Electronic Supplementary Information (ESI)

for

Heteroleptic phenoxyimino tin(II) *bis*(trimethylsilyl)amides for the synthesis of poly(diester-*alt*-ethers) from cyclohexene oxide and succinic anhydride

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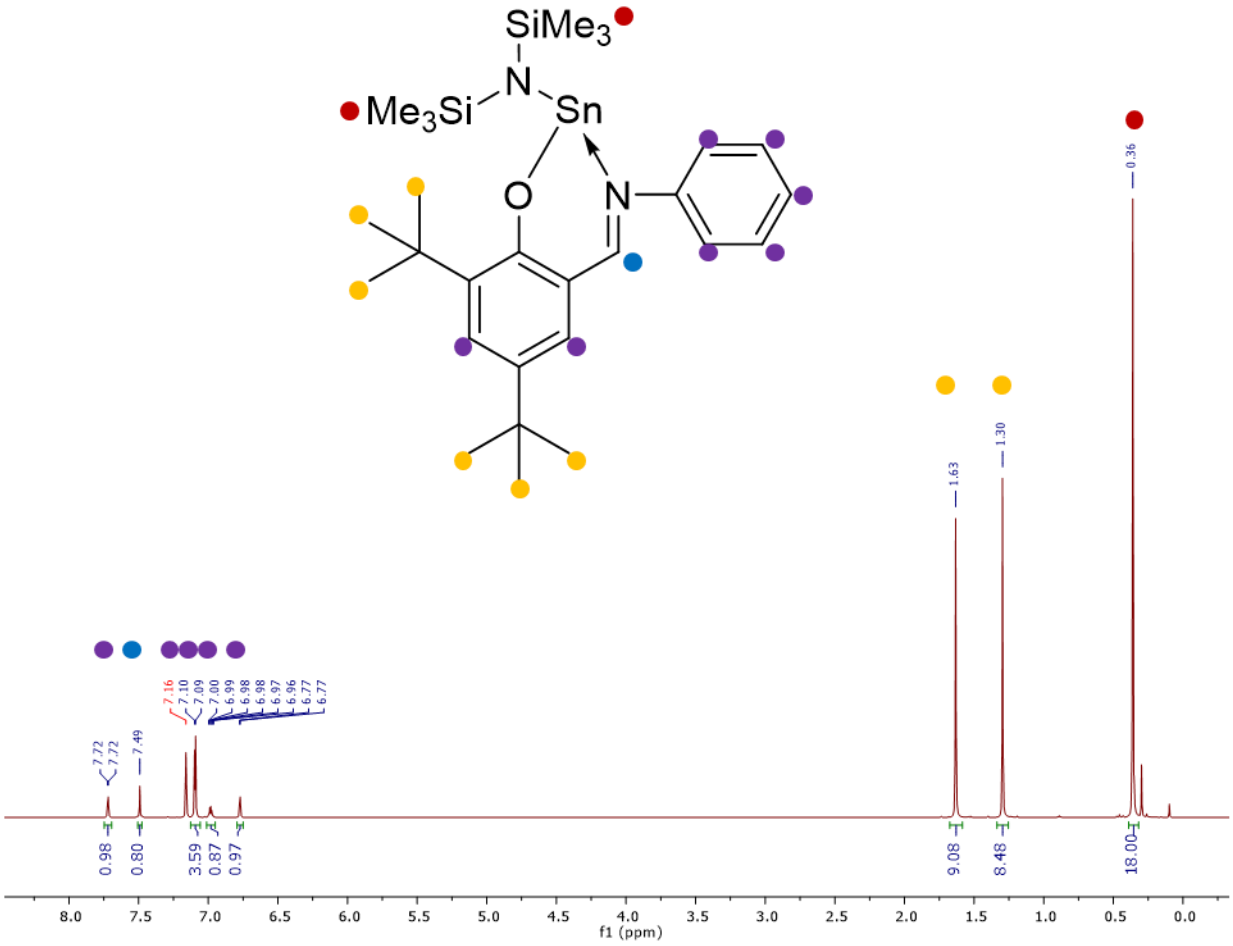


Fig. S1 ^{1}H NMR spectrum (600 MHz, C_6D_6, 30 °C) of Catalyst **1**.

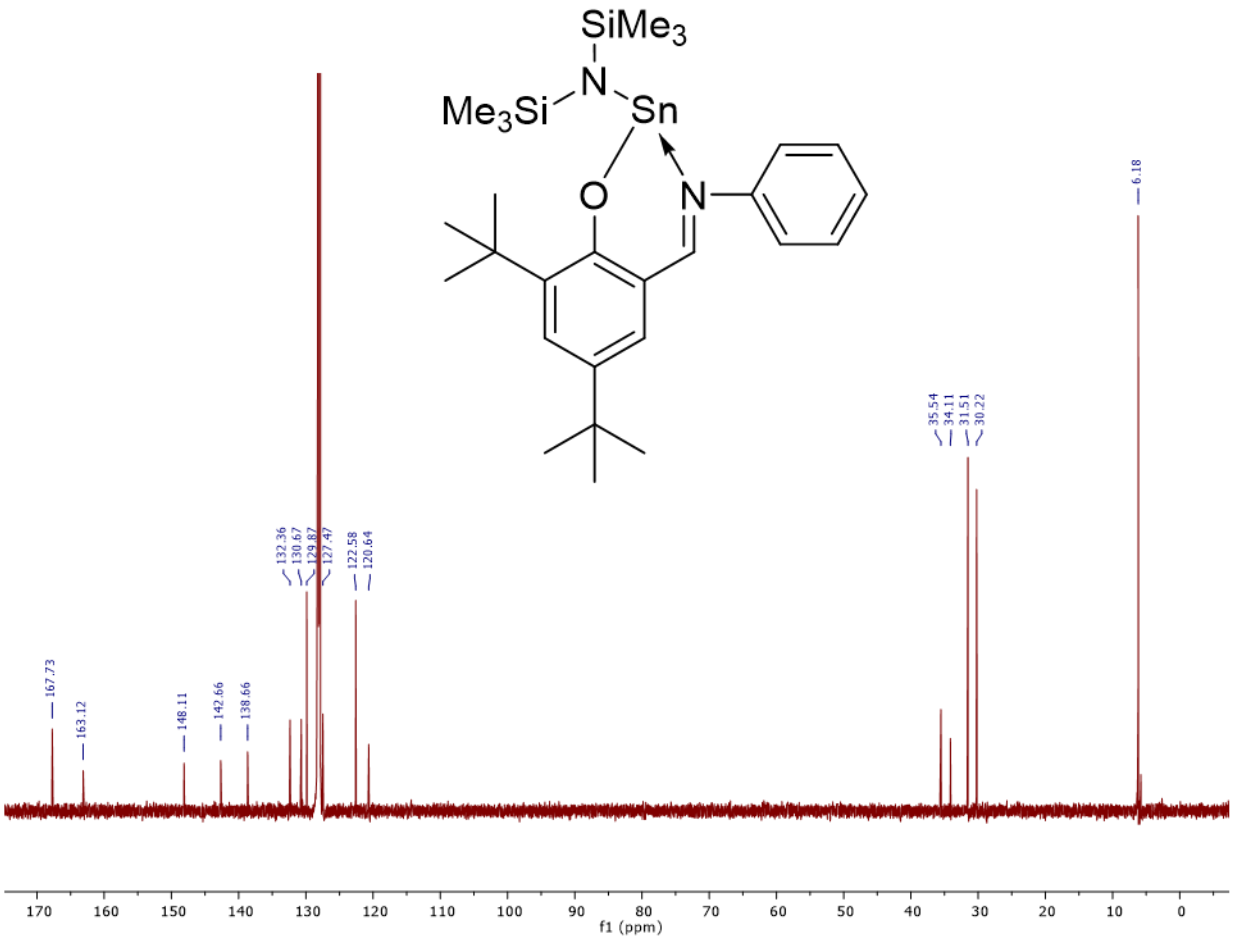


Fig. S2 ^{13}C NMR spectrum (150 MHz, C_6D_6, 30 °C) of Catalyst **1**.

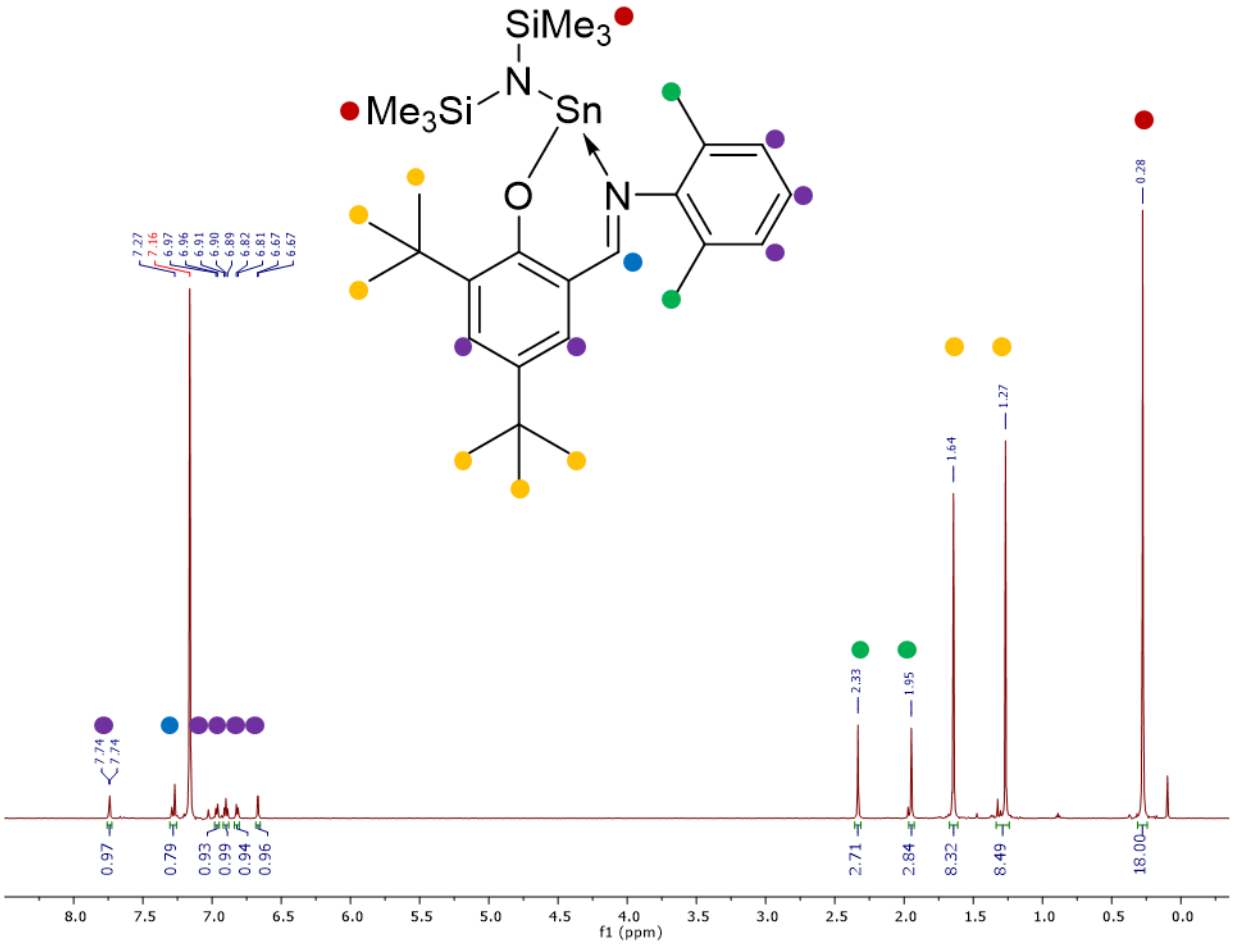


Fig. S3 ^{1}H NMR spectrum (600 MHz, C_6D_6, 30 °C) of Catalyst **2**.

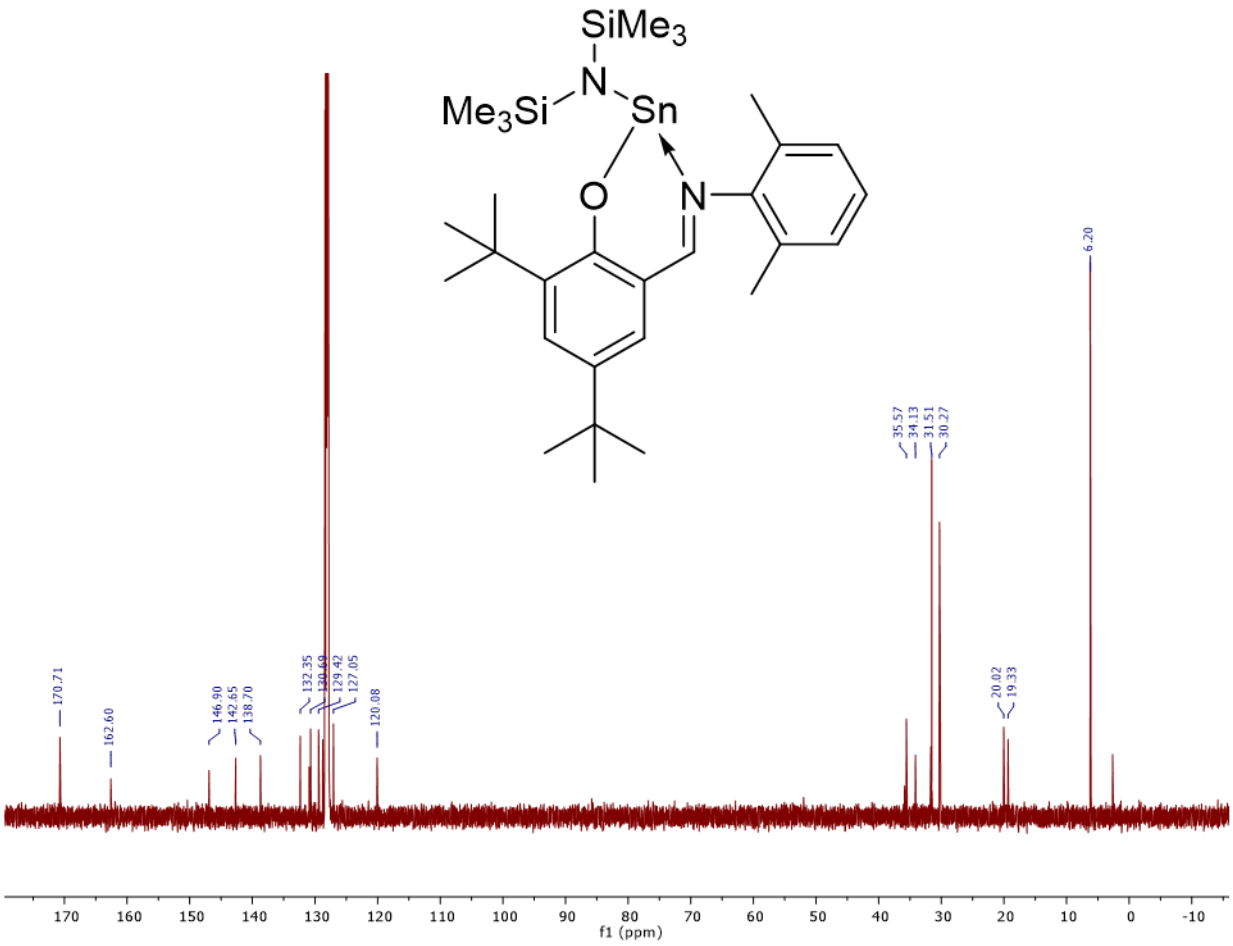


Fig. S4 ^{13}C NMR spectrum (150 MHz, C_6D_6, 30 °C) of Catalyst **2**.

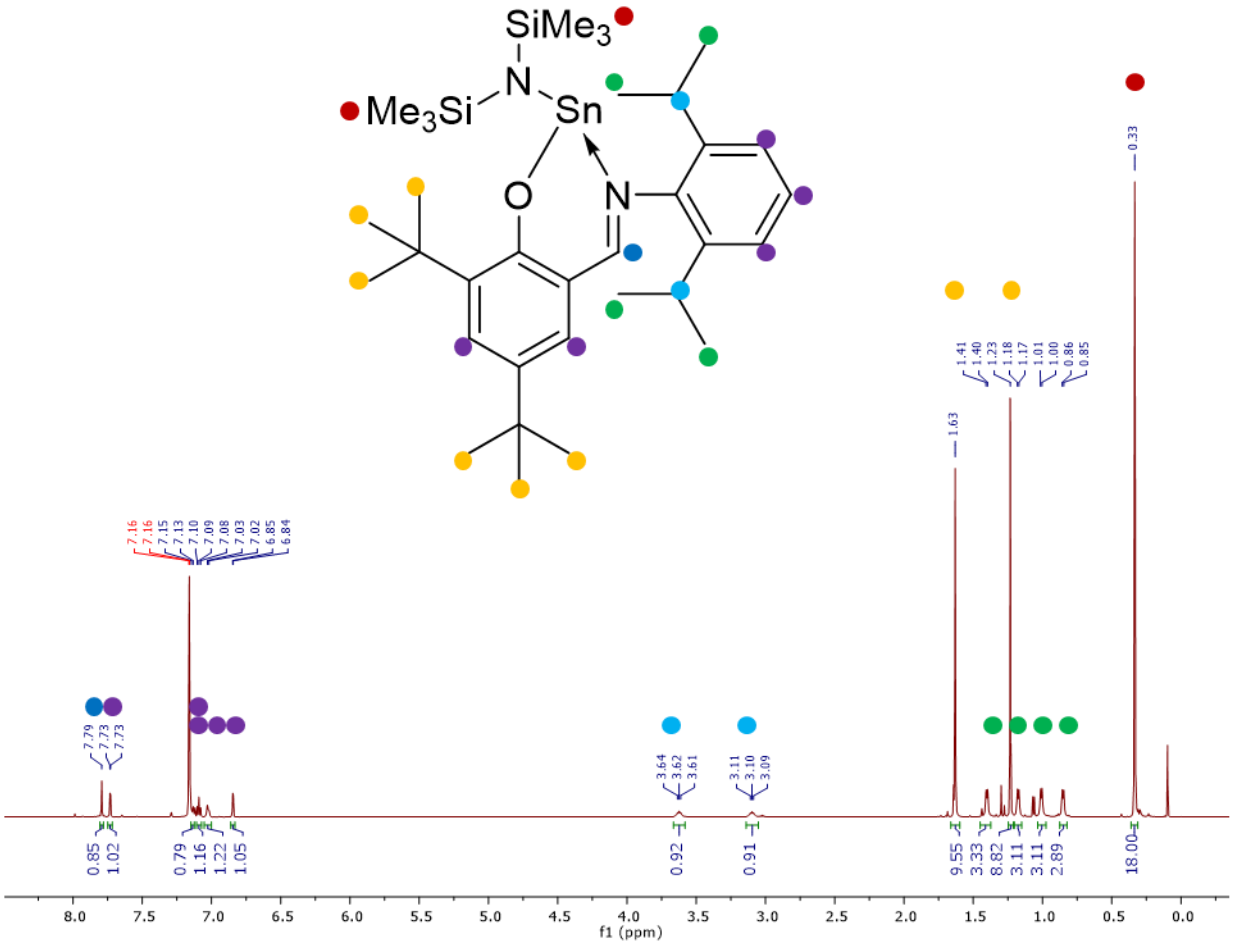


Fig. S5 ^{1}H NMR spectrum (600 MHz, C_6D_6, 30 °C) of Catalyst **3**.

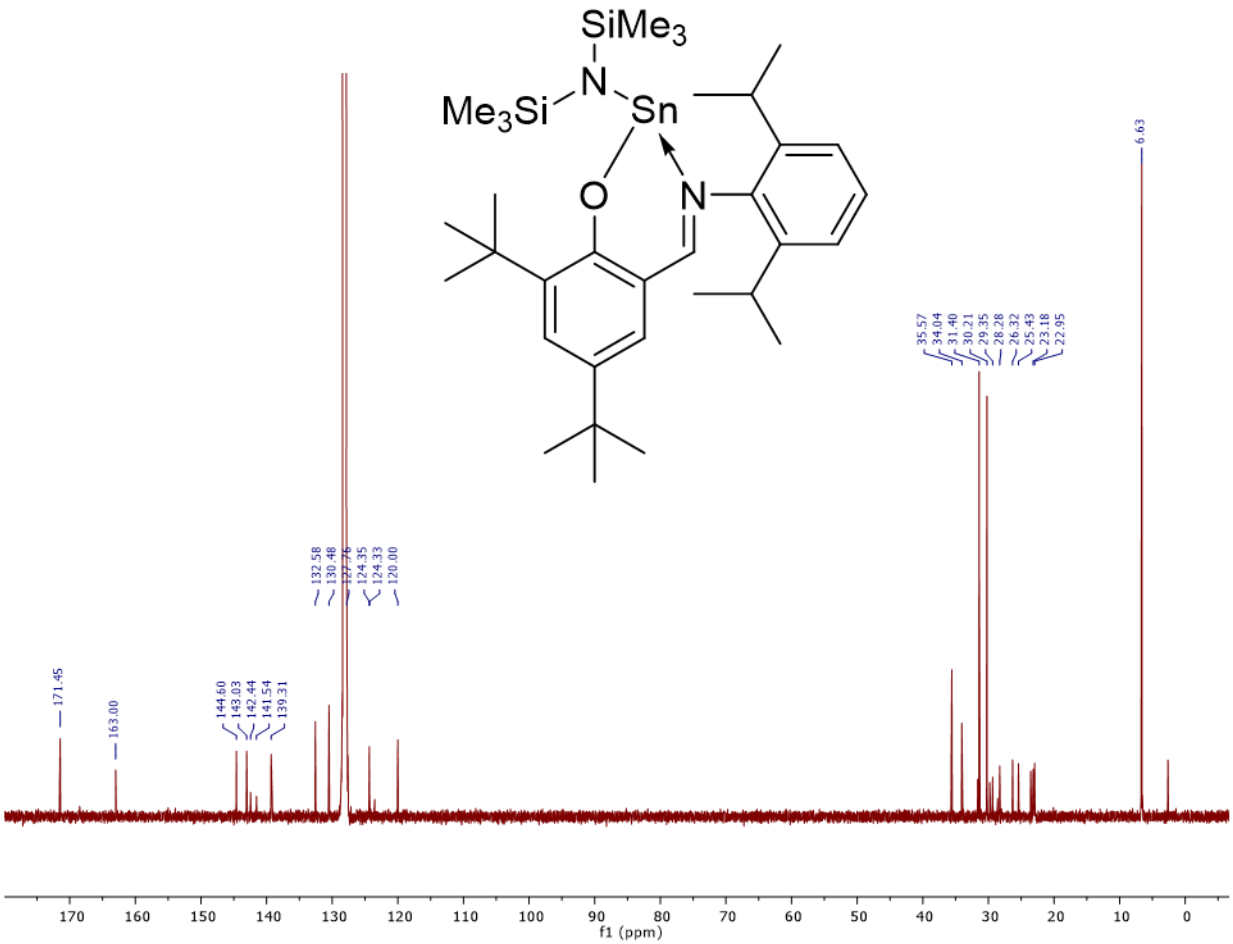


Fig. S6 ^{13}C NMR spectrum (150 MHz, C_6D_6, 30 °C) of Catalyst **3**.

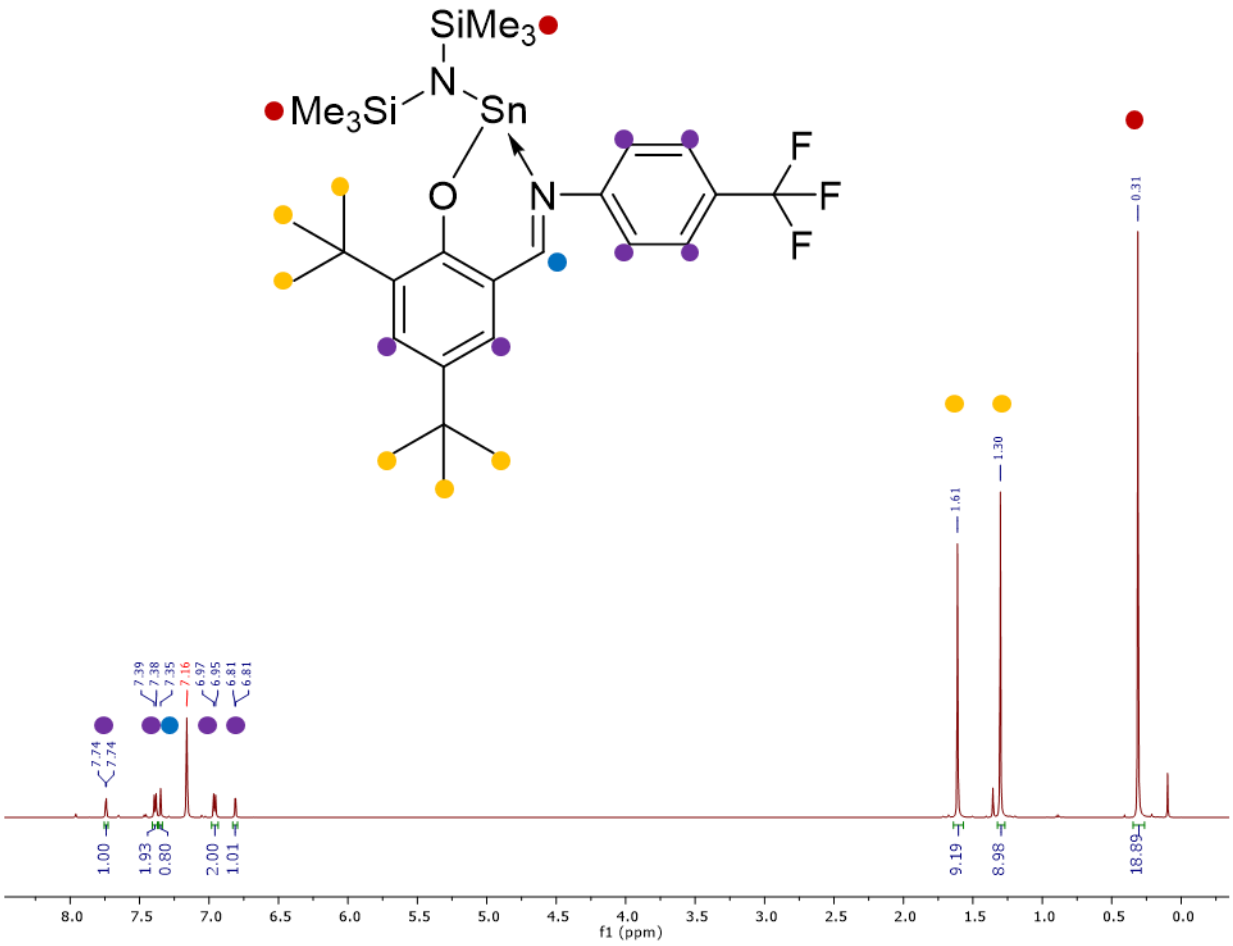


Fig. S7 ^{1}H NMR spectrum (600 MHz, C_6D_6, 30 °C) of Catalyst **4**.

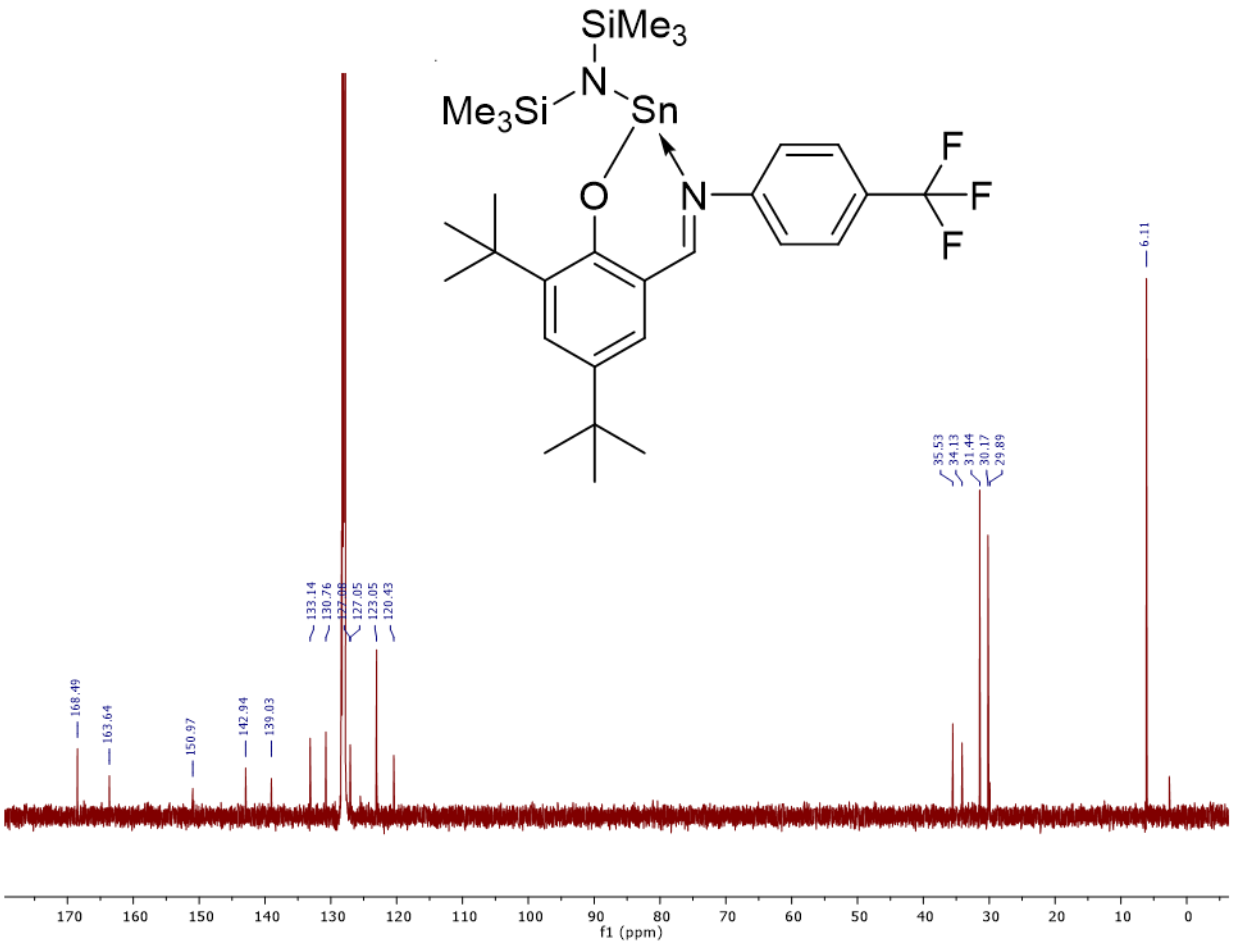


Fig. S8 ^{13}C NMR spectrum (150 MHz, C_6D_6, 30 °C) of Catalyst **4**.

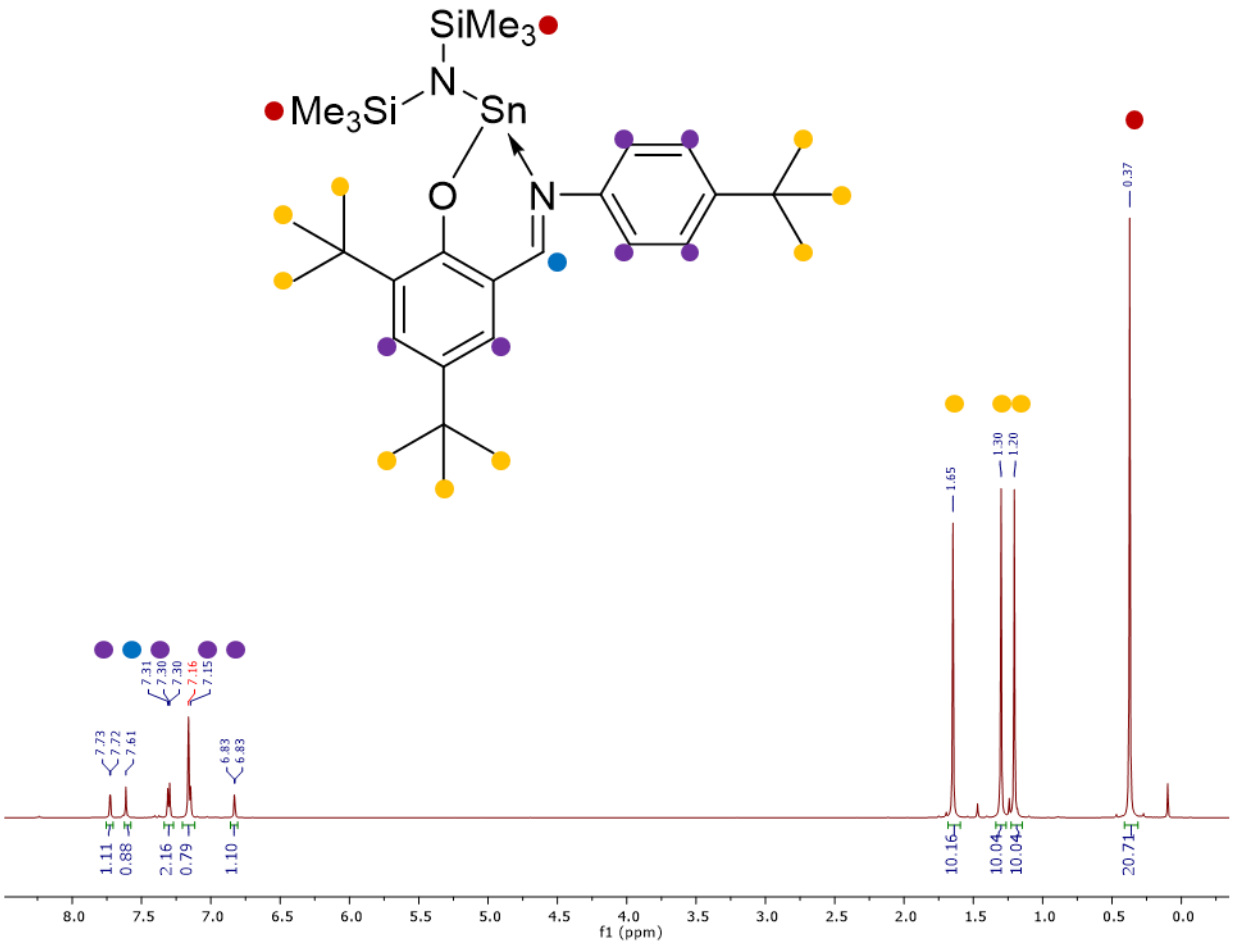


Fig. S9 ^{1}H NMR spectrum (600 MHz, C_6D_6, 30 °C) of Catalyst **5**.

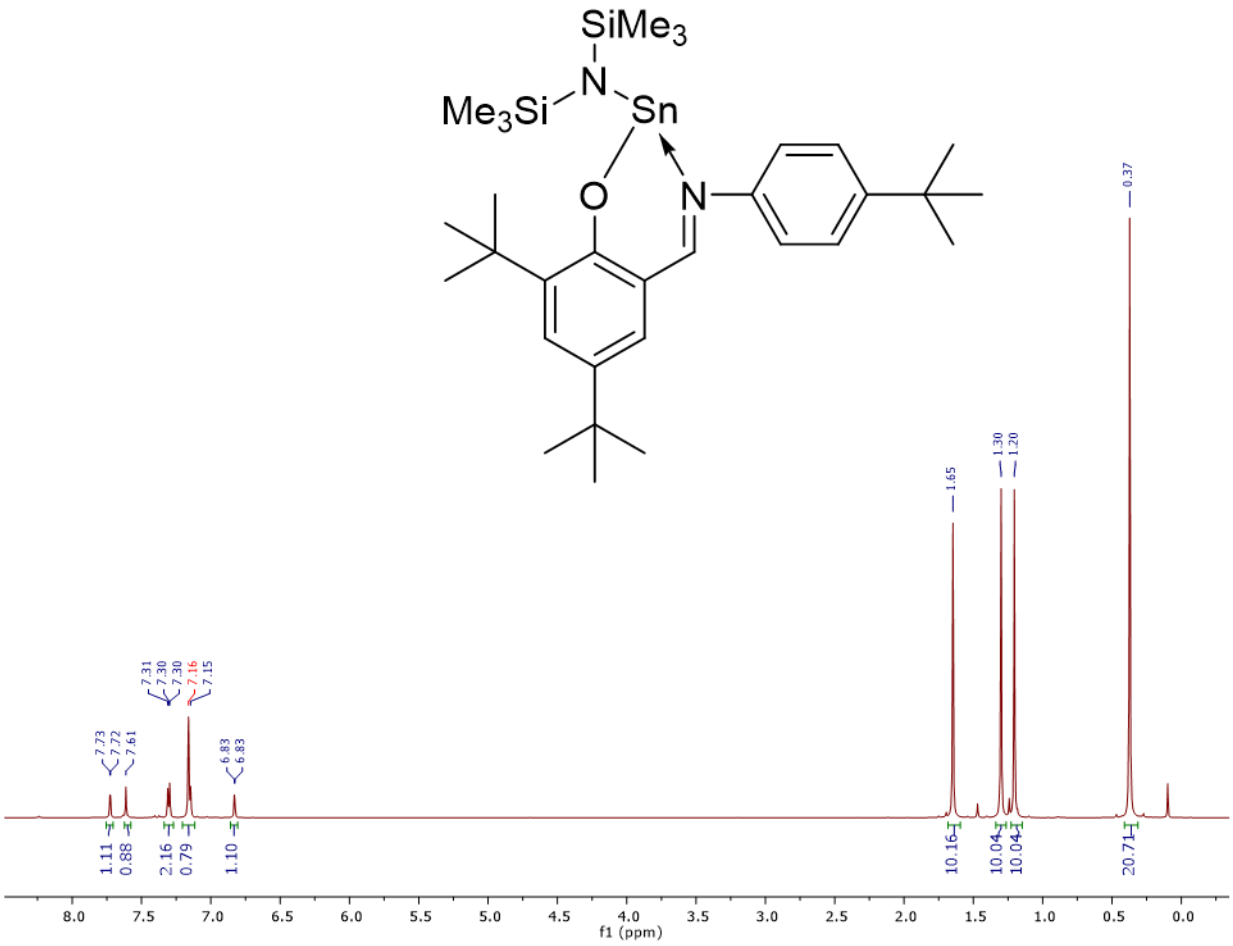


Fig. S10 ^{13}C NMR spectrum (150 MHz, C_6D_6, 30 °C) of Catalyst **5**.

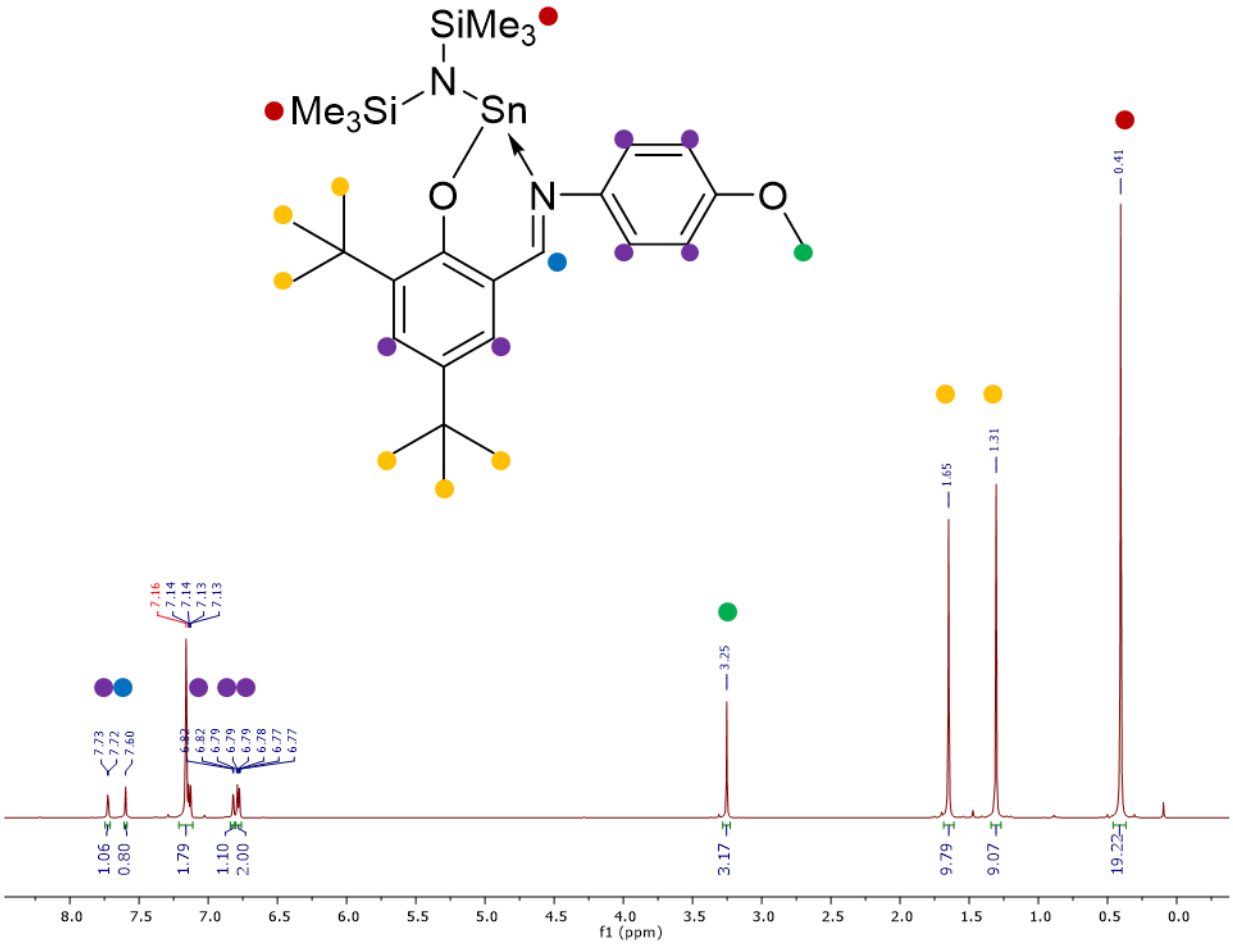


Fig. S11 ^{1}H NMR spectrum (600 MHz, C_6D_6, 30 °C) of Catalyst **6**.

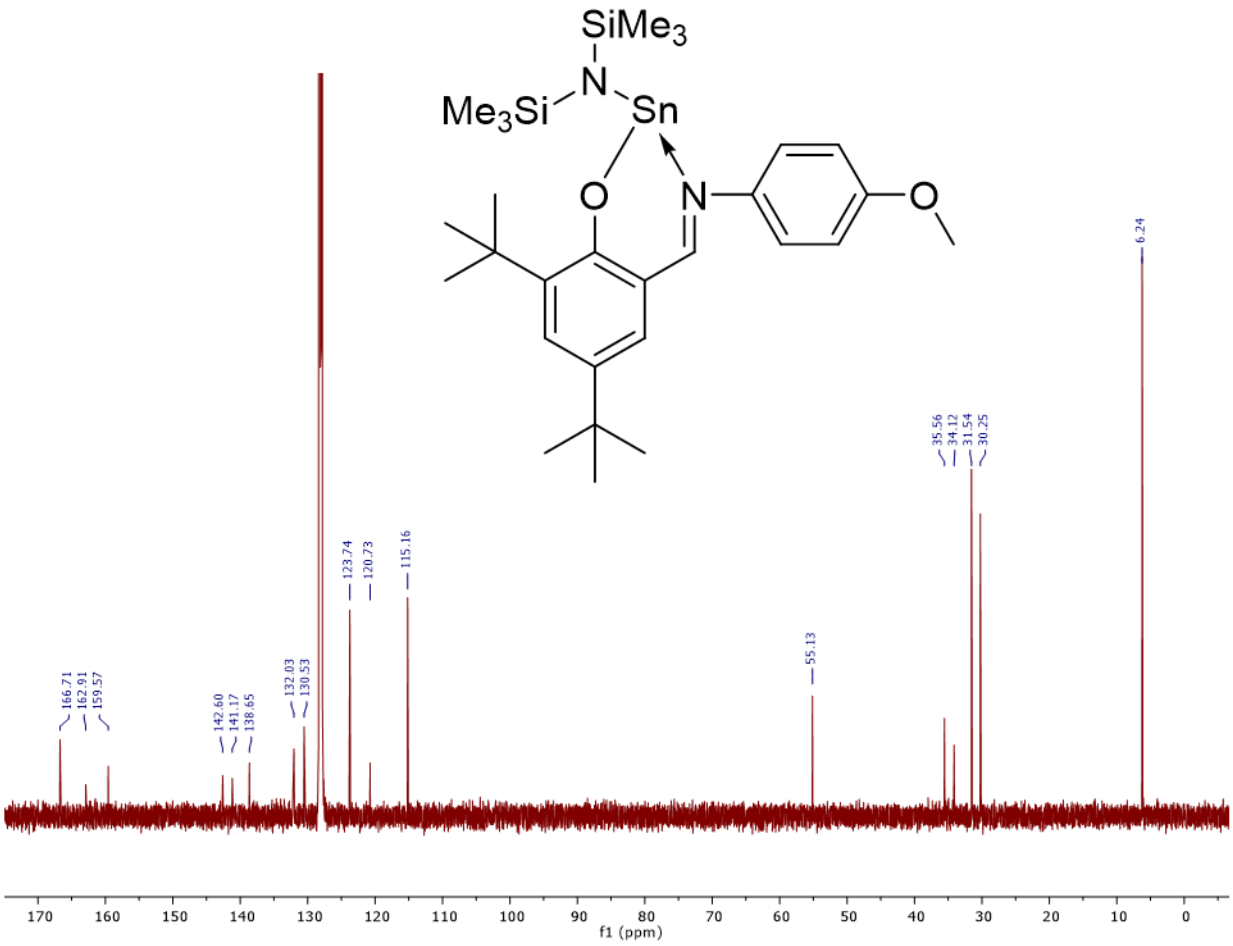


Fig. S12 ^{13}C NMR spectrum (150 MHz, C_6D_6, 30 °C) of Catalyst **6**.

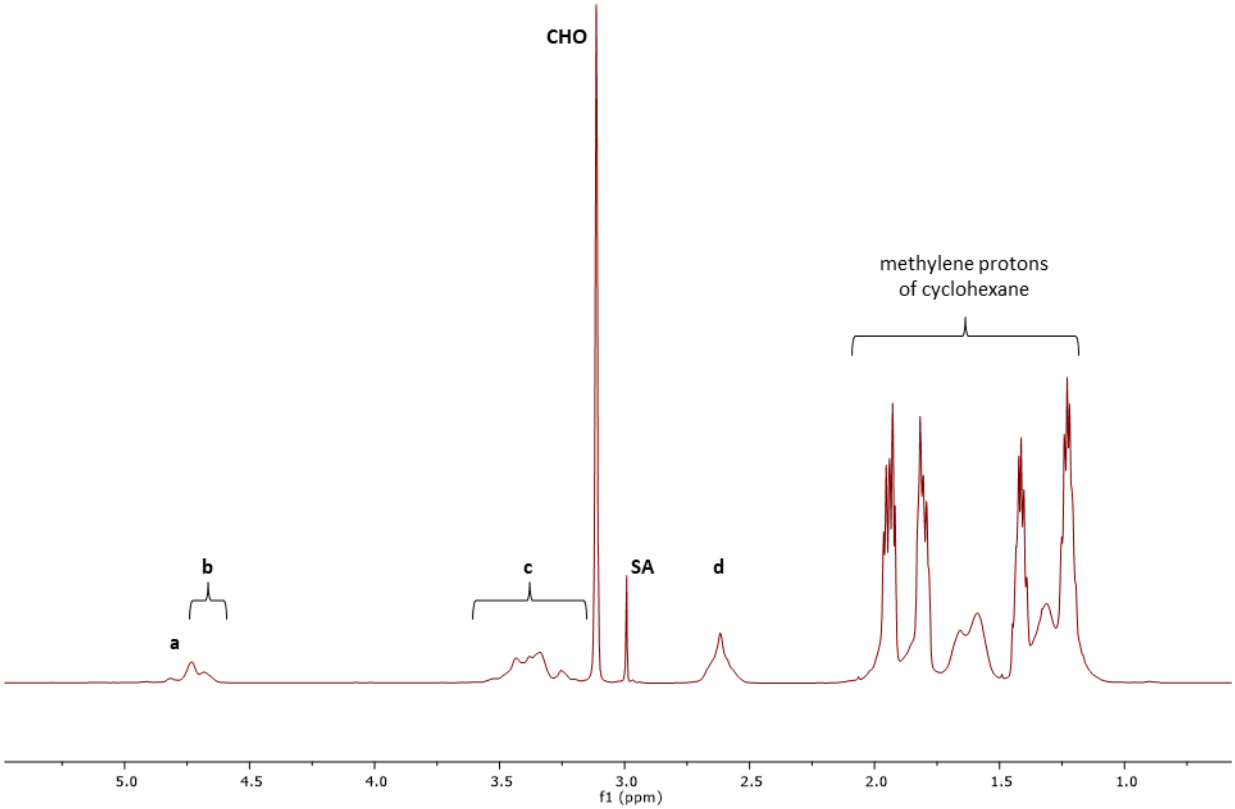


Fig. S13 ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 30 °C) of crude product of a representative polymerisation reaction (Table 2, entry 3).

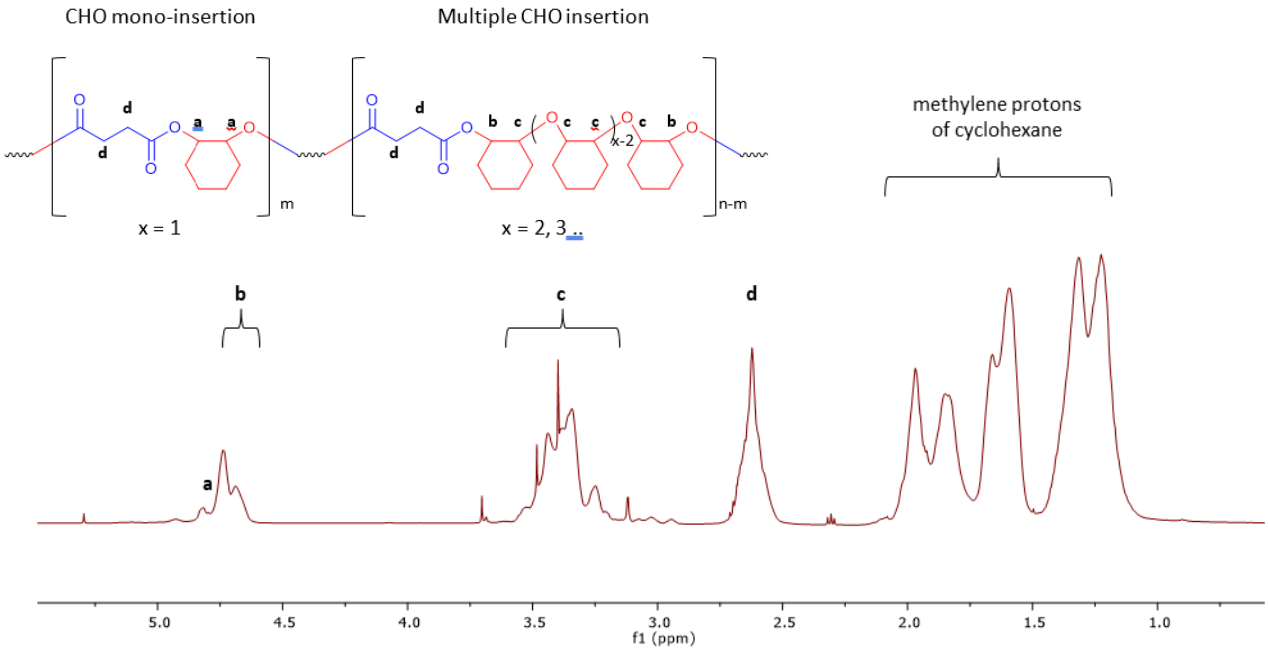
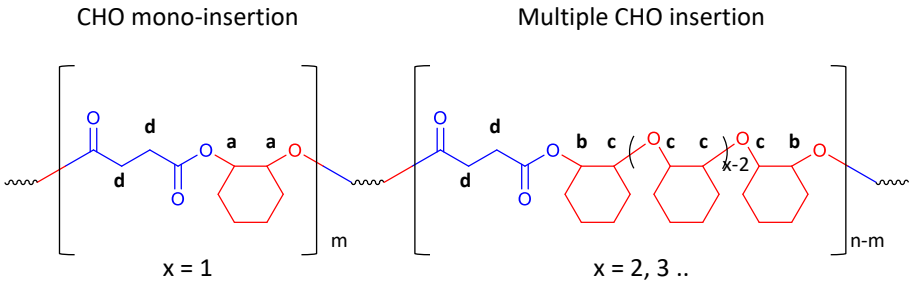


Fig. S14 ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 30 °C) of representative isolated polymer (Table 2, entry 3).

Method for the calculation of copolymer compositions from NMR data



Take the NMR in Figure S13 as an example. From the crude sample (before polymer purification), we need to integrate for the peaks as shown below.

- a : This is the CH proton from CHO of the mono-insertion (x = 1).
- b : This is the CH proton from CHO of the multiple CHO insertion at both ends.
- c : This is the CH proton from CHO connected by ether linkages.
- d : This is CH_2 proton from SA in the polymer.
- SA : This is CH2 proton from unreacted SA monomer.
- CHO : This is CH proton from unreacted CHO monomer.

The incorporation ratio [B/A ratio] can be obtained by dividing the sum of the integrated CHO peaks by half that of SA, because the SA peaks correspond to four protons while only two protons per CHO are represented in the integrated sections.

B/A ratio = (a + b + c) / (d / 2)

SA conversion [convSA] is determined by dividing the signal of the polymerised SA (**d**) by the sum of monomer and polymerised SA signals:

convSA = d / (SA + d)

The degree of polymerisation [DP-SA] may be calculated by multiplying the loading ratio of each monomer to the catalyst:

DP-SA = convSA * loadedSA

Turnover frequency [TOF] of SA is calculated from the reaction time and the degree of polymerization of SA:

TOF = DP-SA / time

The degree of polymerisation of CHO can be found by multiplying that of SA with the incorporation ratio:

DP-CHO = DP-SA * B/A ratio

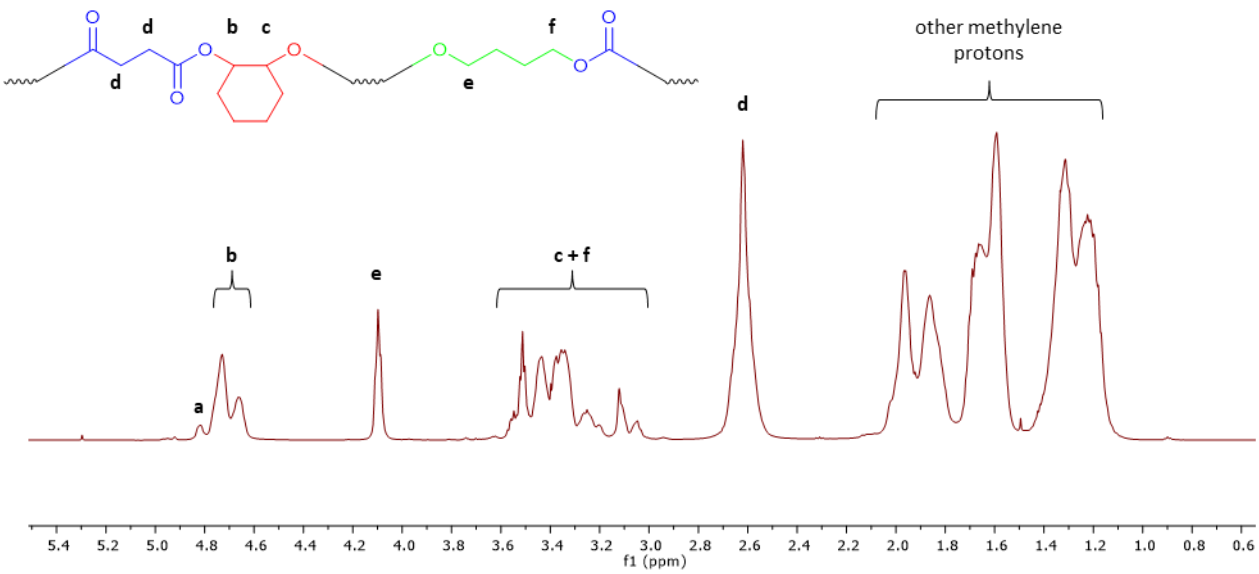
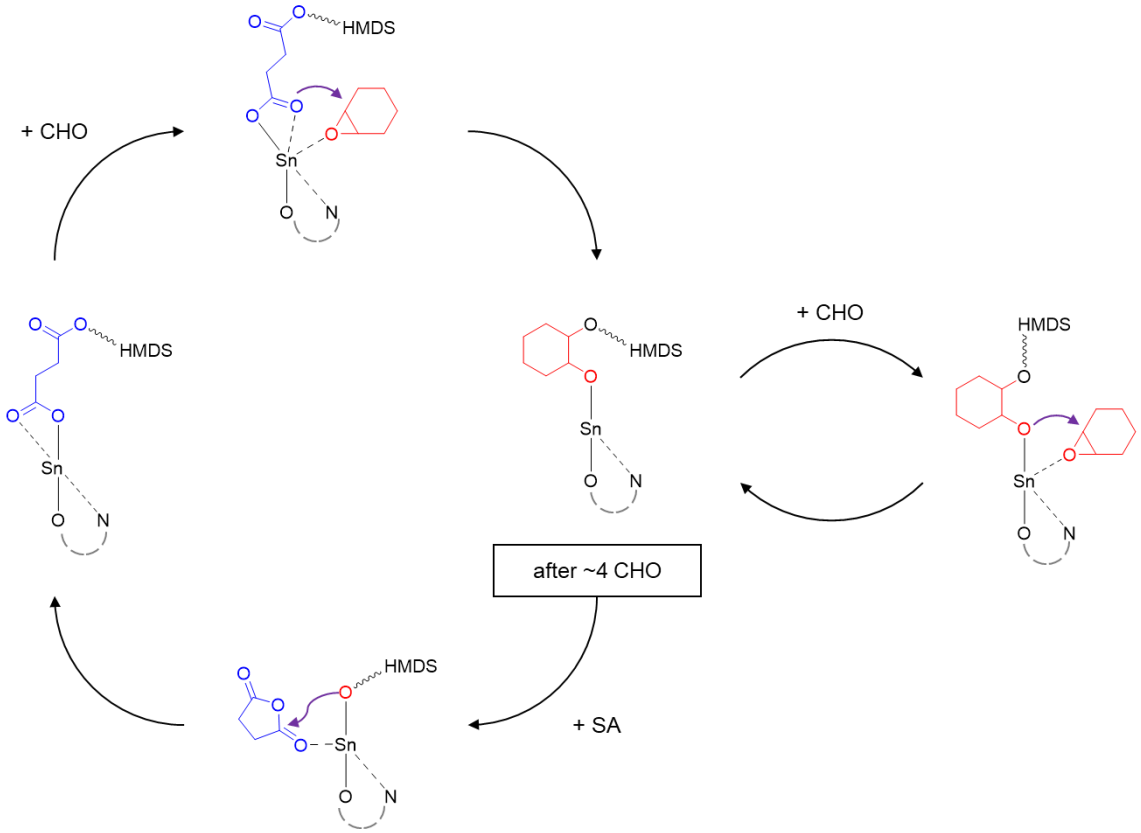


Fig. S15 ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 30 °C) of isolated terpolymer (Table 3, entry 1).



Scheme S1 Proposed mechanism for the copolymerisation reaction.

DOSY NMR

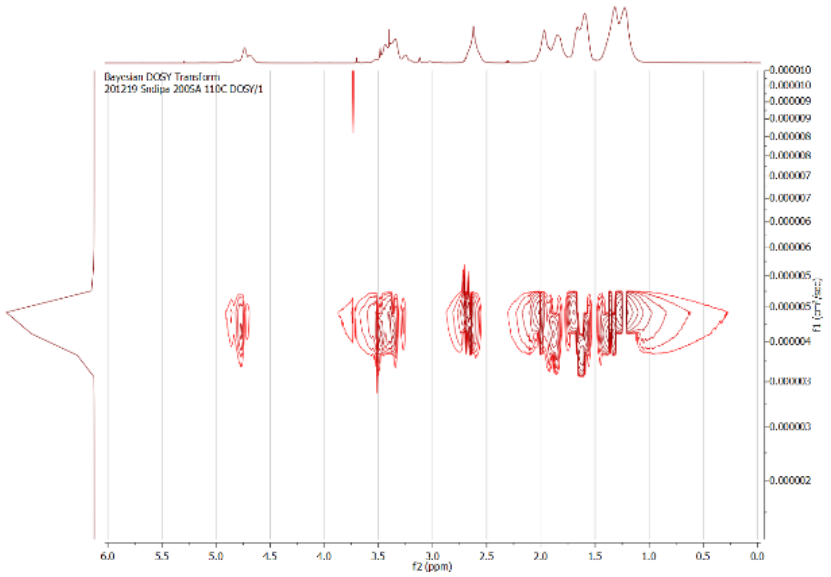


Fig. S16 DOSY NMR spectrum of isolated polymer sample in $CDCl_3$ (Table 2, entry 3).

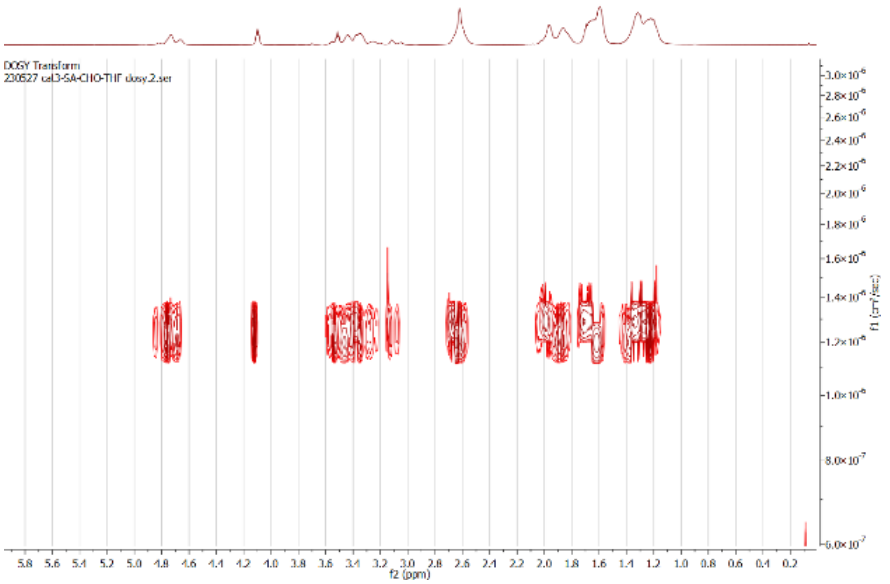


Fig. S17 DOSY NMR spectrum of isolated ter-polymer in $CDCl_3$ (Table 3, entry 1).

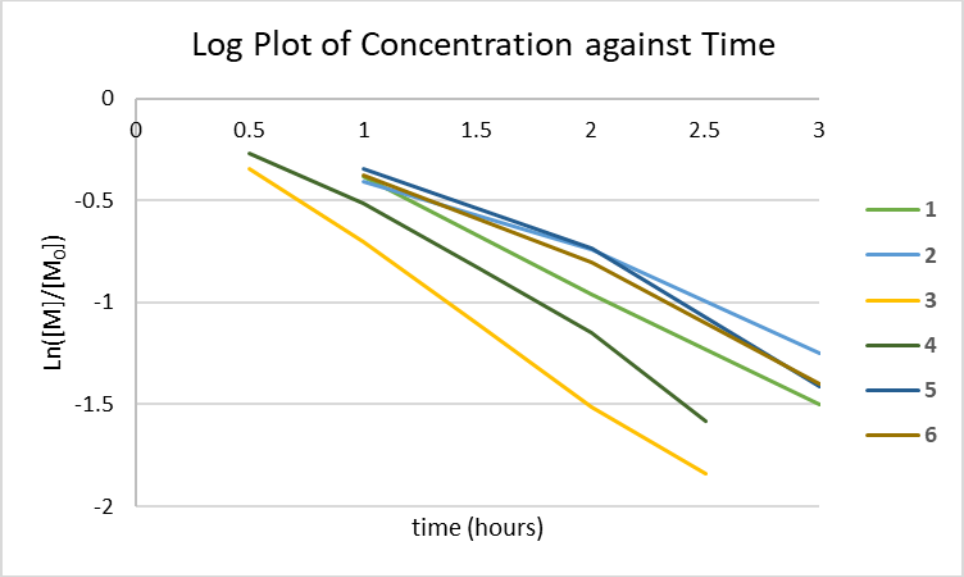


Fig. S18 The SA consumption of the polymerisations described in Table 2, entries 1-6.

Electrospray Ionisation – Mass Spectrometry

Samples of polymers were hydrolysed. The hydrolysis products were extracted from the organic layer and analysed by electrospray ionisation mass spectrometry.

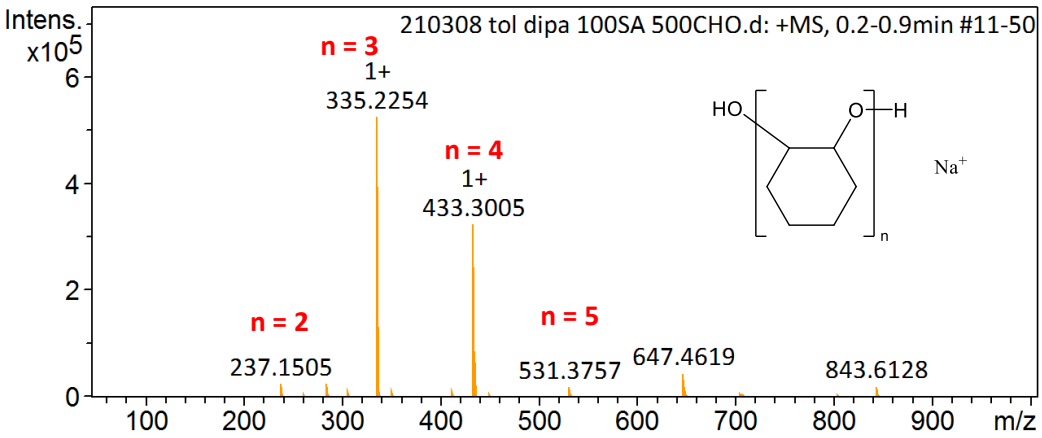
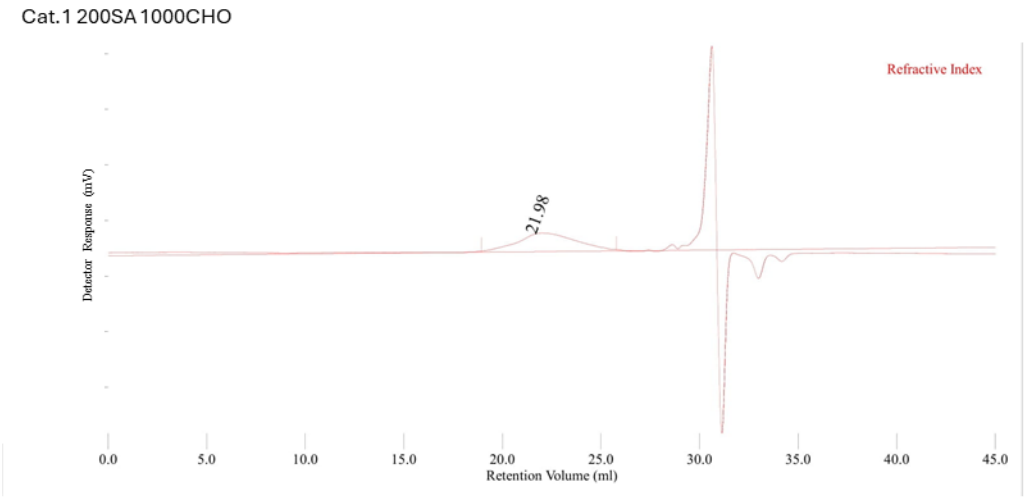
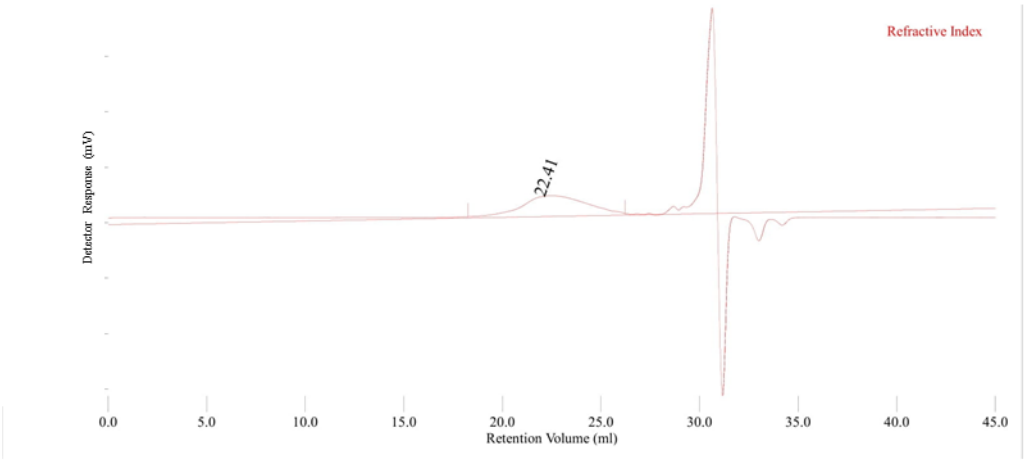


Fig. S19 ESI-MS spectra of hydrolysed copolymer (Table 1, entry 9).



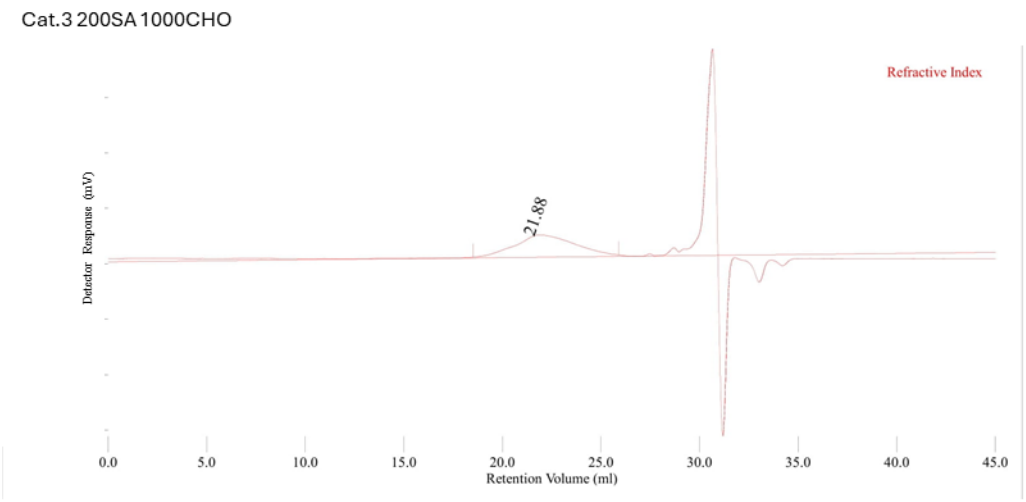
Peak RV - (ml)	21.983
Mn - (Daltons)	4,323
Mw - (Daltons)	6,480
Mz - (Daltons)	9,205
Mp - (Daltons)	6,230
Mw / Mn	1.499

Fig. S20 GPC trace of isolated copolymer (Entry 1, Table 2).



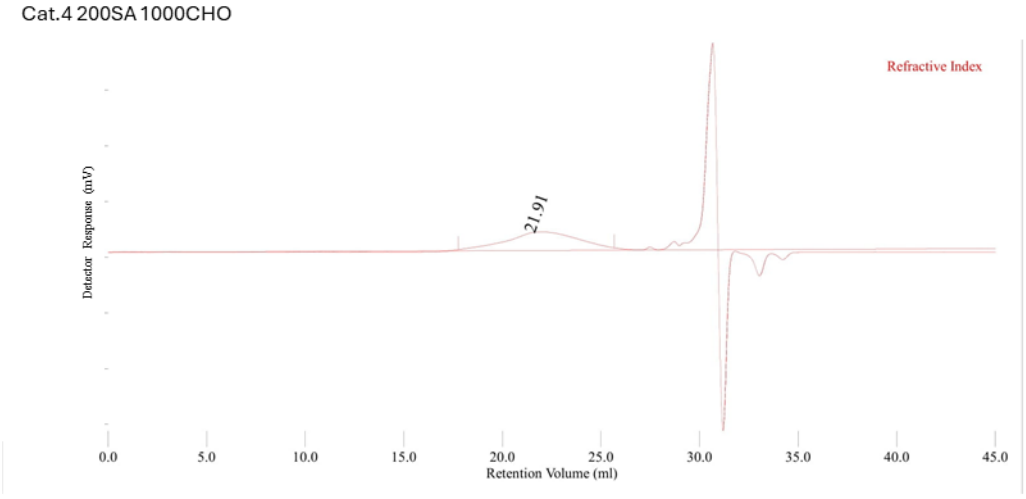
Peak RV - (ml)	22.413
Mn - (Daltons)	3,505
Mw - (Daltons)	6,039
Mz - (Daltons)	10,457
Mp - (Daltons)	5,160
Mw / Mn	1.723

Fig. S21 GPC trace of isolated copolymer (Entry 2, Table 2).



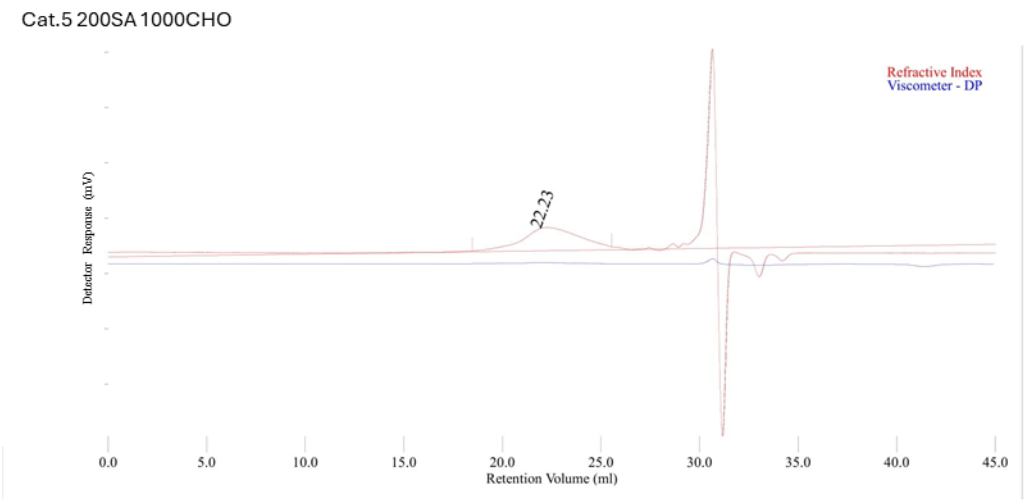
Peak RV - (ml)	21.883
Mn - (Daltons)	4,395
Mw - (Daltons)	6,884
Mz - (Daltons)	10,203
Mp - (Daltons)	6,503
Mw / Mn	1.566

Fig. S22 GPC trace of isolated copolymer (Entry 3, Table 2).



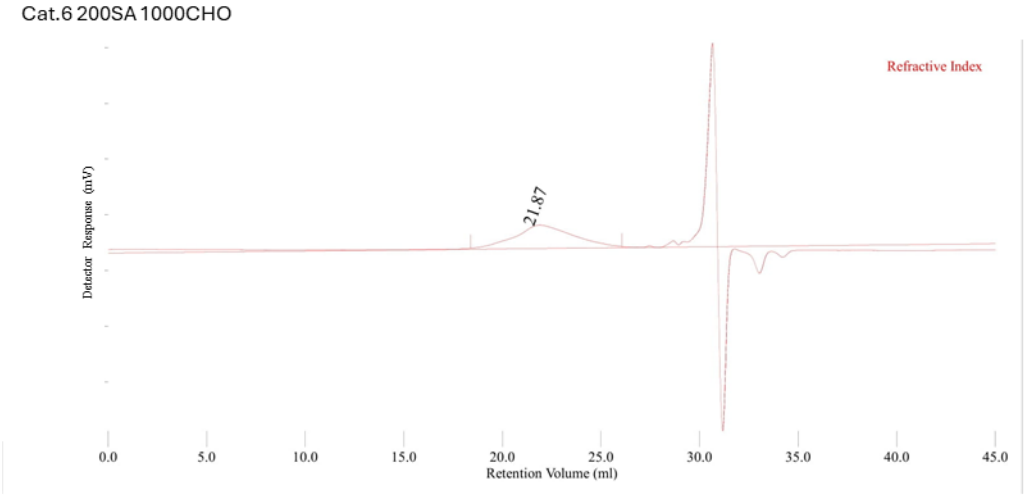
Peak RV - (ml)	21.913
Mn - (Daltons)	4,623
Mw - (Daltons)	8,508
Mz - (Daltons)	15,743
Mp - (Daltons)	6,415
Mw / Mn	1.840

Fig. S23 GPC trace of isolated copolymer (Entry 4, Table 2).



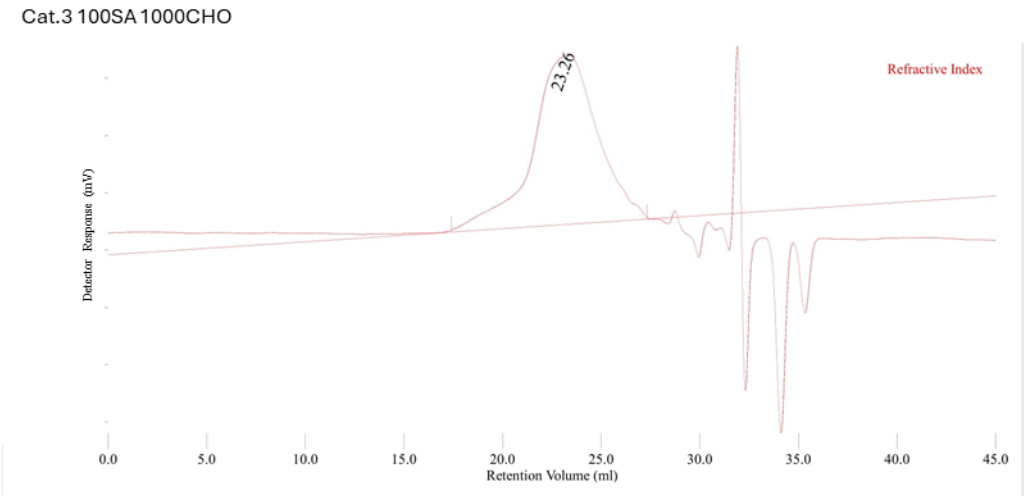
Peak RV - (ml)	22.227
Mn - (Daltons)	4,884
Mw - (Daltons)	7,790
Mz - (Daltons)	12,392
Mp - (Daltons)	7,106
Mw / Mn	1.595

Fig. S24 GPC trace of isolated copolymer (Entry 5, Table 2).



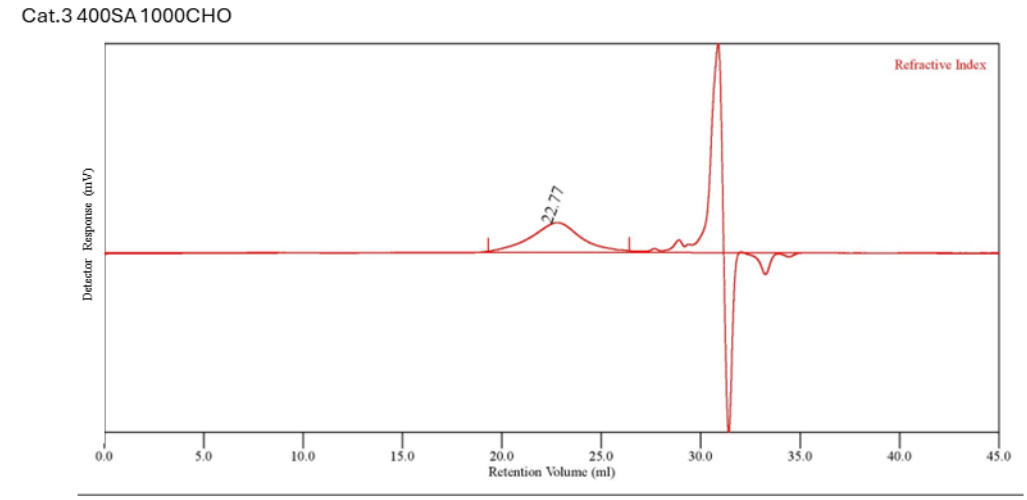
Peak RV - (ml)	21.873
Mn - (Daltons)	4,420
Mw - (Daltons)	7,145
Mz - (Daltons)	10,923
Mp - (Daltons)	6,536
Mw / Mn	1.616

Fig. S25 GPC trace of isolated copolymer (Entry 6, Table 2).



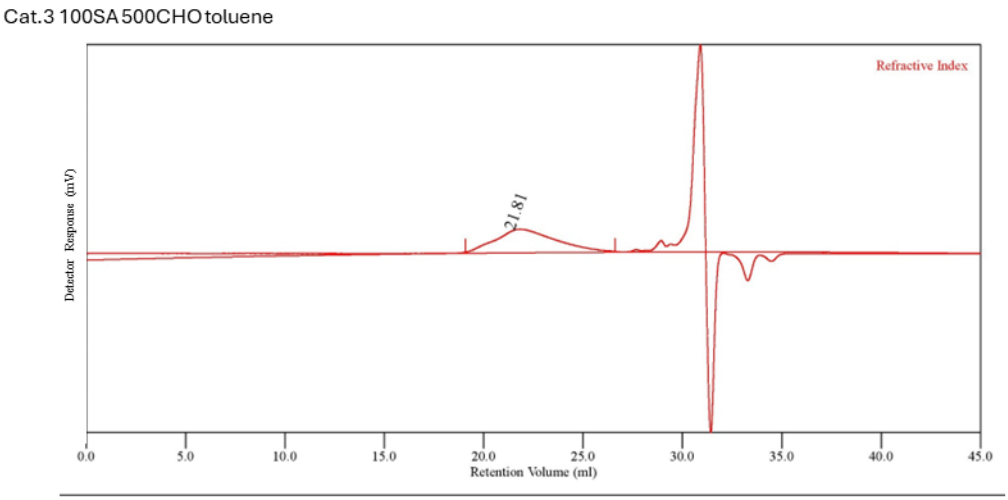
Peak RV - (ml)	23.263
Mn - (Daltons)	3,642
Mw - (Daltons)	7,804
Mz - (Daltons)	19,959
Mp - (Daltons)	4,883
Mw / Mn	2.142

Fig. S26 GPC trace of isolated copolymer (Entry 7, Table 2).



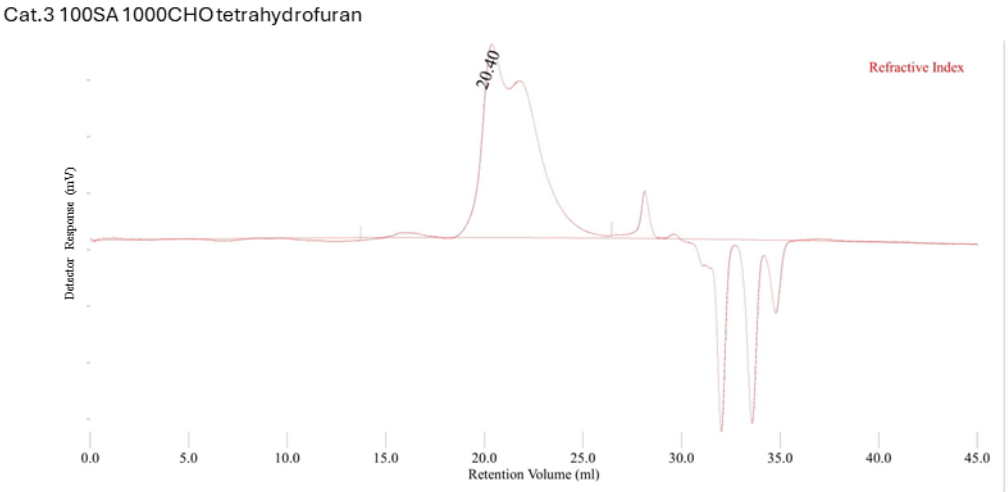
Peak RV - (ml)	22.773
Mn - (Daltons)	3,544
Mw - (Daltons)	5,269
Mz - (Daltons)	7,334
Mp - (Daltons)	4,402
Mw / Mn	1.487

Fig. S27 GPC trace of isolated copolymer (Entry 8, Table 2).



Peak RV - (ml)	21.810
Mn - (Daltons)	4,063
Mw - (Daltons)	6,626
Mz - (Daltons)	9,285
Mp - (Daltons)	6,720
Mw / Mn	1.631

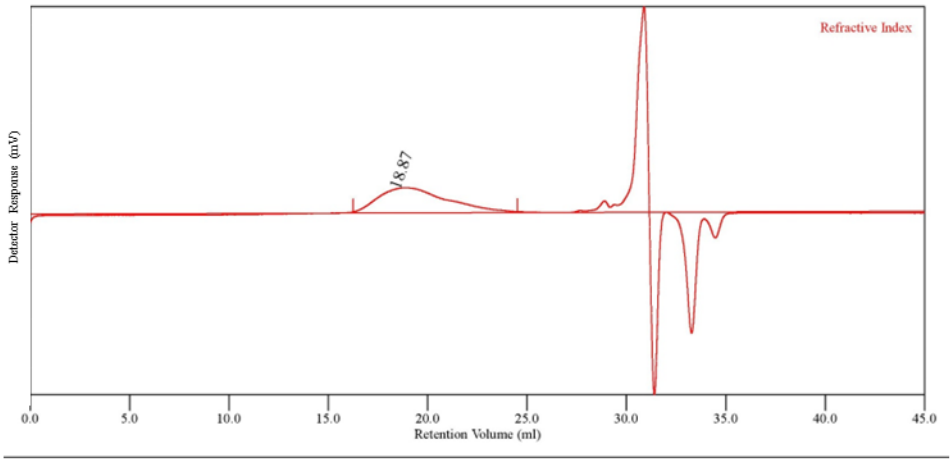
Fig. S28 GPC trace of isolated copolymer (Entry 9, Table 2).



Peak RV - (ml)	20.400
Mn - (Daltons)	6,399
Mw - (Daltons)	9,032
Mz - (Daltons)	11,505
Mp - (Daltons)	12,598
Mw / Mn	1.411

Fig. S29 GPC trace of isolated terpolymer (Entry 1, Table 3).

Cat.3 1000CHO



Peak RV - (ml)	18.870
Mn - (Daltons)	14,152
Mw - (Daltons)	29,586
Mz - (Daltons)	52,872
Mp - (Daltons)	27,574
Mw / Mn	2.090

Fig. S30 GPC trace of isolated polymer (Entry 5, Table 3).