Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Zebra reaction or the recipe for heterodimeric zinc complexes synthesis

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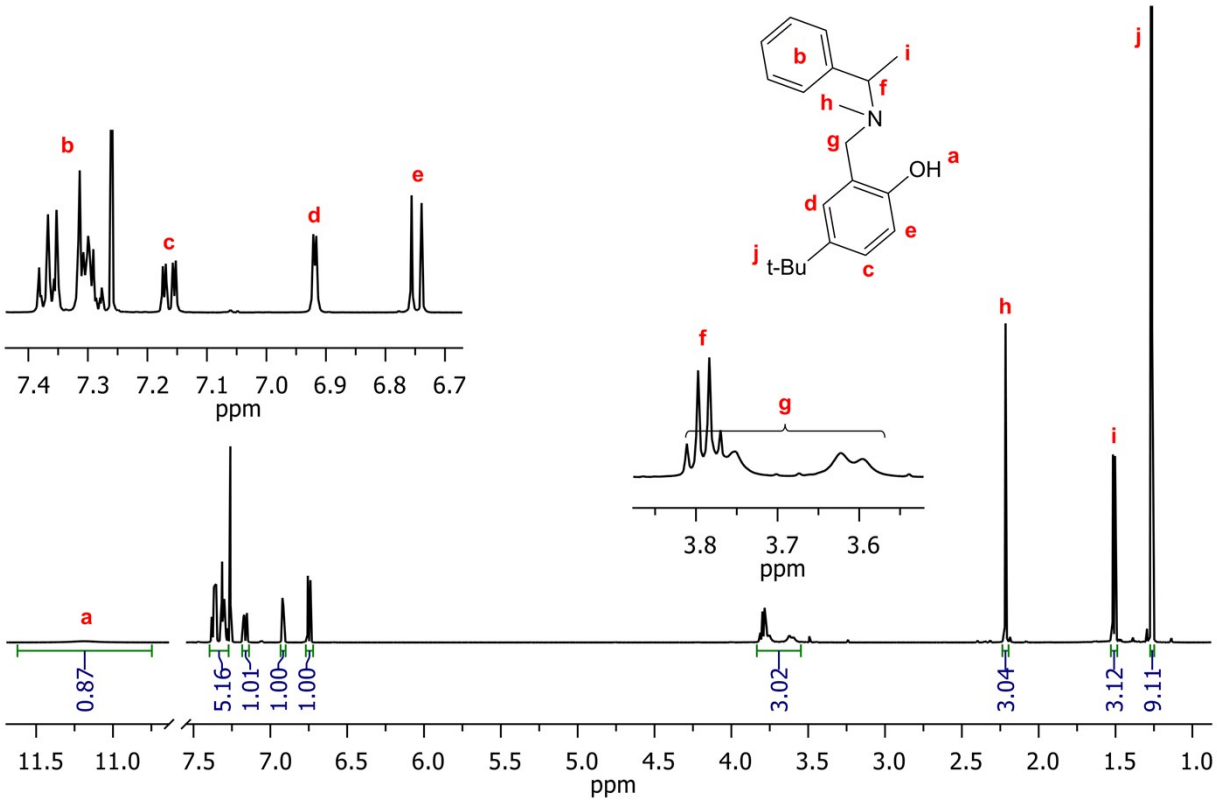


Figure S1. ^{1}H NMR of L^{R}-H in $CDCl_3$.

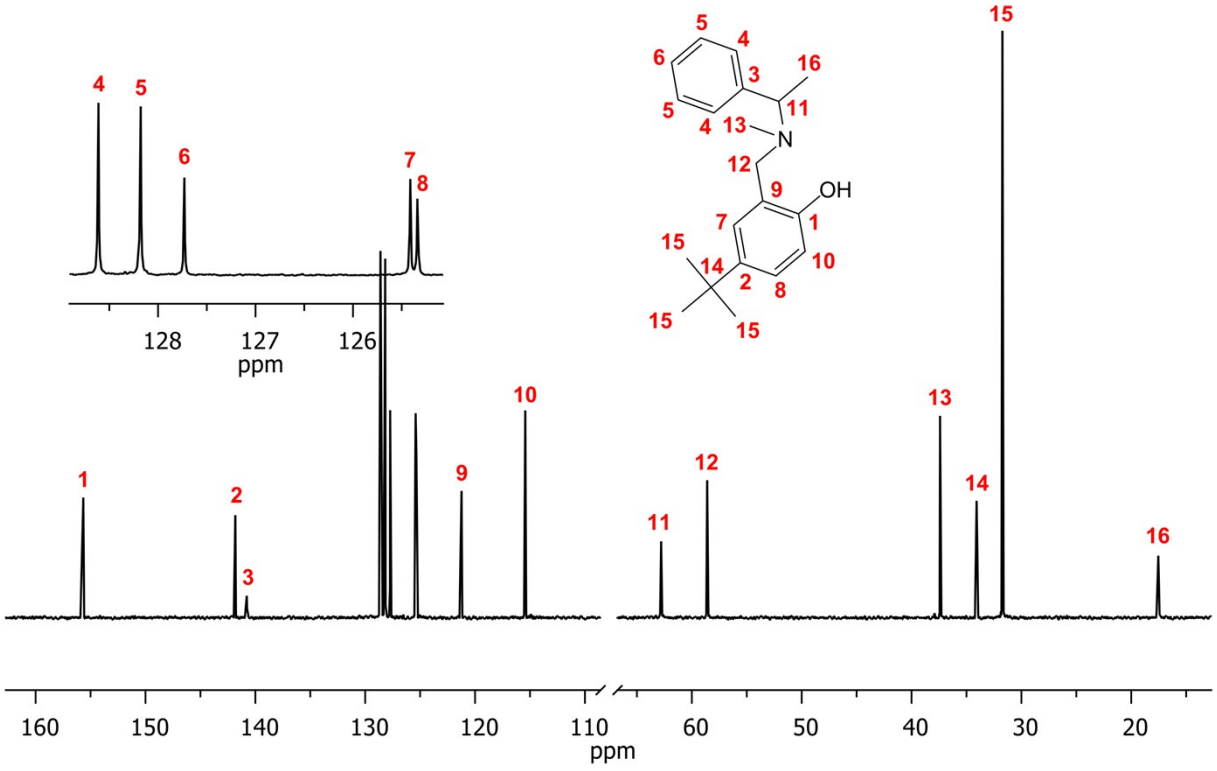


Figure S2. ^{13}C NMR of L^{R}-H in $CDCl_3$.

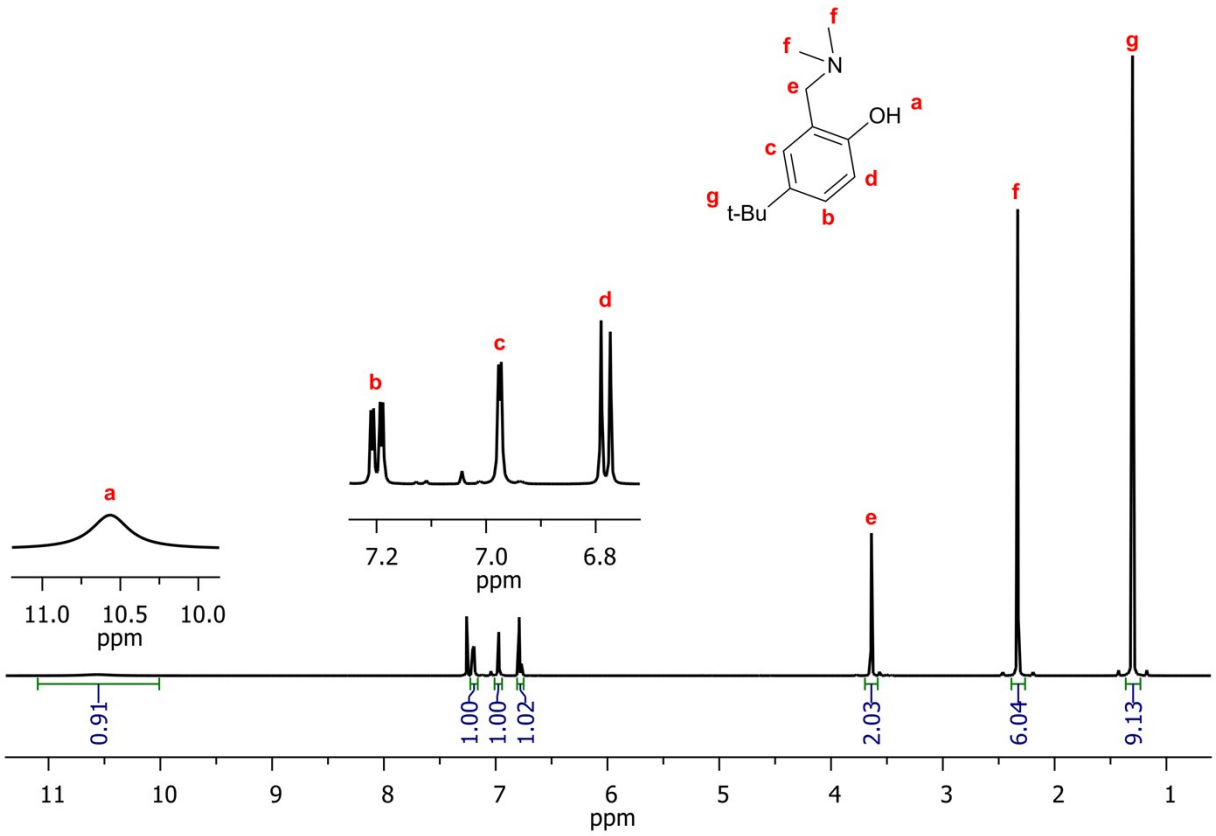


Figure S3. ^{1}H NMR of L^{Me}-H in $CDCl_3$.

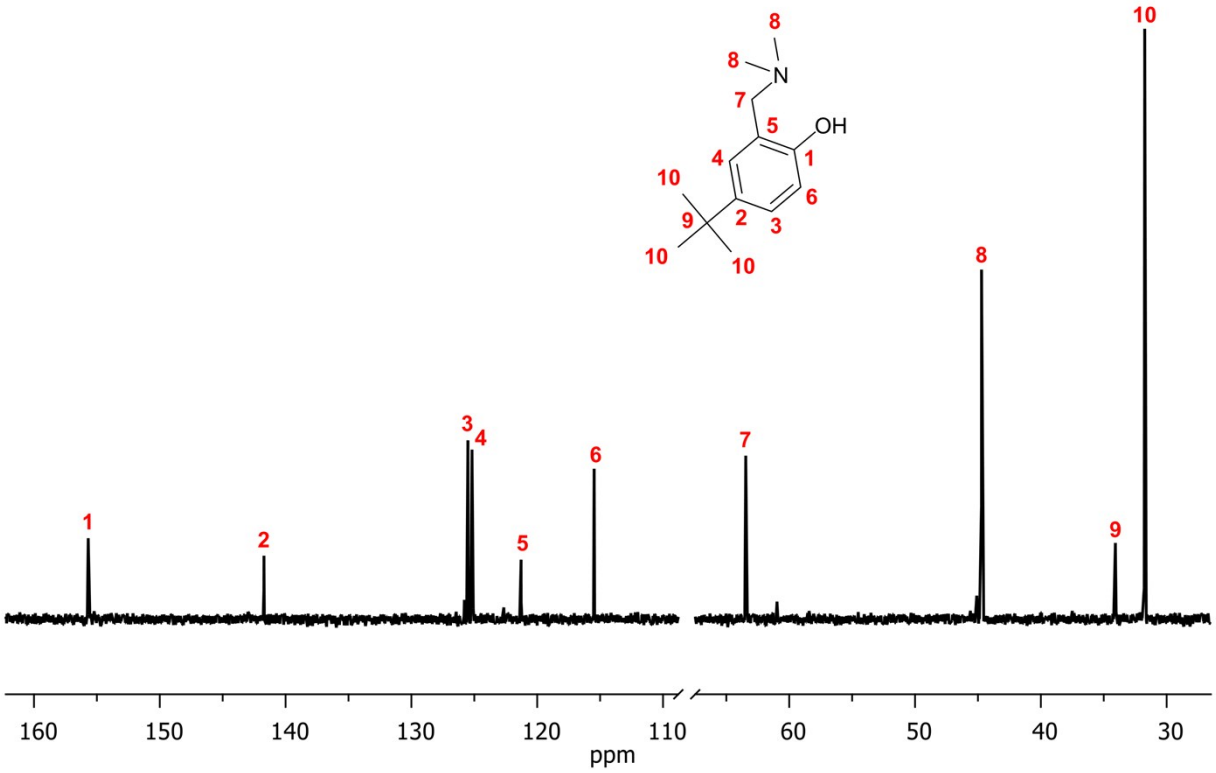


Figure S4. ^{13}C NMR of L^{Me}-H in $CDCl_3$.

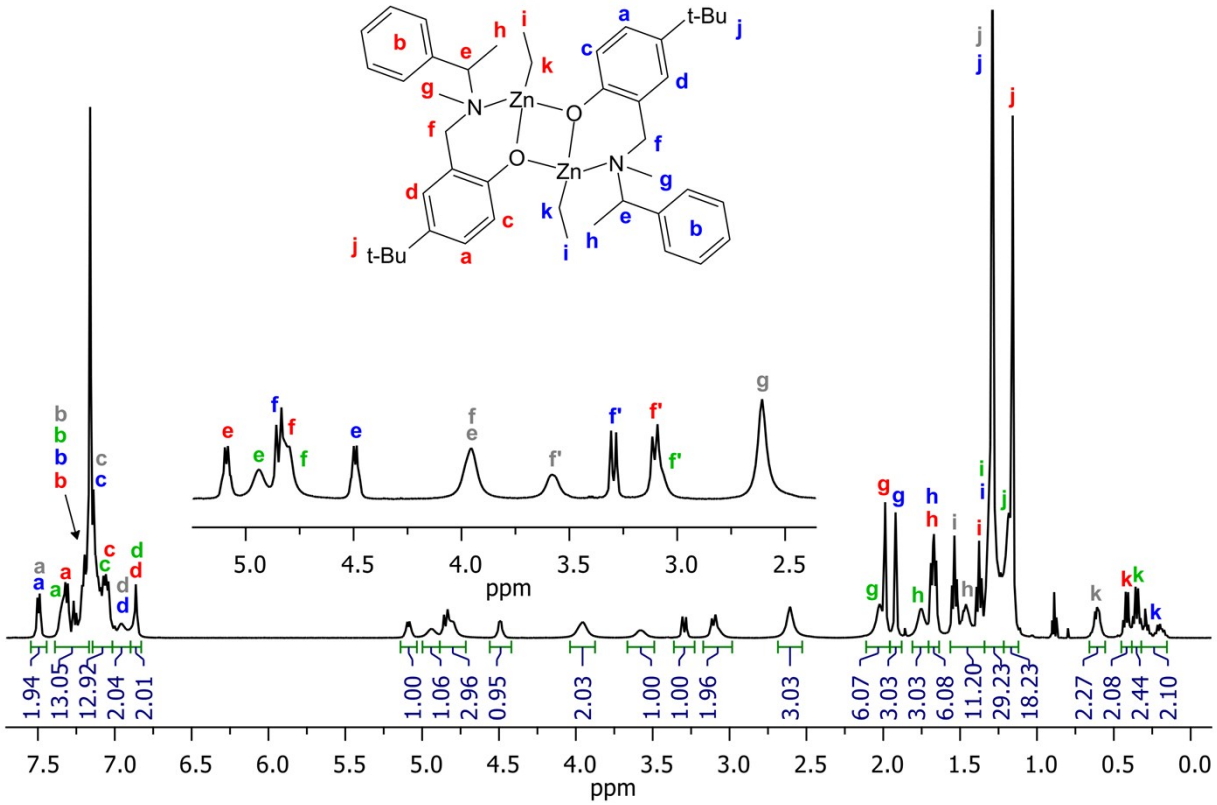


Figure S5. ^{1}H NMR of *RR*-Zn in benzene-d_6. Assigments based on DFT studies (**Table S5**).

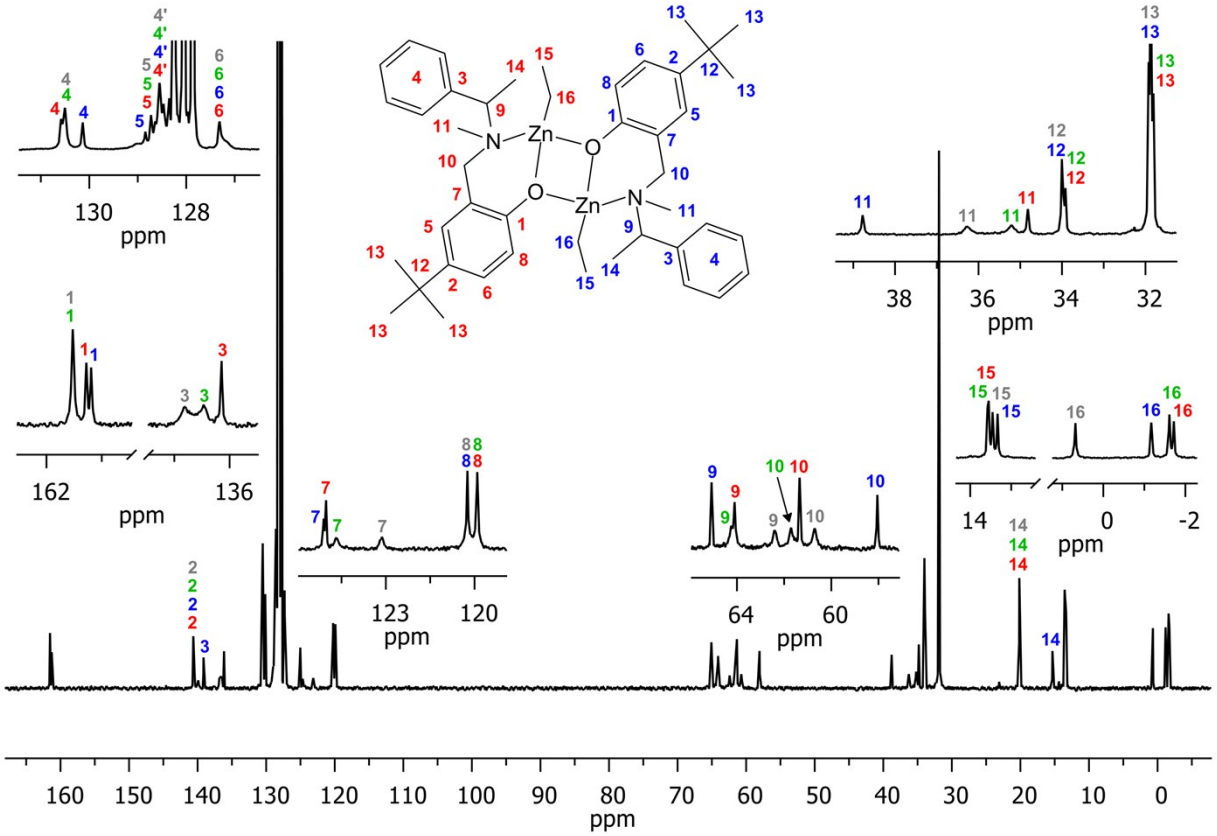


Figure S6. ^{13}C NMR of *RR*-Zn in benzene-d_6.

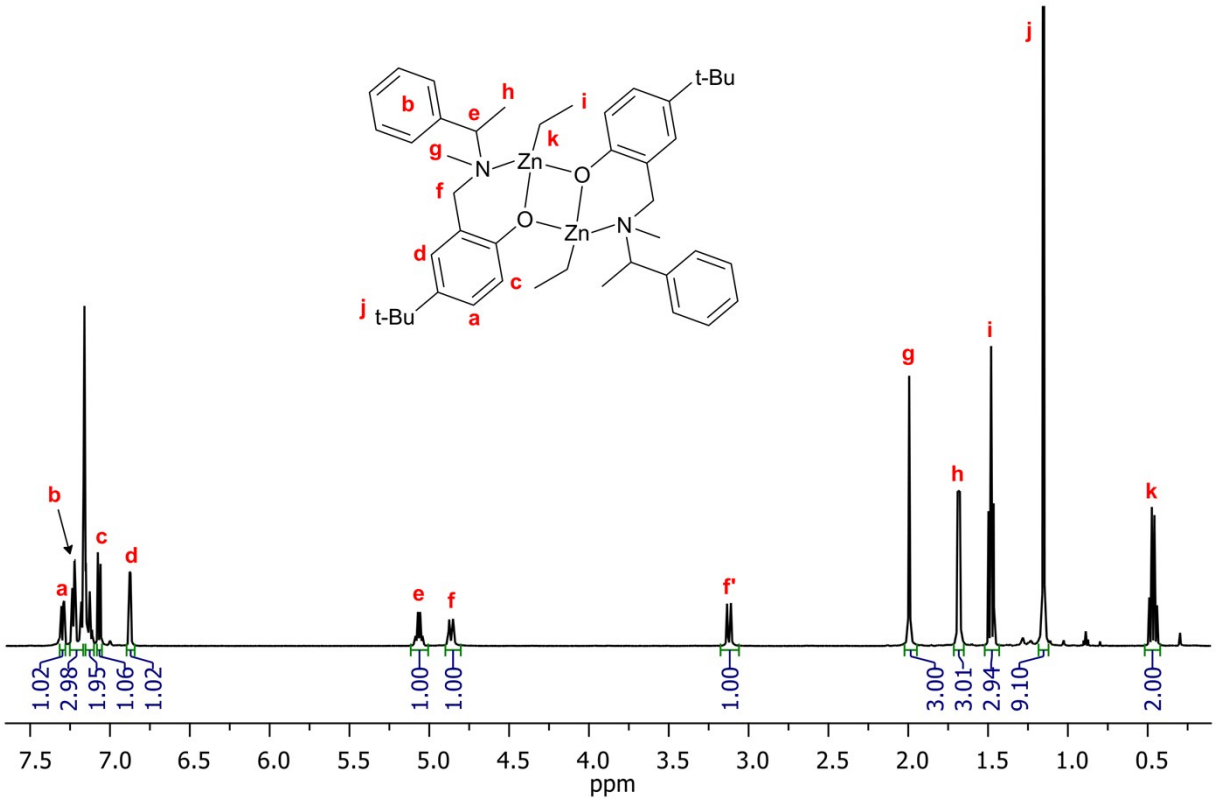


Figure S7. ^{1}H NMR of *RS*-Zn in benzene-d_6.

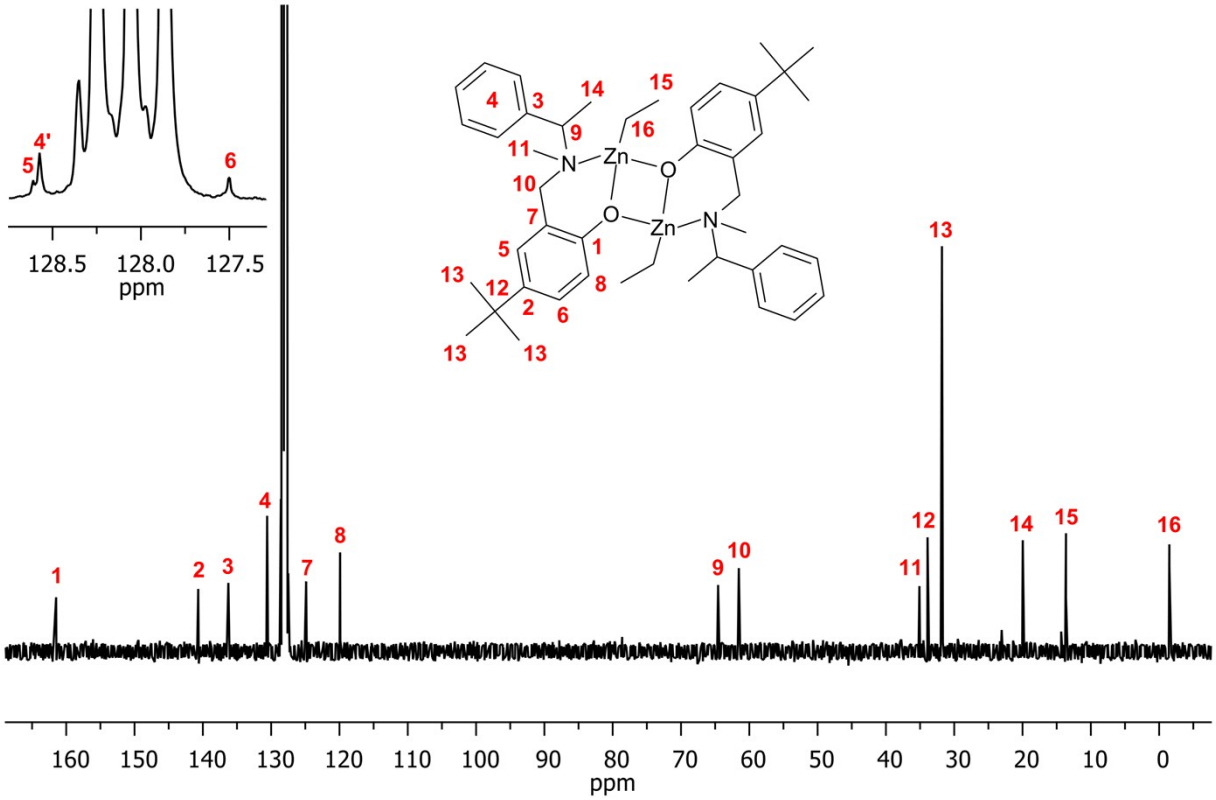


Figure S8. ^{1}H NMR of *RS*-Zn in benzene-d_6.

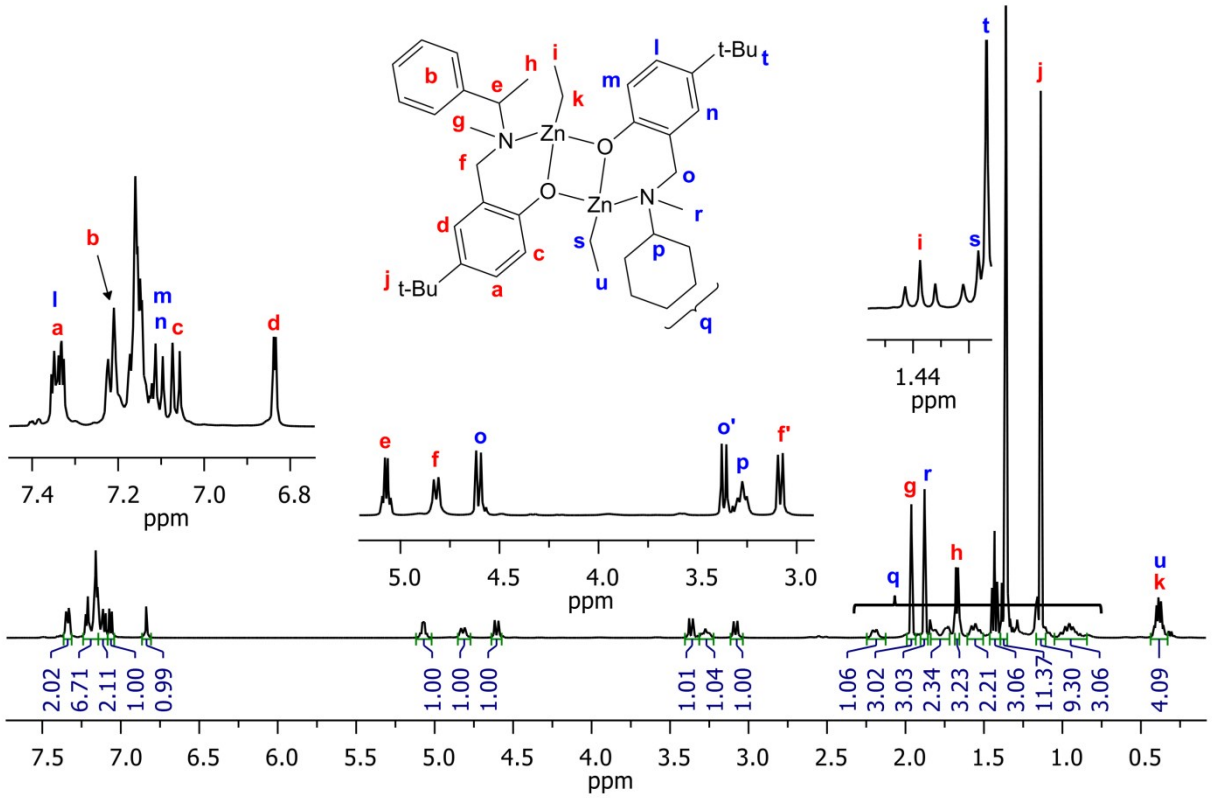


Figure S9. ^{1}H NMR of *RCy*-Zn in benzene-d_6.

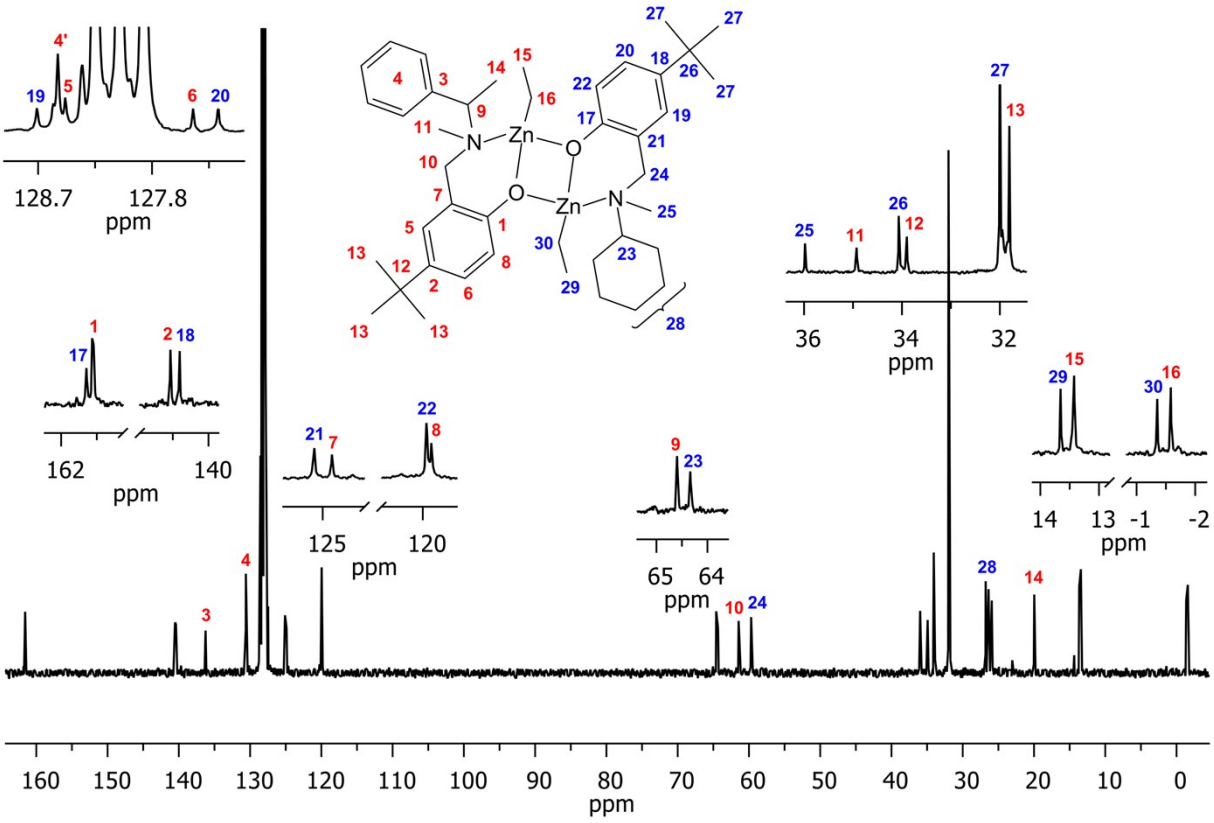


Figure S10. ^{13}C NMR of *RCy*-Zn in benzene-d_6.

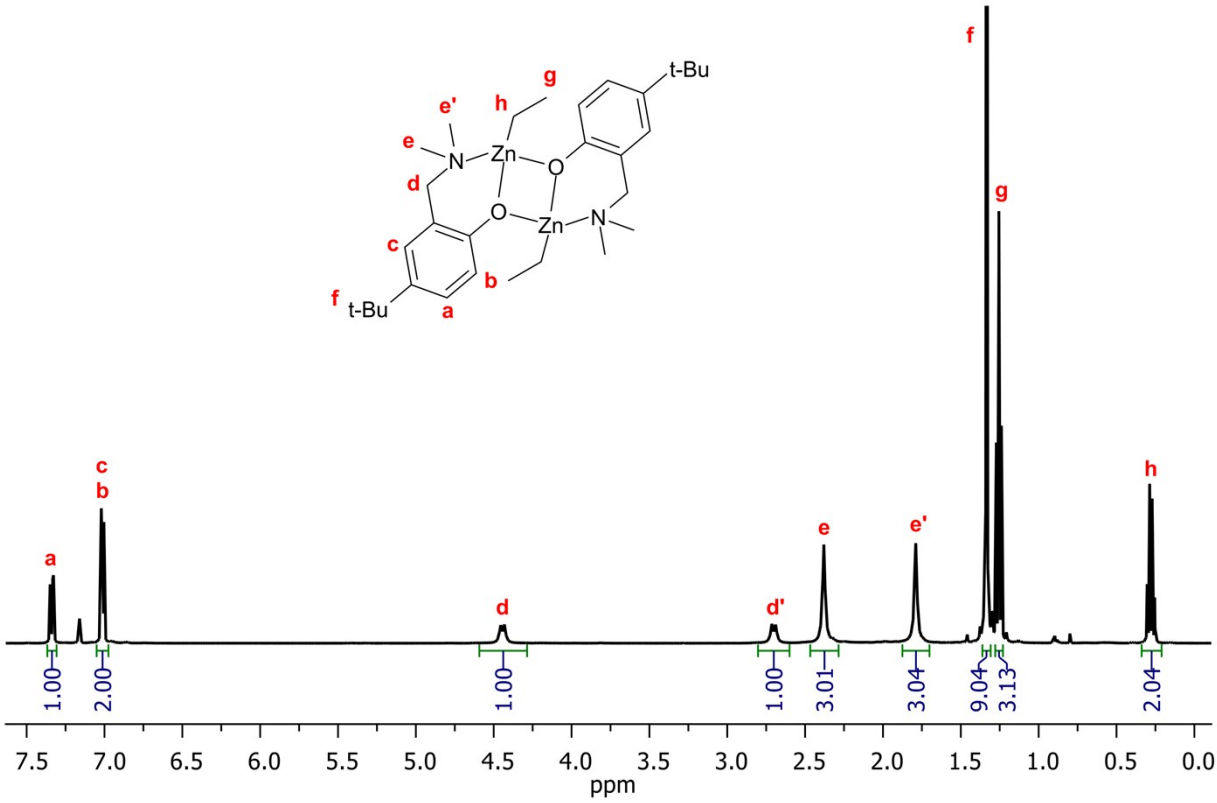


Figure S11. ^{1}H NMR of *Me*-Zn in benzene-d_6.

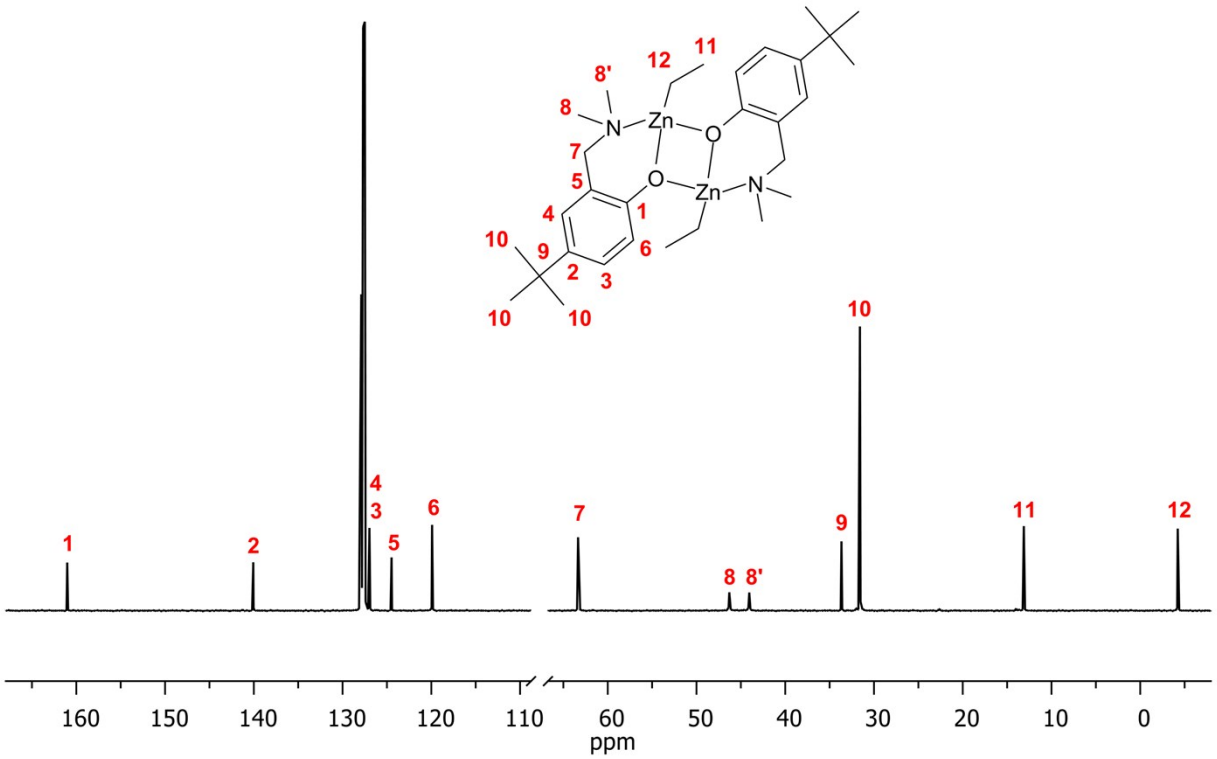


Figure S12. ^{13}C NMR of *Me*-Zn in benzene-d_6.

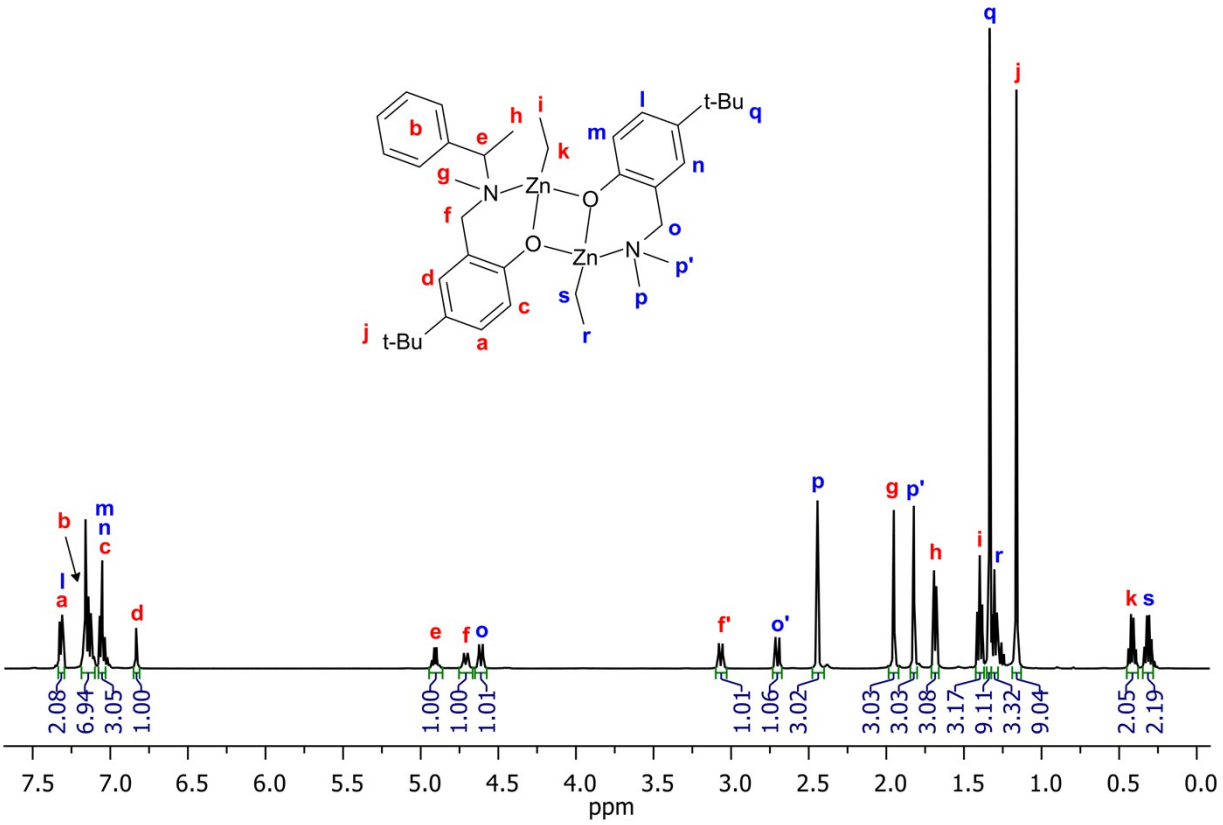


Figure S13. ^{1}H NMR of *RMe*-Zn in benzene-d$_6$.

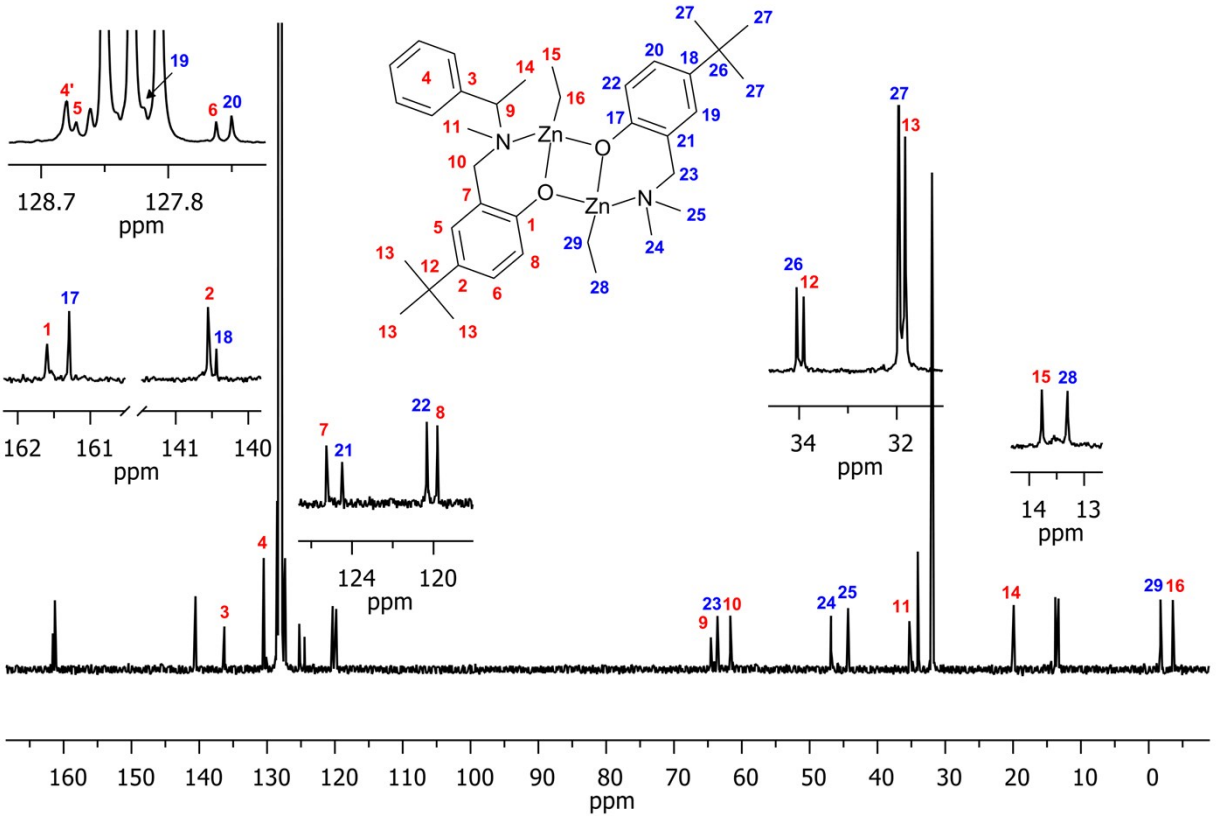


Figure S14. ^{13}C NMR of *RMe*-Zn in benzene-d$_6$.

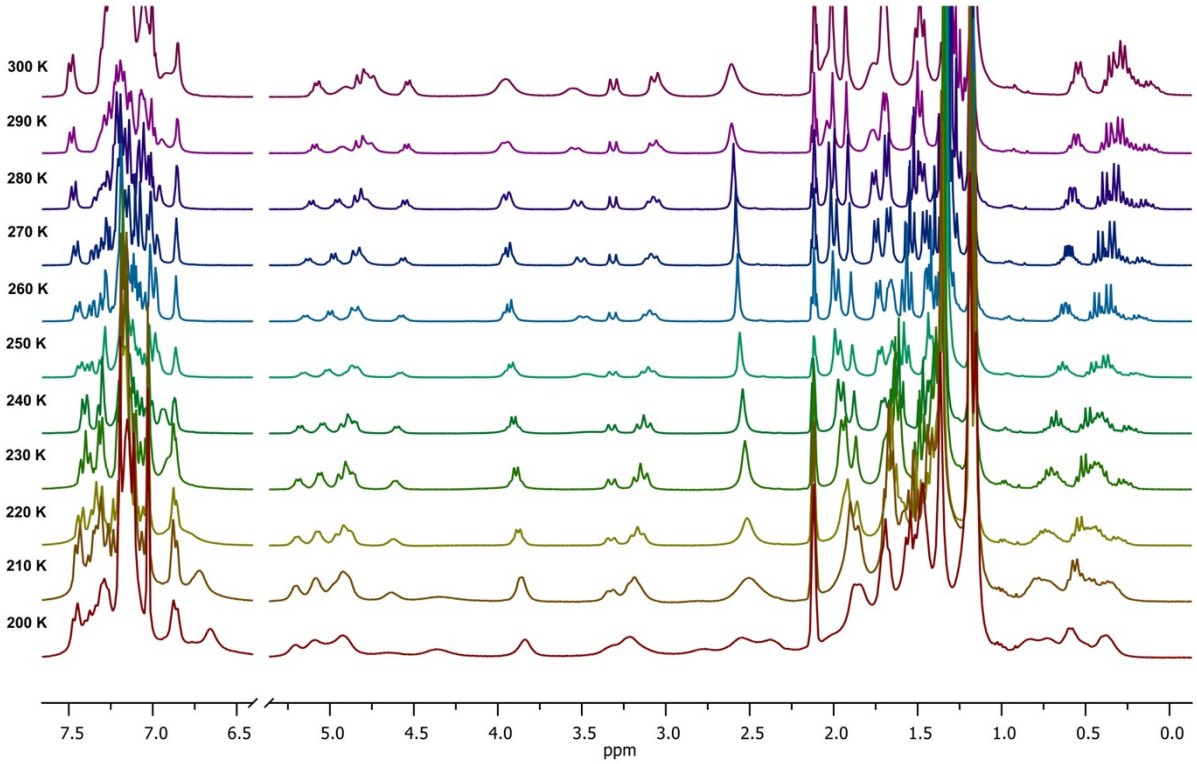


Figure S15. Variable temperature ^{1}H NMR of *RR*-Zn in toluene-d_8.

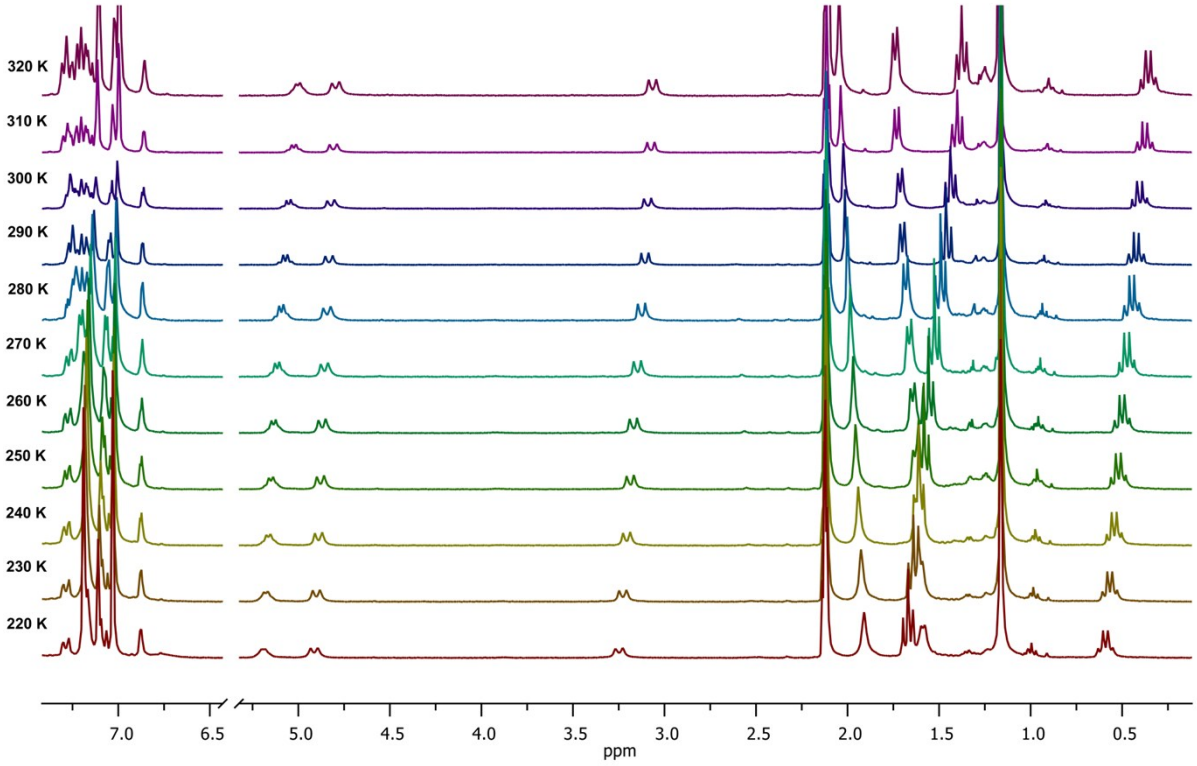


Figure S16. Variable temperature ^{1}H NMR of *RS*-Zn in toluene-d_8.

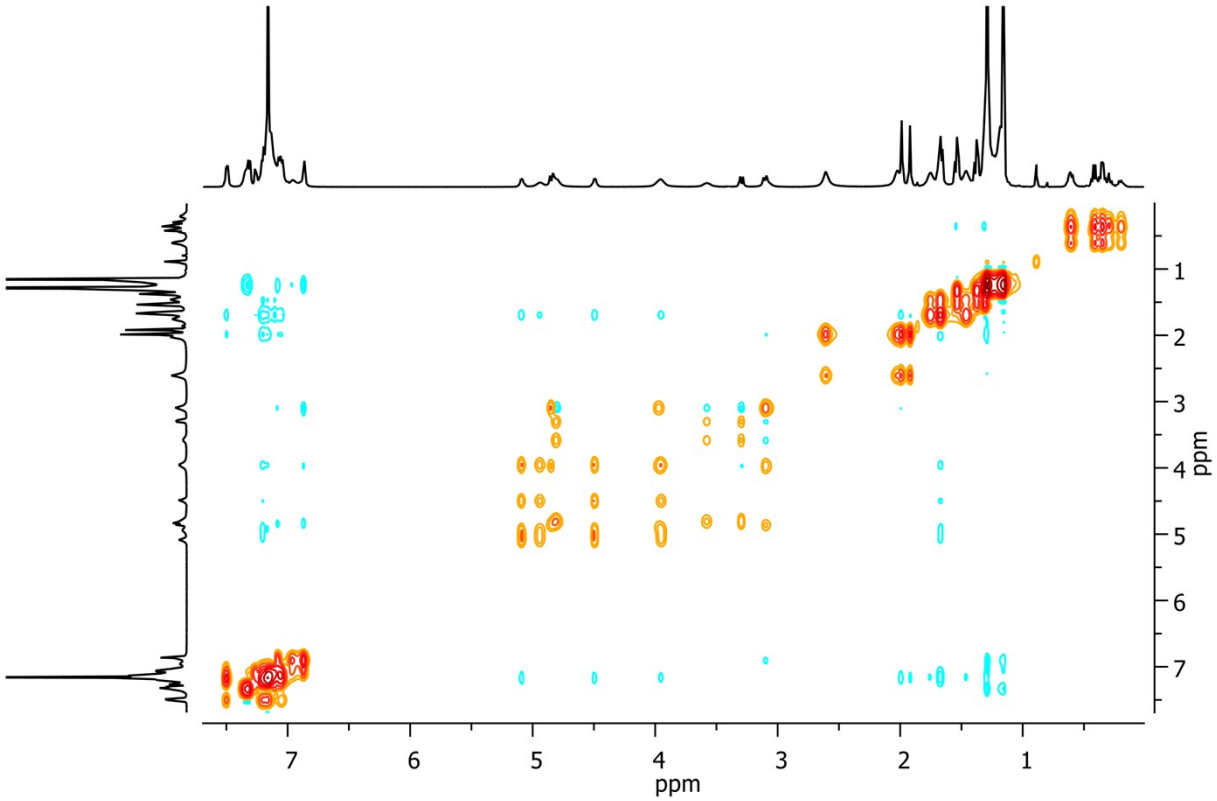


Figure S17. ^{1}H NOESY NMR of *RR*-Zn in benzene-d_6.

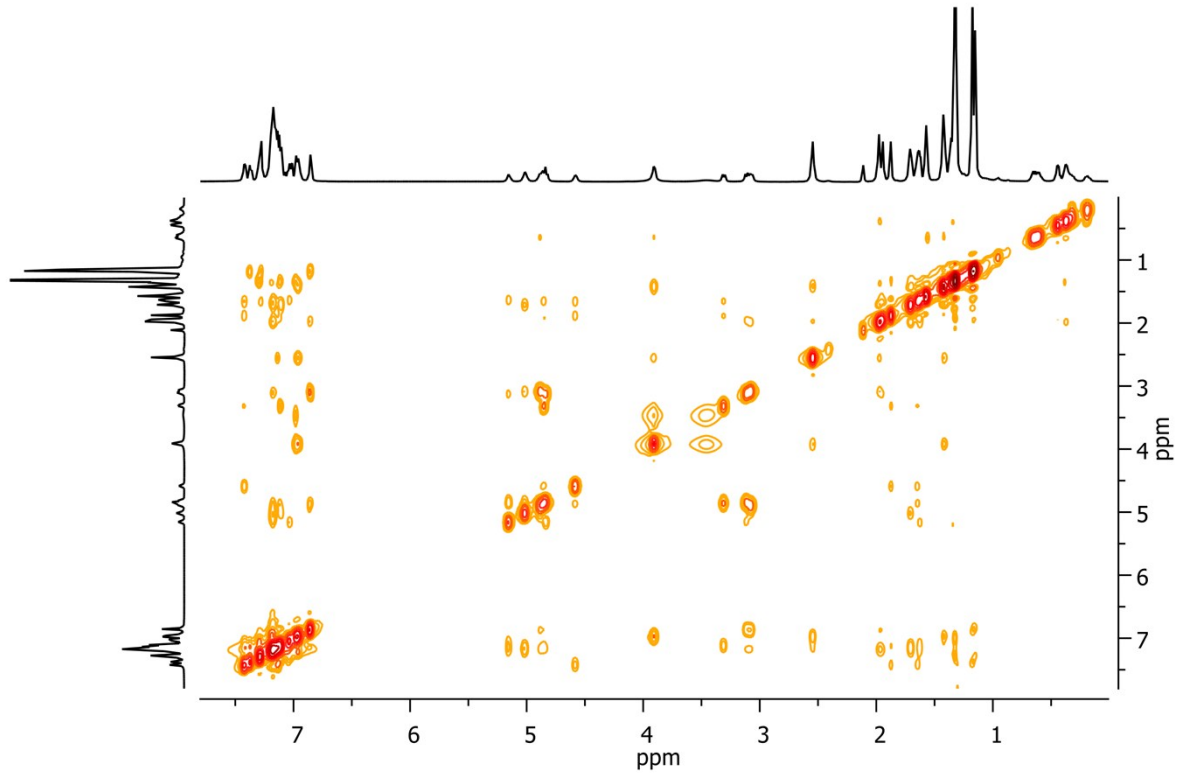


Figure S18. ^{1}H NOESY NMR of *RR*-Zn in toluene-d_8.

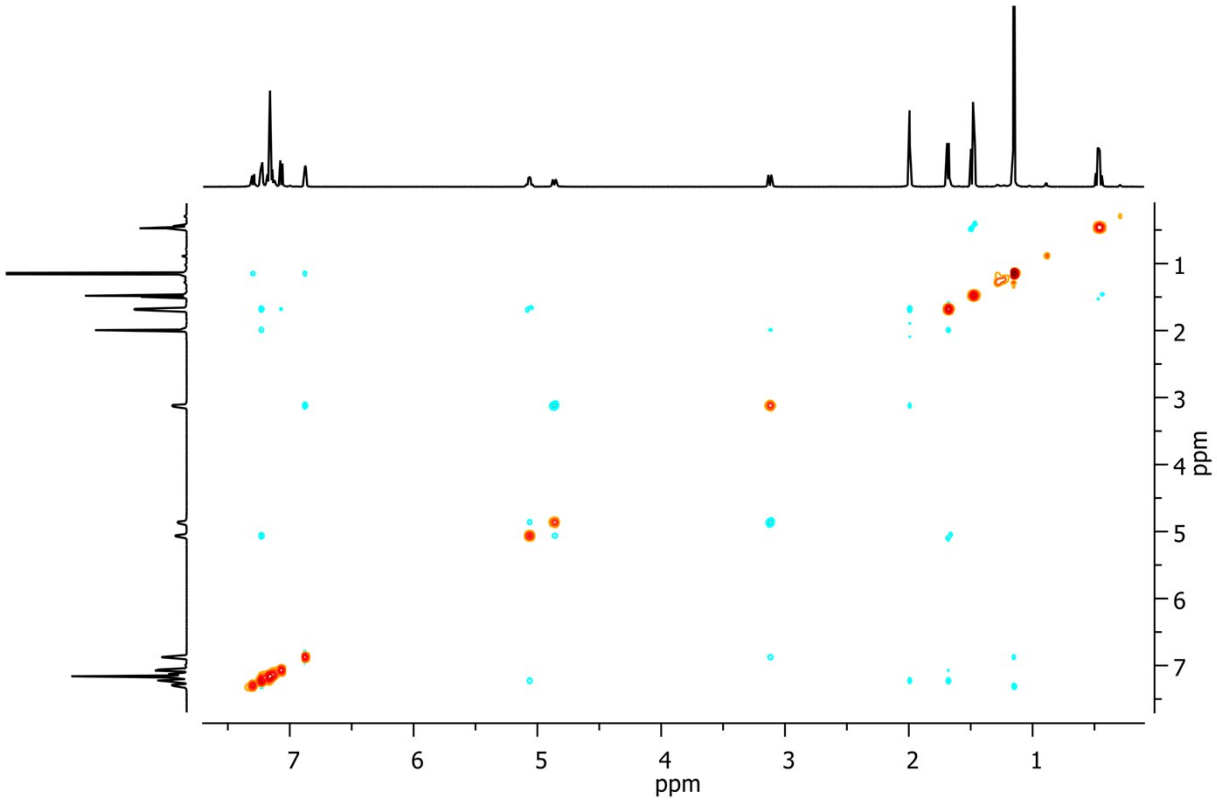


Figure S19. ^{1}H NOESY NMR of *RS*-Zn in benzene-d_6.

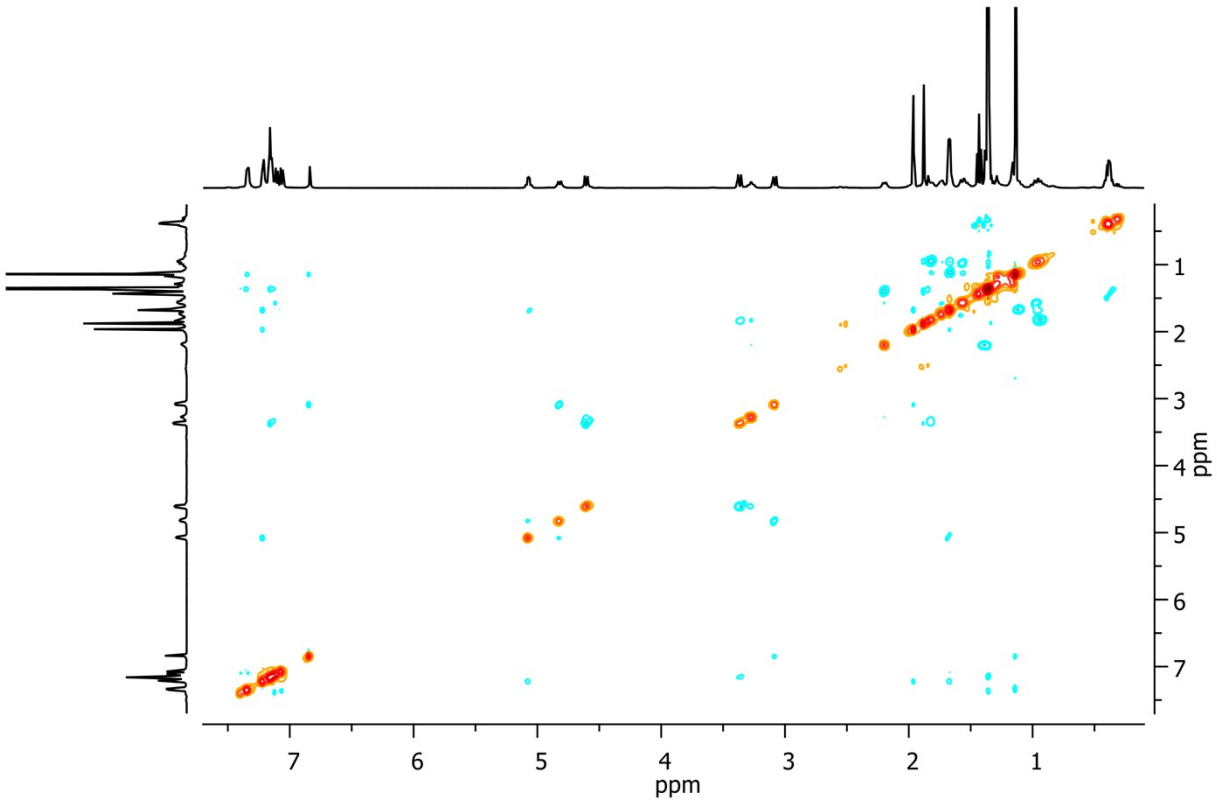


Figure S20. ^{1}H NOESY NMR of *RCy*-Zn in benzene-d_6.

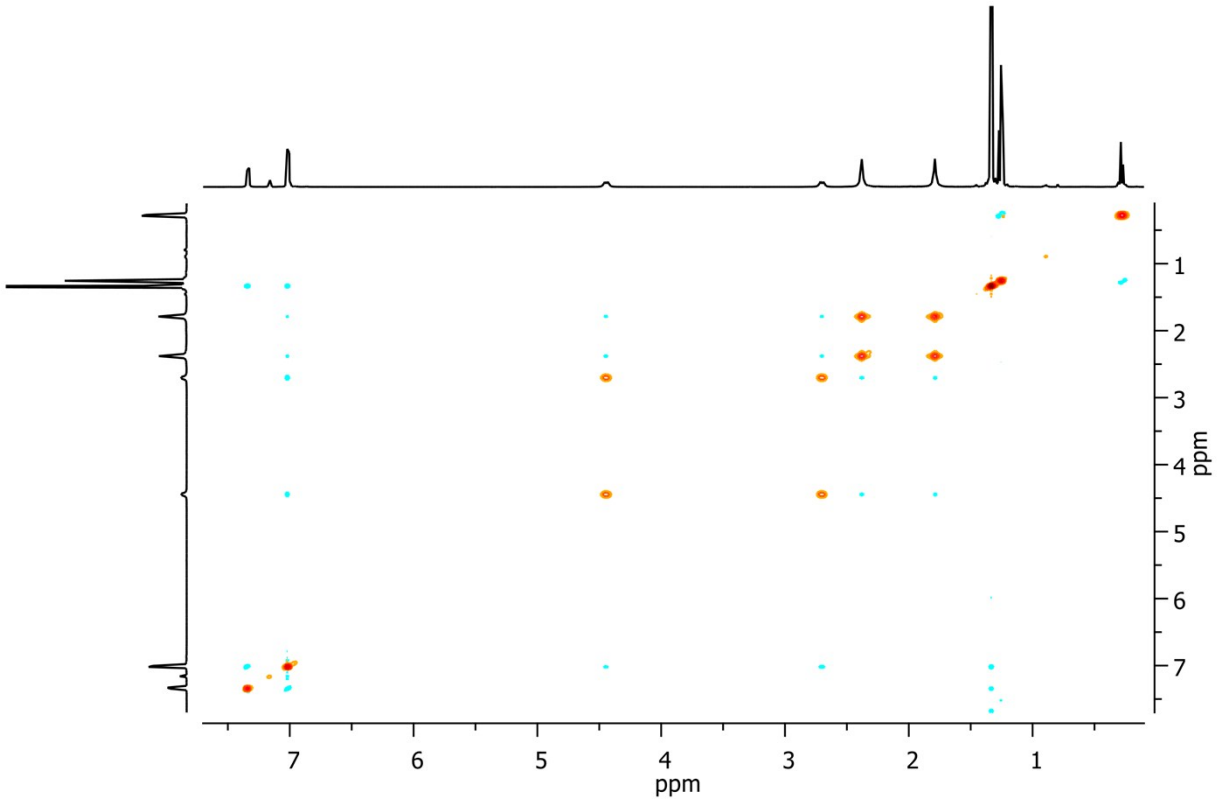


Figure S21. ^{1}H NOESY NMR of *Me*-Zn in benzene-d_6.

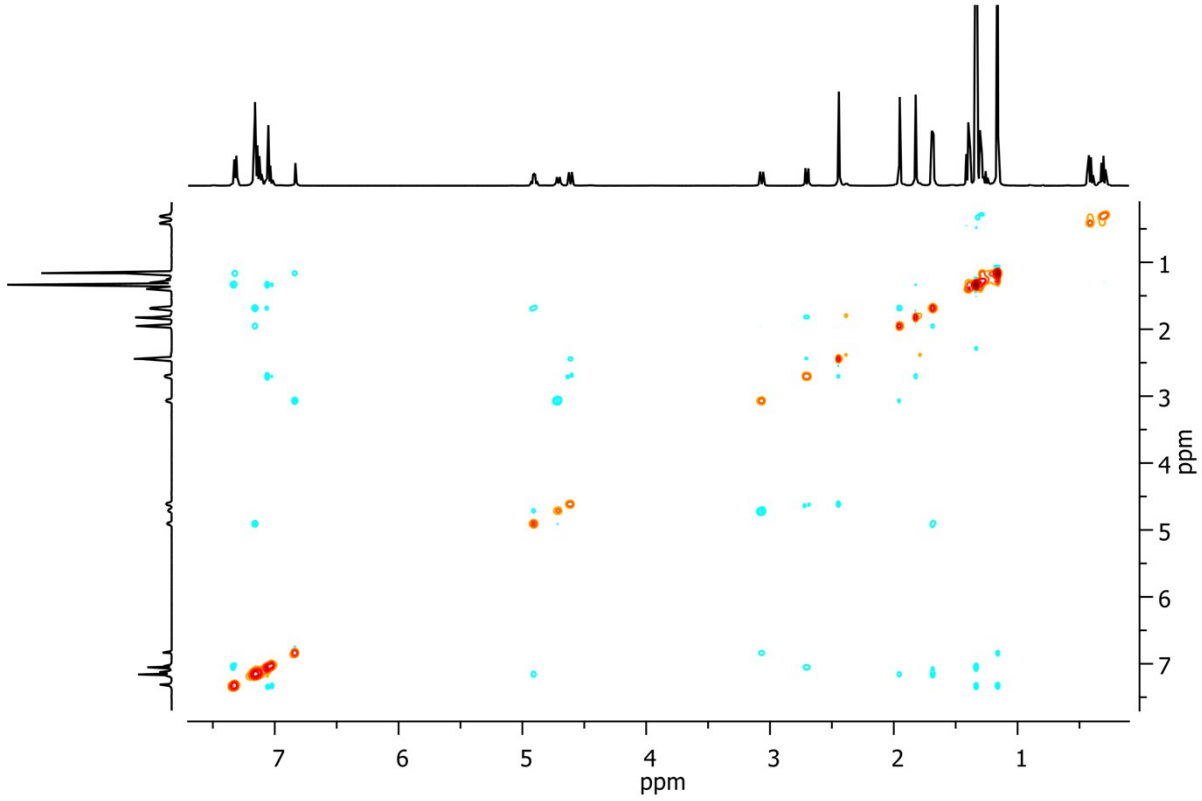


Figure S22. ^{1}H NOESY NMR of *RMe*-Zn in benzene-d_6.

	***RR*-Zn**	***SS*-Zn**	***RS*-Zn**	***RCy*-Zn**	***SMe*-Zn**
Empirical formula	$C_{44}H_{62}N_2O_2Zn_2$	$C_{44}H_{62}N_2O_2Zn_2$	$C_{44}H_{62}N_2O_2Zn_2$	$C_{42}H_{64}N_2O_2Zn_2$	$C_{37}H_{56}N_2O_2Zn_2 \cdot C_6D_6$
Formula weight	781.69	781.69	781.69	759.69	775.72
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	*P* 1	*P* 1	$P2_1/c$	$P2_1$	*P* 1
a (Å)	7.031 (2)	7.030 (2)	14.582 (5)	13.914 (4)	9.024 (3)
b (Å)	10.364 (3)	10.327 (3)	10.542 (3)	10.463 (3)	9.930 (3)
c (Å)	15.232 (5)	15.279 (6)	13.030 (4)	14.174 (5)	12.671 (4)
α (°)	70.75 (3)	70.36 (2)	90	90	78.01 (3)
β (°)	82.43 (2)	82.48 (3)	98.64 (3)	102.27 (3)	86.50 (3)
γ (°)	82.66 (3)	82.65 (3)	90	90	72.57 (2)
V (Å^3)	1034.5 (6)	1031.6 (6)	1980 (1)	2016.3 (11)	1059.7 (6)
Z	1	1	2	2	1
Crystal description	Block, colourless	Block, colourless	Block, colourless	Block, colourless	Block, colourless
Crystal size (mm)	0.45 × 0.35 × 0.18	0.26 × 0.19 × 0.10	0.55 × 0.46 × 0.13	0.50 × 0.26 × 0.20	0.30 × 0.26 × 0.10
d_{calc} (g/cm^3)	1.255	1.256	1.311	1.25	1.216
μ (mm^{-1})	1.20	1.20	1.25	1.72	1.17
F(000)	416	416	832	812	410
Diffractometer	Kuma KM-4 CCD	Xcalibur, CCD Ruby	Kuma KM-4 CCD	Xcalibur, CCD Onyx	Kuma KM-4 CCD
λ (Å)	0.71073 (Mo)	0.71073 (Mo)	0.71073 (Mo)	1.54184 (Cu)	0.71073 (Mo)
T (K)	100	129	100	100	180
Θ min/max (°)	2.9/28.7	2.8/28.7	3.0/32.5	3.2/70.2	2.9/28.7
h, *k*, *l* min/max	-9/7, -13/13, -19/20	-9/7, -7/13, -18/20	-18/20, -14/13, -17/13	-16/16, -12/10, -17/17	-12/12, -13/13, -16/16
Reflections collected	7051	7164	14537	10651	9259
Independent reflections	5647	5807	5239	5285	7036
Reflections [$I>2\sigma(I)$]	5058	5382	4552	5176	5758
R (int.)	0.034	0.016	0.028	0.056	0.040
Flack parameter	-0.030 (13)	-0.004 (9)	-	0.03 (3)	-0.015 (18)
data/restraints/params	5647/57/524	5807/69/525	5239/0/232	5285/19/475	7036/302/547
$R[F^2 > 2\sigma(F^2)]$	0.045	0.027	0.034	0.051	0.048
$wR(F^2)$	0.126	0.062	0.102	0.150	0.058
GooF	1.10	1.00	1.11	1.21	1.00
$\Delta\rho_{max}/\Delta\rho_{min}$ (e·Å^{-3})	0.49/-0.51	0.32/-0.29	0.71/-0.41	0.67/-0.81	0.34/-0.60

Table S1. X-ray experimental data and refinement.

Atoms	*RR*-Zn	*SS*-Zn	*RS*-Zn	*RCy*-Zn	*SMe*-Zn
Bond distance [Å]					
Zn1-C21	1.964(9)	1.977(6)	1.9866(17)	1.990(6)	1.971(9)
Zn2-C51[a]	1.999(8)	1.986(5)		2.002(6)	1.974(9)
Zn1-O1	2.006(5)	2.009(4)	2.0155(11)	2.033(3)	2.036(5)
Zn2-O2	2.008(5)	2.002(4)		2.029(3)	2.030(5)
Zn1-O1[i]	2.068(5)	2.062(4)	2.0485(11)	2.046(4)	2.037(5)
Zn2-O1	2.055(5)	2.059(4)		2.038(4)	2.043(5)
Zn1-N1	2.164(6)	2.173(5)	2.1426(15)	2.164(4)	2.166(7)
Zn2-N2	2.163(7)	2.157(5)		2.151(4)	2.132(8)
Zn1-Zn1[i,b]	3.0946(11)	3.0967(10)	3.0415(9)	3.0581(12)	3.0576(11)
O1-O1[i,b]	2.641(4)	2.634(2)	2.696(2)	2.690(4)	2.684(4)
Angles [°]					
C21-Zn1-O1	128.1(3)	138.5(2)	124.86(6)	126.3(2)	127.9(4)
C51[a]-Zn2-O2	135.4(4)	127.15(17)		125.57(19)	125.3(3)
C21-Zn1-O1[i]	122.9(3)	119.3(2)	121.40(6)	126.04(18)	127.2(4)
C51[a]-Zn2-O1	119.6(3)	122.51(18)		120.43(19)	128.8(4)
O1-Zn1-O1[i]	80.81(19)	80.63(15)	83.10(5)	82.52(14)	82.42(19)
O1-Zn2-O2	81.05(19)	80.86(15)		82.83(14)	82.65(18)
C21-Zn1-N1	118.4(3)	110.5(2)	125.39(6)	122.23(18)	118.1(4)
C51[a]-Zn2-N2	112.3(4)	119.1(2)		123.2(2)	119/1(4)
O1-Zn1-N1	93.0(2)	92.35(16)	92.85(5)	94.04(14)	94.3(2)
O2-Zn2-N2	92.5(2)	93.37(15)		93.27(14)	93.6(2)
O1[i]-Zn1-N1	105.2(2)	110.76(16)	98.70(5)	95.02(14)	97.4(2)
O1-Zn2-N2	110.8(2)	105.27(16)		102.08(15)	97.4(2)
Zn1-O1-Zn1[i]	99.27(19)	99.16(14)	96.90(5)	97.37(13)	97.4(2)
Zn1-O2-Zn2	98.79(19)	99.28(14)		97.24(14)	97.5(2)
Sum of the interior angles of the core Zn_2O_2 [°]					
	359.9(8)	359.9(6)	360	359.9(6)	360.0(8)

i = −x+1, −y+1, −z+1 for ***RS*-Zn**

O1[i] = O2, Zn1[i] = Zn2 for ***RR*-Zn**, ***SS*-Zn**, ***RCy*-Zn, *SMe*-Zn**

C51[a] = C49 for ***RCy*-Zn**, C44 for ***SMe*-Zn**

[b] Values in parentheses refer to the non-bonding interactions.

Table S2. Selected bond distances (Å) and angles (°).

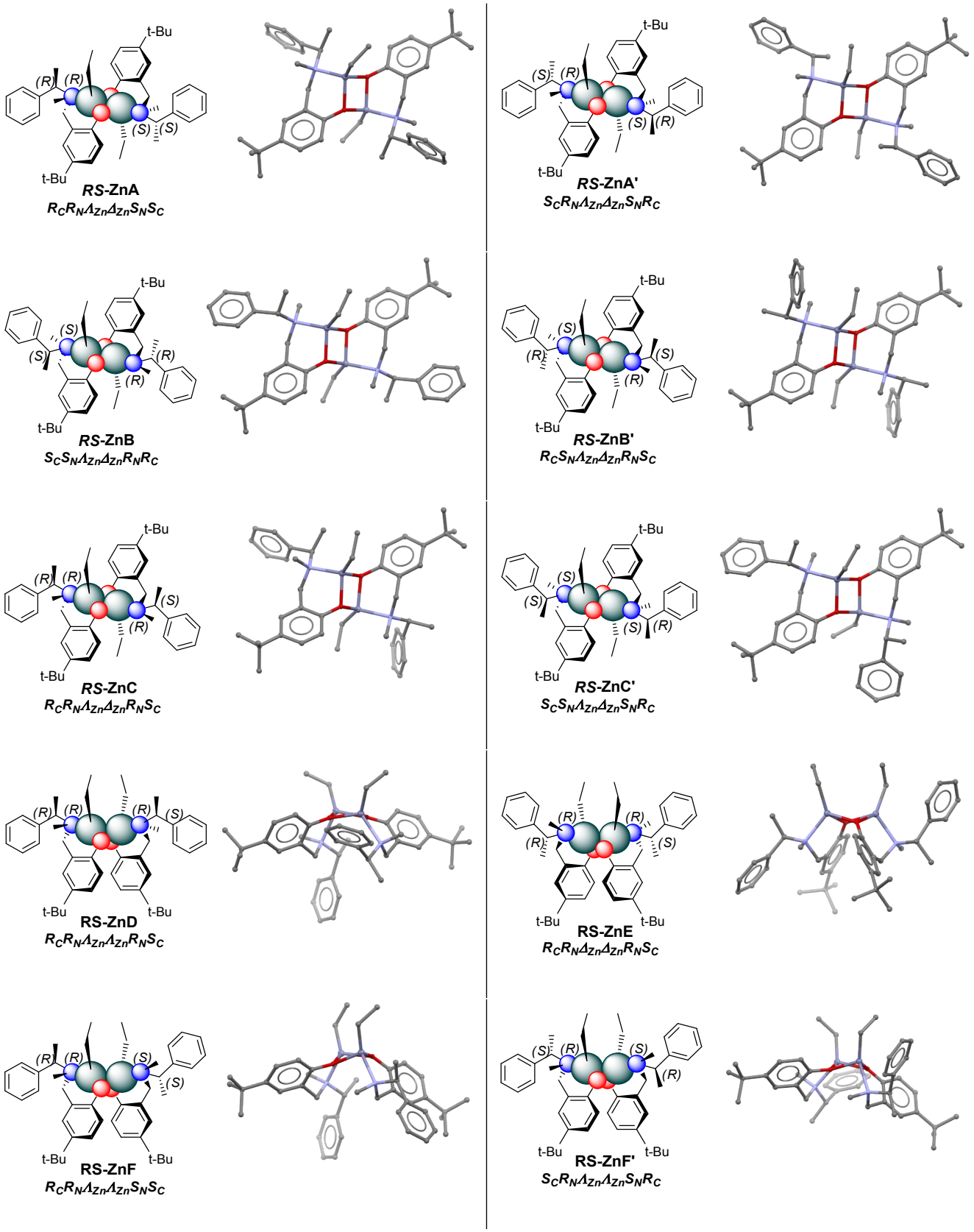


Figure S23. Structures of *RS*-Zn isomers (schematic on left, DFT optimised on right). Red - oxygen atoms, green – zinc atoms, blue – nitrogen atoms.

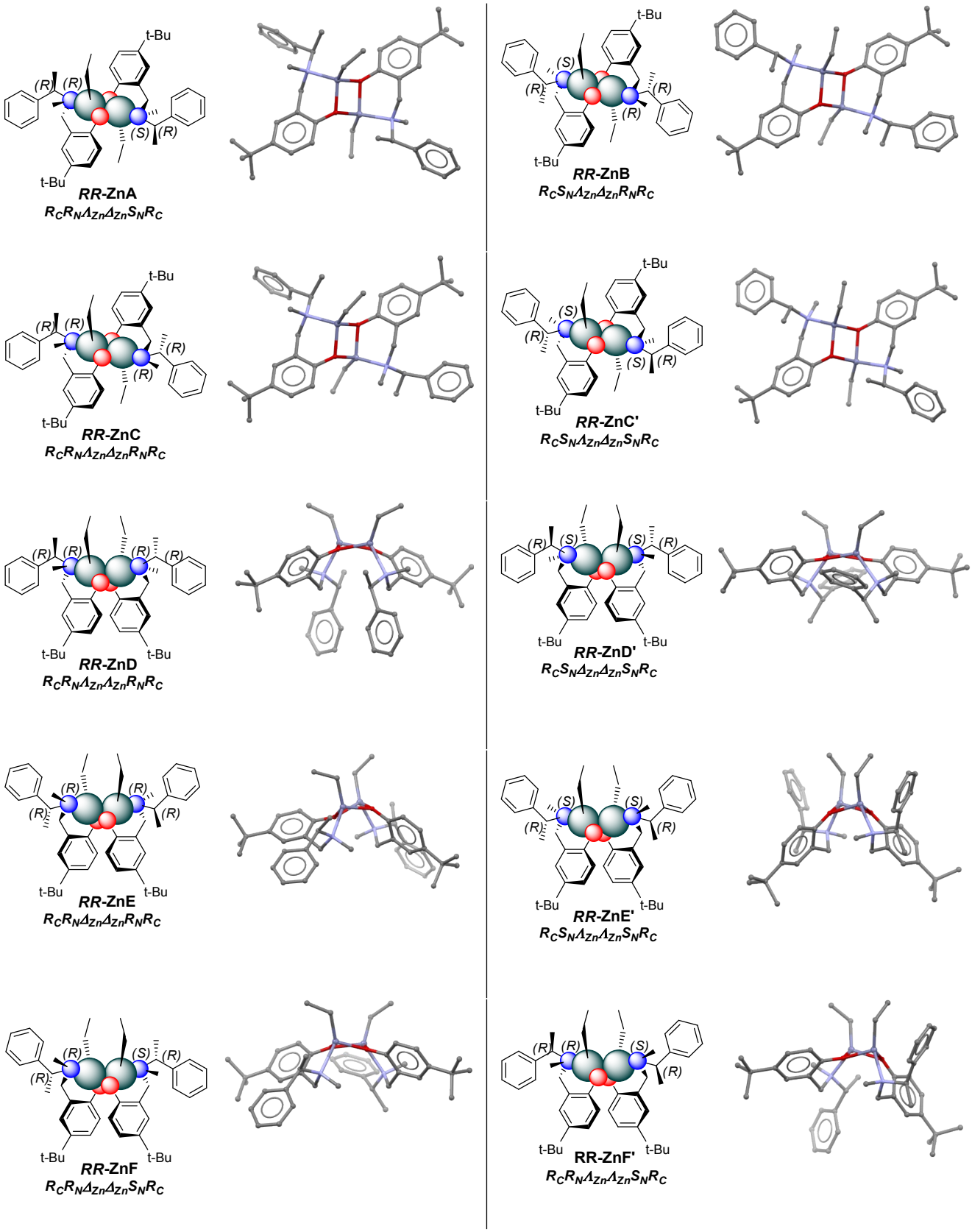


Figure S24. Structures of *RR*-Zn isomers (schematic on left, DFT optimised on right). Red - oxygen atoms, green – zinc atoms, blue – nitrogen atoms.

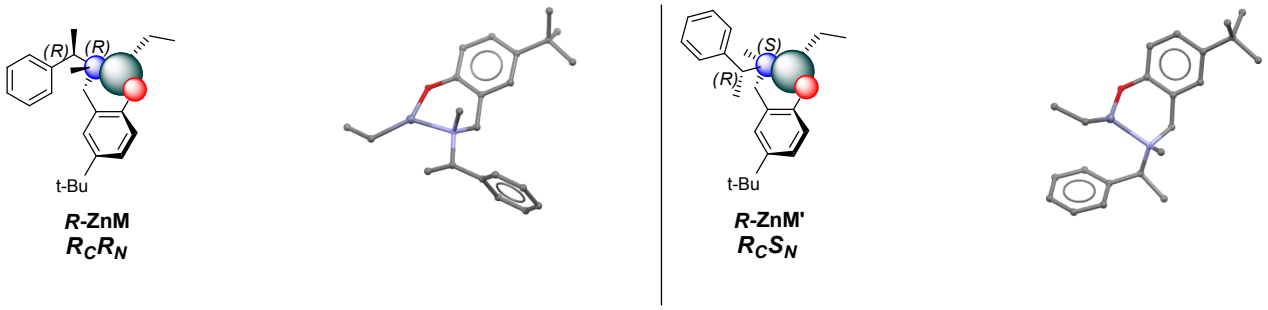


Figure S25. Structures of *RS/RR*-Zn monomers (schematic on left, DFT optimised on right). Red - oxygen atoms, green – zinc atoms, blue – nitrogen atoms.

Isomer	E (hartree)	ZPE (kcal/mol)	ΔE_{zpe} (kcal/mol)	ΔE_{zpe} (kJ/mol)
RS-ZnA	-5532.41059547	608.41	0.00	0.00
RS-ZnA'	-5532.40546920	609.25	4.05	16.97
RS-ZnB	-5532.40345722	609.10	5.17	21.62
RS-ZnB'	-5532.39742961	609.06	8.91	37.26
RS-ZnC	-5532.40390400	608.59	4.38	18.32
RS-ZnC'	-5532.40157326	608.75	6.00	25.11
RS-ZnD	-5532.39817291	607.76	7.14	29.89
RS-ZnE	-5532.39168361	608.78	12.23	51.19
RS-ZnF	-5532.39902345	608.28	7.13	29.82
RS-ZnF'	-5532.39139122	608.46	12.10	50.62
RR-ZnA	-5532.40781100	608.48	1.82	7.61
RR-ZnB	-5532.40344840	609.11	5.18	21.69
RR-ZnC	-5532.40692280	608.81	2.70	11.29
RR-ZnC'	-5532.40473200	608.87	4.13	17.30
RR-ZnD	-5532.40164801	608.15	5.35	22.40
RR-ZnD'	-5532.39476523	608.24	9.77	40.86
RR-ZnE	-5532.39455236	608.94	10.60	44.35
RR-ZnE'	-5532.38795849	608.27	14.07	58.85
RR-ZnF	-5532.39470040	608.44	10.00	41.84
RR-ZnF'	-5532.39628418	608.34	8.91	37.30
R-ZnM	-2766.17691992	303.83	34.87*	145.89*
R-ZnM'	-2766.17436811	303.74	37.89*	158.51*

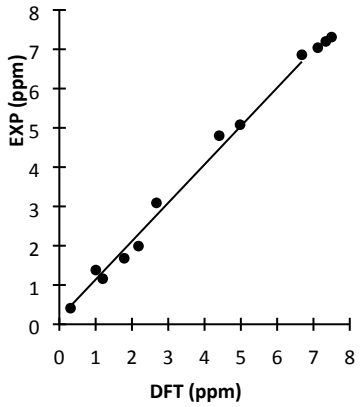
Table S3. Energies of *RS/RR*-Zn isomers in *vacuo*. * - Calculated as for two monomers.

Isomer	E (hartree)	ZPE (kcal/mol)	ΔE_{zpe} (kcal/mol)	ΔE_{zpe} (kJ/mol)
RS-ZnA	-5532.41590724	608.16	0.00	0.00
RS-ZnA'	-5532,41129476	608.39	3.13	13.10
RS-ZnB	-5532.40949091	608.82	4.69	19.61
RS-ZnB'	-5532.40397911	608.61	7.93	33.20
RS-ZnC	-5532.40980849	608.19	3.86	16.14
RS-ZnC'	-5532.40742782	608.54	5.70	23.85
RS-ZnD	-5532.40460263	607.54	6.48	27.11
RS-ZnE	-5532.39871329	608.44	11.07	46.32
RS-ZnF	-5532.40564158	608.27	6.56	27.43
RS-ZnF'	-5532.39878805	608.09	10.68	44.68
RR-ZnA	-5532.41350352	608.13	1.48	6.19
RR-ZnB	-5532.40901733	608.76	4.92	20.60
RR-ZnC	-5532.41255037	608.47	2.42	10.12
RR-ZnC'	-5532.41035451	608.56	3.89	16.28
RR-ZnD	-5532.40769320	607.88	4.88	20.41
RR-ZnD'	-5532.40121644	607.76	8.82	36.89
RR-ZnE	-5532.40124819	608.64	9.68	40.51
RR-ZnE'	-5532.39532702	607.95	12.71	53.18
RR-ZnF	-5532.40154967	608.11	8.96	37.49
RR-ZnF'	-5532.40304981	608.12	8.04	33.62
R-ZnM	-2766.18470309	303.86	28.75*	120.29*
R-ZnM'	-2766.18169909	303.47	31.72*	132.73*

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

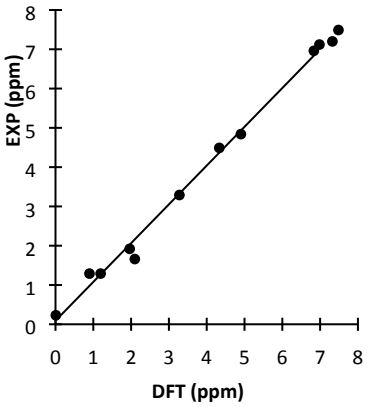
***RR*-ZnA ($R_CR_N\Lambda_{Zn}$ part)**

	DFT	EXP
a	7.50	7.31
b	7.34	7.20
c	7.12	7.04
d	6.68	6.86
e	4.98	5.08
f	4.40	4.8
f'	2.67	3.09
g	2.18	1.99
h	1.79	1.68
i	1.20	1.16
j	1.00	1.38
k	0.31	0.41



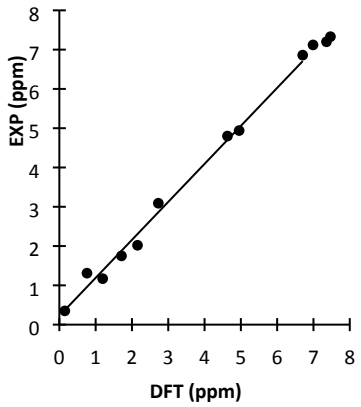
***RR*-ZnA ($R_CS_N\Delta_{Zn}$ part)**

	DFT	EXP
a	7.49	7.49
b	7.32	7.20
c	6.98	7.12
d	6.83	6.96
e	4.33	4.49
f	4.90	4.84
f'	3.28	3.29
g	1.96	1.92
h	2.10	1.66
i	1.19	1.29
j	1.30	1.29
k	0.21	0.23



***RR*-ZnC ($R_CR_N\Lambda_{Zn}$ part)**

	DFT	EXP
a	7.47	7.33
b	7.36	7.20
c	6.99	7.12
d	6.70	6.86
e	4.95	4.94
f	4.63	4.8
f'	2.73	3.09
g	2.15	2.02
h	1.71	1.75
i	1.19	1.17
j	0.76	1.31
k	0.15	0.35



***RR*-ZnC ($R_CR_N\Delta_{Zn}$ part)**

	DFT	EXP
a	7.53	7.49
b	7.32	7.20
c	7.06	7.12
d	7.02	6.96
e	3.99	3.95
f	4.18	3.95
f'	3.15	3.58
g	2.69	2.61
h	1.64	1.46
i	1.31	1.29
j	1.01	1.54
k	0.41	0.62

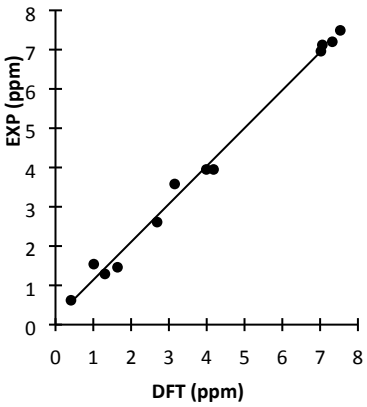


Table S5. Comparison of ^{1}H NMR chemical shifts in benzene-d_6 (EXP) with calculated (DTF) for *RR*-Zn. The best R^2 values were achievied for *RR*-ZnA, *RR*-ZnC isomers.

***RS*-ZnA**

	DFT	EXP
a	7.48	7.30
b	7.37	7.16
c	7.02	7.07
d	6.68	6.87
e	5.14	5.06
f	4.69	4.86
f'	2.87	3.12
g	2.00	1.99
h	1.77	1.68
i	0.96	1.48
j	1.17	1.15
k	0.31	0.47

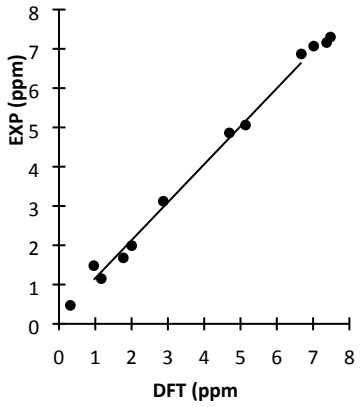


Table S6. Comparison of ^{1}H NMR chemical shifts in benzene-d_6 (EXP) with calculated (DTF) for *RS*-Zn.

Cy-Zn		
	DFT	EXP
a	7.53	7.4
b	6.98	7.13
c	6.96	7.12
d	4.34	4.59
d'	3.37	3.33
e	3.28	3.27
f	1.89	1.84
g	1.28	1.35
h	1.27	1.34
J	0.01	0.33

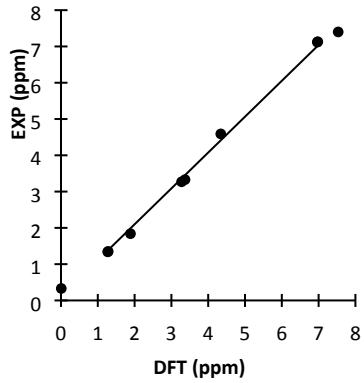


Table S7. Comparison of ^{1}H NMR chemical shifts in benzene-d_6 (EXP) with calculated (DTF) for *Cy*-Zn.

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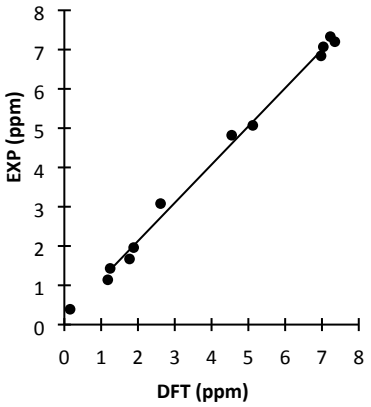
RCy-Zn (L^R part)		
	DFT	EXP
a	7.23	7.33
b	7.35	7.2
c	7.04	7.07
d	6.97	6.84
e	5.12	5.07
f	4.55	4.82
f'	2.61	3.08
g	1.88	1.96
h	1.77	1.67
I	1.24	1.43
J	1.18	1.14
k	0.16	0.39



RCy-Zn (L^{Cy} part)		
	DFT	EXP
l	7.52	7.35
m	7.00	7.12
n	6.98	7.10
o	4.41	4.61
o'	3.36	3.37
p	3.55	3.35
r	1.90	1.88
s	0.91	1.38
t	1.27	1.36
u	0.26	0.39

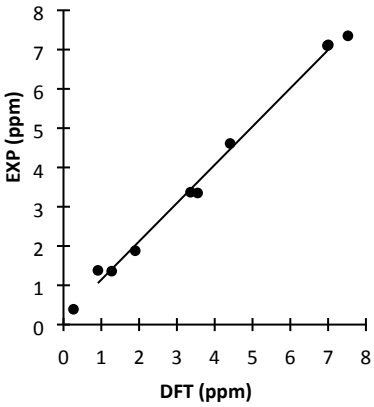


Table S8. . Comparison of ^{1}H NMR chemical shifts in benzene-d_6 (EXP) with calculated (DTF) for *RCy*-Zn.

Me-Zn		
	DFT	EXP
a	7.51	7.34
b	6.98	7.01
c	6.94	7.01
d	4.54	4.44
d'	2.70	2.70
e	2.49	2.38
e'	1.98	1.79
f	1.27	1.33
g	1.15	1.26
h	0.09	0.28

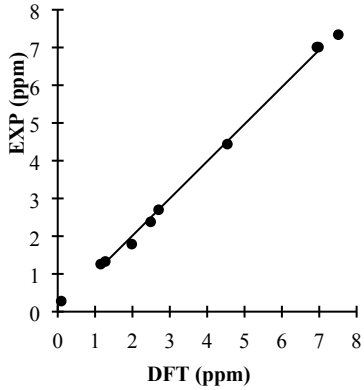


Table S9. Comparison of ^{1}H NMR chemical shifts in benzene-d_6 (EXP) with calculated (DTF) for *Me*-Zn.

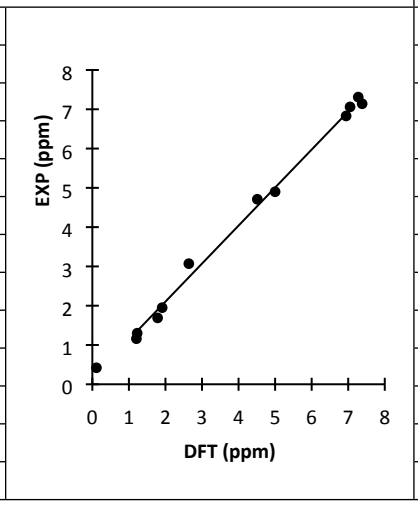
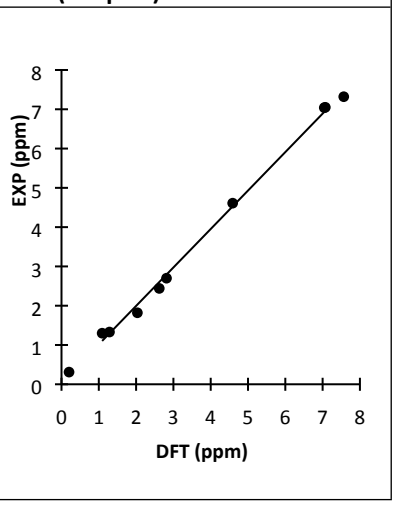
RMe-Zn (L^{R} part)				*RMe*-Zn (L^{Me} part)			
	DFT	EXP			DFT	EXP	
a	7.27	7.31		l	7.57	7.32	
b	7.38	7.14		m	7.07	7.05	
c	7.05	7.06		n	7.04	7.04	
d	6.94	6.83		o	4.59	4.61	
e	5.00	4.9		o'	2.82	2.7	
f	4.51	4.71		p	2.62	2.44	
f'	2.64	3.07		p'	2.03	1.82	
g	1.91	1.95		q	1.29	1.33	
h	1.79	1.69		r	1.09	1.30	
i	1.23	1.3		s	0.20	0.31	
j	1.21	1.16					
k	0.11	0.42					

Table S10. Comparison of ^{1}H NMR chemical shifts in benzene-d$_6$ (EXP) with calculated (DTF) for *RMe*-Zn.

	V^{vdW} [Å^3]	V^{SES} [Å^3]	D^{vdW} [10^{-10} m^2/s]	D^{SES} [10^{-10} m^2/s]	D_f^{vdW} [10^{-10} m^2/s]	D_f^{SES} [10^{-10} m^2/s]	D^{EXp} [10^{-10} m^2/s]
***RR*-ZnA**	681.70	854.24	6.45	6.54	6.32	6.41	6.34
***RR*-ZnC**	681.63	845.01	6.45	6.57	6.32	6.44	
***RS*-ZnA**	681.19	856.88	6.45	6.53	6.34	6.42	6.30
***Me*-Zn**	512.82	645.38	8.15	7.36	7.82	7.07	7.42
***Cy*-Zn**[a]	645.98	818.02	6.75	6.66	6.64	6.55	6.65
***RMe*-Zn**	596.96	743.39	7.17	6.93	7.04	6.80	6.88
***RCy*-Zn**	629.45	774.56	6.74	6.81	6.62	6.68	6.72

Table S11. Van der Waals volumes V^{vdW}, Connolly volumes V^{SES}, theoretical diffusion coefficients D^{vdW}, D^{SES} and theoretical diffusion coefficients corrected by the shape factor D_f^{vdW} , D_f^{SES} for DFT optimized strucures and corresponding experimental diffusion coefficients D^{EXP}. [a] Previously published, D. Jędrzkiewicz, J. Ejfler, N. Gulia, Ł. John, S. Szafert, *Dalton Trans*., 2015, **44**, 13700;