SUPPORTING INFORMATION

Versatile NHC-based zinc and magnesium complexes for the synthesis and chemical recycling of aliphatic polyesters and polycarbonates

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General Information

All the operations of synthesis and handling of air-sensitive chemicals were performed in an inert atmosphere, using Schlenk techniques and/or a glove-box in nitrogen atmosphere. The used glassware was dried in an oven at 120 °C and subsequently subjected to vacuum-nitrogen cycles. Solvents used for polymerization experiments and for the synthesis of substances instable toward air and moisture, were distilled prior to use on the opportune drying agent. In particular, THF, toluene, and benzene were dried by refluxing over sodium and benzophenone and stored under nitrogen. Dichloromethane was dried over calcium hydride and distilled prior to use. Benzyl alcohol and isopropanol were dried by refluxing over sodium. Deuterated solvents were purchased from Sigma–Aldrich and dried over activated 3-Å molecular sieves prior to use. All the reagents used for the synthesis of the complexes were purchased from Sigma Aldrich, while trimethylene carbonate was purchased from TCI. L-LA was crystallized in toluene and then dried over P_2O_5, ε-caprolactone was dried over CaH_2 and distilled under nitrogen, while TMC was purified twice by recrystallization from dry THF and stored in a glovebox before use. The NMR spectra were recorded with BRUKER AVANCE instruments operating at 600, 400 and 300 MHz for ^{1}H. Molecular masses (M_n and M_w) and their dispersities (M_w/M_n) were measured by gel permeation chromatography (GPC), using THF as the eluent (1.0 mL min^{-1}) and narrow polystyrene standards as the reference. MALDI mass spectra were recorded using a Bruker solariX XR Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer (Bruker Daltonik GmbH,Bremen, Germany) equipped with a 7 T refrigerated actively shielded superconducting magnet (Bruker Biospin, Wissembourg, France). The samples were prepared at the concentration of 1.0 mg mL^{-1} in THF, while the matrix (DCTB) was mixed at a concentration of 10.0 mg mL^{-1}.

Synthesis of the Complexes

Zinc and magnesium complexes were synthesized, according to the synthetic procedure reported in the literature,[1] using zinc bis [bis (trimethylsilyl) amide] $Zn[N(TMS)_2]_2$ and magnesium bis(hexamethyldisilazide) $Mg[N(TMS)_2]_2$ as metal precursor. All complexes were then characterized by NMR spectroscopy.

Synthesis of Zinc Complex 1a

The reaction was carried out in a glove box: in a vial, 0.200 g (4.545×10^{-4} mol) of NHC precursor ligand[2] was weighed, dissolved in 8 mL of anhydrous benzene and transferred into a 20 mL vial, equipped with a magnetic stirrer. In another vial, 0.176 g (4.545×10^{-4} mol) of $Zn[N(TMS)_2]_2$ was weighed and dissolved in 8 mL of anhydrous benzene. The solution of the metal precursor was transferred to the solution of the salt and the mixture was left stirring for one hour at room temperature. The solvent was subsequently removed under reduced pressure and the complex was obtained as white powdery solid (Yield = 80%).

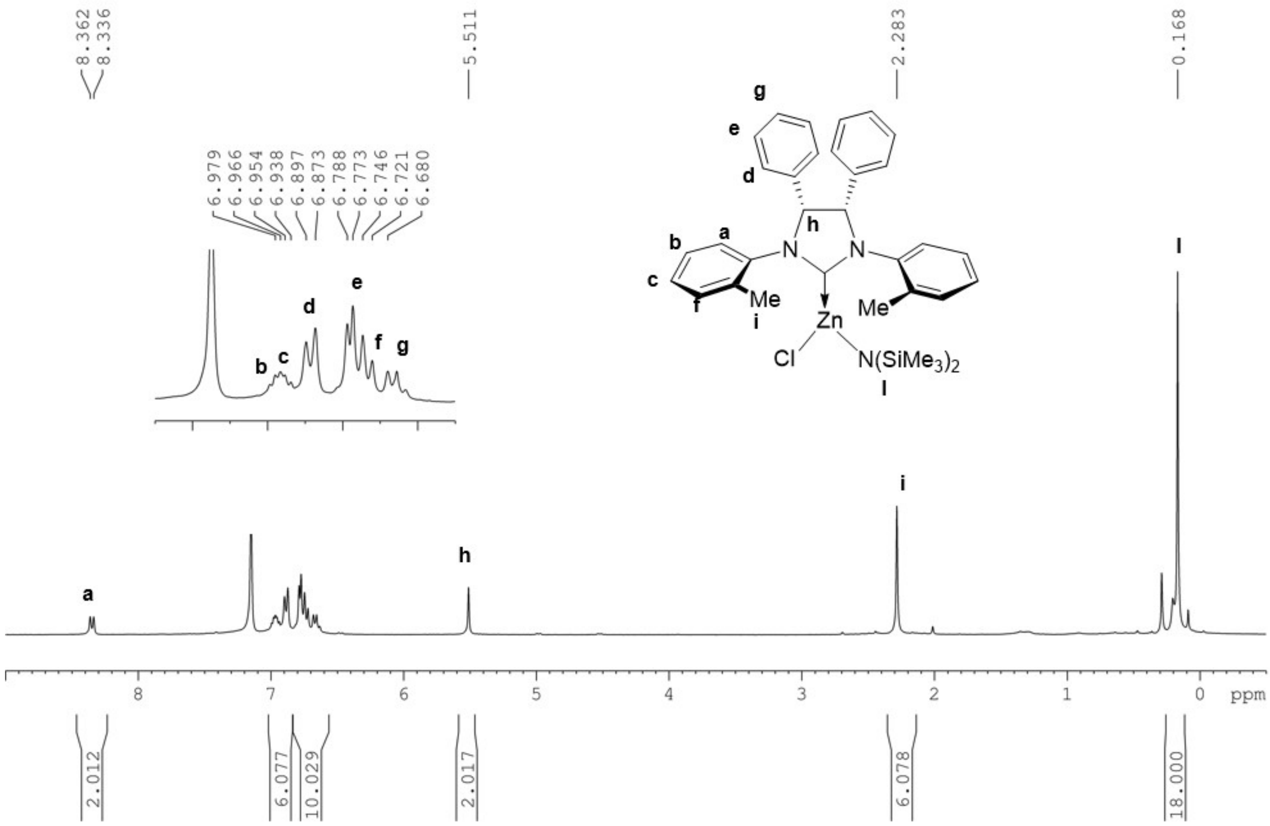


Figure S1: ^{1}H-NMR spectrum of complex **1a** (solvent: C_6D_6, 400 MHz, 298 K).

^1H NMR (400 MHz, C_6D_6, 298 K): δ 0.17 (s, 18H, $Si(CH_3)_3$), 2.28 (s, 6H, CH_3), 5.51 (s, 2H, N-CH), 6.67 (t, 2H, Ar-H), 6.74 (d, 2H, Ar-H), 6.78 (t, 2H, Ar-H), 6.88 (d, 4H, Ar-H), 6.95 (t, 2H, Ar-H), 6.97 (t, 2H, Ar-H), 8.35 (d, 2H, Ar-H).

Synthesis of Zinc Complex 2a

The reaction carried out in a glove box: in a vial, 0.200 g (4.545 x 10^{-4} mol) of NHC precursor ligand[3] was weighed, dissolved in 8 mL of anhydrous benzene and transferred into a 20 mL vial, equipped with a magnetic stirrer. In another vial, 0.176 g (4.545 x 10^{-4} mol) of $Zn[N(TMS)_2]_2$ was weighed and dissolved in 8 mL of anhydrous benzene. The solution of the metal precursor was transferred to the solution of the salt and the mixture was left stirring for one hour at room temperature. The solvent was subsequently removed under reduced pressure and the complex obtained was a white powdery solid (Yield = 85%).

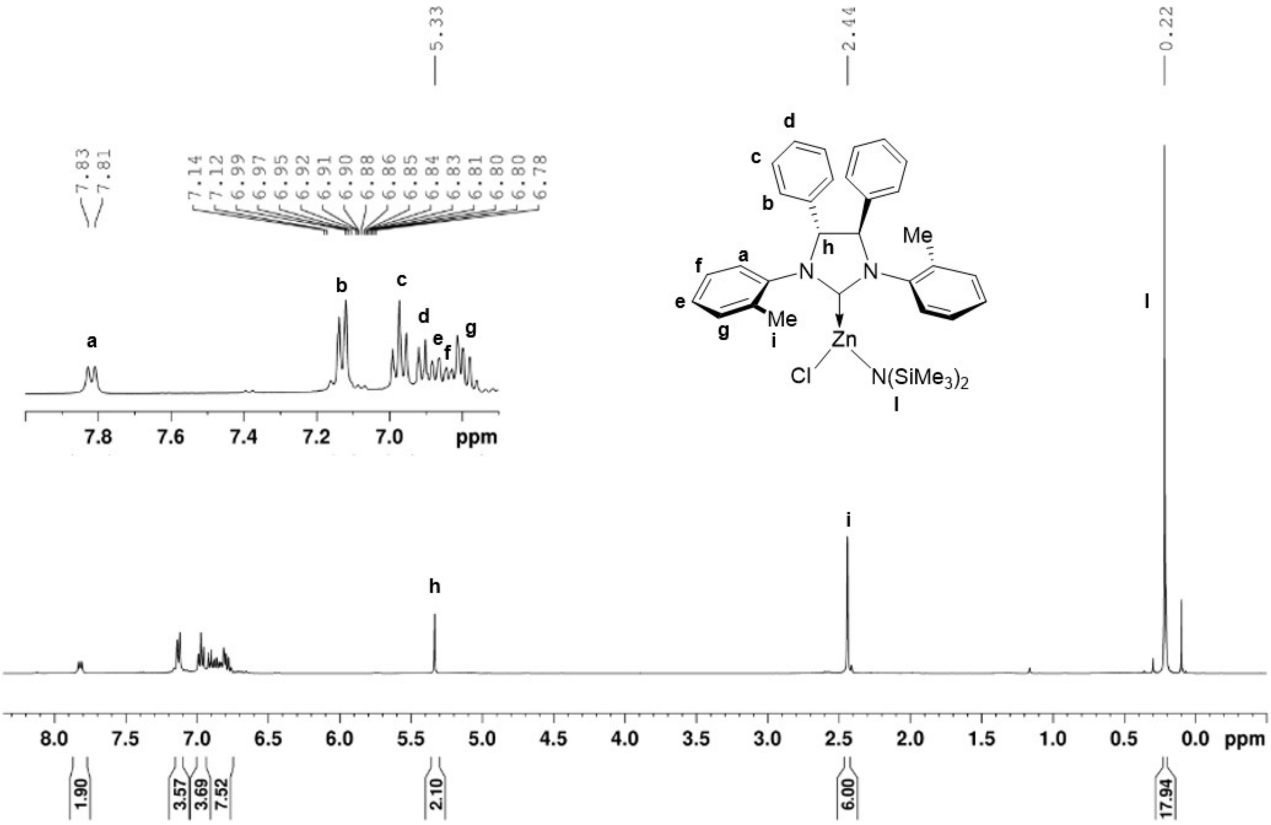


Figure S2: ^1H-NMR spectrum of complex **2a**. (Solvent: C_6D_6, 400 MHz, 298 K.)

^1H NMR (400 MHz, C_6D_6, 298 K): δ 0.22 (s, 18H, $Si(CH_3)_3$), 2.44 (s, 6H, CH_3), 5.33 (s, 2H, N-CH), 6.79 (d, 2H, Ar-H), 6.81 (t, 2H, Ar-H), 6.86 (tr, 2H, Ar-H), 6.91 (t, 2H, Ar-H), 6.97 (t, 4H, Ar-H), 7.13 (d, 4H, Ar-H), 7.82 (d, 2H, Ar-H).

Synthesis of Magnesium Complex 1b

The reaction was carried out in a glove box: in a vial, 0.100 g (2.273 x 10^{-4} mol) of NHC precursor ligand was weighed, dissolved in 4 mL of anhydrous benzene and transferred into a 20 mL vial, equipped with a magnetic stirrer. In another vial, 0.0784 g (2.273 x 10^{-4} mol) of $Mg[N(TMS)_2]_2$ was weighed and dissolved in 4 mL of anhydrous benzene. The solution of the metal precursor was transferred to the solution of the salt and the mixture was left stirring for 30 minutes at room temperature. The solvent was subsequently removed under reduced pressure and the complex obtained was a white powdery solid (Yield = 85%).

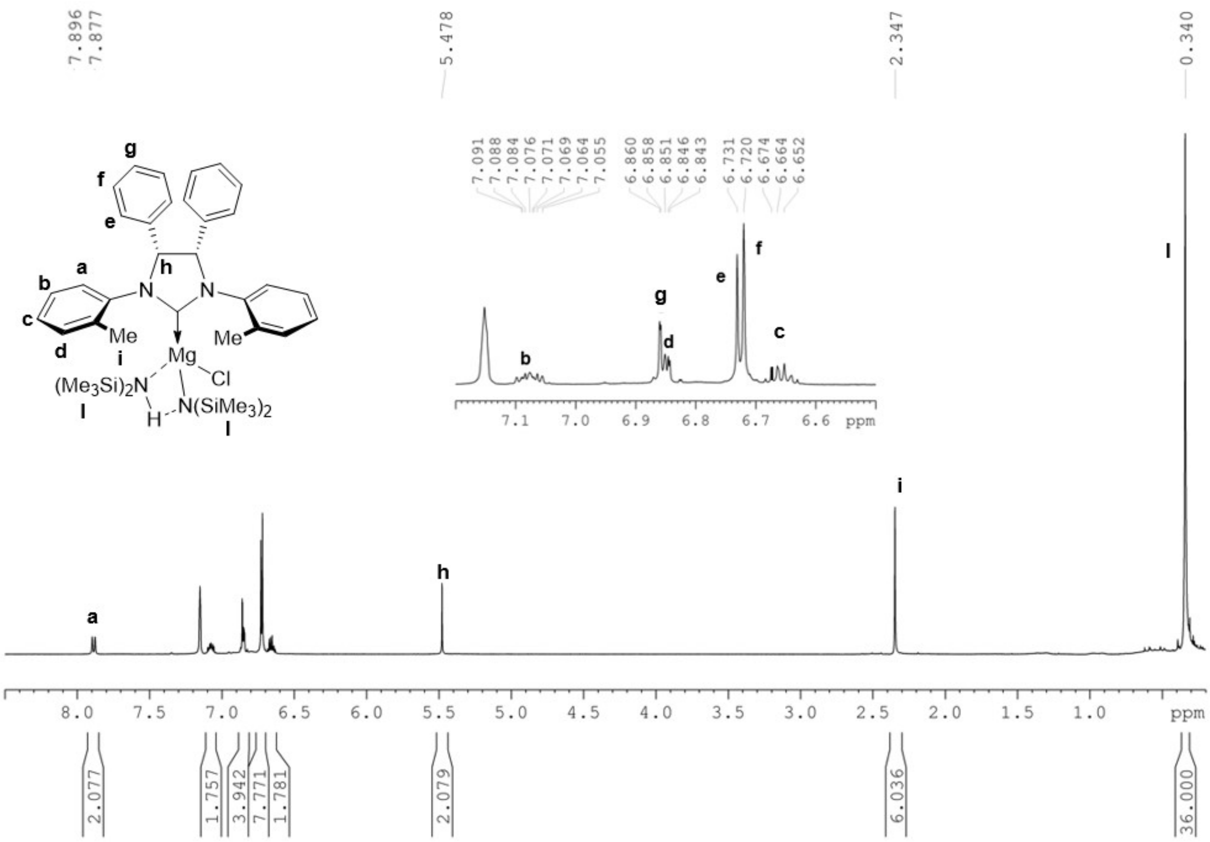


Figure S3: ^{1}H-NMR spectrum of complex **1b**. (Solvent: C_6D_6, 400 MHz, 298 K.)

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 0.34 (s, 36H, $Si(CH_3)_3$), 2.35 (s, 6H, CH_3), 5.48 (s, 2H, N-CH), 6.66 (t, 2H, Ar-H), 6.72 (t, 4H, Ar-H), 6.73 (d, 4H, Ar-H), 6.84 (d, 2H, Ar-H), 6.86 (d, 2H, Ar-H), 7.07 (m, 2H, Ar-H), 7.88 (d, 2H, Ar-H).

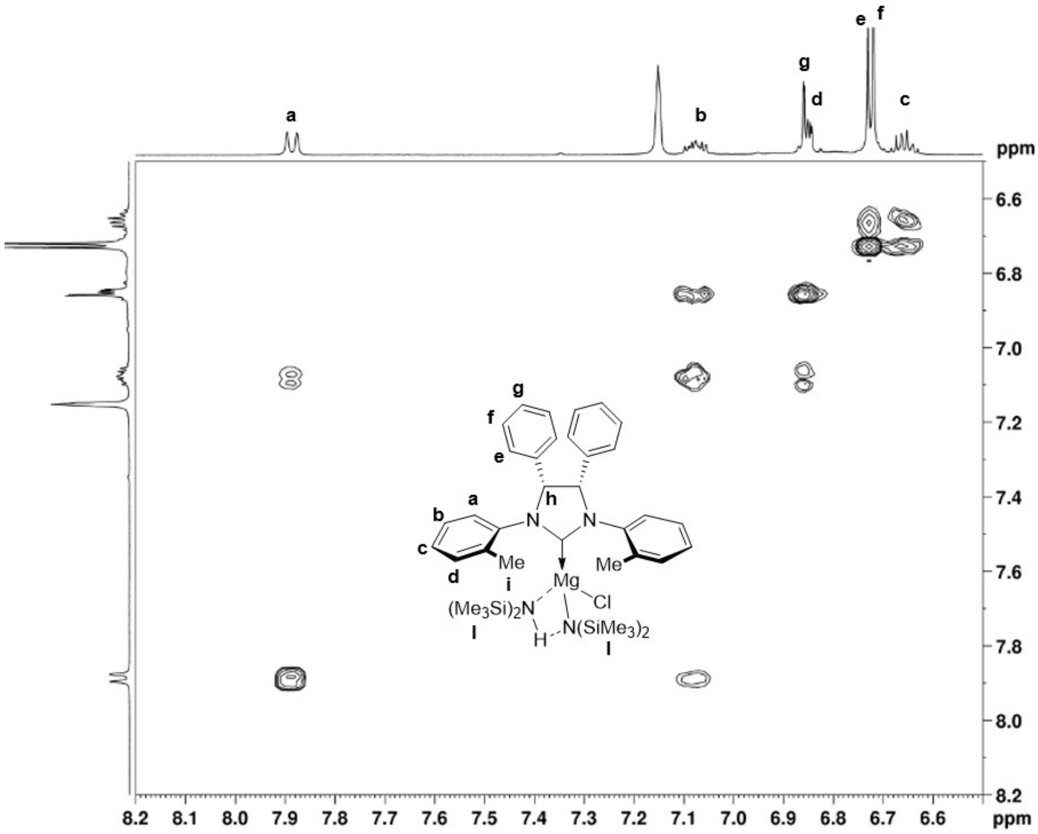


Figure S4: Aromatic region of the 2D-COSY spectrum of complex **1b** (Solvent: C_6D_6, 400 MHz, 298 K.)

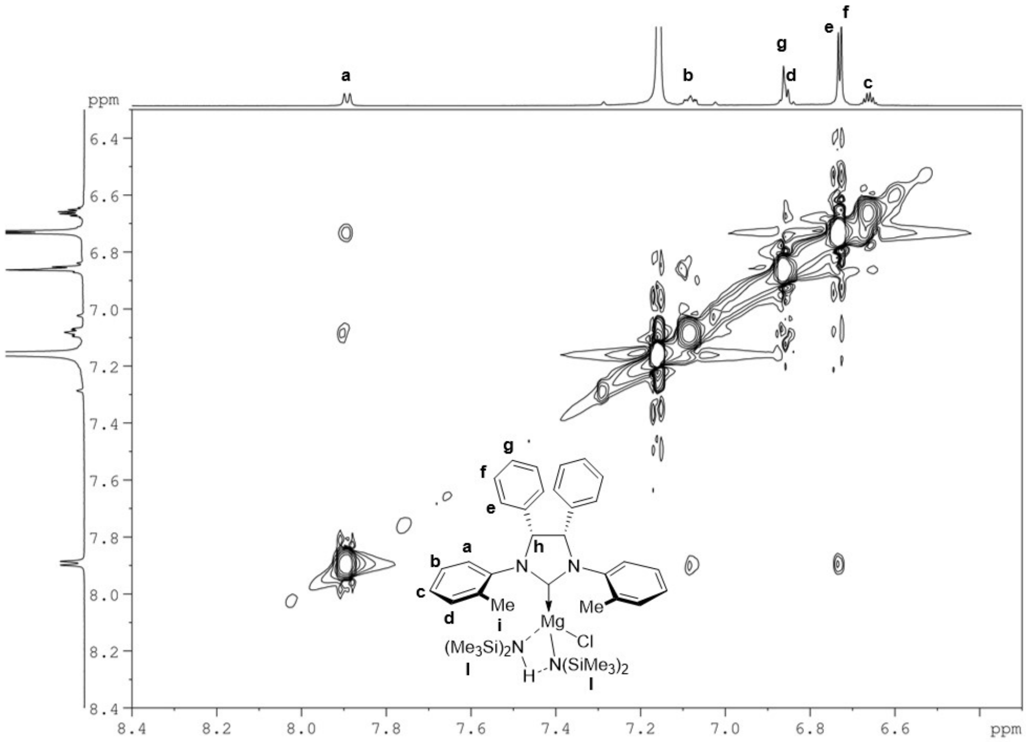


Figure S5: Aromatic region of the 2D-NOESY spectrum of complex **1b**. (Solvent: C_6D_6, 400 MHz, 298 K.)

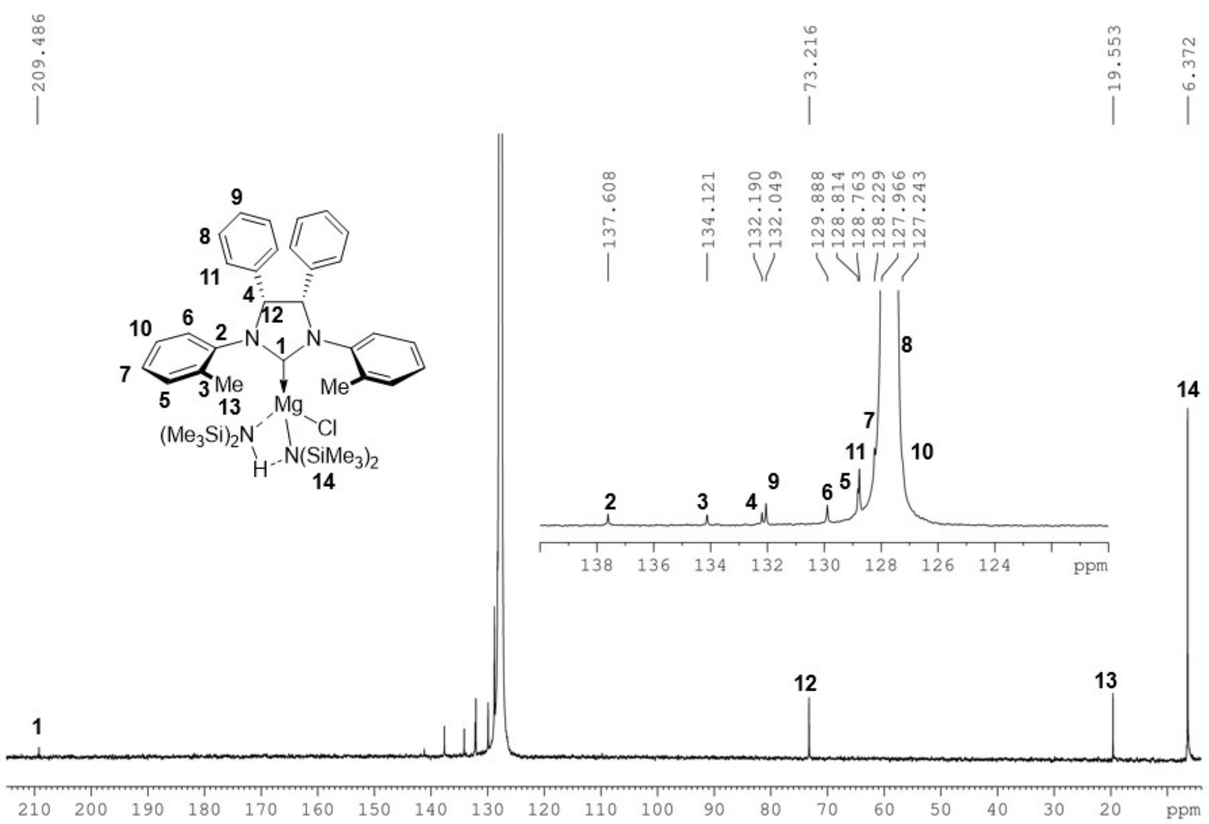


Figure S6: ^{13}C spectrum of complex **1b**. (Solvent: C_6D_6, 100,6 MHz, 298 K).

^{13}C NMR (100.6 MHz, C_6D_6, 298 K): δ 6.37 ($Si(CH_3)_3$), 19.55 (2 CH_3), 73.22 (2 CH), 127.24 (2 CH) 127.97 (2 CH), 128.23 (2 CH) 128.76 (2 CH), 128.81 (2 CH), 129.89 (2 CH), 132.05 (2 CH), 132.19 (2 Cq), 134.12 (2 Cq), 137.61 (2 CqN), 209.49 (C Carbenic).

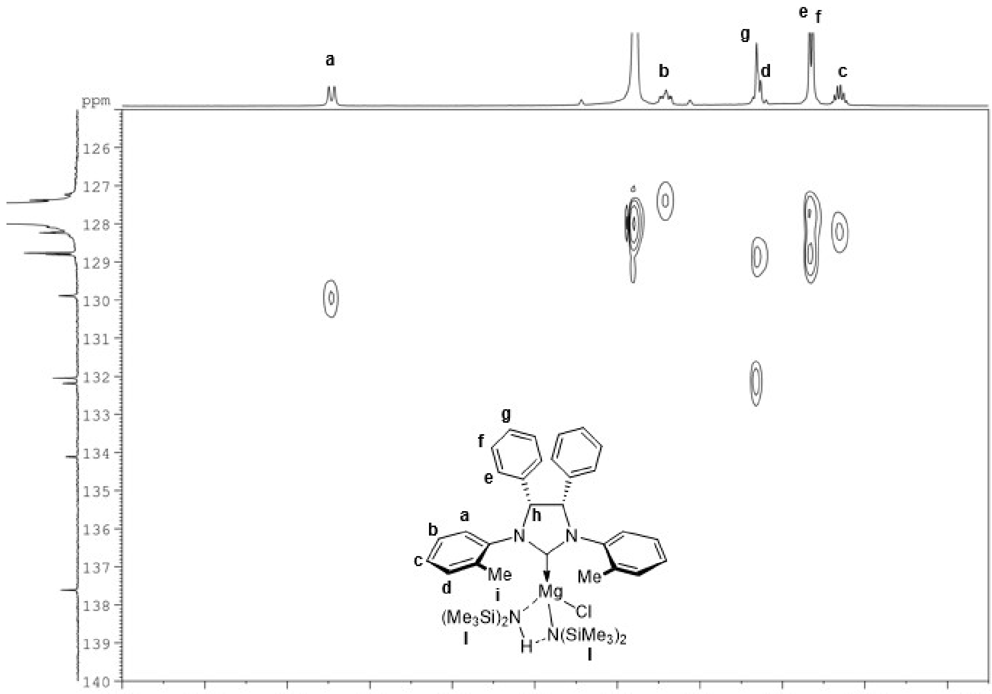


Figure S7: Aromatic region of 2D-HSQC spectrum of complex **1b**. (Solvent: C_6D_6, 600 MHz, 298 K.)

Synthesis of Magnesium Complex 2b

The reaction was carried out in a glove box: in a vial, 0.100 g (2.273 x 10^{-4} mol) of NHC precursor ligand was weighed, dissolved in 4 mL of anhydrous benzene and transferred into a 20 mL vial, equipped with a magnetic stirrer. In another vial, 0.0784 g (2.273 x 10^{-4} mol) of $Mg[N(SiMe_3)_2]_2$ was weighed and dissolved in 4 mL of anhydrous benzene. The solution of the metal precursor was transferred to the solution of the salt and the mixture was left stirring for 30 minutes at room temperature. The solvent was subsequently removed under reduced pressure and the complex obtained was a yellow powdery solid (Yield = 80%).

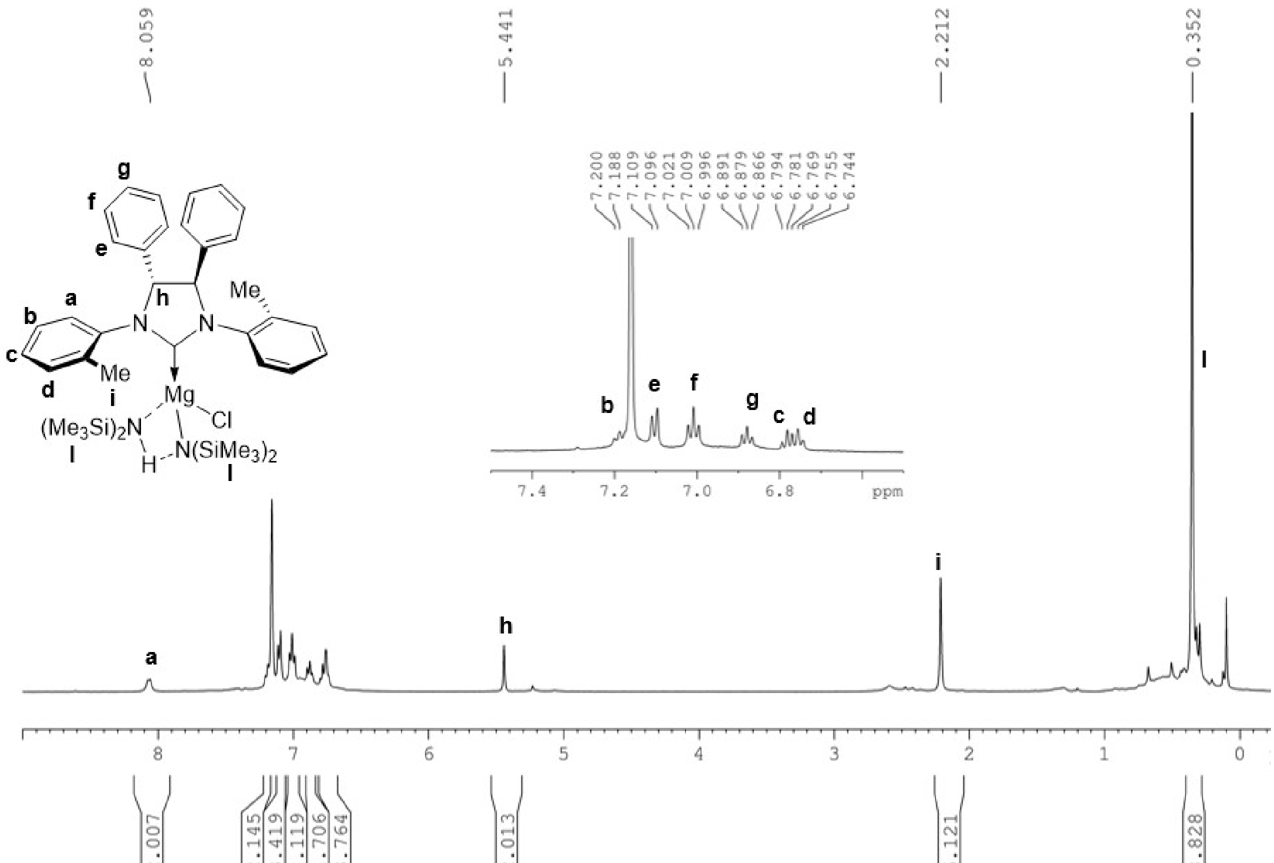


Figure S8: ^{1}H-NMR spectrum of complex **2b**. (Solvent: C_6D_6 400 MHz, 298 K.)

^{1}H NMR (400 MHz, C6D6, 298 K): δ 0.35 (s, 36H, $Si(CH_3)_3$), 2.21 (s, 6H, CH_3), 5.44 (s, 2H, N-CH), 6.76 (d, 2H, Ar-H), 6.80 (t, 2H, Ar-H), 6.88 (t, 2H, Ar-H), 7.01 (t, 4H, Ar-H), 7.10 (d, 4H, Ar-H), 7.19 (d, 2H, Ar-H), 8.06 (d, 2H, Ar-H).

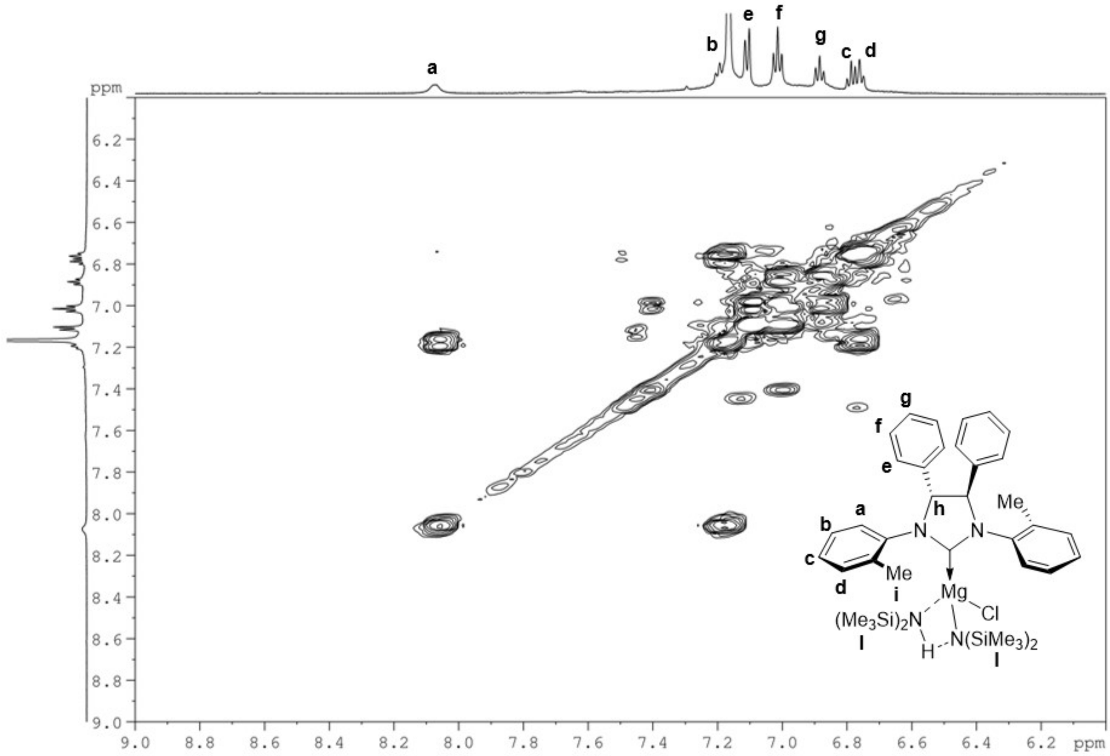


Figure S9: Aromatic region of 2D-COSY spectrum of complex **2b** (Solvent: C_6D_6, 400 MHz, 298 K.)

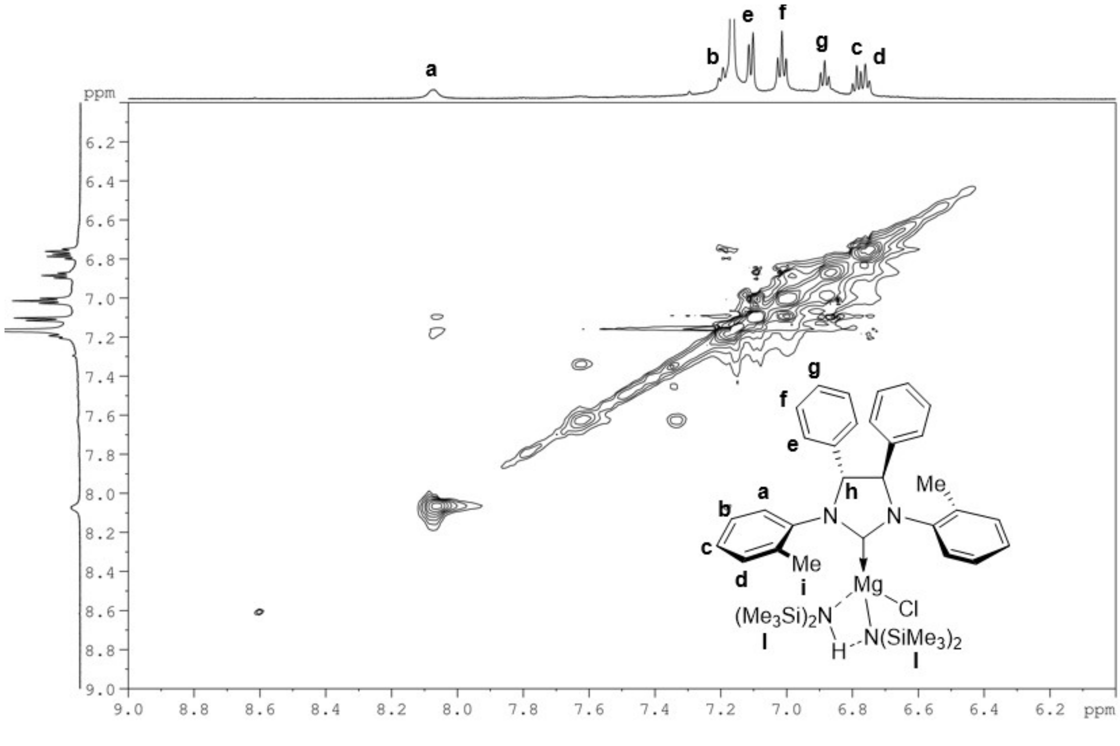


Figure S10: Aromatic region of 2D-NOESY spectrum of complex **2b.** (Solvent: C_6D_6, 400 MHz, 298 K.)

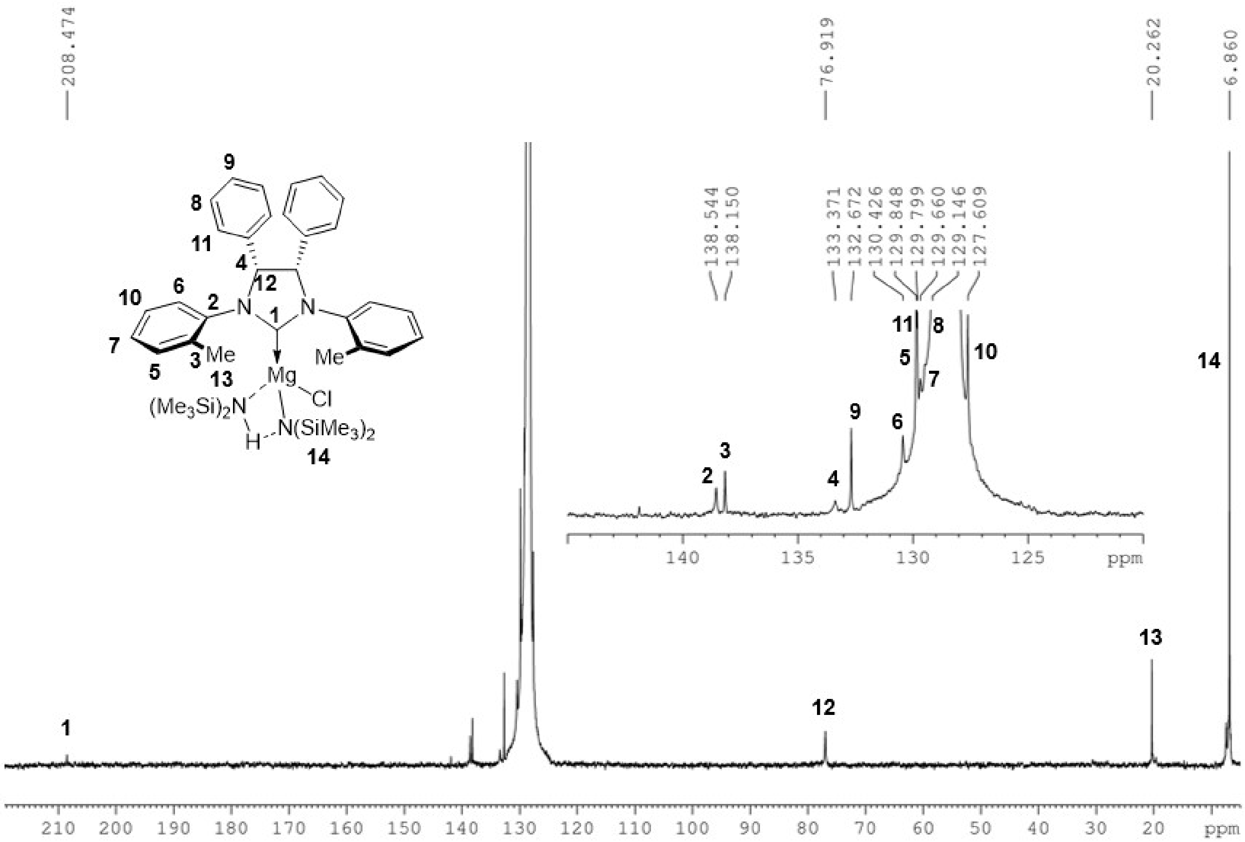


Figure S11: ^{13}C spectrum of complex **2b**. (Solvent: C_6D_6, 100.6 MHz, 298 K.)

^{13}C NMR (100.6 MHz, C_6D_6, 298 K): δ 6.86 ($Si(CH_3)_3$), 20.26 (2 CH_3), 76.92 (2 CH), 127.61 (2 CH) 129.15 (2 CH), 129.66 (2 CH), 129.80 (2 CH), 129.85 (2 CH), 130.43 (2 CH), 132.67 (2 CH), 133.37 (2 Cq), 138.15 (2 Cq), 138.54 (2 CqN), 208.45 (C Carbenic).

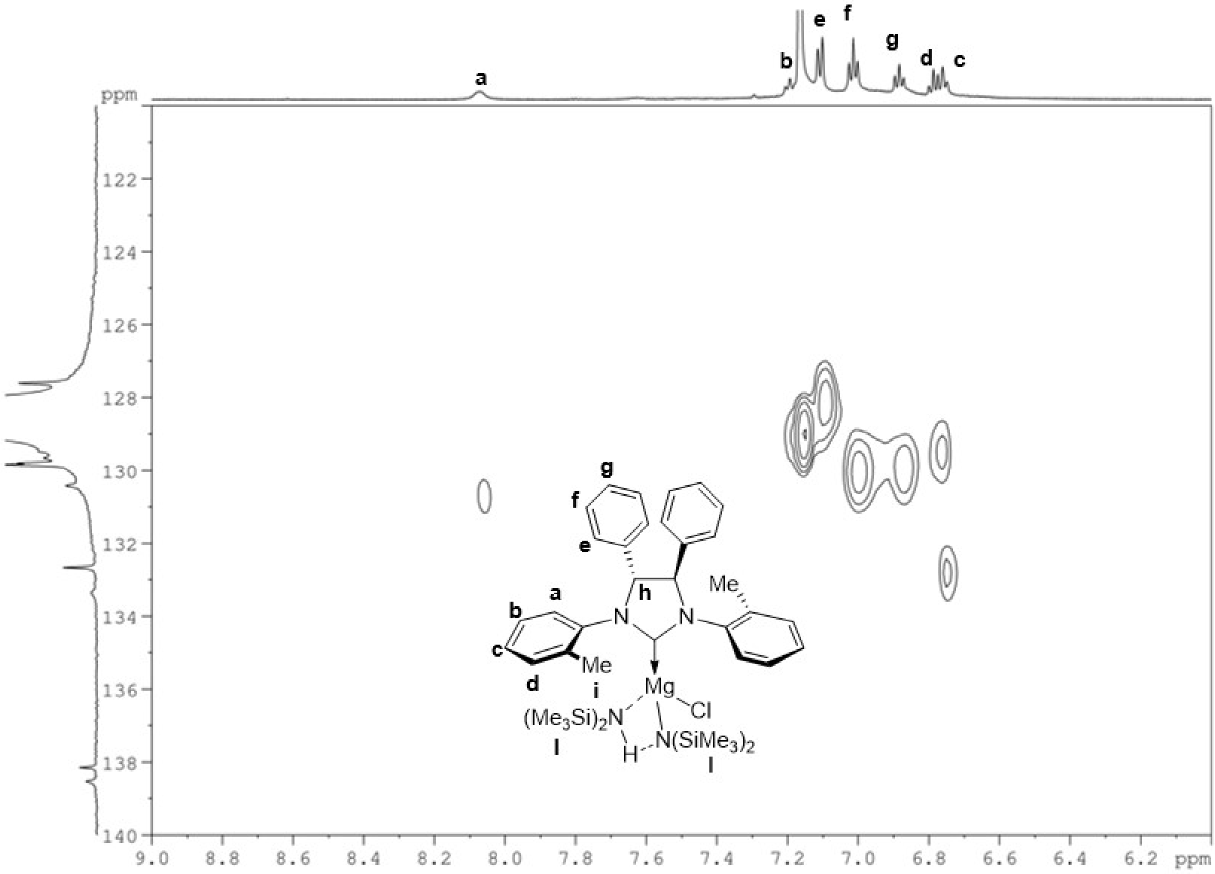


Figure S12: HSQC spectrum of complex **2b**. (Solvent: C_6D_6, 400 MHz, 298 K.)

DOSY-NMR experiments details

A measurement of diffusion has been carried out by observing the attenuation of the NMR signals during a pulsed field gradient experiment using the double stimulated echo pulse sequence. In particular, 2D DOSY PGSE NMR spectra were performed on a Bruker Avance 600 spectrometer at 298 K without spinning. Tetrakis(trimethylsilyl)silane (TMSS) was added as the internal standard. The dependence of the resonance intensity (I) on the gradient strength (G) is described by the following equation:

$$I(G) = I_0 \exp\{-D\gamma^2 G^2 \delta^2 (\Delta - \delta/3)\}$$

where I is the observed intensity (attenuated signal intensity), I_0 is the reference intensity unattenuated signal intensity), D is the diffusion coefficient, γ is the nucleus gyromagnetic ratio, G is the gradient strength, δ is the gradient duration, and Δ is the diffusion delay. The parameters δ and Δ were kept constant during the experiments (1800 μs and 0.15 s, respectively) whereas G varied from 5 to 95% in 100 steps. A nonlinear regression on I and G2 data gave the coefficients D for the samples and the corresponding internal standard signals (D_{sample} and D_{TMSS}, respectively). The molecular masses in solution (MM) were simply estimated using Graham's law of diffusion: $D = K(T/MM)^{1/2}$, where the constant K depends on geometric factor. By assuming the same K for both species in solution and a constant temperature, the relative diffusion rate of the sample and the TMSS is given by

$$D_{sample}/D_{TMSS} = (MM_{TMSS}/MM_{sample})^{1/2}$$

This allows the calculation of an unknown molecular mass. This method is useful when a highly accurate value is not required for the molecular mass.

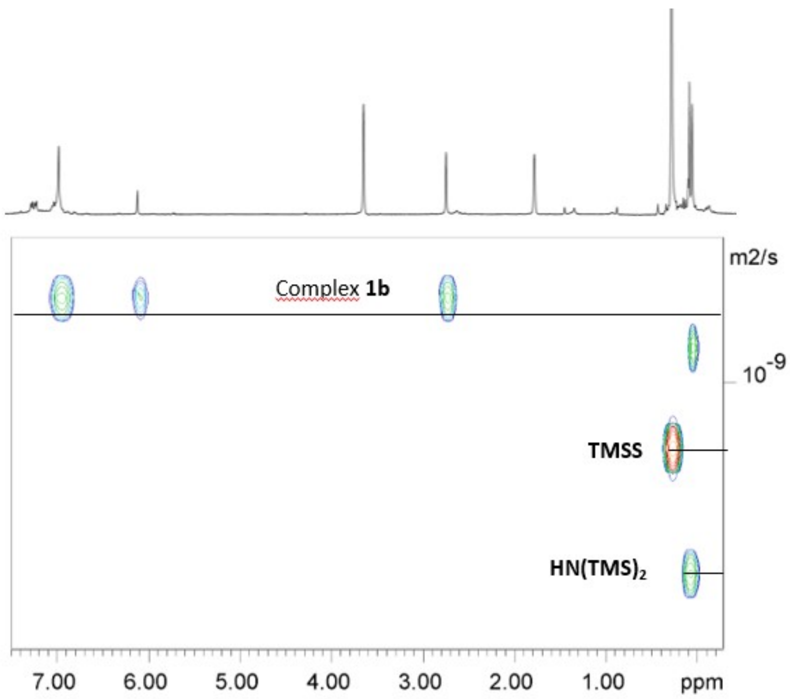


Figure S13: DOSY spectrum (THF-d8, 298 K, 400 MHz) of complex **1b** (D = 8.8 10^{-10} m^2 /s) in the presence of TMSS as standard (D = 1.10 x 10 $^{-9}$ m^2/s), with the formation of free amine $HN(TMS)_2$ (D= 1.42 x 10 $^{-9}$ m^2/s).

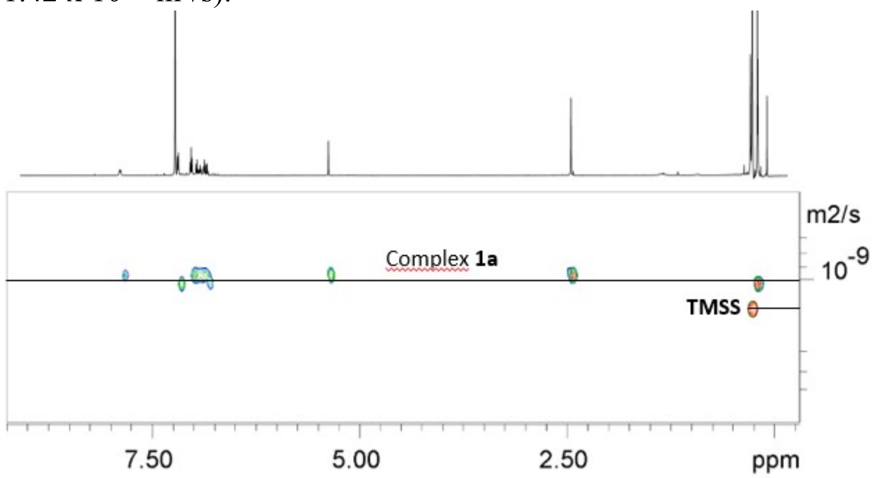


Figure S14: DOSY spectrum (C_6D_6, 298 K, 400 MHz) of complex **1a** (D = 9.9 10^{-10} m^2 /s) in the presence of TMSS as standard (D = 1.3 x 10 $^{-9}$ m^2/s).

TABLE S1: Diffusion coefficients and estimated molecular mass of complex **1b**, using TMSS as internal reference species

Complex	D_{Sample} (x$10^{-10}$$m^2$/ s)	D_{TMSS} (x10^{-10} m^2/s)	MM^{est} (Da)	FW (Da)	FW_{amine} (Da)	FW_{THF} (Da)	FW_2 (Da)
[a]**1b**	5.4	9.3	886	624	**786**	-	1410
[b]**1b**	8.8	11	605	624	786	**696**	1410
[a]**1a**	9.9	13	553	**665**	827	-	1330

[a]C_6D_6 at 298 K. [b]THF-d8 at 298 K. MM^{est} = estimated molecular mass, FW = formula weight.

DFT Section

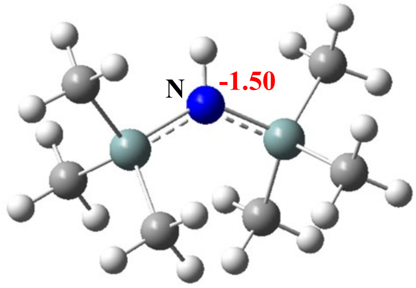


Figure S15. NBO charge values of the nitrogen atom in the produced $HN(SiMe_3)_2$. The structures are represented in balls and sticks. C, H, N and Si, are depicted in gray, white, blue and light green, respectively. The NBO charge values of the metals are in red.

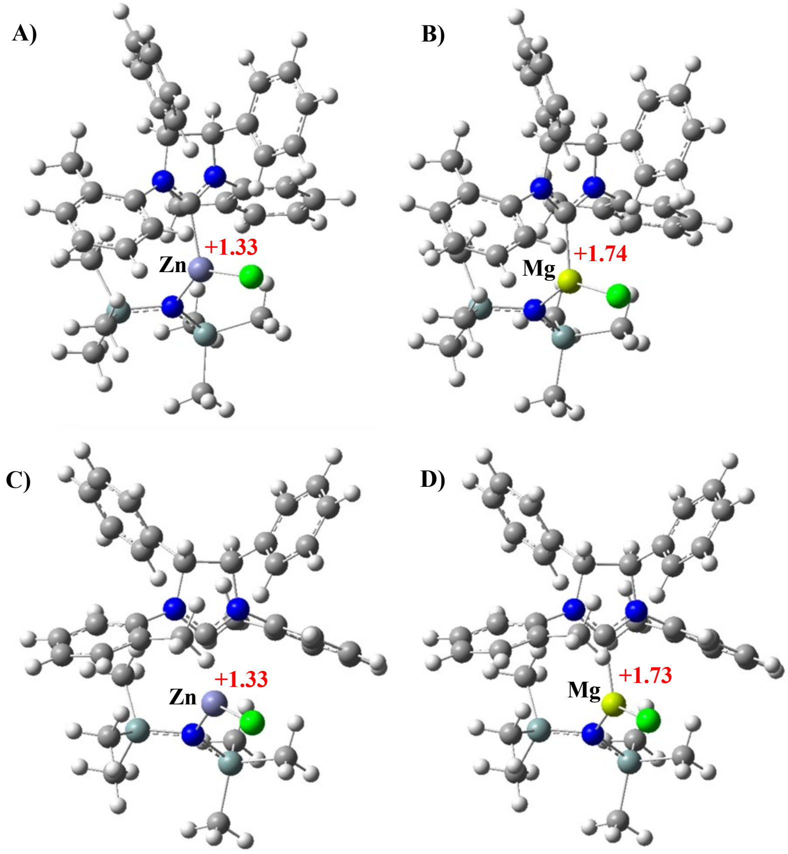
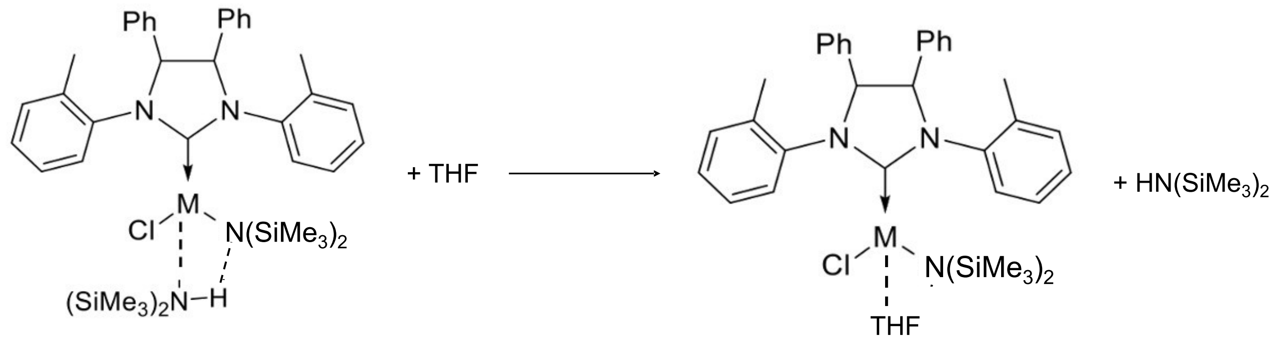


Figure S16. NBO charge values of the metals in the *syn* and *anti* monomeric Zn and Mg complexes **1a, 1b** (panel A and B) and **2a, 2b** (panel C and D), respectively. The structures are represented in balls and sticks. C, H, N, Si, Cl, Zn and Mg are depicted in grey, white, blue, light green, green, light purple and yellow, respectively. The NBO charge values of the metals are in red.



ΔG_{syn} (Mg) = -12.5 kcal/mol

Scheme S1. Free energy difference in THF as solvent between the *syn* Mg complex interacting with $HN(SiMe_3)_2$ and with a THF molecule (ΔG_{syn} (Mg)).

TABLE S2: XYZ Coordinates.

L1HCl	**Zn[N(SiMe$_3$)$_2$]$_2$**	**Mg[N(SiMe$_3$)$_2$]$_2$**
Cl -1.51711500 -1.66096400 -2.51930900	Zn 0.00000000 0.00005400 0.00001100	Mg 0.00002100 0.00637100 0.00213700
C 0.77851900 0.18855900 1.26206500	Si 2.65868800 1.38412900 -0.71153000	N 1.92695100 0.00286700 0.00317900
C -0.63137100 0.84340200 1.05795600	Si 2.65858900 -1.38413700 0.71156500	Si 2.65361500 1.26126800 -0.91962900
C -0.65329100 -1.30689800 0.24684600	C 1.35623600 2.28925500 -1.74610500	Si 2.65055800 -1.26011400 0.92229000
N 0.63013400 -1.06861500 0.48092800	H 0.94274100 1.64365800 -2.52772400	C 1.23767200 2.09242200 -1.88070300
N -1.45297500 -0.34675500 0.70525900	H 0.52284000 2.66004000 -1.13779900	H 0.73496100 1.39398900 -2.56022600
C 1.70946700 -1.87575900 -0.01219400	H 1.78904200 3.16321600 -2.24205900	H 0.47832500 2.53180500 -1.22020300
C 1.72296300 -2.18647900 -1.37150700	C 4.09237800 0.89337100 -1.83251100	H 1.60921800 2.91560600 -2.49789100
C 2.71332400 -2.32521000 0.85814600	H 4.54114200 1.77257100 -2.30492900	C 3.92927100 0.63198600 -2.15673200
C 2.76281300 -2.94938400 -1.88903600	H 4.88169900 0.38414500 -1.27186200	H 4.31250300 1.44175900 -2.78527100
H 0.90512400 -1.85169800 -2.00421200	H 3.75714800 0.21698900 -2.62347200	H 4.78430400 0.18293300 -1.64218700
C 3.75481000 -3.07141600 0.30195300	C 3.29453400 2.58424000 0.59591200	H 3.49878600 -0.13231000 -2.80964500
C 3.78887100 -3.38012100 -1.05412900	H 4.05583400 2.11528600 1.22495000	C 3.46577200 2.57792000 0.15885200
H 2.76592600 -3.19684500 -2.94338000	H 3.73747200 3.47664500 0.14233700	H 4.28903900 2.15389600 0.74054200
H 4.54267900 -3.42988600 0.95512300	H 2.48059600 2.90877900 1.25130800	H 3.86857700 3.40158700 -0.43898000
H 4.60838200 -3.96693100 -1.45217600	C 4.09255400 -0.89356300 1.83227200	H 2.74543500 2.99542300 0.86873000
C -2.88022100 -0.33451000 0.71222700	H 4.54122600 -1.77282100 2.30467100	C 3.93808500 -0.63870700 2.15104300
C -3.51462100 0.91112500 0.76927500	H 4.88188000 -0.38452800 1.27145700	H 4.31975700 -1.45074900 2.77760100
C -3.64387800 -1.51954200 0.72610100	H 3.75758800 -0.21706700 2.62324700	H 4.79292000 -0.19570100 1.63095300
C -4.89821200 1.00498000 0.81207300	C 1.35617000 -2.28902100 1.74639100	H 3.51681700 0.12875300 2.80624800
C -5.03432100 -1.38553300 0.76350500	H 0.52262200 -2.65971800 1.13823800	C 1.23561200 -2.08212600 1.89225500
C -5.66818700 -0.15064800 0.80230500	H 1.78892800 -3.16302100 2.24232000	H 0.46795100 -2.51465200 1.23687700
H -5.36439800 1.98210500 0.84313700	H 0.94289300 -1.64331900 2.52803700	H 1.60548800 -2.90894600 2.50558300
H -5.63057700 -2.29068300 0.76521200	C 3.29402400 -2.58440300 -0.59593800	H 0.74333100 -1.38046300 2.57596500
H -6.74963300 -0.09503000 0.82814100	H 4.05524600 -2.11556700 -1.22516000	C 3.44767700 -2.58188300 -0.16126000
C 2.68448600 -2.06224000 2.34109800	H 3.73695900 -3.47683400 -0.14240700	H 4.26955200 -2.16290500 -0.74855100
H 2.99286000 -1.03929200 2.57508600	H 2.47991800 -2.90889000 -1.25115000	H 3.84951600 -3.40783700 0.43406300
H 1.68522000 -2.21757400 2.75605400	N -1.89528300 0.00002700 -0.00003100	H 2.72018100 -2.99525400 -0.86625800
H 3.36769700 -2.73750100 2.85731800	Si -2.65859700 -1.38413500 -0.71156600	N -1.92689900 0.00116000 -0.00063700

H -2.92960700 1.81744000 0.74654100	Si -2.65868000 1.38413100 0.71152900	Si -2.64768500 -1.26159500 -0.92225900
C -3.07008000 -2.91262900 0.70178400	C -1.35613400 -2.28910500 -1.74626200	Si -2.65646500 1.25965300 0.91976900
H -2.73078500 -3.17398500 -0.30532200	H -0.94273900 -1.64343500 -2.52787300	C -1.22932700 -2.08470500 -1.88638700
H -2.23313400 -3.03074400 1.39665600	H -0.52267000 -2.65984700 -1.13802300	H -0.73282600 -1.38345100 -2.56750000
H -3.83800100 -3.63030700 0.99124500	H -1.78889500 -3.16308000 -2.24223100	H -0.46535700 -2.51877000 -1.22775600
H -0.97971800 1.24547400 2.00896100	C -4.09245000 -0.89352300 -1.83240100	H -1.59758900 -2.91054800 -2.50199800
H 0.87384900 -0.08430600 2.31543000	H -4.54114900 -1.77277000 -2.30479100	C -3.92977300 -0.63953600 -2.15637300
C -0.65565900 1.92240200 -0.00281600	H -4.88178000 -0.38440700 -1.27166400	H -4.30957600 -1.45140600 -2.78428900
C -0.34077200 3.22876700 0.37719900	H -3.75738200 -0.21708500 -2.62338200	H -4.78633400 -0.19570500 -1.63983400
C -0.90208900 1.62782900 -1.34349700	C -3.29419200 -2.58433700 0.59591600	H -3.50525400 0.12744600 -2.81004300
C -0.25358300 4.23518500 -0.57779900	H -4.05550200 -2.11548100 1.22501600	C -3.45003300 -2.58273200 0.15815400
H -0.14516700 3.45619200 1.41990800	H -3.73705600 -3.47679400 0.14237000	H -4.27409000 -2.16322500 0.74199500
C -0.82005300 2.64133500 -2.29530800	H -2.48016600 -2.90878200 1.25124900	H -3.84989000 -3.40849500 -0.43876700
H -1.15978300 0.62119000 -1.66442000	C -4.09247700 0.89341000 1.83239000	H -2.72568800 -2.99647200 0.86616800
C -0.49111800 3.94087800 -1.91933200	H -4.54119900 1.77261700 2.30483300	C -3.93827800 0.63087100 2.15073300
H -0.00174400 5.24514500 -0.27627000	H -4.88180400 0.38427900 1.27166300	H -4.32358000 1.44070000 2.77793100
H -1.01626800 2.40220100 -3.33365500	H -3.75734600 0.21695500 2.62333100	H -4.79140500 0.18291400 1.63208700
H -0.42599300 4.72414600 -2.66573400	C -1.35627200 2.28917600 1.74622700	H -3.51147900 -0.13415300 2.80520800
C 1.95481700 1.03586500 0.86951700	H -0.52279200 2.65991400 1.13800600	C -1.24416300 2.08907700 1.88756000
C 2.65108900 1.71916400 1.86634700	H -1.78907400 3.16316300 2.24214000	H -0.48065200 2.52688100 1.23078400
C 2.32507300 1.20734800 -0.46596300	H -0.94289200 1.64355100 2.52788300	H -1.61740600 2.91319900 2.50247000
C 3.69675500 2.57776300 1.53763700	C -3.29437400 2.58430100 -0.59593500	H -0.74620200 1.38989200 2.56975400
H 2.36961500 1.58435000 2.90595900	H -4.05558700 2.11536400 -1.22509100	C -3.46261100 2.57747800 -0.16183000
C 3.37273000 2.05876300 -0.79384400	H -3.73738300 3.47667900 -0.14237500	H -4.28353800 2.15435200 -0.74747300
H 1.78941500 0.68817200 -1.24797600	H -2.48035800 2.90888200 -1.25121200	H -3.86747400 3.40125900 0.43445400
C 4.05820000 2.74843000 0.20459200	N 1.89528300 0.00003900 0.00004700	H -2.73868600 2.99465300 -0.86825200
H 4.22846900 3.10652600 2.31979900		
H 3.65025500 2.18766000 -1.83291500	E_{BENZ} = -1811.86870693	E_{BENZ} = -1747.28132206
H 4.87305800 3.41343900 -0.05620900	Thermal correction= 0.387813	Thermal correction= 0.382444
H -0.99568400 -2.17385100 -0.28857600		
E_{BENZ} = -1690.49153051		
Thermal correction= 0.426844		

1a	**1b**	**$HN(SiMe_3)_2$**
Zn -1.51908000 0.01150500 0.91661500	Mg -1.64167300 -0.01581300 1.08852900	N 0.00001100 0.00035000 -0.81411400
C 2.08596300 -1.32276000 -1.11633100	C 0.16403100 -0.12881600 -0.16484200	Si -1.58770100 0.00808600 -0.08766200
C 0.26171300 -0.13030700 -0.26345200	N 1.14086100 0.76687100 -0.36325900	Si 1.58770400 -0.00801500 -0.08765100
N 1.24426000 0.76039000 -0.43319400	N 0.54652300 -1.29619500 -0.69381900	C -2.81011500 0.60410100 -1.38856000
N 0.64275000 -1.30288800 -0.77495100	C 1.13639600 2.06633100 0.22891200	H -2.57586700 1.62080200 -1.71625800
C 1.22875800 2.06178100 0.15569200	C 1.01710300 2.14792100 1.61754300	H -2.80103300 -0.04502800 -2.26985700
C 1.07171400 2.14669600 1.53985600	C 1.23489600 3.22218200 -0.55867300	H -3.83075600 0.60532600 -0.99474300
C 1.35353700 3.21391300 -0.63319100	C 0.98335300 3.38748300 2.24538700	C -1.59720600 1.17118300 1.39316400
C 1.02621700 3.38825000 2.16253900	H 0.94886600 1.23743700 2.20076200	H -2.58501500 1.19134900 1.86350300
H 0.98258500 1.23833600 2.12313600	C 1.21459100 4.45422200 0.09977300	H -0.87907700 0.86266800 2.15818100
C 1.31859300 4.44805800 0.02053600	C 1.09076000 4.54532000 1.48236300	H -1.34517900 2.19098300 1.09042400

C 1.15744800 4.54331600 1.39904000	H 0.87540100 3.44010600 3.32152400	C -2.09242200 -1.71037600 0.49640700
H 0.88848400 3.44468300 3.23503300	H 1.27835900 5.35972000 -0.49322700	H -1.39369100 -2.09158400 1.24617900
H 1.40204100 5.35153200 -0.57307700	H 1.06604500 5.51800200 1.95867200	H -3.09184900 -1.70388200 0.94300500
H 1.12281800 5.51747700 1.87172400	C -0.32023900 -2.43047900 -0.82165100	H -2.10127600 -2.41822300 -0.33760700
C -0.23223600 -2.42898100 -0.91908200	C -0.15063100 -3.54010400 0.00644300	C 1.59673900 -1.17175500 1.39265700
C -0.04950700 -3.56224900 -0.12664800	C -1.33117900 -2.39717800 -1.79714600	H 2.58449600 -1.19234600 1.86308400
C -1.25991700 -2.36682000 -1.87524300	C -0.98573100 -4.64277300 -0.13254200	H 0.87860500 -0.86342400 2.15774100
C -0.89057100 -4.65795700 -0.27889200	C -2.15689300 -3.51854500 -1.91368100	H 1.34452900 -2.19136200 1.08942700
C -2.09195500 -3.48241200 -2.00453000	C -1.98841700 -4.63153400 -1.09726700	C 2.81014600 -0.60373900 -1.38865500
C -1.91317000 -4.61715400 -1.22175300	H -0.86001500 -5.49728300 0.52059900	H 2.80151000 0.04589800 -2.26958400
H -0.75431100 -5.53042100 0.34788300	H -2.94793200 -3.50971800 -2.65436000	H 3.83070000 -0.60556500 -0.99461000
H -2.89605900 -3.45130300 -2.73038300	H -2.64817200 -5.48401300 -1.20674100	H 2.57557900 -1.62015800 -1.71699100
H -2.57865500 -5.46382000 -1.34088400	C 1.33869900 3.16513300 -2.05922000	C 2.09284000 1.71008800 0.49715100
C 1.50226900 3.15072300 -2.12971500	H 2.34958500 2.89244600 -2.37634500	H 1.39419500 2.09113500 1.24708800
H 2.52109300 2.87235400 -2.41492000	H 0.64243800 2.43698800 -2.47963300	H 3.09227600 1.70320100 0.94372100
H 0.81554200 2.42443300 -2.56870800	H 1.10457700 4.13744500 -2.49366800	H 2.10183600 2.41829000 -0.33656500
H 1.28600400 4.12250700 -2.57444500	H 0.62008200 -3.52744500 0.76285600	H 0.00000100 0.00145200 -1.82594700
H 0.73570400 -3.57372400 0.61455500	C -1.55443900 -1.18659500 -2.66206200	
C -1.49725700 -1.13844900 -2.71074000	H -2.05500200 -0.39858300 -2.09422400	E_{BENZ} = -873.787557664
H -2.02036300 -0.37567600 -2.12869600	H -0.61409600 -0.77457400 -3.03510300	E_{THF}= -873.788501684
H -0.56196500 -0.69880200 -3.06384000	H -2.18465300 -1.43555100 -3.51644400	Thermal correction= 0.195486
H -2.11396400 -1.37870500 -3.57753500	H 2.09791400 -1.80029500 -2.04809600	
H 2.23701800 -1.82780600 -2.06998500	H 1.96785800 0.49870900 -2.27446500	
H 2.12114700 0.47325000 -2.31911700	C 2.85741300 -1.96436300 -0.04723600	
C 2.92719600 -1.97385200 -0.04127300	C 4.06033900 -2.54238100 -0.45206600	
C 4.14560600 -2.55207700 -0.39648900	C 2.54412200 -1.91898800 1.31338800	
C 2.56212900 -1.91886600 1.30597700	C 4.94697100 -3.06049300 0.48669600	
C 4.99712300 -3.06113900 0.57895500	H 4.31225500 -2.57272100 -1.50666100	
H 4.43728500 -2.58949100 -1.44054000	C 3.42821700 -2.44242600 2.25209300	
C 3.41141300 -2.43333600 2.28105500	H 1.61039300 -1.48768200 1.65469400	
H 1.61395800 -1.49045400 1.60928800	C 4.63291900 -3.00963500 1.84253300	
C 4.63198900 -3.00059000 1.92158600	H 5.87984100 -3.50451500 0.15980500	
H 5.94250700 -3.50552100 0.29085700	H 3.16850200 -2.40515200 3.30332900	
H 3.11149700 -2.38925400 3.32124900	H 5.32035900 -3.41559700 2.57534400	
H 5.29206400 -3.39951300 2.68287000	C 3.60980900 0.71305600 -0.94853600	
C 3.72743800 0.68733500 -0.94930300	C 4.48132100 0.93259200 -2.01676900	
C 4.62940000 0.89567700 -1.99421900	C 4.07552900 0.89367000 0.35569800	
C 4.15738900 0.87332300 0.36644400	C 5.80146300 1.31226200 -1.79104200	
C 5.94484000 1.26951900 -1.73389800	H 4.12398300 0.80210800 -3.03324300	
H 4.29985000 0.76103800 -3.01949000	C 5.39134500 1.27942100 0.58241500	
C 5.46843600 1.25343800 0.62741400	H 3.41531400 0.72644000 1.19385200	
H 3.47332900 0.71431600 1.18688800	C 6.25875400 1.48656900 -0.48801600	
C 6.36646000 1.44932600 -0.41965100	H 6.46736800 1.47656800 -2.62996900	
H 6.63478500 1.42515800 -2.55483600	H 5.74009500 1.41551900 1.59904900	
H 5.78945300 1.39380700 1.65254400	H 7.28424800 1.78635400 -0.30705400	
H 7.38814300 1.74469800 -0.21191000	C 2.21920900 0.22944100 -1.24477500	
C 2.34322700 0.20946700 -1.28133700	Cl -0.76602600 -0.76776300 3.08202500	

Cl -0.75637100 -0.75596800 2.95055900	N -3.32280700 0.59571300 0.27719400	
N -3.23519500 0.57938800 0.17701100	Si -4.57038800 -0.58742000 0.33242100	
Si -4.50058600 -0.58948000 0.28991800	Si -3.41128500 2.19564200 -0.34495100	
Si -3.30390600 2.19676700 -0.41282900	C -3.84380100 -2.14223600 1.13908700	
C -3.80884300 -2.15688900 1.08696500	H -2.96479600 -2.52729100 0.61214200	
H -2.96010600 -2.57004000 0.53449100	H -3.56553300 -1.97497000 2.18479300	
H -3.48366500 -1.98099700 2.11625200	H -4.57922600 -2.95266500 1.13198800	
H -4.57583900 -2.93760500 1.11354200	C -5.20194800 -1.06870100 -1.38667400	
C -5.17545300 -1.05896200 -1.41609800	H -5.98905500 -1.82724100 -1.32548700	
H -5.96905600 -1.80915000 -1.33724400	H -5.61648100 -0.20352700 -1.91259800	
H -5.59089600 -0.19123800 -1.93631900	H -4.39323300 -1.47243200 -2.00036900	
H -4.38307000 -1.47372700 -2.04412800	C -6.06918900 -0.08043500 1.36421000	
C -5.95760900 -0.01736100 1.34671600	H -6.61204800 0.75101300 0.90801500	
H -6.48637900 0.82369300 0.89176900	H -6.77030900 -0.91403500 1.47638600	
H -6.68091900 -0.82724000 1.48797900	H -5.75641400 0.23292200 2.36457200	
H -5.61017300 0.29878300 2.33463600	C -2.56309100 3.39457500 0.84571400	
C -2.55103700 3.38500900 0.84730300	H -1.50453000 3.15607100 0.98378700	
H -1.49398000 3.17048100 1.02784300	H -2.60732500 4.42469300 0.47811000	
H -2.61148000 4.42374000 0.50679500	H -3.04045800 3.36704100 1.82978800	
H -3.07143800 3.31048600 1.80653900	C -2.48641600 2.34785700 -1.99360200	
C -2.28087500 2.39035700 -1.99713500	H -1.45960300 1.98817200 -1.88219100	
H -1.26540200 2.01649400 -1.84121400	H -2.96465600 1.75396900 -2.77807700	
H -2.71817800 1.83228800 -2.83003900	H -2.43993300 3.38634400 -2.33684300	
H -2.20427700 3.44049200 -2.29662000	C -5.17336600 2.81586300 -0.63139800	
C -5.05666600 2.78787700 -0.79383100	H -5.72839200 2.88478400 0.30769500	
H -5.66180100 2.85218700 0.11375200	H -5.15398800 3.81350600 -1.08168600	
H -5.02214800 3.78616100 -1.24184400	H -5.73470500 2.16177800 -1.30452800	
H -5.57285600 2.12873100 -1.49671900	C 1.97659500 -1.30504100 -1.08487600	
E_{BENZ} = -2628.62335051	E_{BENZ} = -2564.04155895	
Thermal correction= 0.621109	Thermal correction= 0.622332	

1a · HN(SiMe$_3$)$_2$	**1b · HN(SiMe$_3$)$_2$**	**L2HCl**
Zn -1.27498200 0.46921500 0.26144900	Mg -1.37560400 0.50056800 0.30847800	Cl 0.23259500 -2.19683700 2.29363500
N 1.87517100 0.89499400 -0.32203600	Cl -1.06706900 2.27119400 1.80456200	N 1.03652000 -0.75565900 -0.57244600
N 1.37393700 -1.03676500 -1.17440500	N 1.83864700 0.89918800 -0.32527000	N -1.14003200 -0.78980200 -0.16152800
C 1.78118400 2.23856900 0.18043500	N 1.33360000 -1.04108500 -1.15032200	C 2.36900100 -1.24455800 -0.76367400
C 1.37793500 3.27408100 -0.67097500	C 1.74210700 2.24999400 0.15685400	C 3.10855700 -0.82032600 -1.87871400
C 2.16888000 2.49282500 1.49018200	C 1.32237200 3.27009200 -0.70575400	C 2.90158600 -2.12973000 0.17215400
C 1.35658200 4.56914400 -0.14965100	C 2.13668400 2.52691500 1.45997300	C 4.41140400 -1.30498300 -2.00917900
C 2.15259100 3.78865200 1.98462800	C 1.29305400 4.57210900 -0.20284800	C 4.19659100 -2.60746900 0.00445300
C 1.74128900 4.82950700 1.16021100	C 2.11093200 3.82941700 1.93651800	C 4.95662500 -2.18797700 -1.08218900
H 1.01959400 5.38131800 -0.78382200	C 1.68423000 4.85452100 1.10058800	H 4.99954600 -0.99236300 -2.86505600
H 2.43414900 3.97855800 3.01278300	H 0.94357200 5.37203000 -0.84574800	H 4.60902300 -3.29473700 0.73313500
H 1.70615000 5.84382700 1.53978500	H 2.39706800 4.03643200 2.96009000	H 5.96952500 -2.55006300 -1.21441900
C 0.68663400 -2.08566400 -1.86681100	H 1.64134000 5.87358100 1.46635300	C -2.44481200 -1.36317600 -0.08612200
C 0.90643700 -3.41148500 -1.48958900	C 0.64125900 -2.10216700 -1.81834300	C -2.85169700 -2.12639900 -1.18296700

C -0.06317300 -1.78025700 -3.01372000	C 0.85781000 -3.42083900 -1.41419400	C -3.28925900 -1.17478800 1.01908200
C 0.32751400 -4.45011600 -2.20806600	C -0.11504100 -1.81901300 -2.96702500	C -4.10139300 -2.73071000 -1.20171700
C -0.63658900 -2.84268000 -3.71726000	C 0.27170600 -4.47270600 -2.10706300	C -4.55133100 -1.77445900 0.95991600
C -0.45591800 -4.16254400 -3.32081500	C -0.69557100 -2.89453100 -3.64471700	C -4.96009800 -2.54373500 -0.12361700
H 0.49051200 -5.47493200 -1.89768800	C -0.51662400 -4.20628000 -3.22171000	H -4.40326500 -3.32677100 -2.05417700
H -1.22769900 -2.62376900 -4.59826500	H 0.43312300 -5.49127300 -1.77586600	H -5.21730800 -1.64819600 1.80587600
H -0.91529700 -4.96380900 -3.88763500	H -1.29134400 -2.69248800 -4.52658800	H -5.94318500 -2.99927300 -0.12220600
H 1.53051700 -3.62565400 -0.63486100	H -0.98147200 -5.01785200 -3.76909600	H -2.18094800 -2.22917600 -2.02843500
C -0.24413700 -0.36630600 -3.47909100	H 1.48559100 -3.61877600 -0.55819800	C -2.87666800 -0.41360600 2.24873700
H -0.93216800 0.16338700 -2.81605700	C -0.29914900 -0.41474100 -3.46039300	H -1.89994300 -0.75913100 2.59789800
H 0.70526400 0.17454500 -3.48951800	H -0.99645800 0.12334500 -2.81370000	H -2.83159100 0.66265700 2.05754400
H -0.66131600 -0.33963300 -4.48545300	H 0.64656300 0.13209700 -3.47111500	H -3.60311900 -0.57410800 3.04610100
H 3.11399200 -1.26008800 -2.35153400	H -0.70716400 -0.40917500 -4.47093200	H -0.68194000 0.66112600 1.26865400
C 3.58472700 -1.85450000 -0.35355500	H 3.07020300 -1.28320100 -2.32975800	C -1.67355200 1.66252300 -0.34567700
C 4.81488500 -2.40213400 -0.71389300	C 3.54672300 -1.84814800 -0.32457100	C -1.83129300 2.83954600 0.38757600
C 3.09149100 -2.08022400 0.93218800	C 4.77408800 -2.40409100 -0.68155500	C -2.31764600 1.53131900 -1.57752300
C 5.54776400 -3.15687000 0.19760600	C 3.05952100 -2.05219800 0.96722800	C -2.62109500 3.87500600 -0.10424500
H 5.20769200 -2.22667500 -1.70942900	C 5.50994800 -3.14561100 0.23844300	H -1.32975000 2.94296400 1.34322200
C 3.81924500 -2.83681100 1.84412500	H 5.16248900 -2.24548900 -1.68163600	C -3.11537500 2.56199400 -2.06408300
H 2.13864800 -1.66240500 1.22222700	C 3.79012100 -2.79551400 1.88777700	H -2.20820100 0.61732700 -2.14767300
C 5.05198100 -3.37538300 1.48028600	H 2.10893700 -1.62739500 1.25489400	C -3.26749200 3.73637700 -1.32976800
H 6.50370500 -3.57514400 -0.09446300	C 5.02003400 -3.34253800 1.52680100	H -2.73630000 4.78512100 0.47236800
H 3.42383600 -3.00315100 2.83949600	H 6.46367100 -3.57041700 -0.05147700	H -3.62232400 2.44665900 -3.01489300
H 5.61992300 -3.96494800 2.19021300	H 3.39953500 -2.94487700 2.88778300	H -3.89060700 4.53749800 -1.70942900
C 3.07296000 0.54722100 -1.14644700	H 5.59024700 -3.92172600 2.24342300	C 0.68243700 0.68562800 -0.41043900
C 2.85195900 -0.96815200 -1.33494400	C 3.03251200 0.54136500 -1.15021300	C -0.75608100 0.59807800 0.18247700
N -2.69236900 0.49963200 -1.18305400	C 2.81057500 -0.97645000 -1.31684600	H 0.63371400 1.14250700 -1.40000800
Si -3.59406000 -0.92402900 -1.55957600	N -2.76285000 0.50945000 -1.16907200	C 1.64542600 1.44964200 0.45394300
Si -3.14472800 2.02218700 -1.89157600	Si -3.65914900 -0.91588500 -1.53931600	C 2.15027300 2.67137500 0.01043900
C -2.75098200 -2.51017600 -0.93162400	Si -3.21470100 2.01153000 -1.91441400	C 2.01487500 0.95783200 1.71023300
H -1.67317000 -2.42512200 -0.80614900	C -2.81687400 -2.49028800 -0.87323400	C 3.02040700 3.40556500 0.81326100
H -3.18571500 -2.85567900 0.01262200	H -1.73723500 -2.40960000 -0.75511200	H 1.85640100 3.05301000 -0.96164400
H -2.91635500 -3.31590600 -1.65138200	H -3.24929700 -2.81343600 0.08019400	C 2.88979100 1.69010800 2.50467100
C -3.88018700 -1.13813200 -3.42255500	H -2.98756700 -3.31258700 -1.57278300	H 1.61835600 0.00828900 2.06017600
H -4.37053800 -2.09658500 -3.62151500	C -3.93153400 -1.17399600 -3.39910400	C 3.39345000 2.91250700 2.06019700
H -4.52778900 -0.35081300 -3.81726100	H -4.41383400 -2.13985000 -3.58115200	H 3.40680900 4.35581500 0.46378600
H -2.94844500 -1.11215500 -3.98867000	H -4.58302500 -0.39945300 -3.81261400	H 3.17860700 1.30245300 3.47440700
C -5.33013700 -1.01856000 -0.79884400	H -2.99744700 -1.15185800 -3.96142600	H 4.07543900 3.47802200 2.68464800
H -5.98145200 -0.20979000 -1.13374000	C -5.40188600 -1.00653800 -0.79107500	H 2.29610800 -2.41479000 1.02632300
H -5.79821000 -1.96585500 -1.08974100	H -6.05468200 -0.20911000 -1.14985300	C 2.53761700 0.10212100 -2.92366100
H -5.30598300 -0.98751700 0.29231400	H -5.86308300 -1.96269900 -1.06316500	H 1.50000200 -0.14887600 -3.15695300
C -5.02368300 2.26159300 -1.99775800	H -5.38683000 -0.94946100 0.29945300	H 2.56271700 1.14533000 -2.59420500
H -5.23745700 3.25644000 -2.40228400	C -5.09237000 2.26187300 -2.02946800	H 3.11613200 0.03647100 -3.84594300
H -5.51124000 1.53325700 -2.65079800	H -5.30127800 3.25140700 -2.44921900	C -0.03131600 -1.50698300 -0.33173700
H -5.49172800 2.19701300 -1.01223500	H -5.58066900 1.52567700 -2.67337300	H -0.03704100 -2.57763500 -0.44403400
C -2.49915100 3.51683800 -0.94617200	H -5.56472200 2.21325900 -1.04493500	
H -1.42478700 3.50098000 -0.76468100	C -2.56549400 3.52435700 -0.99574600	E_{BENZ} = -1690.49998045

H -2.73232800 4.41647300 -1.52689900	H -1.49140800 3.51211300 -0.81017800	Thermal correction= 0.425909
H -2.97149700 3.61096400 0.03265600	H -2.79330300 4.41314100 -1.59496600	
C -2.52886500 2.22936900 -3.67864200	H -3.04080800 3.64238200 -0.02064800	
H -2.85250000 1.40840600 -4.32249300	C -2.59484900 2.18754200 -3.70390900	
H -2.93425700 3.15759600 -4.09548200	H -2.92264000 1.35864500 -4.33544700	
H -1.44010400 2.29342500 -3.74192400	H -2.99292300 3.11172100 -4.13648700	
H 2.45034900 1.66578200 2.12605300	H -1.50545800 2.24279700 -3.76625200	
C 0.96800400 3.02203000 -2.09746200	H 2.43163700 1.71187900 2.10531200	
H 1.83927200 2.88574100 -2.74738500	C 0.90062300 2.99268700 -2.12417000	
H 0.34560800 2.13303900 -2.18828100	H 1.76479700 2.82279100 -2.77540300	
H 0.39782800 3.86483300 -2.48743800	H 0.26042800 2.11397200 -2.19042500	
N -2.13631300 -0.89544200 1.93653600	H 0.34465900 3.83680900 -2.53134400	
Si -0.87606100 -1.78882800 2.84274500	N -2.19209100 -0.81942300 1.95424100	
Si -3.45902200 -0.04590200 2.85516400	Si -0.93581300 -1.70436000 2.88514700	
C -0.23842700 -3.11131800 1.68048000	Si -3.52407000 0.03027800 2.87120600	
H -1.01610500 -3.84466100 1.45196000	C -0.29018300 -3.03806600 1.74083600	
H 0.09217500 -2.68747200 0.73651500	H -1.06511400 -3.77303600 1.50874700	
H 0.60625800 -3.64643400 2.12337700	H 0.05217700 -2.62156900 0.79748800	
C -1.52797900 -2.70554400 4.35551400	H 0.54976000 -3.56944700 2.19701700	
H -0.70008200 -3.26449700 4.80479600	C -1.59881300 -2.60117800 4.40348900	
H -1.94395300 -2.05843900 5.12774500	H -0.77173700 -3.15018700 4.86620700	
H -2.29472400 -3.43166700 4.07235900	H -2.02381200 -1.94620200 5.16386100	
C 0.48789400 -0.61100000 3.34965300	H -2.35927900 -3.33502300 4.12359300	
H 0.11441900 0.17293600 4.00979800	C 0.42561600 -0.51811000 3.37690100	
H 1.27952300 -1.15828000 3.87199000	H 0.05046600 0.28205100 4.01605800	
H 0.92047700 -0.10525600 2.48582900	H 1.21190300 -1.05674300 3.91598000	
C -2.79699000 0.71273100 4.43715700	H 0.86748200 -0.03307000 2.50556100	
H -3.62997600 1.22000400 4.93546200	C -2.86622200 0.81285700 4.44209800	
H -2.38529100 -0.00791000 5.14473300	H -3.70274500 1.31890600 4.93565100	
H -2.04039000 1.46194200 4.20315500	H -2.44538200 0.10616000 5.15814700	
C -4.31739300 1.26811200 1.83606900	H -2.11756300 1.56595400 4.19454300	
H -4.28536900 1.04003500 0.77240400	C -4.38341000 1.32819300 1.83210400	
H -5.36519200 1.34267600 2.14349200	H -4.36384100 1.07982200 0.77223200	
H -3.83098000 2.23246000 1.98071300	H -5.42807500 1.41248000 2.14762400	
C -4.71562200 -1.39145200 3.27841100	H -3.89335100 2.29385500 1.95493600	
H -4.29819900 -2.15567400 3.93734200	C -4.77299800 -1.31956800 3.29790100	
H -5.57757800 -0.94846100 3.78707100	H -4.35559000 -2.07764000 3.96363700	
H -5.09299600 -1.88984600 2.38040600	H -5.63965300 -0.87775900 3.79936500	
H -2.60138500 -1.57509400 1.33521200	H -5.14350000 -1.82457500 2.40075000	
C 0.86513400 0.02445300 -0.50951600	H -2.66356400 -1.52000500 1.38040600	
C 4.40525200 0.99579100 -0.61432200	C 0.82291000 0.02852500 -0.49660300	
C 5.27874400 1.64903400 -1.48460200	C 4.36772000 0.99730200 -0.63137100	
C 4.81607600 0.76127100 0.70069200	C 5.23740000 1.63687600 -1.51558600	
C 6.54415000 2.04832500 -1.06164300	C 4.78510500 0.78280400 0.68501900	
H 4.96356000 1.85099300 -2.50291500	C 6.50496500 2.04213200 -1.10493800	
C 6.07522400 1.16290200 1.12745900	H 4.91732400 1.82351100 -2.53530300	
H 4.15430200 0.25952300 1.39060500	C 6.04649500 1.19031300 1.09954400	

C 6.94529800 1.80464200 0.24764600	H 4.12653400 0.29197500 1.38576400	
H 7.20873900 2.55515700 -1.75128300	C 6.91253000 1.81827200 0.20592200	
H 6.37813200 0.97508000 2.15071600	H 7.16628900 2.53821500 -1.80546600	
H 7.92651600 2.11816300 0.58420700	H 6.35432300 1.01792100 2.12406800	
H 2.92722100 1.02516500 -2.12070000	H 7.89547200 2.13652900 0.53289600	
Cl -1.01876600 2.20385600 1.80752200	H 2.88268100 1.00515800 -2.13079000	
E_{BENZ} = -3502.42007344	E_{BENZ} = -3437.84654929	
Thermal correction = 0.851401	E_{THF} = -3437.85541490	
	Thermal correction= 0.852699	

2a	**2b**	**2a · HN(SiMe$_3$)$_2$**
Zn -1.55977200 -0.25367200 1.06029000	Mg 1.66465100 0.31781300 1.20898000	Zn -1.28132100 -0.36855600 -0.35084500
C 2.41795000 -0.88010700 -0.65858000	C -0.36887700 0.02867600 0.38593100	N 1.84482900 -0.76517800 -0.55890700
C 0.45044200 -0.02490300 0.32595100	N -1.27974900 -0.94553800 0.44886000	N 1.58357100 0.85265200 0.88084300
N 1.35935500 0.94468400 0.42360400	N -0.89762900 1.06566200 -0.27093400	C 1.62025800 -2.04945600 -1.14686000
N 0.98351300 -1.06396100 -0.31680500	C -1.11953700 -2.17486200 1.16929200	C 1.98908800 -2.31227300 -2.47021900
C 1.18179300 2.17002000 1.14676500	C -1.27889900 -2.18718600 2.56377600	C 1.07555900 -3.04328000 -0.33922000
C 1.27741300 2.16722500 2.54685900	C -0.83251600 -3.34160300 0.46337500	C 1.80208100 -3.61062800 -2.94360400
C 0.94094600 3.34565300 0.43859400	C -1.09090800 -3.40586100 3.22264600	C 0.88031300 -4.32399900 -0.83695000
C 1.07418900 3.38221600 3.20776400	C -0.66811800 -4.54354800 1.14054000	C 1.25591200 -4.60977900 -2.14459900
C 0.76071400 4.54347300 1.11900800	C -0.78764800 -4.57114200 2.52611000	H 2.05971600 -3.82986000 -3.97368300
C 0.81726000 4.55716700 2.50879400	H -1.19219800 -3.43521200 4.30153800	H 0.43590100 -5.08477100 -0.20780000
H 1.12566600 3.40067100 4.29037200	H -0.43242500 -5.44545700 0.58926800	H 1.10903300 -5.60406600 -2.54921200
H 0.56068400 5.45303600 0.56629200	H -0.64660600 -5.49963200 3.06676400	C 1.11322300 1.44229900 2.10034300
H 0.66234900 5.48247600 3.05106600	C -0.17779700 2.26402200 -0.59507400	C 1.23675100 2.82188400 2.27783400
C 0.26140600 -2.25547100 -0.66069100	C -0.14164700 3.31082300 0.32447400	C 0.66000700 0.62382100 3.15002300
C 0.18933800 -3.29875500 0.25944200	C 0.46957000 2.36172900 -1.83750700	C 0.86317000 3.41491700 3.47679800
C -0.35228600 -2.34749200 -1.91960700	C 0.52019100 4.49194800 0.00496800	C 0.28628300 1.24740800 4.34380800
C -0.47721700 -4.47252000 -0.07518200	C 1.12243000 3.55905200 -2.13624200	C 0.37610700 2.62393100 4.51166600
C -1.01124200 -3.53754000 -2.23345400	C 1.14103900 4.61808100 -1.23288400	H 0.95197700 4.48780200 3.59604600
C -1.06676400 -4.59396400 -1.32876000	H 0.55900300 5.29809700 0.72643600	H -0.07448600 0.63180400 5.15894100
H -0.54588000 -5.27609900 0.64690900	H 1.63754300 3.65189100 -3.08530000	H 0.07685300 3.07384400 5.45099000
H -1.50206400 -3.62629200 -3.19570100	H 1.66317100 5.53247000 -1.48822700	H 1.61881200 3.42970700 1.47243800
H -1.59347200 -5.50237000 -1.59578200	H -0.61282000 3.18691000 1.28851900	C 0.56562400 -0.87009300 3.02411500
H 0.63303400 -3.17590600 1.23646200	C 0.50035700 1.20128800 -2.79417400	H -0.29250500 -1.15397000 2.41072700
C -0.34389800 -1.18903500 -2.87920500	H 0.99664200 0.34182800 -2.33768300	H 1.46212500 -1.28988000 2.56364800
H -0.83555100 -0.31964200 -2.43683900	H -0.50482000 0.88950900 -3.08952900	H 0.44582700 -1.32972400 4.00530800
H 0.67234100 -0.89483900 -3.15484300	H 1.04840400 1.46313800 -3.69935800	H 3.54823900 0.56523400 1.58581200
H -0.87687900 -1.44473800 -3.79512600	H -2.42165700 0.97202100 -1.73327800	C 3.57766400 2.20253700 0.21418200
H 2.54370400 -0.96516000 -1.73886200	C -3.23886300 1.86409200 0.02469700	C 4.56314300 2.85665400 0.94999000
C 3.31005800 -1.88401500 0.02779100	C -4.22365500 2.51896900 -0.71199100	C 3.06473700 2.81176300 -0.93519800
C 4.29365100 -2.55423700 -0.69643000	C -3.13685000 2.10638600 1.39780400	C 5.03155500 4.10647200 0.54839100
C 3.18321000 -2.12855400 1.39841900	C -5.10341100 3.40114700 -0.08744600	H 4.95724000 2.39037000 1.84598100
C 5.14795500 -3.45407300 -0.06182200	H -4.30133200 2.33983900 -1.77896400	C 3.52620200 4.05985000 -1.33415600
H 4.39025400 -2.37352200 -1.76156200	C -4.01143700 2.98824800 2.02155300	H 2.28762600 2.31884900 -1.50705900

C 4.03216500 -3.02806200 2.03211200	H -2.35956100 1.62071600 1.97519800	C 4.51182800 4.71137500 -0.59183700
H 2.40618000 -1.63092400 1.96599600	C -4.99875100 3.63670700 1.27985100	H 5.79740400 4.60722200 1.12883000
C 5.01858900 -3.69193100 1.30290900	H -5.86373700 3.90747500 -0.67036300	H 3.11652000 4.52666500 -2.22226700
H 5.90770300 -3.97216700 -0.63503400	H -3.91779200 3.17543800 3.08470900	H 4.87107800 5.68520500 -0.90285000
H 3.91946100 -3.21697400 3.09310600	H -5.67797000 4.32669700 1.76633600	C 3.23442400 -0.24189100 -0.42196900
H 5.67789500 -4.39558500 1.79713500	C -2.56678900 -0.60289600 -0.21978700	C 3.05991200 0.85642500 0.65339800
C 2.66480900 0.59259800 -0.20548500	Cl 1.29027900 1.38387300 3.20305500	N -2.43179500 -1.05333000 1.15783400
Cl -1.34675000 -1.35692200 3.05746600	N 3.16183600 -0.28482700 0.08720900	Si -3.16303500 0.04684600 2.26611400
N -3.06807500 0.33332100 -0.03531100	Si 4.30833600 0.91071400 -0.37449500	Si -2.74169000 -2.75788700 1.27665200
Si -4.22233100 -0.86420200 -0.49185200	Si 3.17016300 -1.95561500 -0.30335200	C -2.44712900 1.80521500 2.12329400
Si -3.04397300 2.00257500 -0.44724500	C 3.78632300 2.55404600 0.40251400	H -1.43180000 1.84780800 1.73155600
C -3.74076300 -2.51189600 0.28863000	H 2.78011700 2.85836600 0.10232000	H -3.08492100 2.45353500 1.51238900
H -2.74106800 -2.83529500 -0.01030400	H 3.81122800 2.51474300 1.49603200	H -2.41296800 2.26327900 3.11530400
H -3.75900900 -2.46219100 1.38077500	H 4.45954100 3.35887700 0.09101100	C -2.95927900 -0.48817300 4.07471200
H -4.43568400 -3.29914200 -0.02098100	C 4.37736700 1.14935200 -2.25284500	H -3.38333400 0.26622600 4.74542000
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H -5.00644500 -1.84520200 -2.66988800	H 4.64465200 0.21700100 -2.76012400	H -1.91100600 -0.62439800 4.34315900
H -4.50751800 -0.16386800 -2.88555800	H 3.40472100 1.46794900 -2.63640900	C -5.02817700 0.29926300 2.03080900
H -3.28734100 -1.43168700 -2.73516100	C 6.06841900 0.55412300 0.21426700	H -5.59847300 -0.61380700 2.20954000
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H -6.65240900 -1.30609900 -0.12590500	H 6.07998700 0.36729600 1.29214400	C -4.49114800 -3.15867700 1.89241500
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H -1.60903200 2.69468100 1.50879500	H 2.51513500 -4.00371500 1.01127800	H -3.44317500 -3.45541800 -1.00594600
H -2.46772300 4.07801600 0.85384000	H 3.35284100 -2.81712400 2.02266700	C -1.57603400 -3.62053200 2.50604400
H -3.32804000 2.89354900 1.85164500	C 1.95559600 -2.33176500 -1.71183400	H -1.63895200 -3.16914500 3.49966500
C -1.76666900 2.34652200 -1.80747200	H 2.27651900 -1.83694500 -2.63389500	H -1.84871200 -4.67678500 2.60226900
H -2.06119300 1.85401900 -2.73947600	H 1.86839600 -3.40391400 -1.91538600	H -0.52967400 -3.58222900 2.19182000
H -1.65345600 3.41623900 -2.01103300	H 0.96097000 -1.95632700 -1.46064000	H 3.51437200 0.22511500 -1.36540800
H -0.78817400 1.95652400 -1.51858900	H -3.36597700 -0.64573400 0.52184000	C 4.26392300 -1.28658800 -0.08057400
H 3.43798600 0.62037100 0.56382700	C -2.89727200 -1.53312400 -1.35980600	C 5.43859600 -1.36637100 -0.82637500
C 3.04174700 1.53127300 -1.32346300	C -4.11992300 -2.19970000 -1.39006600	C 4.07809400 -2.16394900 0.99068200
C 4.25724600 2.21057200 -1.29013700	C -1.98419200 -1.73520400 -2.39928800	C 6.41674100 -2.30671900 -0.50977900
C 2.17586200 1.73393900 -2.40252900	C -4.43287500 -3.05494900 -2.44548600	H 5.58864500 -0.68800700 -1.65909800
C 4.60976500 3.07941100 -2.32165400	H -4.82784800 -2.05411700 -0.58153700	C 5.04841900 -3.10672300 1.30542100
H 4.92802000 2.06460300 -0.45064300	C -2.29165600 -2.59030200 -3.45020200	H 3.16368700 -2.12238500 1.56879600
C 2.52273400 2.60260300 -3.42974200	H -1.02048700 -1.24290400 -2.37359800	C 6.22182100 -3.18001300 0.55531200
H 1.21721900 1.23158500 -2.42662700	C -3.51972300 -3.25194700 -3.47631100	H 7.32526600 -2.35904700 -1.09800400
C 3.74346700 3.27719000 -3.39199100	H -5.38591800 -3.57046100 -2.45695500	H 4.88783300 -3.78946400 2.13132900
H 5.55679200 3.60462100 -2.28391200	H -1.57115000 -2.74679600 -4.24429400	H 6.97693100 -3.91781800 0.79935500
H 1.83862300 2.75945200 -4.25529800	H -3.75902800 -3.92070100 -4.29459700	H 0.79987300 -2.79996000 0.67759200
H 4.01346000 3.95637300 -4.19192100	H -0.72309900 -3.29744500 -0.61003700	C 2.49634600 -1.23176300 -3.38399300

H 0.87946100 3.31193300 -0.63903400	C -1.64801800 -0.94634400 3.33164400	H 1.94517400 -0.30350800 -3.22573000
C 1.59611700 0.91438700 3.31727800	H -0.85169200 -0.19796000 3.31140000	H 3.56263100 -1.03430800 -3.23186900
H 0.79743500 0.17201800 3.24251300	H -2.54950700 -0.48312200 2.92141300	H 2.36040600 -1.52340200 -4.42572300
H 2.51709200 0.45183800 2.95139300	H -1.84360300 -1.19083700 4.37618100	N -2.42373400 1.48283100 -1.19159100
H 1.73430500 1.14358200 4.37430400	C -2.32106400 0.87592000 -0.65119700	Si -1.39334000 2.76441500 -1.90840300
		Si -3.90710900 0.95372400 -2.10030500
E_{BENZ} = -2628.62635441	E_{BENZ} = -2564.04422510	C -0.42657100 3.52995400 -0.50371800
Thermal correction= 0.619631	Thermal correction= 0.620699	H -1.07464600 3.93793300 0.27512800
		H 0.22111600 2.78884800 -0.04450100
		H 0.20759300 4.33993500 -0.87530200
		C -2.39086200 4.15883700 -2.69375000
		H -1.69503300 4.92013900 -3.06198400
		H -3.01186100 3.84776200 -3.53418100
		H -3.03807200 4.63929700 -1.95474700
		C -0.20696100 2.03160100 -3.15599800
		H -0.71936400 1.56952100 -3.99986500
		H 0.45165900 2.81888100 -3.53819200
		H 0.40036200 1.24943200 -2.69809700
		C -3.57541500 0.93325000 -3.94576800
		H -4.48846800 0.59578500 -4.44727300
		H -3.30896400 1.90191700 -4.37035900
		H -2.78521100 0.21463600 -4.16775100
		C -4.51159200 -0.73552000 -1.58110800
		H -4.45569700 -0.88399900 -0.50439100
		H -5.55366600 -0.84979800 -1.89737100
		H -3.91248600 -1.51006100 -2.05913700
		C -5.24305700 2.22147500 -1.68659800
		H -4.99179100 3.22286500 -2.04162500
		H -6.19040200 1.93076500 -2.15107700
		H -5.41800000 2.28033200 -0.60801700
		H -2.75084800 1.84224700 -0.29505400
		C 0.93738200 -0.08923900 0.15970500
		Cl -1.13596800 -1.25717900 -2.52373100
		E_{BENZ} = -3502.42597866
		Thermal correction= 0.850138

2b · HN(SiMe$_3$)$_2$	**1b · THF**	**THF**
Mg 1.38744800 -0.37402100 0.40396400	Mg -1.44516400 0.13494700 0.86529600	C 1.18253400 -0.46195300 0.00000000
Cl 1.18812500 -1.28019900 2.56611700	Cl -0.39937600 0.26545700 2.99434900	O 0.00000200 -1.25696800 0.00000000
N -1.80263600 -0.76884000 0.57143500	N 1.50726600 0.83684400 -0.40140400	C -1.18253200 -0.46195700 -0.00000100
N -1.54331000 0.84284800 -0.87192000	N 0.85631700 -1.12546900 -1.04557500	C -0.77278000 1.02553500 0.00000100
C -1.57443500 -2.05148600 1.16124500	C 1.52185000 2.17531000 0.11365300	C 0.77277600 1.02553700 0.00000000
C -1.94608600 -2.31553500 2.48371100	C 1.37710700 3.25833000 -0.76478400	H 1.77629300 -0.71586700 0.88497600
C -1.01714800 -3.04263100 0.35810100	C 1.74042500 2.37218400 1.47401600	H 1.77629400 -0.71586700 -0.88497600
C -1.74997300 -3.61136000 2.96032100	C 1.44601100 4.54456200 -0.22471600	H -1.77629100 -0.71587200 -0.88497700
C -0.81421000 -4.32111100 0.85883700	C 1.80921000 3.66139800 1.98712100	H -1.77629200 -0.71587300 0.88497400

C -1.19262700 -4.60754700 2.16548500	C 1.66452700 4.74962900 1.13337400	H -1.16698600 1.53906200 -0.87811200
H -2.00916100 -3.83059900 3.98999800	H 1.31643400 5.39511000 -0.88460200	H -1.16698500 1.53906000 0.87811500
H -0.36136300 -5.07944300 0.23278300	H 1.95508000 3.80784700 3.04981500	H 1.16698000 1.53906400 -0.87811400
H -1.03909300 -5.59976300 2.57266500	H 1.70612700 5.75910000 1.52523100	H 1.16698100 1.53906400 0.87811400
C -1.06683900 1.43880600 -2.08561900	C 0.01930100 -2.16205900 -1.54527400	
C -1.18635000 2.81982600 -2.25614600	C 0.35352900 -3.49232600 -1.27170300	E_{THF} = -232.360555953
C -0.60726900 0.62598700 -3.13721300	C -1.06189700 -1.85085600 -2.38821800	Thermal correction = 0.089390
C -0.80376300 3.41943900 -3.44899100	C -0.40795700 -4.53087300 -1.79064500	
C -0.22407100 1.25611700 -4.32467500	C -1.81051700 -2.91887700 -2.89364800	
C -0.31088400 2.63368800 -4.48519100	C -1.50367500 -4.24106800 -2.59902400	
H -0.89016800 4.49315800 -3.56267600	H -0.14355200 -5.55710800 -1.56559500	
H 0.14186700 0.64483800 -5.14076700	H -2.64763800 -2.69849000 -3.54471300	
H -0.00451900 3.08860600 -5.41981500	H -2.10730700 -5.04067100 -3.01146200	
H -1.57291900 3.42338900 -1.44955500	H 1.21102300 -3.70564300 -0.64756500	
C -0.51425600 -0.86888000 -3.01984600	C -1.40154400 -0.43909500 -2.78782300	
H 0.34515500 -1.15744000 -2.41023500	H -1.90025000 0.11723100 -1.98879800	
H -1.40940000 -1.29021000 -2.55841400	H -0.50120200 0.12006900 -3.05559700	
H -0.39781600 -1.32322300 -4.00397000	H -2.06752900 -0.44475200 -3.65152400	
H -3.50536100 0.55017800 -1.58362300	H 2.56222400 -1.61981000 -2.20102200	
C -3.54181100 2.18888400 -0.21387900	C 3.02201400 -1.94158900 -0.12882300	
C -4.52544500 2.84110300 -0.95372500	C 4.20970200 -2.61484600 -0.41265100	
C -3.03365900 2.80049300 0.93646800	C 2.54016800 -1.93173400 1.18316800	
C -4.99656200 4.09107400 -0.55555200	C 4.91232100 -3.26766900 0.59629900	
H -4.91592800 2.37324000 -1.85047800	H 4.59339600 -2.61815800 -1.42720000	
C -3.49781900 4.04862400 1.33221200	C 3.24170400 -2.58427400 2.19193600	
H -2.25830100 2.30878600 1.51186900	H 1.62917900 -1.40382400 1.43550900	
C -4.48151100 4.69821500 0.58554600	C 4.42939900 -3.25329200 1.90219300	
H -5.76089500 4.59017600 -1.13942000	H 5.83476600 -3.78594500 0.36226600	
H -3.09215700 4.51700600 2.22138600	H 2.85861700 -2.56028900 3.20528200	
H -4.84293100 5.67206000 0.89400300	H 4.97438000 -3.76101900 2.68932000	
C -3.19463500 -0.25441600 0.42589400	C 2.62956800 0.34067600 -1.25412400	
C -3.01983400 0.84320700 -0.65023700	C 2.32778700 -1.17506100 -1.23467900	
N 2.49783300 -1.07237400 -1.13431900	N -3.07203000 1.03847200 0.10347000	
Si 3.22338000 0.02066600 -2.24856800	Si -4.50297400 0.29225900 -0.50027800	
Si 2.80792600 -2.77275600 -1.27151300	Si -3.00207300 2.76900000 0.17193400	
C 2.50827500 1.78150800 -2.09374500	C -4.25530600 -1.53450800 -0.97780700	
H 1.48989500 1.82556700 -1.70838600	H -3.33104300 -1.97352700 -0.60559900	
H 3.14410900 2.42629300 -1.47673000	H -5.08828900 -2.14219000 -0.60979600	
H 2.47844800 2.24671200 -3.08258600	H -4.24712900 -1.63469600 -2.06561100	
C 3.01309000 -0.49804200 -4.06147600	C -5.15859300 1.10666900 -2.08527500	
H 3.43265000 0.26257900 -4.72795700	H -6.03976200 0.56654600 -2.44806400	
H 3.53063900 -1.43809400 -4.26909900	H -5.44885800 2.15004200 -1.94308600	
H 1.96442900 -0.63590900 -4.32756600	H -4.40185500 1.07889600 -2.87529500	
C 5.09018300 0.27743000 -2.02280900	C -5.93676300 0.32952800 0.74391000	
H 5.66100900 -0.63227400 -2.21714300	H -6.26654500 1.35236700 0.93731800	
H 5.44557600 1.04801500 -2.71606500	H -6.79712400 -0.23374100 0.36650500	
H 5.33645000 0.60755600 -1.01039100	H -5.65143900 -0.10131700 1.70857700	

C 4.55567900 -3.18372200 -1.88784000	C -4.63208600 3.61681500 0.63814500	
H 4.67854100 -4.27142100 -1.91865300	H -4.47726900 4.70037400 0.67531700	
H 4.76640500 -2.80288500 -2.88999800	H -5.44193900 3.42627900 -0.06948200	
H 5.31637100 -2.78608100 -1.21048300	H -4.96843000 3.29601300 1.62800500	
C 2.65541900 -3.69553100 0.36597200	C -1.76230500 3.33182300 1.47324000	
H 1.75965800 -3.46154700 0.93983200	H -0.74645500 2.98570500 1.28559800	
H 2.65686600 -4.77273200 0.16549900	H -1.72115100 4.42538600 1.49216100	
H 3.51098500 -3.48019500 1.00997400	H -2.03955900 2.98543300 2.47204900	
C 1.63901300 -3.63228700 -2.50068100	C -2.45489500 3.50153600 -1.48782700	
H 1.70063400 -3.17899000 -3.49360100	H -3.20335000 3.32904900 -2.26559000	
H 1.90838800 -4.68910500 -2.59978500	H -2.27970500 4.58014100 -1.41805500	
H 0.59329300 -3.59126500 -2.18402000	H -1.52520300 3.03128300 -1.81483000	
H -3.48394600 0.21231200 1.36670700	H 1.80620500 1.51532400 2.12788400	
C -4.21606100 -1.30570200 0.07984300	C 1.16943300 3.06652000 -2.24373700	
C -5.39463300 -1.39174900 0.81881500	H 2.12678500 2.93434400 -2.75927300	
C -4.01864600 -2.18364500 -0.98889900	H 0.55064900 2.19300000 -2.45415300	
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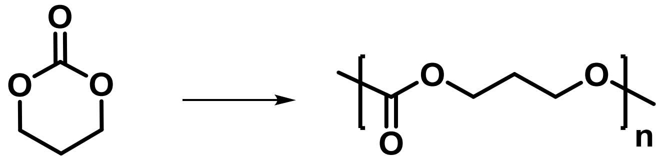
H -5.55367800 -0.71316000 1.64971000	C 0.45818500 0.00069400 -0.40912400	
C -4.98137600 -3.13272300 -1.30800800	C 4.00949500 0.77524200 -0.85219600	
H -3.10100400 -2.13744400 -1.56147200	C 4.89238600 1.18734200 -1.85189100	
C -6.15874300 -3.21213900 -0.56474600	C 4.45235700 0.75073200 0.47295500	
H -7.27675200 -2.39563100 1.08098800	C 6.19952000 1.55414400 -1.54255900	
H -4.81172300 -3.81567300 -2.13194400	H 4.55274200 1.22188700 -2.88197600	
H -6.90789200 -3.95490900 -0.81212200	C 5.75408400 1.12298000 0.78467400	
H -0.74013000 -2.79967900 -0.65863900	H 3.78254700 0.43919000 1.26019300	
C -2.46568300 -1.23787800 3.39390200	C 6.63278600 1.52219100 -0.22072100	
H -1.92014400 -0.30577500 3.23840900	H 6.87254900 1.87094200 -2.33055700	
H -3.53227900 -1.04718700 3.23530100	H 6.08260800 1.10169200 1.81689900	
H -2.33377600 -1.52805000 4.43654400	H 7.64698500 1.81290700 0.02684100	
N 2.47526900 1.44158400 1.21403900	H 2.44302200 0.69713800 -2.27220200	
Si 1.44749400 2.73145700 1.93467600	C -1.02803900 -2.84979800 1.76926900	
Si 3.96722200 0.92957300 2.13085300	O -1.96708400 -1.84477900 1.31637300	
C 0.48322100 3.49825900 0.52911700	C -3.13832800 -2.04423600 2.15102300	
H 1.13120600 3.90595000 -0.24986600	C -3.29065500 -3.56771400 2.24162400	
H -0.16679600 2.75932600 0.06904100	C -1.87929400 -4.11025600 1.89054900	
H -0.14965700 4.30875700 0.90180100	H -0.23683600 -2.91532900 1.03178200	
C 2.44967900 4.12217000 2.71795900	H -0.61549300 -2.52064300 2.72630900	
H 1.75366500 4.88249500 3.08771800	H -2.93589800 -1.58656300 3.12357900	
H 3.07285800 3.81198900 3.55685900	H -3.97110900 -1.53864100 1.67526000	
H 3.09381500 4.60385800 1.97717400	H -3.61428200 -3.86664900 3.23932200	
C 0.25687500 1.99691500 3.17626500	H -4.03105000 -3.92415100 1.52511900	
H 0.76444500 1.51762300 4.01322600	H -1.48588800 -4.78660300 2.65060500	
H -0.39293500 2.78688100 3.56769600	H -1.89816300 -4.63996200 0.93693600	
H -0.36058500 1.22782100 2.70944700		
C 3.63435600 0.90743300 3.97506300	E_{THF} = -2796.43755313	
H 4.54959200 0.57645100 4.47688400	Thermal correction = 0.736731	
H 3.35972400 1.87331700 4.40044200		

H 2.84946600 0.18201400 4.19449700		
C 4.57619600 -0.75814100 1.60872200		
H 4.50741500 -0.91117100 0.53290300		
H 5.62359800 -0.86268200 1.91012300		
H 3.99243500 -1.53745700 2.09853300		
C 5.29276300 2.20219800 1.70467500		
H 5.03729700 3.20551100 2.05060400		
H 6.24210900 1.92063100 2.17054400		
H 5.46599400 2.25072900 0.62532700		
H 2.81520600 1.81843100 0.32798800		
C -0.89038500 -0.09302600 -0.14572400		
E_{BENZ} = -3437.85221567		
Thermal correction= 0.851798		

Ring-Opening Polymerization (ROP) of cyclic monomers.

Polymerization experiments were performed in a glovebox at room temperature: in a 4 mL vial, the complex was weighed and dissolved in the desired solvent. Subsequently, the solution of the initiator in the same solvent was added to the solution of the complex and left to stir for 5 min. Finally, the monomer solution was added to the reaction mixture. The polymerization was stopped using wet dichloromethane, and then the solvent was removed under reduced pressure. The polymer was washed with methanol to remove the non-reacted monomer. Most of the samples were characterized by NMR spectroscopy, MALDI-ToF mass spectrometry and/or GPC analysis both before and after the washing with methanol.



Scheme S2: Ring-opening polymerization (ROP) of trimethylene carbonate

TABLE S3: ROP of TMC promoted by complex **1a** and **1b**, at 20°C.

Entry	Cat.	Cat/TMC/CoCat.	Solvent	Time	Conv[b] (%)	M_n th [c]	M_n exp [d]	Đ [d]	Ref
1	**1a**	1:30:0	DCM	5.5 h	78	2.4	29.5	2.01	4
2	**1a**	1:30:1	DCM	5.5 h	81	2.5	2.8	1.21	4
3	**1b**	1:100:0	THF	15 min	75	7.7	25.6	2.87	
4	**1b**	1:100:1	THF	10 min	95	9.7	9.9	1.76	Entry 10 Table 1

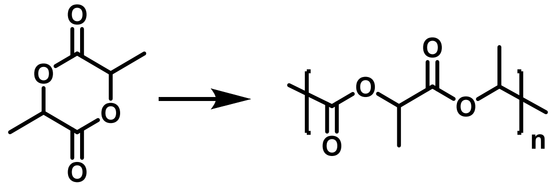
General conditions: [**Cat**] = 8 µmol, CoCat: BnOH (1 equiv). Volume of solvent = 0.8 mL. Temperature: 20 °C. [b] Conversion determined by ^{1}H NMR ($CDCl_3$) integrals of TMC (δ = 4.45 ppm) and PTMC (δ = 4.23 ppm). [c] M_n^{th} (g mol^{-1}) = $MM_{monomer}$ × ([TMC]$_0$/[**Cat**]$_0$) × monomer conversion. [d] Experimental M_n (in g mol^{-1}) and M_w/M_n (Đ) values were determined by GPC in THF using polystyrene standards and corrected of factors indicated in the literature for PTMC.

TABLE S4: ROP of TMC promoted by complex **1b** in different solvents, at 20°C.

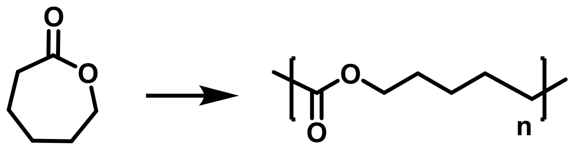
Entry	Solvent	Time	Conv[b] (%)	M_n th [c]	M_n exp [d]	Đ [d]
1	THF	1 min 5 min 10 min 20 min	45 70 89 98	10005	13873	1.71
2	Toluene	1 min 5 min 20 min	45 58 95	9699	11173	1.08
3	1,3 dioxolane	5 min 20 min 35 min 45 min	48 76 85 90	9188	11185	1.70
4	DCM	30 min 1 h	78 88	8984	5736	1.51

5	Me-THF	1 h 2 h 4 h 9 h	52 65 79 88	8984	5577	1.62

General conditions: [**1b**] = 8 µmol, 1 equivalent of BnOH, 100 eq of TMC. Volume of solvent = 0.8 mL ^{b} Conversion determined by ^{1}H NMR ($CDCl_3$) integrals of TMC (δ = 4.45 ppm) and PTMC (δ= 4.23 ppm).. ^{c} M_n^{th} (g mol^{-1}) = $MM_{monomer}$ × ([monomer]$_0$/[**1b**]$_0$) × monomer conversion. ^{d} Experimental M_n (in g mol^{-1}) and M_w/M_n (Đ) values were determined by GPC in THF using polystyrene standards and corrected of 0.73 for PTMC (as indicated in the literature[28] for PTMC with theoretical mass in the range 5000-10000).



Scheme S3: Ring-opening polymerization (ROP) of lactide.



Scheme S4: Ring-opening polymerization (ROP) of ε-caprolactone.

TABLE S5: ROP of cyclic esters and carbonates promoted by complexes **1a**, **1b, 2a** and **2b.**

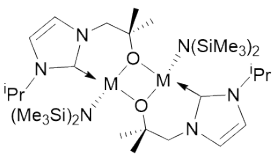
Entry	Complex	Monomer	Cocat	Time	Conv ^{b} (%)
1	**1a**	L-LA	^{i}PrOH	15 min 30 min 1 h 2,5 h	12 31 65 84
2	**1b**	L-LA	^{i}PrOH	30 min 2.5 h 4 h 6 h	2 23 40 55
3	**2a**	L-LA	^{i}PrOH	1 h 2 h 3 h 6 h	20 37 48 61
4	**2b**	L-LA	^{i}PrOH	1 h 2 h 3 h 6 h	10 16 25 49
5	**1a**	ε-CL	^{i}PrOH	30 min 2 h 4 h 6 h 7 h	8 32 50 66 80
6	**1b**	ε-CL	^{i}PrOH	1 min 5 min 10 min 15 min	77 84 95 99
7	**2a**	ε-CL	^{i}PrOH	1 h 2 h	0 0

				4 h 9 h	2 7
8	**2b**	ε-CL	^{i}PrOH	5 min 15 min 30 min	64 81 99
9	**1a**	TMC	BnOH	15 min 30 min 45 min 1 h	50 77 86 92
10	**1b**	TMC	BnOH	1 min 5 min 10 min	71 87 95
11	**2a**	TMC	BnOH	1 h 2 h 3 h 5.5 h	46 70 84 96
12	**2b**	TMC	BnOH	30 sec 1 min 5 min 15 min	43 58 83 96

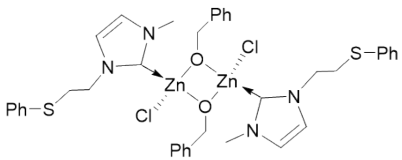
General conditions: [**cat**] = 15 µmol for cyclic esters, 8 µmol for cyclic carbonates, 1 equivalent of alcohol, 100 eq of monomer. [b] Conversion determined by ^{1}H NMR ($CDCl_3$) integrals of LLA (δ = 5.08 ppm) and PLLA (δ = 5.15 ppm) , εCL (δ = 4.25 ppm) and PCL (δ = 4.05 ppm), TMC (δ = 4.45 ppm) and PTMC (δ= 4.23 ppm).

TABLE S6: ROP of LA and TMC by zinc and magnesium complexes supported by NHC-type ligands reported in the literature.

Cat	Monomer (eq)	T (°C)	Cocat (eq)	Solvent	Time (h)	Conv. (%)	M_n^{th} (kDa)	M_n^{exp} (kDa)	Đ	Reference
[Mg(L)N”]$_2$	*rac*-LA (100)	25	-	THF	0.75	98	36.3	26.0	1.57	5
[Zn(L)N”]$_2$	*rac*-LA (100)	25	-	THF	16	78	32.4	27.5	1.30	5
5	*rac*-LA (100)	25	BnOH (1)	DCM	1.5	90	11.5	13.0	1.11	6
5	TMC (100)	25	-	DCM	1	89	9.1	10.1	1.14	7
1	*rac*-LA (100)	25	BnOH (1)	toluene	1	98	-	21.3	1.51	8
2a	*rac*-LA (120)	25	^{i}PrOH (2)	DCM	18	91	7.9	4.6	1.48	9
3	*rac*-LA (120)	25	-	DCM	48	99	17.3	4.0	1.88	9
3	*rac*-LA (120)	110	^{i}PrOH (2)	toluene	1	93	8.0	3.4	1.53	9



M = Mg cat = [Mg(L)N"]$_2$
M = Zn cat = [Zn(L)N"]$_2$



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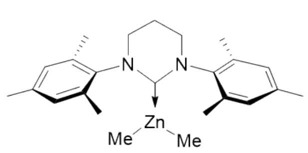

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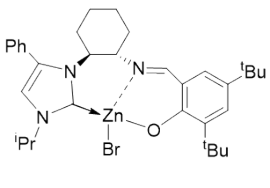
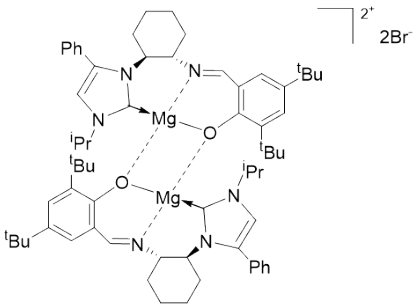


2a



3

Scheme S5 NHC-type zinc and magnesium complexes reported in the literature for the ROP of lactide and trimethylene carbonate

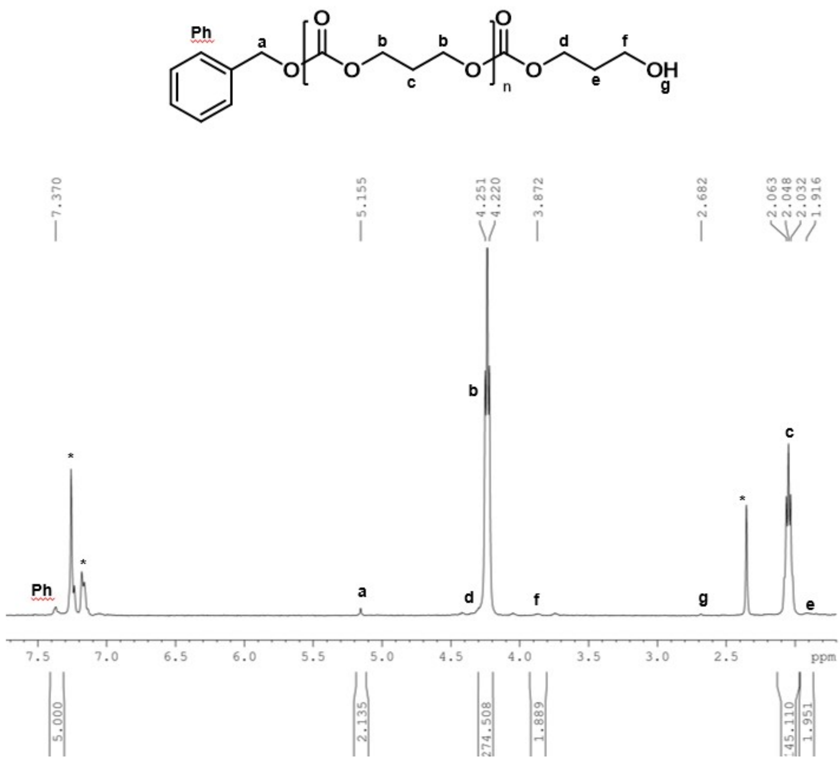


Figure S17: ^{1}H-NMR spectrum of polytrimethylene carbonate (solvent: $CDCl_3$, 400 MHz, 298 K). * = toluene.

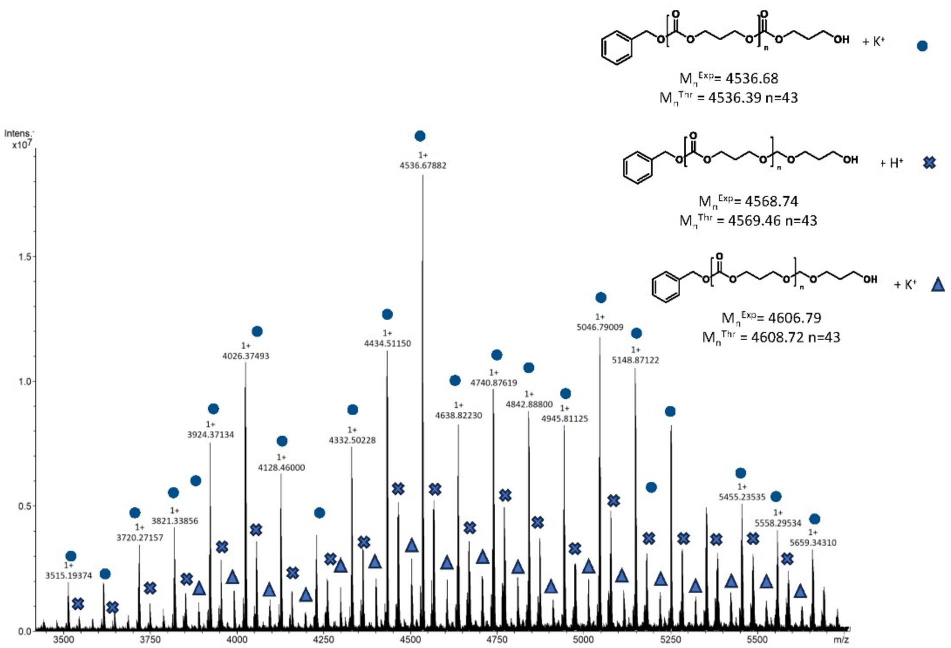


Figure S18: MALDI-TOF mass spectrum (matrix DCTB) of the isolated polymer from TMC polymerization. Polymerization conditions: $[TMC]_0/[BnOH]_0$ /[**1b**] = 50:1:1, temperature: 25 °C, solvent: THF.

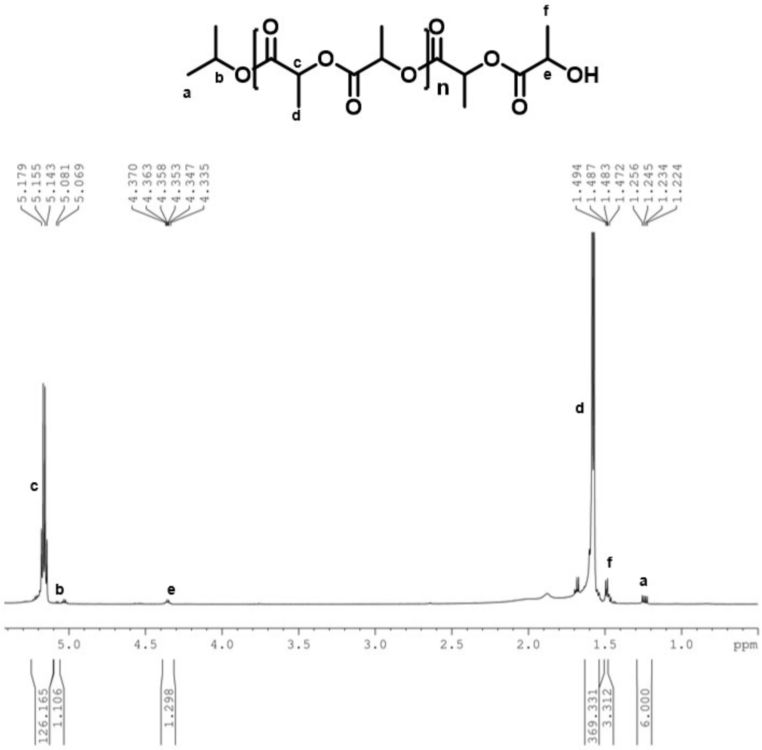


Figure S19: ^{1}H-NMR spectrum of polylactide (solvent: $CDCl_3$, 600 MHz, 298 K).

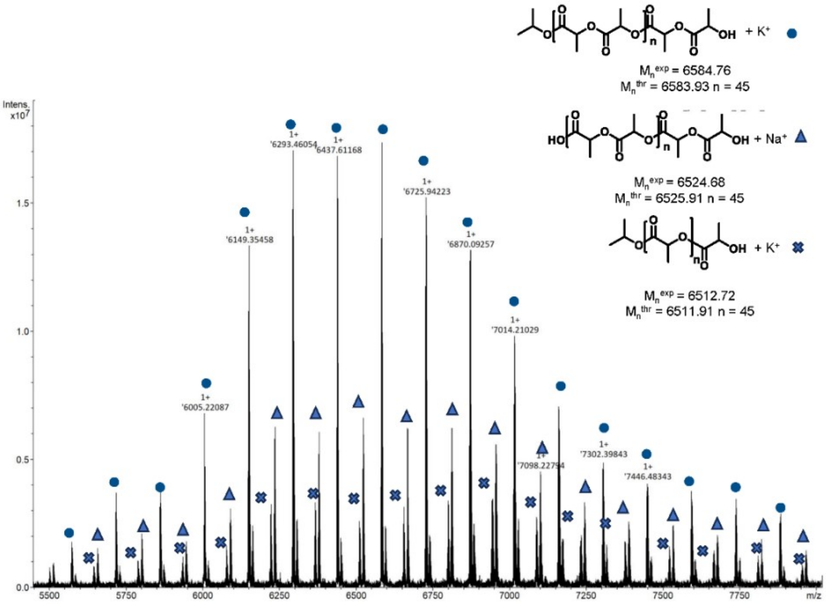


Figure S20: MALDI-TOF mass spectrum (matrix: DCTB) of the isolated polymer from L-LA polymerization (entry 2 in Table 1). Polymerization conditions: $[LLA]_0/[iPrOH]_0/[\mathbf{1b}] = 100:1:1$, temperature: 25 °C, solvent: THF.

Figure S21: ^{1}H-NMR spectrum of polycaprolactone (solvent: $CDCl_3$, 400 MHz, 298 K).

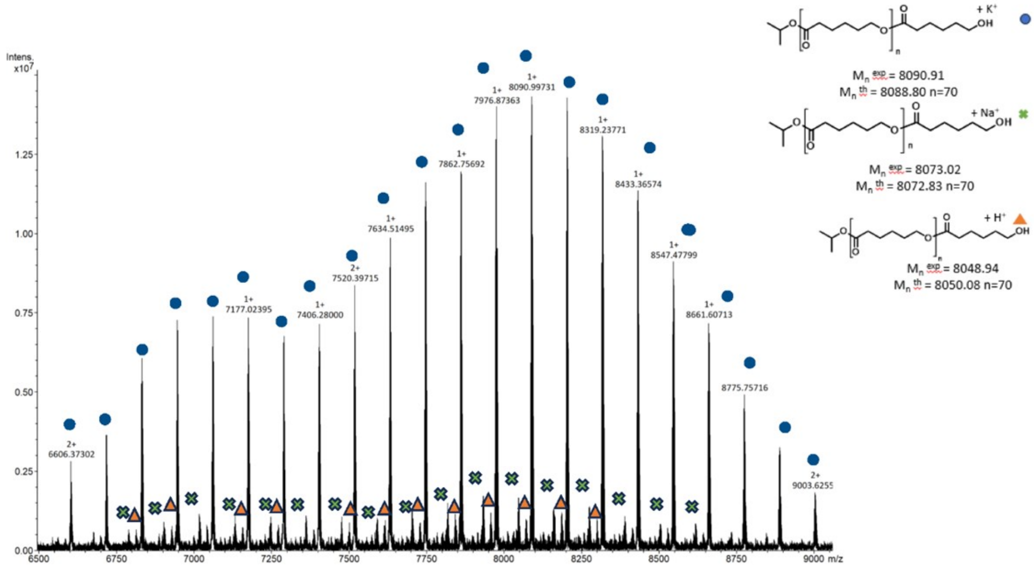
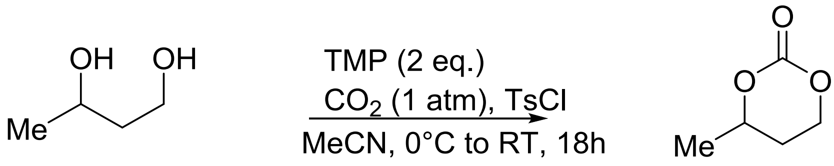


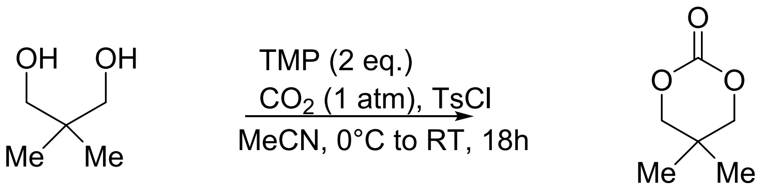
Figure S22: MALDI-TOF mass spectrum (matrix: DCTB) of the isolated polymer from ε-caprolactoene polymerization (entry 5 in Table 1). Polymerization conditions: $[\varepsilon\text{-CL}]_0/[\text{iPrOH}]_0/[\mathbf{1a}]$ = 100:1:1, temperature: 25 °C, solvent: THF.

Synthesis of alkyl substituted trimethylene carbonates

Following literature procedures[10], 1-methyl-trimethylene carbonate (1-Me-TMC) and dimethyl-trimethylene carbonate (DTC) were prepared from CO_2 and respectively from 1,3- butanediol and 2,2 dimethyl-1,3 propandiol.



Scheme S6: Synthesis of Methyl-Trimethylene Carbonate (Me-TMC).



Scheme S7: Synthesis of 2,2 Dimethyl-Trimethylene Carbonate (DTC).

A 0.40 mol L^{-1} solution of the opportune diol (1.70 mmol) and tosylchloride (TsCl 325 mg, 1.7 mmol, 1 equiv.) in anhydrous acetonitrile (4.3 mL) is prepared in a flask. The atmosphere of the flask is exchanged for CO_2 and the solution saturated with CO_2. Under a continuous feed of gas, 2,2,6,6 – Tetramethylpiperidine (TMP 575 μL, 3.40 mmol, 2 equiv.) is added dropwise at 0 °C, then the reaction is left to reach room temperature under stirring. After approximately 20 minutes, a white precipitate forms and CO_2 stopped being fed to the vessel. After 20 hours, the reaction mixture is diluted with non-anhydrous acetonitrile (10 mL) and the liquid phase separated by centrifugation (3 x 5 minutes at 3000 rpm). The solvent is then removed *in vacuo.* Purification by column chromatography (diameter of column = 1.5 cm, product: silica = 1: 19, 1:1 EtOAc:Hex) affords the cyclic carbonate product (Yield % $_{\text{Me-TMC}}$ = 70% , Yield % $_{\text{DTC}}$ = 75%).

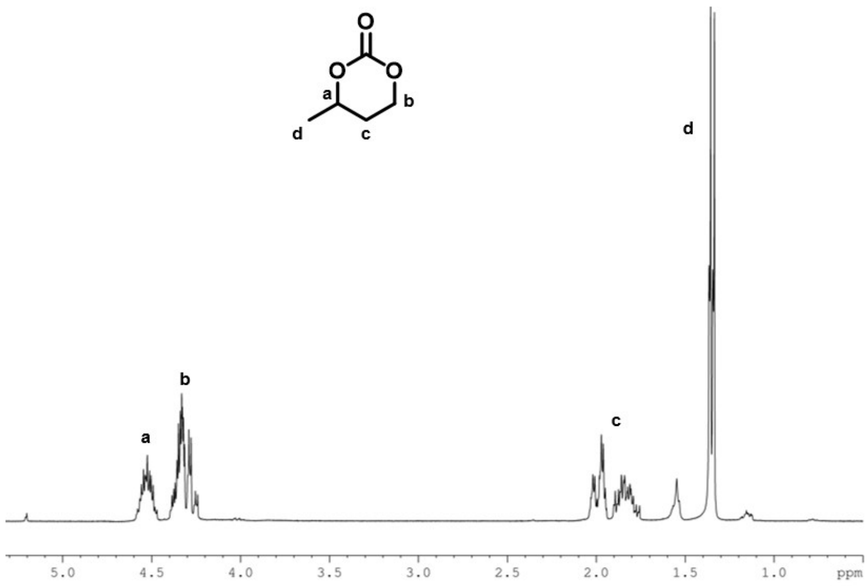


Figure S23: ^{1}H-NMR spectrum of the methyl-trimethylenecarbonate (solvent: $CDCl_3$, 400 MHz, 298 K).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.35 (d, 3H, CH_3), 1.78-1.88 (m, 1H, CH_2), 2.06-2.00 (m, 1H, CH_2), 4.46-4.21 (m, 2H, OCH_2), 4.68-4.44 (m, 1H, CH).

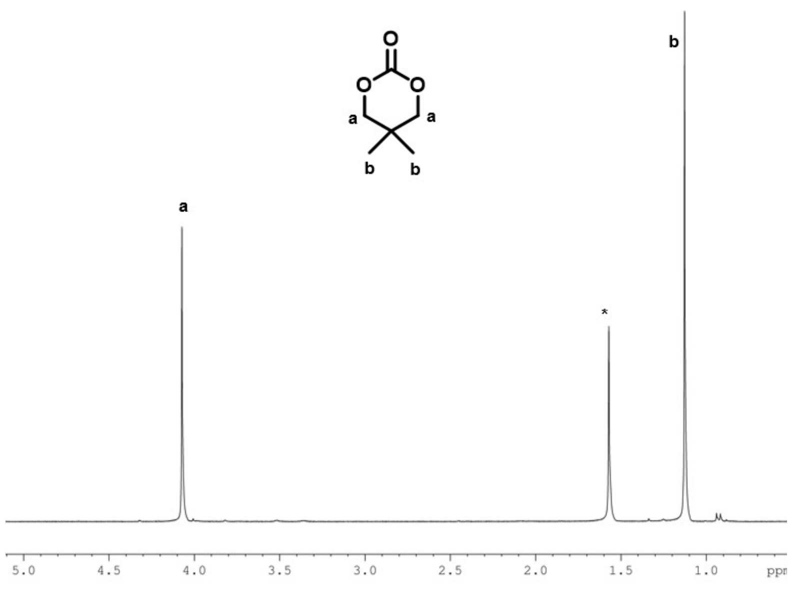
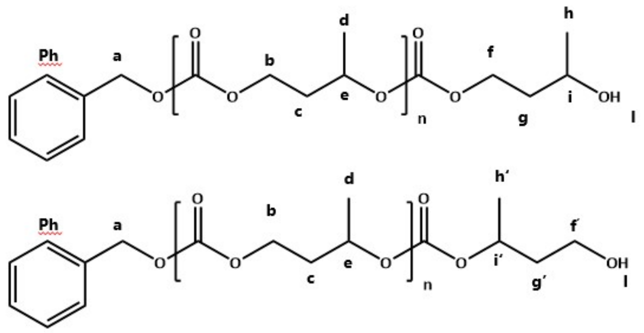


Figure S24: ^{1}H-NMR spectrum of the 2,2-dimethyl-trimethylenecarbonate (solvent: $CDCl_3$, 300 MHz, 298 K).

^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 1.09 (s, 6H, CH_3), 4.04 (s, 4H, CH_2).

Ring Opening Polymerization (ROP) of alkyl substituted trimethylene carbonates

The polymerization experiments in bulk were carried out in a glove box or in a thermostated bath, at desired temperature. In a typical procedure, the complex (8 x 10^{-6} mol) was weighed into a vessel. Subsequently, the initiator was added to the complex and left to stir for a few minutes and the monomer, weighed into a 4 mL vial, was added to the reaction mixture. Conversions have been determined by ^{1}H NMR spectroscopy, with the quantities of polymers and monomers determined by integrating the proper resonances (1-MeTMC: δ = 4.65 ppm; P(MeTMC): δ = 4.90 ppm; DTC: δ = 4.10 ppm and P(DTC): δ = 4.01 ppm). All the polymerization experiments were stopped using wet dichloromethane, after taking the vial out of the glovebox. The solvent was removed under reduced pressure and the polymer was washed with methanol, dried and characterized by NMR spectroscopy, MALDI mass spectrometry and/or GPC analysis.



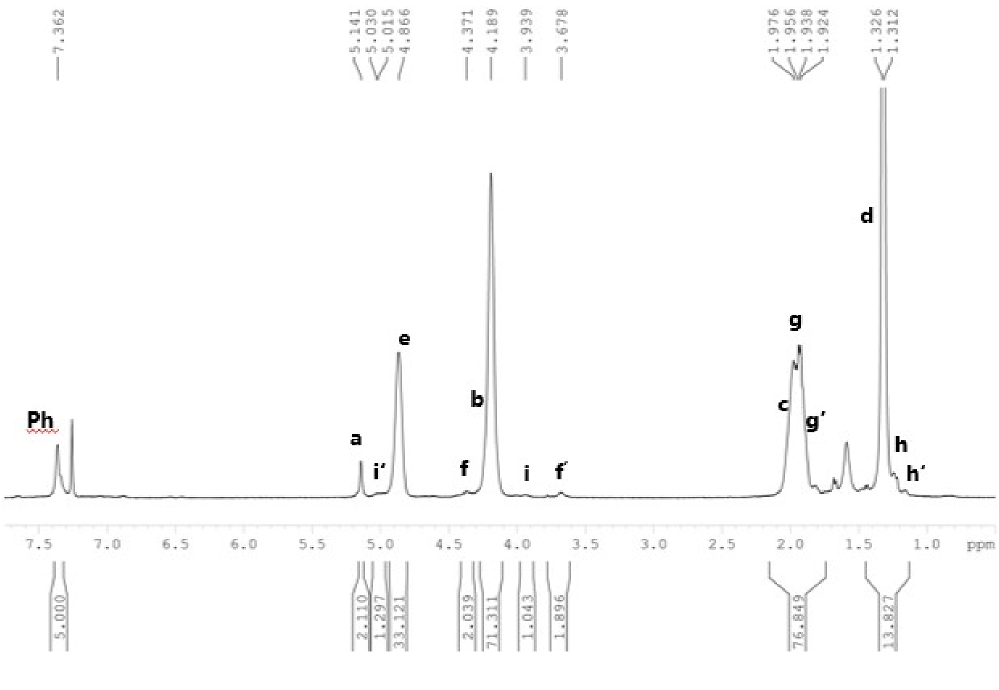


Figure S25: ^{1}H-NMR spectrum of poly-methyl-trimethylenecarbonate (Solvent: $CDCl_3$, 600 MHz, 298K).

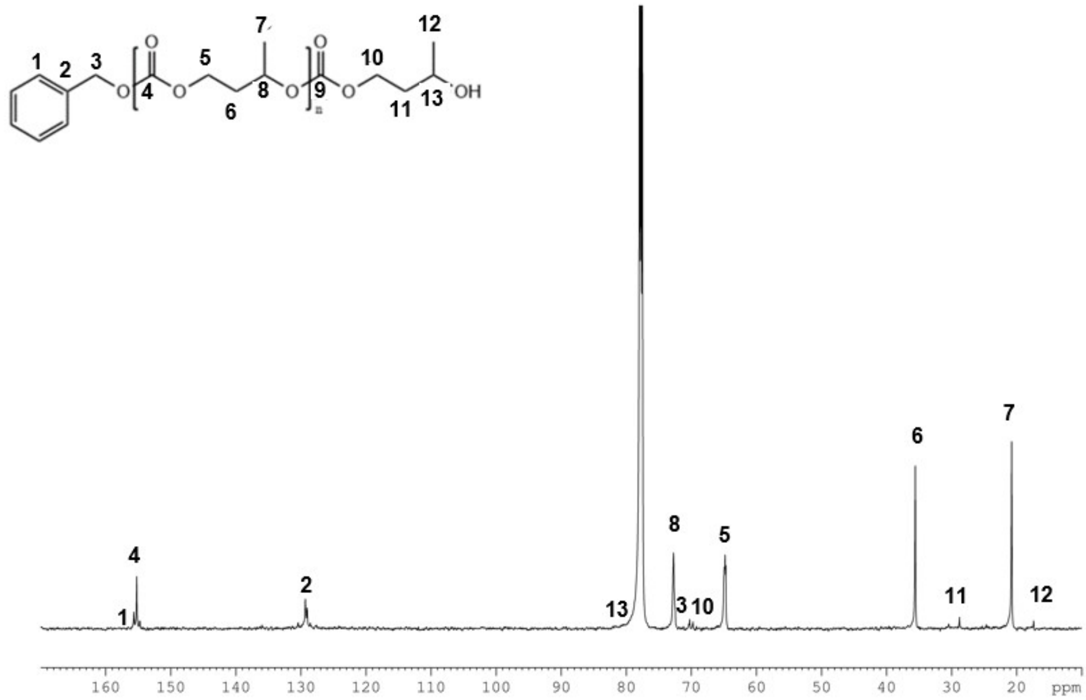


Figure S26: ^{13}C-NMR spectrum of poly-methyl-trimethylenecarbonate (Solvent: $CDCl_3$, 100.6 MHz, 298K).

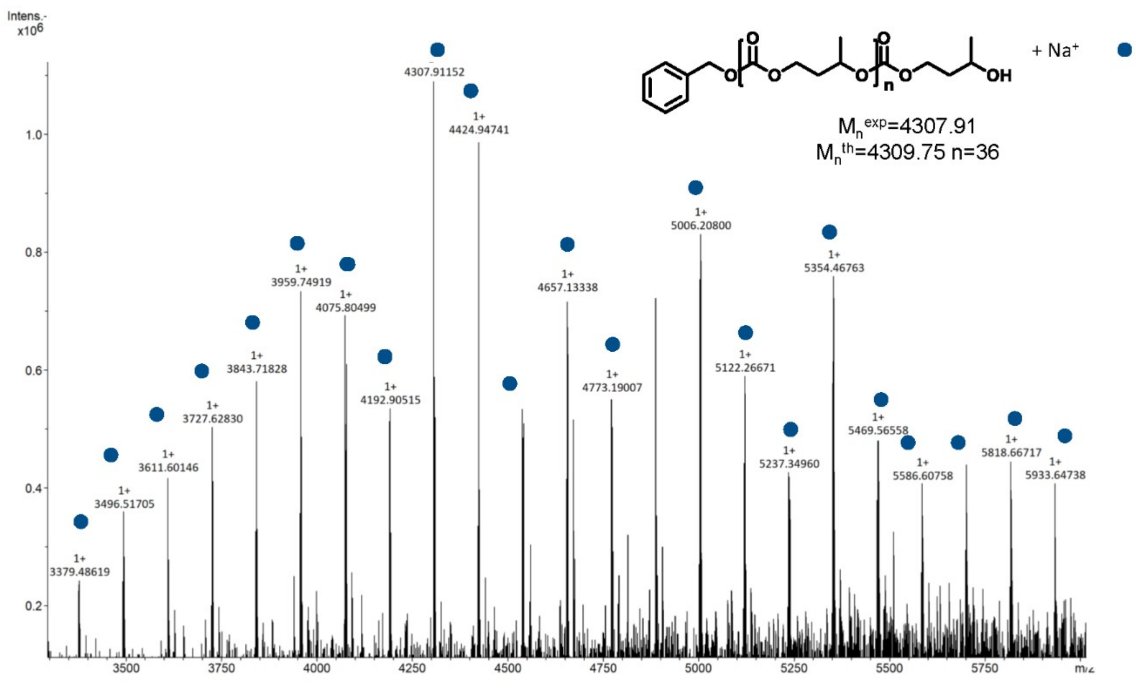


Figure S27: MALDI-TOF mass spectrum (matrix: DCTB) of the isolated polymer from 2,2-dimethyl-trimethylene carbonate polymerization (entry 16 in Table 1). Polymerization conditions: $[\text{Me-TMC}]_0/[\text{BnOH}]_0/[\mathbf{1b}] = 50{:}1{:}1$, temperature: 70 °C.

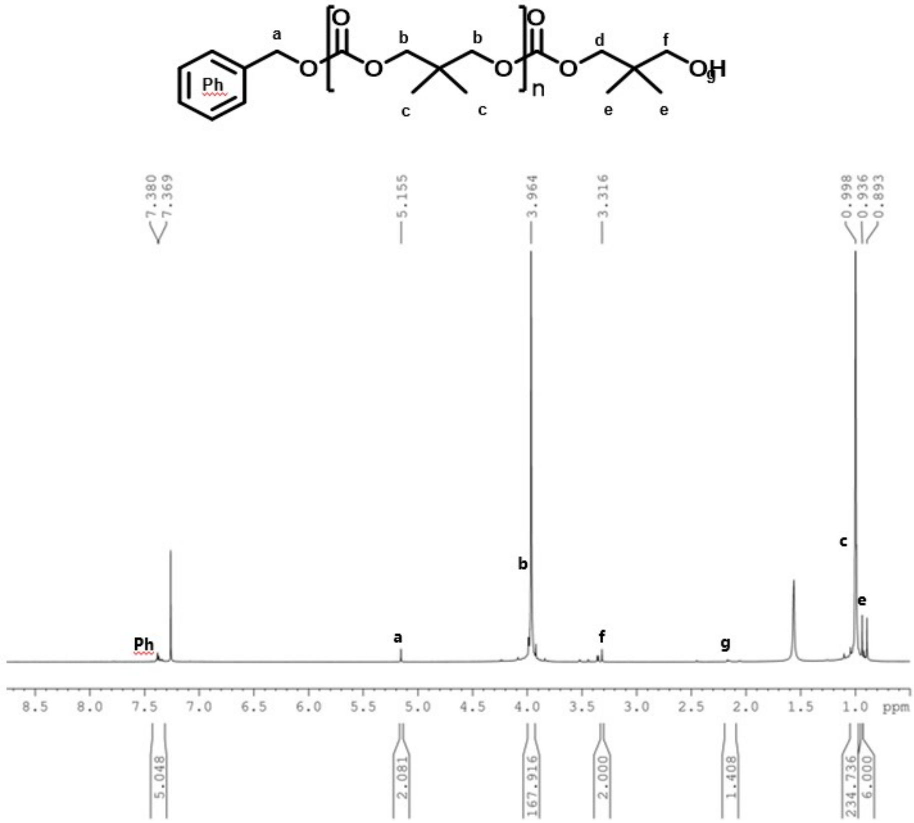


Figure S28 ^1^H-NMR spectrum of poly-2,2-dimethyl-trimethylenecarbonate (Solvent: $CDCl_3$, 600 MHz, 298 K).

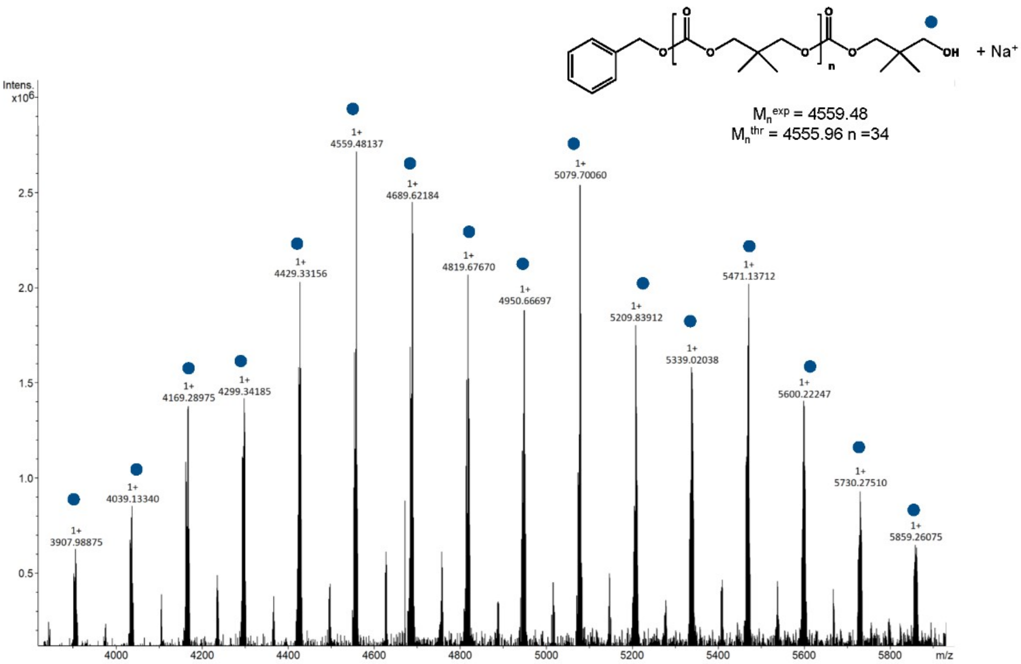
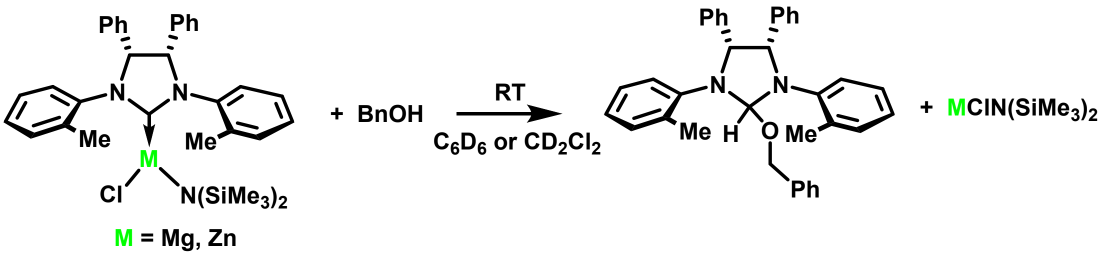


Figure S29: MALDI-TOF mass spectrum (matrix: DCTB) of the isolated polymer from 2,2-dimethyl-trimethylene carbonate polymerization (entry 13 in Table 1). Polymerization conditions: $[DTC]_0/[BnOH]_0$ /[**1a**] = 50:1:1, temperature: 160 °C.

Mechanistic Studies via NMR analysis

A deuterated solution (0.5 mL) of BnOH (1.63 mg, 1.51 x 10^{-5} mol) was added to a deuterated solution (0.3 mL) of complex (1.51 x 10^{-5} mol). Once the addition was complete, the reaction mixture was left to stir for a few minutes and transferred to the J-Young tube at room temperature. The formation of the corrisponding alcohol adduct was observed.



Scheme S8: Synthesis of the alcohol adduct L1HOBn from complex **1a** and **1b.**

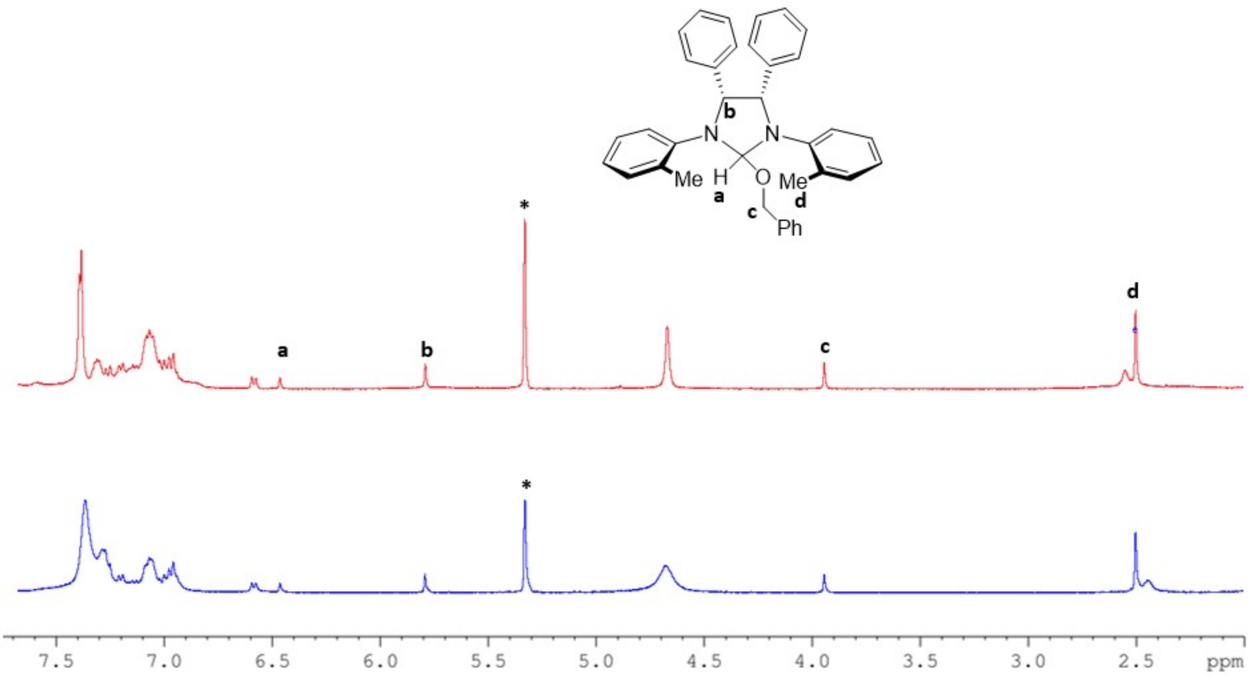


Figure S30: ^{1}H NMR spectra of the products obtained from the reaction of complex **1a** (up spectrum) and complex **1b** (down spectrum) with one equivalent of BnOH in CD_2Cl_2 (400 MHz, 20 °C).* = benzyl alcohol.

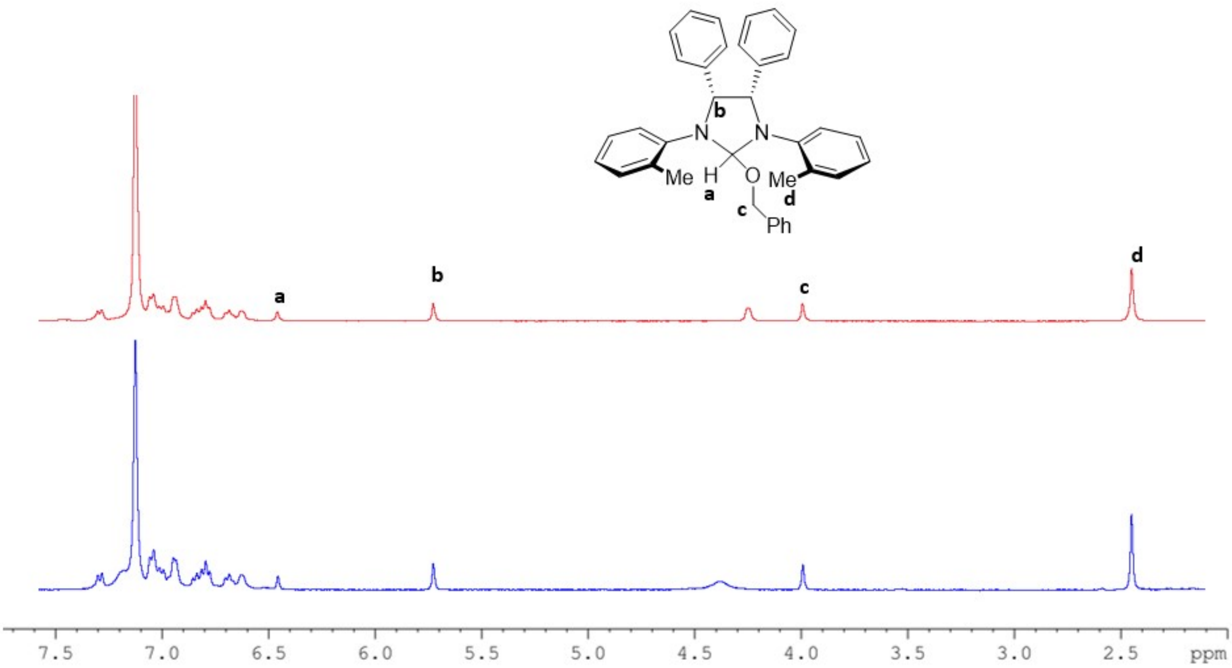


Figure S31: ^{1}H NMR spectra of the products obtained from the reaction of complex **1a** (up spectrum) and complex **1b** (down spectrum) with one equivalent of BnOH in C_6D_6 (400 MHz, 20 °C).

The experiment was carried out in a glove box. A THF d8 solution of BnOH (1.63 mg, 1.51 x 10^{-5} mol) was added to a THF d8 solution of complex **1b** (1.51 x 10^{-5} mol). The formation of the corrisponding alcohol adduct was observed (b). 15 eq of TMC were added to the reaction mixture and the formation of new alcohol adduct was observed (c). After 15 minutes, the addition of BnOH solution led to the formation of the benzyl alcohol adduct (d): subsequently, with the addition of 15 eq of TMC, the formation of alcohol adduct bearing the polymeric chain was observed again (e).

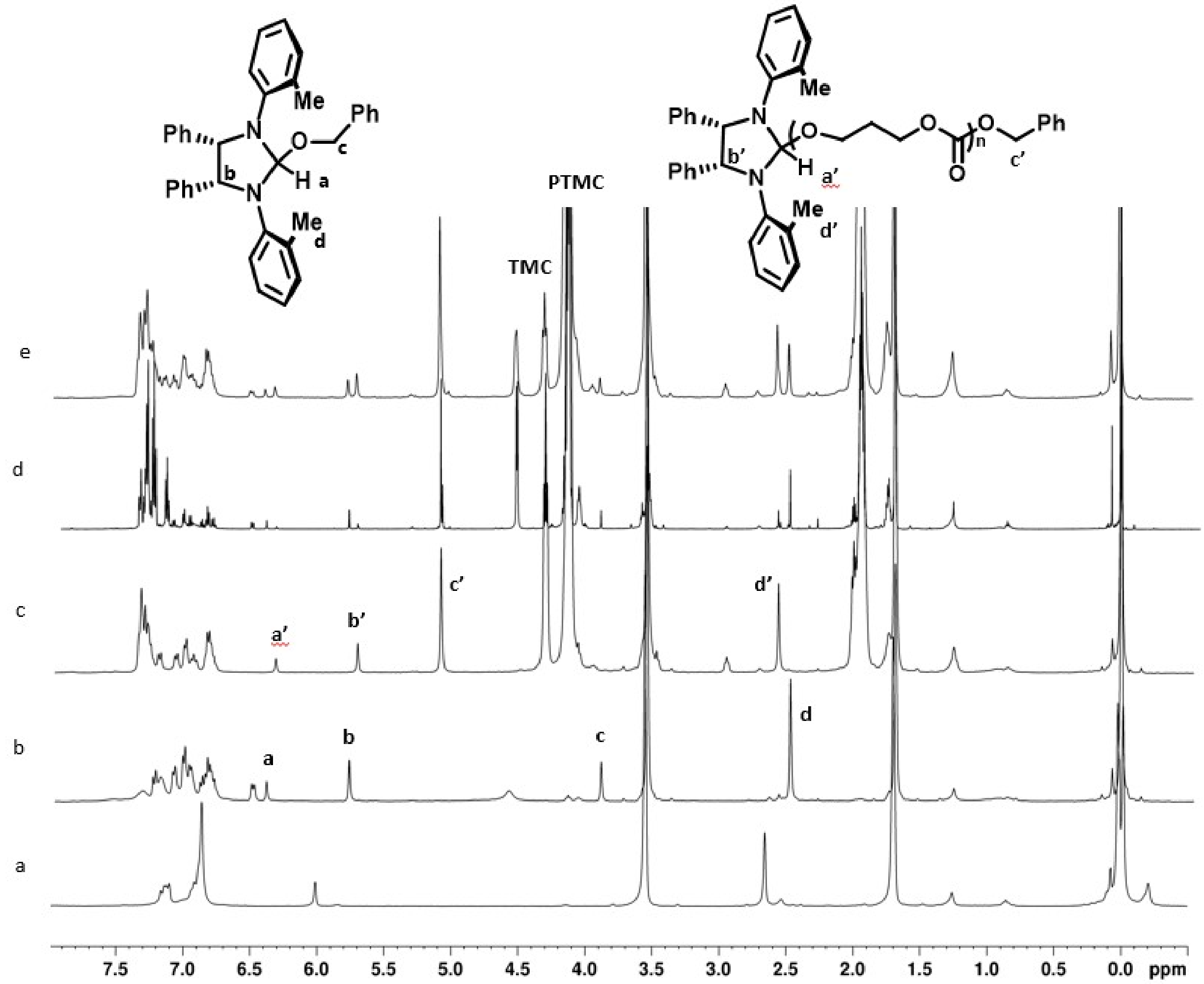


Figure S32: ^{1}H NMR spectra of the sequential addition of one equivalent of BnOH and 15 eq of TMC to complex **1b** in THF-d8 (400 MHz, 20 °C).

Table S7. ROP of LLA and TMC promoted by complex 1a and 1b, alcohol adduct ad its combination with Zn and Mg precursors in THF, 20°C.

Entry	Catalytic system	Monomer	Time	Conv ^{b} (%)	$M_n^{th\ c}$ (KDa)	$M_n^{exp\ d}$ (KDa)	Đ ^{d}	k_{obs} (h^{-1})
1	**L1**HO^{i}Pr	TMC	20 min	-				
2	**1a** + ^{i}PrOH	TMC	30 min 2.5 h 5 h	16 58 85	8.7	7.5	1.28	0.34
3	**L1**HO^{i}Pr + 0.5 $ZnCl_2$ + 0.5 $Zn(NR_2)_2$	TMC	15 min 30 min 1 h 2 h 2.5 h	12 37 57 79 85	8.7	8.8	1.45	0.79
4	**L1**HO^{i}Pr + $Zn(NR_2)_2$	TMC	15 min	78	8.0	19.2	2.34	
5	**1b** + ^{i}PrOH	TMC	1 min 5 min 10 min 15 min	34 75 83 92	9.4	12.6	2.2	13.0
6	**L1**HO^{i}Pr + 0.5 $MgCl_2$ + 0.5 $Mg(NR_2)_2$	TMC	5 min 10 min 15 min 20 min	45 60 85 90	9.2	7.4	2.1	7.1
7	**L1**HO^{i}Pr + $Mg(NR_2)_2$	TMC	15 min	94	9.6	33.3	1.85	
8	$Mg(NR_2)_2$	TMC	15 min	99	10.1	24.4	2.27	
9	**L1**HO^{i}Pr	LLA	20 min	-				
10 Table 1	**1a** + ^{i}PrOH	LLA	15 min 30 min 1 h 2.5 h	12 31 65 84	12.1	8.5	1.27	0.80
11	**L1**HO^{i}Pr + 0.5 $ZnCl_2$ + 0.5 $Zn(NR_2)_2$	LLA	15 min 30 min 45 min 1 h	39 58 70 80	11.5			1.6
12	**L1**HO^{i}Pr + $Zn(NR_2)_2$	LLA	15 min	39	5.6	14.7	1.83	
13 Table 1	**1b** + ^{i}PrOH	LLA	30 min 2.5 h 4 h 6 h	3 23 40 55	7.9	6.0	1.22	0.14
14	**L1**HO^{i}Pr + 0.5 $MgCl_2$ + 0.5 $Mg(NR_2)_2$	LLA	30 min 2 h 4 h 6 h 8 h	6 20 37 54 75	10.8	8.1	1.35	0.13
15	**L1**HO^{i}Pr + $Mg(NR_2)_2$	LLA	15 min	93	13.4	16.4	3.04	
16	$Mg(NR_2)_2$	LLA	15 min	77	11.1	24.4	2.27	

General conditions: [**cat**] = 15 µmol for LLA, 8 µmol for TMC, 100 eq of monomer. ^{b} Conversion determined by ^{1}H NMR ($CDCl_3$) integrals of LLA (δ = 5.08 ppm) and PLLA (δ = 5.15 ppm) , TMC (δ = 4.45 ppm) and PTMC (δ= 4.23 ppm). ^{c} M_n^{th} (g mol^{-1}) = MMmonomer × ([monomer]$_0$/[cat]$_0$) × monomer conversion. ^{d} Experimental M_n (in g mol^{-1}) and M_w/M_n (Đ) values were determined by GPC in THF using polystyrene standards and corrected of 0.73 for PTMC (as indicated in the literature[28] for PTMC with theoretical mass in the range 5000-10000) and of 0.56 for PLLA.

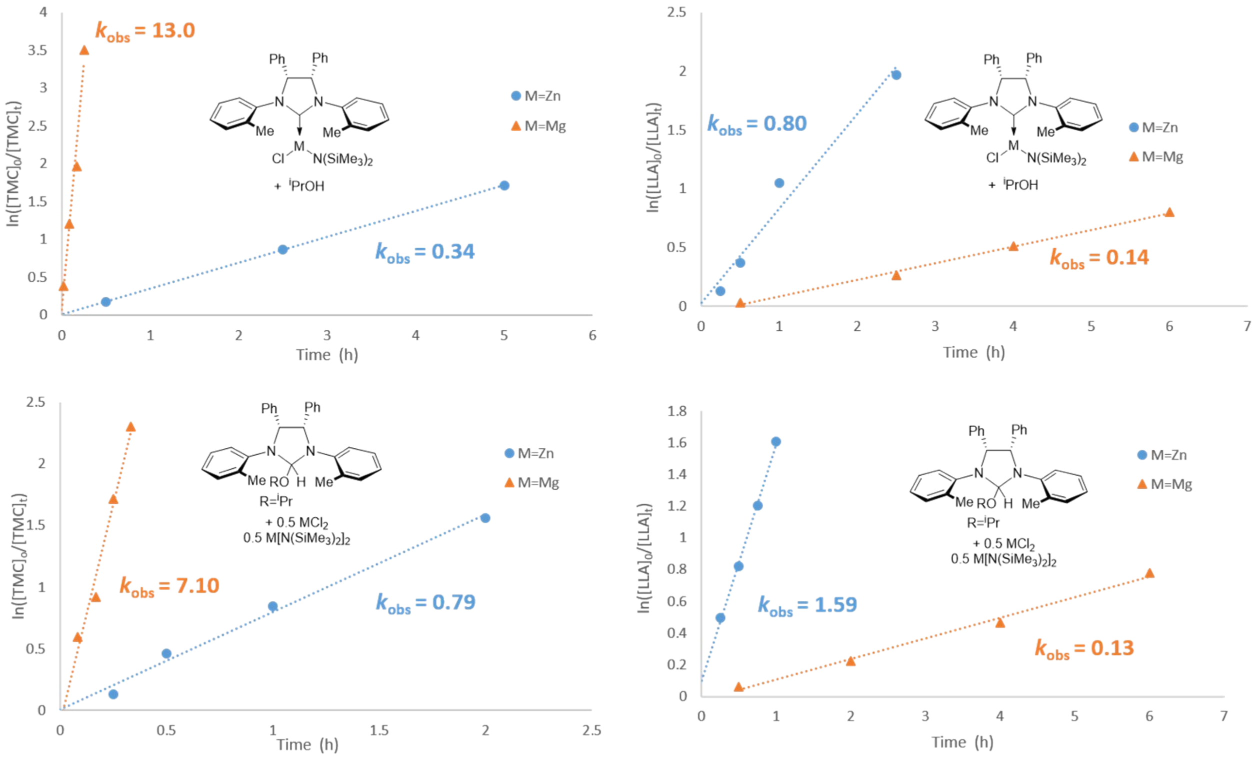
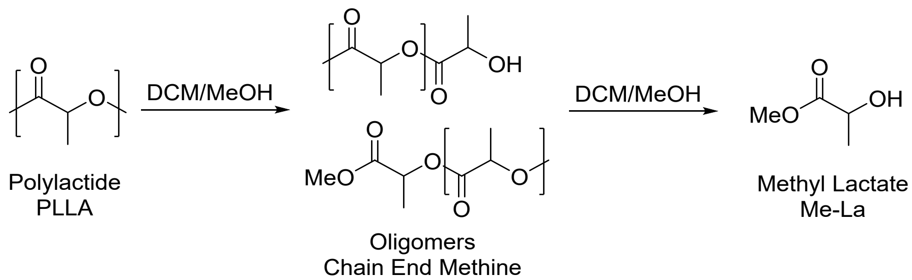


Figure S33. First-order kinetic plots for the consumption of TMC (left) and L-LA (right) by the catalytic systems depicted in the insets.

Chemical recycling of PLLA

Methanolysis reaction performed in DCM solution

Methanolysis experiments were performed in a glovebox at room temperature: in a 4 mL vial, the complex (14.0×10^{-6} mol) was weighed and dissolved in 0.4 mL of DCM. The polymer (200 mg, 2.8×10^{-3} mol) was weighted into another vial and then dissolved in 1 mL of DCM. The solution of the complex was added to the solution of the polymer and left to stir for 5 min. After this time, methanol (56.3 µL, 1.4 mmol) was added and the reaction mixture was stirred at room temperature for 24 h. The reaction was stopped using wet dichloromethane, and an aliquot of the reaction mixture was dissolved in wet CD_2Cl_2 and analyzed by ^1H NMR spectroscopy.



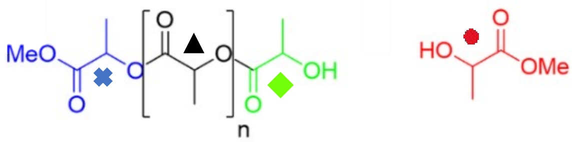
Scheme S9: Methanolysis reaction of PLLA in DCM solution.

The conversion of internal methine units (X_{Int}), Selectivity ($S_{Me\text{-}La}$) and Yield ($Y_{Me\text{-}La}$) of methyl lactate were calculated by the following equations[11]:

Conversion $X_{int} = \frac{Int_0 - Int}{Int_0}$

Selectivity $S_{MeLa} = \frac{MeLa}{Int_0 - Int}$

Yield $Y_{MeLa} = S_{MeLa} X_{Int}$



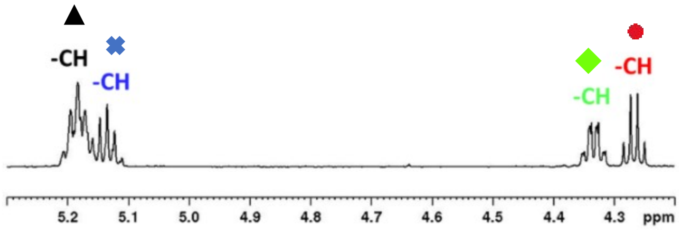
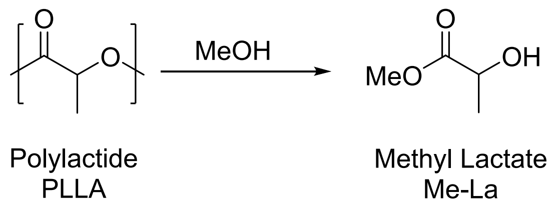


Figure 34: [1]H NMR spectrum of PLA methanolysis with assignment of internal (black triangle), chain end (blue cross and green rumble), and methyl lactate (red circle) alkyl protons. (Solvent = CD_2Cl_2, 400 MHz, 298 K).

Methanolysis reaction performed in solvent-free conditions

Methanolysis experiments were performed in a glovebox at room temperature: in a 4 mL vial, the complex (10.0×10^{-6} mol) was weighed then the polymer and 1 mL of methanol were added.
The reaction mixture was left to stir for the desired time then stopped using wet dichloromethane. An aliquot of the reaction mixture was dissolved in wet CD_2Cl_2 and analyzed by ^1H NMR spectroscopy.



Scheme S10: Methanolysis reaction of PLLA in solvent-free conditions.

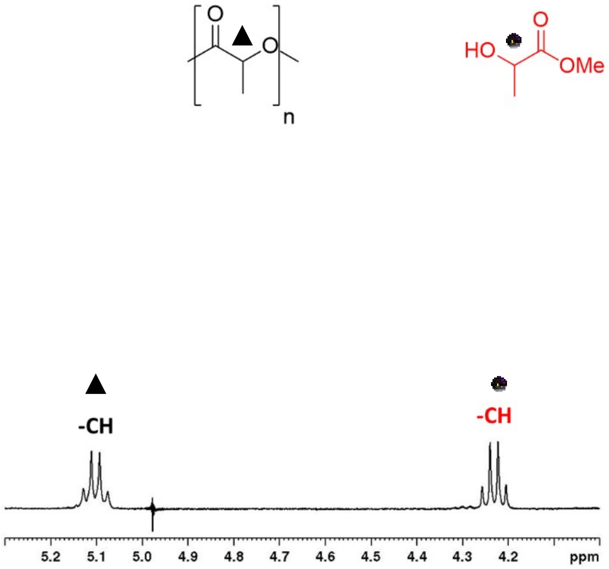
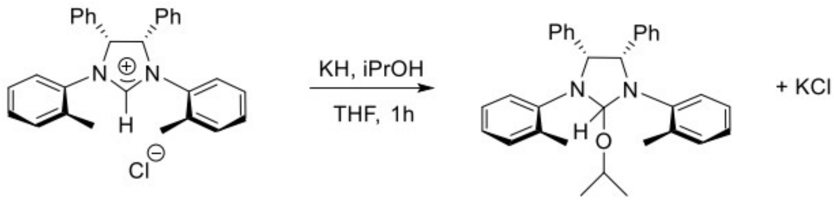


Figure 35: ^{1}H NMR spectrum of PLA methanolysis with assignment of internal (black triangle), and methyl lactate (red circle) alkyl protons. (Solvent = CD_2Cl_2, 400 MHz, 298 K).

Synthesis of the alcoholic adduct L_1HO^iPr

The adduct (L_1HOiPr) was prepared from the corresponding imidazolium salt by deprotonation with potassium hydride and subsequent reaction with isopropanol. The product was characterized by NMR analysis. The ^{1}H-NMR spectrum of L_1HO^iPr showed a pattern in agreement with the formation of the desired product and attributable to the presence of a symmetrical species in solution.



Scheme S11: Synthesis of the alcohol adduct L_1HO^iPr.

The reaction was carried out in the glove-box in a nitrogen atmosphere. A THF suspension (1.25 mL) of KH (0.0238 g, 5.93 x 10^{-4} mol) was added to a THF suspension (4.4 mL) of the L1HCl salt (0.200 g, 4.55 x 10^{-4} mol). Once the addition was complete, the reaction mixture was left to stir for 5 minutes at room temperature. Subsequently, a solution of ^{i}PrOH (0.0251 g, 4.2 x 10^{-4} mol) in THF (1.0 mL) was added and the reaction mixture was left under stirring for 1 hour. Then, the reaction mixture was filtered to remove residual salts and the solvent removed under vacuum. The product was obtained as a white powdery solid.

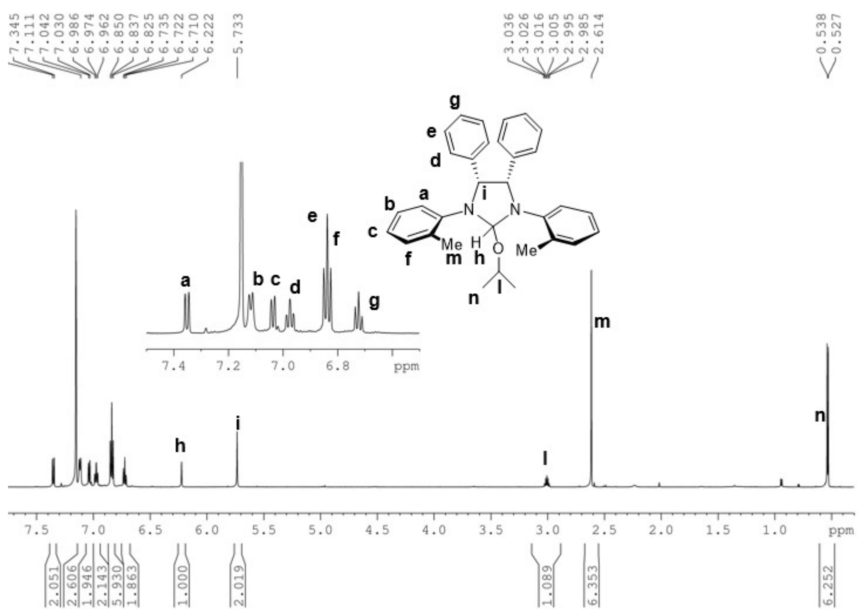


Figure 36: ^{1}H NMR spectra of the alcohol adduct L_1HO^iPr. (Solvent = C_6D_6, 400 MHz, 298 K).

^1H NMR (400 MHz, C_6D_6, 298 K): δ 0.53 (d, 6H, CH_3), 2.61 (s, 6H, CH_3), 3.00 (m, H, CH), 5.73 (s, 2H, CH), 6.22 (s, H, CH), 6.72 (t, 2H, Ar-H), 6.83 (t, 6H, Ar-H), 6.97 (t, 2H, Ar-H), 7.02 (t, 2H, Ar-H), 7.13 (t, 2H, Ar-H), 7.35 (d, 2H, Ar-H).

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