Electronic Supplementary Information

for

Simple magnesium alkoxides: synthesis, molecular structure, and catalytic behavior in the ring-opening polymerization of lactide and macrolactones and for copolymerization of maleic anhydride and propylene oxide.

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Table of Contents

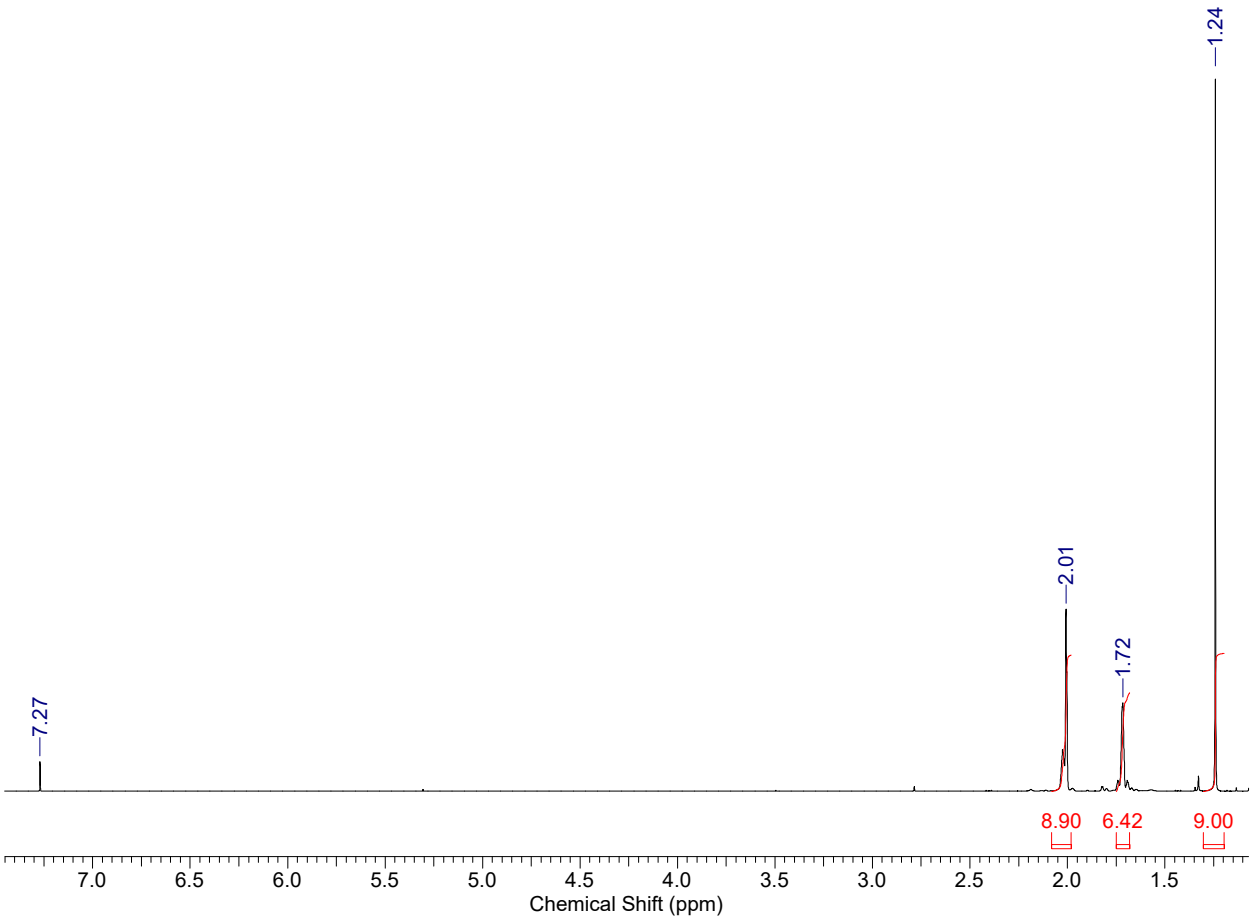

Figure S1. ^{1}H NMR of 1-Adamantyl *tert*-butyl ketone.

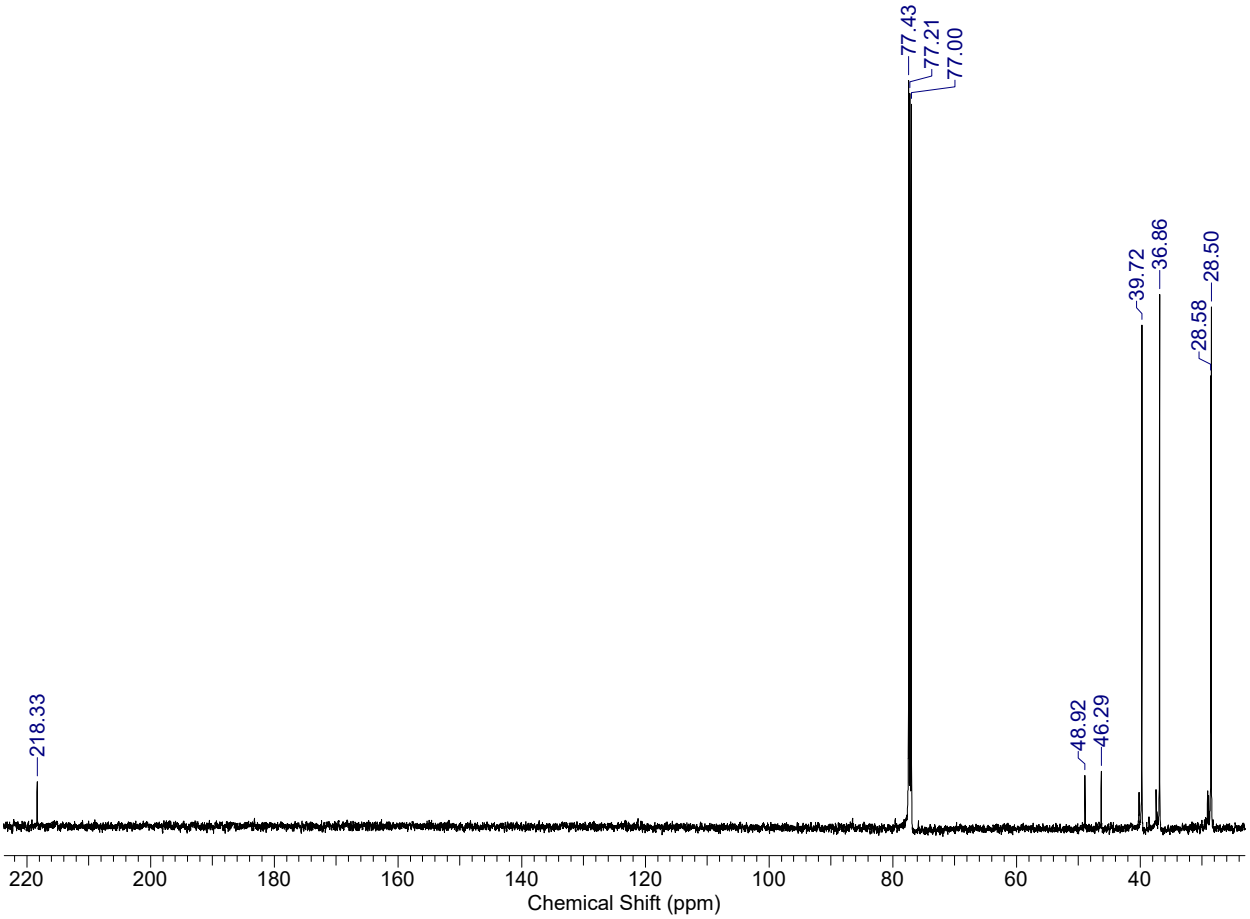

Figure S2. ^{13}C NMR of 1-adamantyl *tert*-butyl ketone.

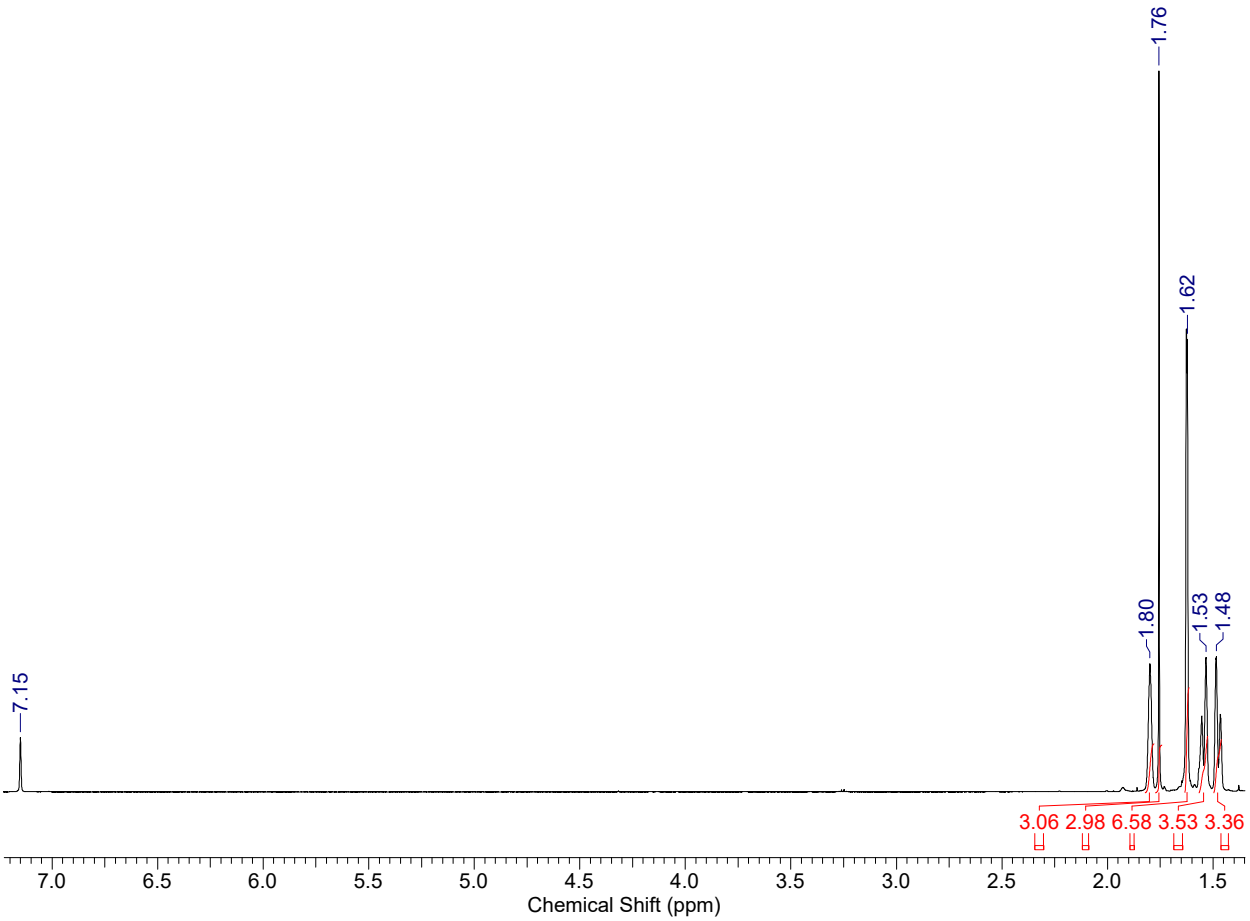

Figure S3. ^{1}H NMR of 1-adamantyl methyl ketone.

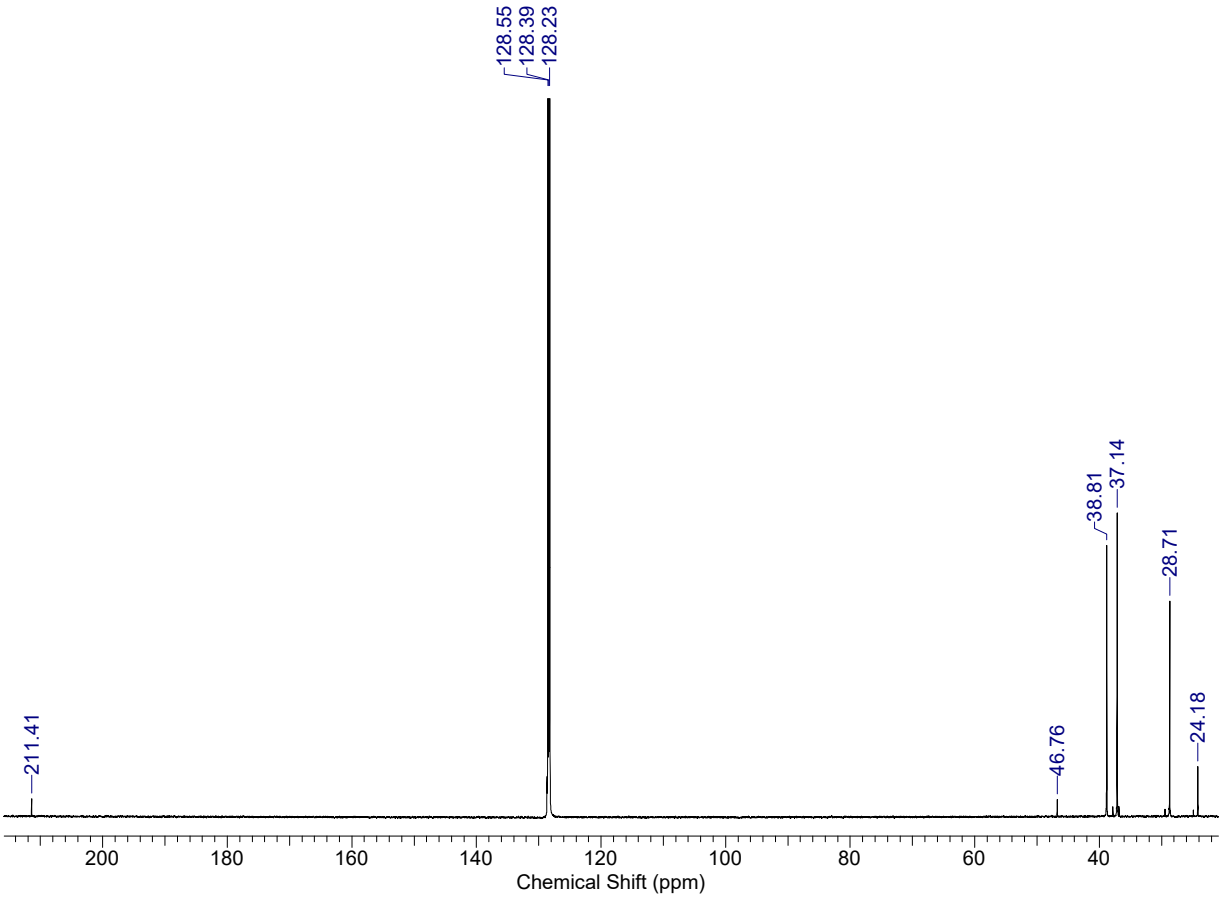

Figure S4. ^{13}C NMR of 1-adamantyl methyl ketone.

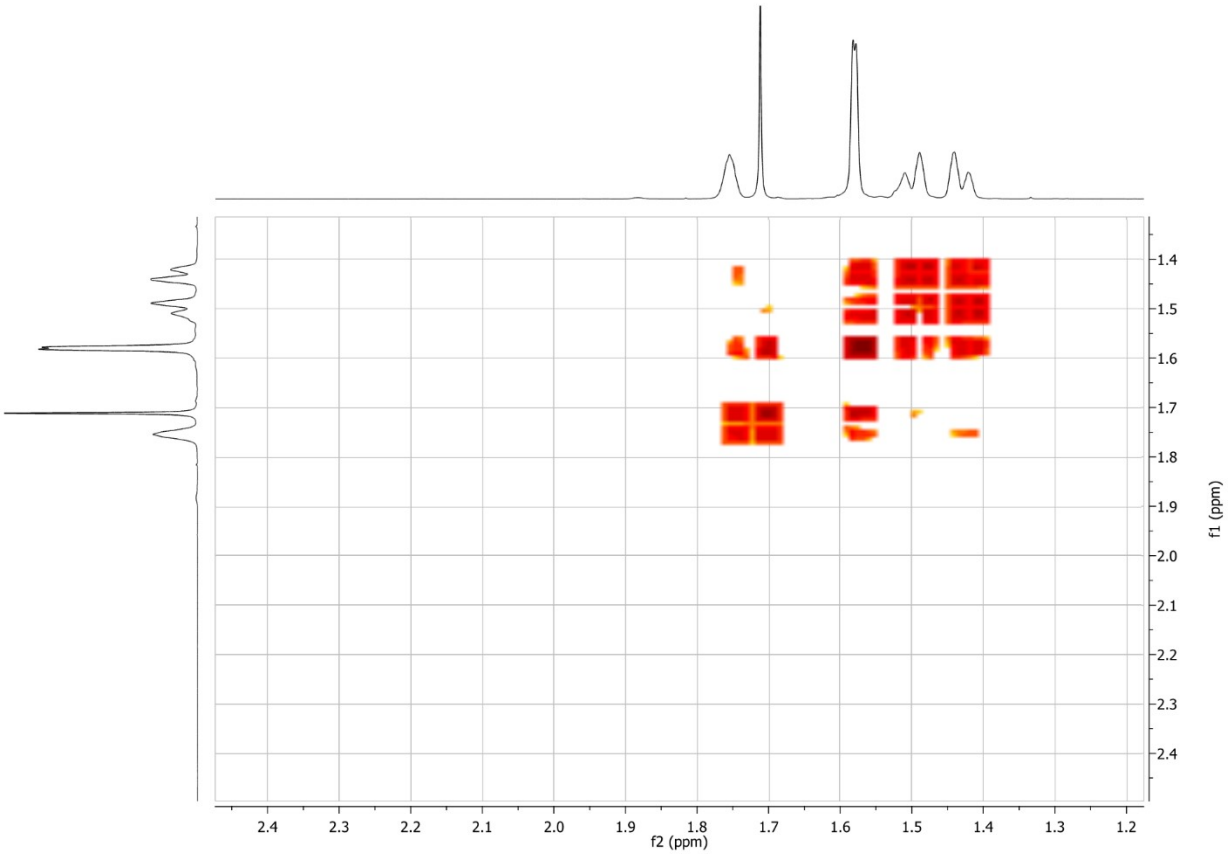

Figure S5. ^{1}H-^{1}H COSY NMR of 1-adamantyl methyl ketone.

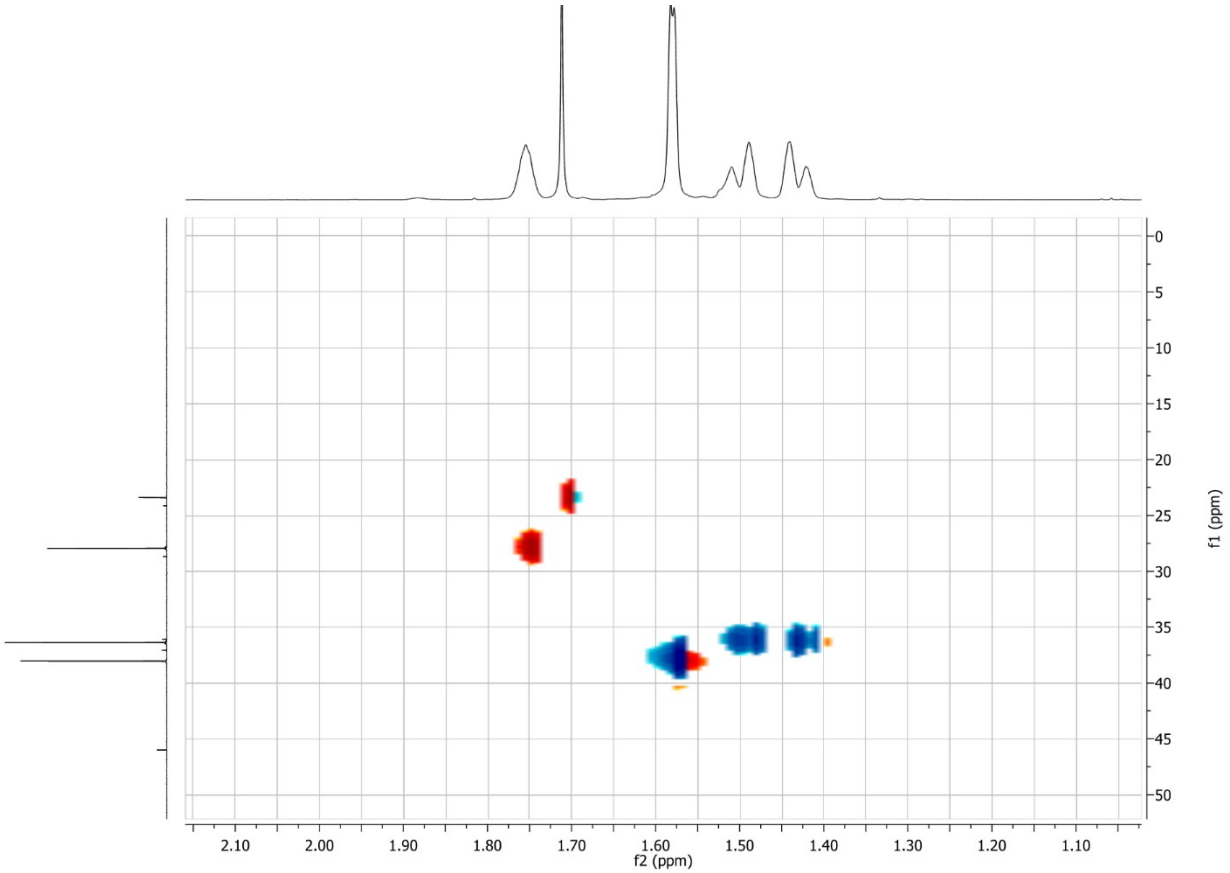

Figure S6. HSQC NMR of 1-adamantyl methyl ketone.

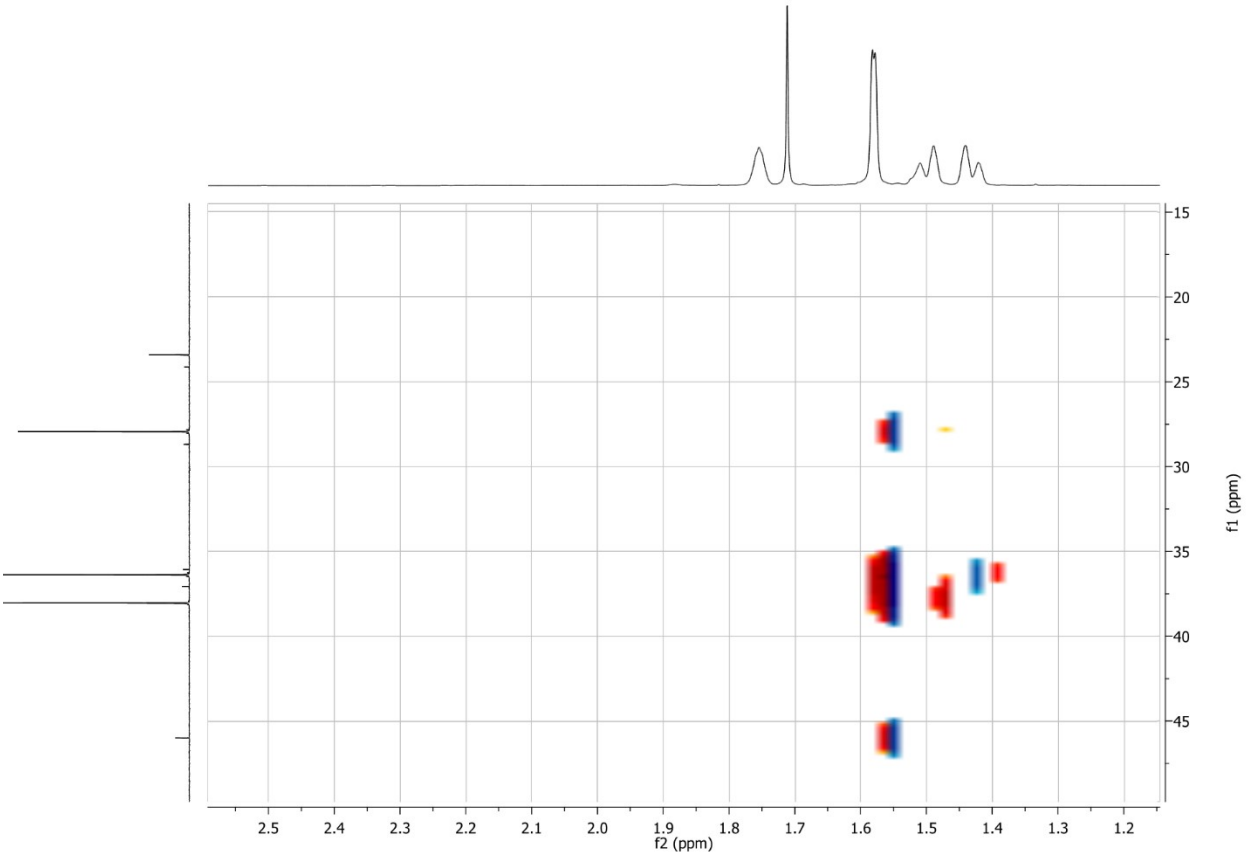

Figure S7. HMBC NMR of 1-adamantyl methyl ketone.

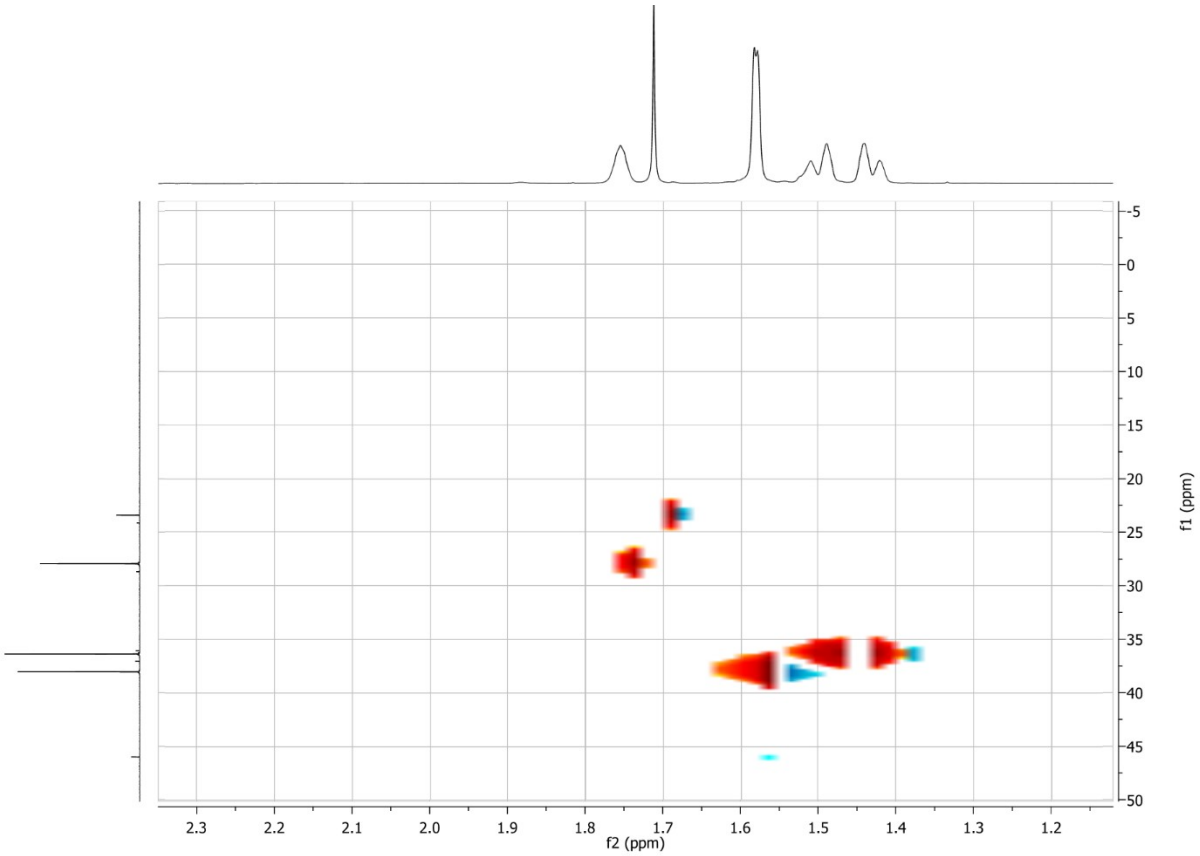

Figure S8. HMQC NMR of 1-adamantyl methyl ketone.

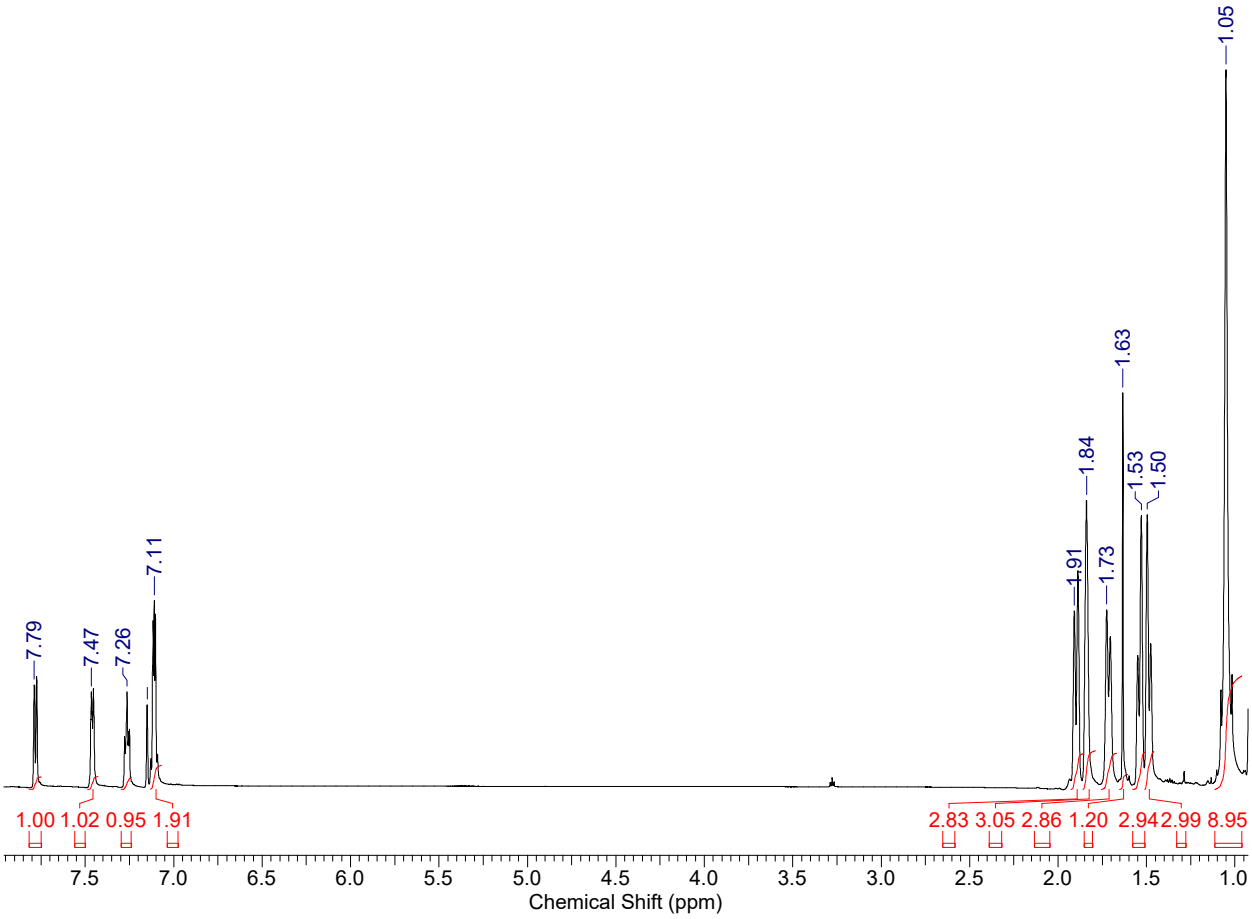

Figure S9. ^{1}H NMR of HO^{t}BuAdPh (HOR^{2}).

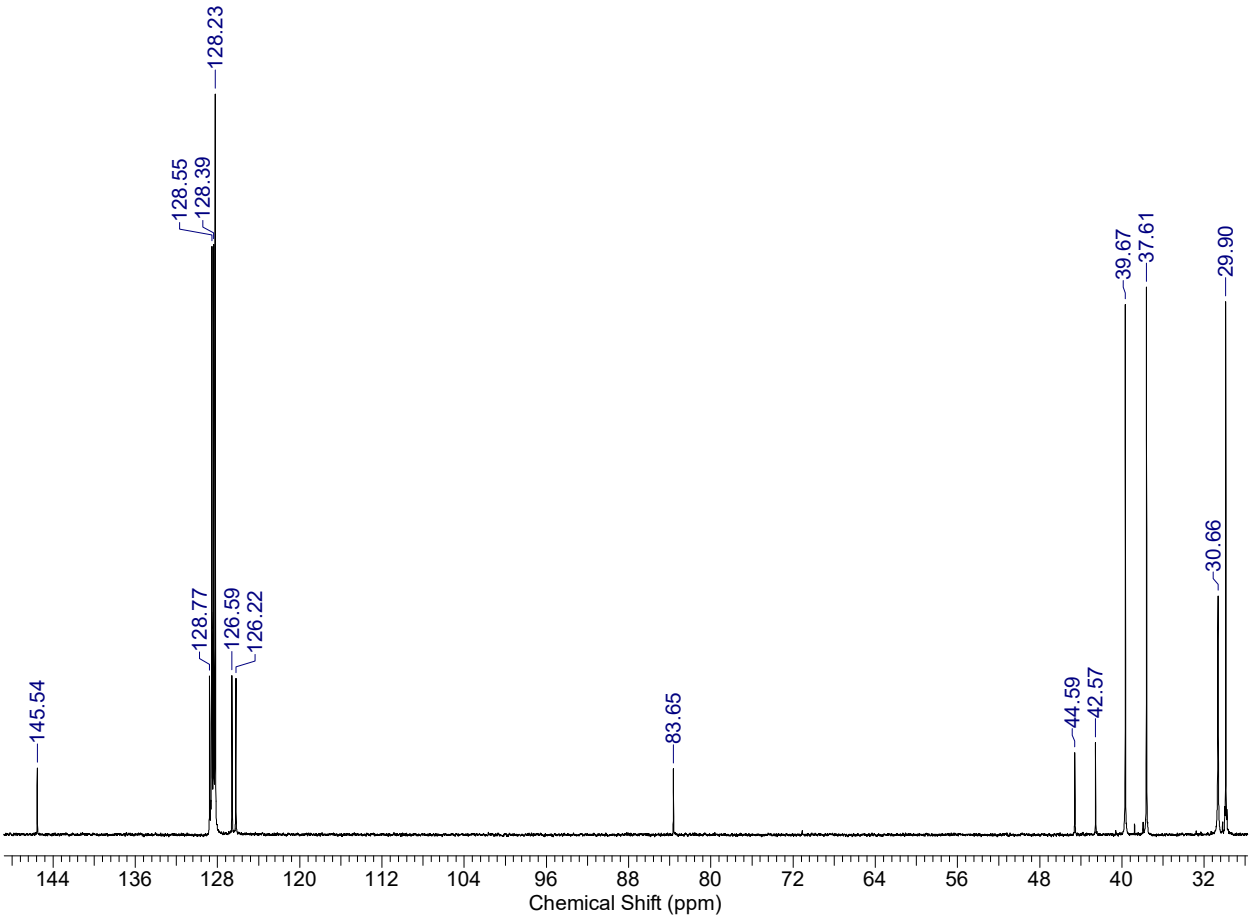

Figure S10. ^{13}C NMR of HO^{t}BuAdPh.

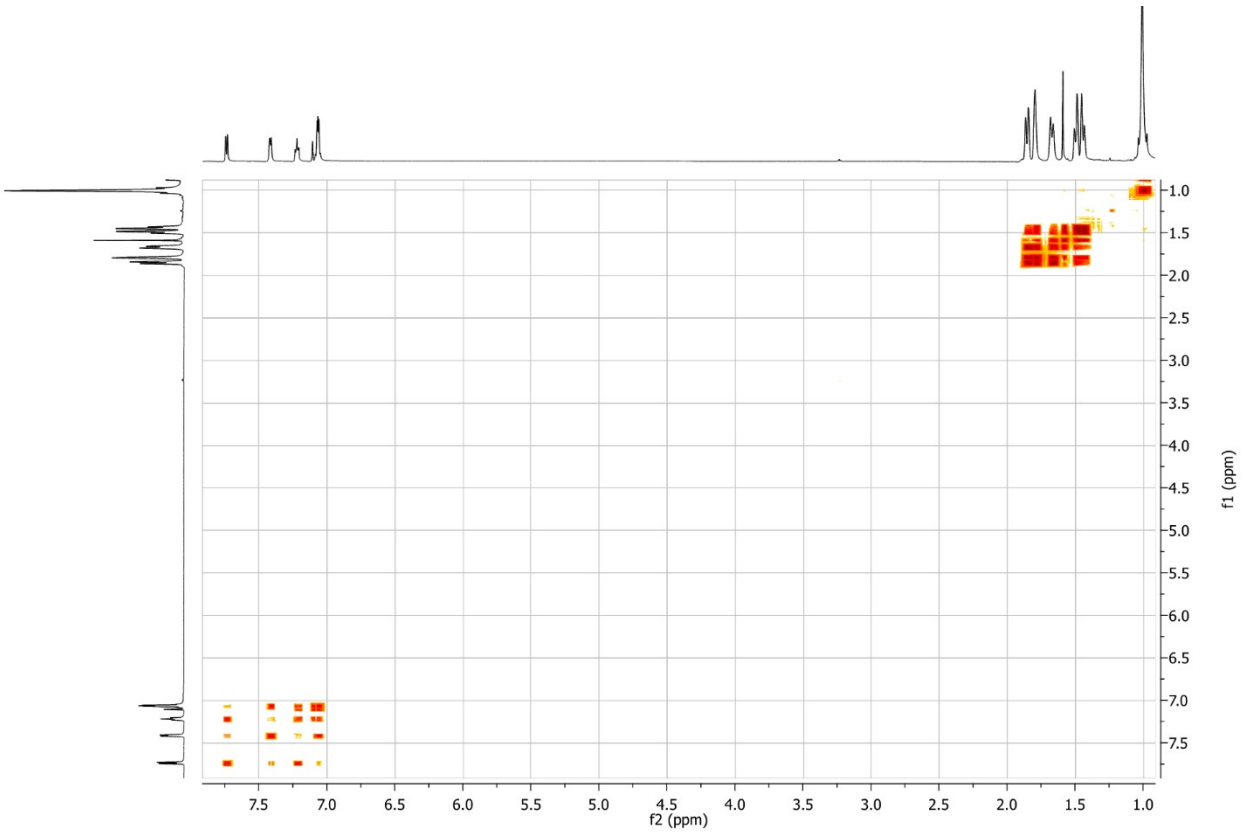

Figure S11. ^{1}H-^{1}H COSY NMR of HO^{t}BuAdPh.

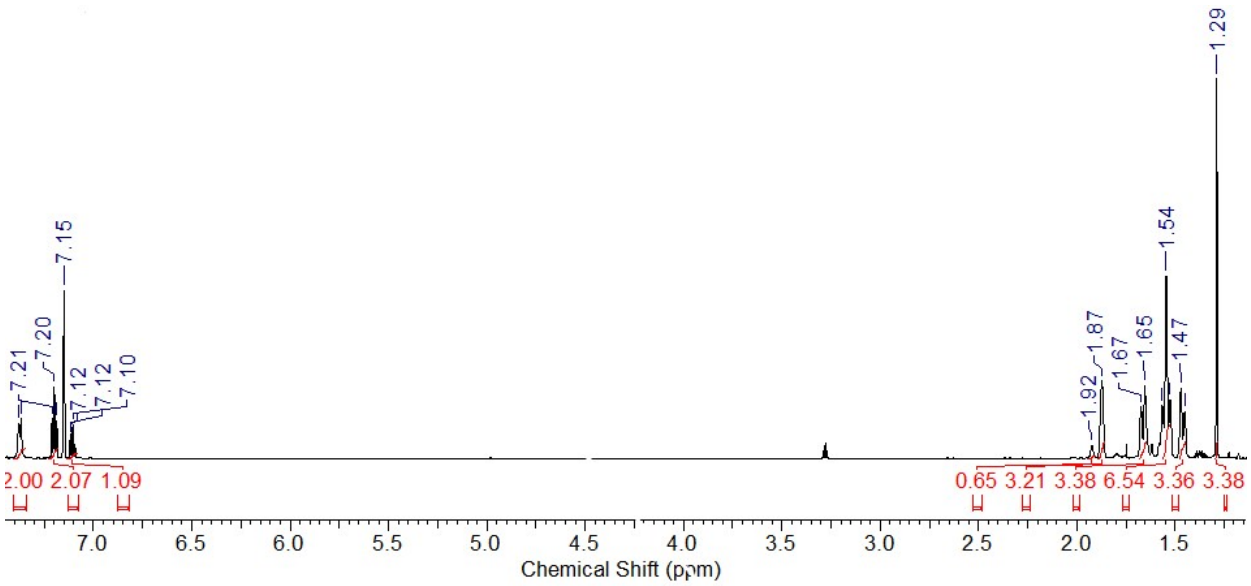

Figure S12. ^{1}H NMR of HOCMeAdPh (HOR^{3}).

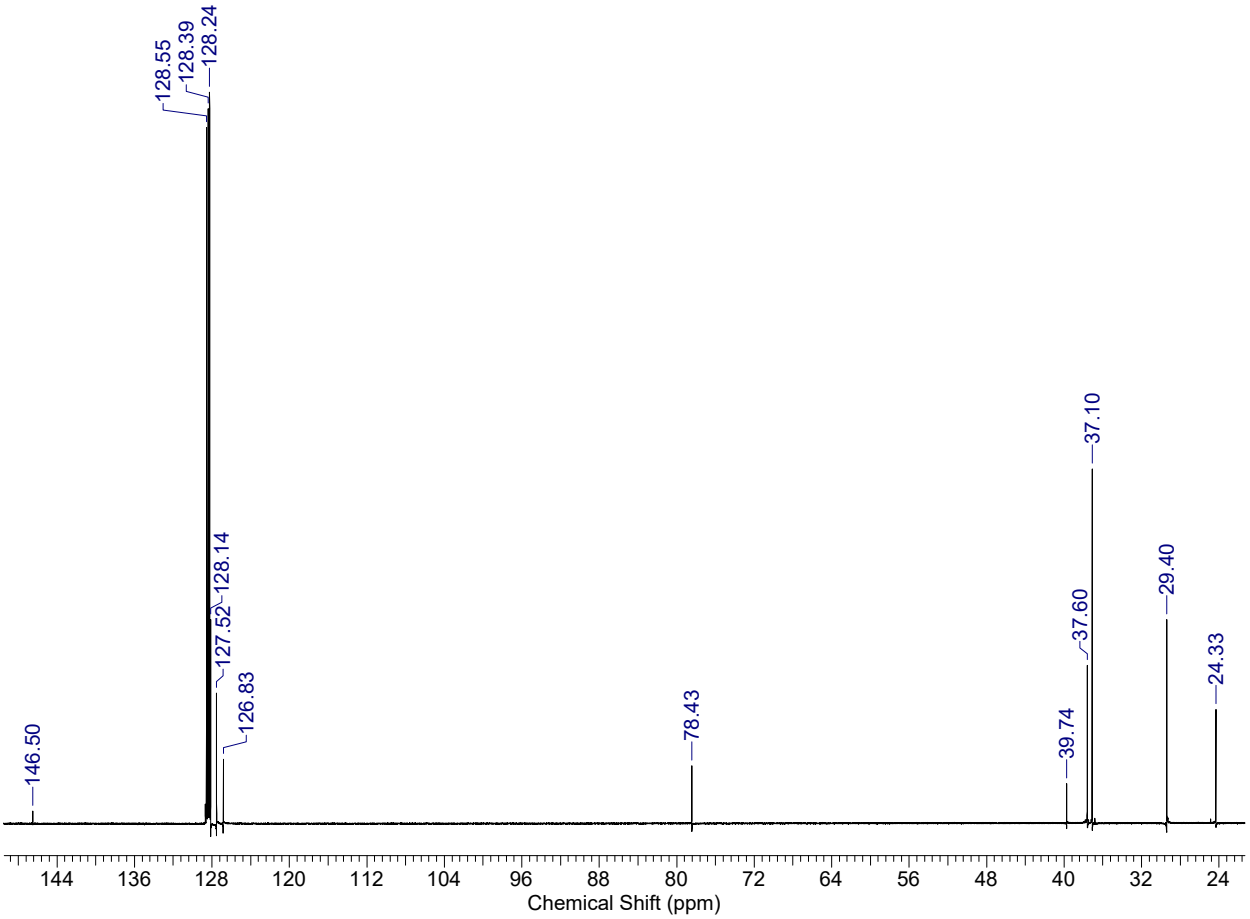

Figure S13. ^{13}C NMR of HOCMeAdPh.

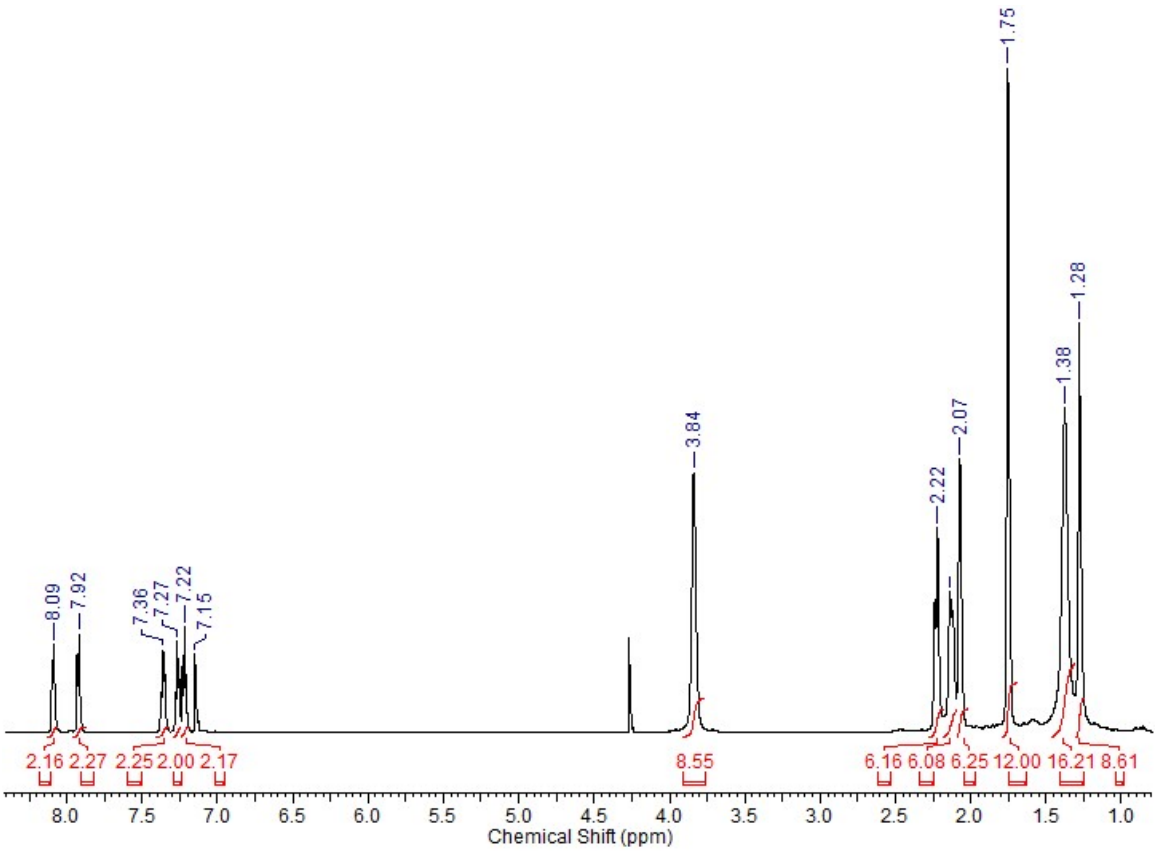

Figure S14. ^{1}H NMR of Mg(OAd^{t}BuPh)$_2$(THF)$_2$ (**2**).

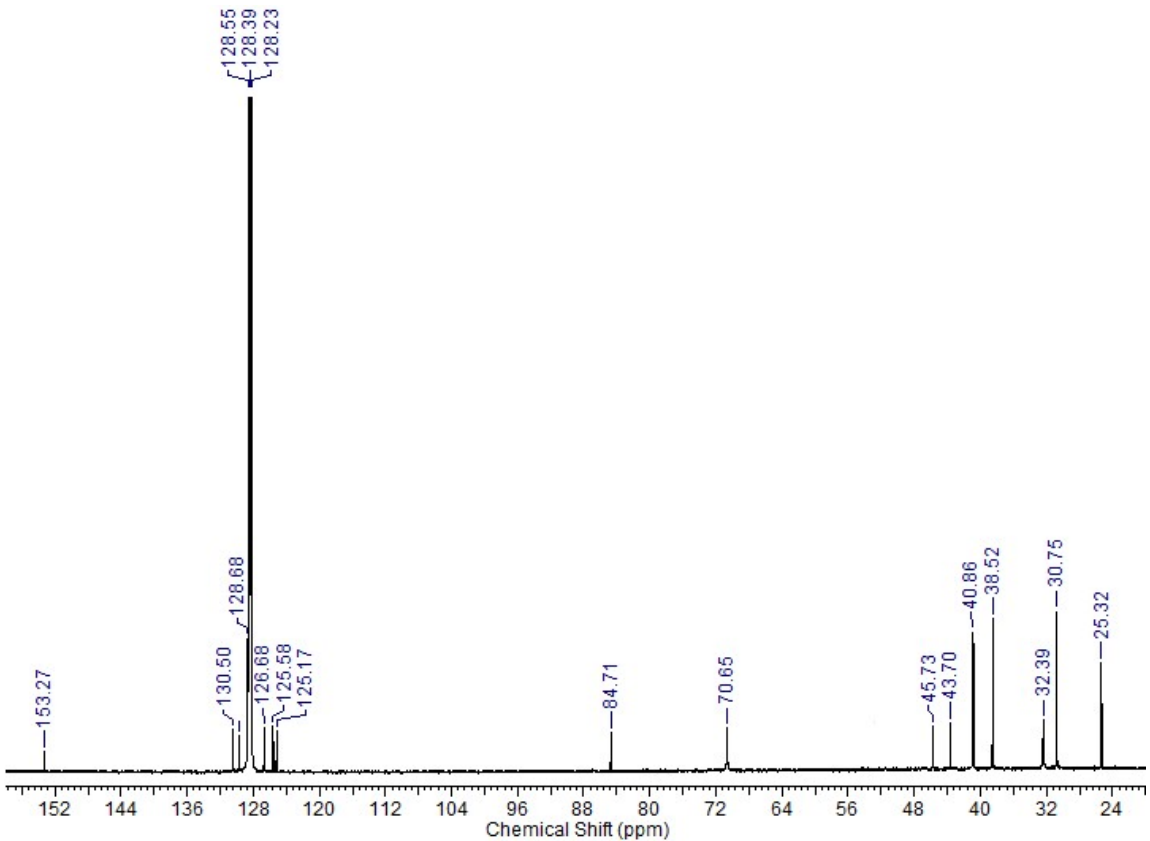

Figure S15. ^{13}C NMR of $Mg(OAd^tBuPh)_2(THF)_2$.

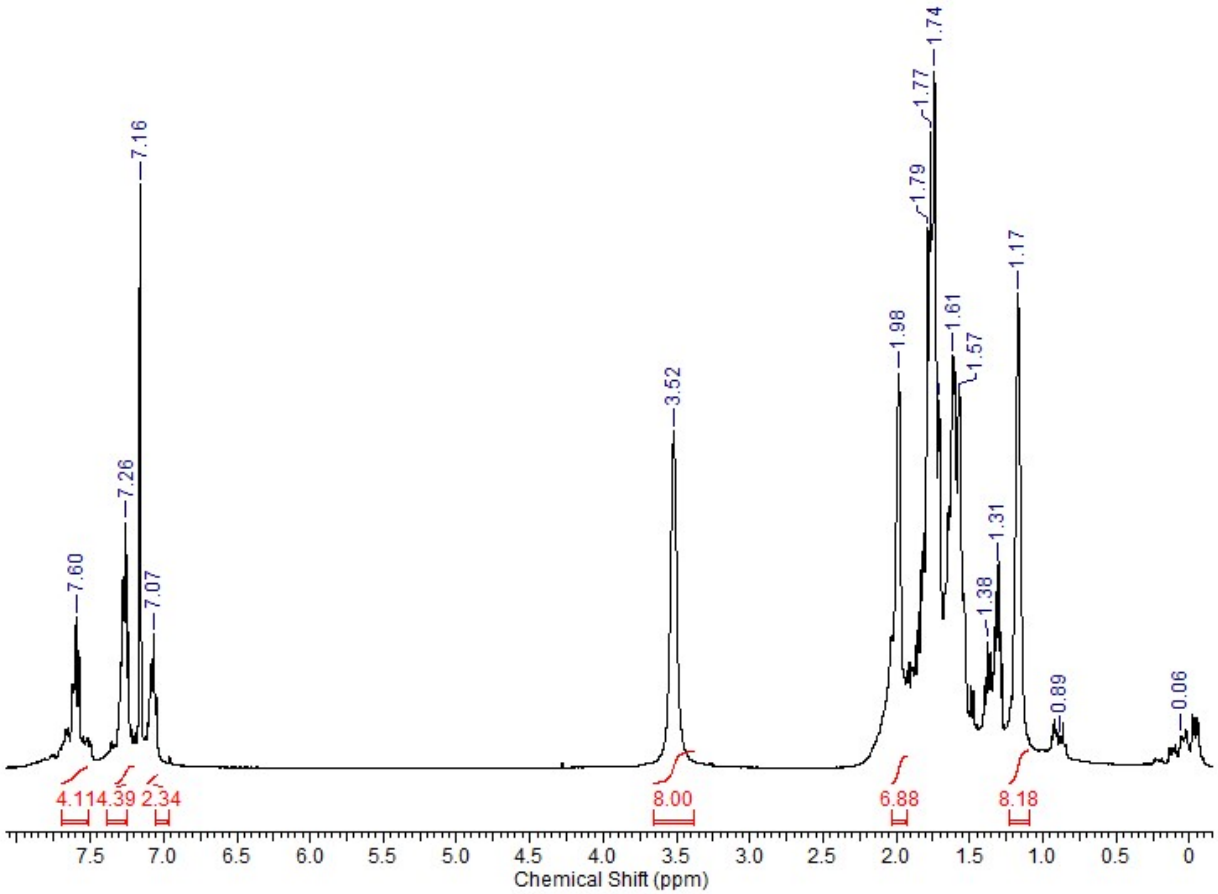

Figure S16. ^{1}H NMR of $Mg_2(OAdMePh)_2(sec\text{-}Bu)_2(THF)_2$ (**3**).

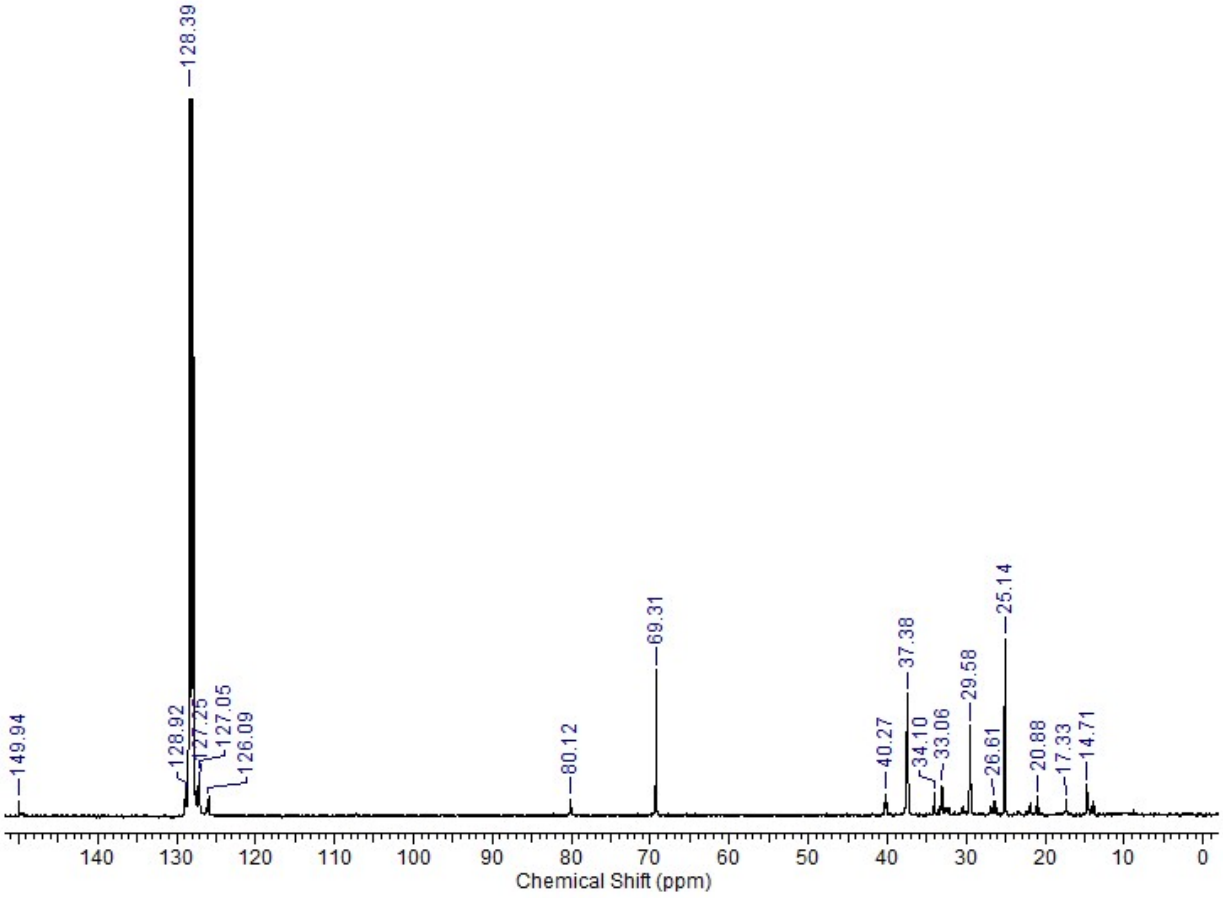

Figure S17. ^{13}C NMR of $Mg_2(OAdMePh)_2(sec\text{-}Bu)_2(THF)_2$ (**3**).

HRMS

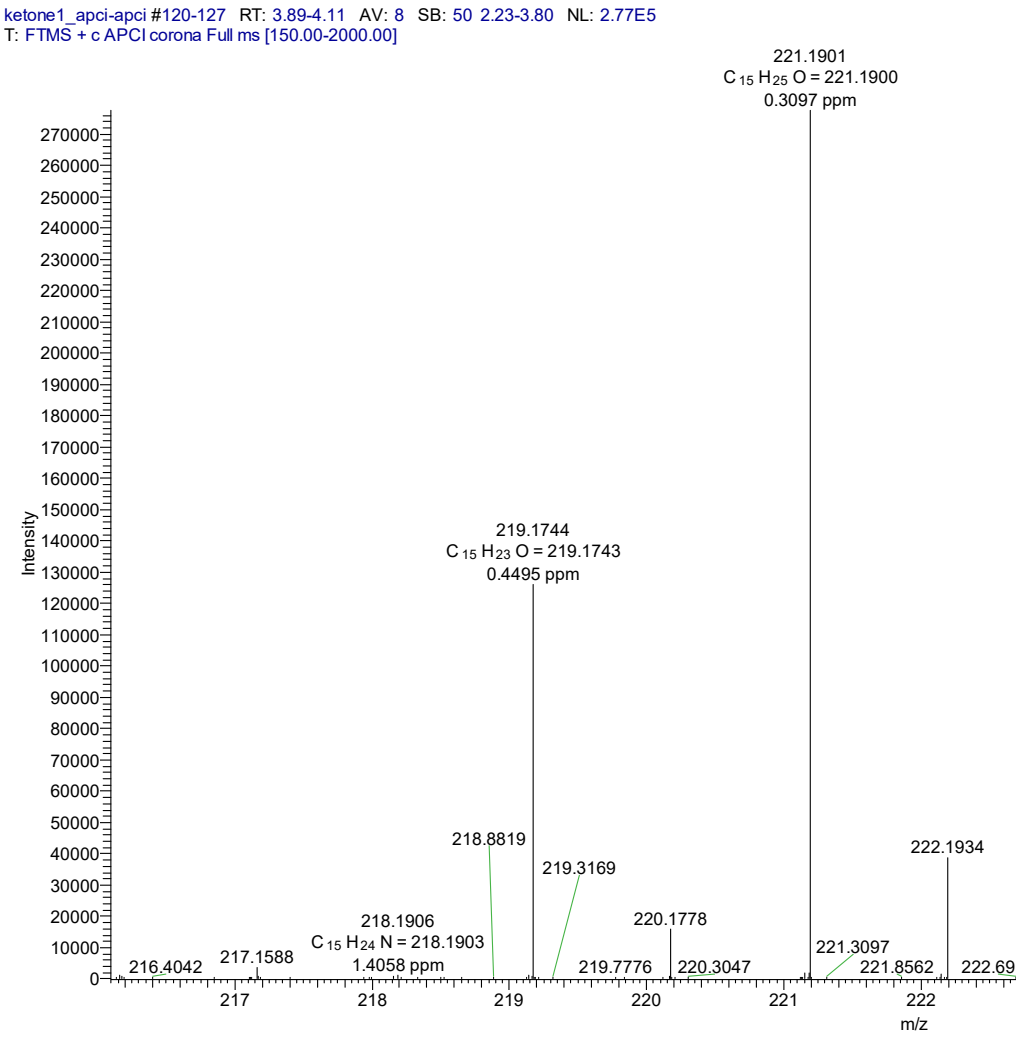

Figure S18. HRMS of 1-adamantyl *tert*-butyl ketone.

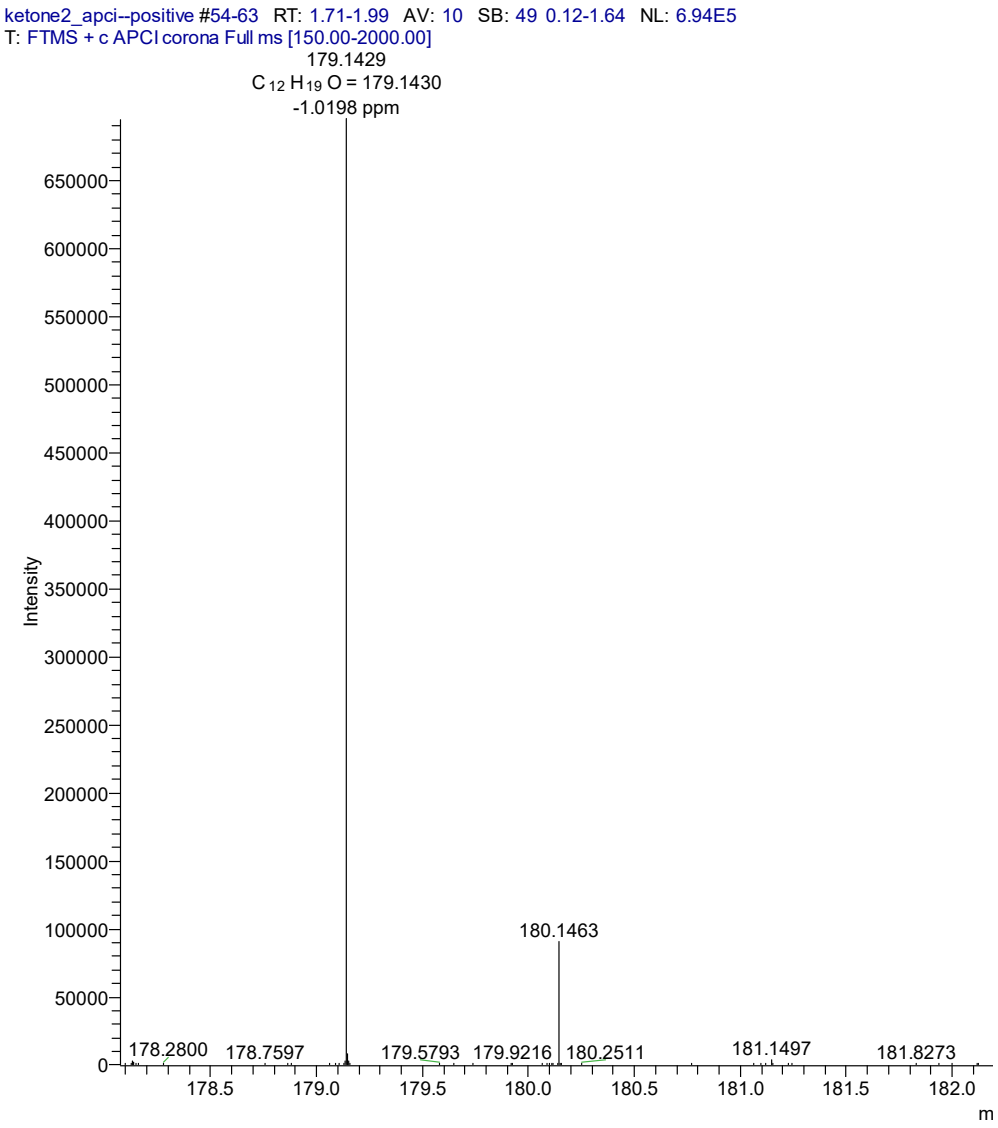

Figure S19. HRMS of 1-adamantyl methyl ketone.

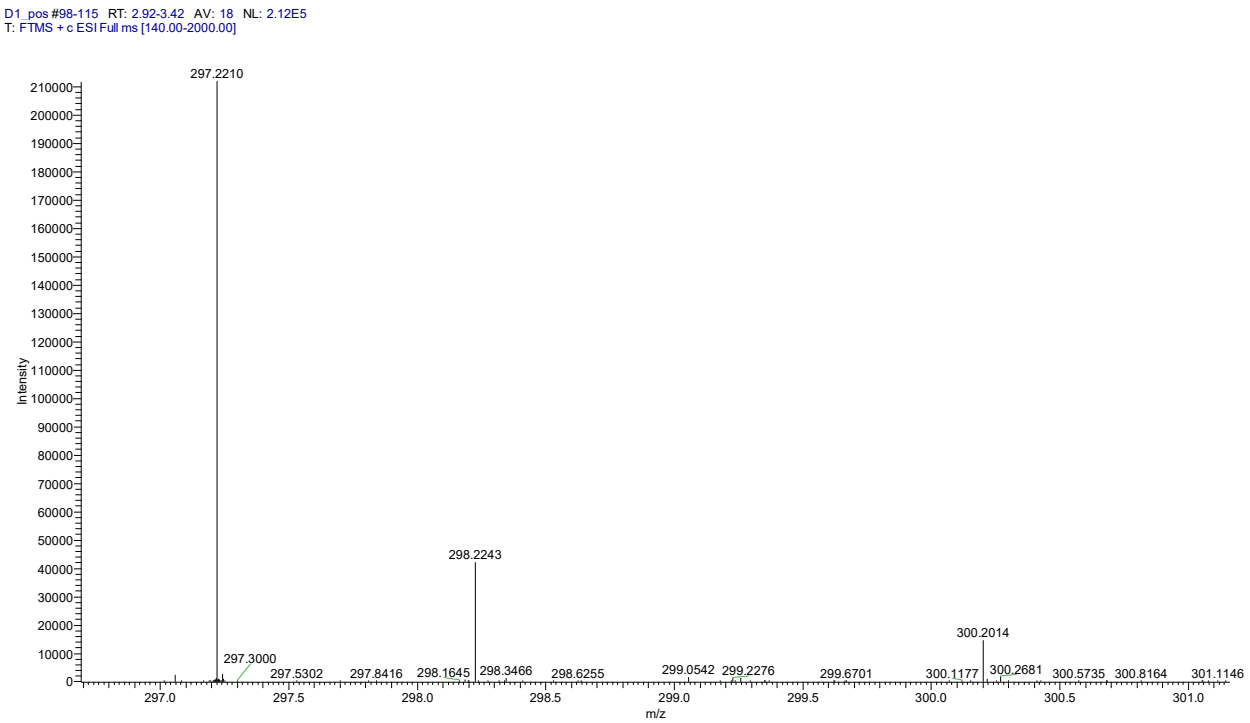

Figure S20. HRMS of HOC′BuAdPh.

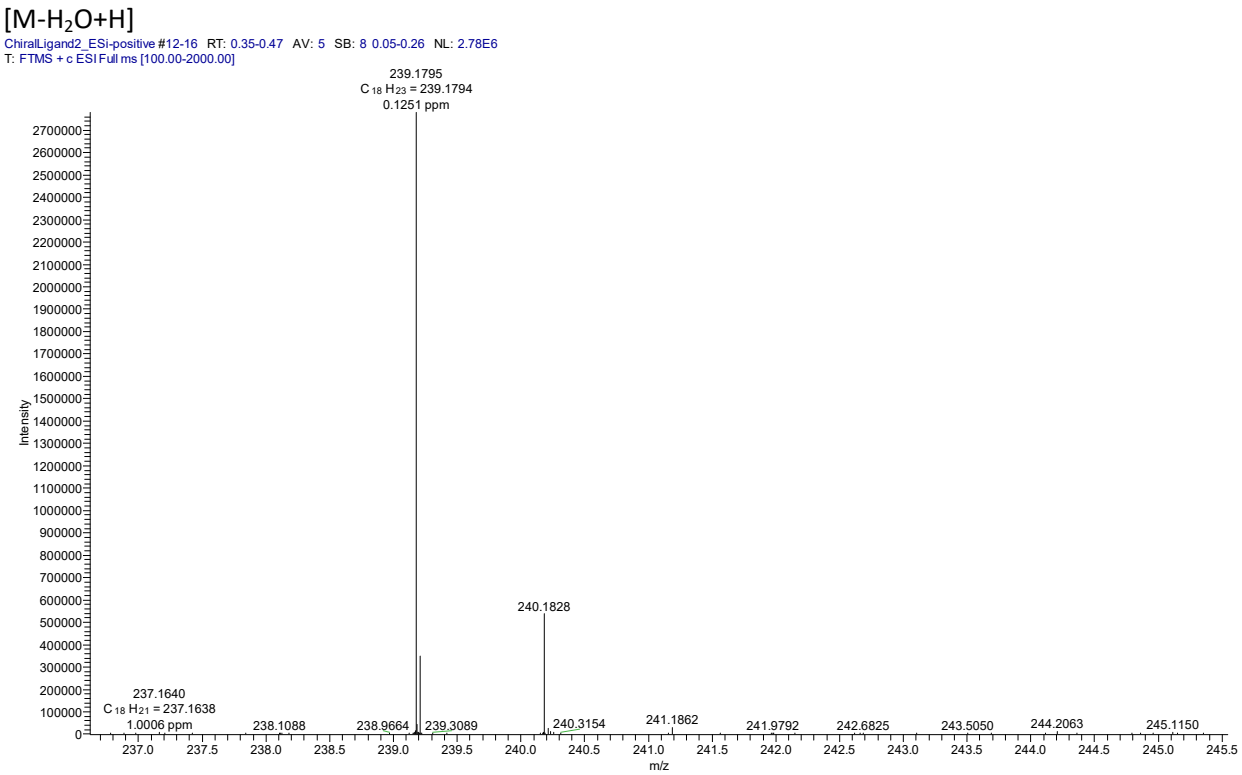

Figure S21. HRMS of HOCMeAdPh.

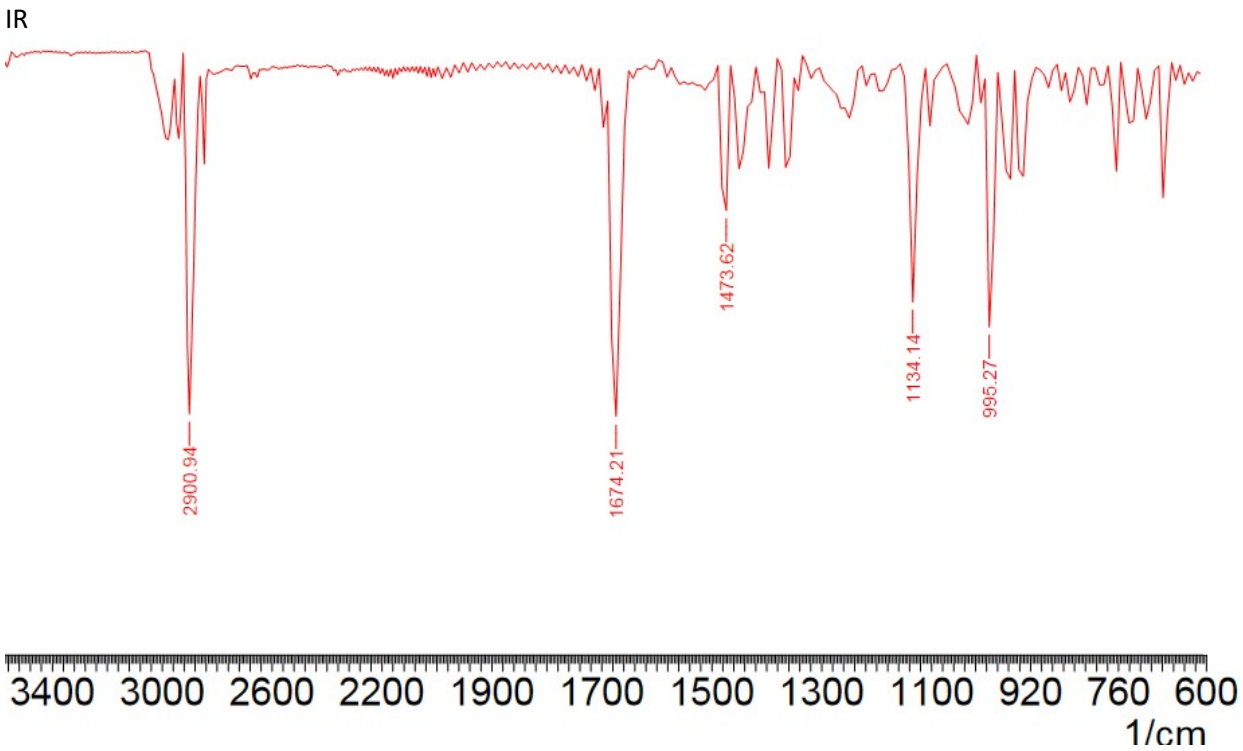

Figure S22. IR spectra of 1-adamantyl *tert*-butyl ketone.

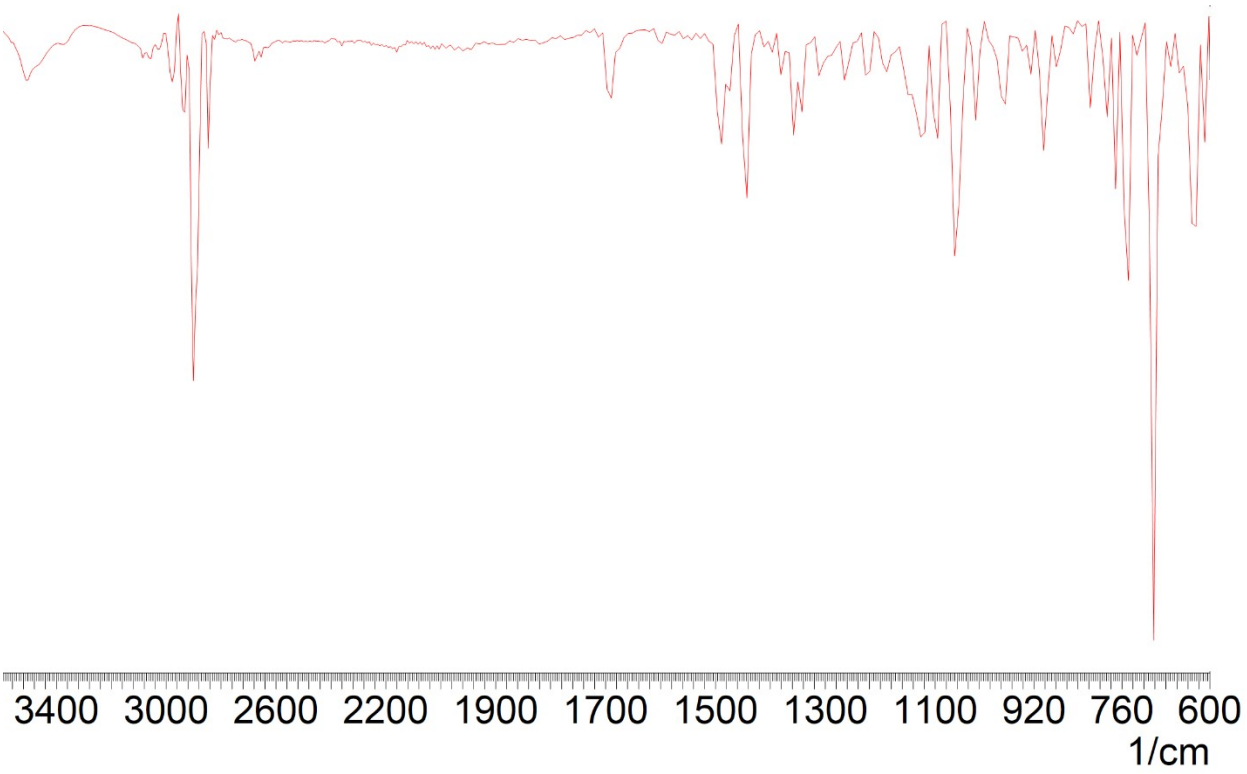

Figure S23. IR spectra of HOC′BuAdPh.

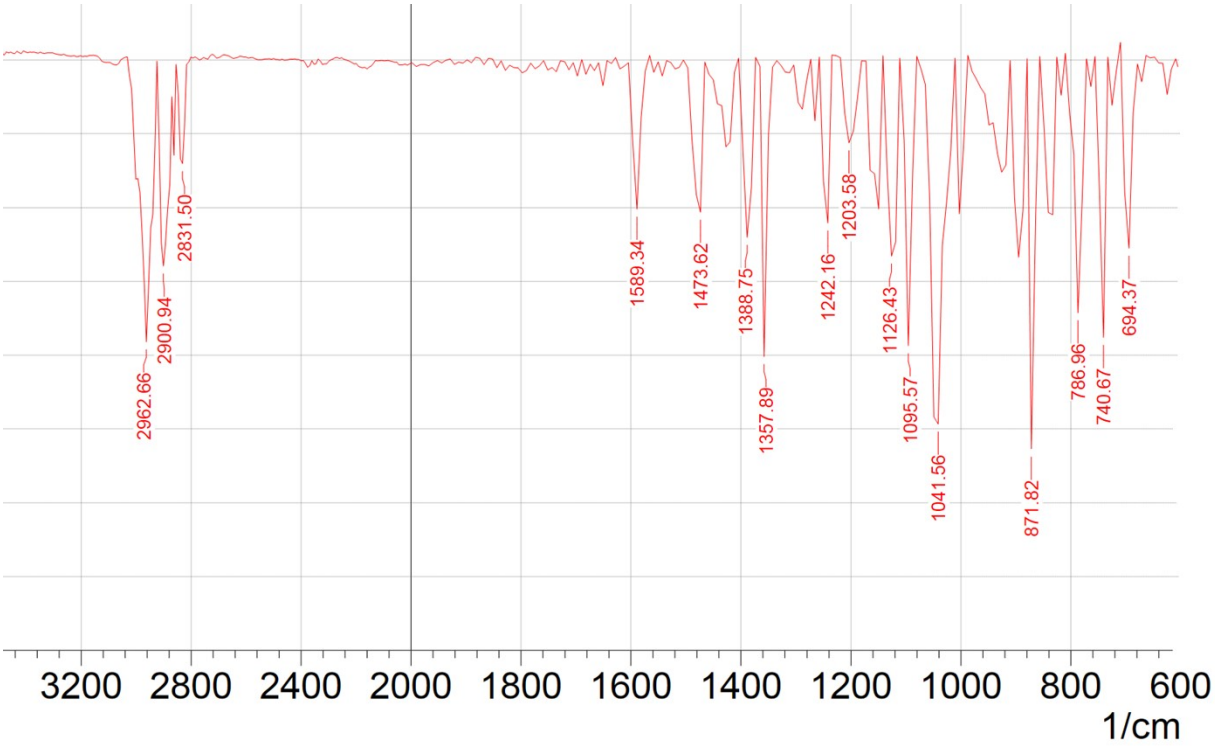

Figure S24. IR spectra of $Mg(OAd^tBuPh)_2(THF)_2$.

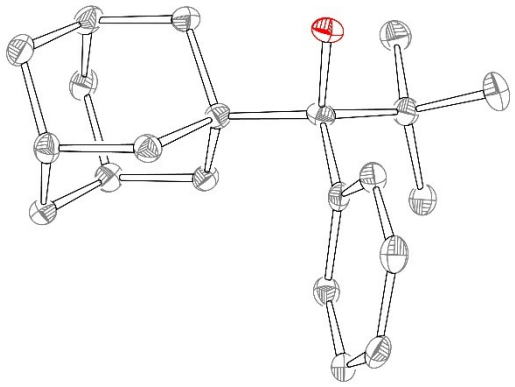

Figure S25. ORTEP diagram (50% probability ellipsoids) of the X-ray structure of HOC^{t}BuAdPh. H atoms were omitted for clarity.

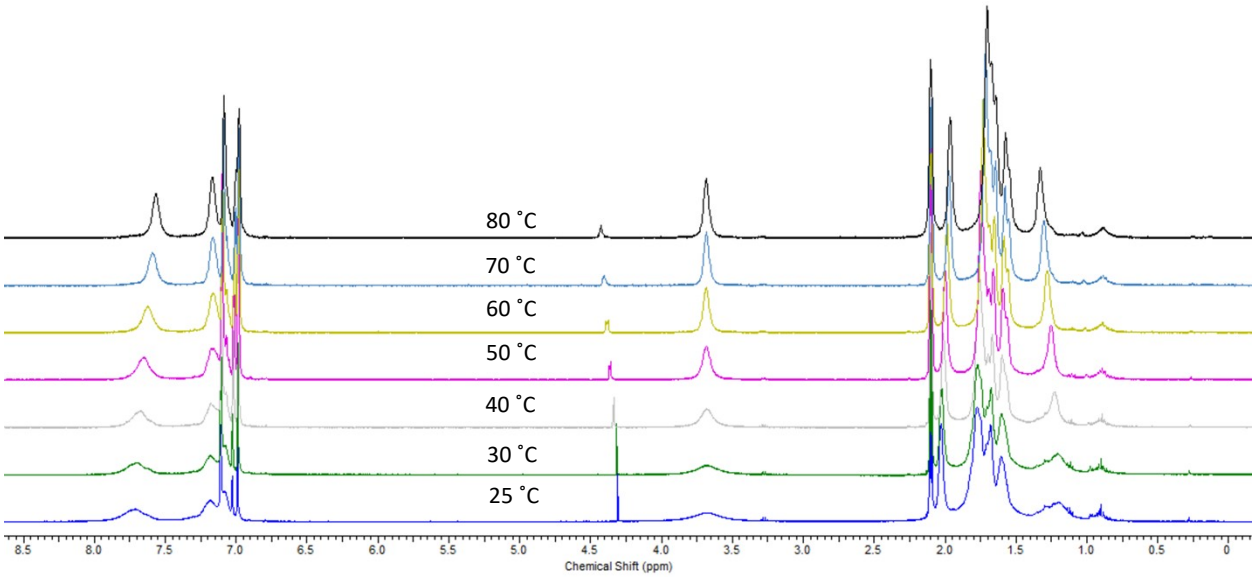

Figure S26. ^{1}H NMR of complex **3** at different temperatures (C_7D_8, 400 MHz).

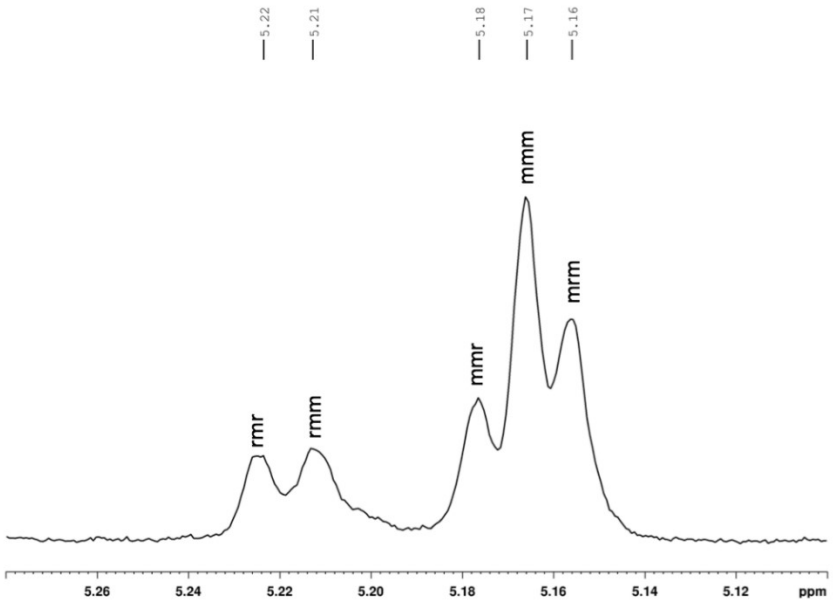

Figure S27. Homonuclear decoupled ^{1}H NMR spectrum of the methine region of polylactide synthesized by **2 (run 2, Table 1).**

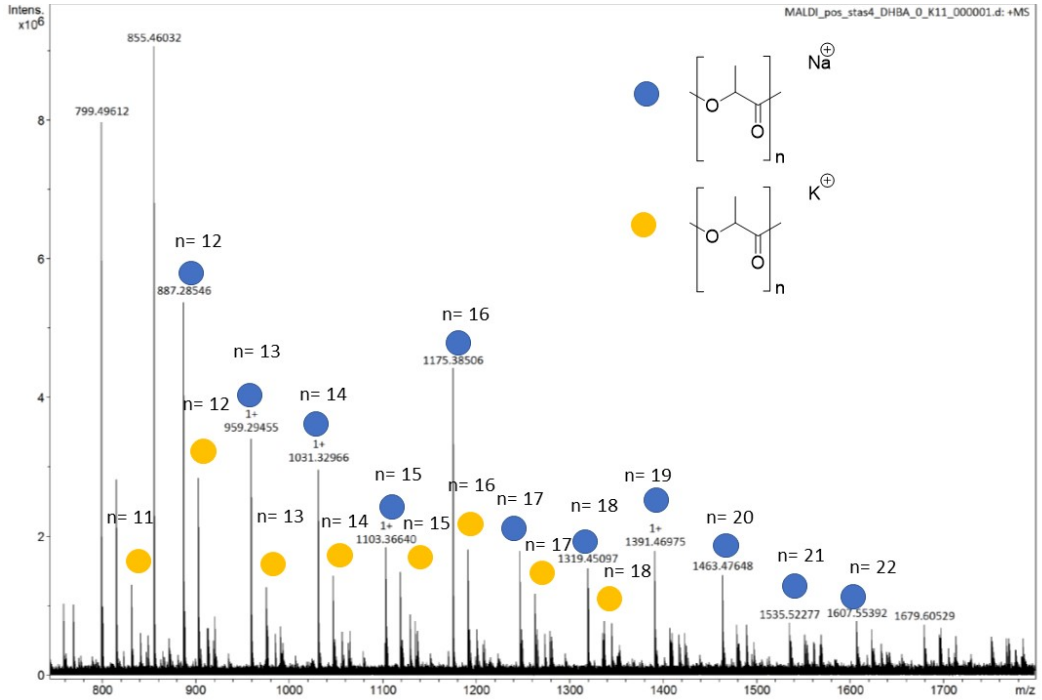

Figure S28. MALDI-ToF-MS spectrum of PLA synthesized by **2 (run 1, Table 1).**

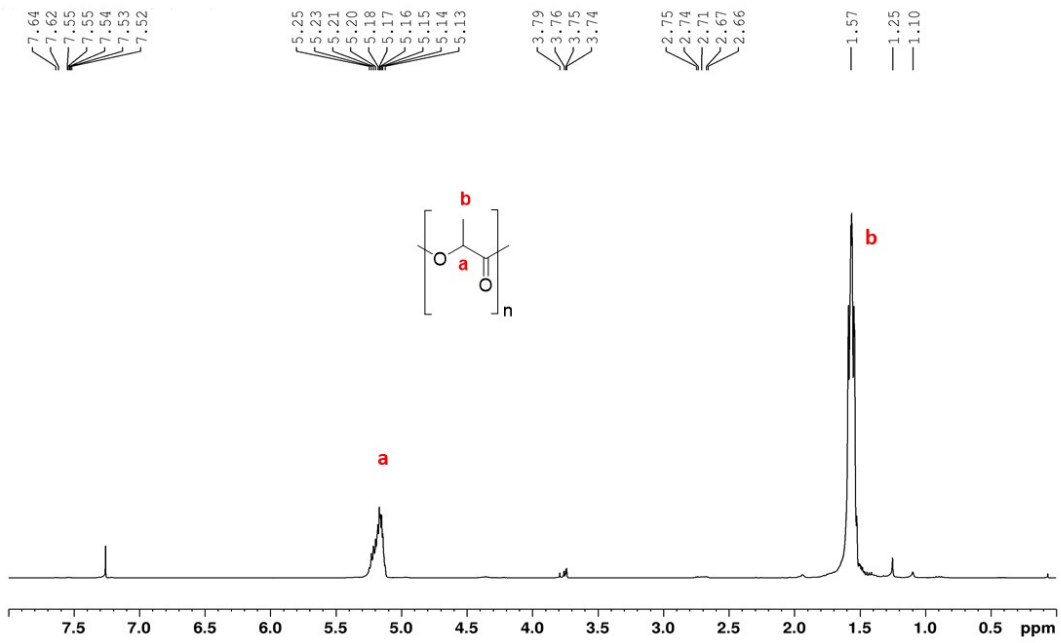

Figure S29. ^{1}H NMR spectrum of PLA synthesized by **2 (run 1, Table 1).**

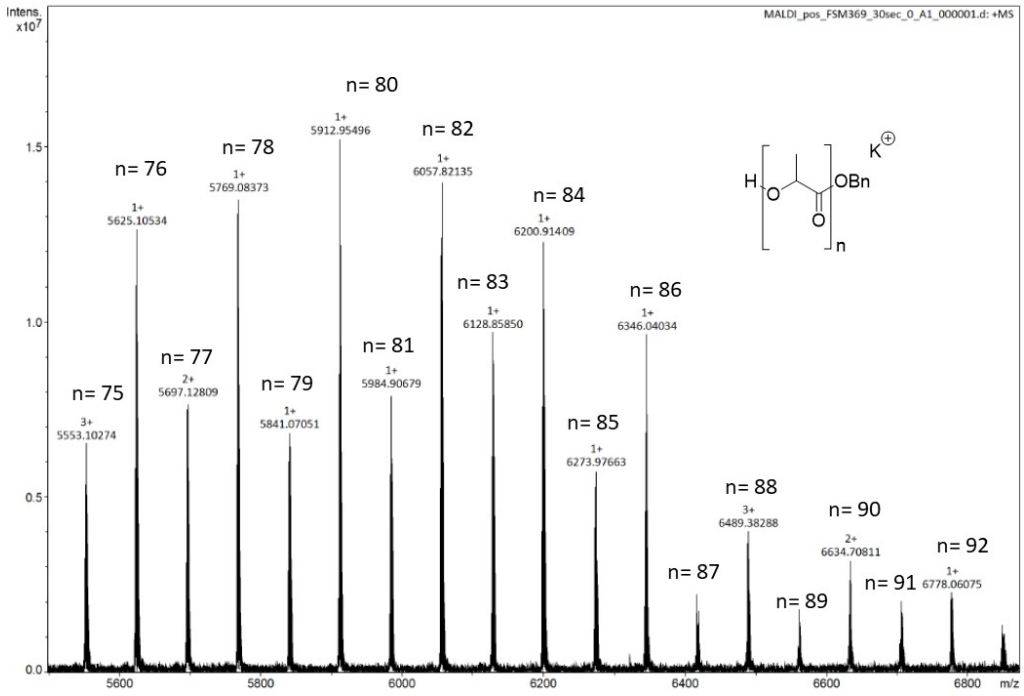

Figure S30. MALDI-TOF of the polymer sample obtained in run 17 of Table 1.

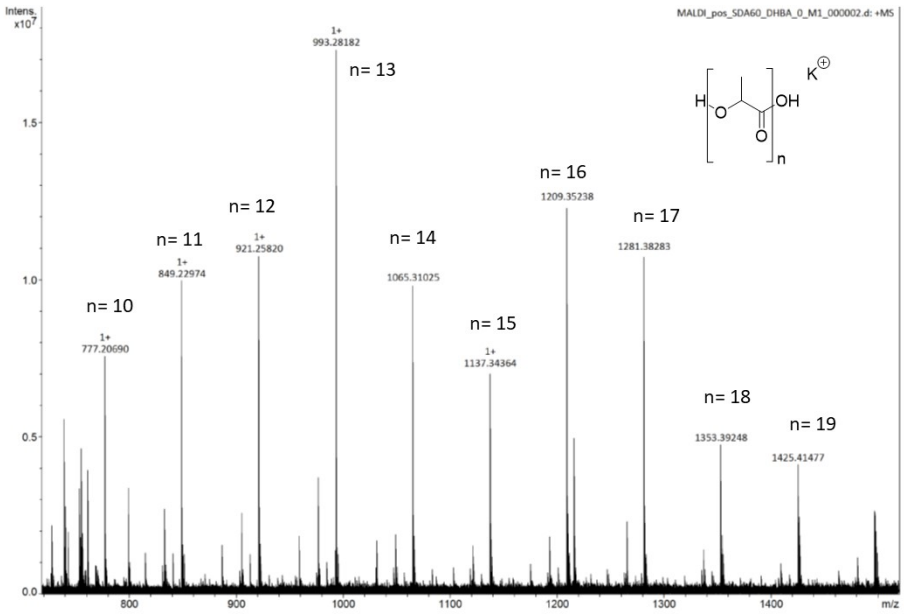

Figure S31. MALDI-ToF-MS spectrum of PLA synthesized by **2 (run 19, Table 1).**

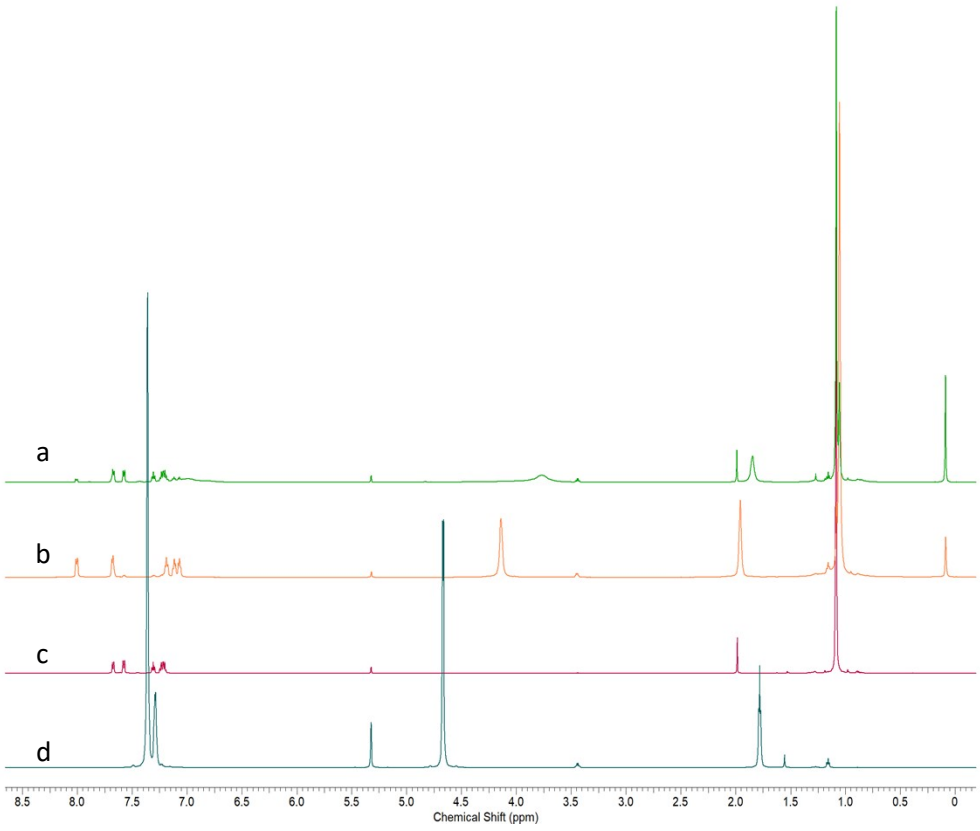

Figure S32. Stacked ^{1}H NMR spectra (CD_2Cl_2, 600 MHz, 25°C) of (a) BnOH : $Mg(OR^1)_2(THF)_2$ 1:1, (b) $Mg(OR)_2(THF)_2$, (c) ROH, (d) BnOH

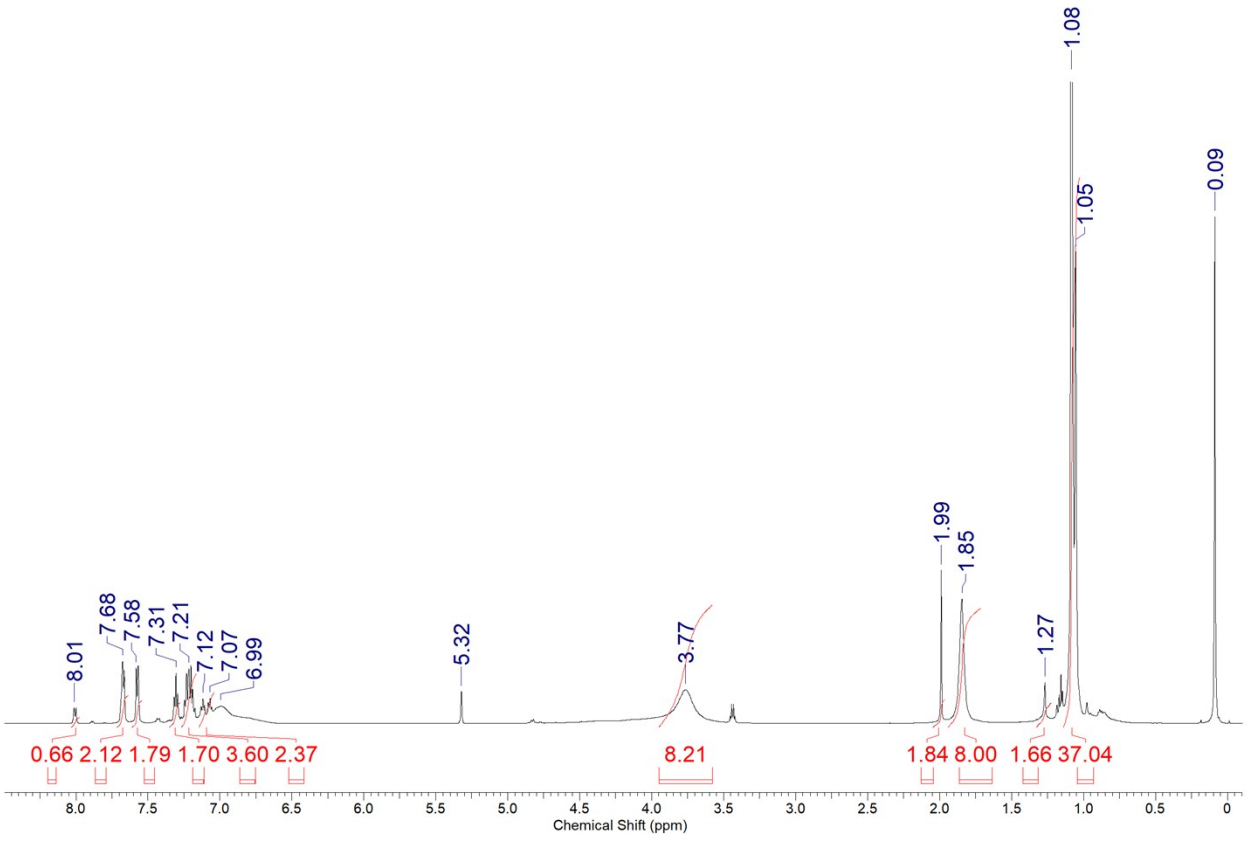

Figure S33 (a). ^{1}H NMR of 1:1 reaction between $Mg(OR)_2(THF)_2$ and BnOH (CD_2Cl_2, 600 MHz)

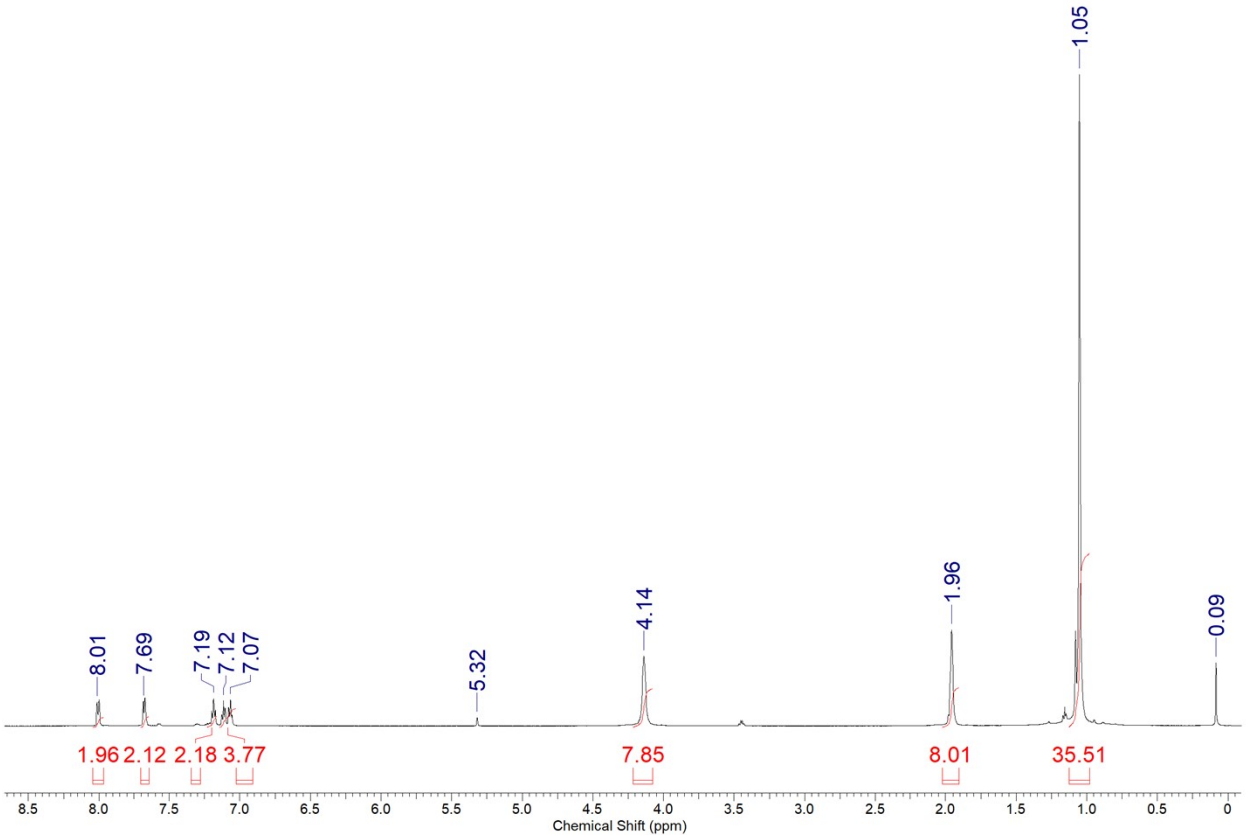

Figure S33 (b): ^{1}H NMR of $Mg(OR)_2(THF)_2$ (CD_2Cl_2, 600 MHz)

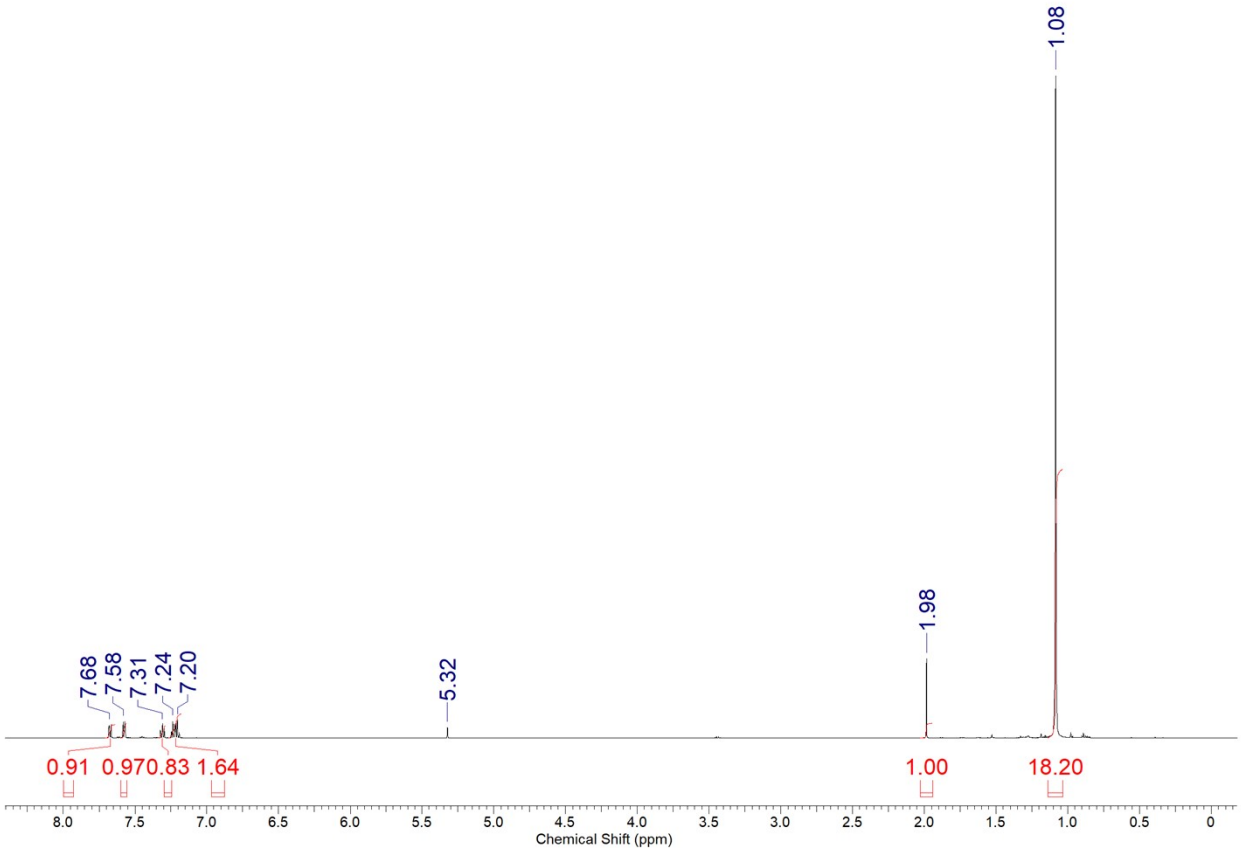

Figure S33 (c): ^{1}H NMR of ROH (CD_2Cl_2, 600 MHz)

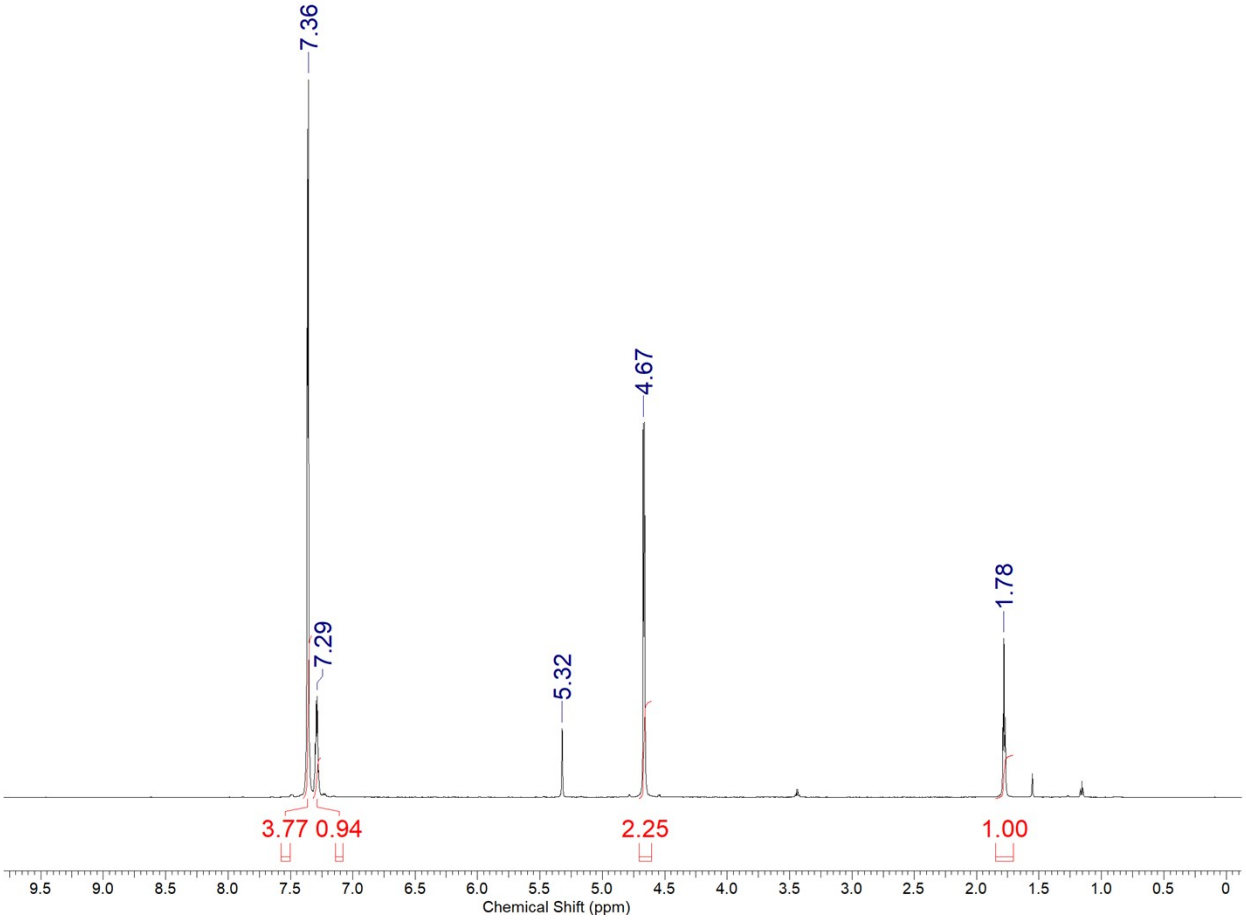

Figure S33 (d): ^{1}H NMR of BnOH (CD_2Cl_2, 600 MHz)

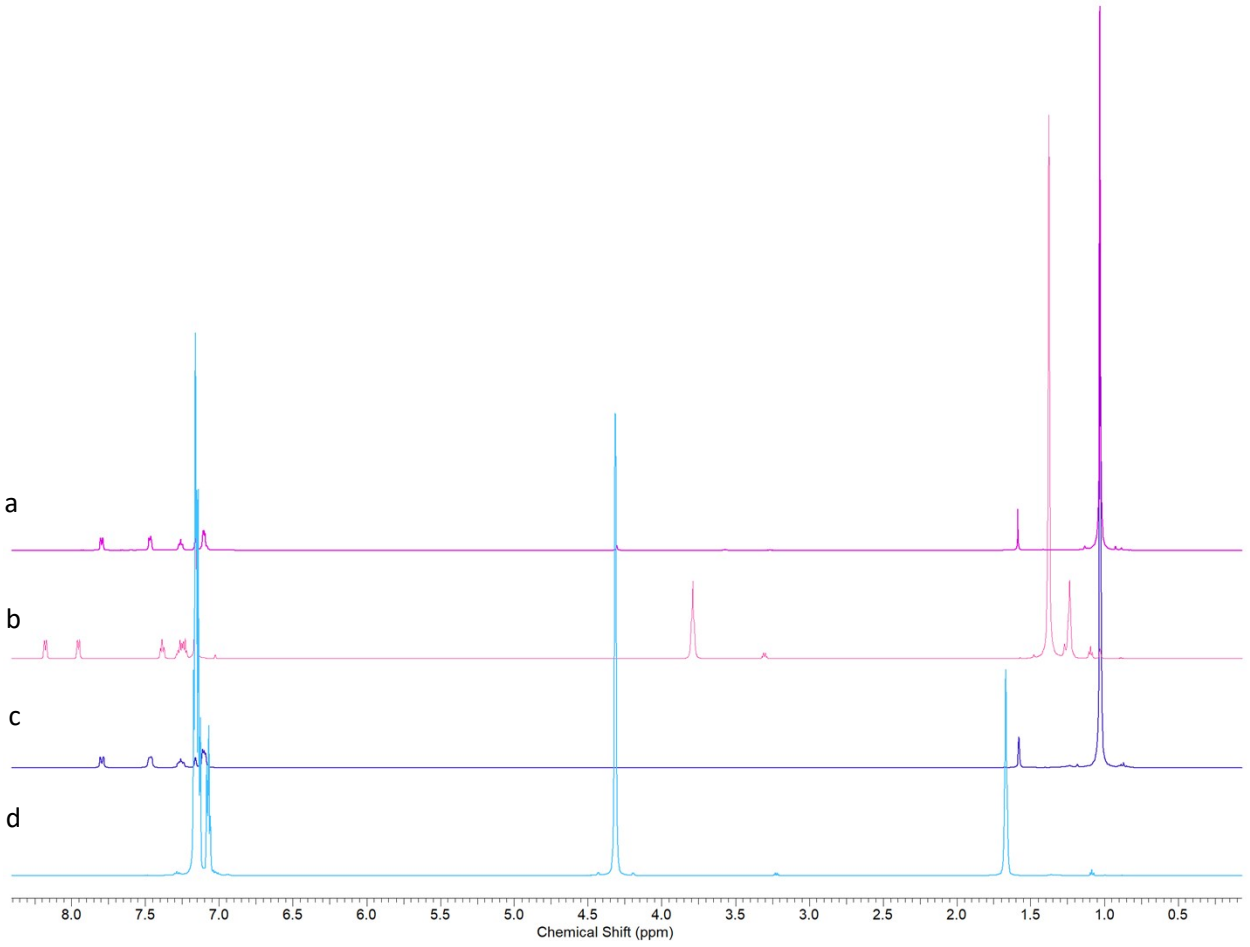

Figure S34 : Stacked ^{1}H NMR spectra of (a) BnOH : $Mg(OR)_2(THF)_2$ 2:1, (b) $Mg(OR)_2(THF)_2$, (c) ROH, (d) BnOH (C_6D_6, 600 MHz)

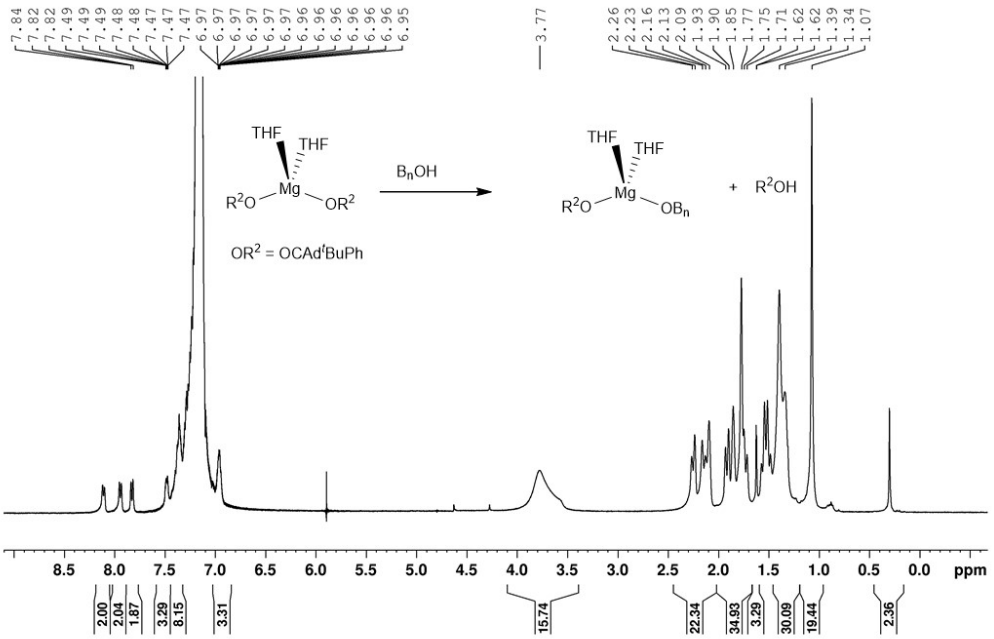

Figure S35. ^{1}H NMR spectrum (C_6D_6, 400 MHz, 25°C) of BnOH : $Mg(OR^2)_2(THF)_2$ 1:1.

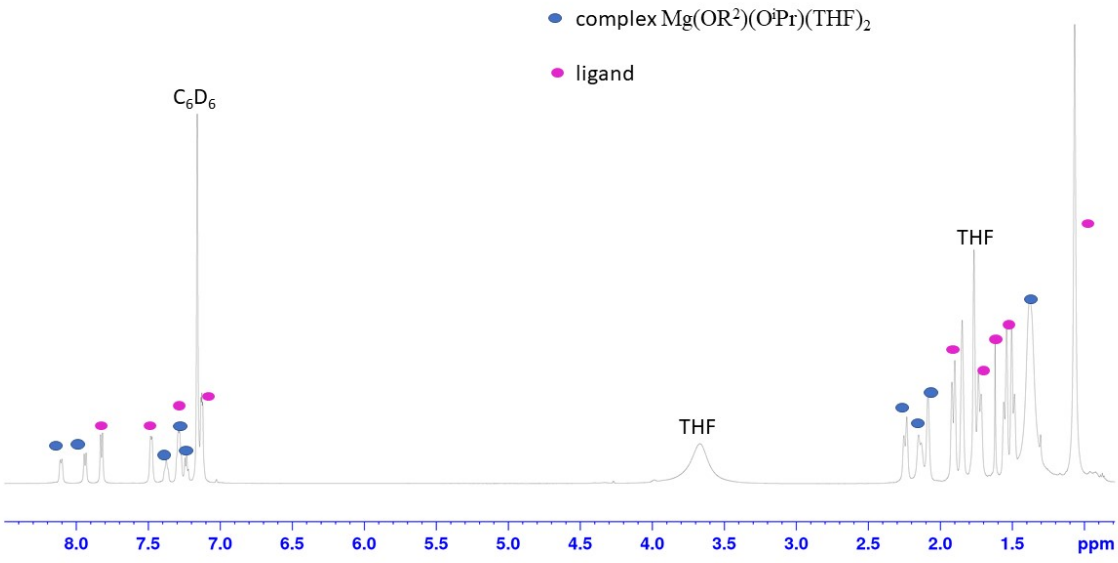

Figure S36 ^{1}H NMR of 1:1 reaction between $Mg(OR)_2(THF)_2$ and iPrOH (C_6D_6, 600 MHz)

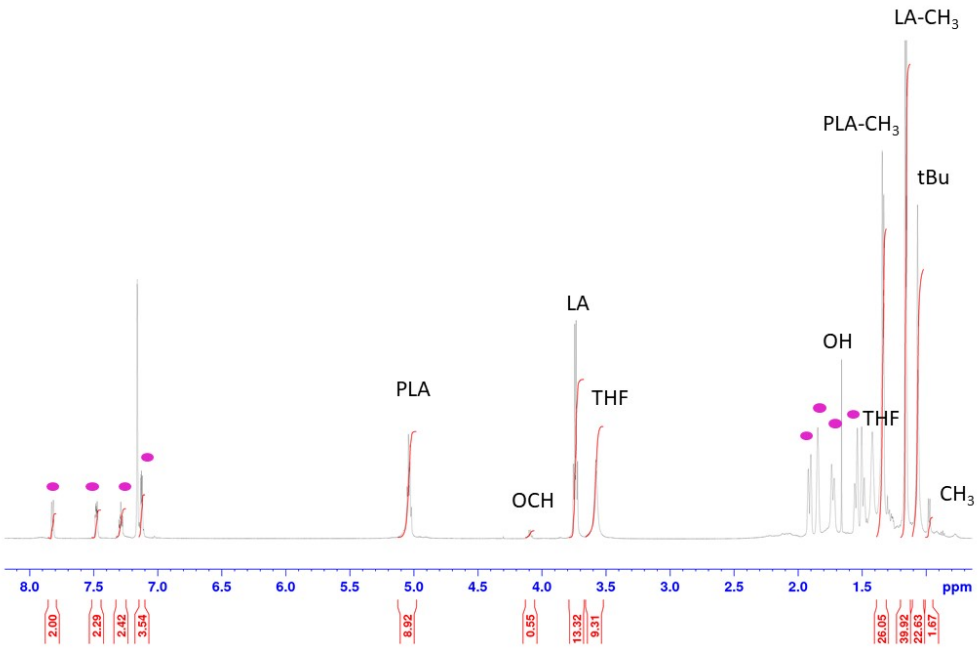

Figure S37 ^{1}H NMR of 1:1 reaction between $Mg(OR)_2(THF)_2$ and iPrOH and 10 equivalent of LA(C_6D_6, 600 MHz)

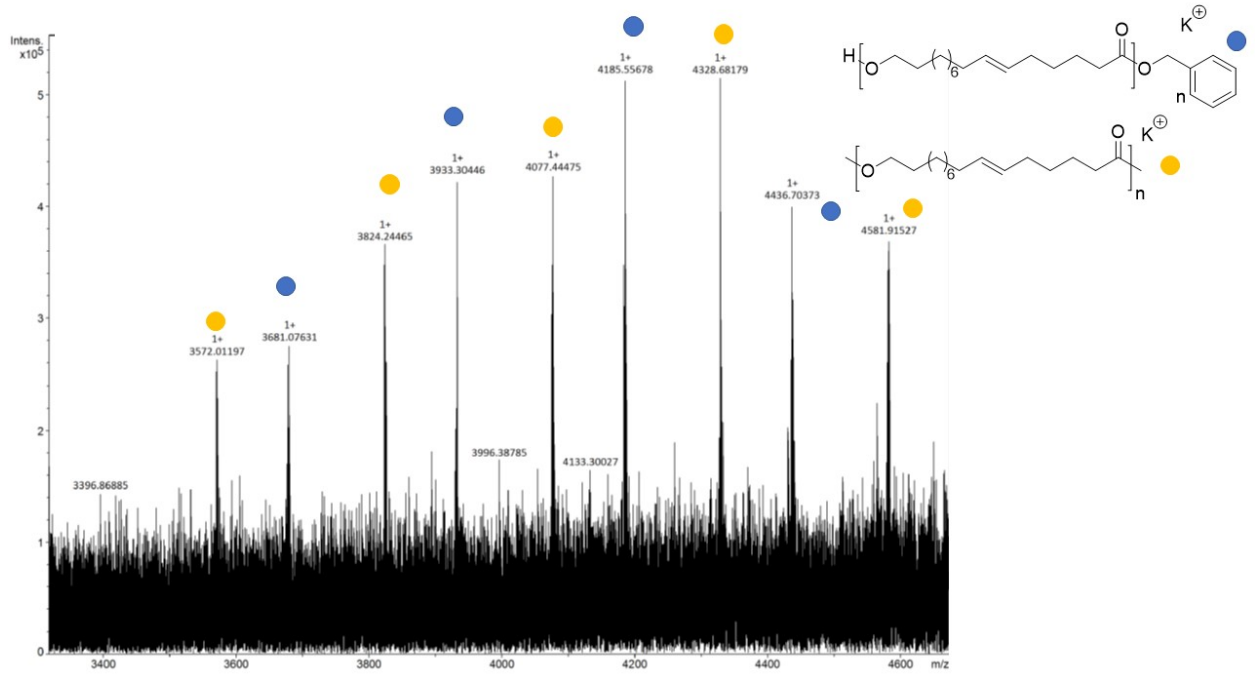

Figure S38. Enlargement of MALDI-ToF-MS spectrum of Figure 5.

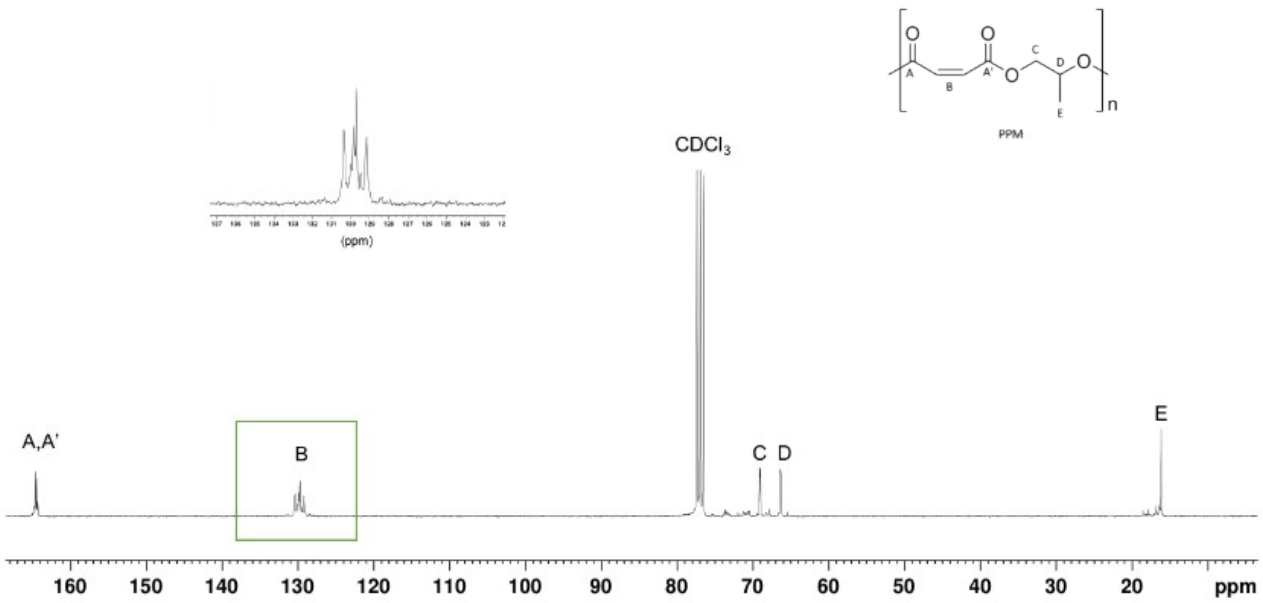

Figure S39. ^{13}C NMR (300 MHz, $CDCl_3$, 298 K) spectrum of poly(propylene maleate).

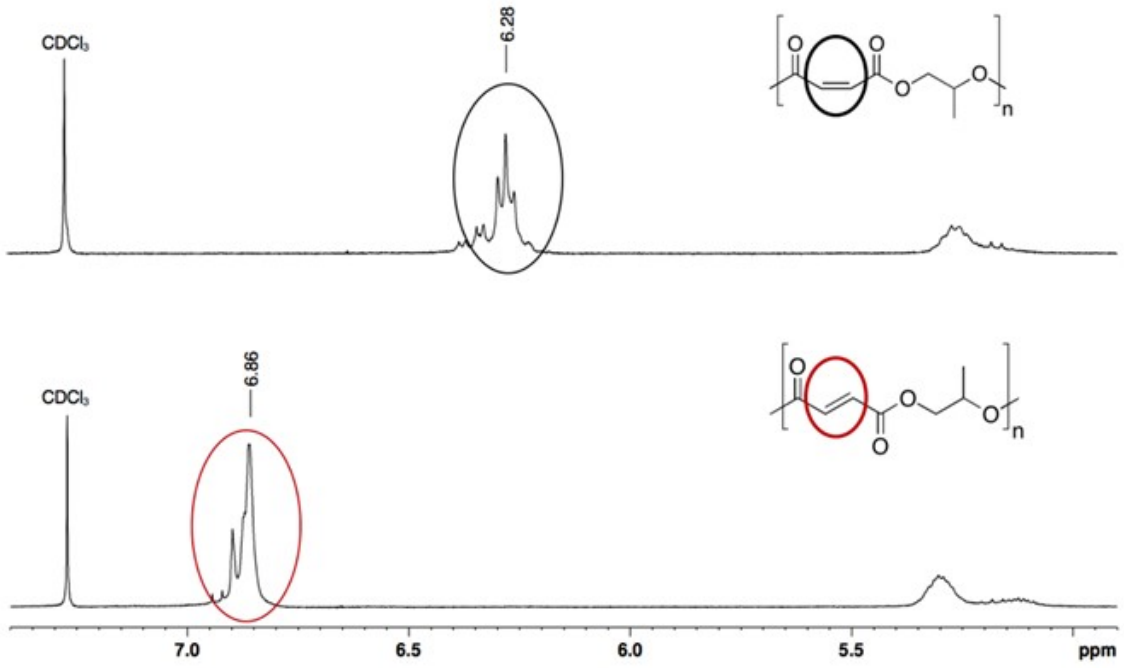

Figure S40. ^{1}H NMR spectrum of poly(propylene maleate) (top) and of poly(propylene fumarate) (bottom) obtained after isomerization reaction.

Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	18010	7738	17850	29690	42116	16284	2.307

Peak Information

	Start (mins)	End (mins)
Baseline region 1	4.78333	5.33333
Baseline region 2	11.75000	12.63333
Peak 1	6.08333	8.23333

Peak Trace Information

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	6.88333	37.366	0.738

Chromatogram Plot

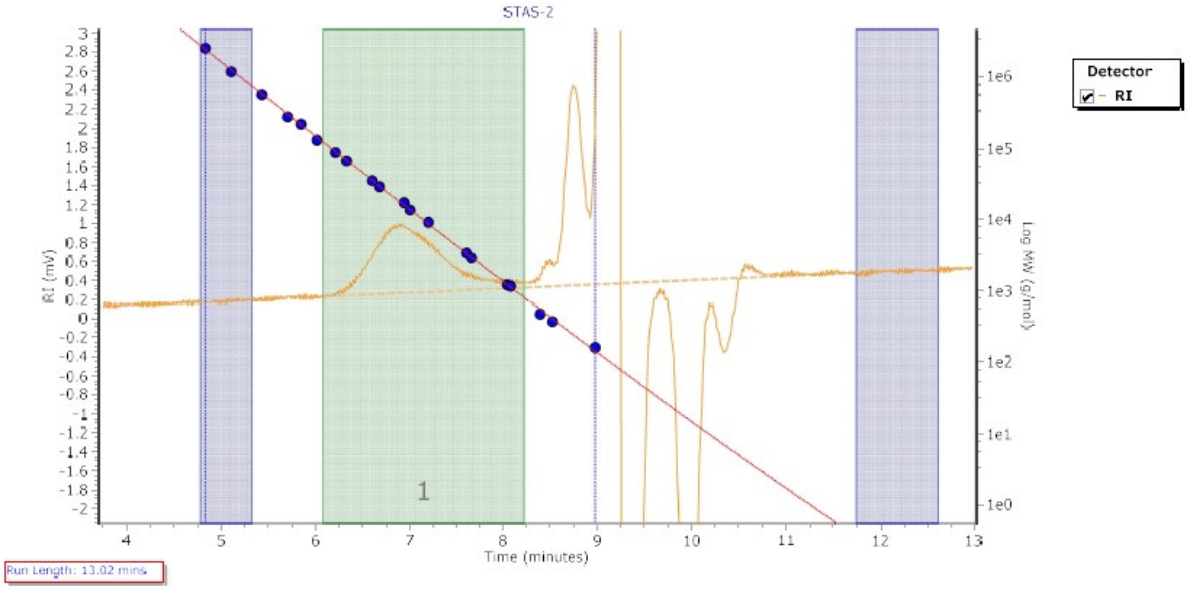

Figure S41. GPC trace of the polymer sample obtained in run 6 of Table 1.

Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	32501	15684	32943	50660	67287	30458	2.1

Peak Information

	Start (mins)	End (mins)
Baseline region 1	4.15000	5.21667
Baseline region 2	11.71667	12.45000
Peak 1	5.95000	8.01667

Peak Trace Information

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	6.63333	39.924	0.834

Chromatogram Plot

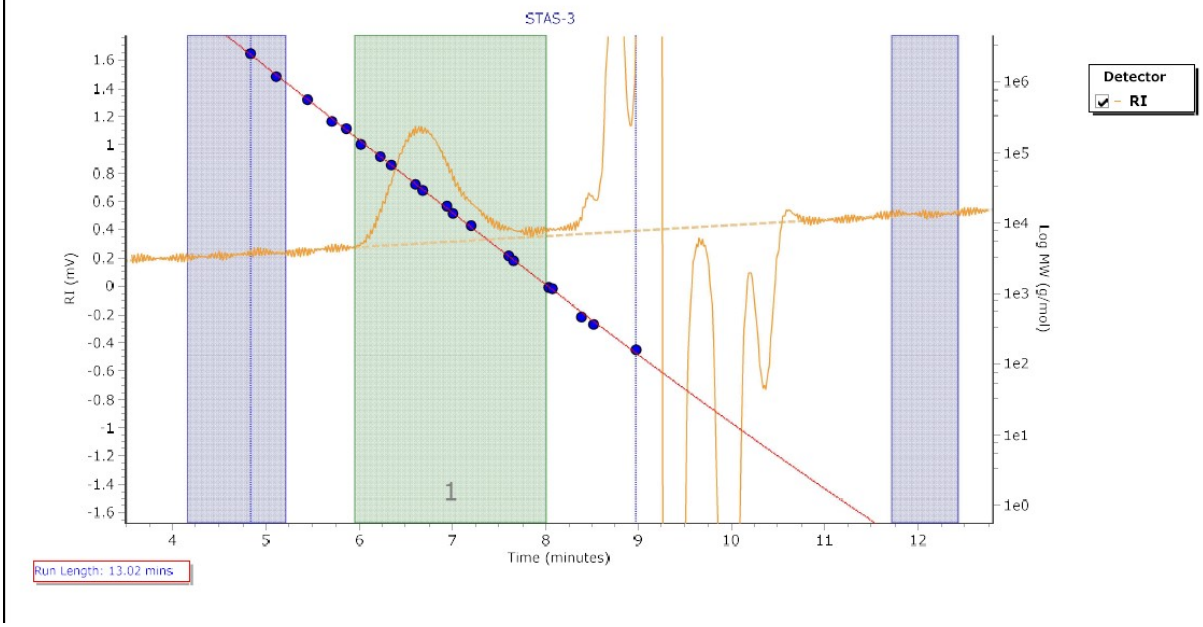

Figure S42. GPC traces of the polymer sample obtained in run 7 of Table 1.

Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	94446	52074	92590	132826	172849	86899	1.778

Peak Information

	Start (mins)	End (mins)
Baseline region 1	3.48333	4.35000
Baseline region 2	11.58333	12.58333
Peak 1	5.43333	7.43333

Peak Trace Information

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	6.18333	36.999	0.903

Chromatogram Plot

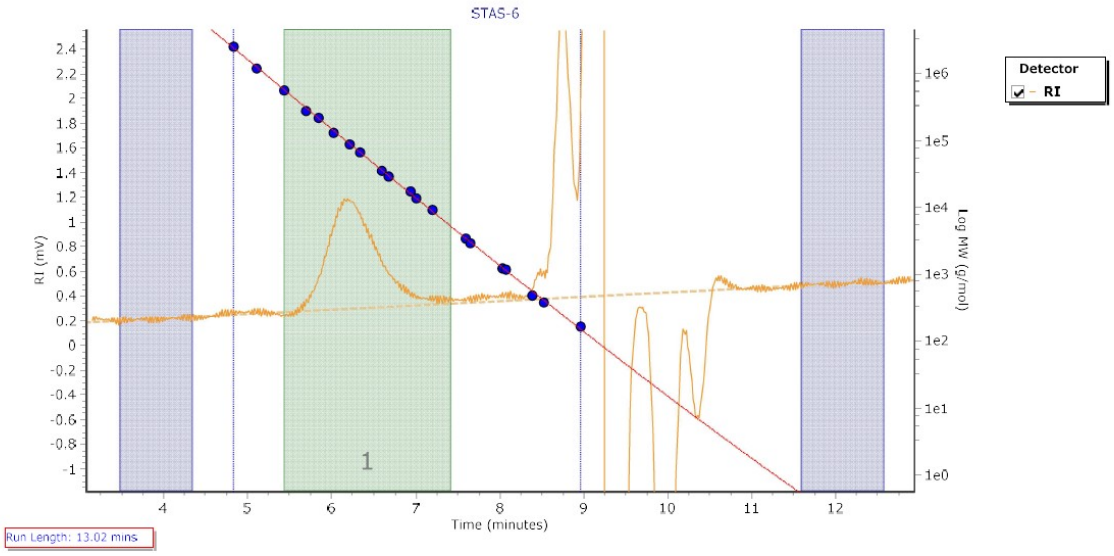

Figure S43. GPC traces of the polymer sample obtained in run 8 of Table 1.

Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	21077	11190	29334	59155	94456	25966	2.621

Peak Information

	Start (mins)	End (mins)
Baseline region 1	4.90000	5.30000
Baseline region 2	11.80000	12.50000
Peak 1	5.81667	8.10000

Peak Trace Information

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	6.81667	45.720	0.783

Chromatogram Plot

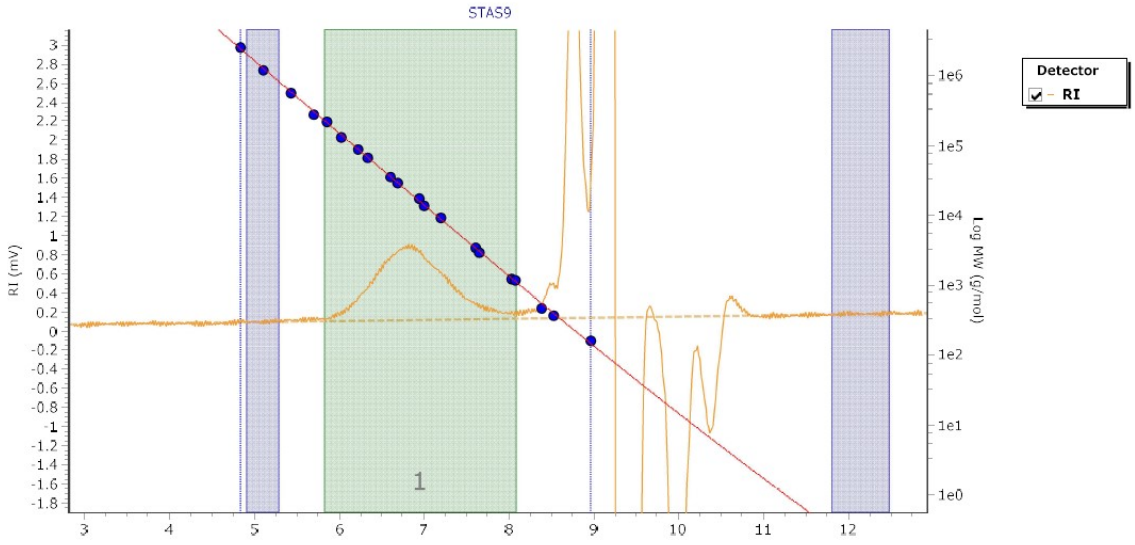

Figure S44. GPC traces of the polymer sample obtained in run 11 of Table 1.

Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	10896	9160	11307	13321	15403	11010	1,234

Peak Information

	Start (mins)	End (mins)
Baseline region 1	3,33333	4,48333
Baseline region 2	11,51667	12,40000
Peak 1	6,60000	7,90000

Peak Trace Information

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	7,11667	27,053	1,110

Chromatogram Plot

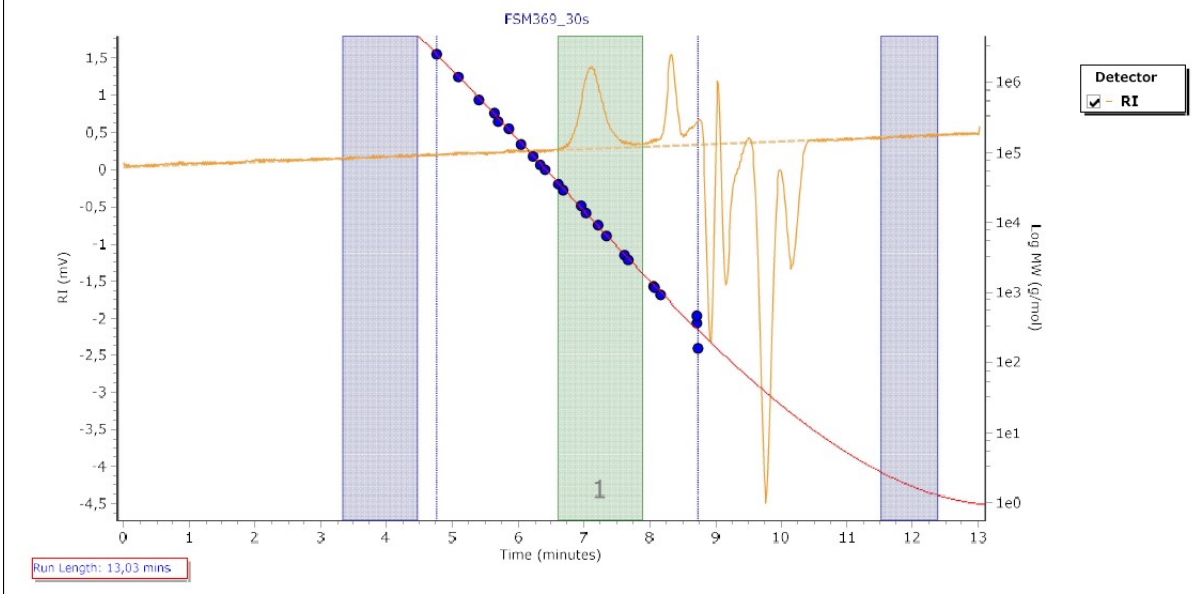

Figure S45. GPC traces of the polymer sample obtained in run 17 of Table 1.

Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	129668	61666	196782	417460	689571	172269	3,191

Peak Information

	Start (mins)	End (mins)
Baseline region 1	3,38333	3,88333
Baseline region 2	11,91667	12,71667
Peak 1	4,91667	7,58333

Peak Trace Information

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	6,05000	192,401	3,011

Chromatogram Plot

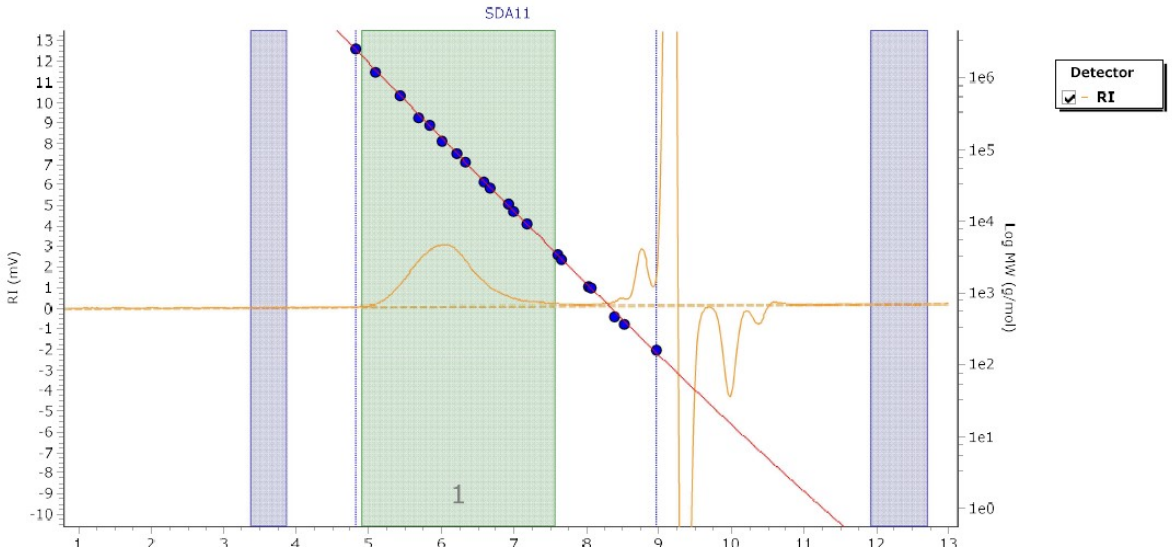

Figure S46. GPC traces of the polymer sample obtained in run 3 of Table 2.

Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	7033	3144	5967	10226	19275	5512	1,898

Peak Information

	Start (mins)	End (mins)
Baseline region 1	5,41667	5,80000
Baseline region 2	11,86667	12,43333
Peak 1	6,26667	8,50000

Peak Trace Information

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	7,28333	156,761	3,933

Chromatogram Plot

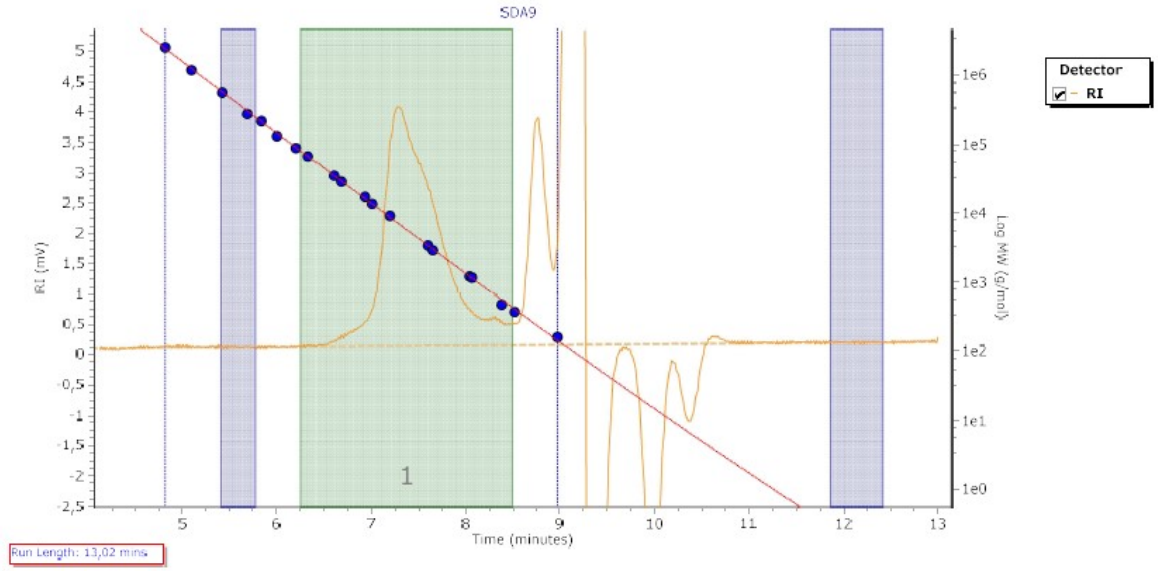

Figure S47. GPC traces of the polymer sample obtained in run 1 of Table 3.

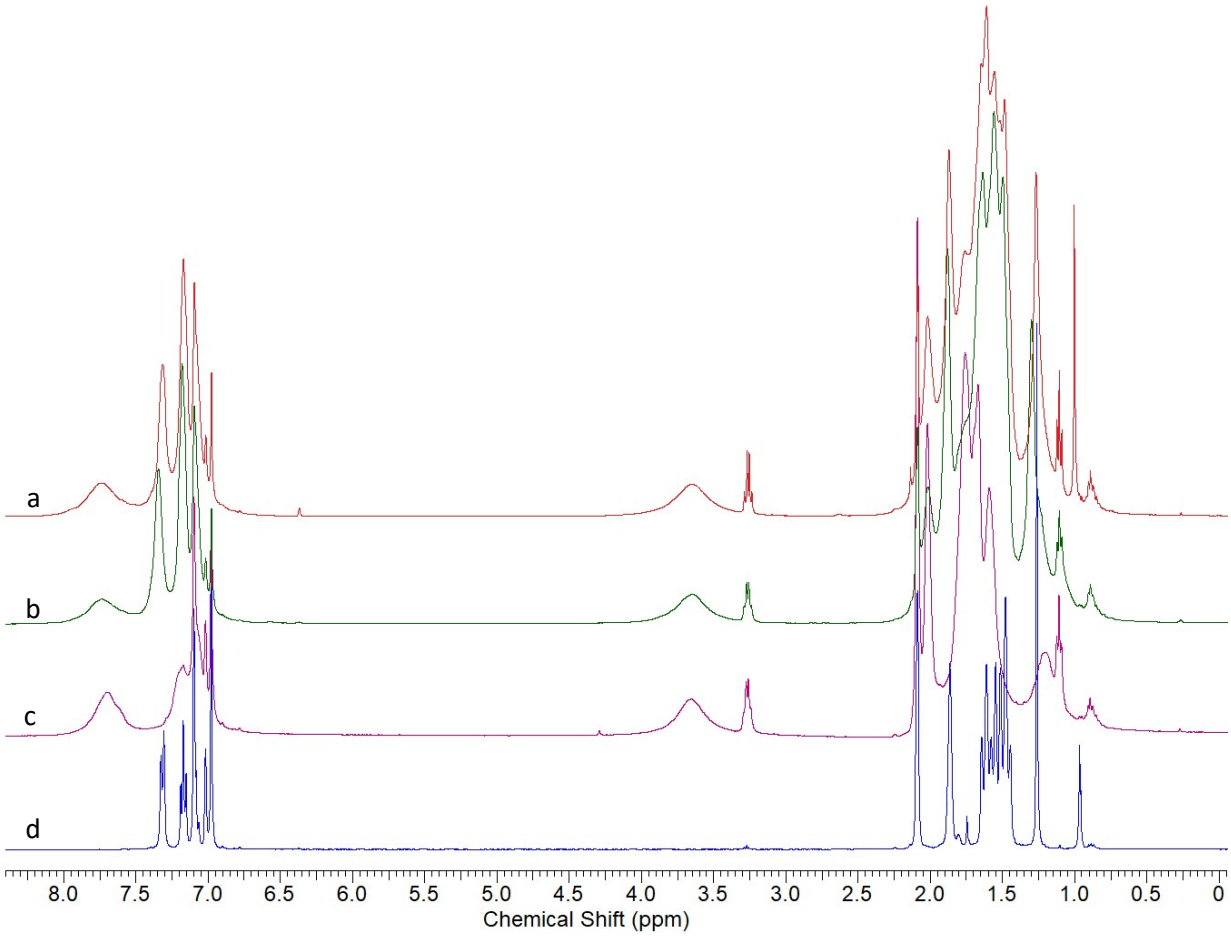

Figure S48. Stacked ^{1}H NMR spectra (C_7D_8, 400 MHz) of (a) a solution containing **3** and HOR^3 (1:2 ratio) heated to 80 °C for 1 hour, (b) a solution containing **3** and HOR^3 (1:2 ratio) at room temperature), (c) **3**, (d) HOR^3.

DOSY spectrum of complex 3

The DOSY data were collected on a Bruker NEO 500 spectrometer using a 5 mm iProbe. The pulse sequence, ledbpgp2s, used stimulated echos and LED with bipolar gradient pulses. The diffusion time, D, and gradient length, d, were optimized to achieve ~95% attenuation of the signals for the complex between 2% and 95% gradient strength. This led to values for D of 100 ms and d of 1.8 ms. The DOSY experiment was then run with a gradient ramp from 2-95% with 16 linear steps. There were 16 transients collected at each gradient, with an acquisition time of 6.5 seconds and a relaxation delay of 4 seconds. A line broadening of 0.5 Hz was applied, and baseline correction was performed. The resulting array was transformed in MestreNova using the Bayesian transform with a resolution factor of 4.

The resulting data show three distinct ranges. The d8-Toluene residual proton signals along with some trace amount of ether appear in the area of -8.6 - -8.8 on the diffusion dimension represented as log[m^2/sec]. The complex of interest appears in a band at -9.3 on the diffusion axis. And a trace amount of contaminant silicone grease appears at -10.3.

The complex was prepared at concentrations of 5 and 10 mM, and DOSY experiments were performed on each. The resulting diffusion data were consistent between the samples. This suggests the complex is intact in the toluene solution, without a significant population of dissociated components.

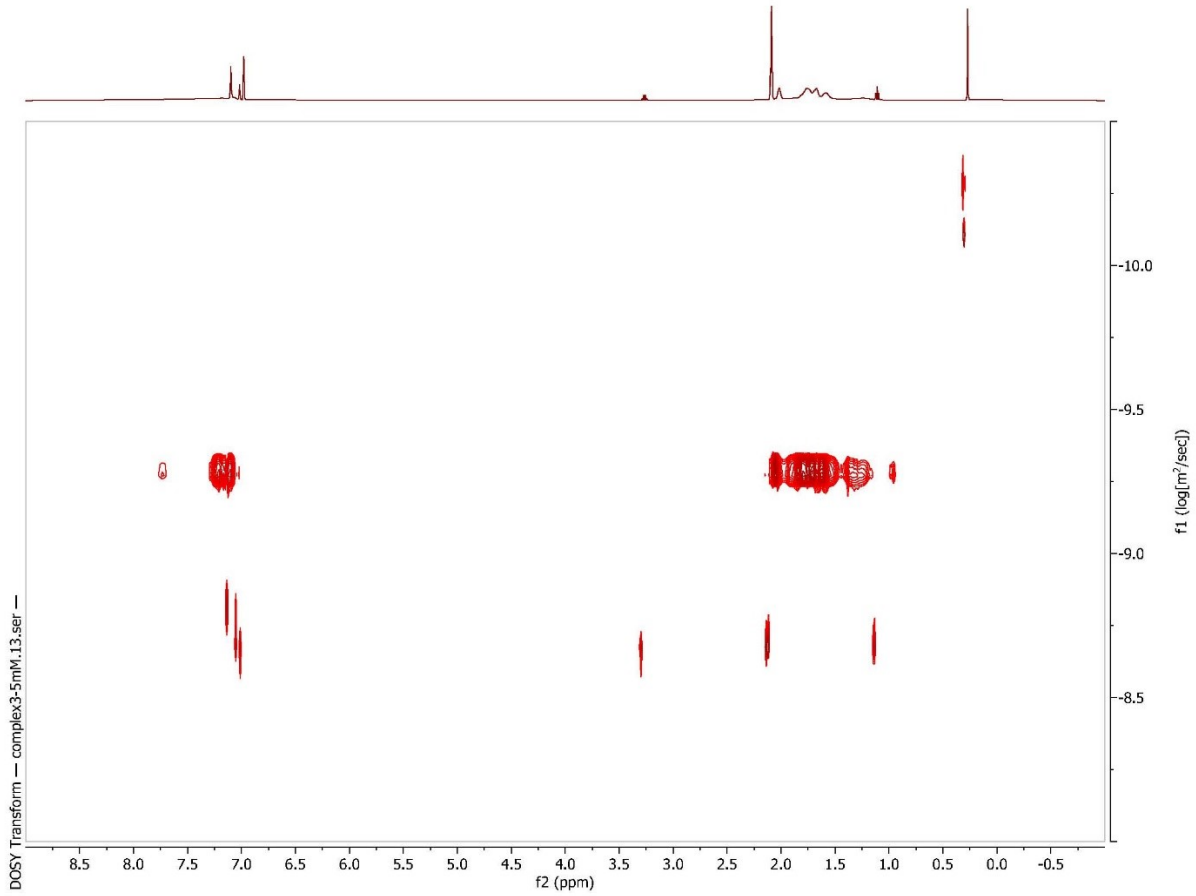

Figure S49. DOSY spectrum of complex **3**.