Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Designing of ancillary ligand for heteroleptic/homoleptic zinc complexes formation: synthesis, structures and application in ROP of lactides

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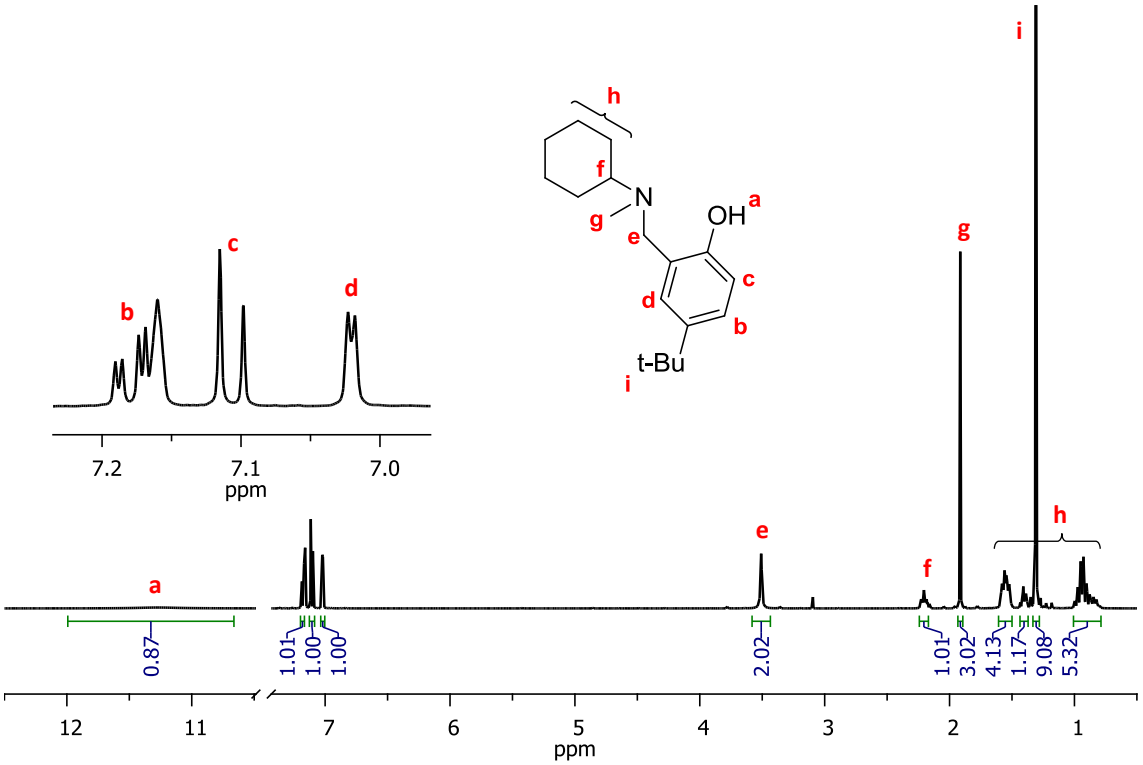


Figure S1. ^{1}H NMR of L^{1}-H in benzene-d$_6$.

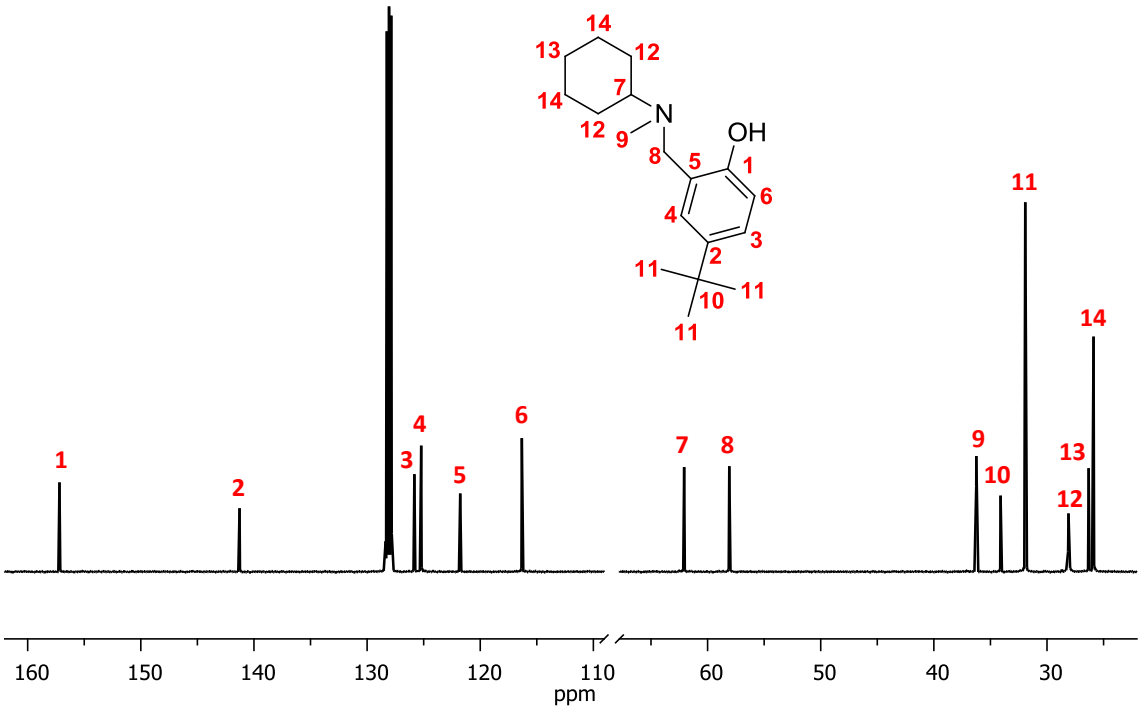


Figure S2. ^{13}C NMR of L^{1}-H in benzene-d$_6$.

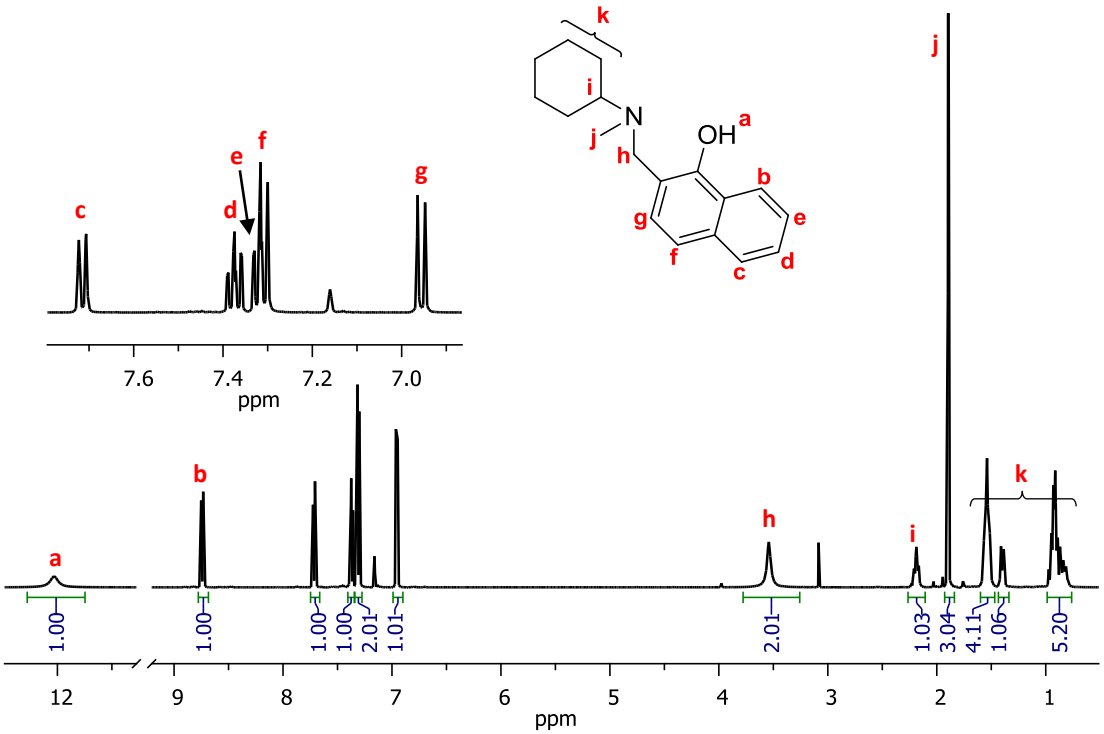


Figure S3. ^{1}H NMR of L^{2}-H in benzene-d$_{6}$.

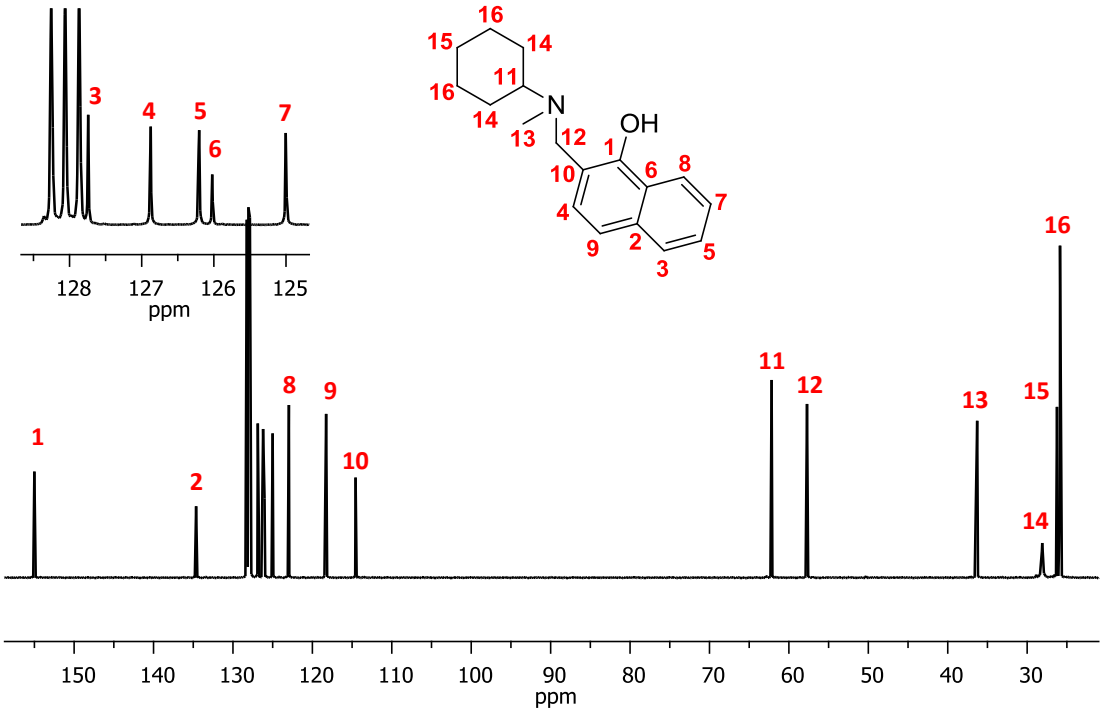


Figure S4. ^{13}C NMR of L^{2}-H in benzene-d$_{6}$.

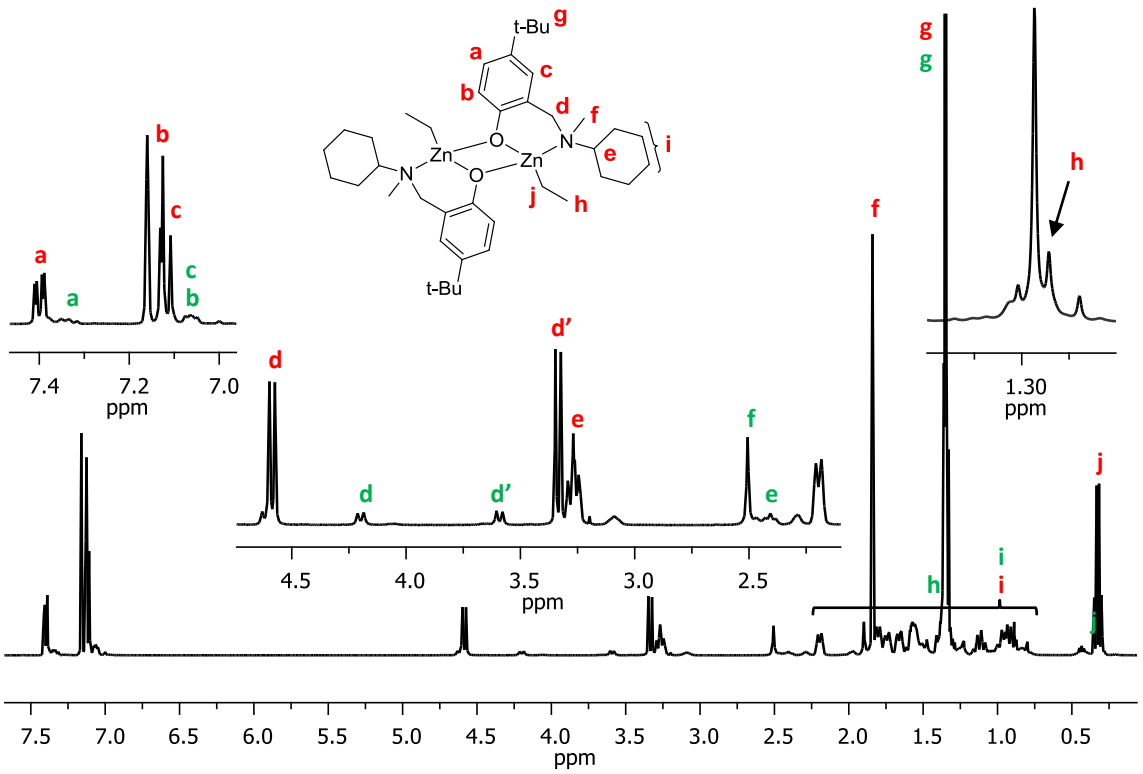


Figure S5. ^{1}H NMR of 1-Zn in benzene-d_6.

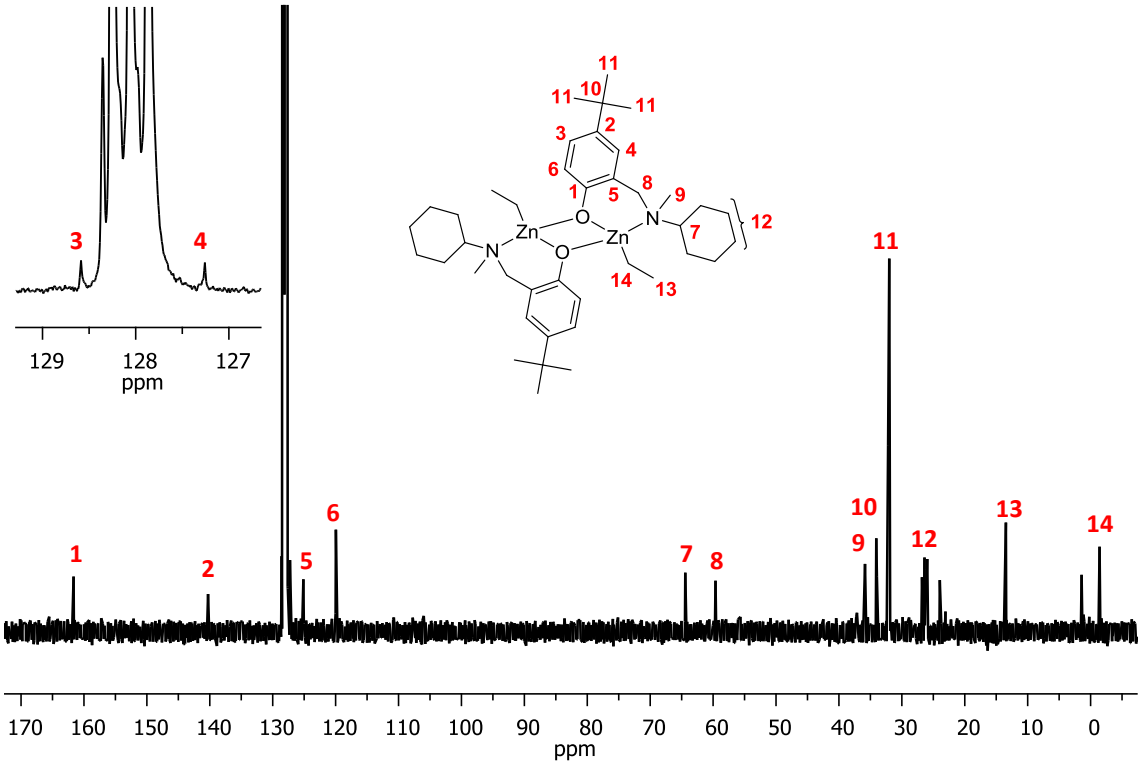


Figure S6. ^{13}C NMR of 1-Zn in benzene-d_6.

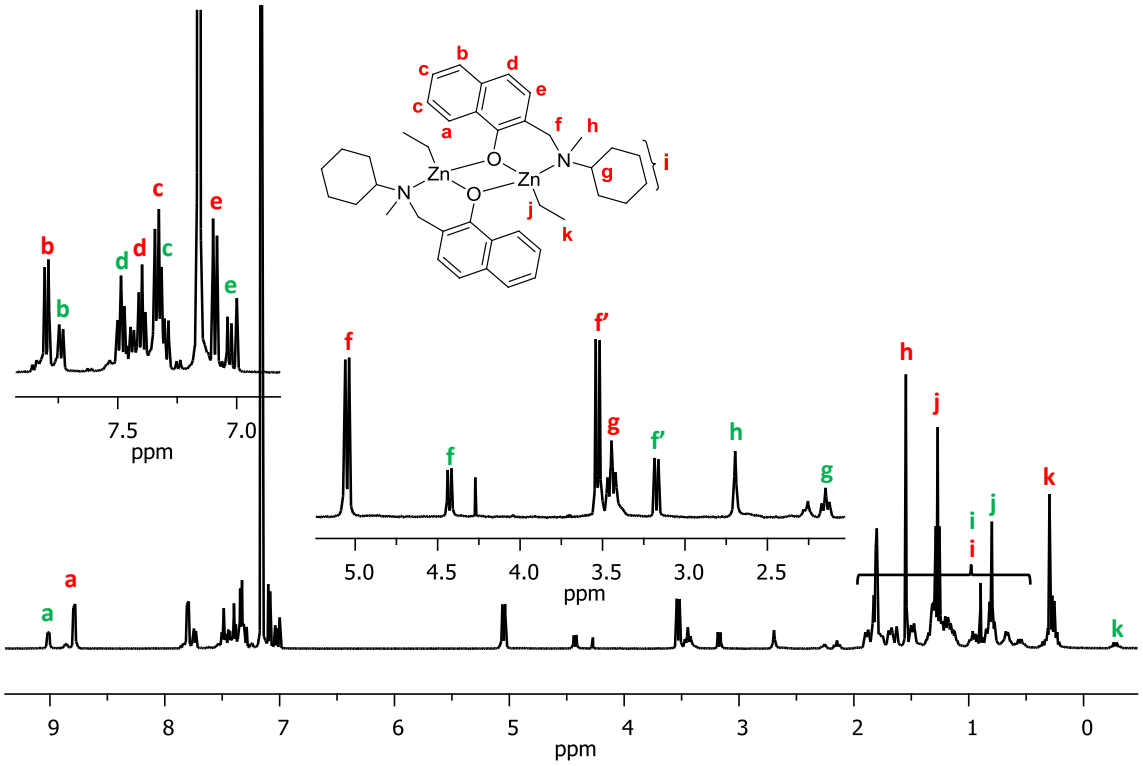


Figure S7. ^{1}H NMR of *2-Zn* in benzene-d_6.

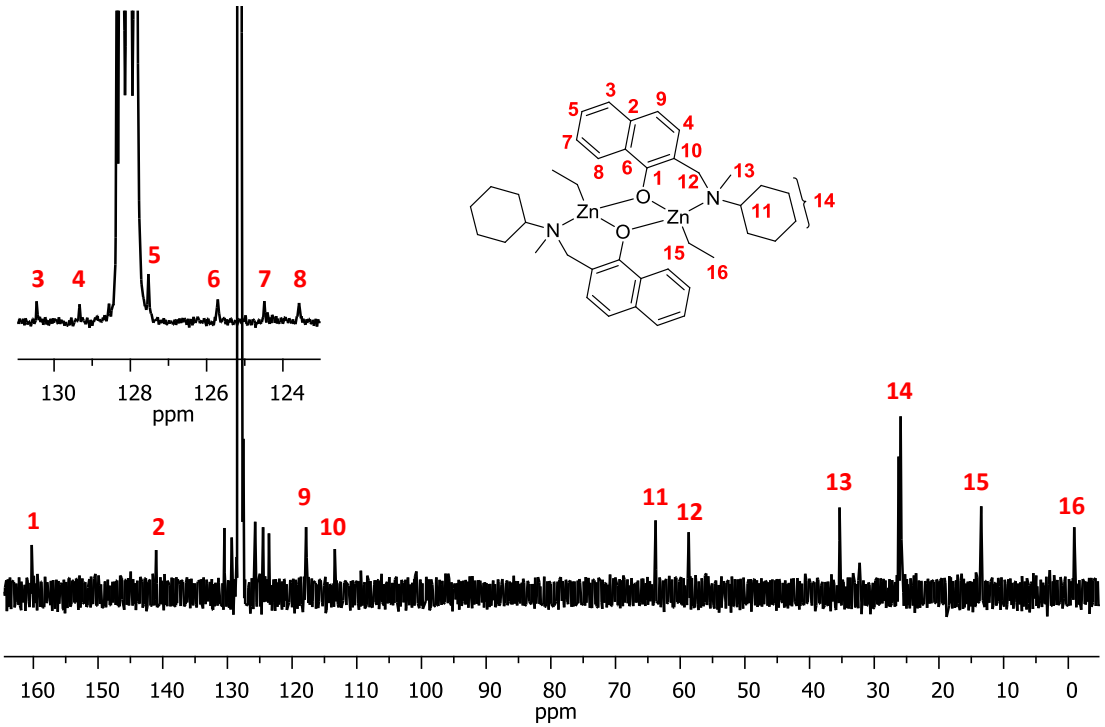


Figure S8. ^{13}C NMR of *2-Zn* in benzene-d_6

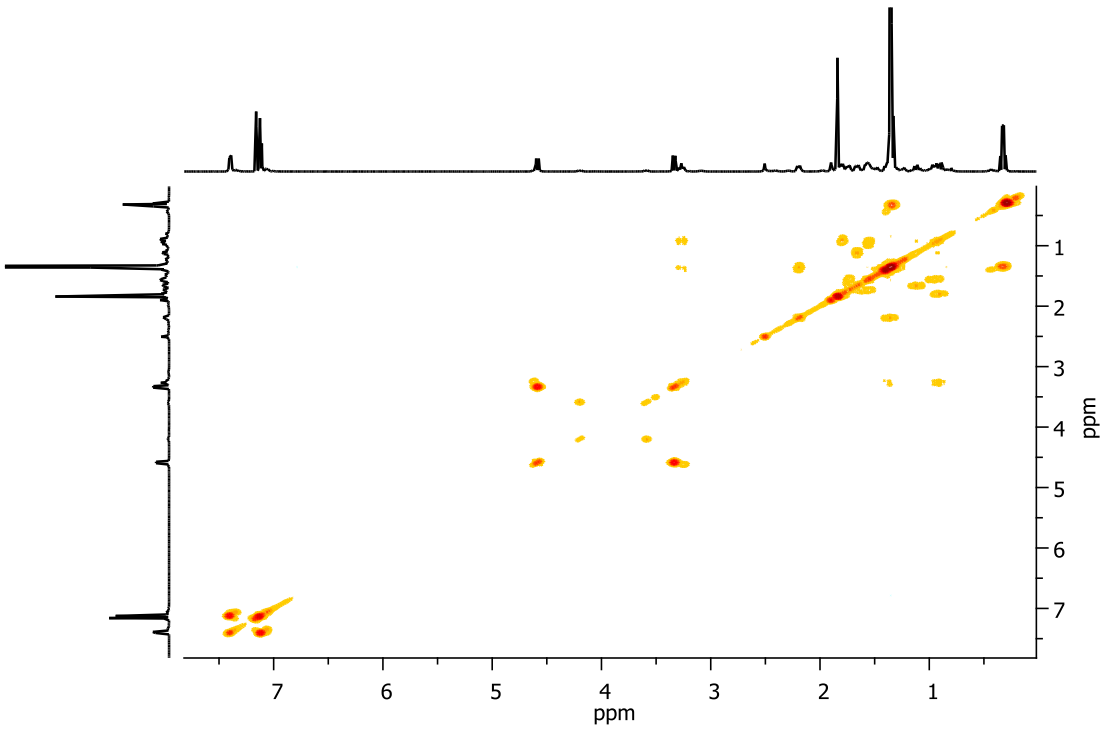


Figure S9. ^{1}H COSY of *1-Zn* in benzene-d_6.

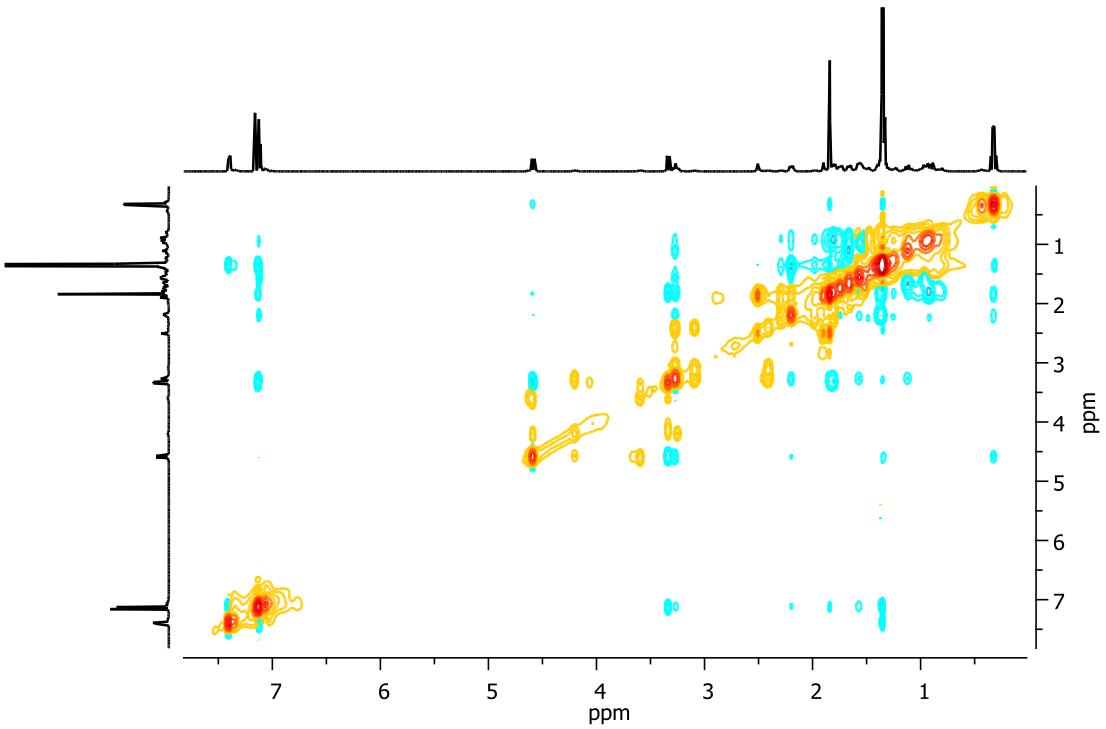


Figure S10. ^{1}H NOESY of *1-Zn* in benzene-d_6

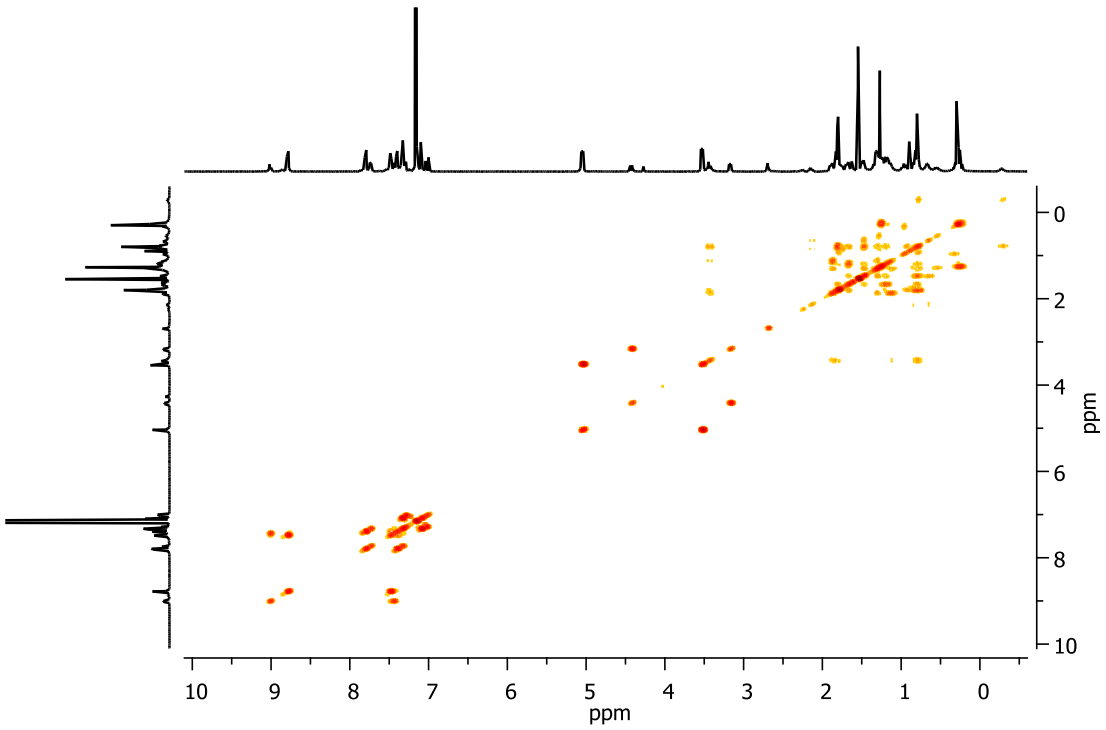


Figure S11. ^{1}H COSY of *2-Zn* in benzene-d_6.

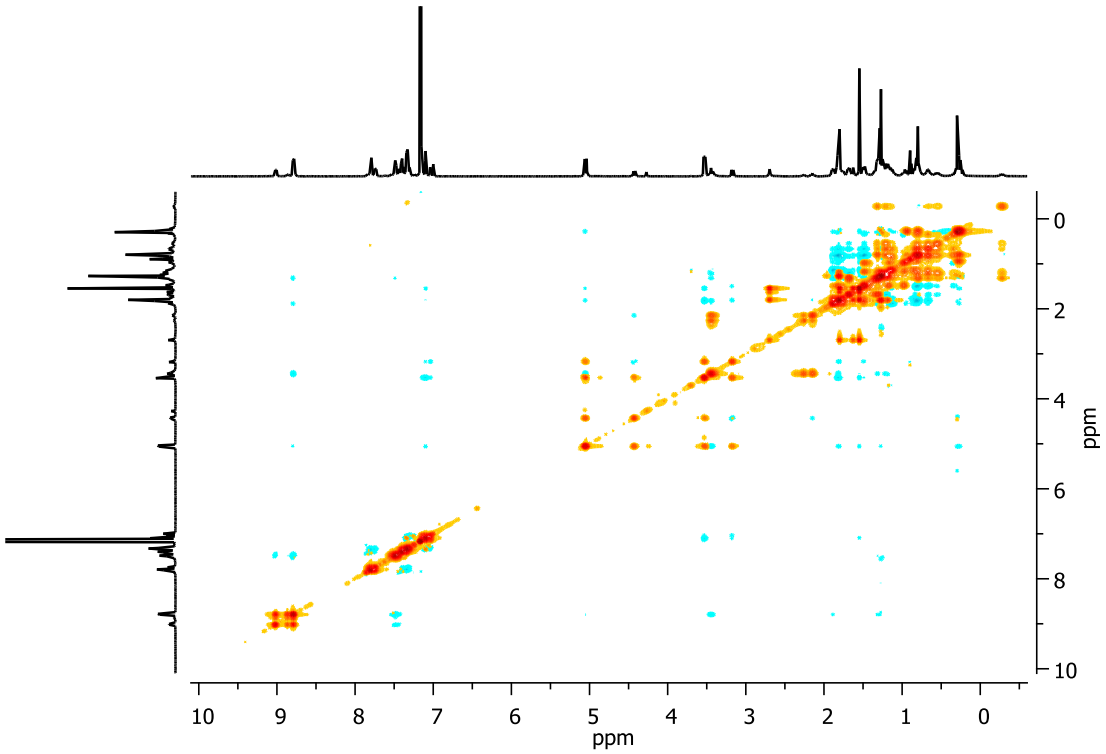


Figure S12. ^{1}H NOESY of *2-Zn* in benzene-d_6

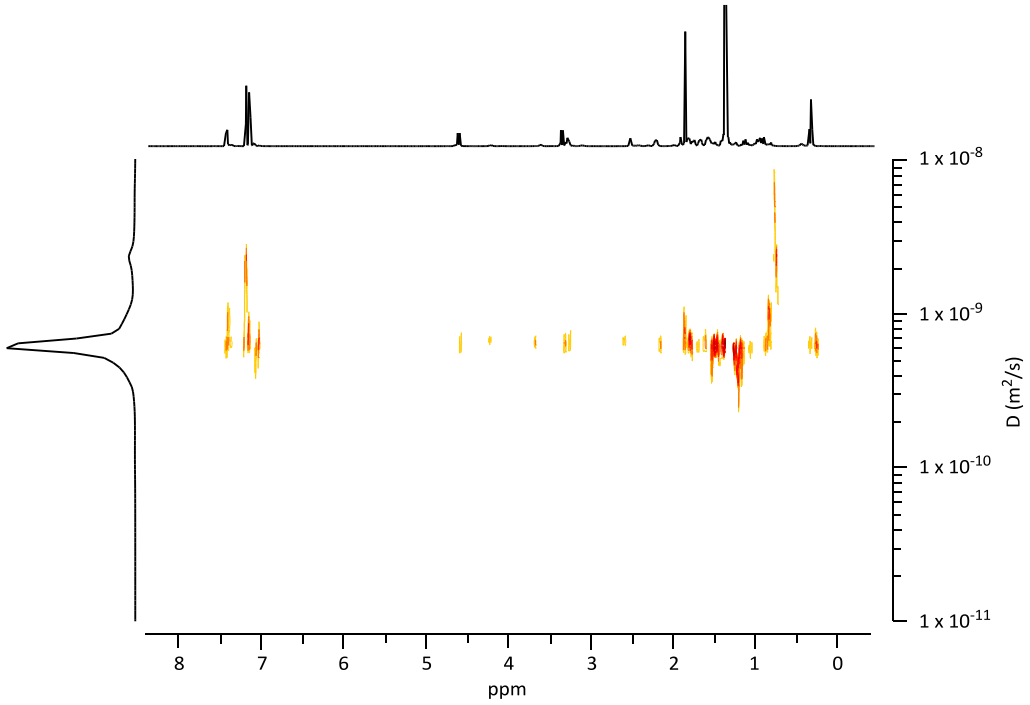


Figure S13. ^{1}H DOSY for 1-*Zn* in benzene-d_6.

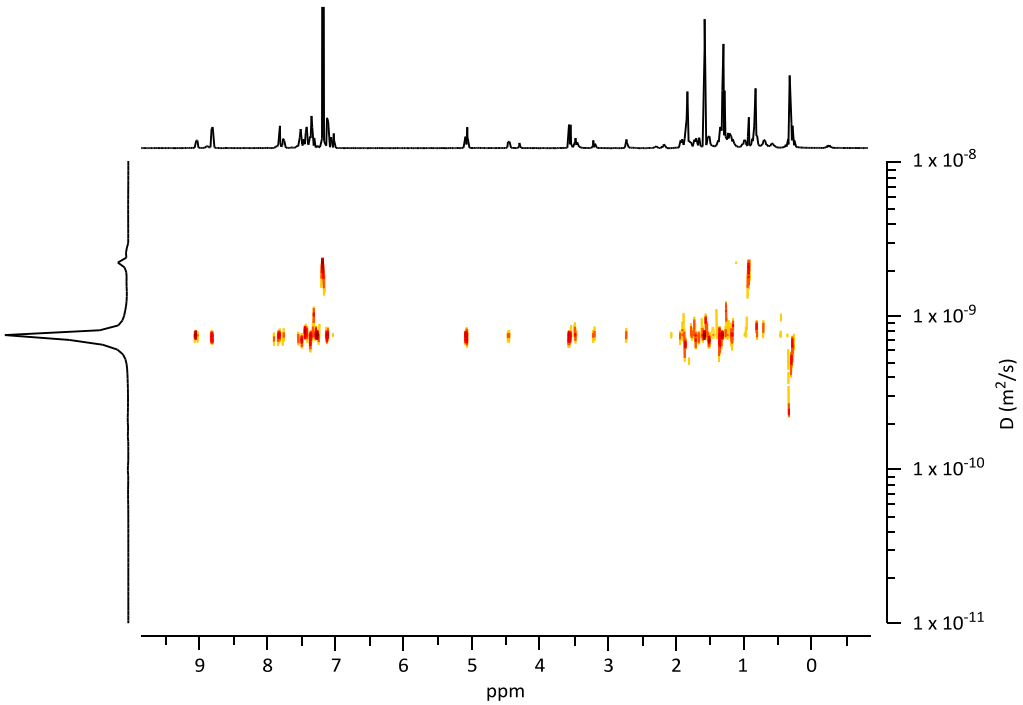


Figure S14. ^{1}H DOSY for *2*-Zn in benzene-d_6.

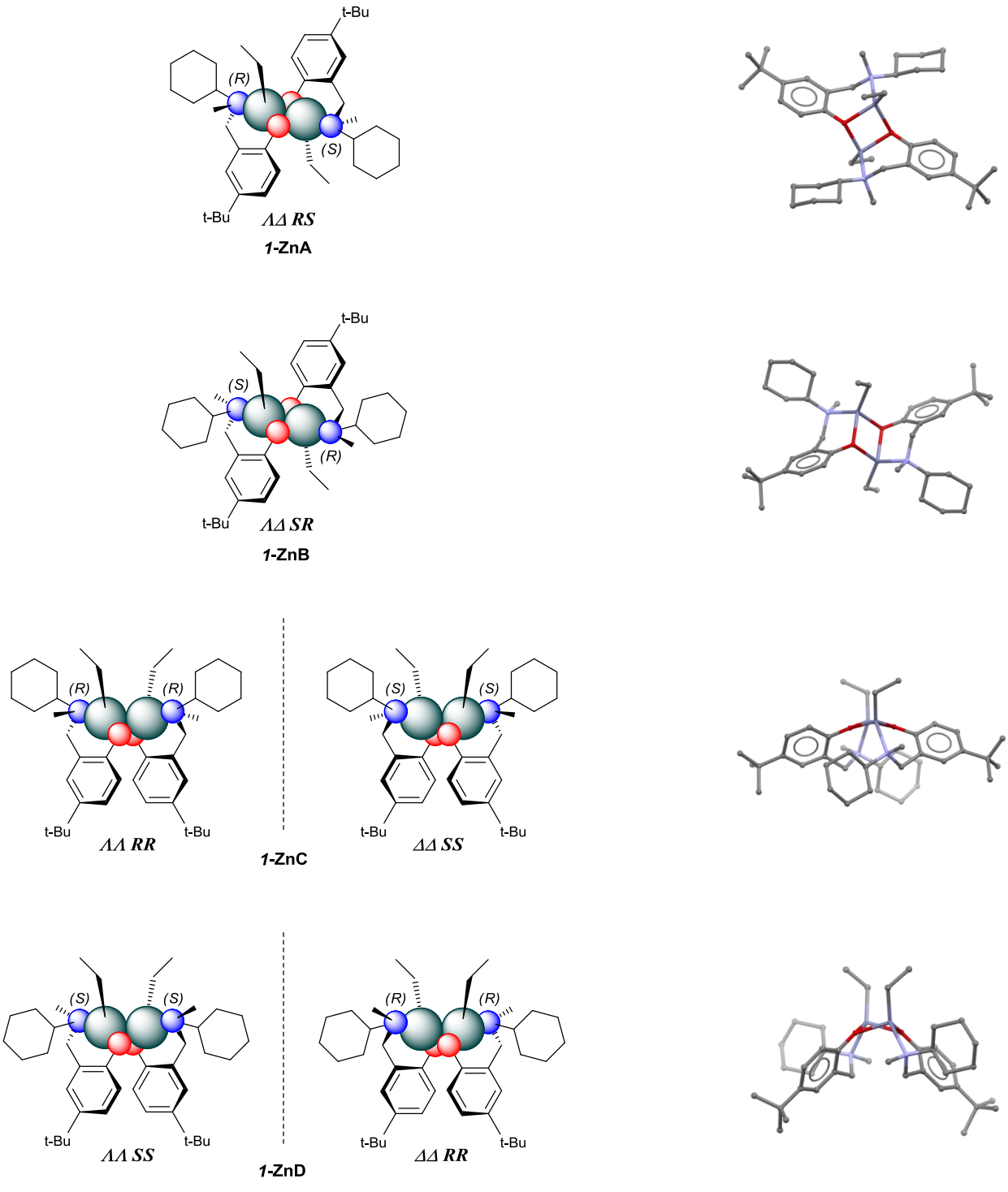


Figure S15. Structures of 1-Zn isomers (schematic on left, DFT optimised on right). Red - oxygen atoms, green – zinc atoms, blue – nitrogen atoms.

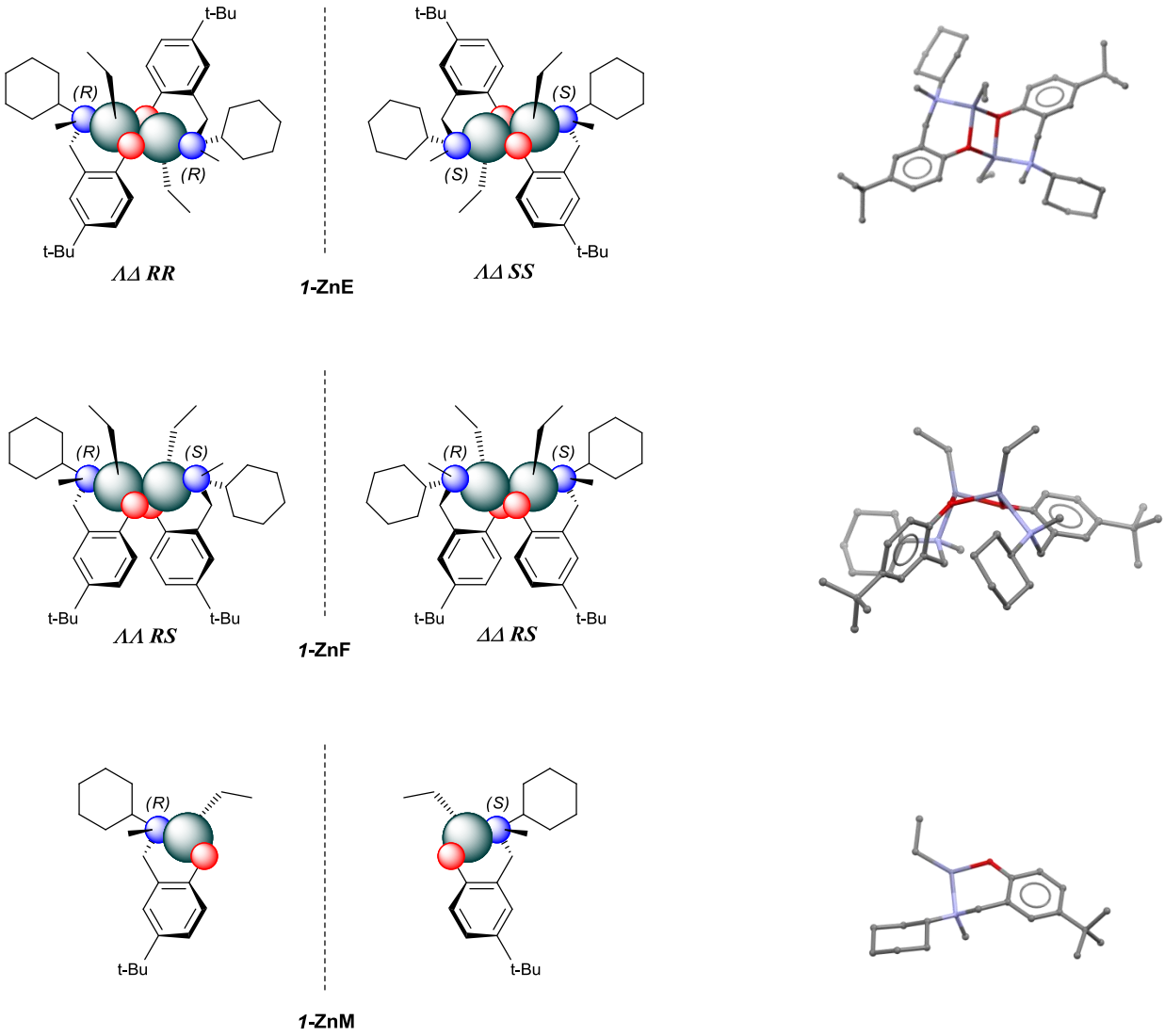
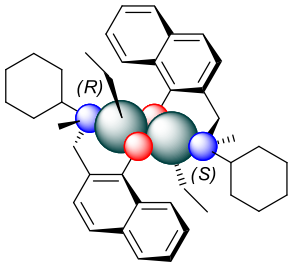
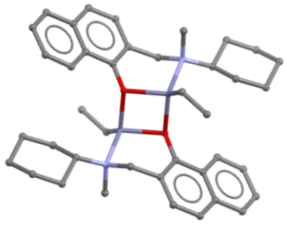


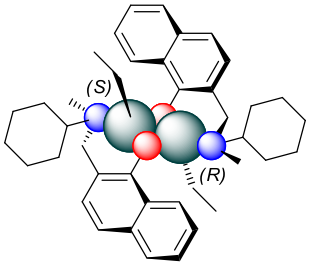
Figure S16. Structures of 1-Zn isomers (schematic on left, DFT optimised on right). Red - oxygen atoms, green – zinc atoms, blue – nitrogen atoms.



ΛΔ RS

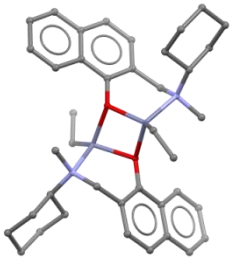
2-ZnA

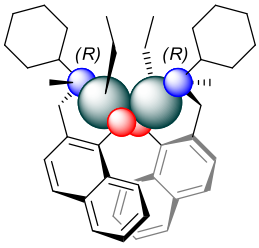




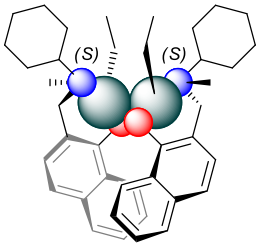
ΛΔ SR

2-ZnB



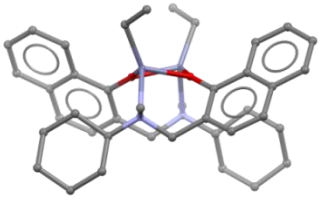


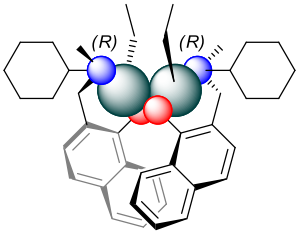
ΛΛ RR



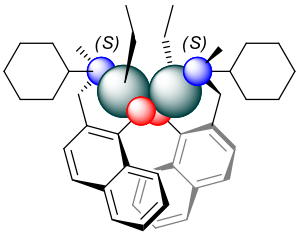
ΔΔ SS

2-ZnC





ΛΛ SS



ΔΔ RR

2-ZnD

Figure S17. Structures of 2-Zn isomers (schematic on left, DFT optimised on right). Red - oxygen atoms, green – zinc atoms, blue – nitrogen atoms.

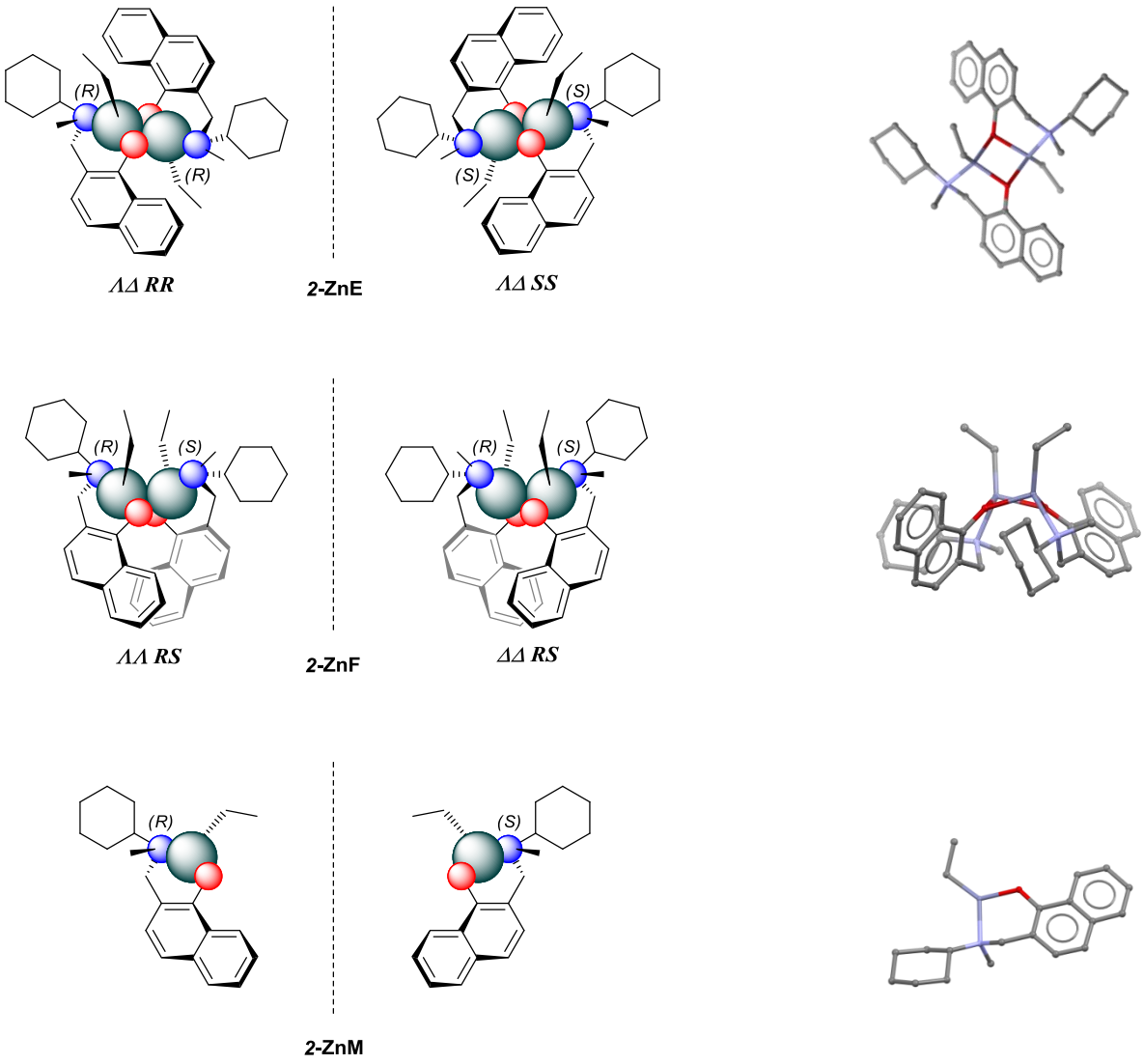


Figure S18. Structures of 2-Zn isomers (schematic on left, DFT optimised on right). Red - oxygen atoms, green – zinc atoms, blue – nitrogen atoms.

Isomer	E (hartree)	ZPE (kcal/mol)	ΔE_{zpe} (kcal/mol)	ΔE_{zpe} (kJ/mol)
1-ZnA	-5382.42180344	624.96	0.00	0.00
1-ZnB	-5382.41892115	625.57	2.42	10.12
1-ZnC	-5382.41494575	624.64	3.98	16.67
1-ZnD	-5382.40950284	625.51	8.27	34.60
1-ZnE	-5382.42055758	625.31	1.14	4.76
1-ZnF	-5382.41277518	624.68	6.39	26.72
1-ZnM	-2691.18363784	312.32	33.91*	141.87*

Table S1. Energies of 1-Zn isomers in vacuo. * - Calculated as for two monomers.

Isomer	E (hartree)	ZPE (kcal/mol)	ΔE_{zpe} (kcal/mol)	ΔE_{zpe} (kJ/mol)
1-ZnA	-5382.42621192	624.57	0.00	0.00
1-ZnB	-5382.42410797	625.13	1.89	7.89
1-ZnC	-5382.41975058	624.34	3.83	16.02
1-ZnD	-5382.41537387	625.01	7.25	30.31
1-ZnE	-5382.42534661	625.04	1.02	4.25
1-ZnF	-5382.41604745	624.23	6.04	25.27
1-ZnM	-2691.19019201	312.14	28.47*	119.12*

Table S2. Energies of 1-Zn isomers in benzene. * - Calculated as for two monomers.

Isomer	E (hartree)	ZPE (kcal/mol)	ΔE_{zpe} (kcal/mol)	ΔE_{zpe} (kJ/mol)
2-ZnA	-5375.17859388	542.72	0.00	0.00
2-ZnB	-5375.17351067	543.40	3.87	16.18
2-ZnC	-5375.17841970	543.22	0.61	2.55
2-ZnD	-5375.17551865	543.21	2.42	10.13
2-ZnE	-5375.17879653	543.17	0.32	1.33
2-ZnF	-5375.17581800	542.91	1.93	8.08
2-ZnM	-2687.56688380	271.04	27.49*	115.03*

Table S3. Energies of 2-Zn isomers in vacuo. * - Calculated as for two monomers.

Isomer	E (hartree)	ZPE (kcal/mol)	ΔE_{zpe} (kcal/mol)	ΔE_{zpe} (kJ/mol)
2-ZnA	-5375.18393686	542.98	0.00	0.00
2-ZnB	-5375.17894190	543.14	3.30	13.79
2-ZnC	-5375.18500575	542.46	-1.19	-4.99
2-ZnD	-5375.18164746	542.70	1.16	4.85
2-ZnE	-5375.18459013	543.14	-0.25	-1.04
2-ZnF	-5375.18312827	543.21	0.74	3.08
2-ZnM	-2687.57438737	271.25	21.58*	90.29*

Table S4. Energies of 2-Zn isomers in benzene. * - Calculated as for two monomers.

	1-Zn	2-Zn
Atoms Bond distance [Å]		
Zn1-C21	1.98264	1.98538
Zn2-C51		1.98540
Zn1-O1	2.03333	2.04486
Zn2-O2		2.04478
Zn1-O1^{i}	2.04557	2.05718
Zn2-O1		2.05719
Zn1-N1	2.15964	2.16995
Zn2-N2	3.09025	2.16998
Zn1-Zn1^{i,a}		3.11647
O1-O1^{i,a}	2.66231	2.66726
Angels [°]		
C21-Zn1-O1	125.62147	122.91299
C51-Zn2-O2		122.91459
C21-Zn1-O1^{i}	123.46471	124.10730
C51-Zn2-O1		124.10851
O1-Zn1-O1^{i}	81.49095	81.11679
O1-Zn2-O2		81.11842
C21-Zn1-N1	120.65228	119.80570
C51-Zn2-N2		119.80109
O1-Zn1-N1	94.73689	93.24436
O2-Zn2-N2		93.24681
O1^{i}-Zn1-N1	101.66471	106.17646
O1-Zn2-N2		106.17681
Zn1-O1-Zn1^{i}	98.50904	98.88093
Zn1-O2-Zn2		98.88386
Sum of the interior angles of the core Zn_2O_2 [°]		
	360	360

Table S5. Selected bond distances (Å) and angles (°) for DFT optimised structures. i = −x+2, −y+1, −z+1 for 1-Zn, O1^{i} = O2, Zn1^{i} = Zn2 for 2-Zn.
[a] Values in parentheses are for the non-bonding interactions

Species	E (hartree)	ZPE (kcal/mol)
$(LZnEt)_2$	-5382.42180330	624.96
L_2Zn	-3444.80488859	543.62
LZnEt	-2691.18298810	312.16
$ZnEt_2$	-1937.56317687	81.05

Table S6. Energies of zinc species with L^1.

System	E (hartree)	ZPE (kcal/mol)	ΔE_{zpe} (kcal/mol)	ΔE_{zpe} (kJ/mol)
$(LZnEt)_2$	-5382.42180330	624.96	0.00	0.00
$L_2Zn + ZnEt_2$	-5382.36806546	624.67	33.43	139.87
2 LZnEt	-5382.36597620	624.31	34.38	143.87

Table S7. Energies of possible equilibrium systems for L^1 compounds.

Species	E (hartree)	ZPE (kcal/mol)
$(LZnEt)_2$	-5375.17859388	542.72
L_2Zn	-3437.57137820	460.99
LZnEt	-2687.56688380	271.04
$ZnEt_2$	-1937.56317687	81.05

Table S8. Energies of zinc species with L^2.

System	E (hartree)	ZPE (kcal/mol)	ΔE_{zpe} (kcal/mol)	ΔE_{zpe} (kJ/mol)
$(LZnEt)_2$	-5375.17859388	542.72	0.00	0.00
$L_2Zn + ZnEt_2$	-5375.13455507	542.03	26.95	112.76
2 LZnEt	-5375.13376760	542.09	27.49	115.03

Table S9. Energies of possible equilibrium systems for L^2 compounds.

Species	E (hartree)	ZPE (kcal/mol)
$(LZnEt)_2$	-5696.88434049	765.78
L_2Zn	-3759.32401891	684.55
LZnEt	-2848.44346254	382.93
$ZnEt_2$	-1937.56317687	81.05

Table S10. Energies of zinc species with L^3.

System	E (hartree)	ZPE (kcal/mol)	ΔE_{zpe} (kcal/mol)	ΔE_{zpe} (kJ/mol)
$L_2Zn + ZnEt_2$	-5696.88719578	765.60	0.00	0.00
2 LZnEt	-5696.88692508	765.86	0.43	1.80
$(LZnEt)_2$	-5696.88434049	765.78	1.97	8.26

Table S11. Energies of possible equilibrium systems for L^3 compounds.

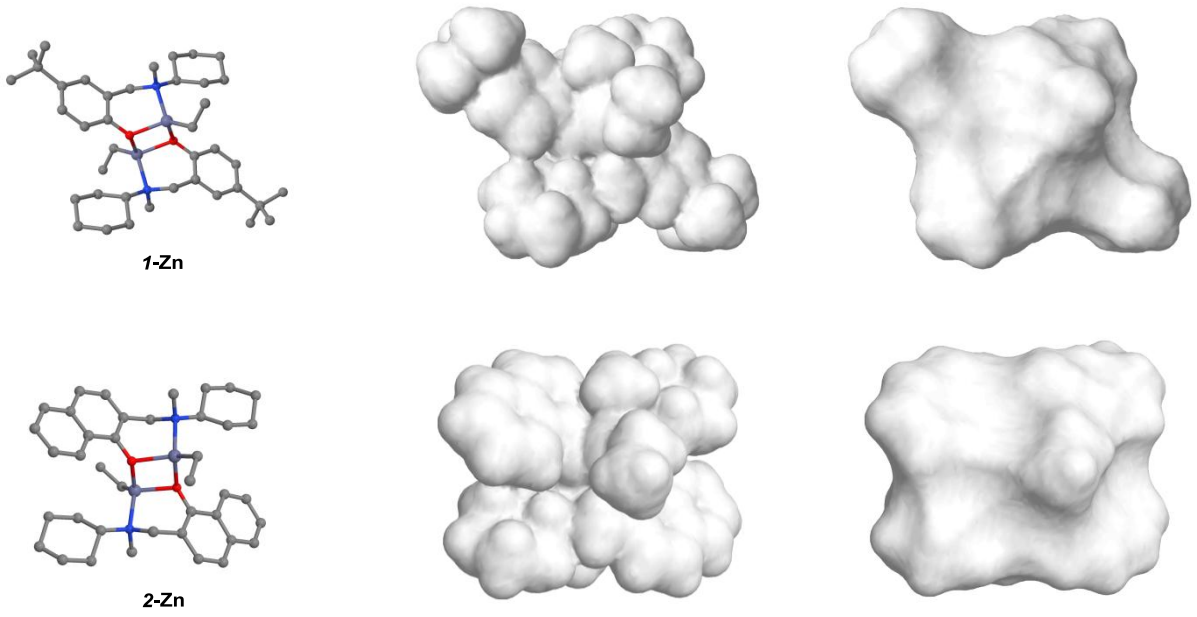


Figure S19. Van der Waals and Connolly surfaces generated around solid-state structures of 1-Zn with probe radius 2.7Å.

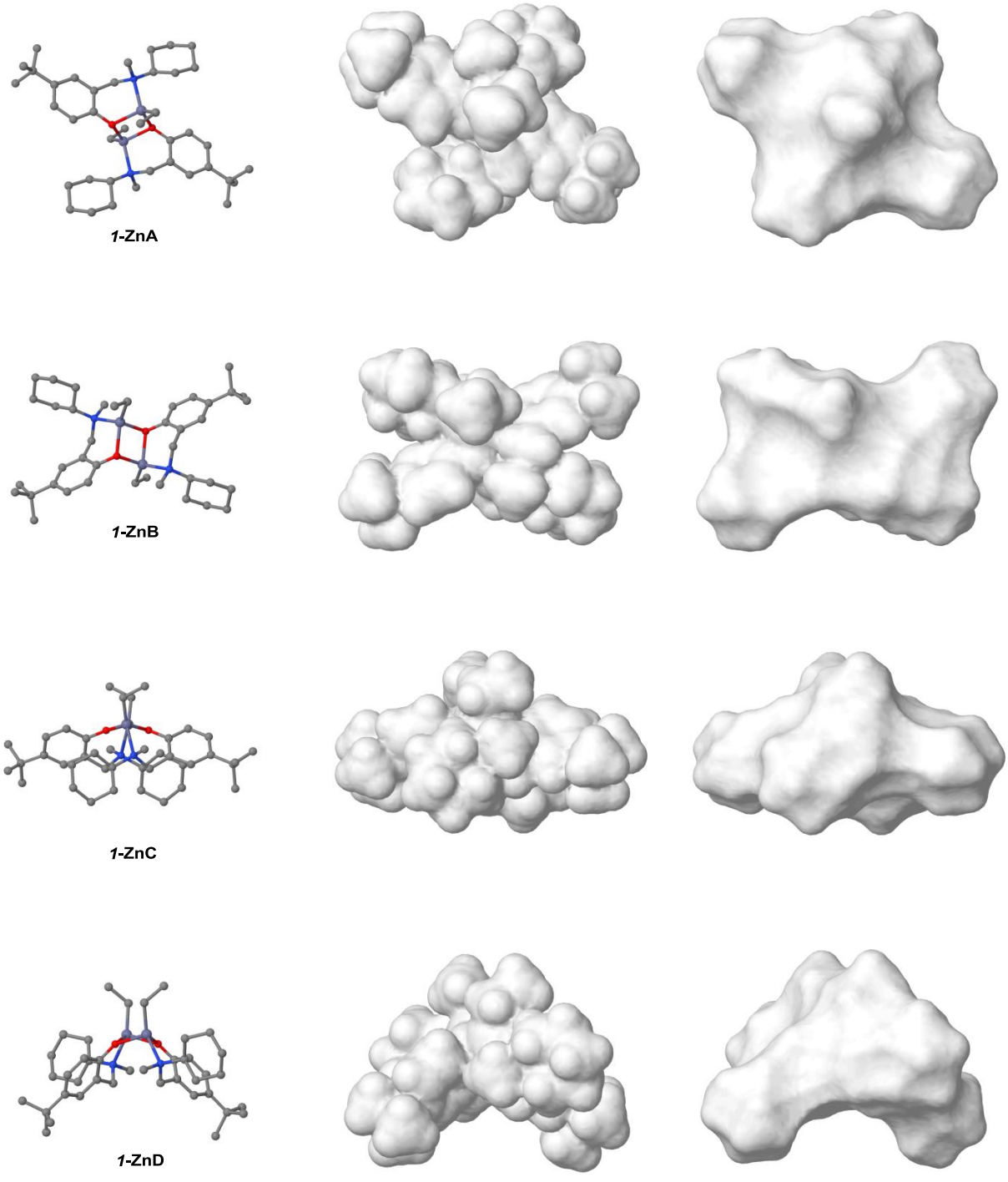


Figure S20. Van der Waals and Connolly surfaces generated around DFT optimised structures of 1-Zn with probe radius 2.7Å.

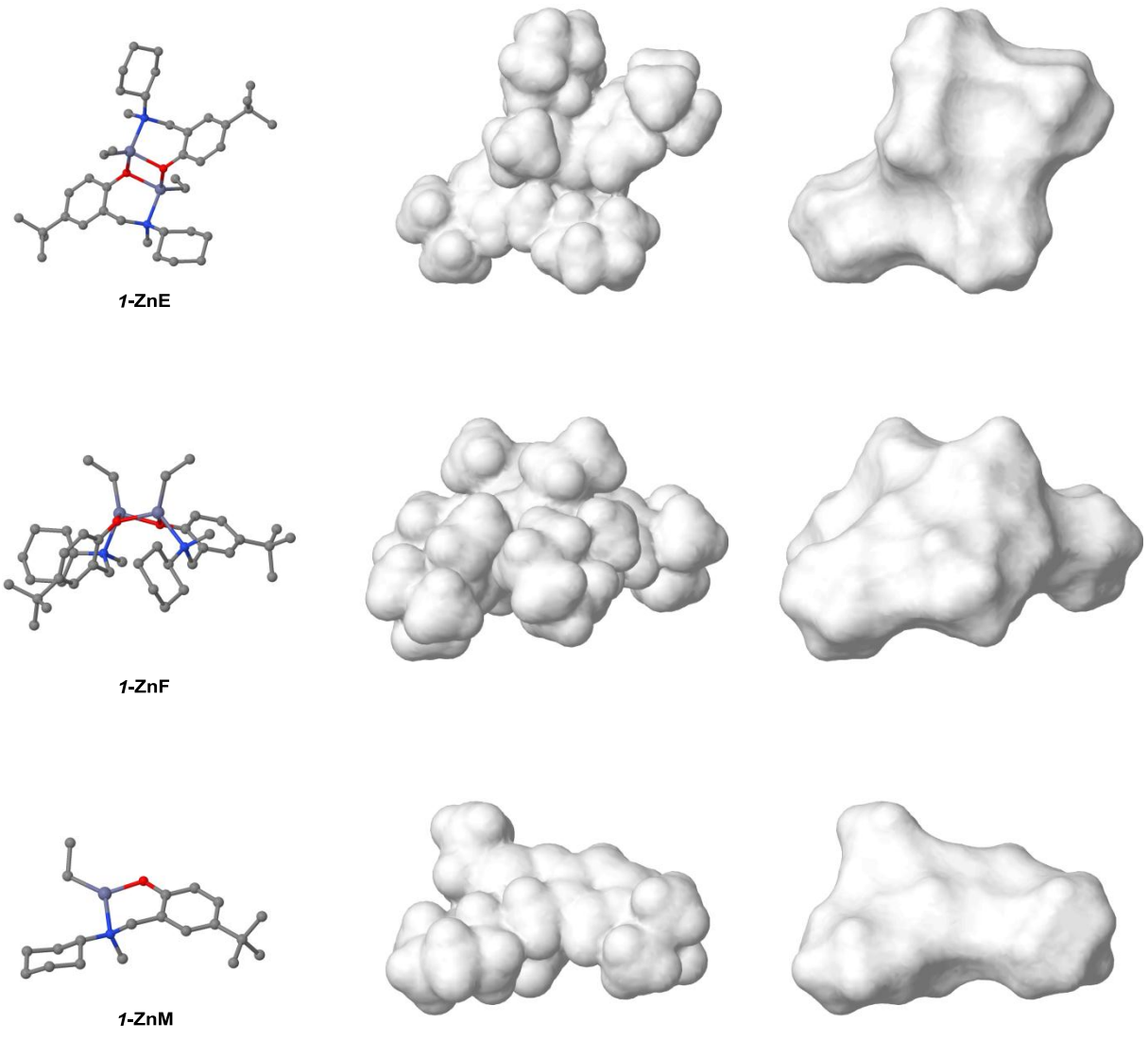


Figure S21. Van der Waals and Connolly surfaces generated around DFT optimised structures of 1-Zn, with probe radius 2.7Å.

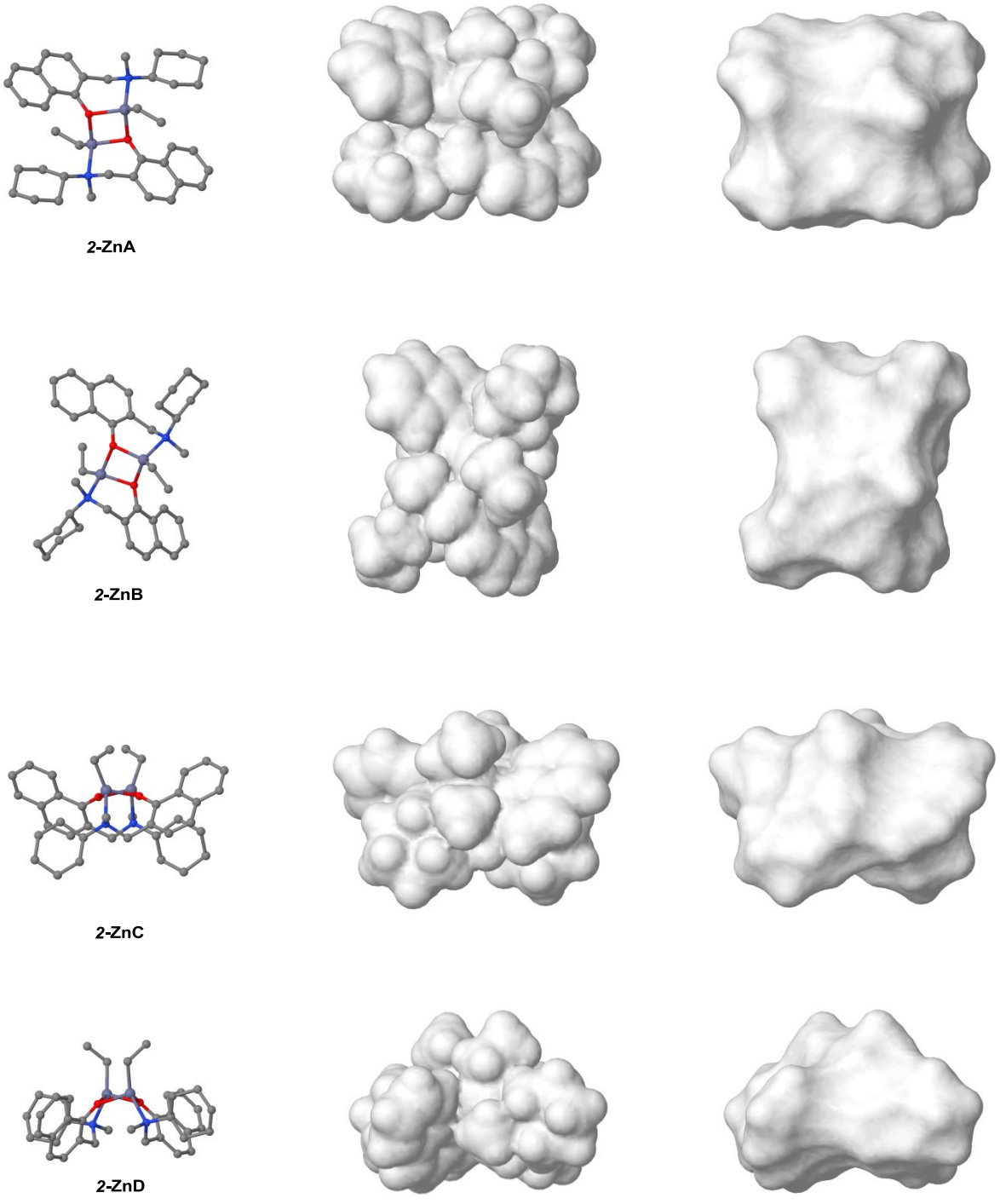


Figure S22. Van der Waals and Connolly surfaces generated around DFT optimised structures of 2-Zn with probe radius 2.7Å.

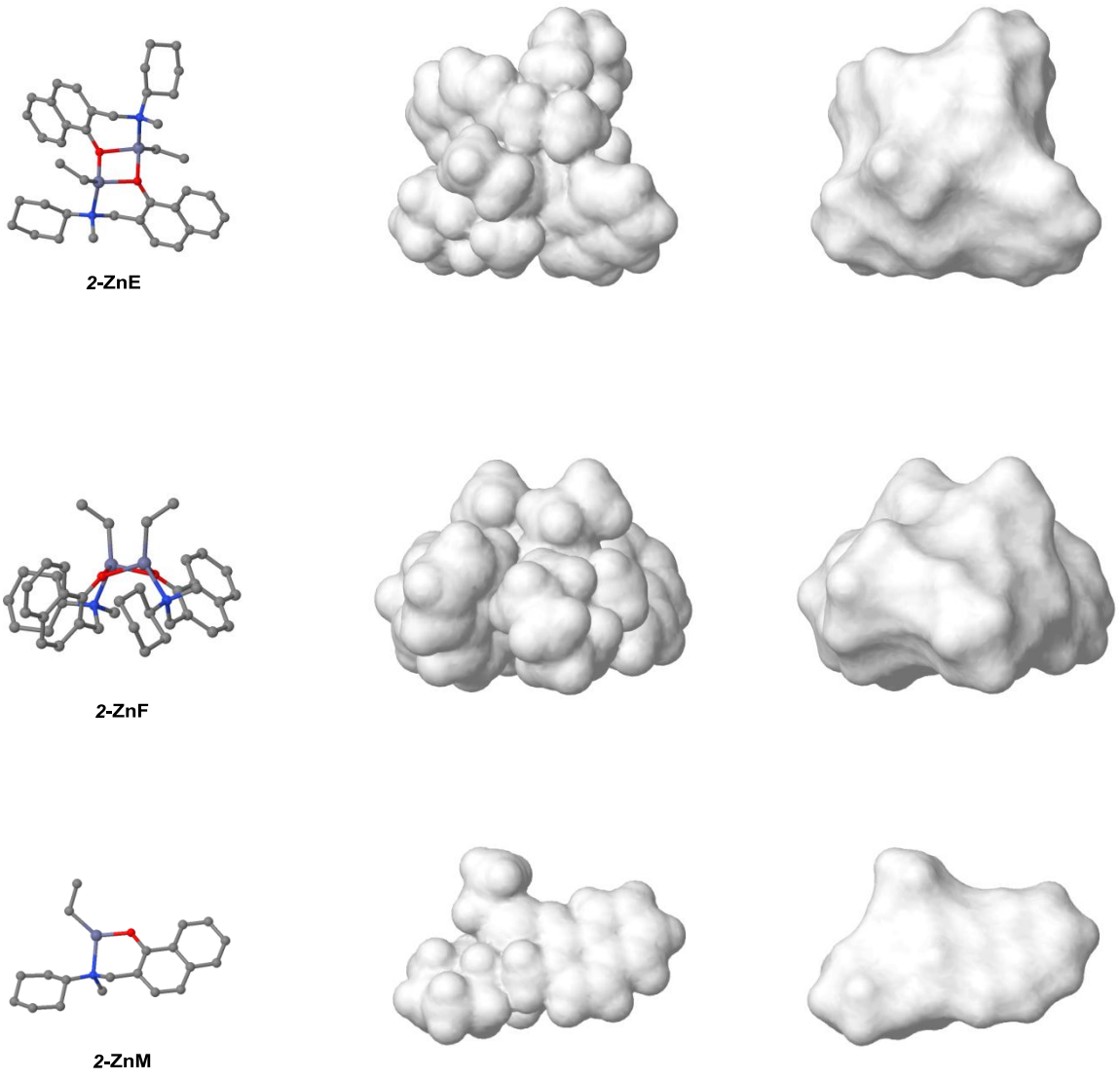


Figure S23. Van der Waals and Connolly surfaces generated around DFT optimised structures of 2-Zn with probe radius 2.7Å.

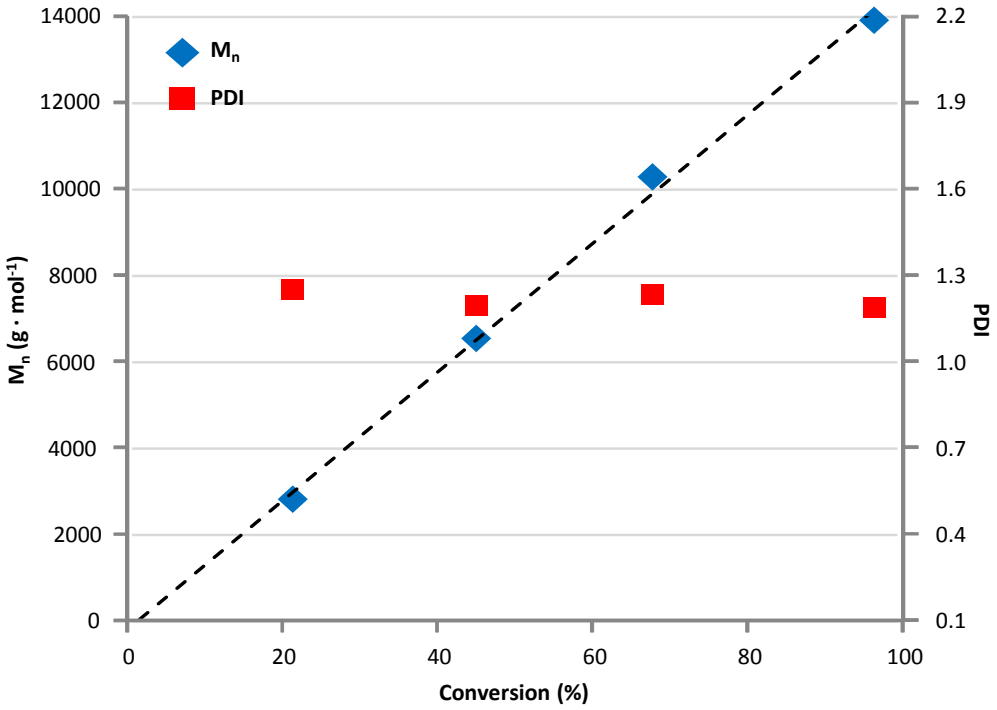


Figure S24. Dependence of M_n and PDI [M_w/M_n] of PLA versus monomer (*L*-LA) conversion with 1-Zn as a catalyst. Reaction conditions: [*L*-LA]/[Zn] = 100, CH_2Cl_2, room temp..

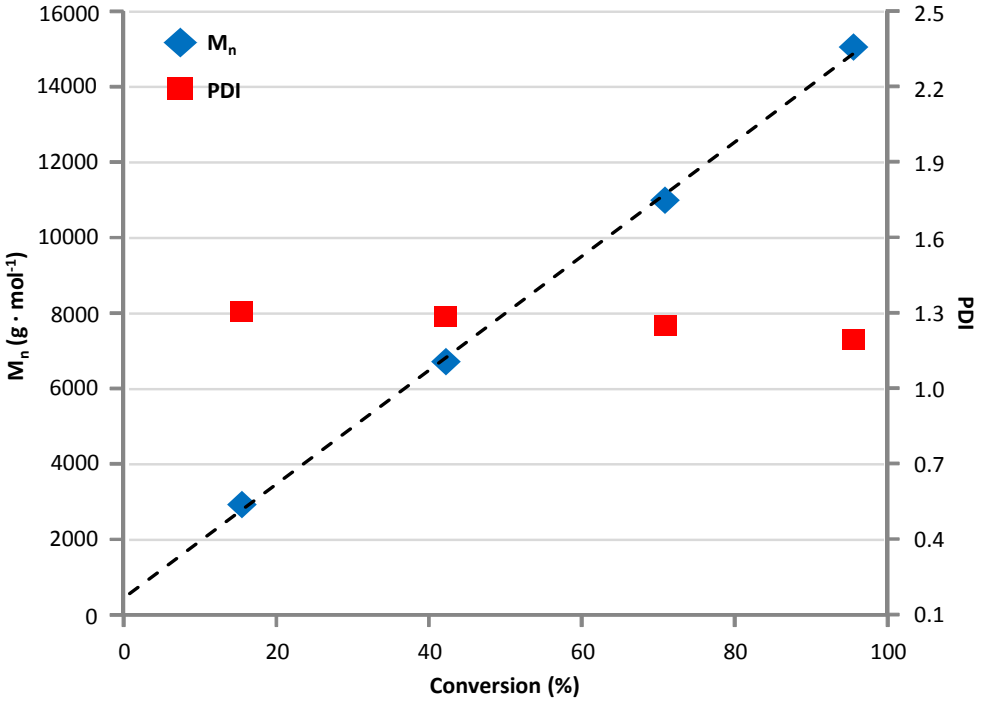


Figure S25. Dependence of M_n and PDI [M_w/M_n] of PLA versus monomer (*L*-LA) conversion with 2-Zn as a catalyst. Reaction conditions: [*L*-LA]/[Zn] = 100, CH_2Cl_2, room temp..

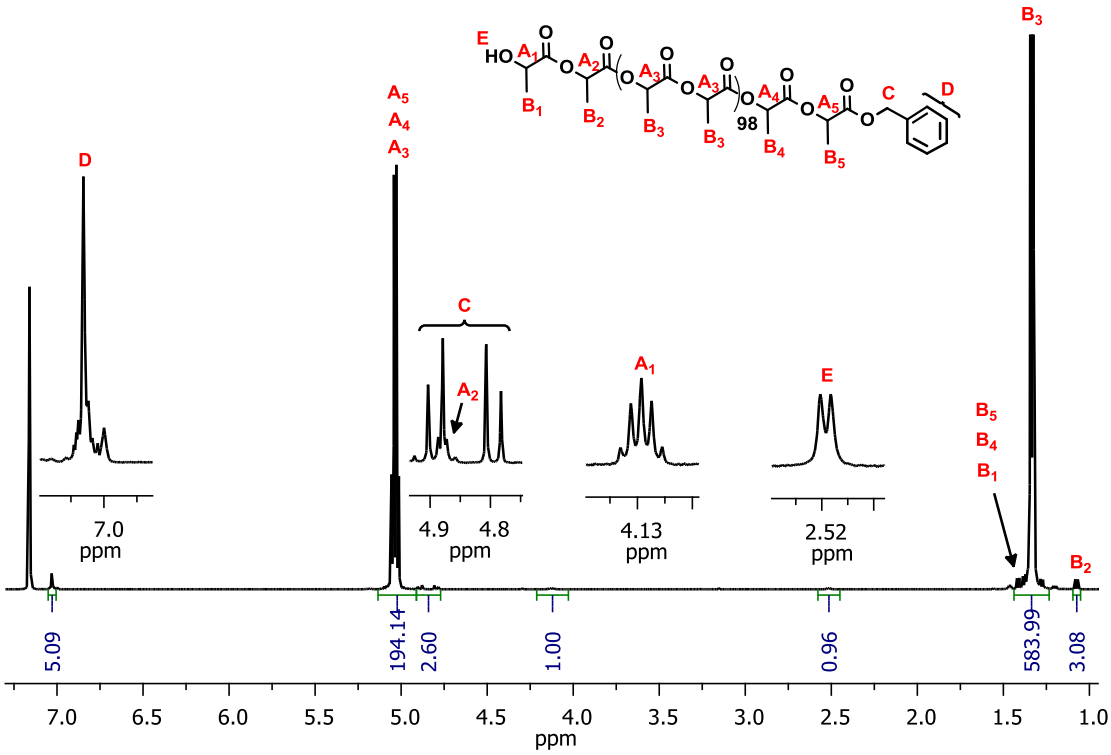


Figure S26. ^{1}H NMR spectrum of Bn-100-PLA obtained with 1-Zn/BnOH catalytic system in benzene-d_6 (Entry no. 2, Table 3).

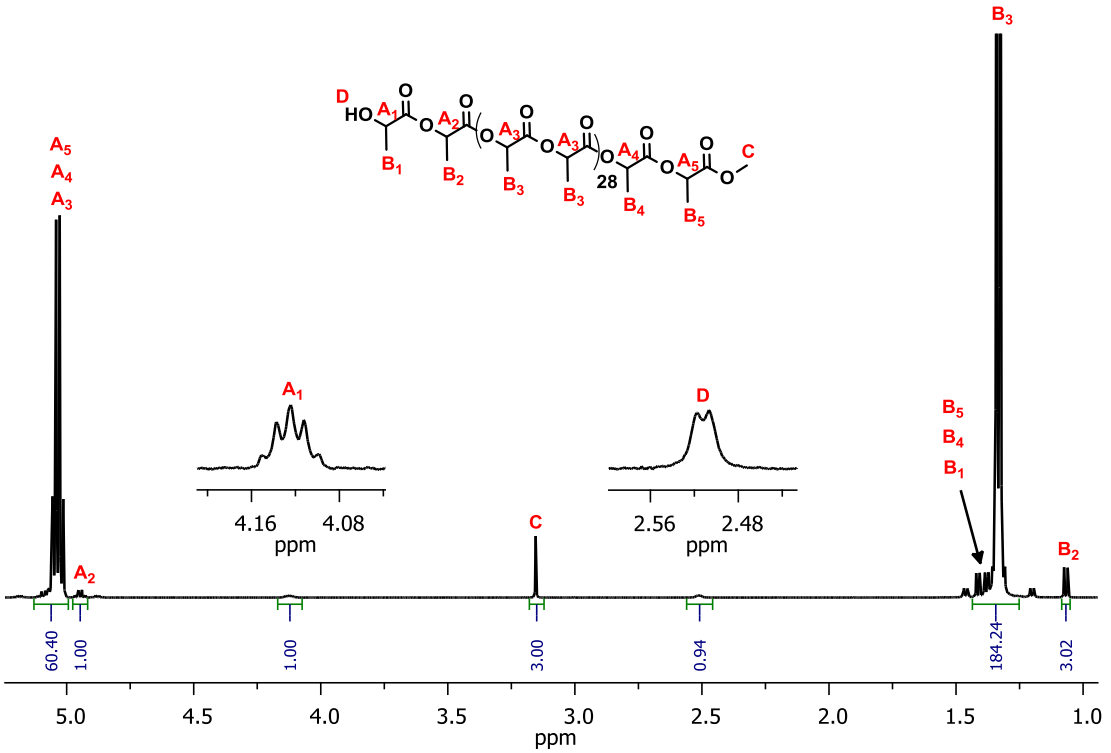


Figure S27. ^{1}H NMR spectrum of Met-30-PLA obtained with 2-Zn/MeOH catalytic system in benzene-d_6 (Entry no. 8, Table 3).

	1-Zn	2-Zn	L^1H
Empirical formula	$C_{40}H_{66}N_2O_2Zn_2$	$C_{40}H_{54}N_2O_2Zn_2$	$C_{18}H_{29}NO$
Formula weight	737.68	725.59	275.42
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	C2/c	$Pna2_1$	$P2_1/n$
a (Å)	15.827 (6)	15.727 (9)	6.519 (5)
b (Å)	12.689 (2)	13.996 (7)	26.13 (2)
c (Å)	20.032 (7)	15.894 (9)	9.596 (6)
α (°)	90	90	90
β (°)	109.81 (3)	90	94.95 (4)
γ (°)	90	90	90
V (Å^3)	3785 (2)	3498 (3)	1629 (2)
Z	4	4	4
Crystal description	Block, colourless	Needle, colourless	Needle, colourless
Crystal size (mm)	0.50 × 0.35 × 0.13	0.29 × 0.12 × 0.10	0.55 × 0.12 × 0.10
d_{calc} (g/cm^3)	1.295	1.378	1.123
μ (mm^{-1})	1.82	1.41	0.07
F(000)	1584	1536	608
Diffractometer	Xcalibur, CCD onyx	Kuma KM-4 CCD	Xcalibur, CCD Ruby
λ (Å)	8.1956, (Cu)	0.71073 (Mo)	0.71073 (Mo)
T (K)	100	100	100
Θ min/max (°)	4.6/87.7	2.9/28.6	3.1/28.7
h, k, l min/max	-19/19, -8/15, -25/25	-16/21, -17/18, -18/21	-8/8, -35/18, -12/7
Reflections collected	12072	14620	7481
Independent reflections	3904	6636	3700
Reflections [I>2σ(I)]	3692	3761	2818
R (int.)	0.038	0.076	0.24
data/restraints/params	3904/0/213	6636/1/419	3700/0/189
R[F^2 > 2σ(F^2)]	0.049	0.066	0.049
wR(F^2)	0.143	0.158	0.109
GooF	1.16	0.89	1.04
$\Delta\rho_{max}/\Delta\rho_{min}$ (e·Å^{-3})	0.69/-1.02	2.88/-0.87	0.34/-0.25

Table S12. X-ray experimental data and refinement.