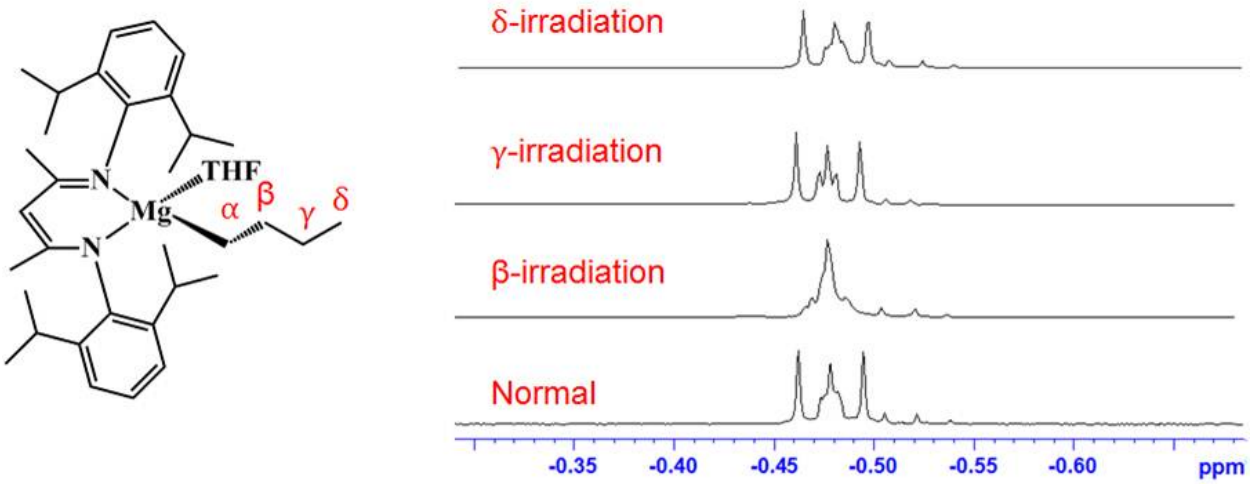
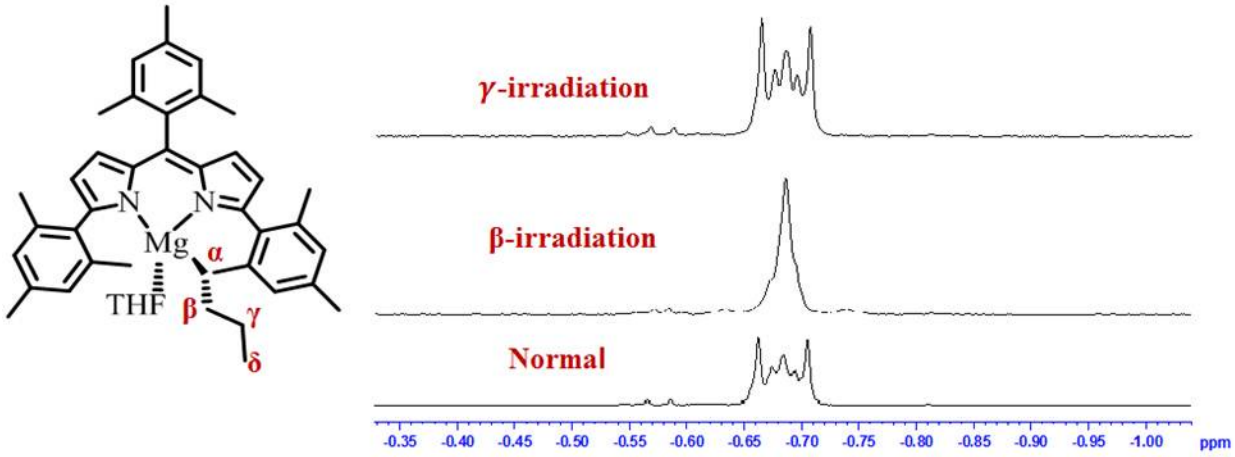
Supporting Information:

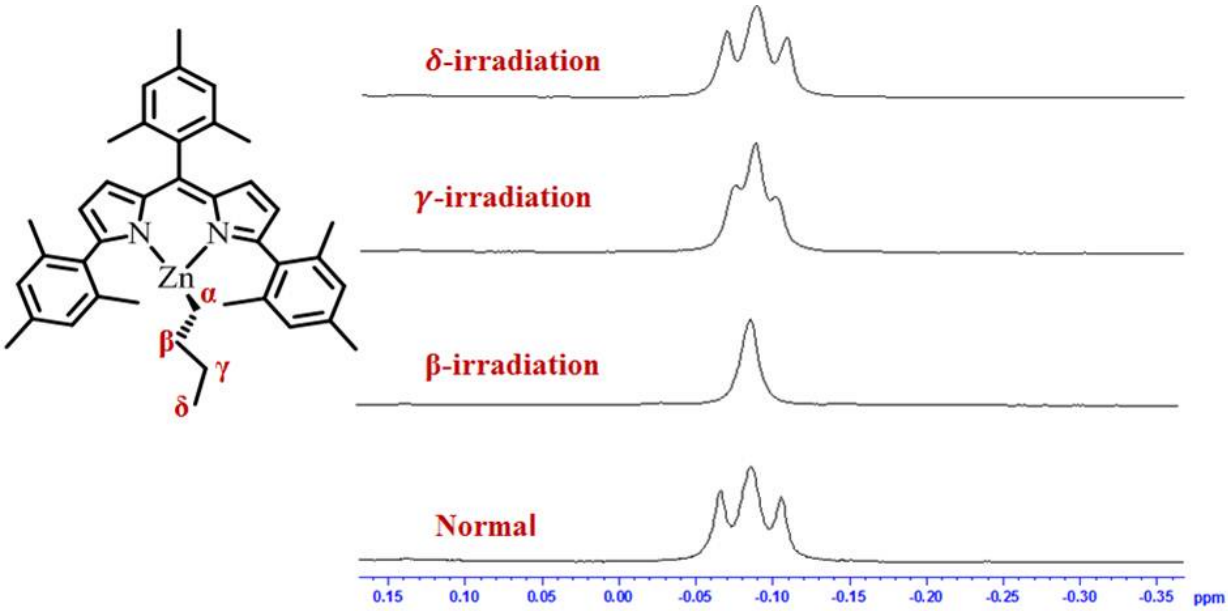
Some Chemistry of Magnesium Alkyls Supported by 1,5,9-trimesityldipyrromethene and 2-[(2,6-diisopropylphenyl)amino]-4-[(2,6-diisopropylphenyl)imino]pent-2-ene. A Comparative Study.



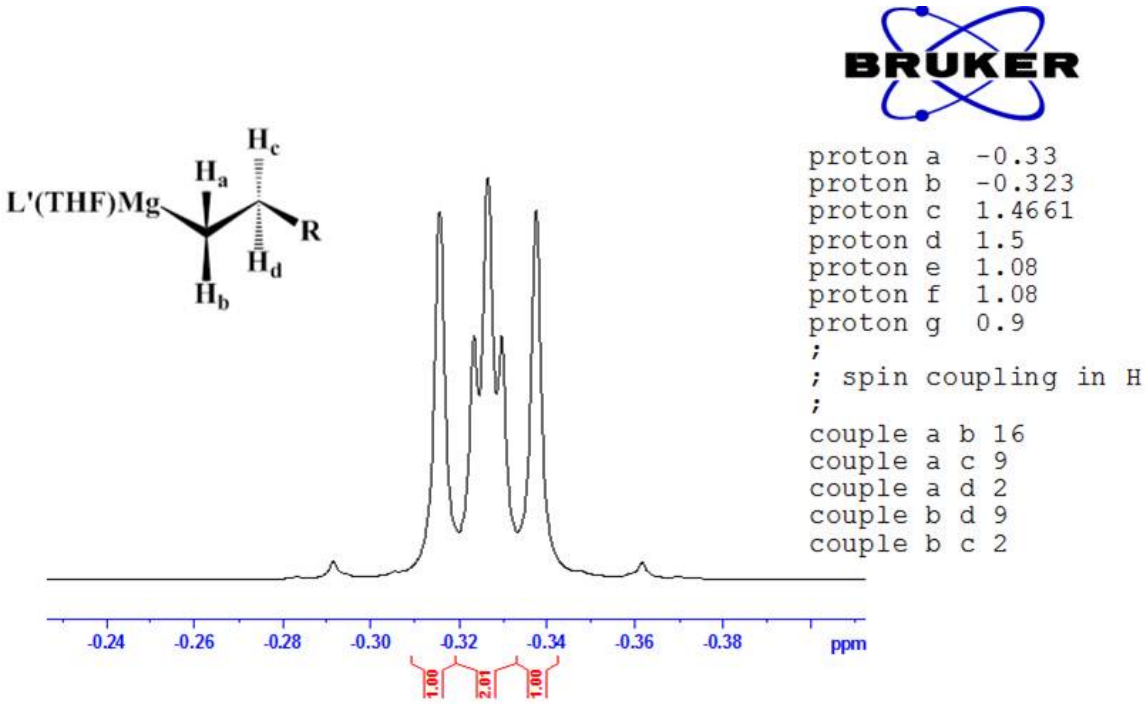
SI 1. Homodecoupled ^{1}H NMR spectra of the α-CH_2 protons in L′MgBu^n(THF) recorded in toluene-d_8 solution.



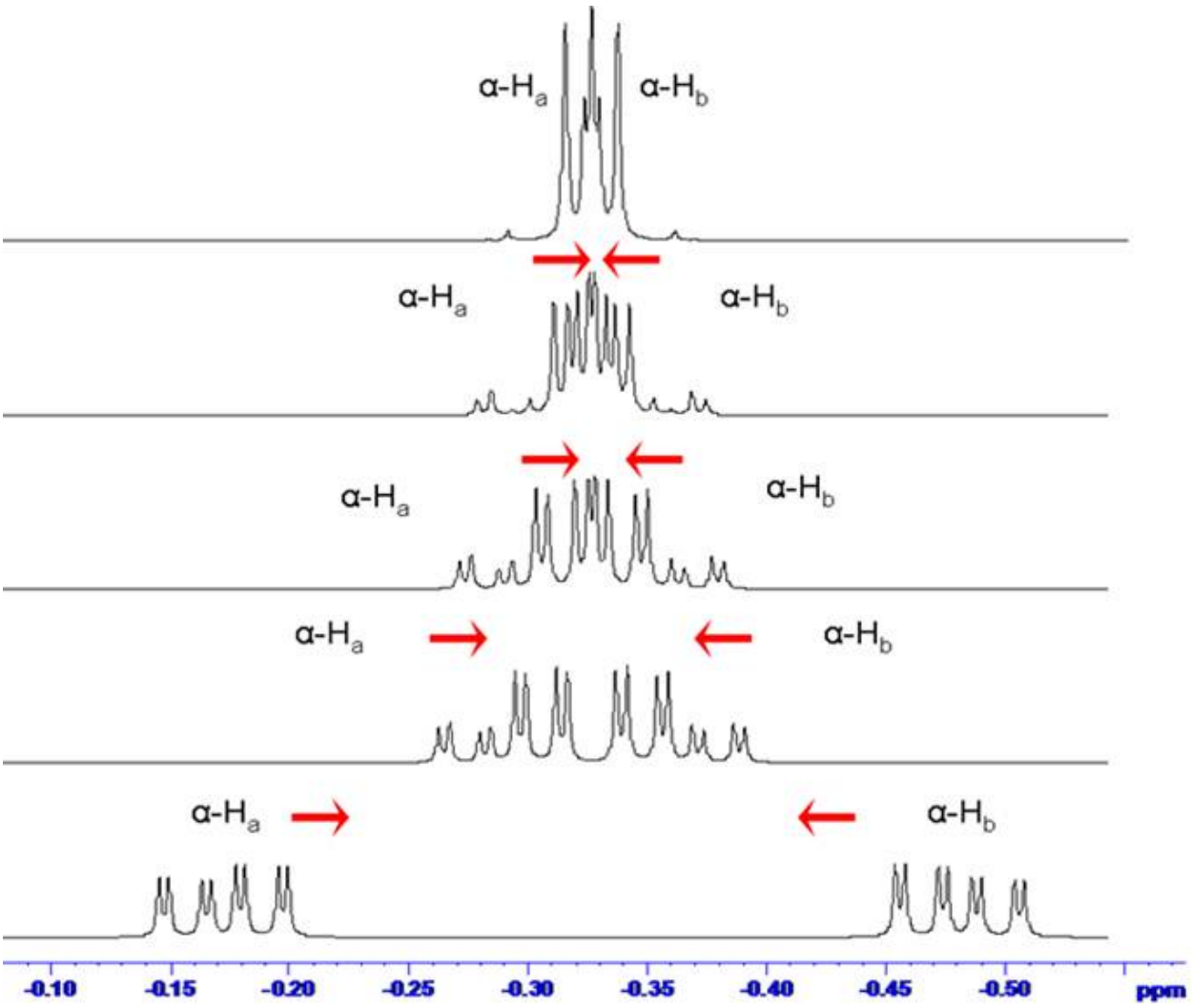
SI 2. Homodecoupled ^{1}H NMR spectra of the α-CH_2 protons in LMgBu^n(THF) recorded in C_6D_6 solution.



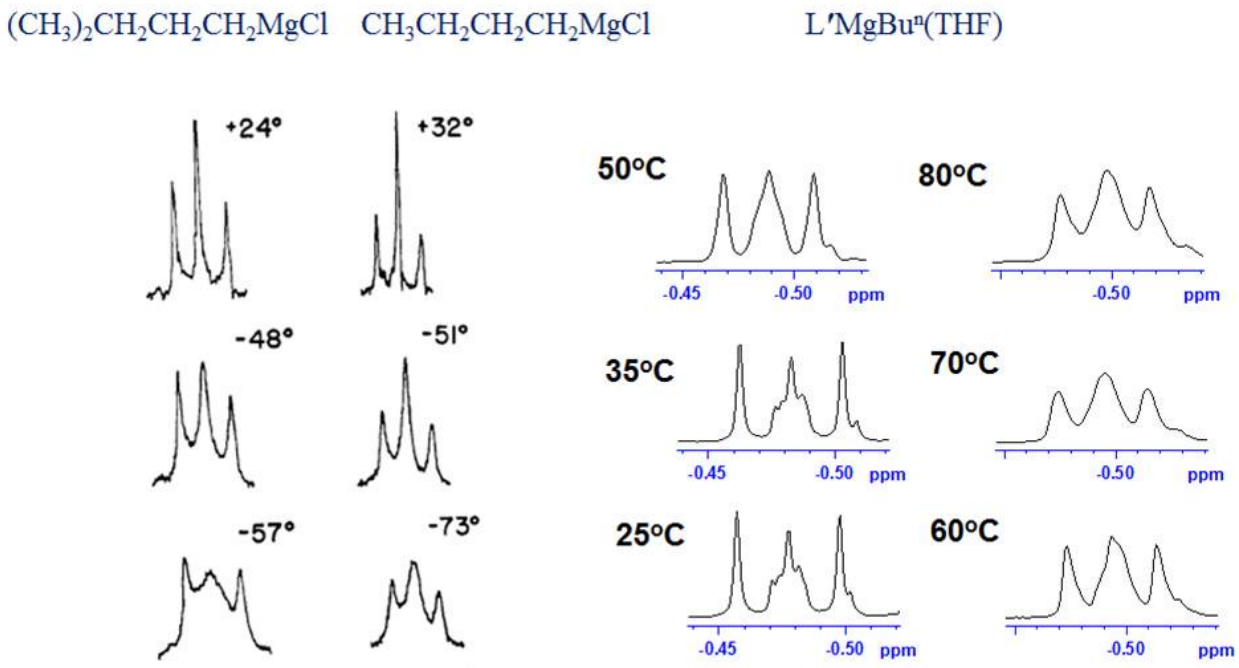
SI 3. Homodecoupled ^{1}H NMR spectra of the α-CH_2 protons in $LZnBu^n$ recorded in C_6D_6 solution.



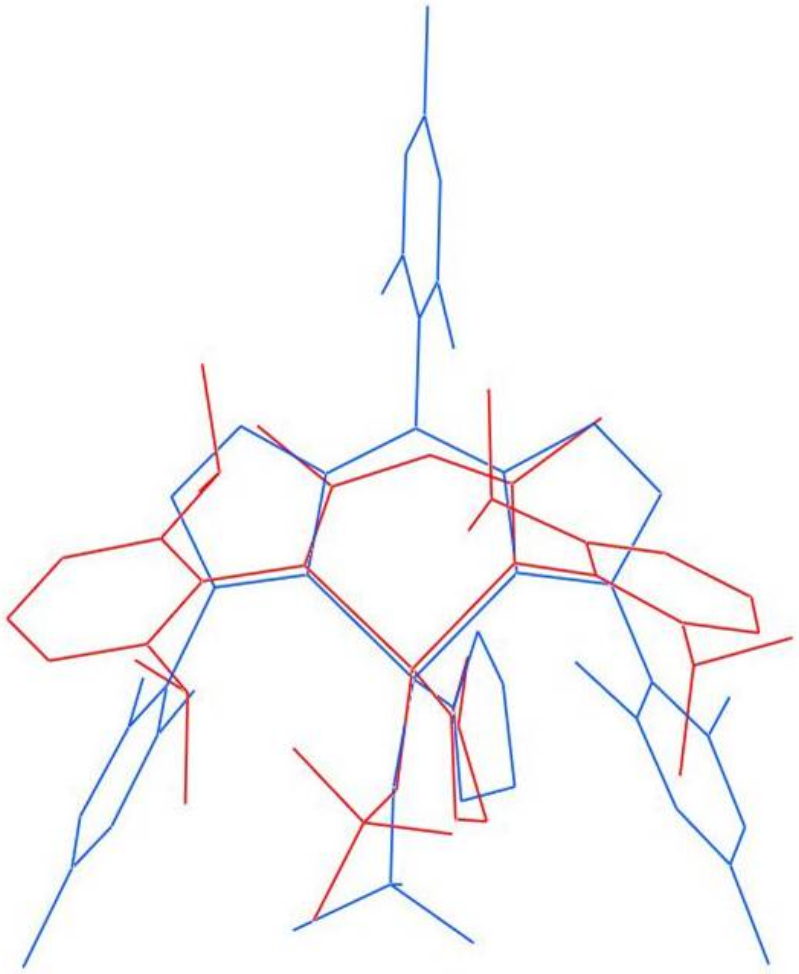
SI 4: The simulation of α–CH_2 of δ-decoupling L′$MgBu^n$(THF) AA′XX′ Spin System



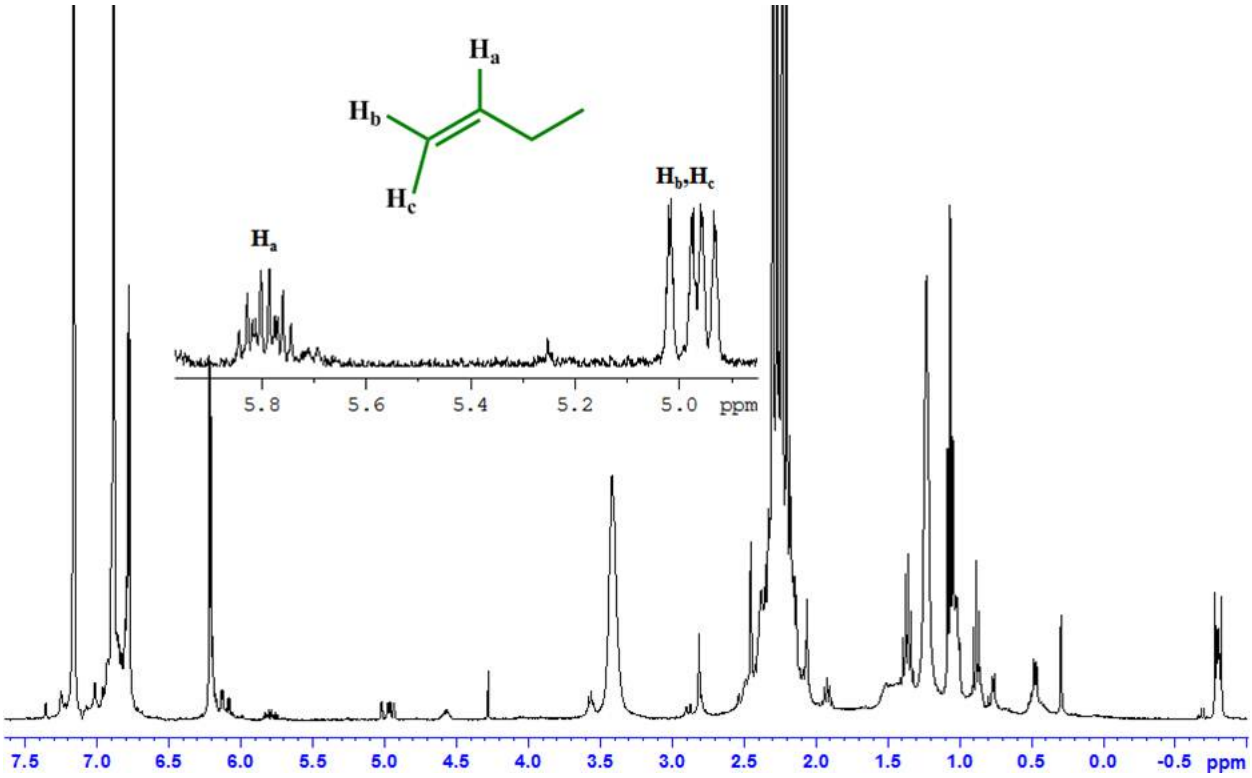
SI 5: The simulated patterns of α–H_a and α–H_b with difference chemical shifts (from ABXY to AA′XX′) by TOPSPIN program.



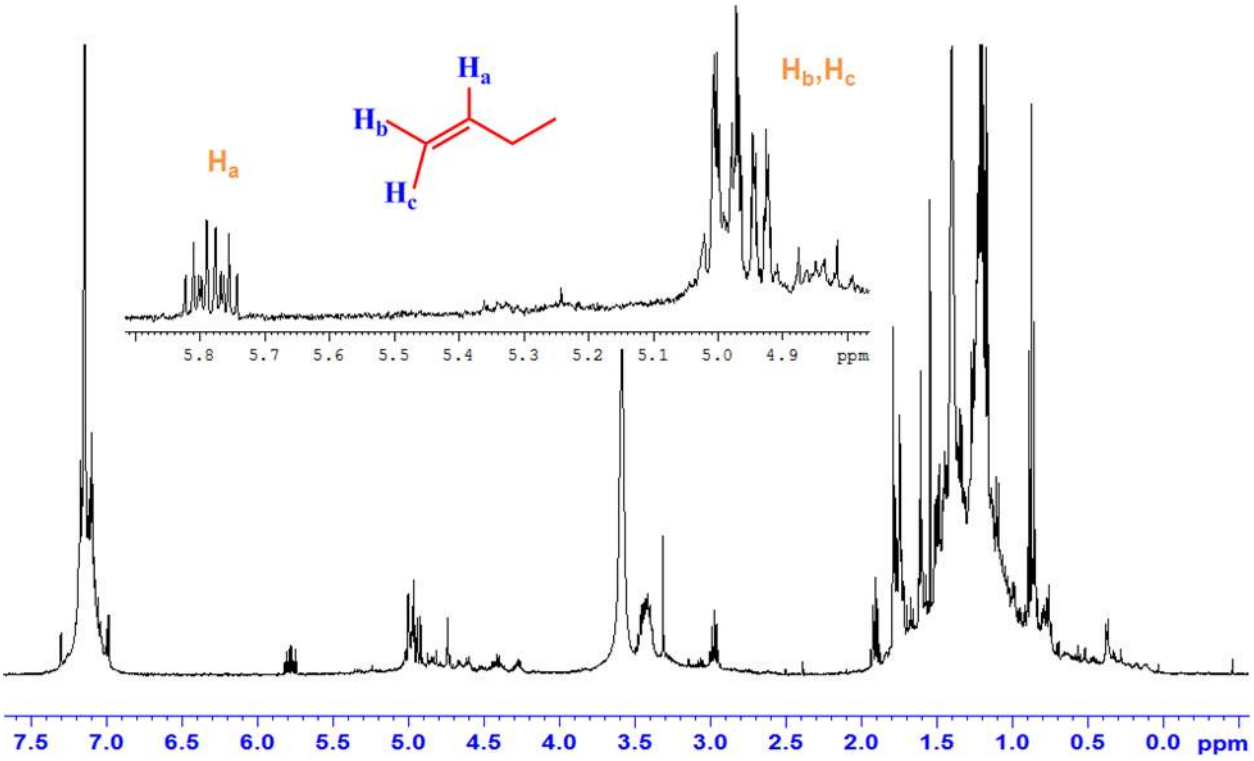
SI 6: V.T. ^{1}H NMR of α-CH_2 for the Grignard reagent Bu^{n}MgBr and 3-Me-BuMgCl in diethyl ether solution vs L′MgBu^{n}(THF) in toluene-d_8 solution. (**G. M. Whitesides and J. D. Roberts, *J. Am. Chem.* Soc., 87, 4878 (1965))**



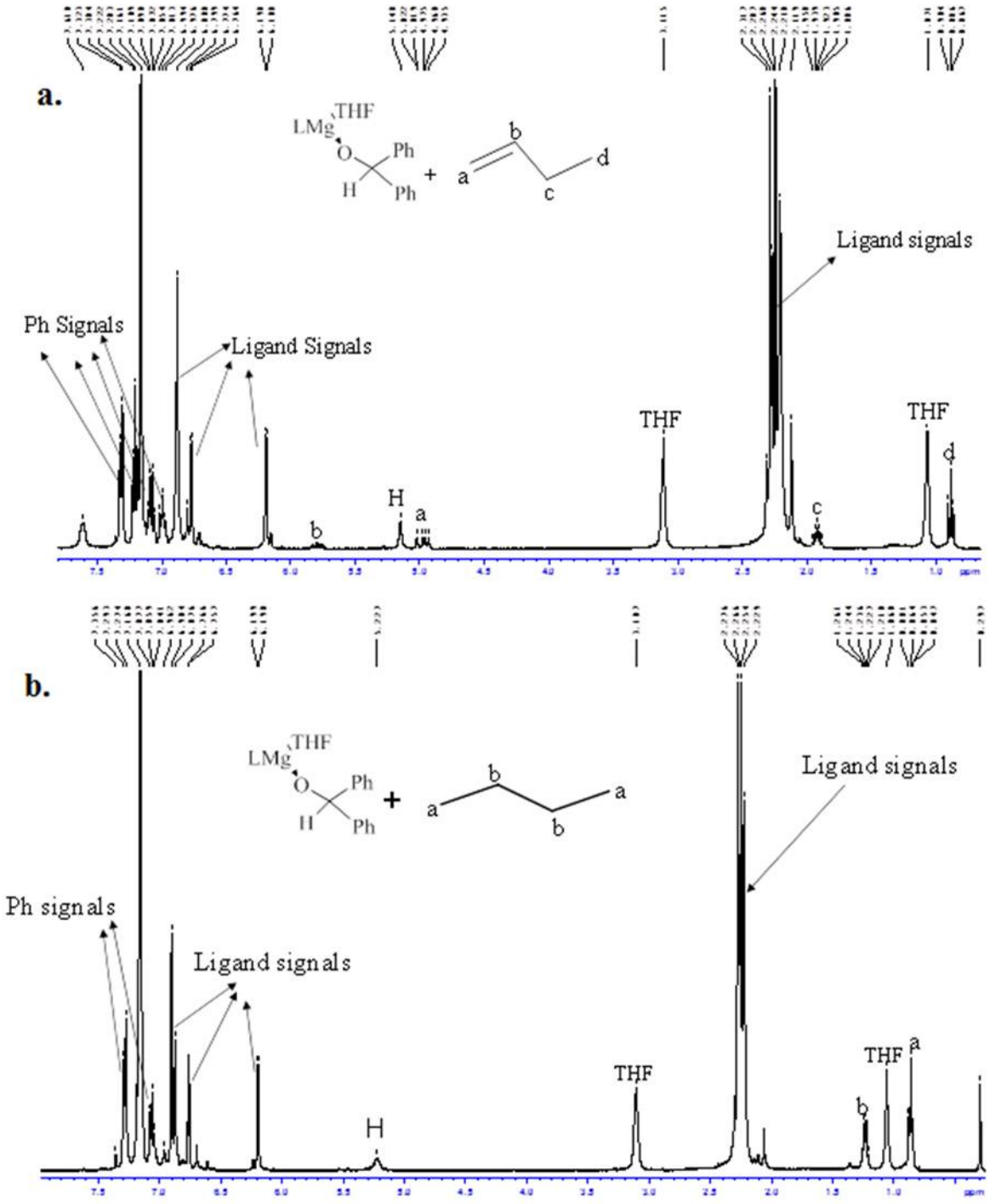
SI 7: Best superposition of the molecular structures of LMgOBu^{i}(THF) and L′MgOBu^{t}(THF) showing the relative disposition of the aryl ligands and the greater steric pressure of mesityl groups in the pyrromethene ligand on the pocket of the *n*-butyl group.



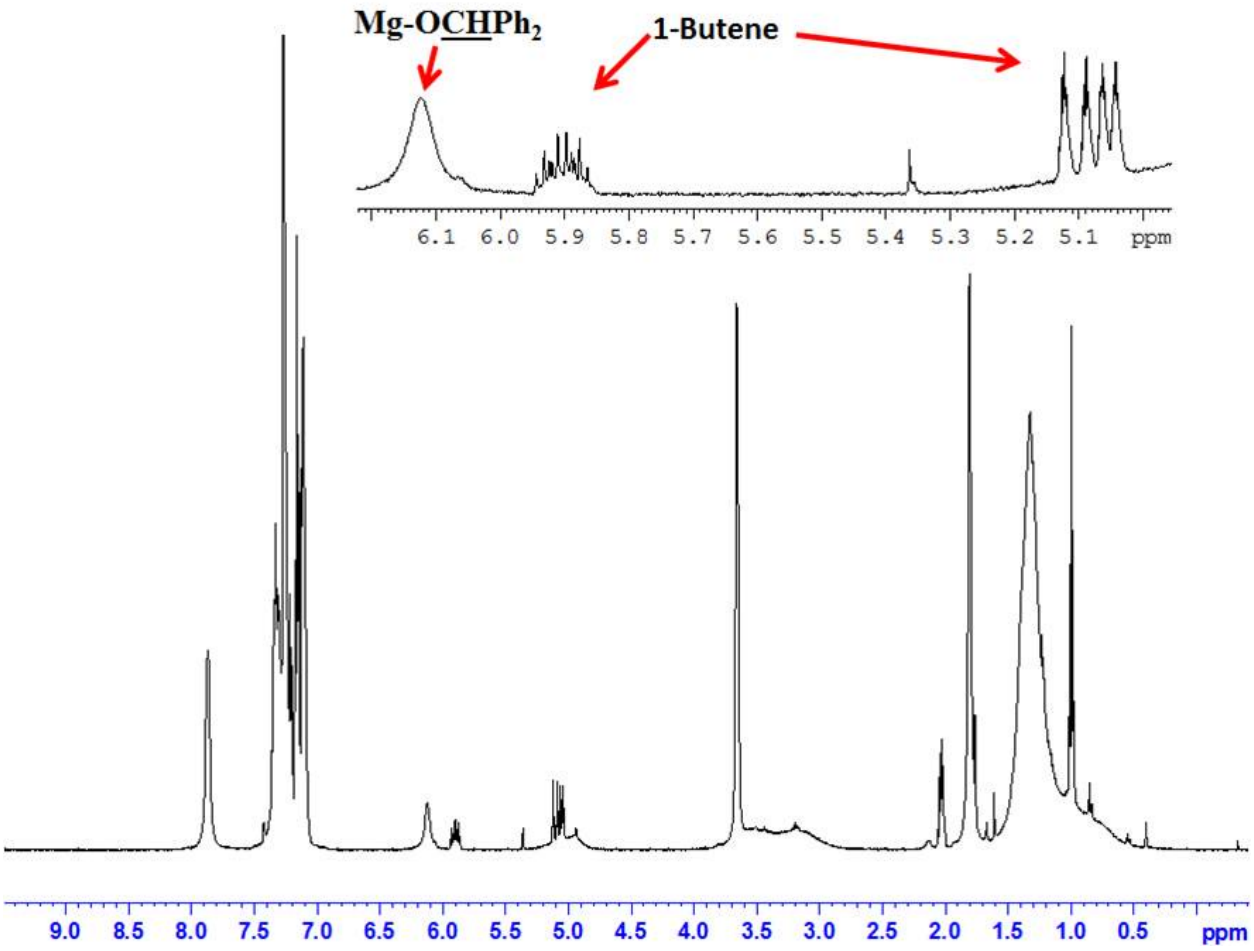
SI 8. The reaction of 1:1 *L*-LA:LMgBu^n(THF) in C_6D_6 showing the formation of the ^{1}H NMR resonances of 1-butene.



SI 9: The reaction of 1:1 *L*-LA: L′MgBu^{n}(THF) in C_6D_6 showing the formation of the ^{1}H NMR resonances of 1-butene.

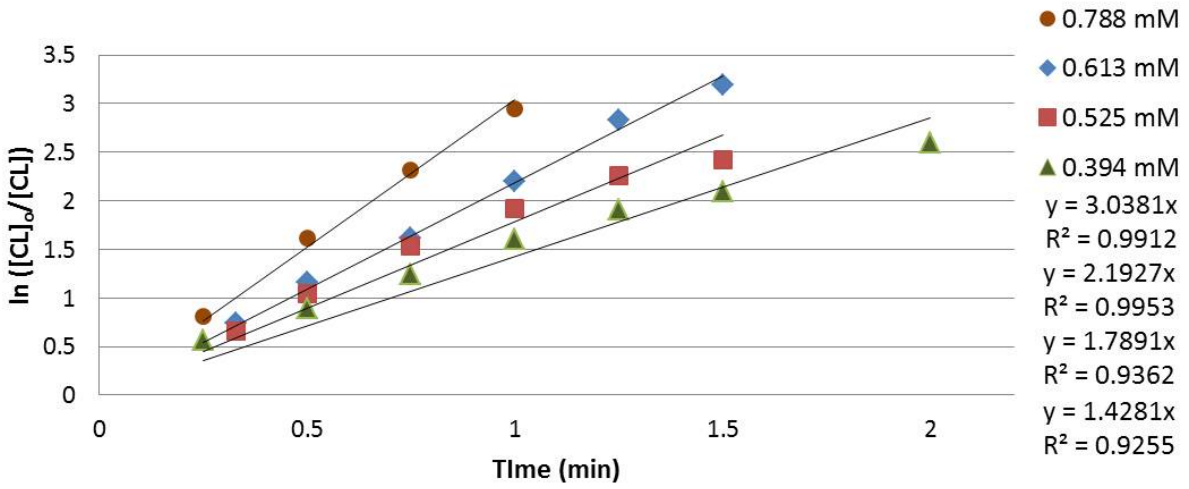


SI 10: a.) ^{1}H NMR spectrum of the reaction between 1:1 of Ph_2CO: $LMgBu^{n}(THF)$ in C_6D_6 showing the formation of 1-butene and the alkoxide ligand $OCHPh_2$ b.) ^{1}H NMR spectrum of the reaction between 1:1 of Ph_2CHOH: $LMgBu^{n}(THF)$ in C_6D_6 showing the formation of butane and the alkoxide ligand $OCHPh_2$.

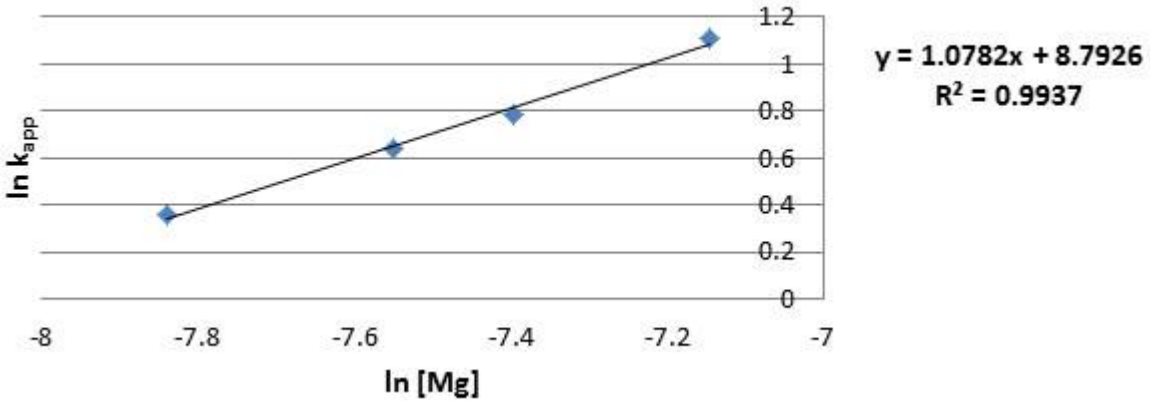


SI 11: ^{1}H NMR spectrum of the reaction between 1:1 of Ph_2CO: L′MgBu^{n}(THF) in C_6D_6 showing the formation of 1-butene and the alkoxide ligand $OCHPh_2$.

Kinetic Studies of ε-caprolactone (CL) Polymerization using L′MgBu^n(THF) as a catalyst initiator.



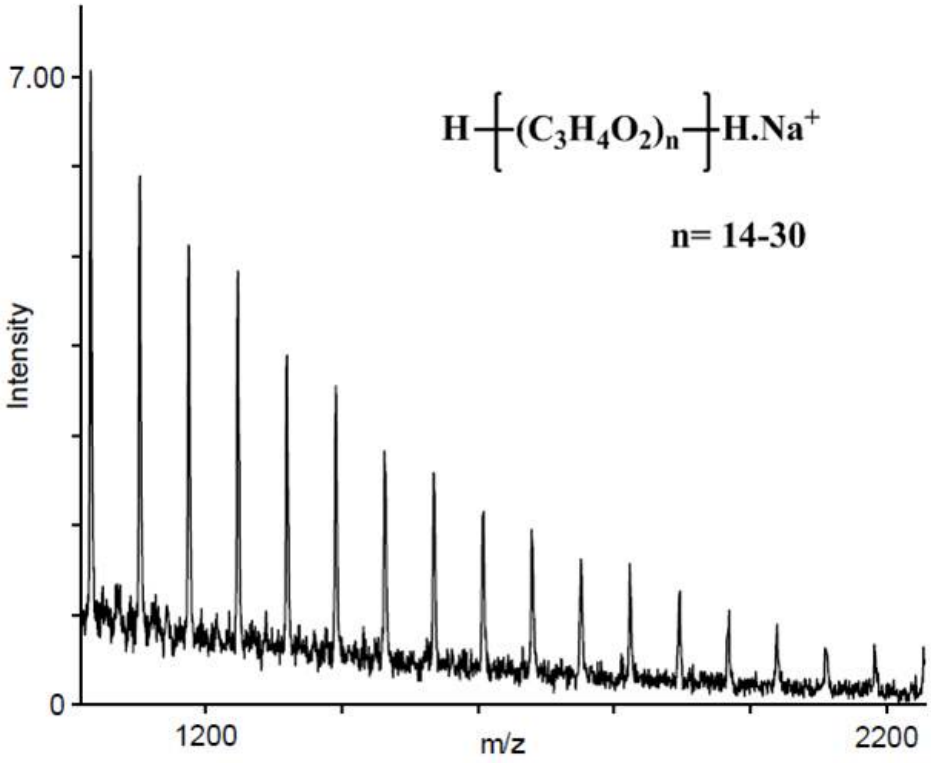
SI 12: Semilogarithmic plots of ε-CL conversion with time in CH_2Cl_2 at 25^{o}C with L′MgBu^n(THF) as initiator ($[CL]_o$= 0.1355 M, ● ; $[CL]_o$/[cat.] = 159, ◆; $[CL]_o$/[cat.] = 204, ■; $[CL]_o$/[cat.] = 239, ▲; $[CL]_o$/[cat.] = 318)



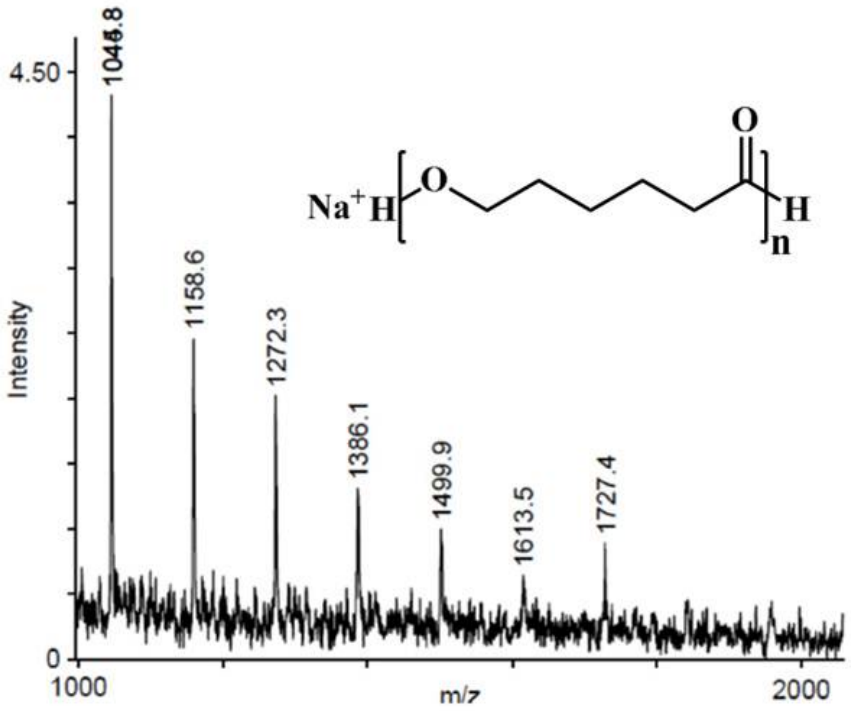
SI 13: Plot of ln k_{app} versus ln [Mg] for the polymerization of CL with L′MgBu^n(THF) as initiator (CH_2Cl_2, 25°C, $[CL]_o$ = 01355 M).

Ratio CL:[Mg]	**Time (second)**	**%coversion**	**M_n (calculation)**	**M_n(GPC) (Dal)**	**PDI (GPC)**
100:1	15	98	11,186	18,633	1.61
500:1	20	99	56,499	68,354	1.90
1000:1	25	98	111,857	100,178	1.87
2000:1	35	44	100,443	85,580	1.26
2000:1	50	97	221,432	143,056	1.72

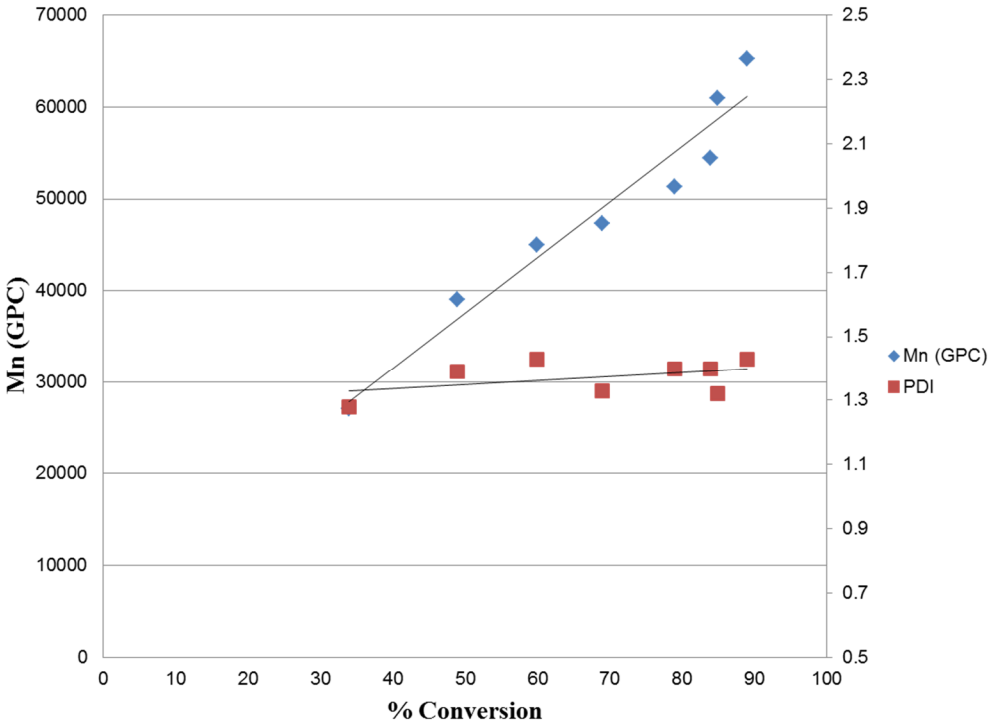
SI 14: ***ε***-CL ROP; Conditions: catalyst: L′MgBu^n(THF), solvent; CH_2Cl_2, total Volume = 5.0 mL, 25°C



SI 15: MALDI-TOF Spectrum: The oligomers of PRLA prepared by L′MgBu^{n}(THF) in CH_2Cl_2, 25^{o}C



SI 16: MALDI-TOF Spectrum; The oligomers of PCL prepared by L′MgBu^{n}(THF) in CH_2Cl_2, 25^{o}C



SI 17**:** Plot of molecular weight (M_n) and polydispersity (PDI) vs %conversion for the polymerization of CL using $LMgBu^n$(THF) as an initiator. Conditions: $[CL]_o$ =0.136 M, [Mg] = 0.876 mM, $[CL]_o$/[Mg] = 155, CH_2Cl_2, 25˚C ((◆)M_n from GPC; (▲) polydispersity index (PDI))