Electronic Supporting Information

DFT calculation as ligand toolbox for the synthesis of active initiators for ROP of cyclic esters

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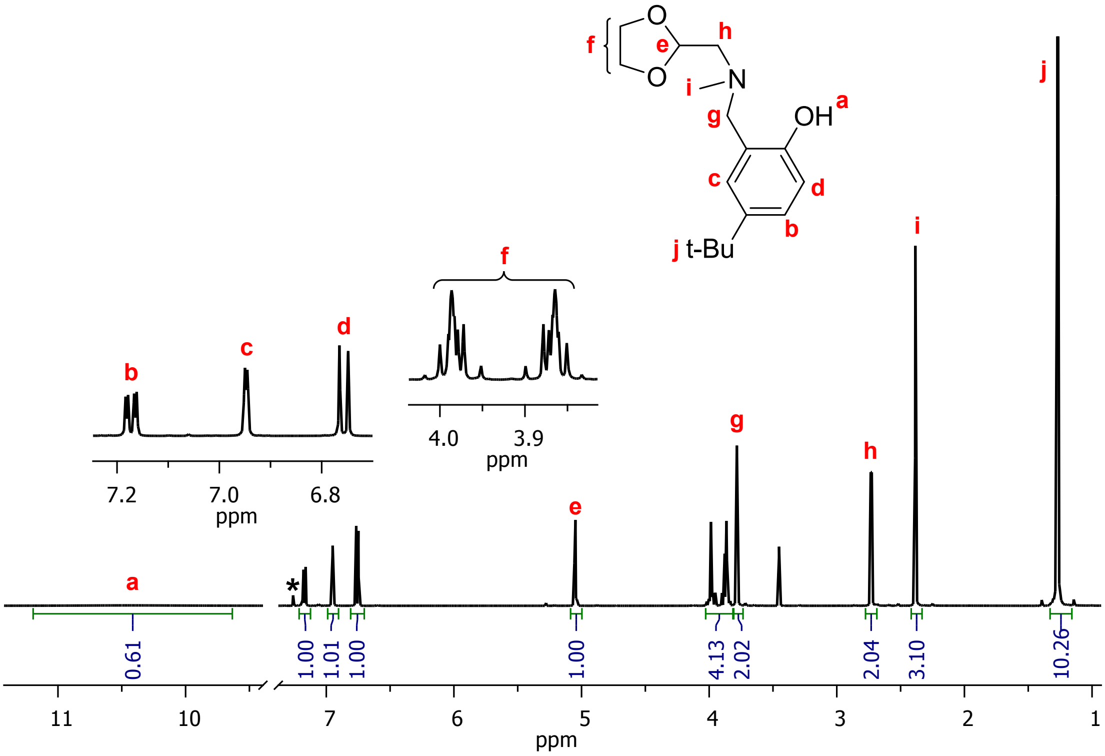

Figure S1. ^{1}H NMR of L^{ox}-H in $CDCl_3$.

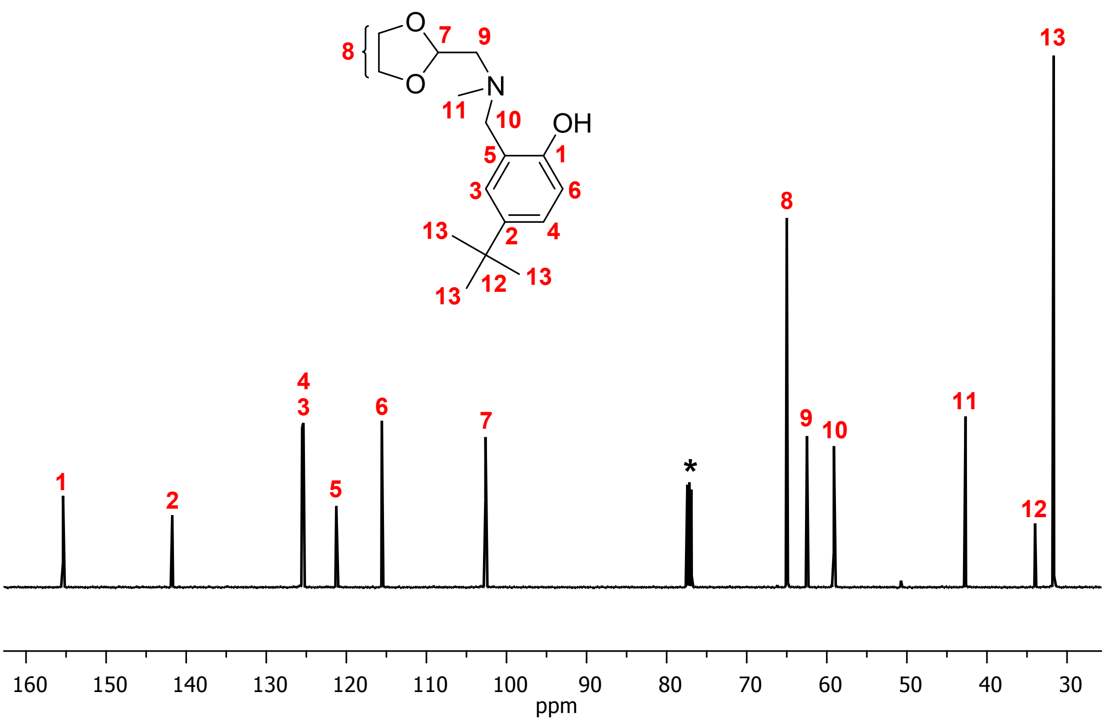

Figure S2. ^{13}C NMR of L^{ox}-H in $CDCl_3$.

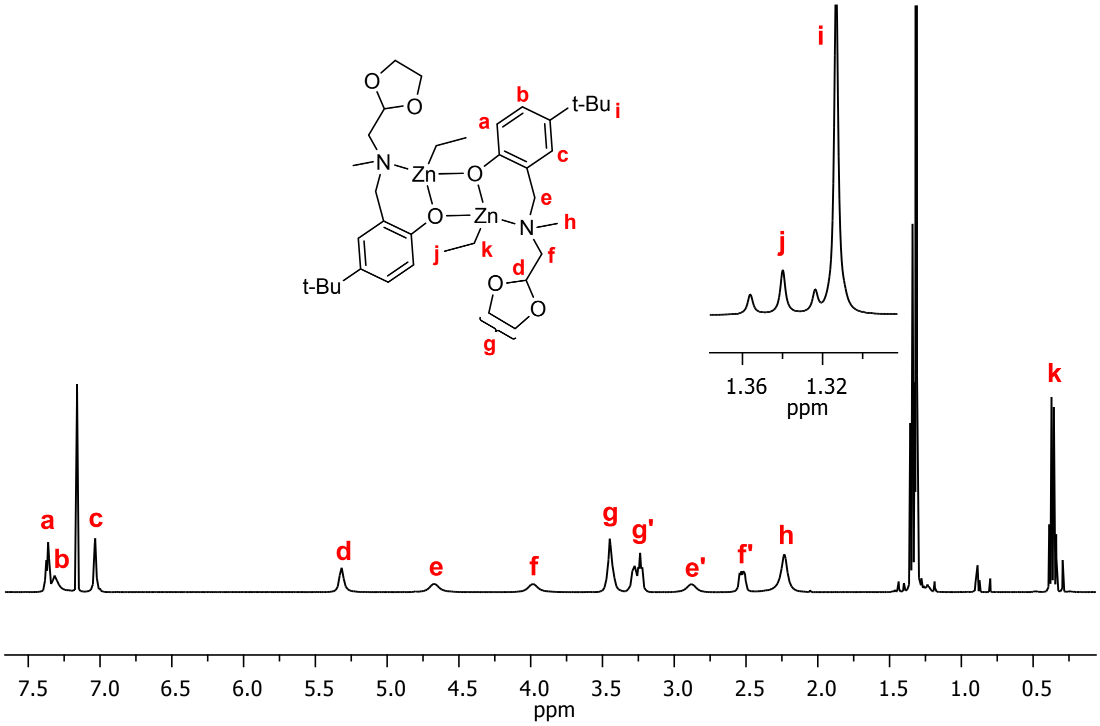

Figure S3. ^{1}H NMR of $(L^{ox}ZnEt)_2$ in benzene-d_6.

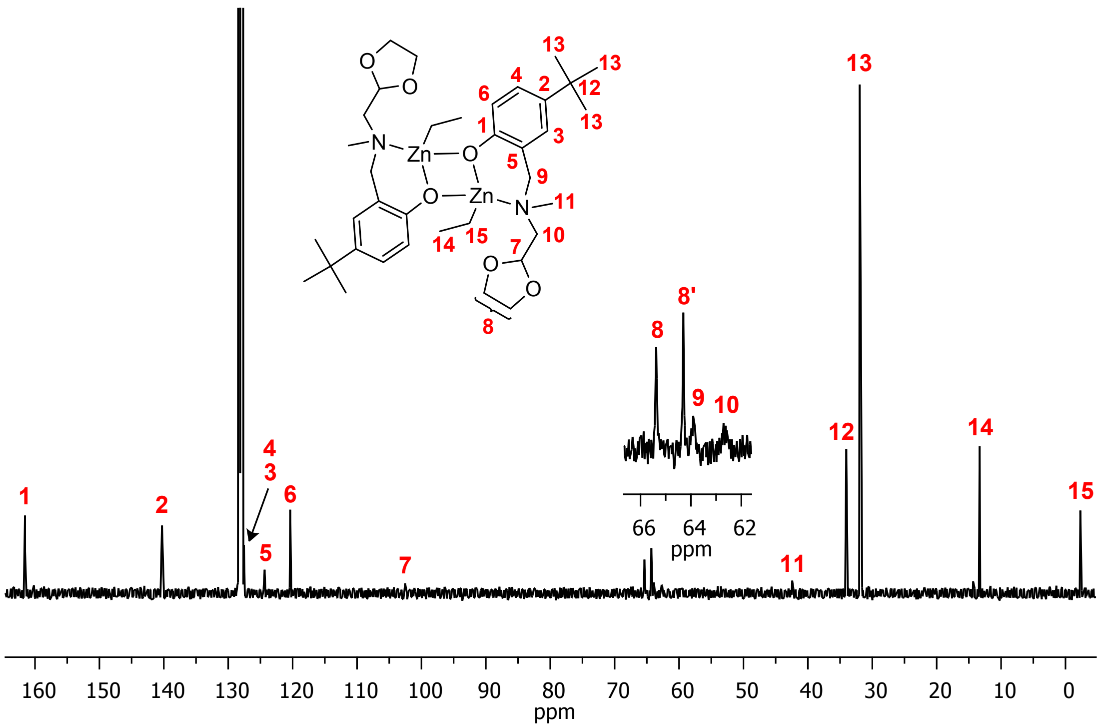

Figure S4. ^{13}C NMR of $(L^{ox}ZnEt)_2$ in benzene-d_6.

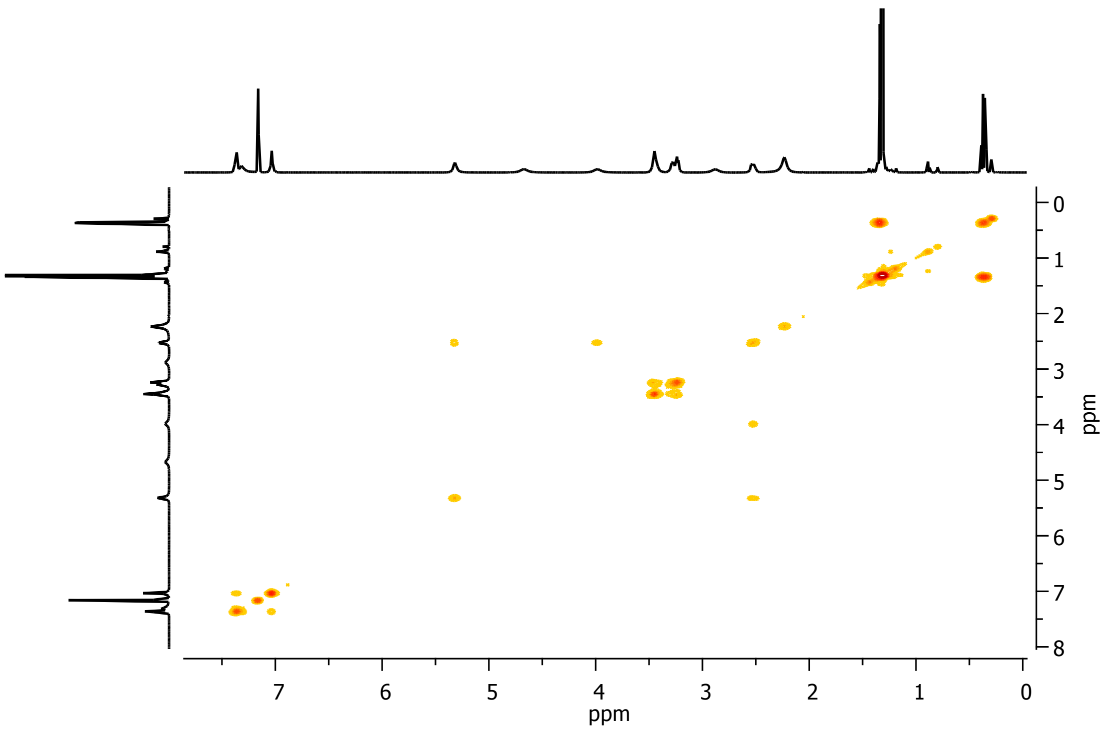

Figure S5. ^{1}H COSY of $(L^{ox}ZnEt)_2$ in benzene-d_6.

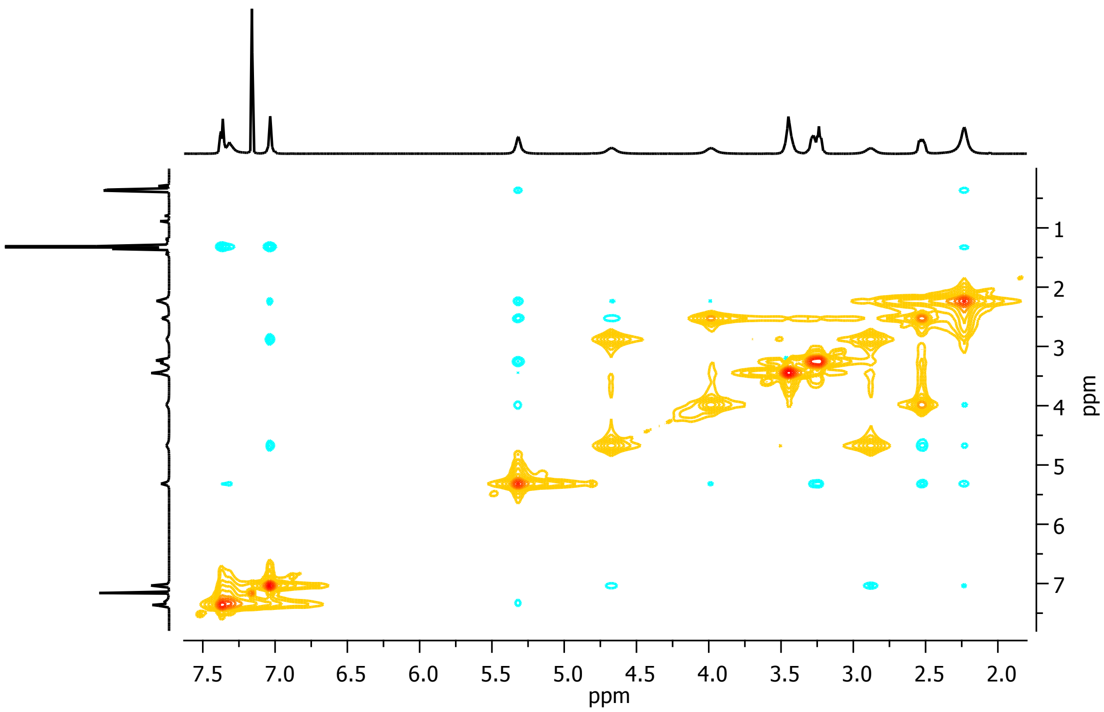

Figure S6. ^{1}H NOESY of $(L^{ox}ZnEt)_2$ in benzene-d_6.

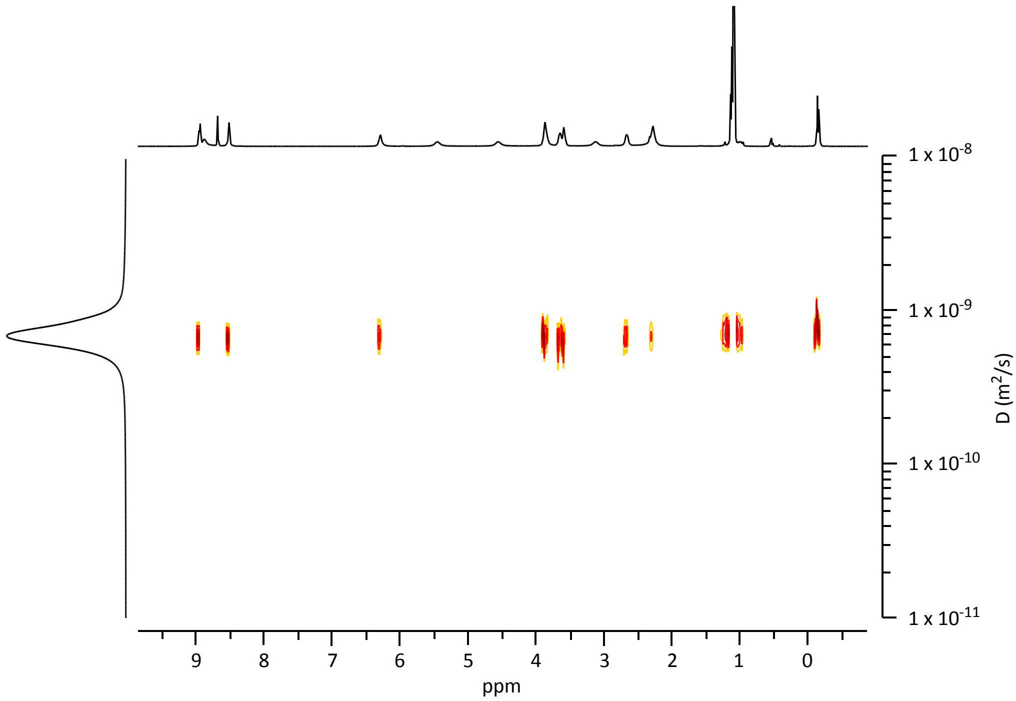

Figure S7. ^{1}H DOSY of $(L^{ox}ZnEt)_2$ in benzene-d_6.

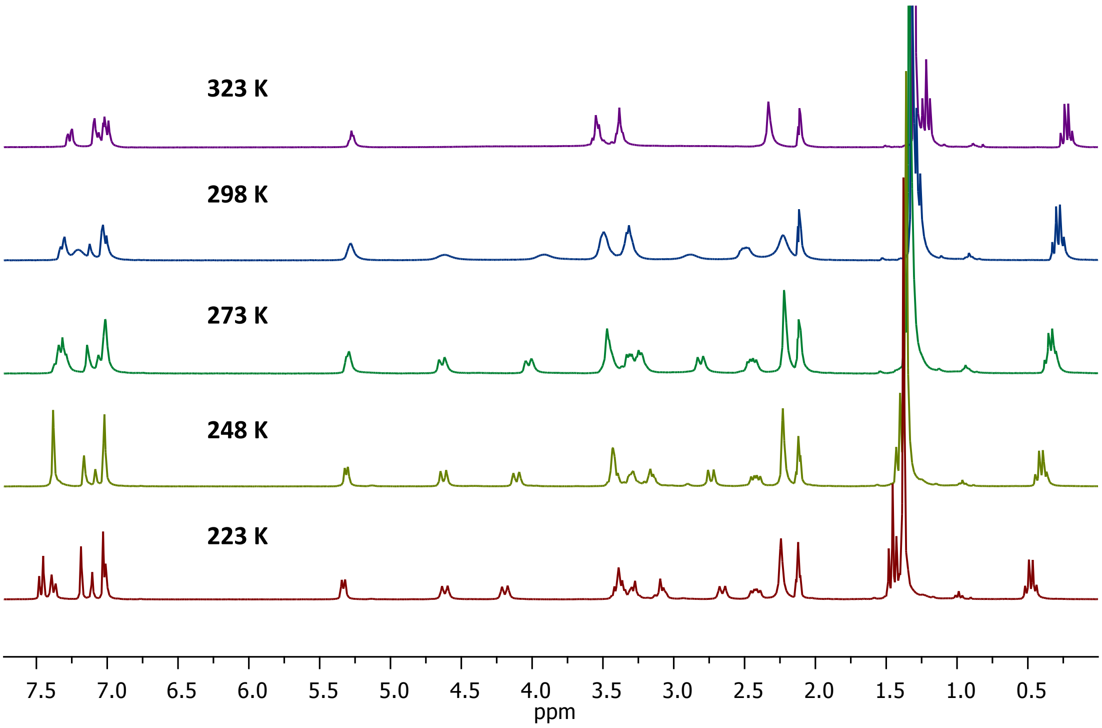

Figure S8. Variable temperature ^{1}H NMR of $(L^{ox}ZnEt)_2$ in toluene-d_8.

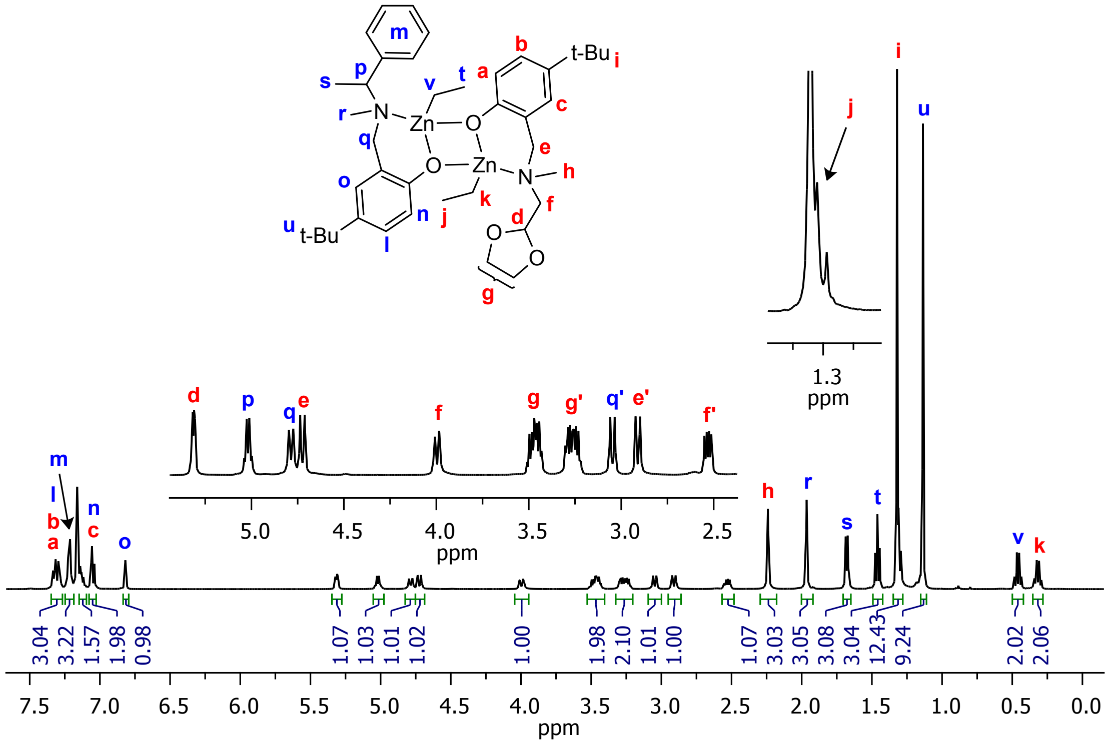

Figure S9. ^{1}H NMR of $L^{R}L^{ox}Zn_2Et_2$ in benzene-d$_6$.

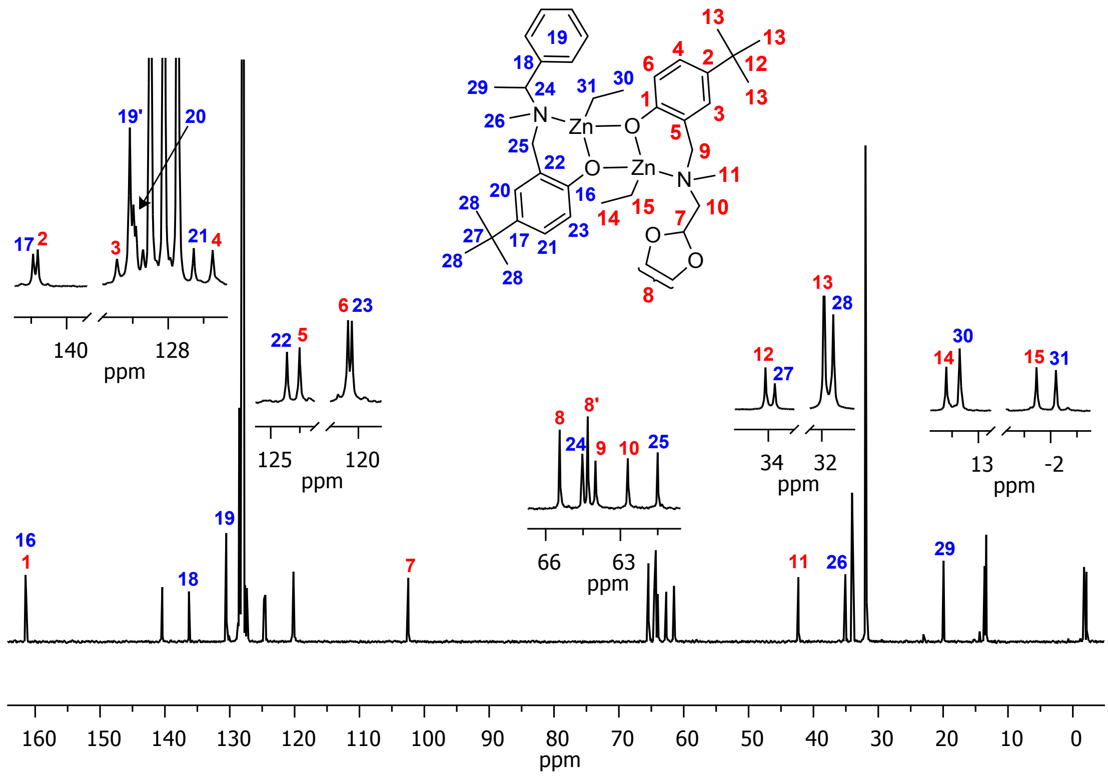

Figure S10. ^{13}C NMR of $L^{R}L^{ox}Zn_2Et_2$ in benzene-d$_6$.

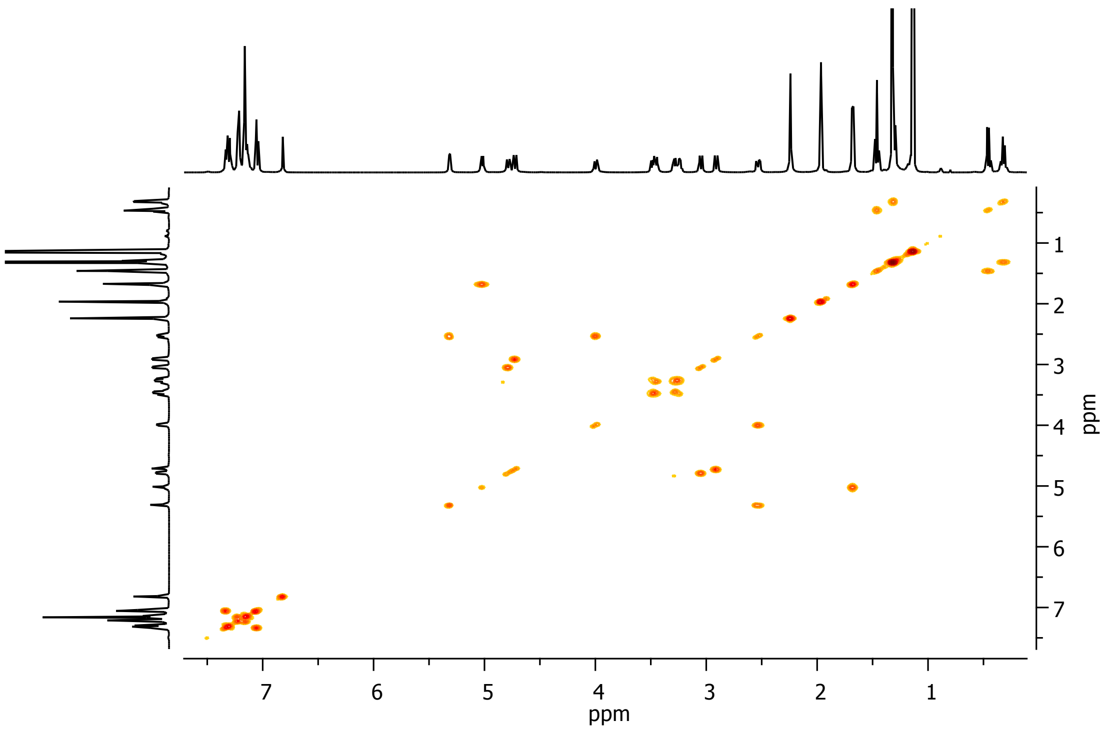

Figure S11. ^{1}H COSY of $L^{R}L^{ox}Zn_2Et_2$ in benzene-d$_6$.

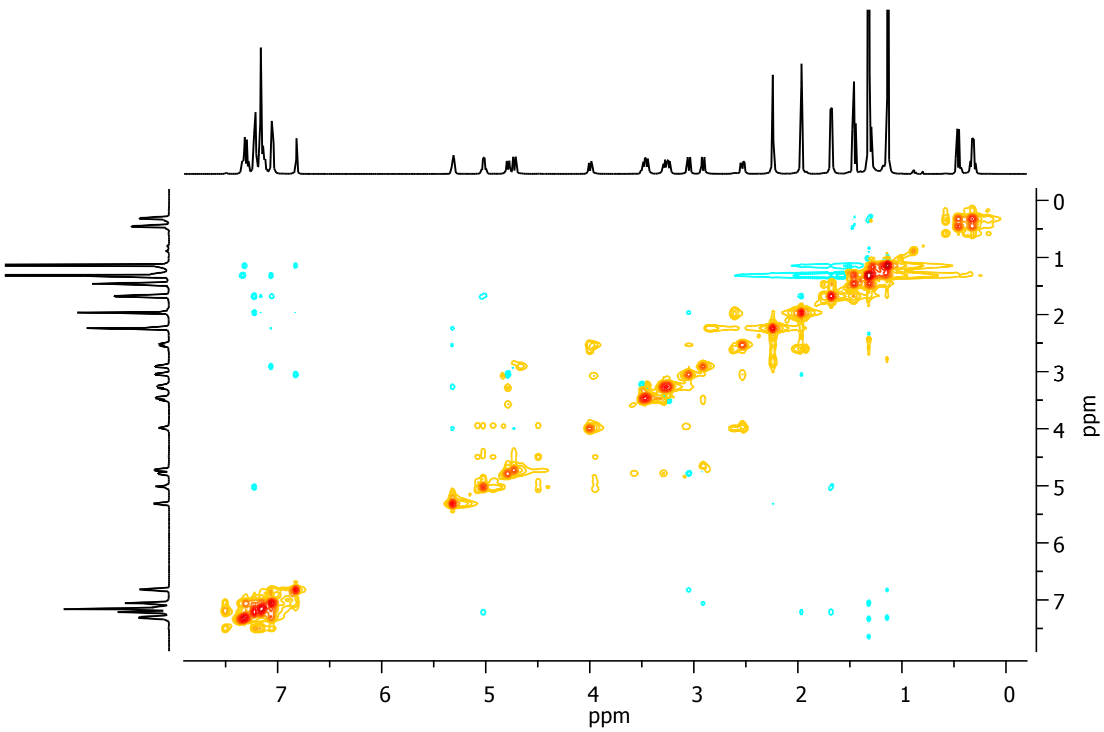

Figure S12. ^{1}H NOESY of $L^{R}L^{ox}Zn_2Et_2$ in benzene-d$_6$.

	$(L^{ox}ZnEt)_2$	**$L^{R}Ł^{cy}Zn_2Et_2$**
Empirical formula	$C_{36}H_{58}N_2O_6Zn_2$	$C_{46}H_{72}N_2O_2Zn_2$
Formula weight	745.58	815.79
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1$
a (Å)	10.612 (7)	13.020 (3)
b (Å)	14.967 (8)	10.104 (2)
c (Å)	12.324 (8)	17.315 (3)
α (°)	90	90
β (°)	112.89 (4)	103.54 (2)
γ (°)	90	90
V (Å^3)	1803.4 (2)	2214.5 (8)
Z	2	2
Crystal description	Block, colourless	Block, colourless
Crystal size (mm)	0.32 × 0.30 × 0.18	0.40 × 0.32 × 0.30
d_{calc} (g/cm^3)	1.373	1.223
μ (mm^{-1})	1.38	1.12
F(000)	792	876
Diffractometer	Kuma KM-4 CCD	Kuma KM-4 CCD
λ (Å)	0.71073 (Mo)	0.71073 (Mo)
T (K)	80	150
Θ min/max (°)	3.3/28.1	3.0/28.1
h, k, l min/max	-14/10, -17/18, -16/14	-17/15, -13/13, -18/22
Reflections collected	8557	22158
Independent reflections	4088	10495
Reflections [$I>2\sigma(I)$]	2273	9773
R (int.)	0.034	0.125
Flack parameter	-	-0.013 (17)
data/restraints/params	4088/0/213	10495/1/482
$R[F^2 > 2\sigma(F^2)]$	0.034	0.061
$wR(F^2)$	0.049	0.156
GooF	0.94	1.07
$\Delta\rho_{max}/\Delta\rho_{min}$ (e·Å^{-3})	0.70/-0.54	0.68/-1.24

Table S1. X-ray experimental data and refinement.

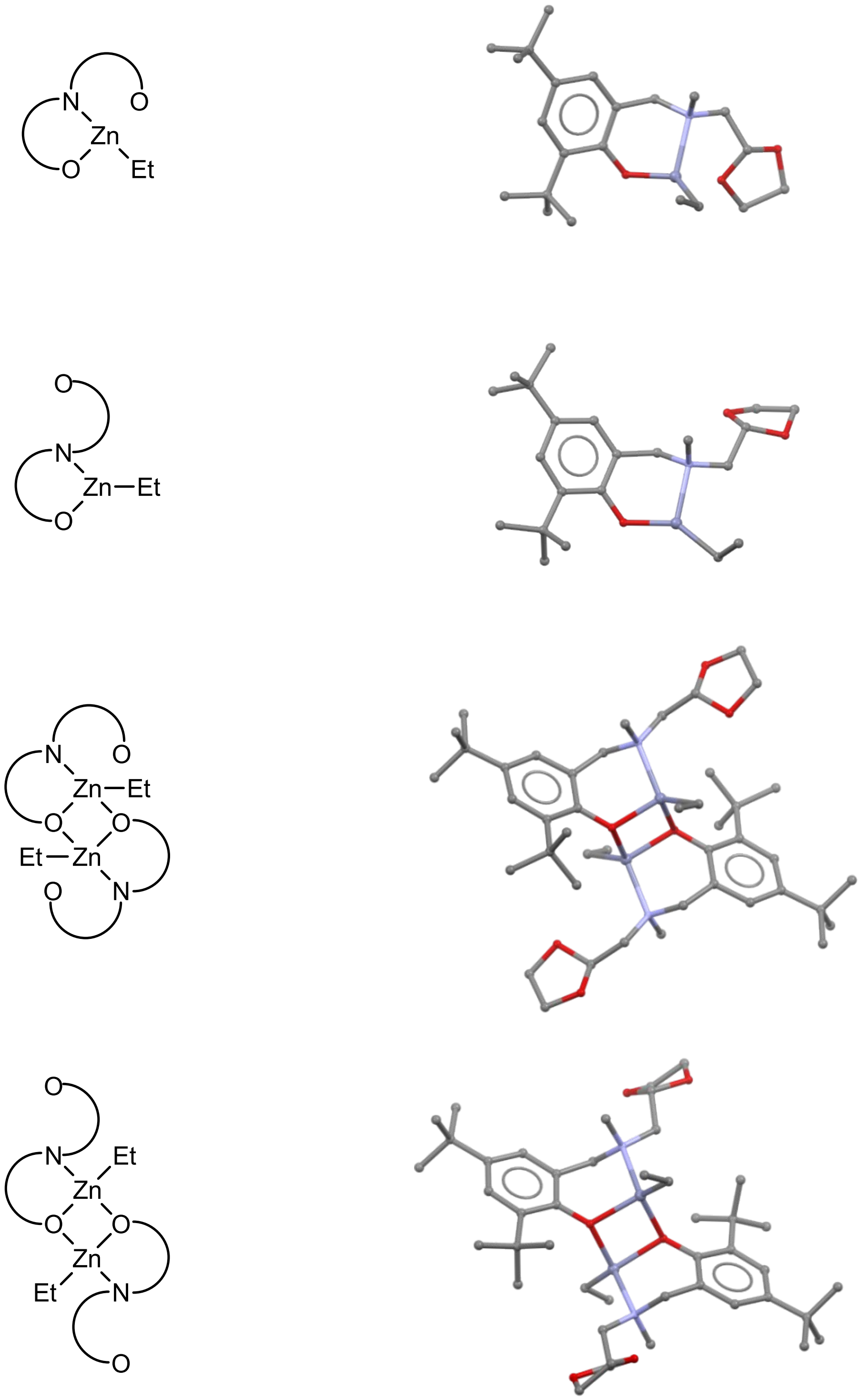

Figure S13. Structures of monomeric and dimeric zinc species with Ł^{ox} (schematic on left, DFT optimised on right).

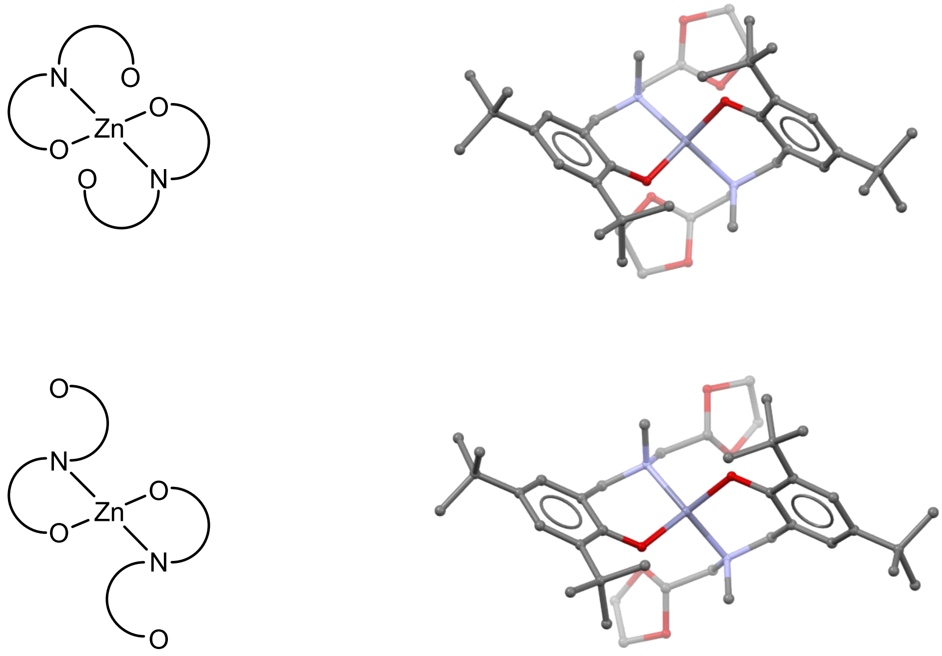

Figure S14. Structures of homoleptic zinc species with Ł^{ox} (schematic on left, DFT optimised on right).

Isomer	E (hartree)	ZPE (kcal/mol)
“closed” Ł^{ox}ZnEt	-2920.23038533	352.00
“closed” (Ł^{ox}ZnEt)$_2$	-5840.47432829	705.63
“closed” (Ł^{ox})$_2$Zn	-3902.89414065	623.84
“opened” Ł^{ox}ZnEt	-2920.22464895	352.07
“opened” (Ł^{ox}ZnEt)$_2$	-5840.47798247	705.83
“opened” (Ł^{ox})$_2$Zn	-3902.89378304	623.36

Table S2. Energies of monomeric, dimeric and homoleptic zinc species with Ł^{ox}.

Isomer	E (hartree)	ZPE (kcal/mol)	ΔE$_{zpe}$ (kcal/mol)	ΔE$_{zpe}$ (kJ/mol)
2 “closed” Ł^{ox}ZnEt	-5840.46077066	703.99	8.96	37.49
“closed” (Ł^{ox}ZnEt)$_2$	-5840.47432829	705.63	2.09	8.73
“closed” (Ł^{ox})$_2$Zn + ZnEt$_2$	-5840.45731752	704.89	12.02	50.29
2 “opened” Ł^{ox}ZnEt	-5840.44929790	704.14	16.30	68.22
“opened” (Ł^{ox}ZnEt)$_2$	-5840.47798247	705.83	0.00	0.00
“opened” (Ł^{ox})$_2$Zn + ZnEt$_2$	-5840.45695991	704.41	11.76	49.22

Table S3. Energies of possible equilibrium systems in relation to the most stable zinc dimer: “opened” (Ł^{ox}ZnEt)$_2$.

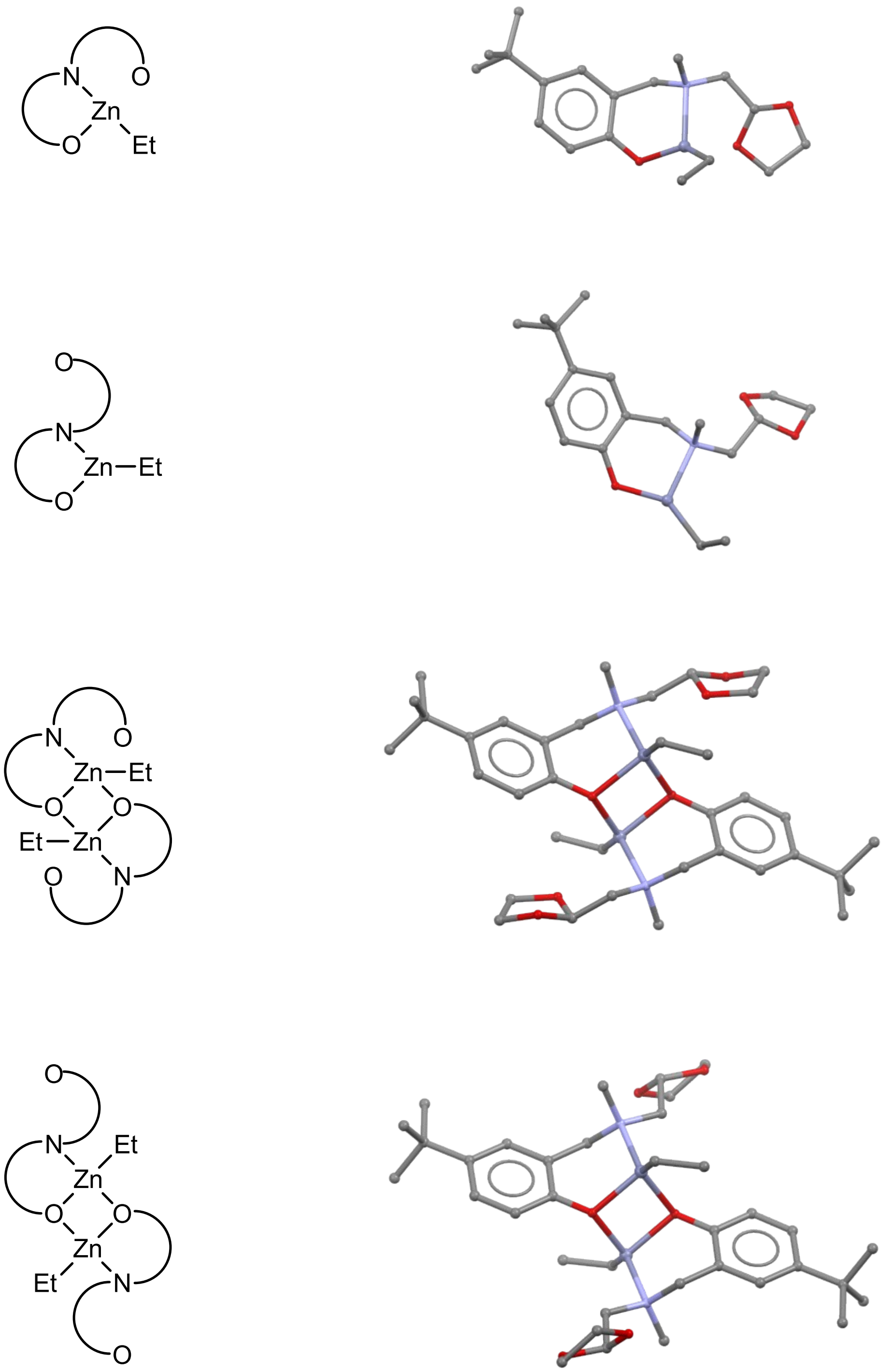

Figure S15. Structures of monomeric and dimeric zinc species with L^{ox} (schematic on left, DFT optimised on right).

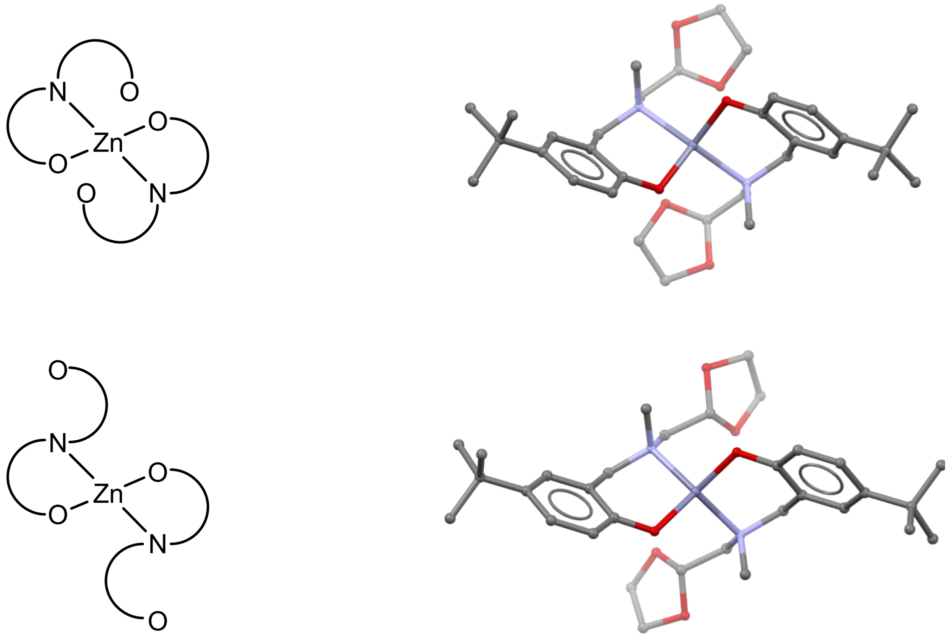

Figure S16. Structures of homoleptic zinc species with L^{ox} (schematic on left, DFT optimised on right).

Isomer	E (hartree)	ZPE (kcal/mol)
“closed” $L^{ox}ZnEt$	-2762.96991569	281.38
“closed” $(L^{ox}ZnEt)_2$	-5525.98548688	564.03
“closed” $(L^{ox})_2Zn$	-3588.37556221	482.66
“opened” $L^{ox}ZnEt$	-2762.96439320	281.24
“opened” $(L^{ox}ZnEt)_2$	-5525.98323595	563.68
“opened” $(L^{ox})_2Zn$	-3588.37512784	482.33

Table S4. Energies of monomeric, dimeric and homoleptic zinc species with L^{ox}.

Isomer	E (hartree)	ZPE (kcal/mol)	ΔE_{zpe} (kcal/mol)	ΔE_{zpe} (kJ/mol)
2 “closed” $L^{ox}ZnEt$	-5525.93983138	562.76	27.37	114.53
“closed” $(L^{ox}ZnEt)_2$	-5525.98548688	564.03	0.00	0.00
“closed” $(L^{ox})_2Zn + ZnEt_2$	-5525.93873908	563.71	29.01	121.39
2 “opened” $L^{ox}ZnEt$	-5525.92878640	562.48	34.02	142.36
“opened” $(L^{ox}ZnEt)_2$	-5525.98323595	563.68	1.06	4.43
“opened” $(L^{ox})_2Zn + ZnEt_2$	-5525.93830471	563.38	28.96	121.16

Table S5. Energies of possible equilibrium systems in relation to the most stable zinc dimer: “closed” $(L^{ox}ZnEt)_2$.

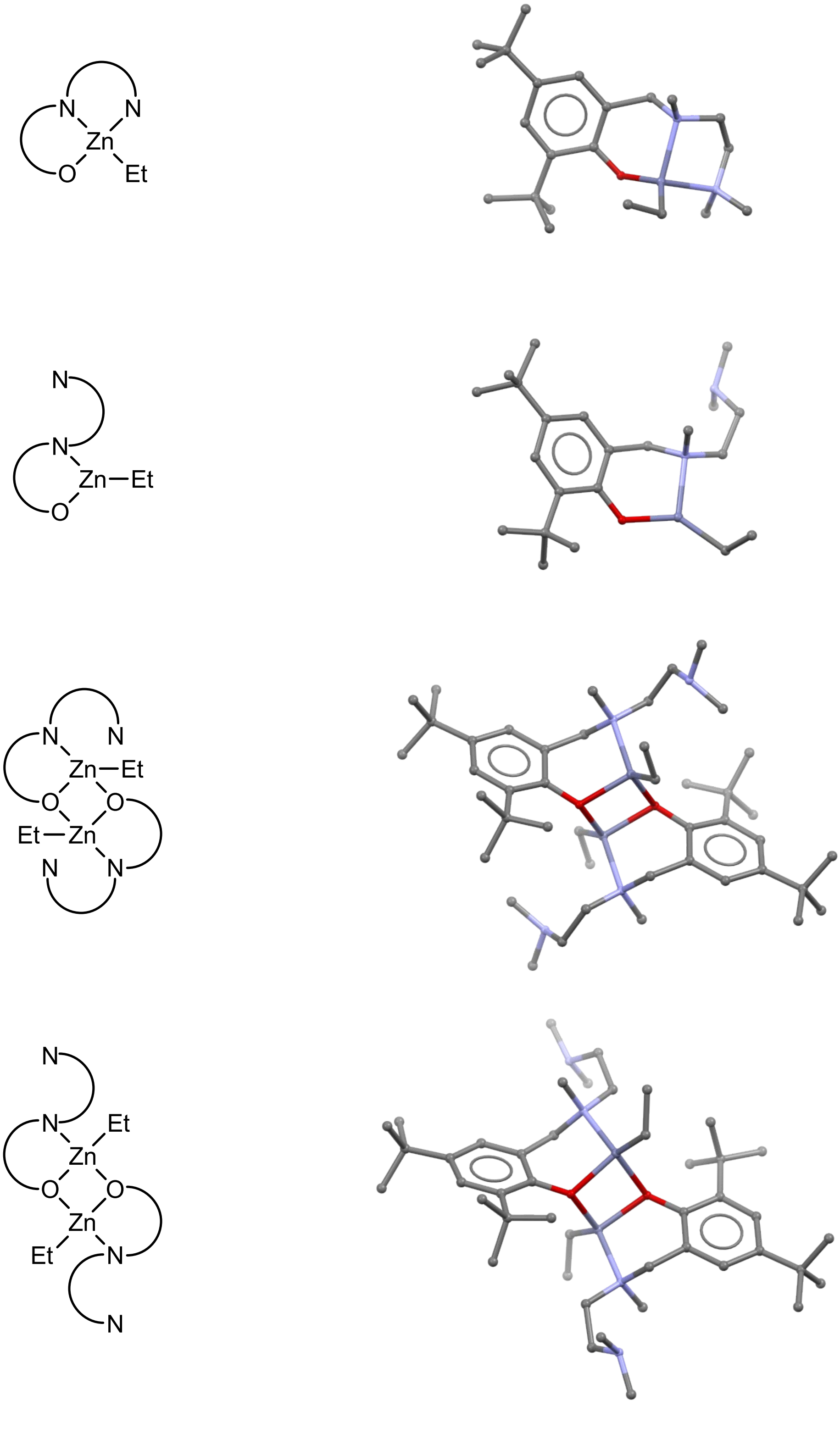

Figure S17. Structures of monomeric and dimeric zinc species with Ł^{T} (schematic on left, DFT optimised on right).

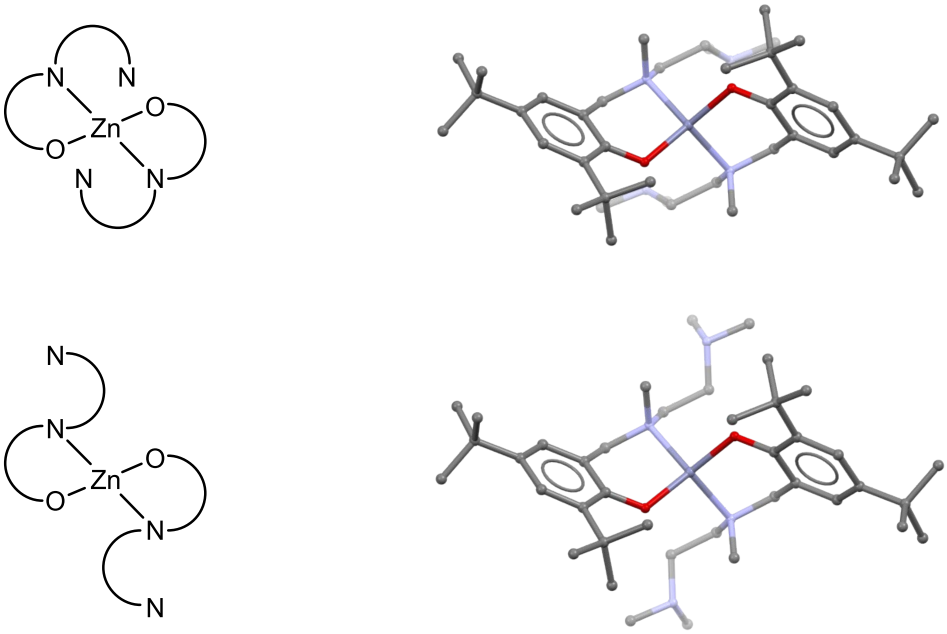

Figure S18. Structures of homoleptic zinc species with Ł^{T} (schematic on left, DFT optimised on right).

Isomer	E (hartree)	ZPE (kcal/mol)
“closed” Ł^{T}ZnEt	-2826.37137436	370.30
“closed” (Ł^{T}ZnEt)$_2$	-5652.71480439	741.11
“closed” (Ł^{T})$_2$Zn	-3715.14656753	659.13
“opened” Ł^{T}ZnEt	-2826.35150416	369.90
“opened” (Ł^{T}ZnEt)$_2$	-5652.73069495	741.18
“opened” (Ł^{T})$_2$Zn	-3715.14190900	658.47

Table S6. Energies of monomeric, dimeric and homoleptic zinc species with Ł^{T}.

Isomer	E (hartree)	ZPE (kcal/mol)	ΔE_{zpe} (kcal/mol)	ΔE_{zpe} (kJ/mol)
2 “closed” Ł^{T}ZnEt	-5652.74274872	740.60	0.00	0.00
“closed” (Ł^{T}ZnEt)$_2$	-5652.71480439	741.11	18.04	75.50
“closed” (Ł^{T})$_2$Zn + ZnEt$_2$	-5652.70974440	740.17	20.28	84.85
2 “opened” Ł^{T}ZnEt	-5652.70300832	739.81	24.14	101.01
“opened” (Ł^{T}ZnEt)$_2$	-5652.73069495	741.18	8.14	34.04
“opened” (Ł^{T})$_2$Zn + ZnEt$_2$	-5652.70508587	739.52	22.55	94.34

Table S7. Energies of possible equilibrium systems in relation to the most stable zinc monomer: “closed” Ł^{T}ZnEt.

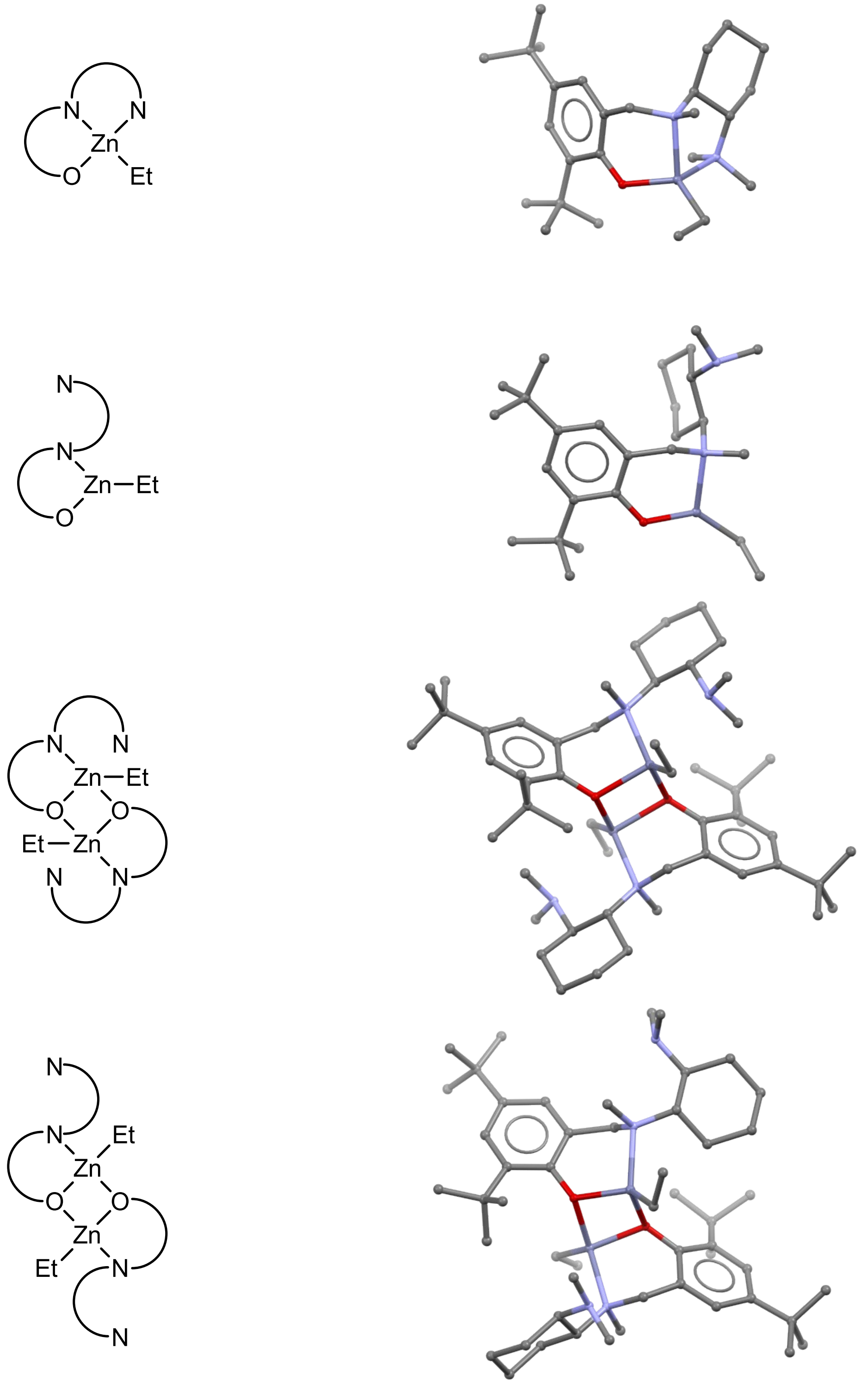

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Figure S19. Structures of monomeric and dimeric zinc species with Ł^{M} (schematic on left, DFT optimised on right).

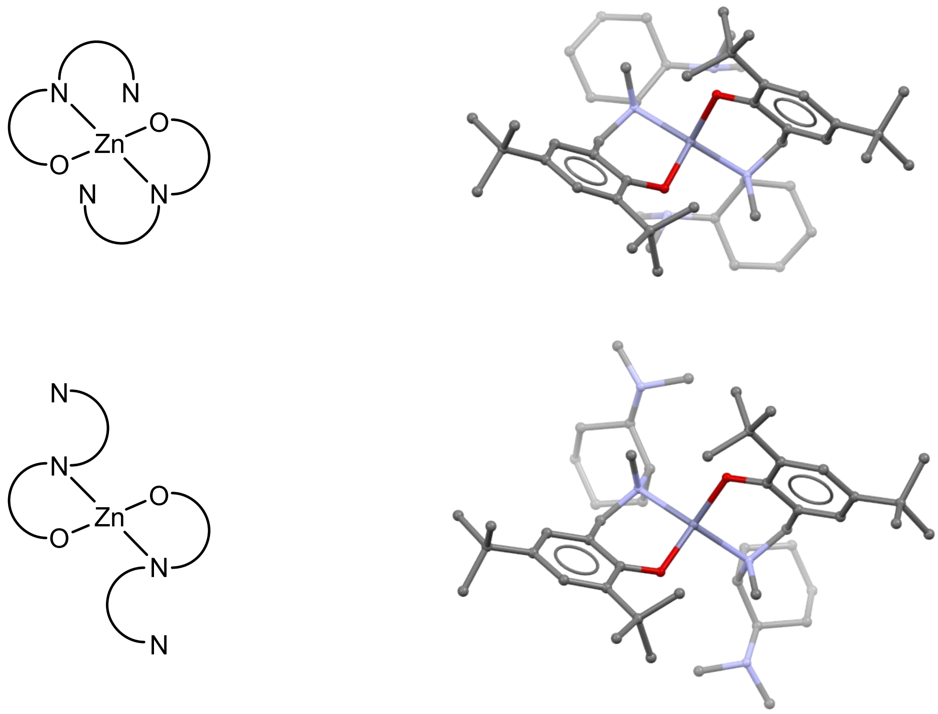

Figure S20. Structures of homoleptic zinc species with Ł^{M} (schematic on left, DFT optimised on right).

Isomer	E (hartree)	ZPE (kcal/mol)
“closed” Ł^{M}ZnEt	-2982.42571645	429.42
“closed” (Ł^{M}ZnEt)$_2$	-5964.80071870	859.15
“closed” (Ł^{M})$_2$Zn	-4027.20066440	777.88
“opened” Ł^{M}ZnEt	-2982.40303061	428.87
“opened” (Ł^{M}ZnEt)$_2$	-5964.80384181	858.99
“opened” (Ł^{M})$_2$Zn	-4027.19438479	777.68

Table S8. Energies of monomeric, dimeric and homoleptic zinc species with Ł^{M}.

Isomer	E (hartree)	ZPE (kcal/mol)	ΔE_{zpe} (kcal/mol)	ΔE_{zpe} (kJ/mol)
2 “closed” Ł^{M}ZnEt	-5964.85143290	858.85	0.00	0.00
“closed” (Ł^{M}ZnEt)$_2$	-5964.80071870	859.15	32.12	134.40
“closed” (Ł^{M})$_2$Zn + ZnEt$_2$	-5964.76384127	858.93	55.05	230.31
2 “opened” Ł^{M}ZnEt	-5964.80606122	857.73	27.36	114.45
“opened” (Ł^{M}ZnEt)$_2$	-5964.80384181	858.99	30.00	125.53
“opened” (Ł^{M})$_2$Zn + ZnEt$_2$	-5964.75756166	858.73	58.78	245.95

Table S9. Energies of possible equilibrium systems in relation to the most stable zinc monomer: “closed” Ł^{M}ZnEt.

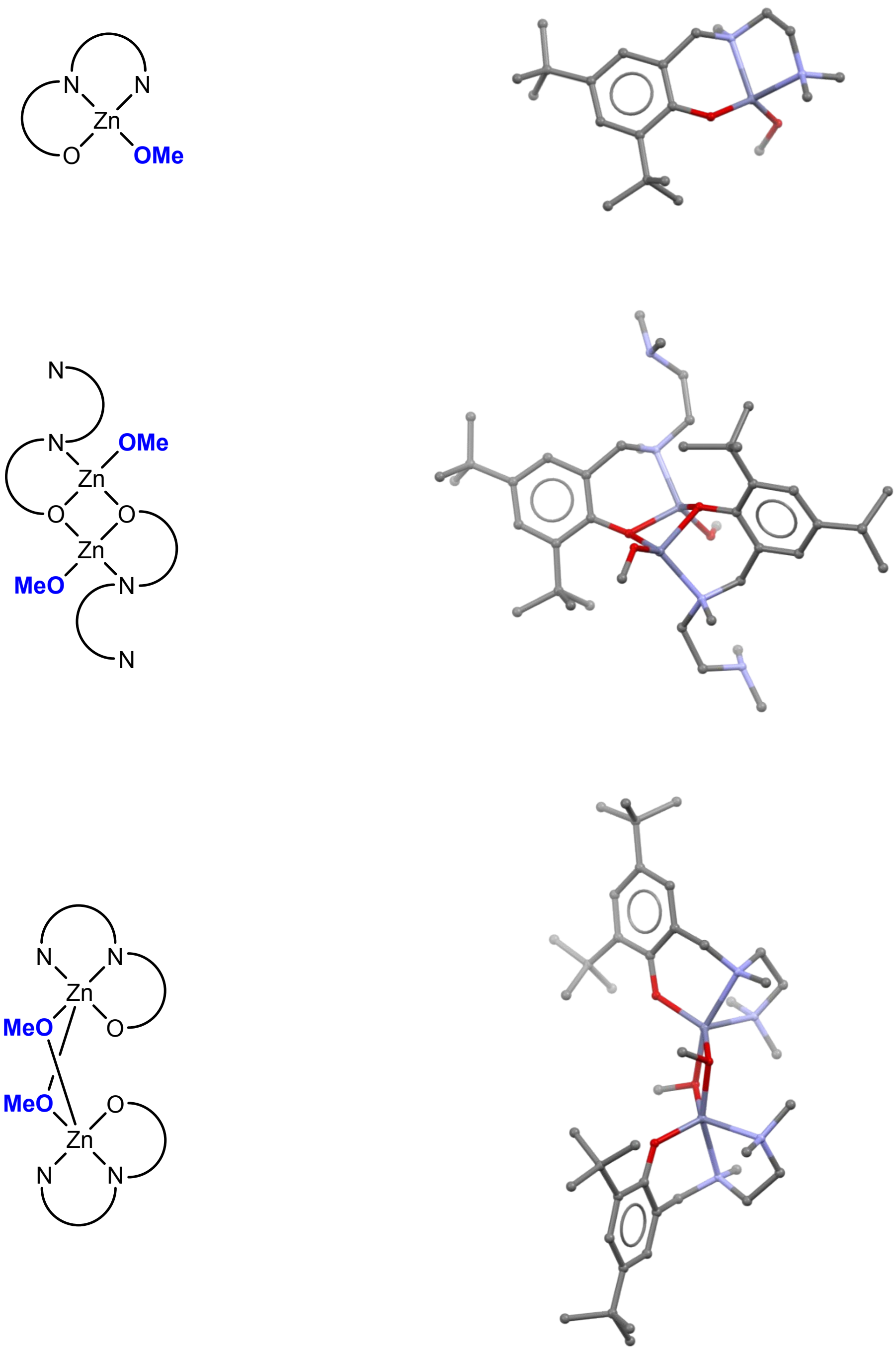

Figure S21. Structures of methoxy zinc species with Ł^{T} (schematic on left, DFT optimised on right).

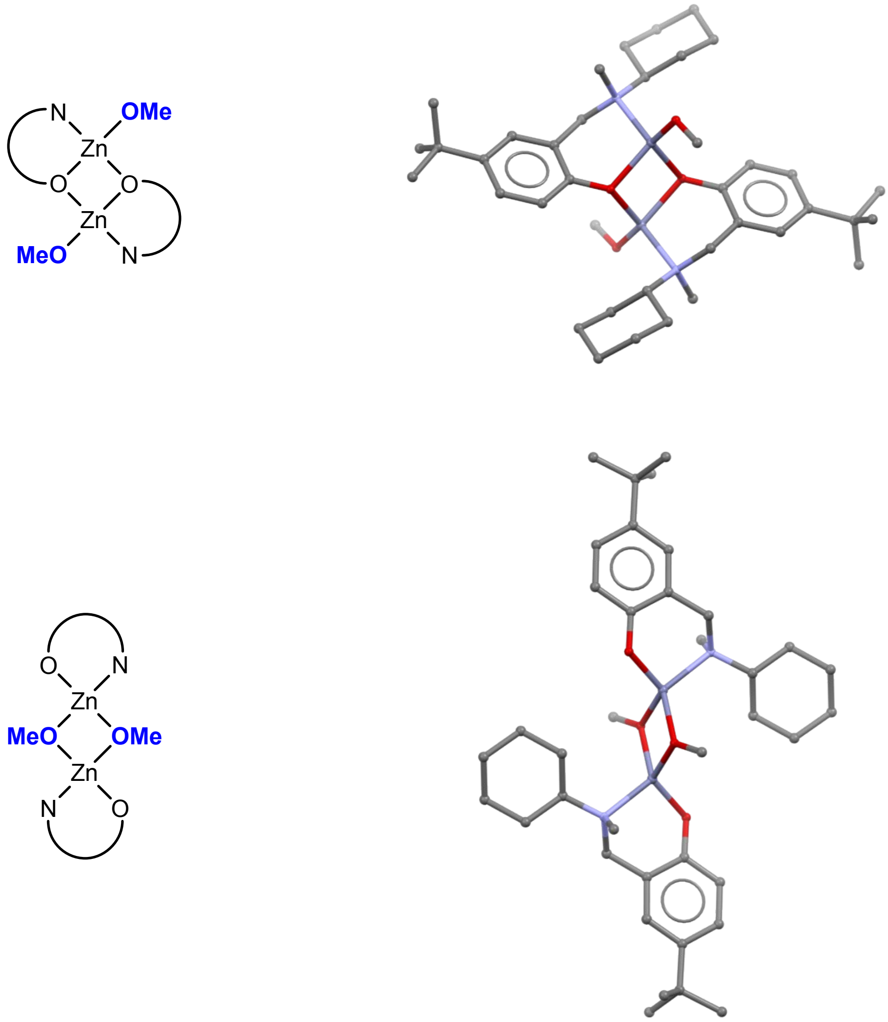

Figure S22. Structures of methoxy zinc species with L^{cy} (schematic on left, DFT optimised on right).

Isomer	E (hartree)	ZPE (kcal/mol)
"opened" Ł^{T}ZnEt : 2 MeOH	-2942.09289429	403.17
"closed" Ł^{T}ZnEt : 2 MeOH	-2942.10181104	403.83
"closed" Ł^{T}ZnOMe	-2862.2990678	355.76
"opened" ((μ-Ł^{T})ZnOMe)$_2$	-5724.5841365	712.31
"closed" (Ł^{T}Zn(μ-OMe))$_2$	-5724.62974043	713.45
MeOH	-115.72185741	32.26
EtH	-79.83720835	47.019

Table S10. Energies of ethyl and methoxy zinc species species with Ł^{T}, methanol (MeOH) and ethane (EtH).

Isomer	E (hartree)	ZPE (kcal/mol)	ΔE_{zpe} (kcal/mol)	ΔE_{zpe} (kJ/mol)
2 “closed” Ł^{T}ZnEt + 2 MeOH	-5884.18646354	805.13	0.00	0.00
“opened” (Ł^{T}ZnEt)$_2$ + 2 MeOH	-5884.17440977	805.71	8.14	34.04
2 “opened” Ł^{T}ZnEt : 2 MeOH	-5884.18578858	806.34	1.63	6.83
2 “closed” Ł^{T}ZnEt : 2 MeOH	-5884.20362208	807.66	-8.24	-34.49
2 “closed” Ł^{T}ZnOMe + 2 EtH	-5884.27255230	805.57	-53.59	-224.22
“opened” (Ł^{T}ZnOMe)$_2$ + 2 EtH	-5884.25855318	806.35	-44.02	-184.20
“closed” (Ł^{T}ZnOMe)$_2$ + 2 EtH	-5884.30415713	807.48	-71.50	-299.16

Table S11. Energies of possible equilibrium systems in relation to the system: 2 “closed” Ł^{T}ZnEt + 2 MeOH.

Isomer	E (hartree)	ZPE (kcal/mol)
(L^{cy}ZnEt)$_2$	-5382.42180344	624.96
“opened” (L^{cy}ZnEt)$_2$: 2 MeOH	-5613.86523800	690.79
“closed” (L^{cy}ZnEt)$_2$: 2 MeOH	-5613.89724862	692.69
((μ-L^{cy})ZnOMe)$_2$	-5454.27507446	595.95
(L^{cy}Zn(μ-OMe))$_2$	-5454.29037844	596.48

Table S12. Energies of ethyl and methoxy zinc species species with Ł^{T}.

Isomer	E (hartree)	ZPE (kcal/mol)	ΔE_{zpe} (kcal/mol)	ΔE_{zpe} (kJ/mol)
(L^{cy}ZnEt)$_2$ + 2 MeOH	-5613.86551826	689.49	0.00	0.00
“opened” (L^{cy}ZnEt)$_2$: 2 MeOH	-5613.86523800	690.79	0.35	1.47
“closed” (L^{cy}ZnEt)$_2$: 2 MeOH	-5613.89724862	692.69	-39.82	-166.62
((μ-L^{cy})ZnOMe)$_2$ + 2 EtH	-5613.94949116	689.99	-105.39	-440.94
(L^{cy}Zn(μ-OMe))$_2$ + 2 EtH	-5613.96479514	690.52	-124.59	-521.30

Table S13. Energies of possible equilibrium systems in relation to the system: (L^{cy}ZnEt)$_2$ + 2 MeOH.

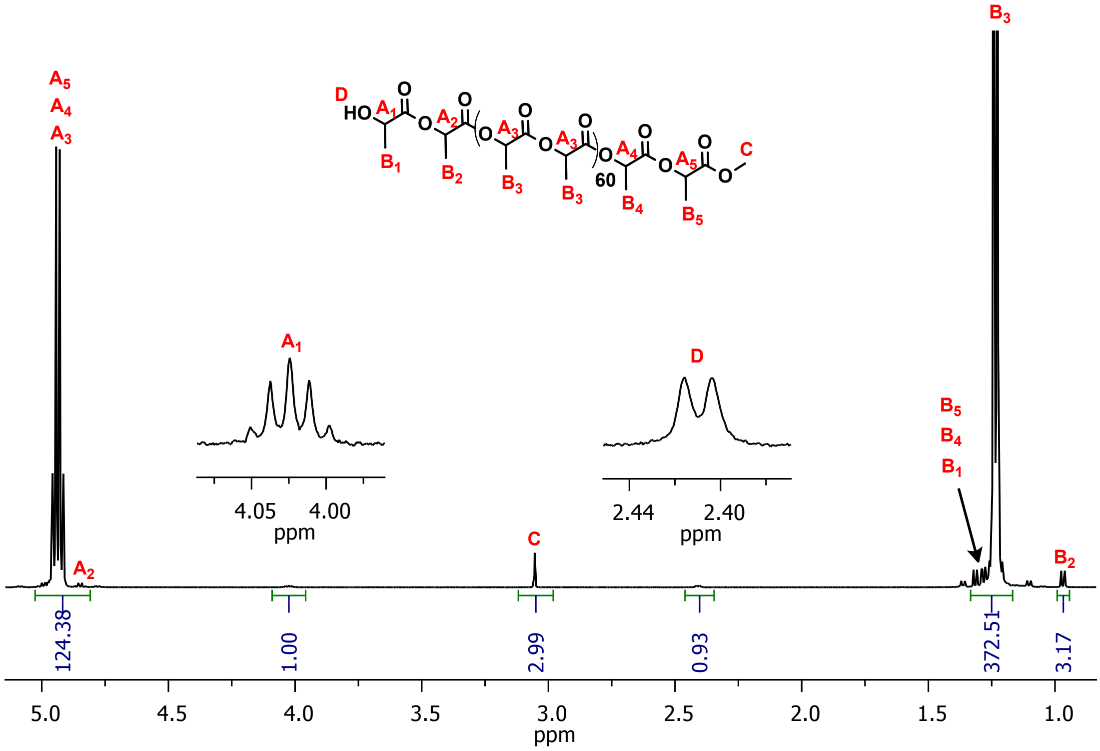

Figure S23. ^{1}H NMR spectrum of Me-50-PLA in benzene-d_6 (Entry no. 4, Table 2).

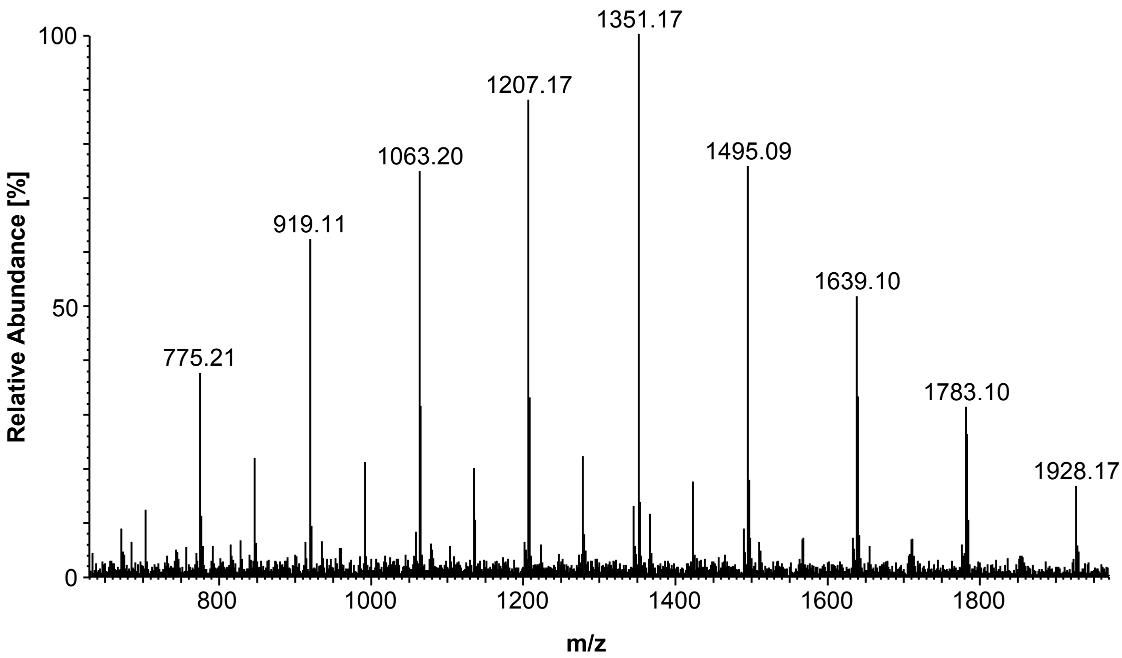

Figure S24. ESI MS spectrum of Me-10-PLA.