

Synthesis of the complex phenoxy-amine (3). To a stirred solution containing 0.230 g (3.09 mmol) of AlMe₃ (97 % wt) in dry benzene was added dropwise a solution of the ligand (1.00 g, 2.88 mmol) in dry benzene. The reaction mixture was stirred for 3 hours at room temperature. The solvent was removed under vacuum forming a gel, which was successively washed with pentane. The complex was dried under vacuum, forming a white solid in almost quantitative yield.

^1H NMR (300 MHz, C_6D_6 , 298 K): δ -0.28 (s, 6H, Al- CH_3), 0.55 (d, 6H, $\text{CH}(\text{CH}_3)_2$), 0.68 (d, 6H, $\text{CH}(\text{CH}_3)_2$), 1.41 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.71 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.77 (m, 2H, CH), 2.47 (dq, 4H, CH_2), 3.43 (s, 2H, N- CH_2), 6.75 (d, 1H, Ar- H), 7.54 (d, 1H, Ar- H).

^{13}C NMR (75 MHz, C_6D_6 , 298 K): δ -8.7 (Al- CH_3), 22.8, 23.3, 23.5, 29.9, 32.1, 35.4, 58.7, 60.2, 119.9, 124.3, 125.4, 137.9, 138.3, 157.3 (C-O).

General procedure for the co-polymerization of epoxides with cyclic anhydrides.

In bulk. The copolymerization was performed at 110 °C with a [epoxide]:[anhydride]:[catalyst] (:[cocatalyst]) ratio of 125:125:1(:1). In a Braun Labmaster glovebox, a magnetically stirred reactor vessel (10 mL) was charged with the anhydride. Subsequently, a solution of catalyst and cocatalyst dissolved in neat epoxide was added. The reaction mixture was stirred at 110 °C. At desired times, small aliquots of the reaction mixture were sampled, dissolved in CDCl_3 and analyzed by ^1H NMR spectroscopy. At the end of the polymerization, the product was dissolved in CH_2Cl_2 and dried under vacuum oven. All analyses were performed on crude samples.

In solution. The copolymerization was performed at the desired temperature in 1 mL toluene with a [epoxide]:[anhydride]:[catalyst] (:[cocatalyst]) ratio of 125:125:1(:1). In a Braun Labmaster glovebox, a magnetically stirred reactor vessel (10 mL) was charged with the anhydride. Subsequently, a solution of catalyst, cocatalyst and epoxide in 1 mL of toluene was added. The reaction mixture was stirred at 110 °C. At desired times, small aliquots of the reaction mixture were sampled, dissolved in CDCl_3 and analyzed by ^1H NMR spectroscopy. At the end of the polymerization, the product was dissolved in CH_2Cl_2 and dried under vacuum oven. All analyses were performed on crude samples.

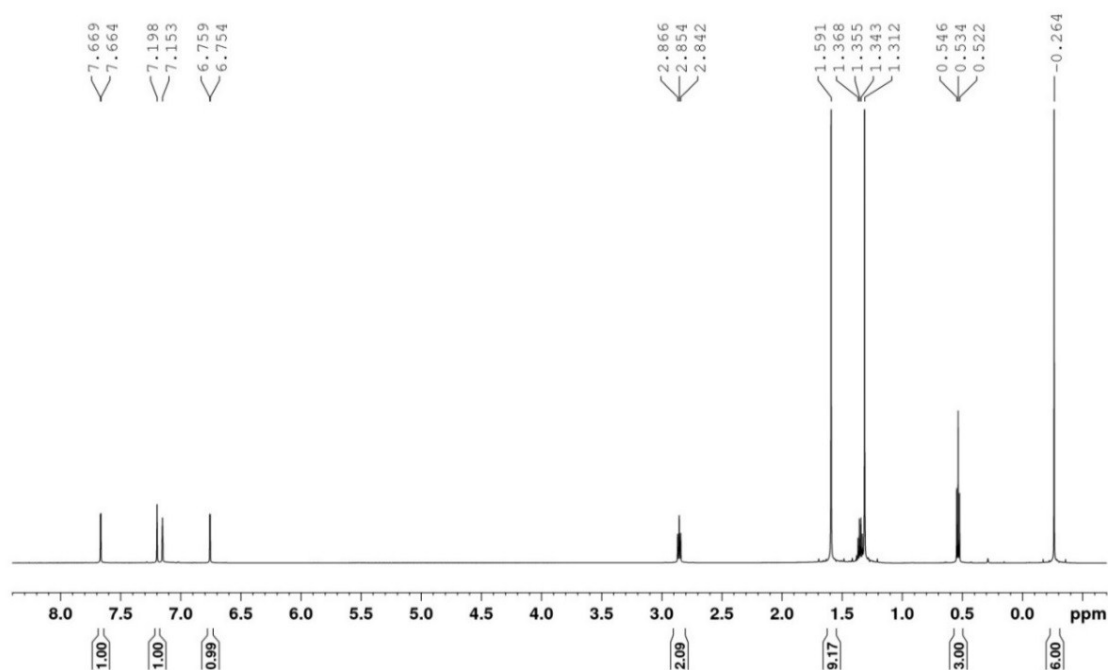


Figure S1. ¹H NMR (400 MHz, C₆D₆, 298 K) of complex phenoxy-imine n-propyl (**1**).

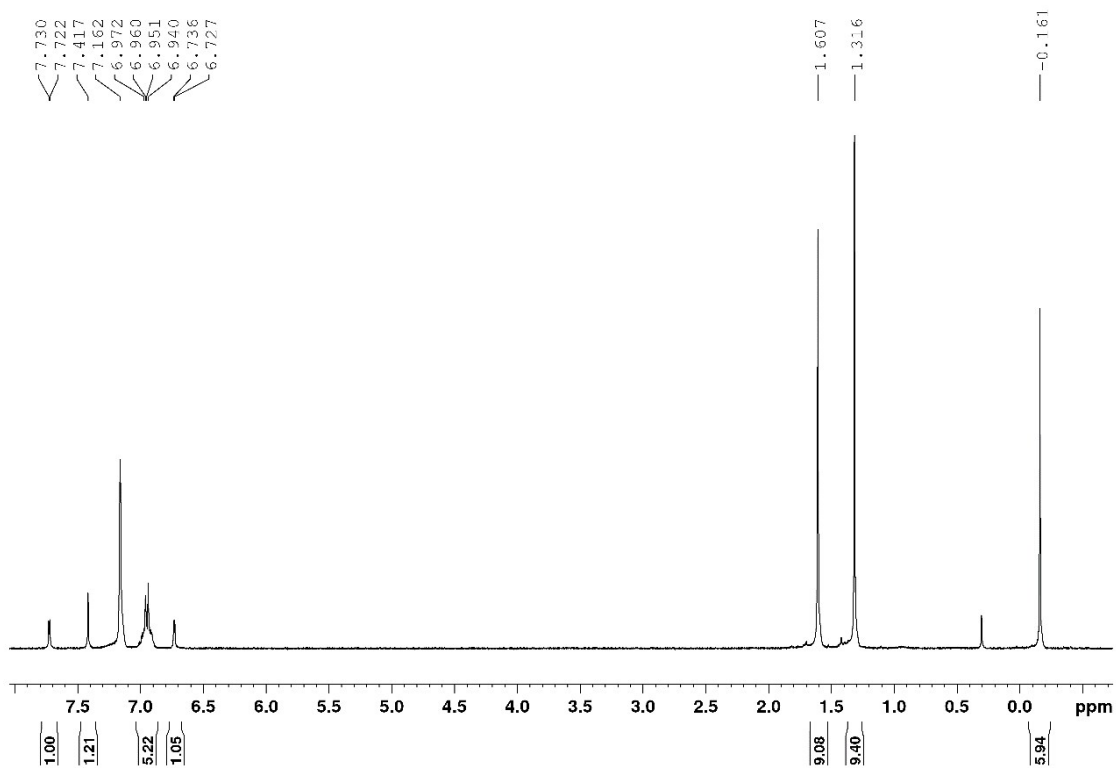


Figure S2. ¹H NMR (300 MHz, C₆D₆, 298 K) of complex phenoxyimine phenyl (**2a**).

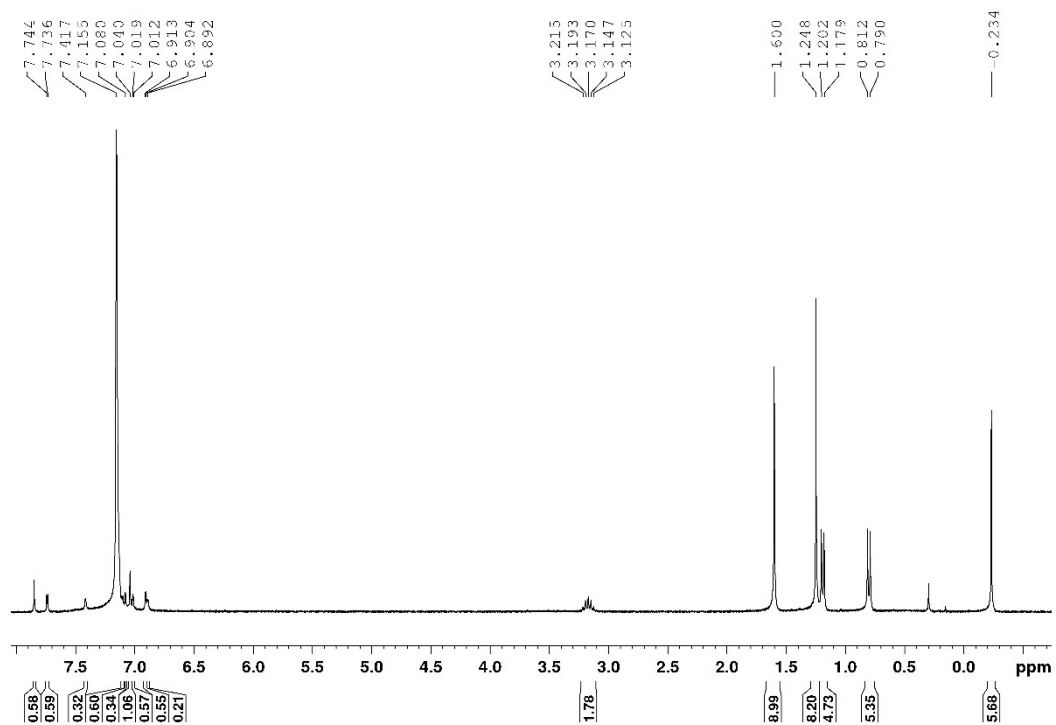


Figure S3. ¹H NMR (300 MHz, C₆D₆, 298 K) of complex phenoxy-imine 2,6-diisopropylphenyl (2b).

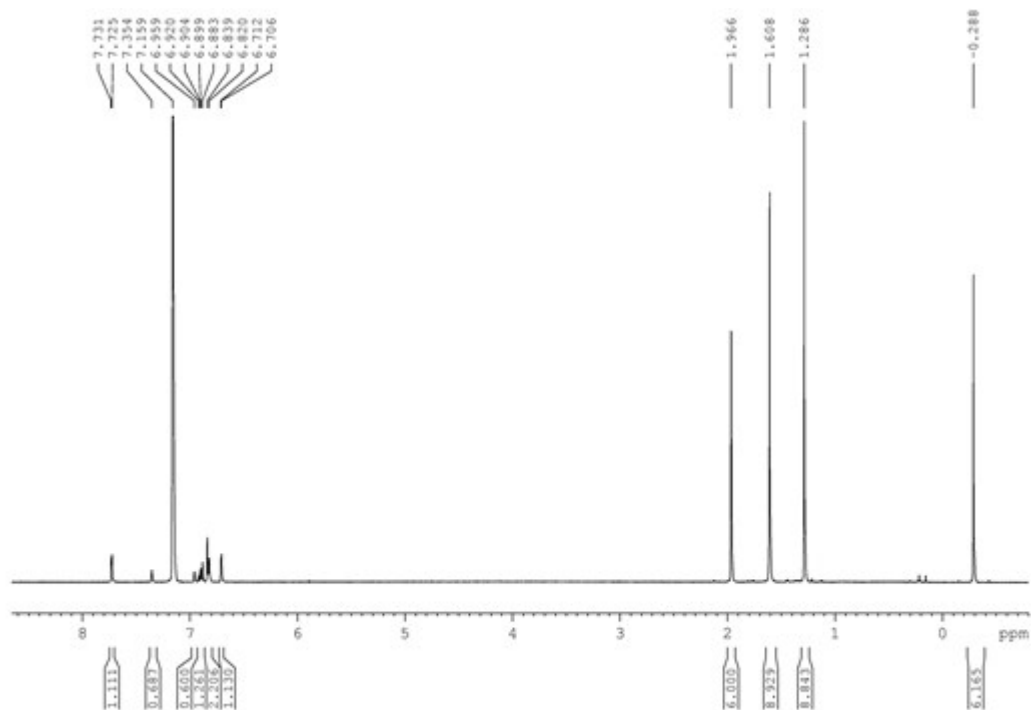


Figure S4. ¹H NMR (400 MHz, C₆D₆, 298 K) of complex phenoxy-imine 2,6-dimethylphenyl (2c).

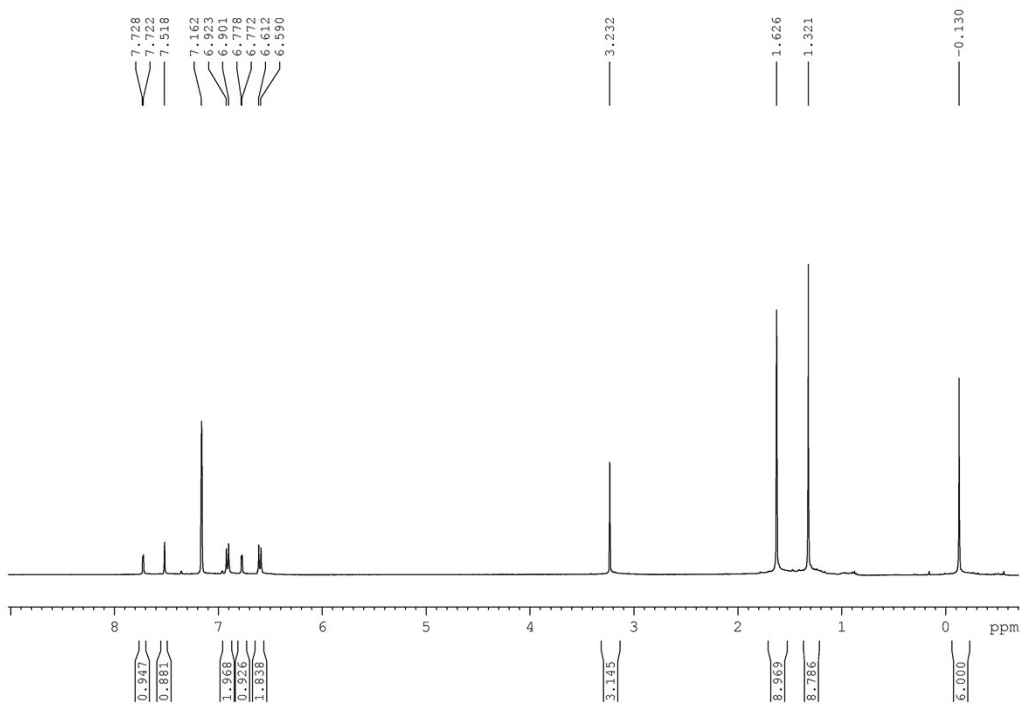


Figure S5. ¹H NMR (400 MHz, C₆D₆, 298 K) of complex phenoxy-imine 4-methoxyphenyl (**2d**).

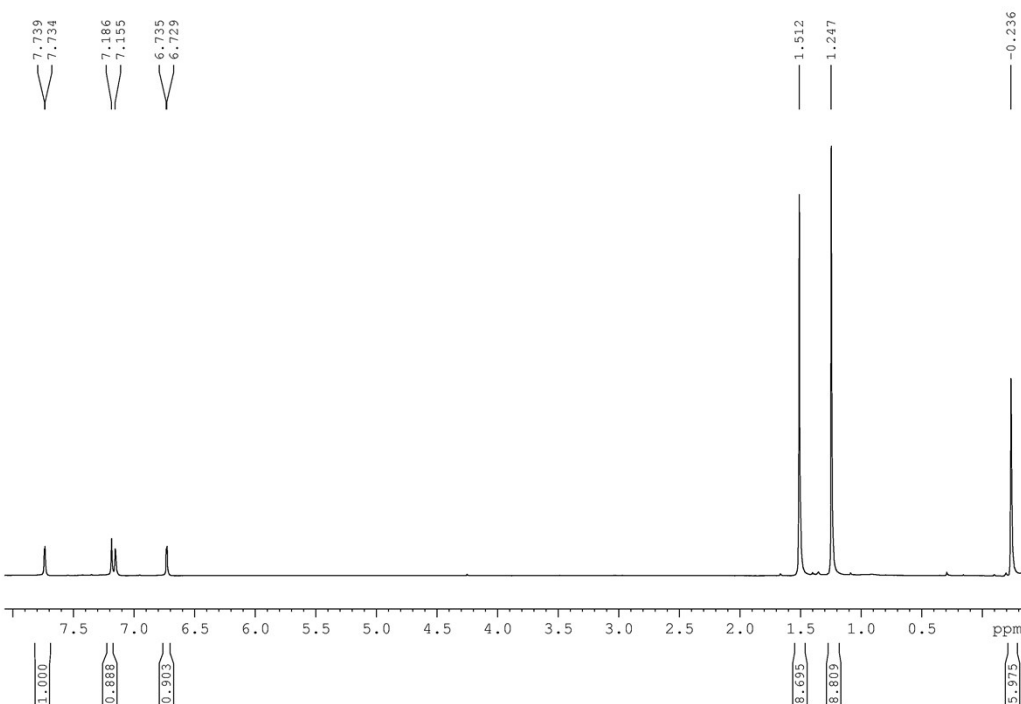


Figure S6. ¹H NMR (400 MHz, C₆D₆, 298 K) of complex phenoxy-imine pentafluorophenyl (**2e**).

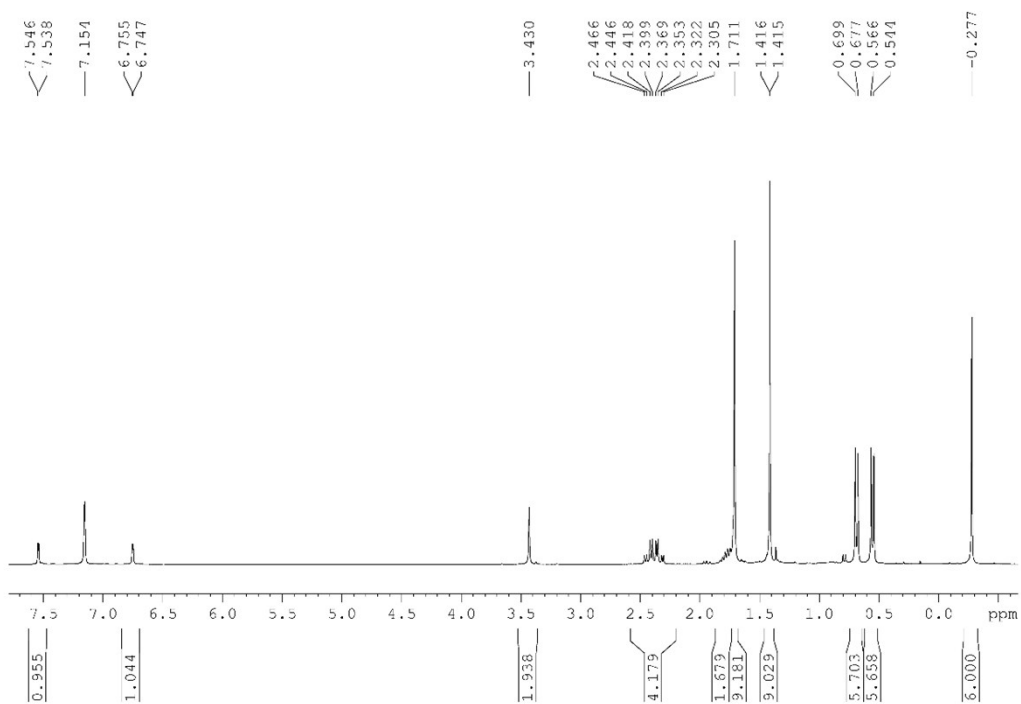


Figure S7. ¹H NMR (300 MHz, C₆D₆, 298 K) of complex phenoxy-amine (**3**).

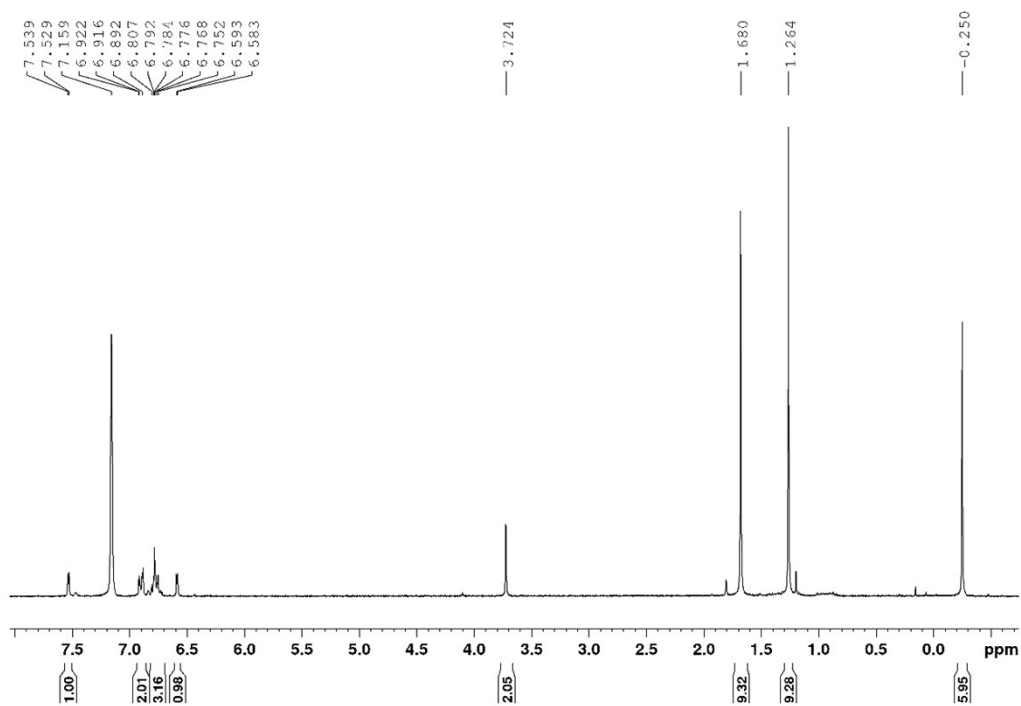


Figure S8. ¹H NMR (250 MHz, C₆D₆, 298 K) of complex phenoxy-thioether (**4**).

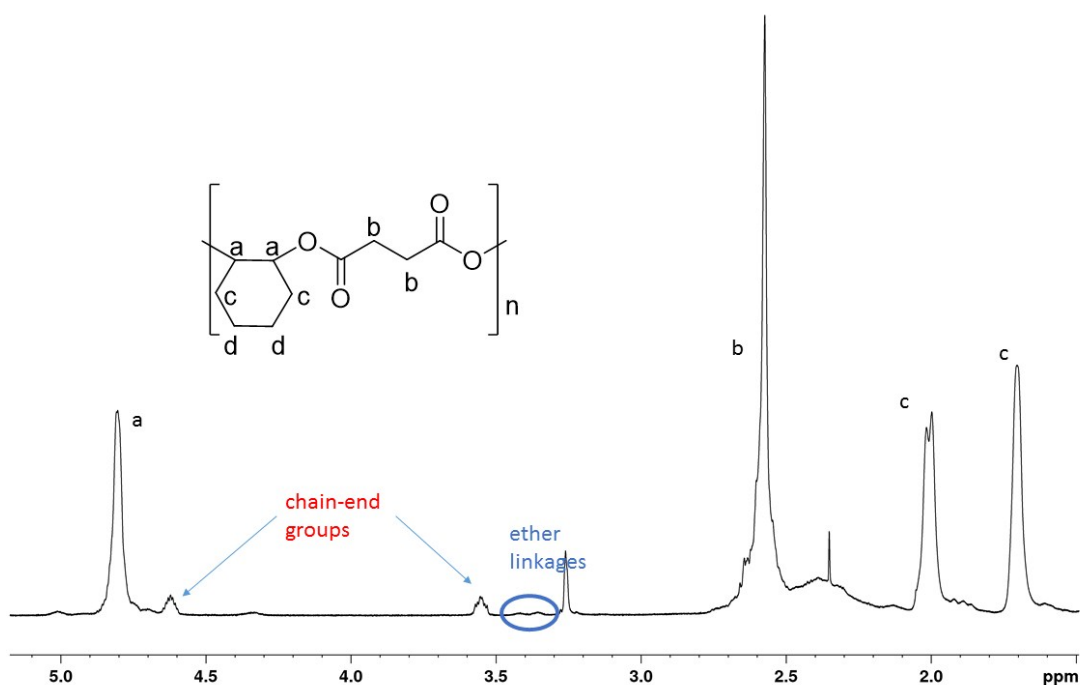
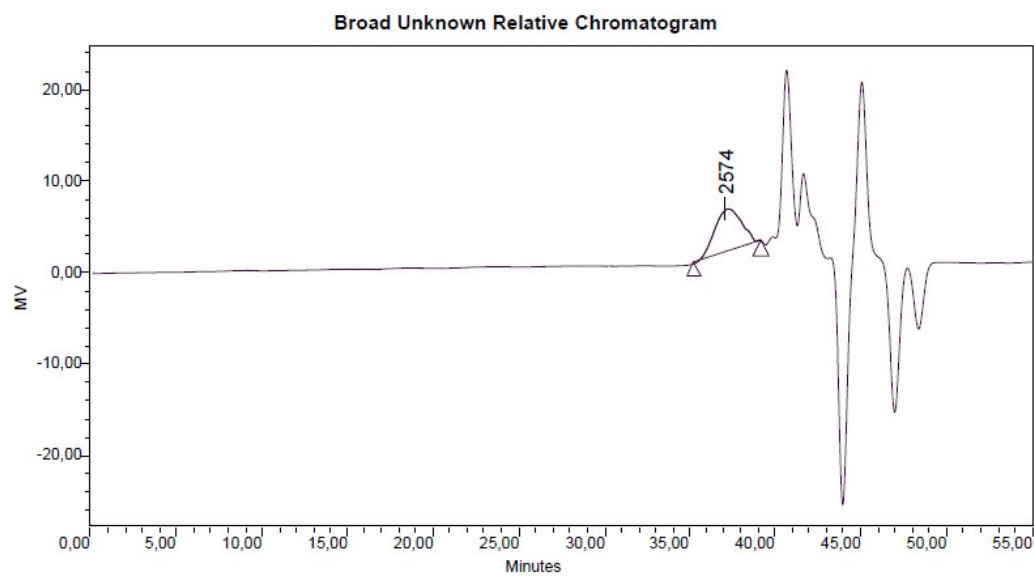


Figure S9. ^1H NMR spectrum (600 MHz, CDCl_3 , 298 K) of polyester CHO/SA synthesized by complex **2a**.



	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		2343	2547	2574	2752	2951	1,087028	1,080444	1,158420

Figure S10. GPC profile of polyester LO/PA by **2d** of $M_n = 2343$ Da (PDI = 1.09).

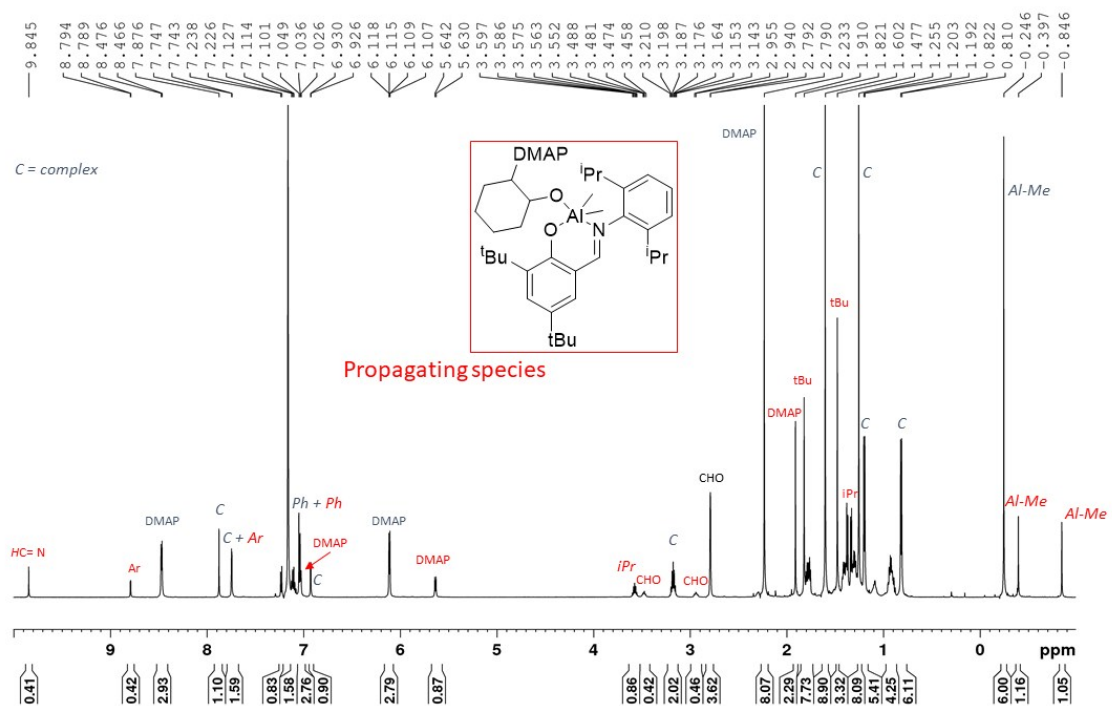


Fig. S11: ^1H NMR spectrum (400 MHz, C_6D_6 , 298 K) of complex **2b*** and **2b** with CHO and DMAP.

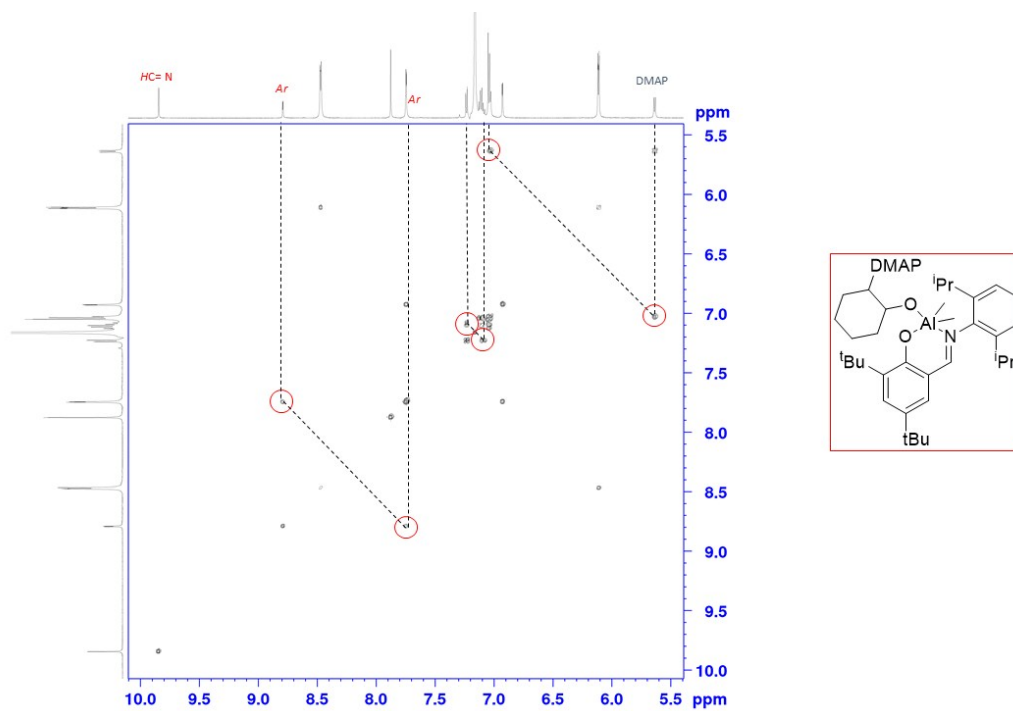


Fig. S12: ^1H - ^1H COSY, (400 MHz, C_6D_6 , 298 K) of complex **2b*** and **2b** with CHO and DMAP.

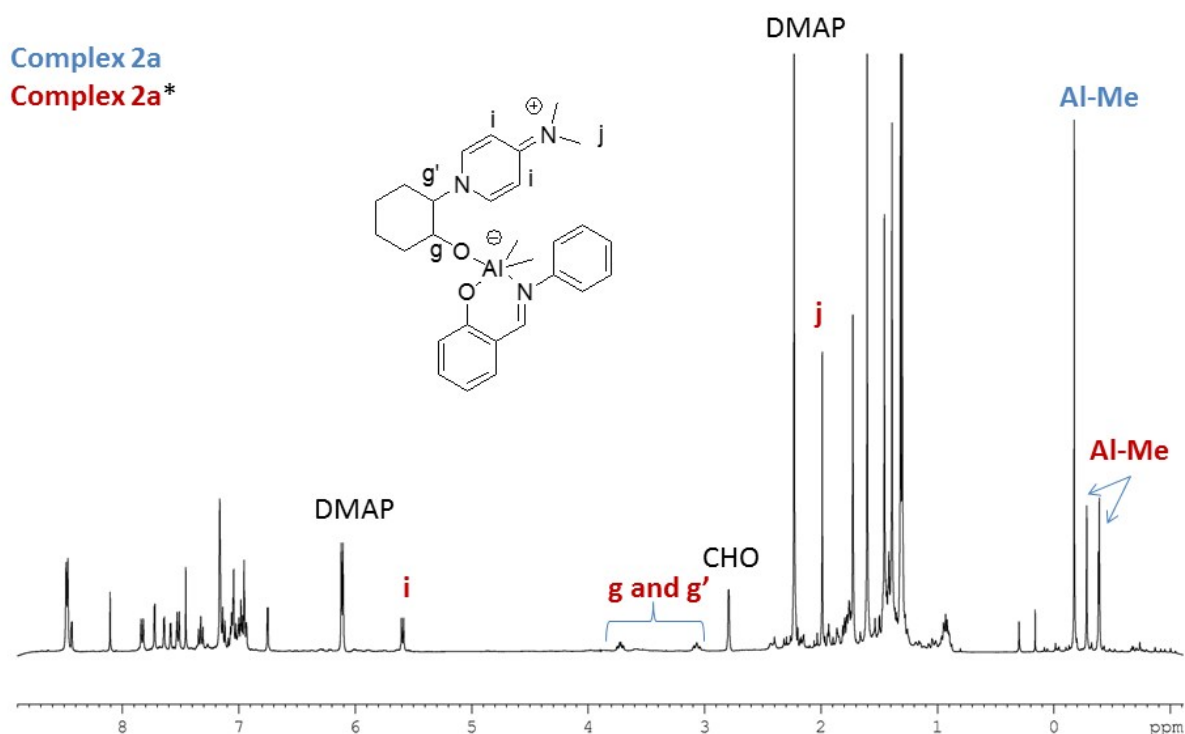


Fig. S13: ^1H NMR spectrum (400 MHz, C_6D_6 , 298 K) of complex **2a*** and **2a** with CHO and DMAP.

Detailed comments for the identification of the reaction intermediates **1*** and **1****

Initially, complex **1** (0.05 M in 0.5 mL of C_6D_6) was mixed with 1 equivalent of CHO and DMAP

After 1 hour at room temperature the spectrum of the mixture revealed to be a simple overlap of the spectra of the starting compounds. The resonances of DMAP and CHO, in the ^1H and ^{13}C NMR spectra, were coincident with those of the two compounds alone which could suggest the absence of interaction with the metal center (see Figure S14).

After heating of the reaction mixture for 12 h at 70 $^\circ\text{C}$, the formation of a different species (**1***) was observed. In which neither CHO and DMAP are involved. In the aromatic region of the ^1H NMR spectrum, three peaks, with equal intensity appeared close to the initial three peaks of the

starting complex **1** (see figure S15). In the high-field region, a singlet integrating for 1.5 protons (at -0.05 ppm), relative to hydrogen atoms of methyl groups bound to aluminum, was observed. The high symmetry of this species and the anomalous ratio between the signals of protons of the ligand moiety and the signals of the methyl groups bound to aluminum (1:1.5) suggested the formation of a multinuclear species, in agreement with the low steric encumbrance offered by the ancillary ligand and the propensity of aluminum to maximize its coordination number. Linear and/or cyclic oligomeric species, consisting of alternating aluminum and oxygen atoms, could be formed, as previously observed for products obtained by an incomplete hydrolysis of aluminum trialkyl species.

Additionally, the presence of a singlet at 0.15 ppm, indicative of the development of methane, suggested the partial hydrolysis of the aluminum-methyl bonds by the adventitious traces of water present or occurring into the sample.

The formation of this species was followed by NMR. After 12 hours the reaction resulted complete (Figures S15 and S16) since the signals of the starting complex disappeared almost completely (<5%). The experiment was repeated in the presence of two equivalents of DMAP, also in this case no opening of the monomer was achieved at room temperature, the DMAP was not coordinated. After heating at 70 °C, the complete conversion of complex **1** into species **1*** occurred within the same time.

After additional 6 hours at 70 °C, the ¹H NMR spectrum revealed the formation of a new species **1**** (Figure S17) and, after prolonged reaction time (5 days at 70 °C), the quantitative conversion of species **1*** into species **1**** was observed. The CHO and DMAP units appeared as free species, not coordinated at the metal center (Figure S17).

The ¹H NMR spectrum of species **1**** revealed to be very simple (figure S18); the full resonance assignment was obtained by following the scalar connectivity in 1D and 2D homo- and hetero-nuclear NMR experiments (¹H-¹H COSY, and ¹H-¹³C HSQC).

In the high-field region of the ¹H NMR spectrum, no signals attributable to methyl groups bound to aluminum were detected, suggesting the exhaustive hydrolysis of the aluminum-alkyl bonds. In the aliphatic region, in addition to the signals diagnostic of free DMAP, CHO and ^tBu groups, the methyl protons of the n-propyl group (H₆) were easily recognized as a triplet at $\delta = 0.53$ ppm (see

Figure S18). A set of four multiplets, attributable to four diastereotopic methylene protons of the n-propyl group were also identified ($H_{4,4'}$ and $H_{5,5'}$). This attribution was confirmed by COSY and HSQC spectra (Figure 6).

In the low field region of the protonic spectrum, two doublets for the aromatic protons and a singlet for the imine proton were observed. The ^{13}C NMR spectrum (see Figure S19) confirmed the absence of resonances attributable to Al-Me bonds.

All the spectral data are coherent with a rigid multinuclear (dimeric or tetrameric) structure of the type $(\text{L-AlO})_n$ ($n = 2$ or 4) in which the aluminum centers are bound via oxygen atom bridges. This species was reasonably formed by the exhaustive hydrolysis of aluminum-alkyl bonds of the species **1** by water that, progressively, could contaminate the sample.

The species **1** was purposely synthesized by adding the opportune amount of deuterated water to a benzene solution of complex **1**.

Initially, by adding sub-stoichiometric equivalents of D_2O to a solution of complex **1** in deuterated benzene, the species **1*** was obtained. After the addition of two equivalents of D_2O , within 10 min at 70°C , **1*** was quantitatively converted into the species **1****. The ^1H NMR spectrum was identical to that obtained by the previously described experiment (Figure S20) and showed the presence of a triplet for the deuterated methane (CH_3D). This confirmed the nature of the species **1****, and that DMAP and/or CHO do not have an active role in the production of this species.

The structure proposed for **1**** was also addressed through pulsed gradient spin-echo (PGSE) NMR spectroscopy. The diffusion coefficient of **1**** was determined by the 2D version of the PGSE experiment (DOSY, Diffusion Ordered Spectroscopy) in C_6D_6 solution, using the ligand (0.3 equivalents) as internal standard (Figure S21 of the SI). The diffusion coefficients of both species have been determined in analogue experiments with identical solvent viscosity and at the same temperature. Since the other parameters are identical, the size of the corresponding species can be compared based on their diffusion coefficients. The diffusion coefficients (D) can be related to the hydrodynamic radius (r) of the species in solution by the Stokes-Einstein equation (Equation 1) where T is the temperature, η is the viscosity of the solvent, r is the hydrodynamic radius of the molecule or assembly, and K is the Boltzmann constant.

Equation
$$D = \frac{KT}{6\pi\eta r}$$

The diffusion coefficient of the ligand was about the double of that evaluated for **1****. Since the other parameters are identical, the size of the corresponding species can be compared based on their diffusion coefficients (*D*) and the molecular masses in solution (*m*) were simply estimated using Graham's law of diffusion: $D = K(T/m)^{1/2}$, where the constant *K* depends on geometric factors, including the area over which the diffusion is occurring. By assuming a constant temperature and that *K* is the same for both species in solution, the molecular mass of **1**** (*m*_{1**}) was easily obtained by the following equation: $D_L/D_{1b} = (m_{1**}/m_L)^{1/2}$

This allows the calculation of the molecular mass unknown species **1****. This method is useful when it is not required a highly accurate value for the molecular mass or when the structures of the studied complexes are far from the spherical one, thus precluding a straightforward application of the Stokes–Einstein equation.

The experimentally determined values of *D* and MM for the ligand and **1**** are listed in Table S1.

Table S1 Diffusion coefficient (*D*), estimated molecular mass (*M*) for the dimer (L-*Al-O*)₂ and the tetramer species (L-*Al-O*)₄ and calculated molecular mass (*F*).

Species	<i>D</i> (x 10 ⁹ m ² s ⁻¹)	<i>M</i> (Da)	<i>F</i> (Da)
L	1.97	275.44	275.44
(L- <i>Al-O</i>) ₂			634.38
(L- <i>Al-O</i>) ₄	0.858	1449	1268.77

The optimal agreement between the molecular mass (*M*) and the value calculated (*F*) for the tetramer (L-*AlO*)₄ supported the hypothesis that **1**** was a discrete tetrameric species.

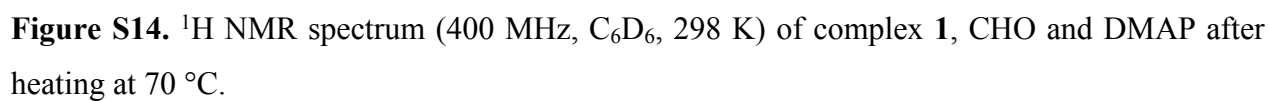


Figure S15. ^1H NMR spectrum (600 MHz, C_6D_6 , 298 K) of species **1***, in the presence of CHO and DMAP.

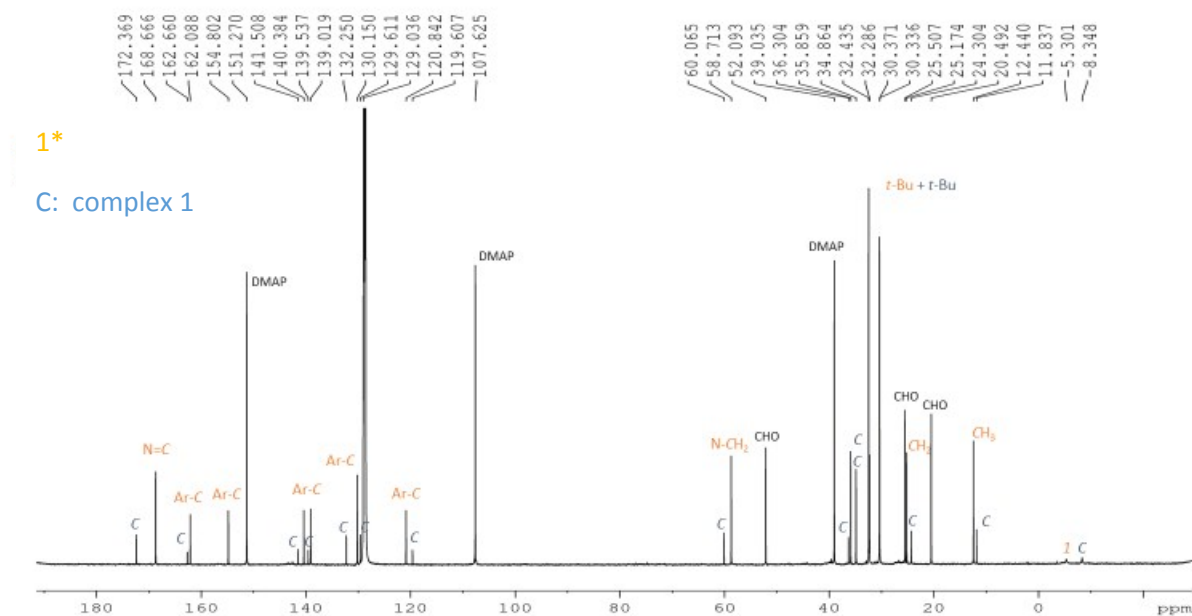


Figure S16. ^{13}C NMR spectrum (150 MHz, C_6D_6 , 298 K) of species **1***, in the presence of CHO and DMAP.

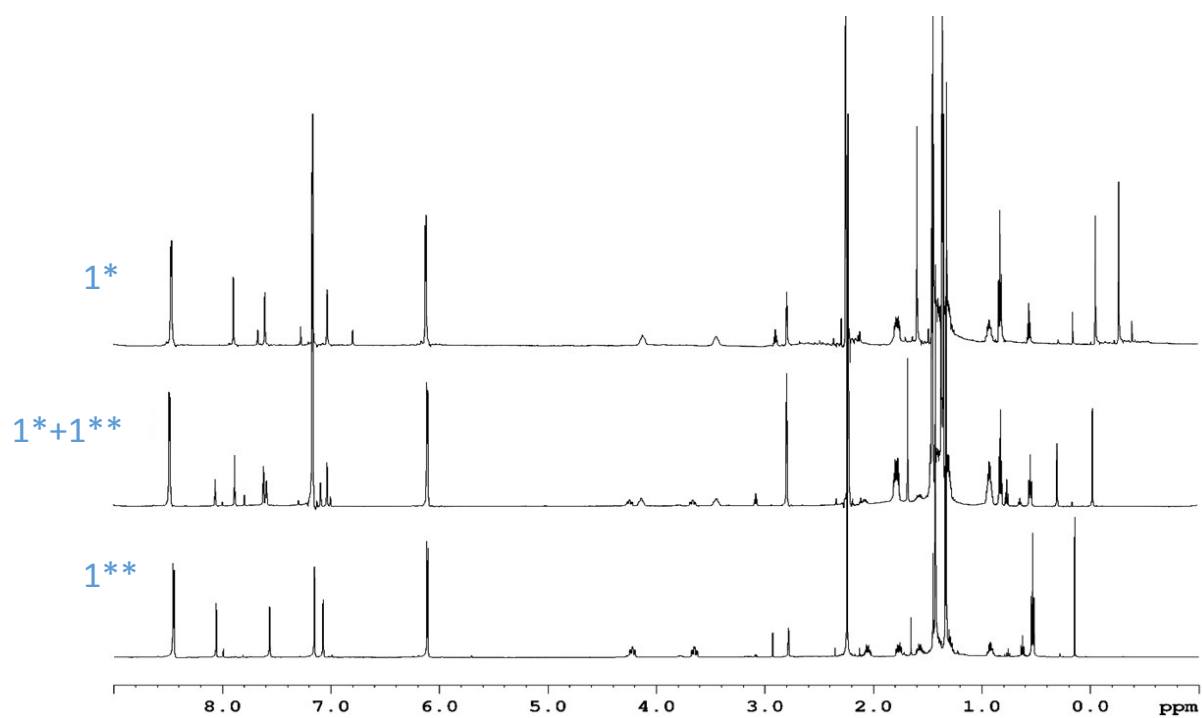


Figure S17. ^1H NMR spectrum (600 MHz, C_6D_6 , 298 K) of the evolution of complex **1**, CHO and DMAP after heating at 70 °C.

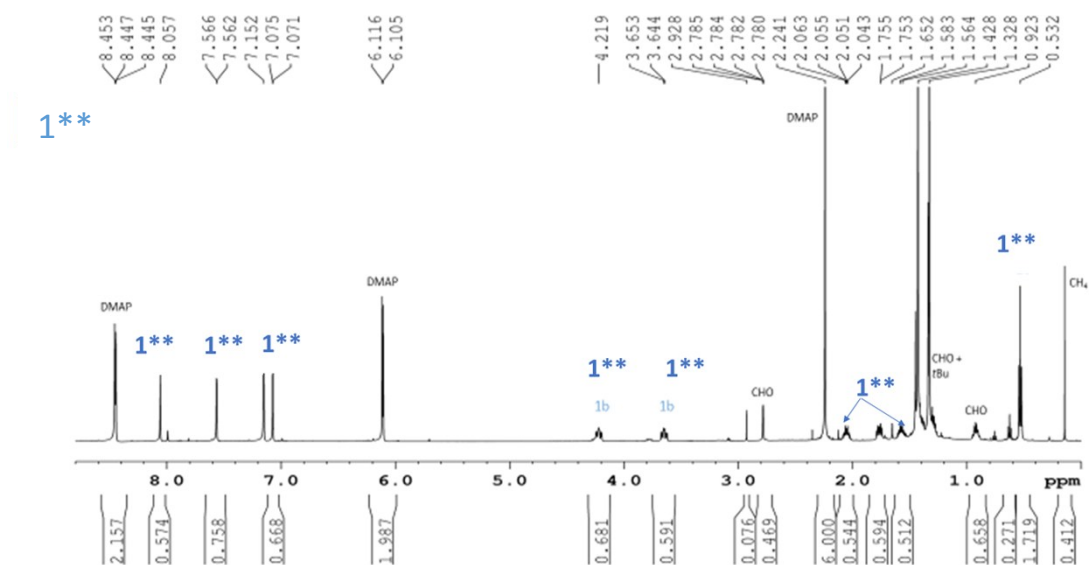


Figure S18. ^1H NMR spectrum (600 MHz, C_6D_6 , 298 K) of species **1****, in the presence of CHO and DMAP.

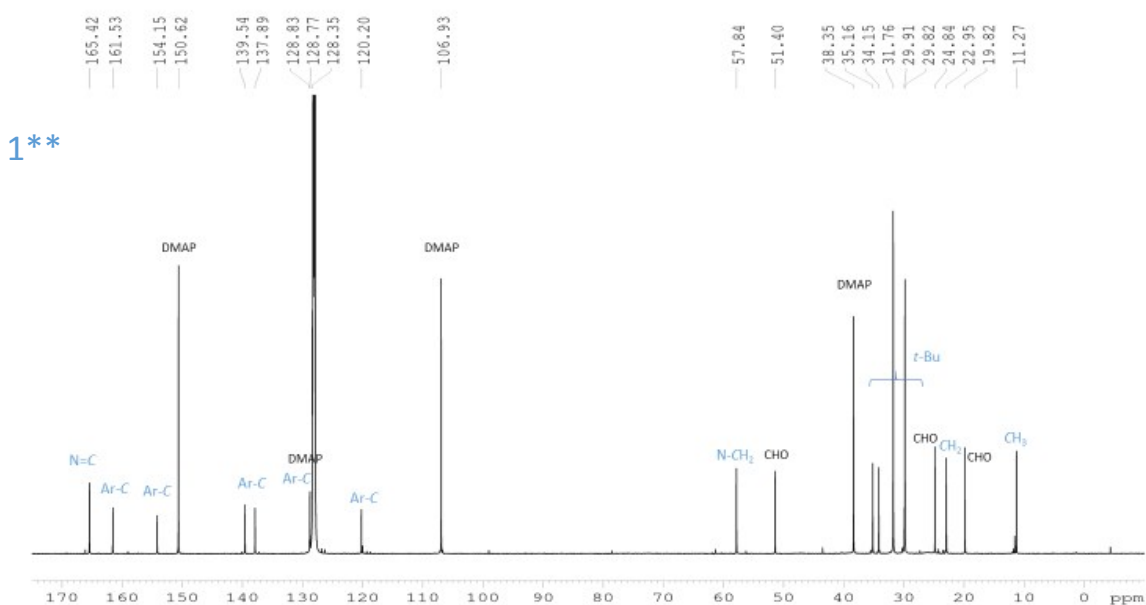


Figure S19. ^{13}C NMR spectrum (150 MHz, C_6D_6 , 298 K) of species **1****, in the presence of CHO and DMAP.

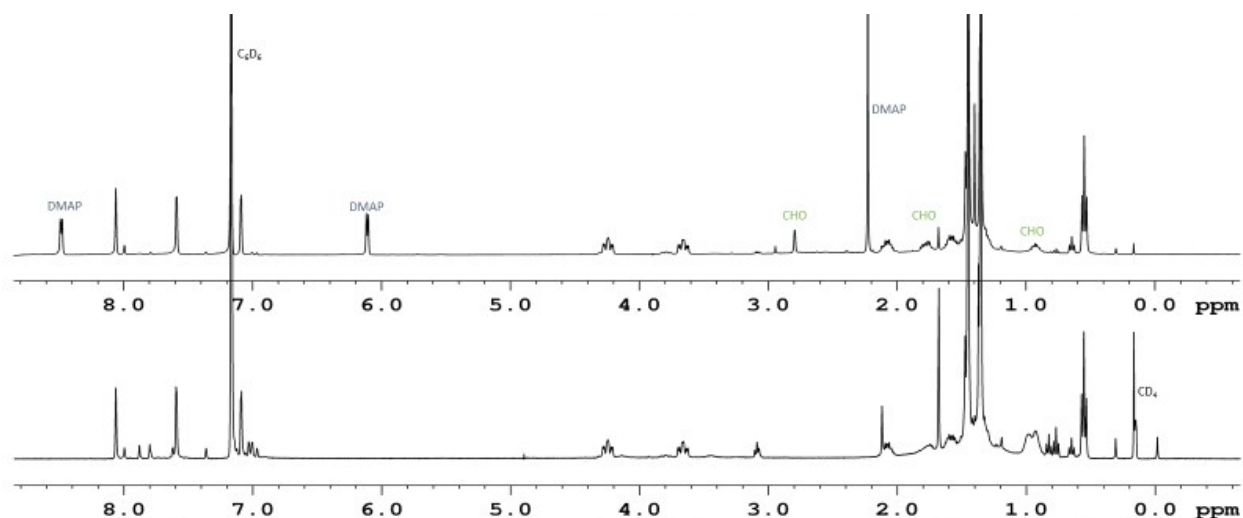


Figure S20. ^1H NMR spectra (600 MHz, C_6D_6 , 298 K) of species **1****. Up: From heating in the presence of CHO and DMAP. Down: From hydrolysis with D_2O .

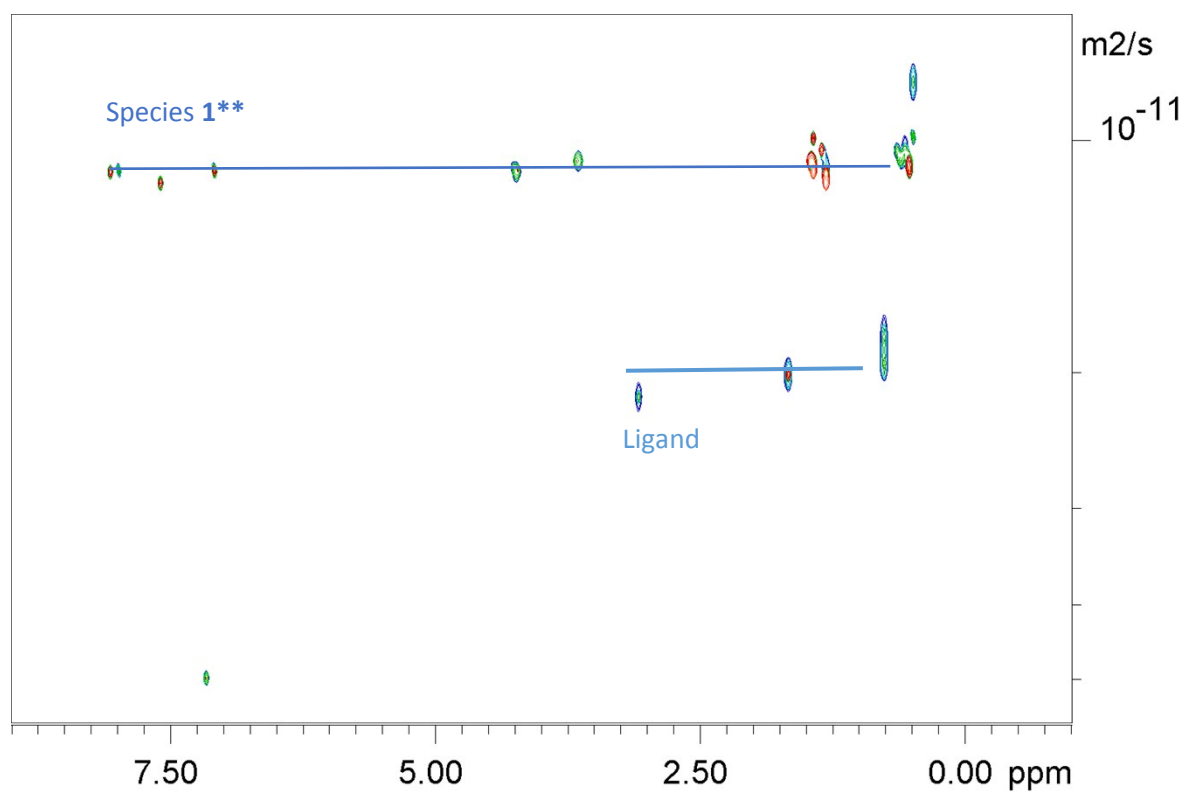


Figure S21. ^1H DOSY spectrum (600 MHz, C_6D_6 , 298 K) of species **1**** in presence of the respective ligand.

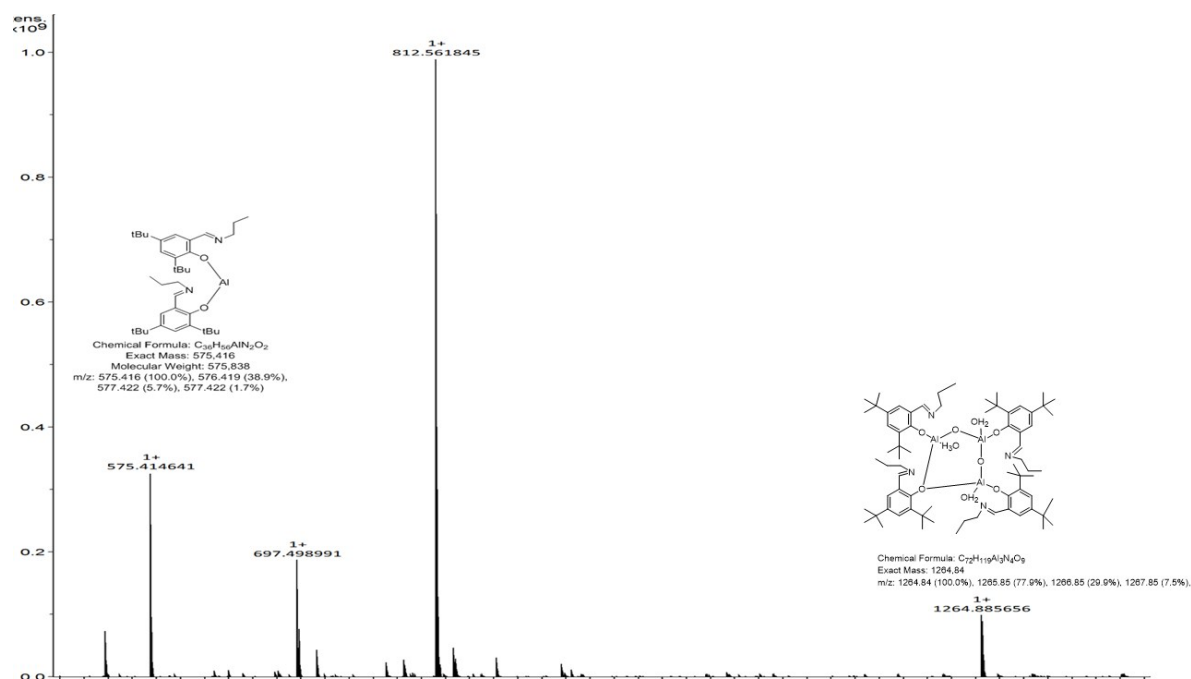


Figure S22. ESI spectrum in CH_2Cl_2 dry of species **1**** (derived from hydrolysis with D_2O).

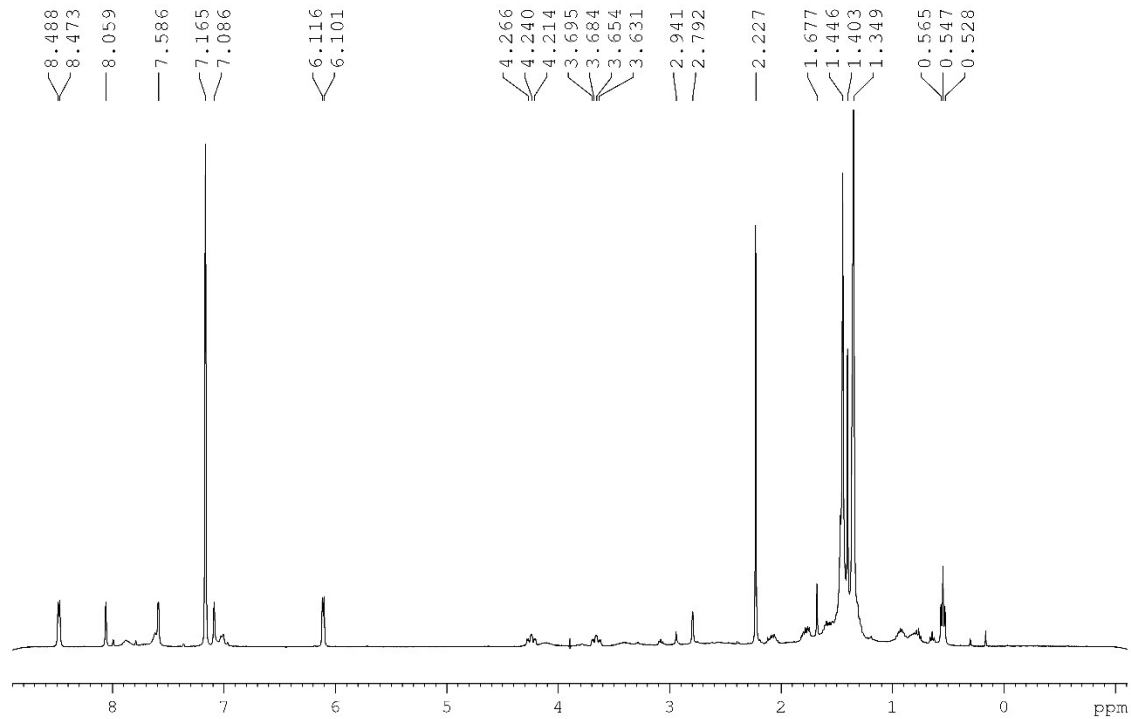


Figure S23. 1H NMR spectrum (400 MHz, C_6D_6 , 298 K) of **[1**]:[DMAP]:[CHO]:[SA] = 1:1:1:1**.

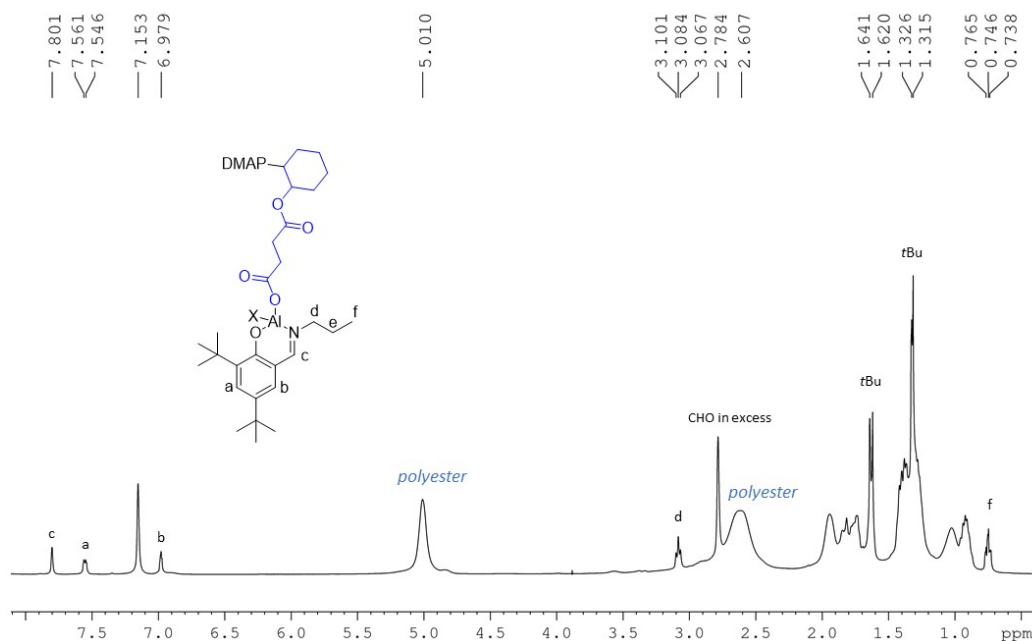


Figure S24. ^1H NMR spectrum (400 MHz, C_6D_6 , 298 K) of **1**** after reaction with 6 equivalents of both monomers

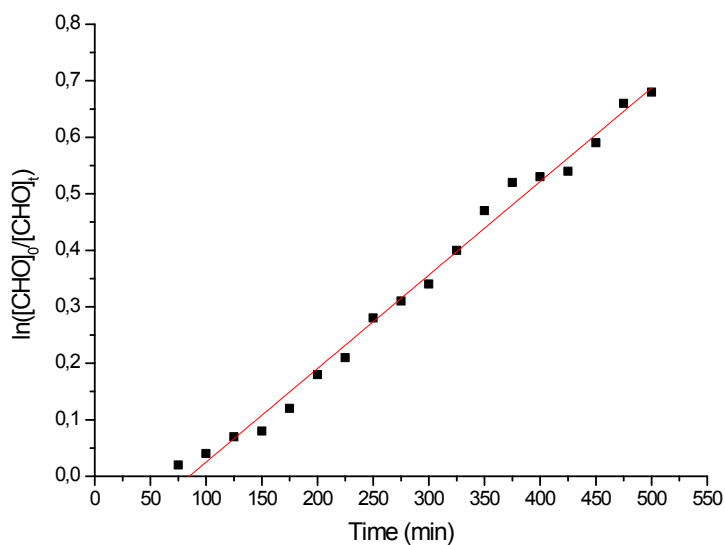


Figure S25 Linear fit depicting a reaction order of unity with respect to monomer concentration

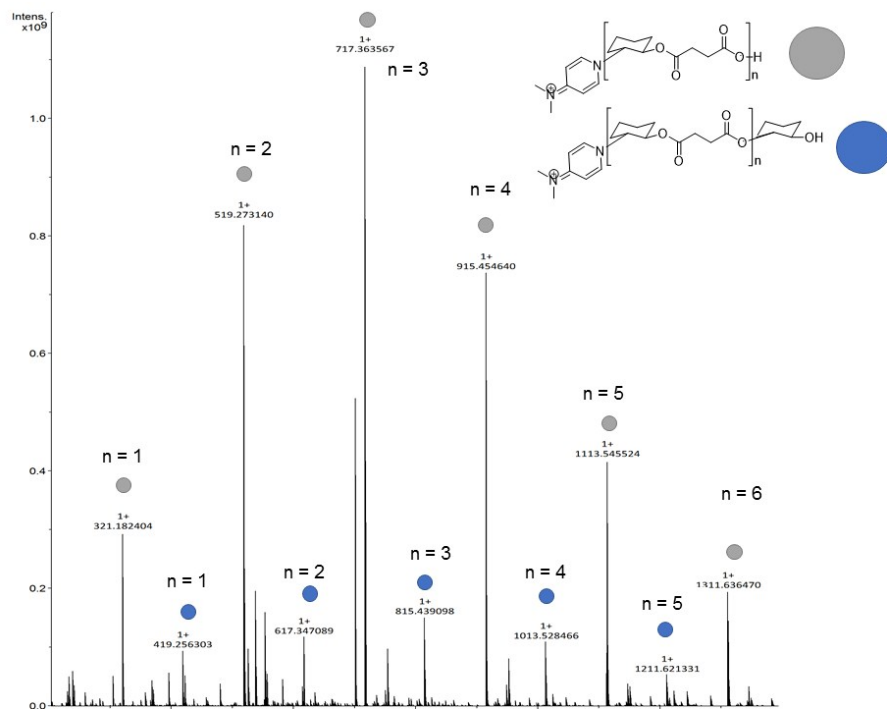
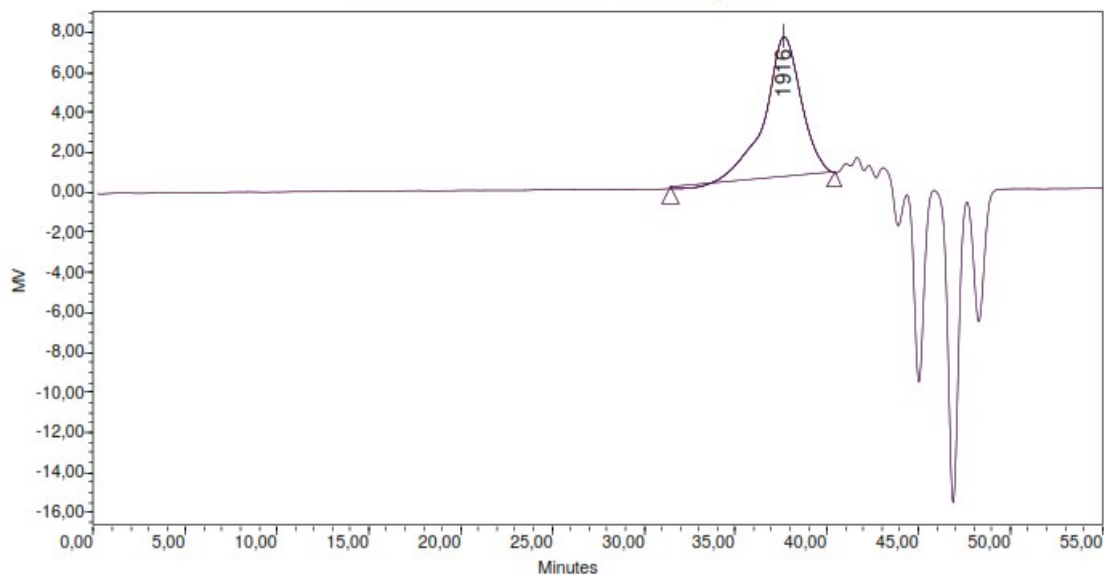


Figure. S26: Maldi TOF of the polyester obtained by 1**

SAMPLE INFORMATION

Sample Name:	FS-8	Acquired By:	System
Sample Type:	Broad Unknown	Date Acquired:	18/05/2016 2.40.49
Vial:	16	Acq. Method:	MG_F1A_RI35C
Injection #:	1	Date Processed:	18/05/2016 9.29.44
Injection Volume:	100,00 ul	Channel Name:	410
Run Time:	55,00 Minutes	Channel Desc.:	RI Detector
Column Type:		Sample Set Name:	SampleSet_17Maggio2016

Broad Unknown Relative Chromatogram



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		1861	2293	1916	2921	3754	1,232203	1,273717	1,637066

Figure. S27: GPC trace of sample obtained by entry 5 Table 2

Dipartimento di Chimica

Project Name: Mariagrazia

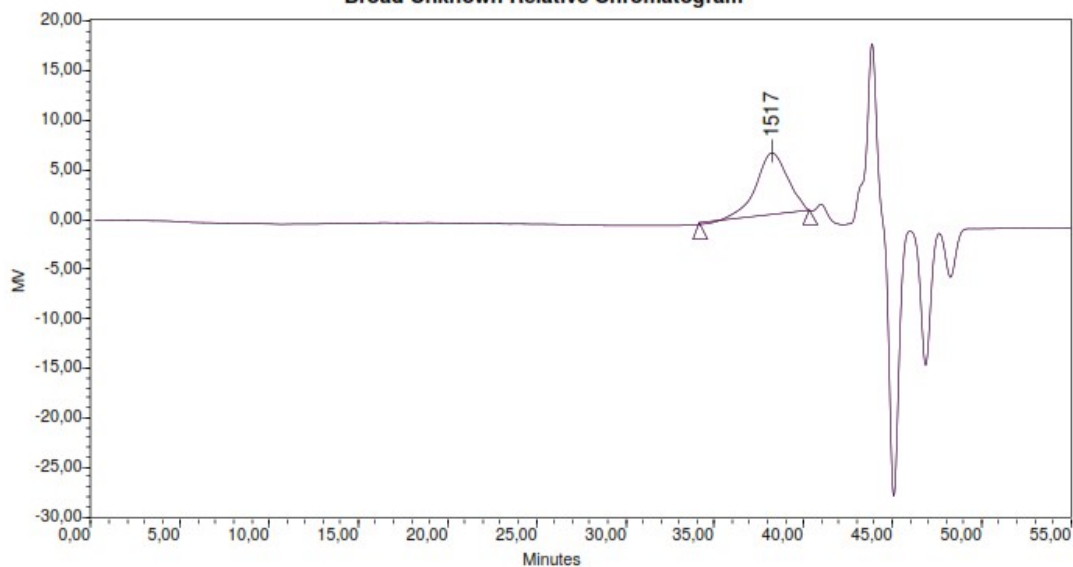
Reported by User: System

Breeze

SAMPLE INFORMATION

Sample Name:	FS 20	Acquired By:	System
Sample Type:	Broad Unknown	Date Acquired:	29/06/2016 12.37.18
Vial:	23	Acq. Method:	MG_F1A_RI35C
Injection #:	1	Date Processed:	29/06/2016 14.46.48
Injection Volume:	100,00 ul	Channel Name:	410
Run Time:	55,00 Minutes	Channel Desc.:	RI Detector
Column Type:		Sample Set Name:	SampleSet_28_6_16

Broad Unknown Relative Chromatogram



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		1450	1686	1517	1992	2376	1,163060	1,181505	1,408995

Figure. S28: GPC trace of sample obtained by entry 8 Table 2

References.

- [1] F. Isnard, M. Lamberti, L. Lettieri, I. D'auria, K. Press, R. Troiano and M. Mazzeo, *Dalton Trans.*, **2016**, 45, 16001-16010.
- [2] M. Lamberti, I. D'Auria, M. Mazzeo, S. Milione, V. Bertolasi, and D. Pappalardo, *Organometallics*, **2012**, 31 (15), 5551–5560.