Electronic Supplementary Material (ESI) for Dalton Transactions.

Factors controlling the structure of alkylzinc amidinates: On the role of N-substituents

Supporting information

Michał Terlecki,[a] Iwona Justyniak,[b] Michał K. Leszczyński,[a,b] Piotr Bernatowicz,[b] Janusz Lewiński*[a,b]

[a]Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland.
[b]Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland.
E-mail: lewin@ch.pw.edu.pl

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1. NMR spectra

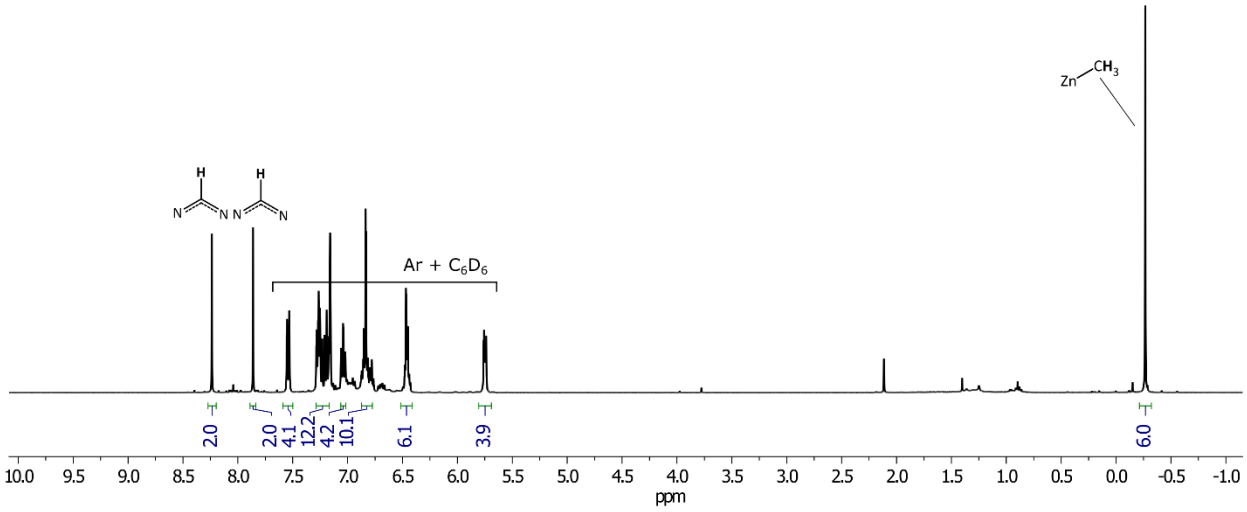


Fig. S1. ^{1}H NMR spectrum of **1^{Me}** in C_6D_6.

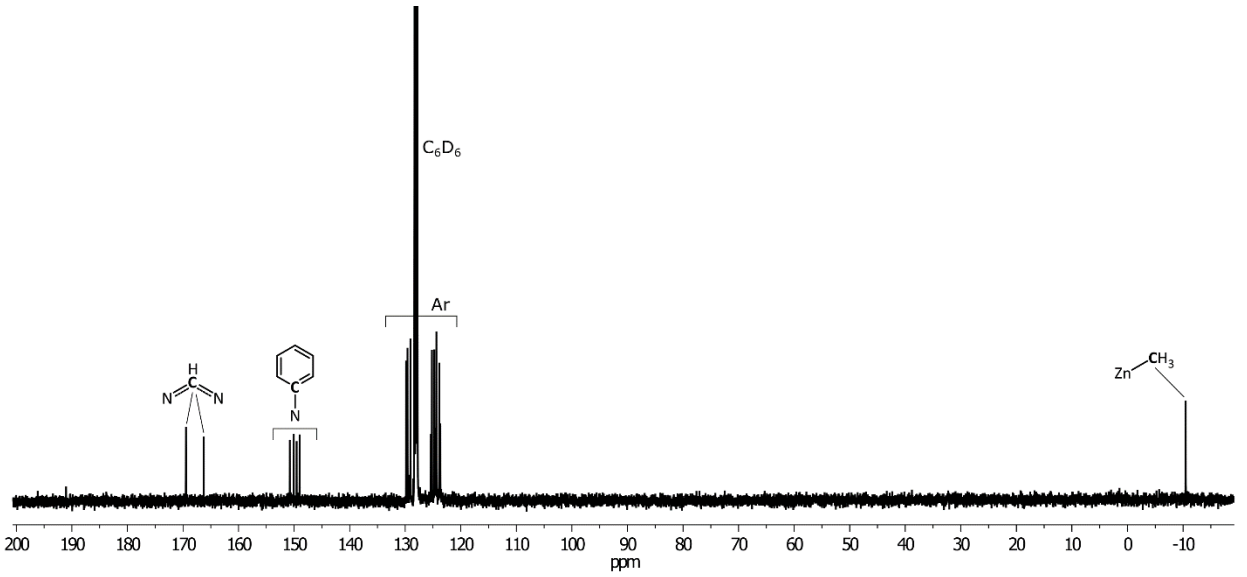


Fig. S2. ^{13}C NMR spectrum of **1^{Me}** in C_6D_6.

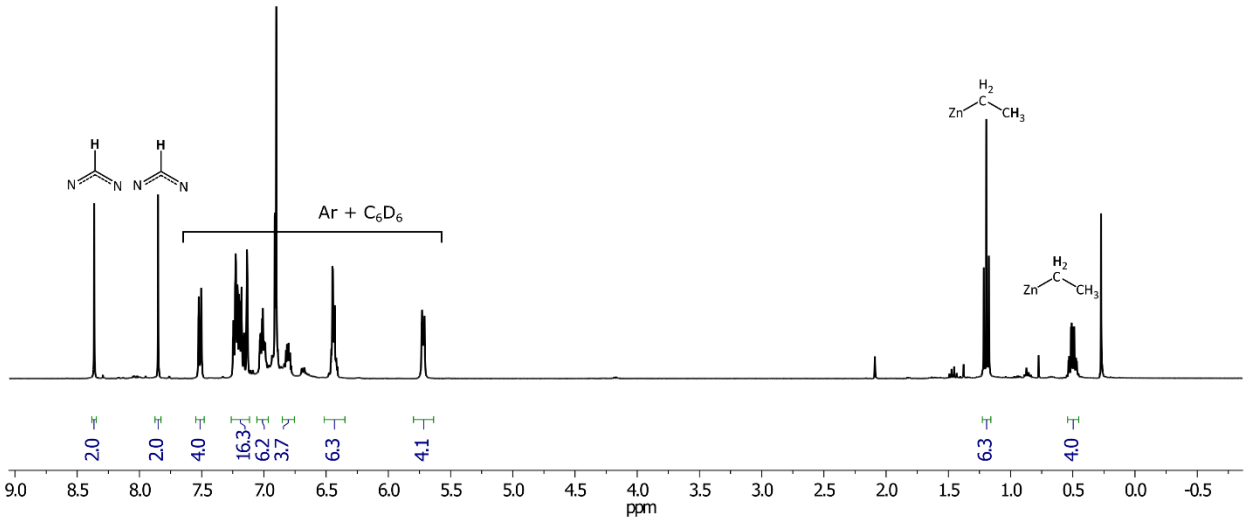


Fig. S3. ^{1}H NMR spectrum of **1^{Et}** in C_6D_6.

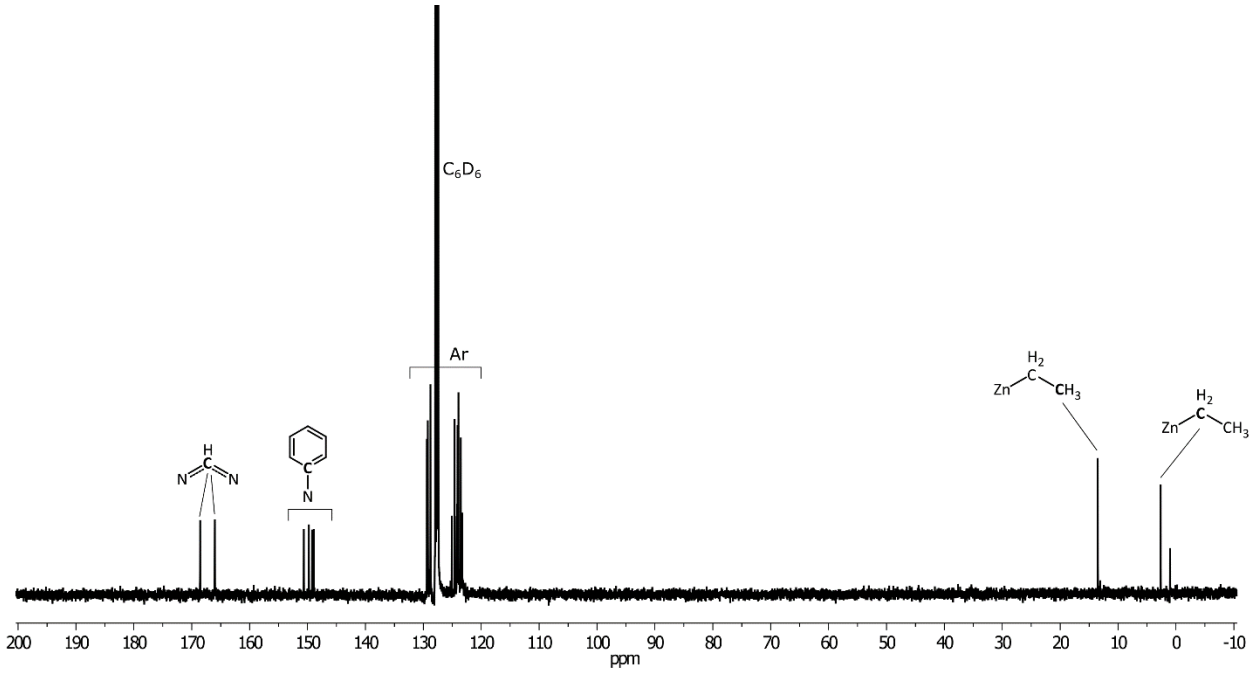


Fig. S4. ^{13}C NMR spectrum of **1^{Et}** in C_6D_6.

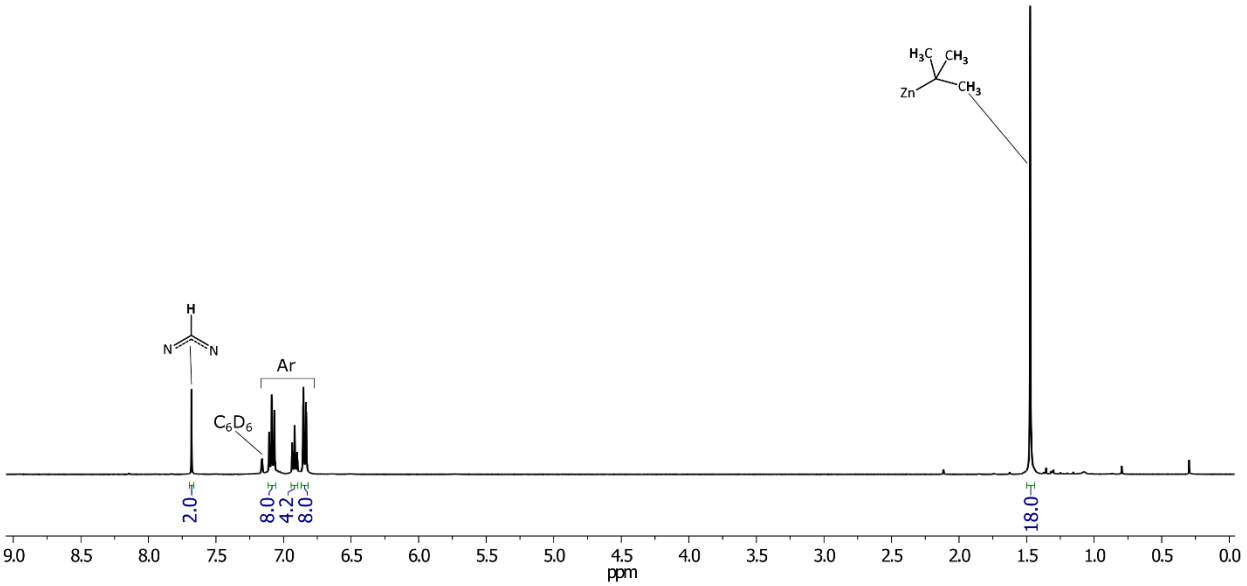


Fig. S5. ^{1}H NMR spectrum of **2** in C_6D_6.

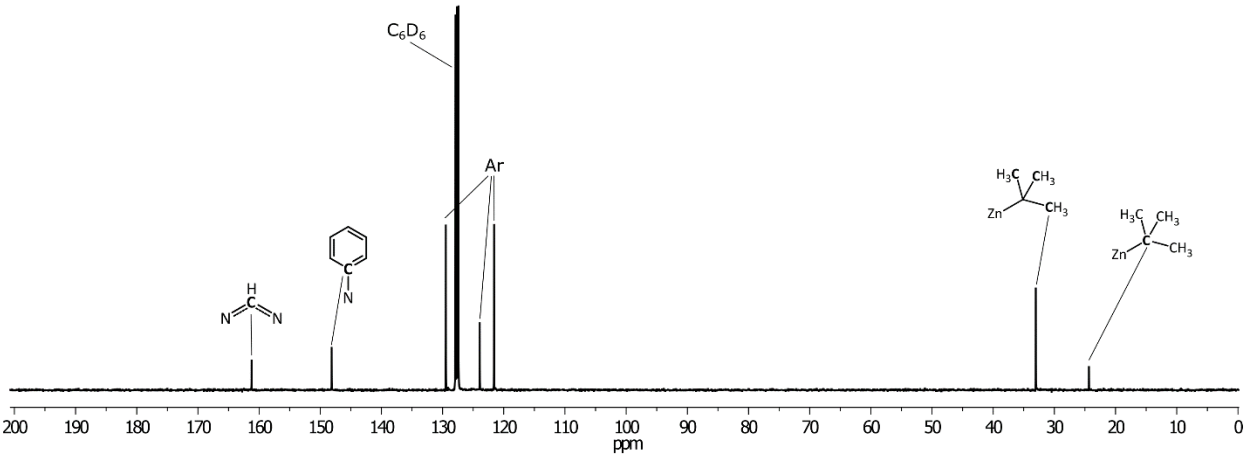


Fig. S6. ^{13}C NMR spectrum of **2** in C_6D_6.

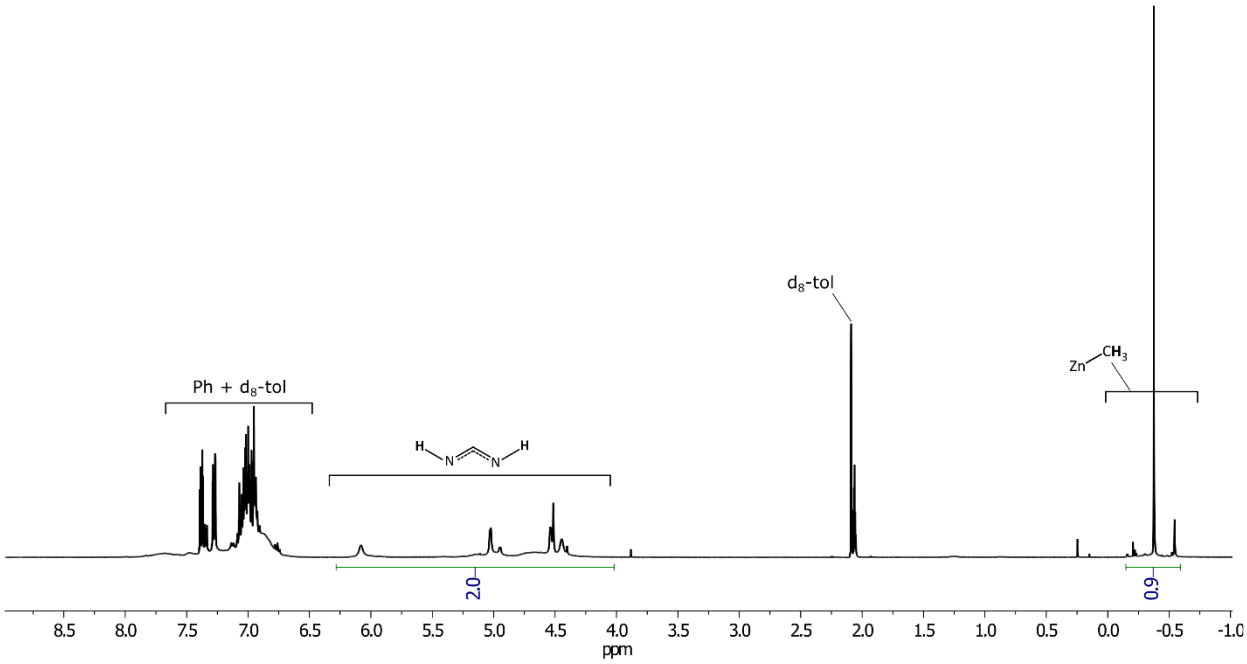


Fig. S7. ^{1}H NMR spectrum of the methylzinc derivative of *bza* in d_8-tol.

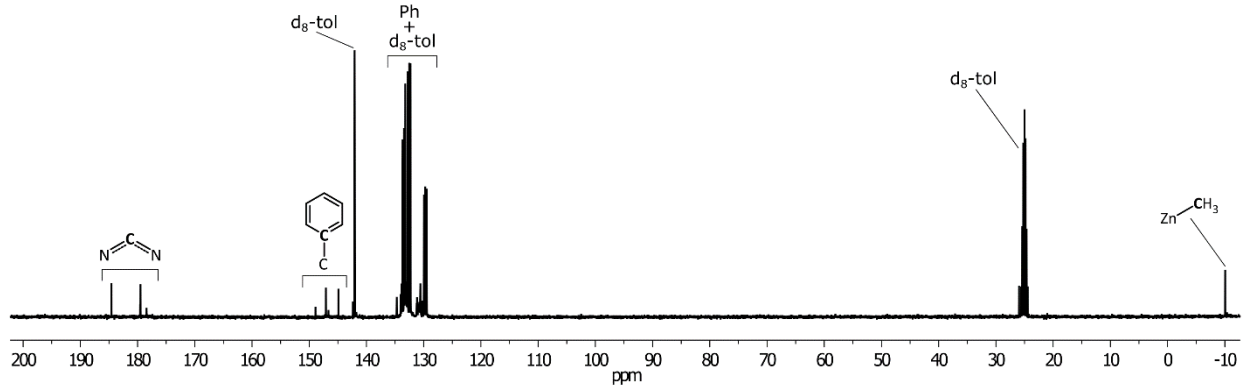


Fig. S8. ^{13}C NMR spectrum of the methylzinc derivative of *bza* in d_8-tol.

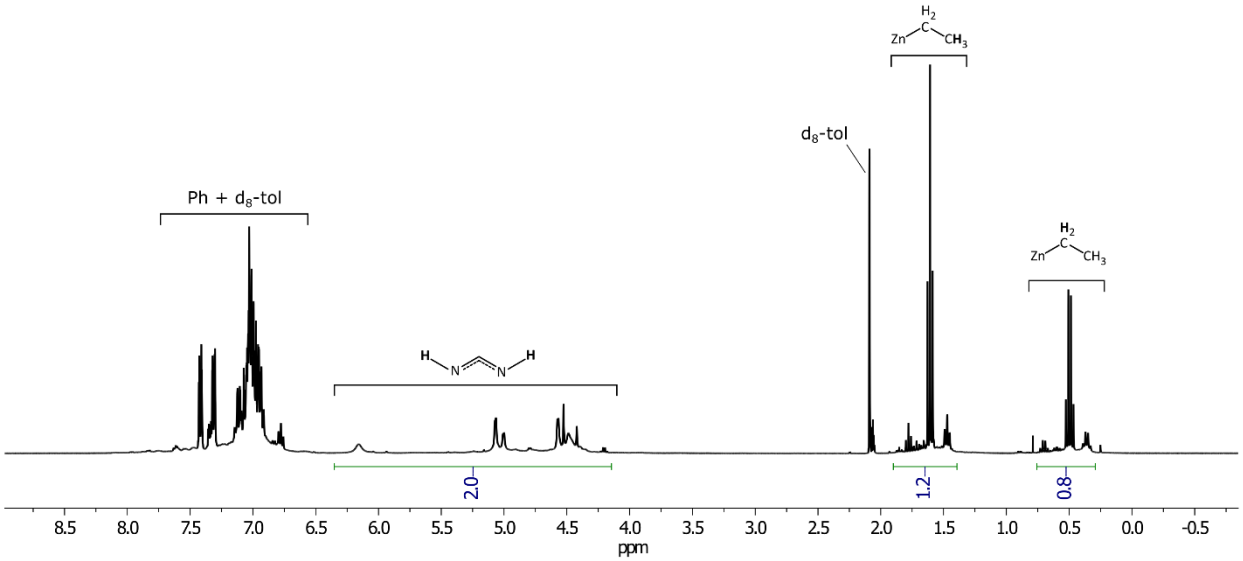


Fig. S9. ^{1}H NMR spectrum of the ethylzinc derivative of *bza* in d_8-tol.

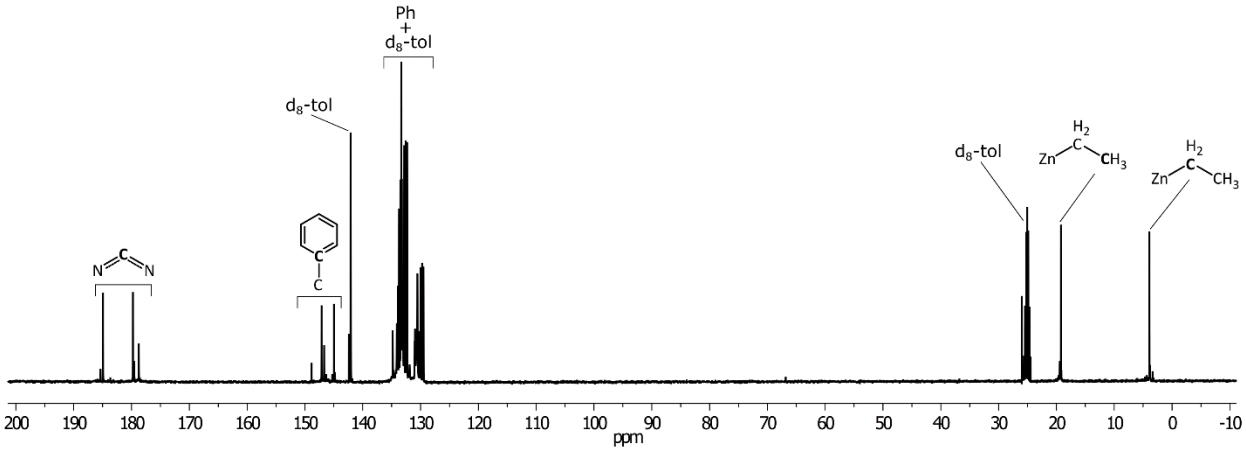


Fig. S10. ^{13}C NMR spectrum of the ethylzinc derivative of *bza* in d_8-tol.

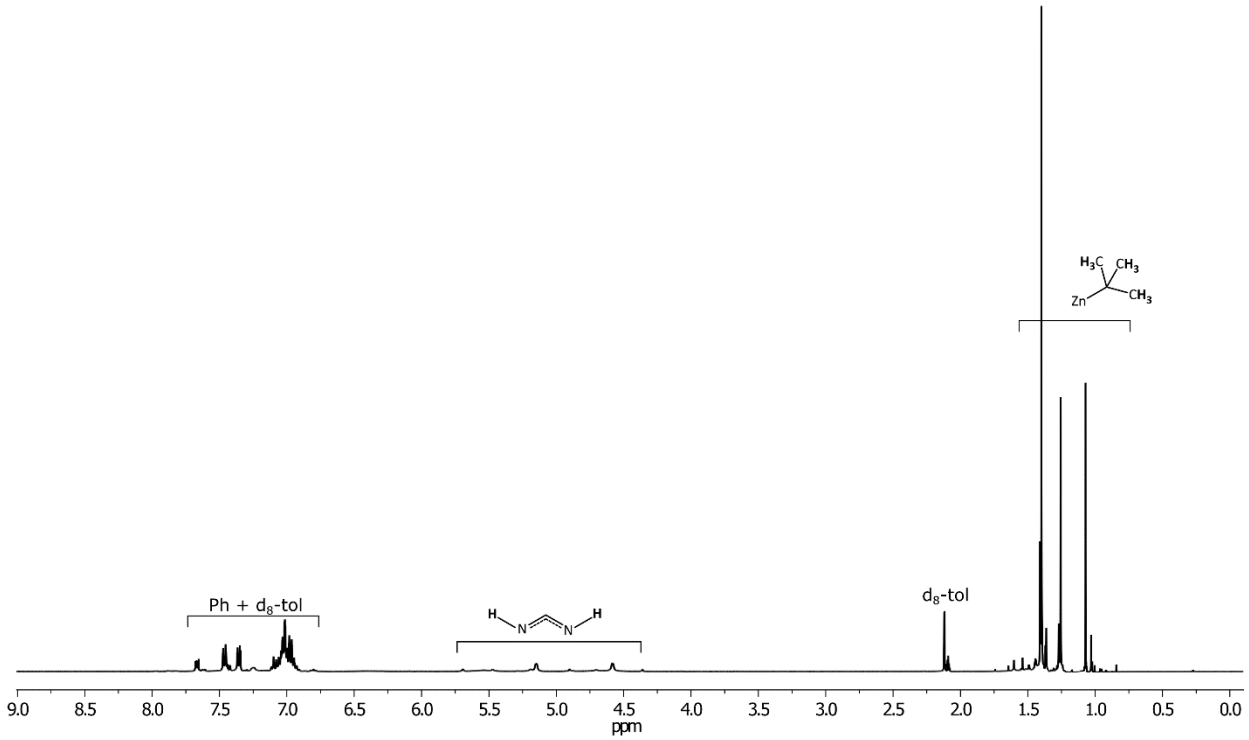


Fig. S11. ^{1}H NMR spectrum of **3** in d_8-tol.

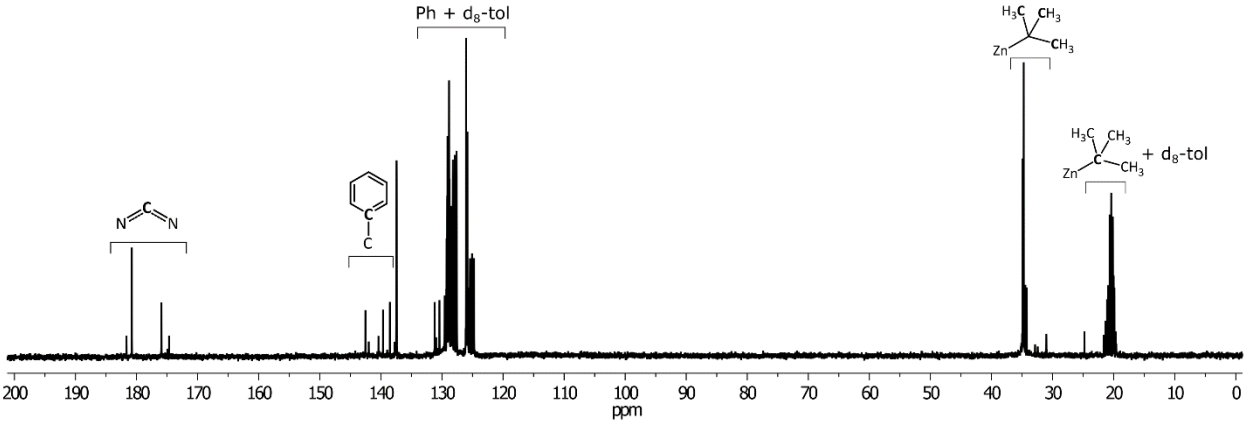


Fig. S12. ^{13}C NMR spectrum of **3** in d_8-tol.

2. DOSY NMR analysis

DOSY ^{1}H NMR spectra were acquired on Bruker AVANCE II (300 MHz) spectrometer. The molecular weights (*MW*) of analyzed compounds were estimated utilizing an external calibration curve (ECC) approach with normalized diffusion coefficients exploiting 1,2,3,4-tetraphenylnaphtalene (TPhN) as an internal reference.[1] The molecular masses calculated for considered alkylzinc complexes were corrected by a correction factor χ_{cor} for molecules with a high van-der Waals density (MDw) [note, that due to the lack of reference data for χ_{cor} in d_8-tol, χ_{cor} calculated for C_6D_6 where used].[2]

2.1. Equimolar reaction of *dipf*-H with $ZnMe_2$

Analysis of the DOSY ^{1}H NMR spectra obtained from a 1:1 reaction of $ZnMe_2$ with *dipf*-H in d_8-toluene indicates the presence of two components with the estimated *MW* of about 762 and 66 g·mol^{-1} (Fig. S15), which fit well to the MW_{cor} of about 746 and 49 g·mol^{-1} calculated for $[Me_2Zn_3(dipf)_4]$ (**1**) and $ZnMe_2$, respectively (Table S1). Furthermore, analysis of the relative intensity of the signals in the ^{1}H NMR spectrum indicates a 1:1 molar ratio of both components.

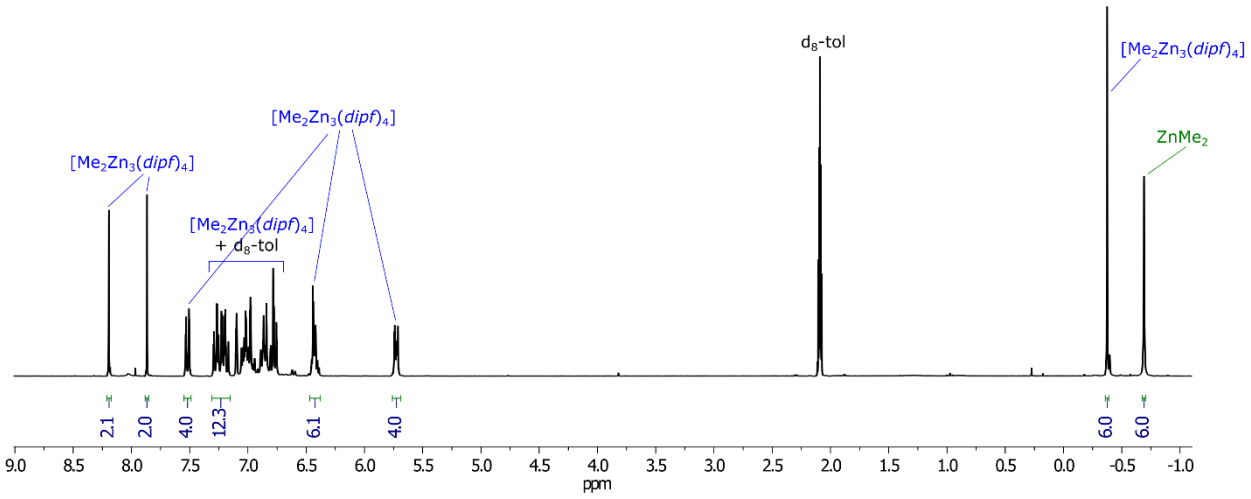


Fig. S13. ^{1}H NMR spectrum from the 1:1 reaction of $ZnMe_2$ with *dipf*-H in d_8-toluene.

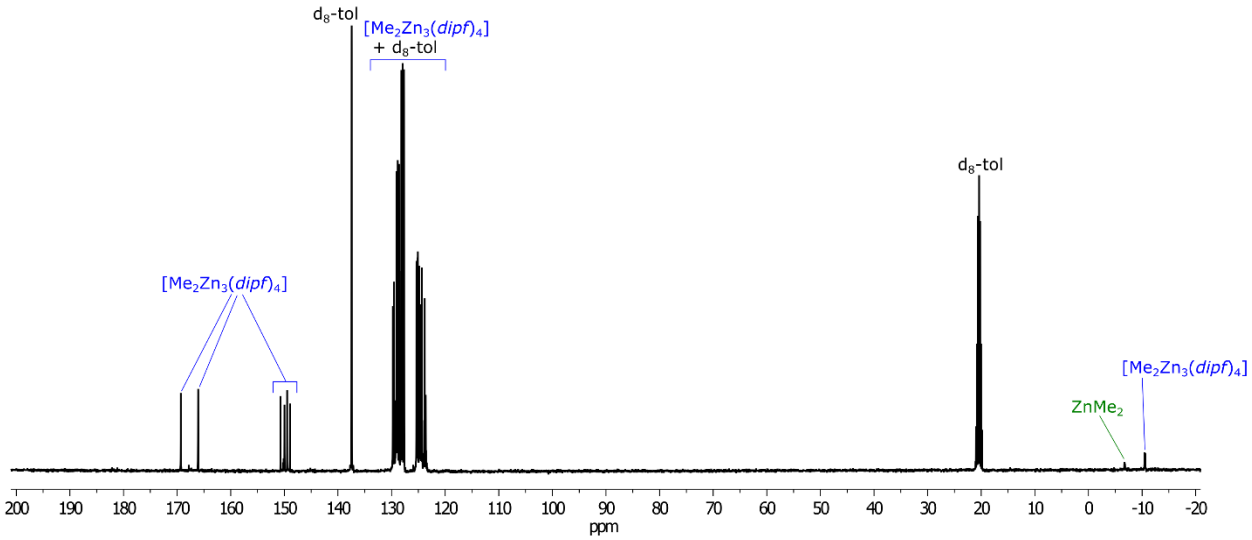


Fig. S14. ^{13}C NMR spectrum from the 1:1 reaction of $ZnMe_2$ with *dipf*-H in d_8-toluene.

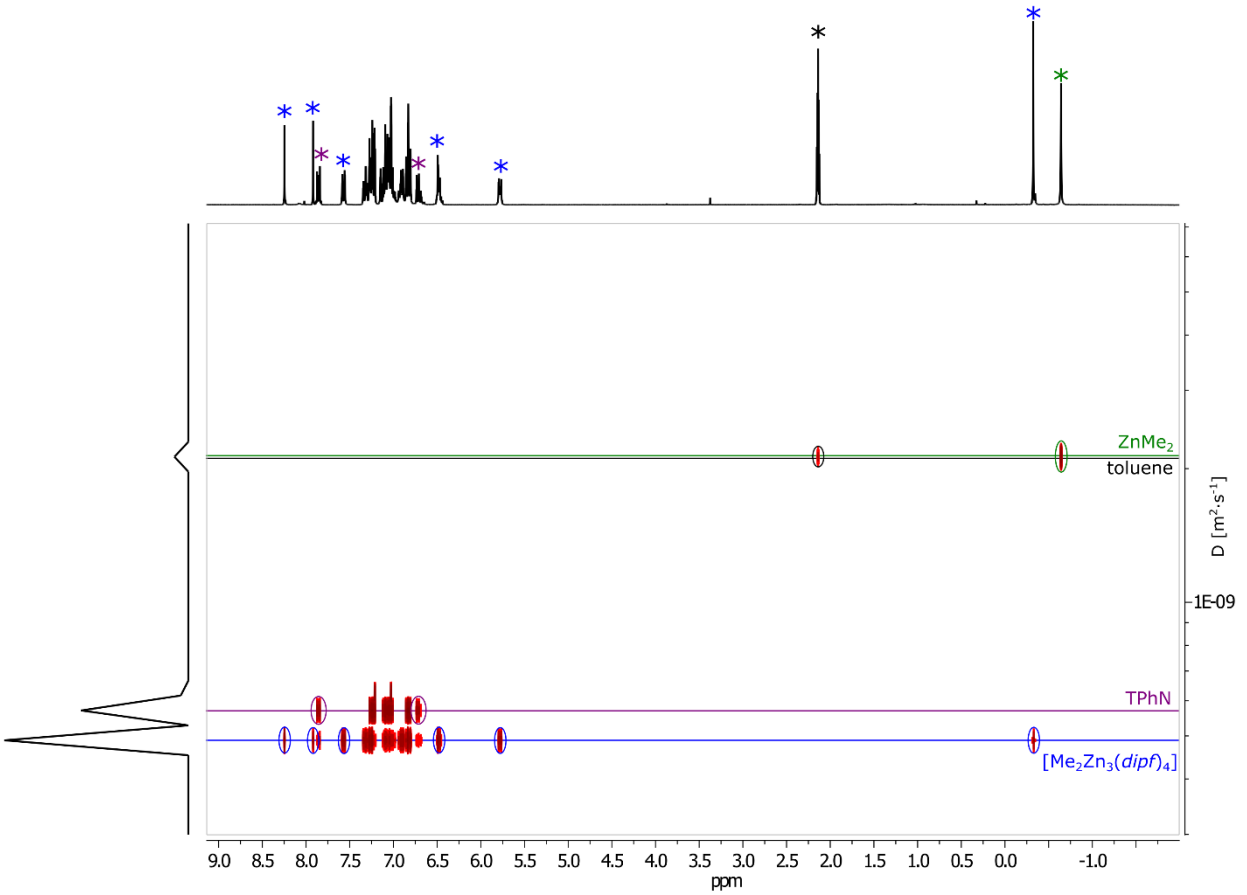


Fig. S15. 2D DOSY-NMR spectrum from the 1:1 reaction of $ZnMe_2$ with *dipf*-H in d_8-toluene (signals used to estimate *MW* are marked with asterisks).

Table S1. Calculated molecular weights (*MW*), van-der Waals densities (MD_W), and corrected molecular weights (MW_{cor}) of respective compounds.

Compound	*MW* [g·mol^{-1}]	MD_W [g·mol^{-1}·m^{-3}]	χ_{cor}	MW_{cor} [g·mol^{-1}]
[Me_2Zn_3(*dipf*)$_4$]	1006	$6.17 \cdot 10^{29}$	1.35	**746**
$ZnMe_2$	95	$9.95 \cdot 10^{29}$	1.94	**49**

Table S2. Determined diffusion coefficients *D* and estimated molecular weights *MW* based on analysis of DOSY ^{1}H NMR spectrum from the 1:1 reaction of $ZnMe_2$ with *dipf*-H in d_8-toluene.

Internal reference (TPhF)		Sample		
[ppm]	*D* [m^2·s^{-1}]	[ppm]	*D* [m^2·s^{-1}]	*MW* [g·mol^{-1}]
7.78-7.83	$6.09 \cdot 10^{-10}$	Complex		
6.62-6.69	$6.13 \cdot 10^{-10}$	8.18-8.22	$4.85 \cdot 10^{-10}$	733
Average Reference *D*	$6.11 \cdot 10^{-10}$	7.86-7.89	$4.69 \cdot 10^{-10}$	773
		7.49-7.56	$4.67 \cdot 10^{-10}$	780
		6.38-6.47	$4.73 \cdot 10^{-10}$	762
		5.70-5.76	$4.70 \cdot 10^{-10}$	771
		-0.41-(-0.35)	$4.77 \cdot 10^{-10}$	753
		Average Estimated *MW*		**762**
		Dialkylzinc		
		-0.72-(-0.67)	$2.11 \cdot 10^{-9}$	**66**
		Toluene		
		2.15-2.05	$1.77 \cdot 10^{-9}$	87

2.2. Equimolar reaction of *dipf*-H with $ZnEt_2$

Analysis of the DOSY ^{1}H NMR spectra obtained from a 1:1 reaction of $ZnEt_2$ with *dipf*-H in d_8-toluene indicates the presence of two components with the estimated *MW* of about 761 and 117 g·mol^{-1} (Fig. S18), which fit well to the MW_{cor} of about 776 and 79 g·mol^{-1} calculated for $[Et_2Zn_3(dipf)_4]$ (**1**) and $ZnMe_2$, respectively (Table S3). Furthermore, analysis of the relative intensity of the signals in the ^{1}H NMR spectrum indicates a 1:1 molar ratio of both components.

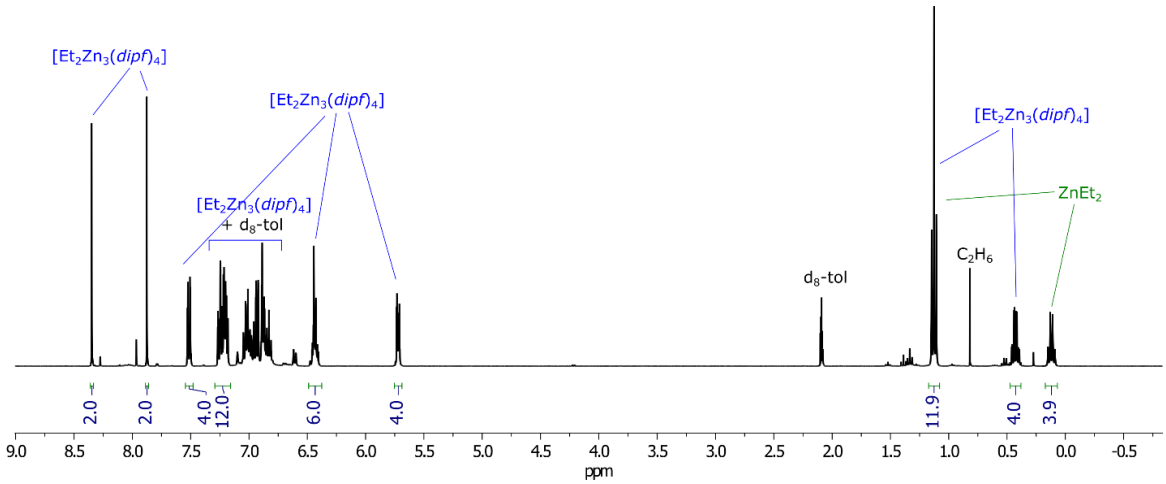


Fig. S16. ^{1}H NMR spectrum from the 1:1 reaction of $ZnEt_2$ with *dipf*-H in d_8-toluene.

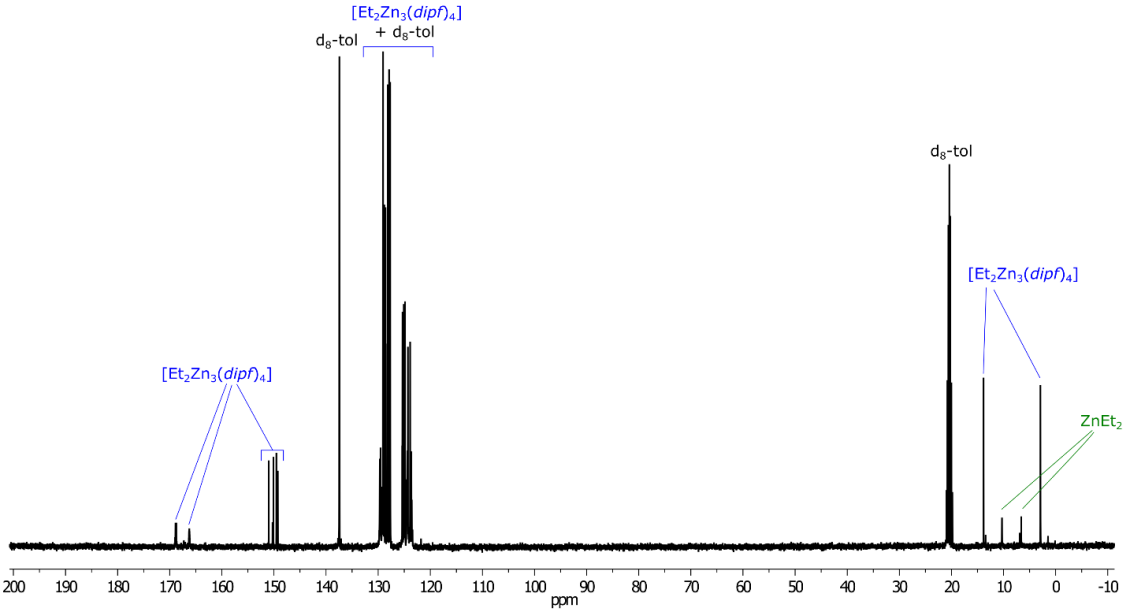


Fig. S17. ^{13}C NMR spectrum from the 1:1 reaction of $ZnEt_2$ with *dipf*-H in d_8-toluene.

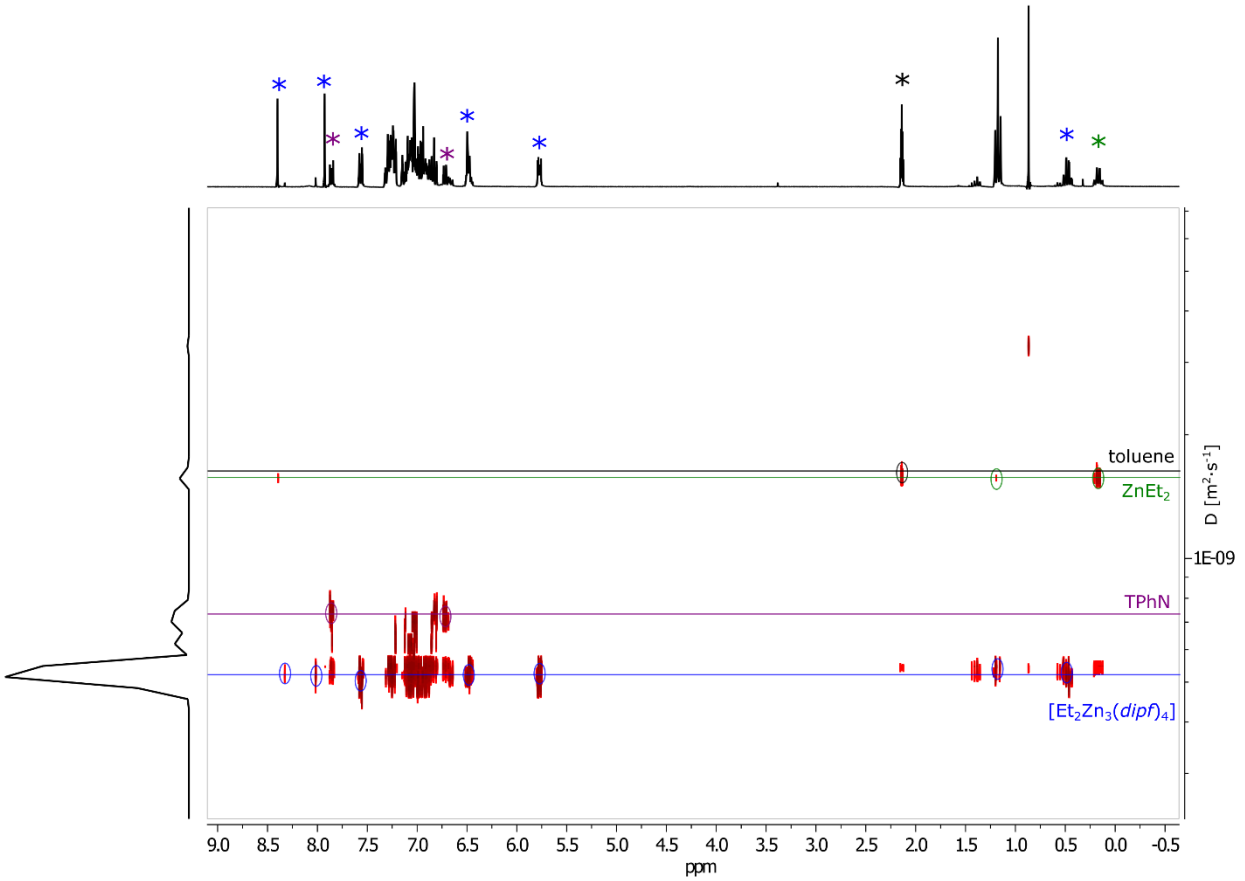


Fig. S18. 2D DOSY-NMR spectrum from the 1:1 reaction of $ZnEt_2$ with *dipf*-H in d_8-toluene (signals used to estimate *MW* are marked with asterisks).

Table S3. Calculated molecular weights (*MW*), van-der Waals densities (MD_W), and corrected molecular weights (MW_{cor}) of respective compounds.

Compound	*MW* [g·mol^{-1}]	MD_W [g·mol^{-1}·m^{-3}]	χ_{cor}	MW_{cor} [g·mol^{-1}]
$[Et_2Zn_3(dipf)_4]$	1034	$6.07 \cdot 10^{29}$	1.33	**776**
$ZnEt_2$	123	$7.44 \cdot 10^{29}$	1.56	**79**

Table S4. Determined diffusion coefficients *D* and estimated molecular weights *MW* based on analysis of DOSY ^{1}H NMR spectrum from the 1:1 reaction of $ZnEt_2$ with *dipf*-H in d_8-toluene.

Internal reference (TPhF)		Sample		
[ppm]	*D* [$m^2 \cdot s^{-1}$]	[ppm]	*D* [$m^2 \cdot s^{-1}$]	*MW* [$g \cdot mol^{-1}$]
7.16-7.28	$6.83 \cdot 10^{-10}$	Complex		
6.80-6.86	$6.28 \cdot 10^{-10}$	8.33-8.36	$5.01 \cdot 10^{-10}$	777
Average Reference *D*	$6.55 \cdot 10^{-10}$	7.85-7.89	$5.28 \cdot 10^{-10}$	713
		7.48-7.55	$4.89 \cdot 10^{-10}$	809
		6.39-6.48	$5.19 \cdot 10^{-10}$	735
		5.69-5.75	$5.06 \cdot 10^{-10}$	766
		0.37-0.47	$5.07 \cdot 10^{-10}$	763
		Average Estimated *MW*		**761**
		Dialkylzinc		
		0.07-0.16	$1.59 \cdot 10^{-9}$	**117**
		Toluene		
		2.15-2.05	$1.92 \cdot 10^{-9}$	86

2.3. Equimolar reaction of *bza*-H with $ZnMe_2$

The ^{1}H and ^{13}C NMR spectra obtained from the 1:1 reaction of $ZnMe_2$ with *bza*-H in d_8-toluene indicate the presence of several various forms of methylzinc *bza* complexes (Fig. S19 and S20). Thus, a significant discrepancy of estimated *MW* based on resonances from the organic ligand and alkylzinc group (Fig. S21 and Table S5) is likely due to the former being collective signals from all *bza* complexes while the latter represents the individual methylzinc derivatives. Analysis of resonances from the methyl groups indicates the presence of two main components with *MW* of about 609 and 86 $g \cdot mol^{-1}$, and at least two other compounds with *MW* of about 735 and 567 $g \cdot mol^{-1}$ in a significant minority. The two former masses fit well to the MW_{cor} of about 610 and 49 $g \cdot mol^{-1}$ calculated for $[Me_3Zn_4(bza)_5]$ and $ZnMe_2$, respectively. The other two signals may be associated with $[Me_4Zn_5(bza)_6]$ and $[MeZn_3(bza)_5]$ with the corresponding MW_{cor} of about 741 and 561 $g \cdot mol^{-1}$. The presence of other forms of *bza* complexes cannot be excluded, however, their analysis using the DOSY technique was hindered by the low intensity of signals.

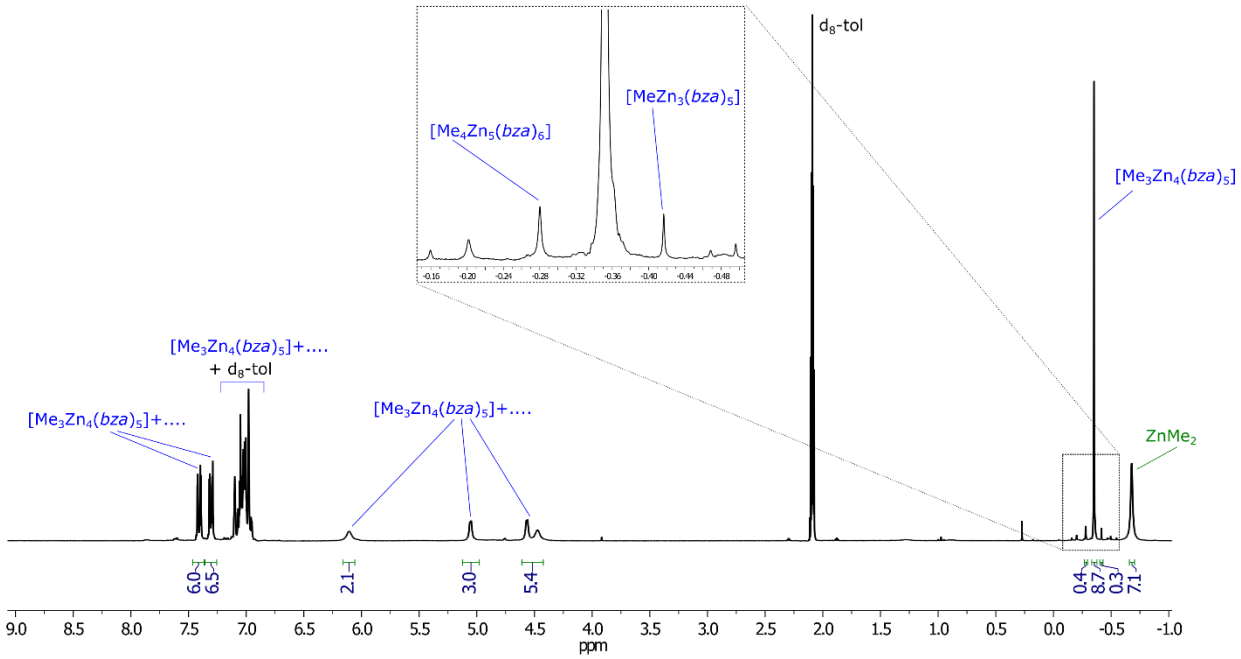


Fig. S19. ^{1}H NMR spectrum from the 1:1 reaction of $ZnMe_2$ with *bza*-H in d_8-toluene.

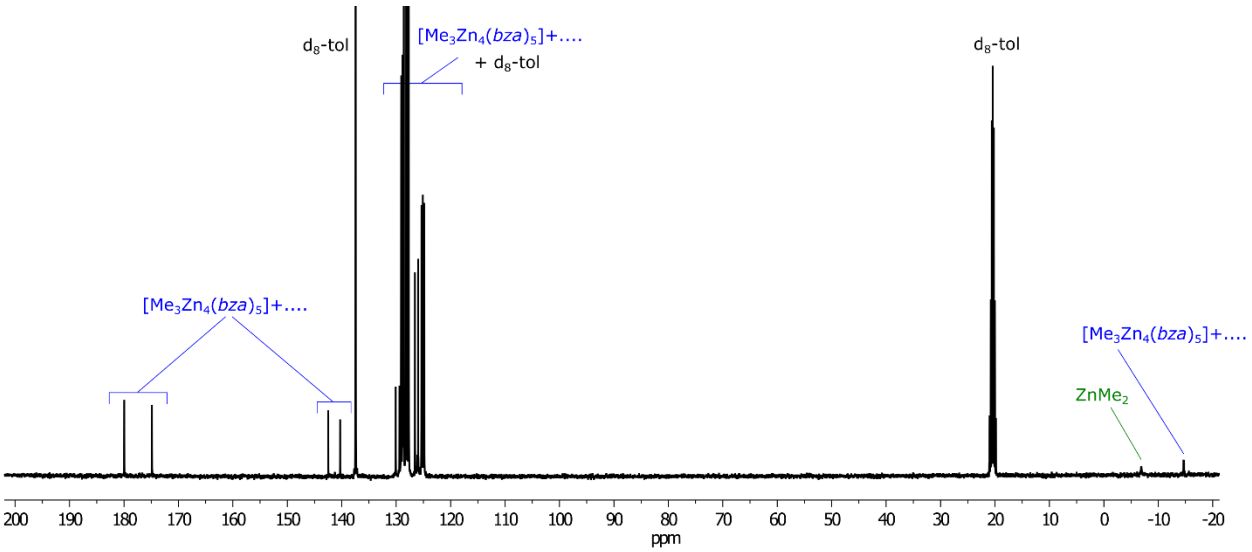


Fig. S20. ^{13}C NMR spectrum from the 1:1 reaction of $ZnMe_2$ with *bza*-H in d_8-toluene.

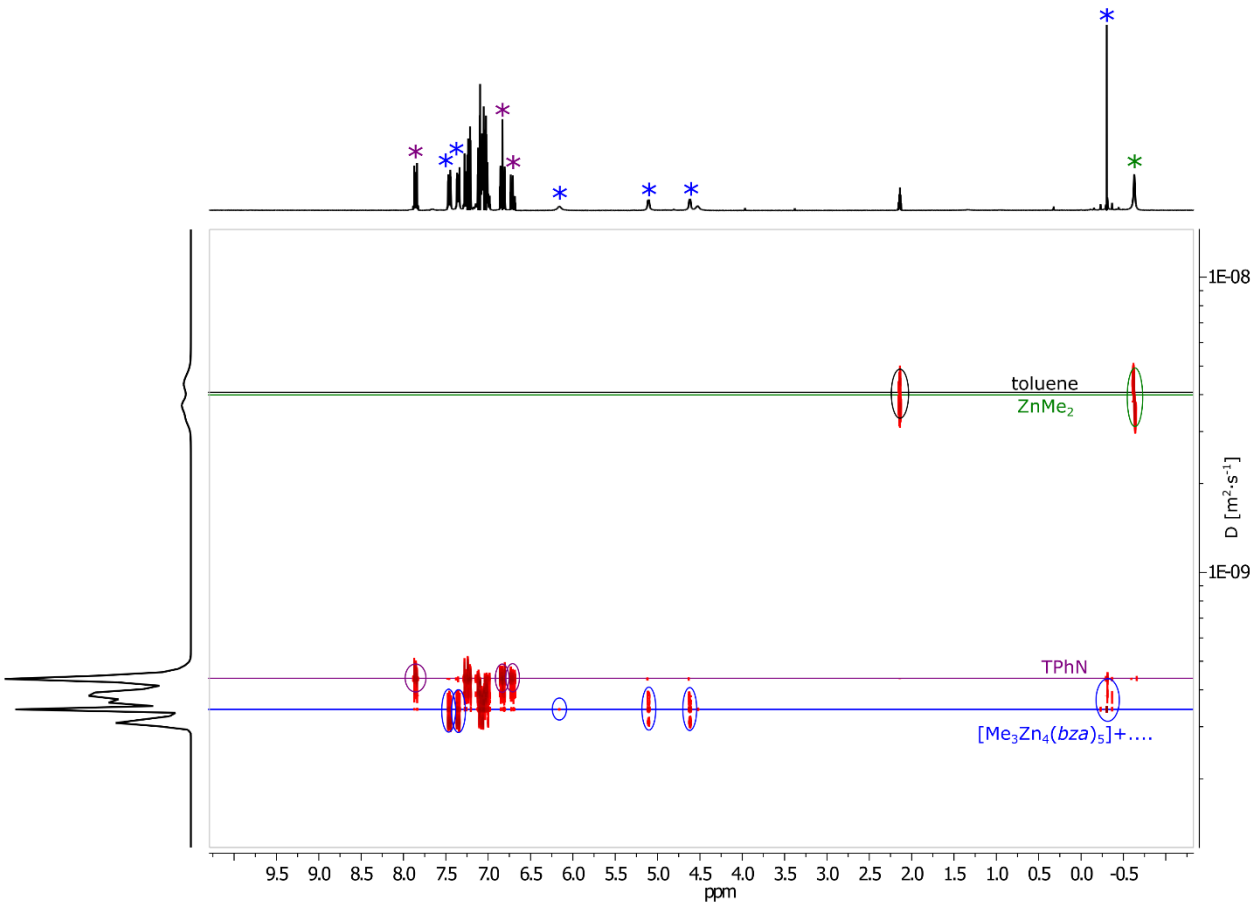


Fig. S21. 2D DOSY-NMR spectrum from the 1:1 reaction of $ZnMe_2$ with *bza*-H in d_8-toluene (signals used to estimate *MW* are marked with asterisks).

Table S5. Calculated molecular weights (*MW*), van-der Waals densities (MD_W), and corrected molecular weights (MW_{cor}) of respective compounds.

Compound	*MW* [g·mol^{-1}]	MD_W [g·mol^{-1}·m^{-3}]	χ_{cor}	MW_{cor} [g·mol^{-1}]
$[Me_3Zn_4(bza)_5]$	902	$6.93 \cdot 10^{29}$	1.48	**610**
$[Me_4Zn_5(bza)_6]$	1101	$6.96 \cdot 10^{29}$	1.48	**741**
$[MeZn_3(bza)_5]$	806	$6.69 \cdot 10^{29}$	1.44	**561**
$ZnEt_2$	95	$9.95 \cdot 10^{29}$	1.94	**49**

Table S6. Determined diffusion coefficients *D* and estimated molecular weights *MW* based on analysis of DOSY ^{1}H NMR spectrum from the 1:1 reaction of $ZnMe_2$ with *bza*-H in d_8-toluene.

Internal reference (TPhF)		Sample		
[ppm]	*D* [$m^2 \cdot s^{-1}$]	[ppm]	*D* [$m^2 \cdot s^{-1}$]	*MW* [$g \cdot mol^{-1}$]
7.78-7.83	$6.90 \cdot 10^{-10}$	Complex		
6.74-6.82	$6.62 \cdot 10^{-10}$	7.37-7.44	$5.58 \cdot 10^{-10}$	677
6.62-6.70	$6.58 \cdot 10^{-10}$	7.27-7.34	$5.64 \cdot 10^{-10}$	665
Average Reference *D*	$6.70 \cdot 10^{-10}$	6.06-6.18	$5.56 \cdot 10^{-10}$	681
		5.02-5.09	$5.67 \cdot 10^{-10}$	659
		4.53-4.60	$5.53 \cdot 10^{-10}$	687
		4.43-4.52	$5.47 \cdot 10^{-10}$	698
		Average Estimated *MW*		678
		-0.29-(-0.27)	$5.30 \cdot 10^{-10}$	**735**
		-0.38-(-0.33)	$5.95 \cdot 10^{-10}$	**609**
		-0.43-(-0.41)	$6.21 \cdot 10^{-10}$	**567**
		Dialkylzinc		
		-0.74-(-0.63)	$1.96 \cdot 10^{-9}$	**86**
		Toluene		
		2.12-2.06	$2.00 \cdot 10^{-9}$	83

2.4. Equimolar reaction of *bza*-H with $ZnEt_2$

DOSY-NMR spectrum from 1:1 reaction of $ZnEt_2$ with *bza*-H in d_8-toluene (Fig. S24 and Table S8) shows, like in the case of methylzinc derivative, the significant discrepancy of estimated *MW* based on signals from the organic ligand and alkylzinc groups, which is likely the result of the presence of several various *bza* complexes in the post-reaction mixture. Analysis of the ethyl signals indicates the presence of two main components of the post-reaction mixture with *MW* of about 653 and 124 $g \cdot mol^{-1}$, which fit well to the MW_{cor} of about 655 and 79 $g \cdot mol^{-1}$ calculated for $[Et_3Zn_4(bza)_5]$ and $ZnEt_2$, respectively. The analysis of other potential minor products is hampered due to the low intensity of signals.

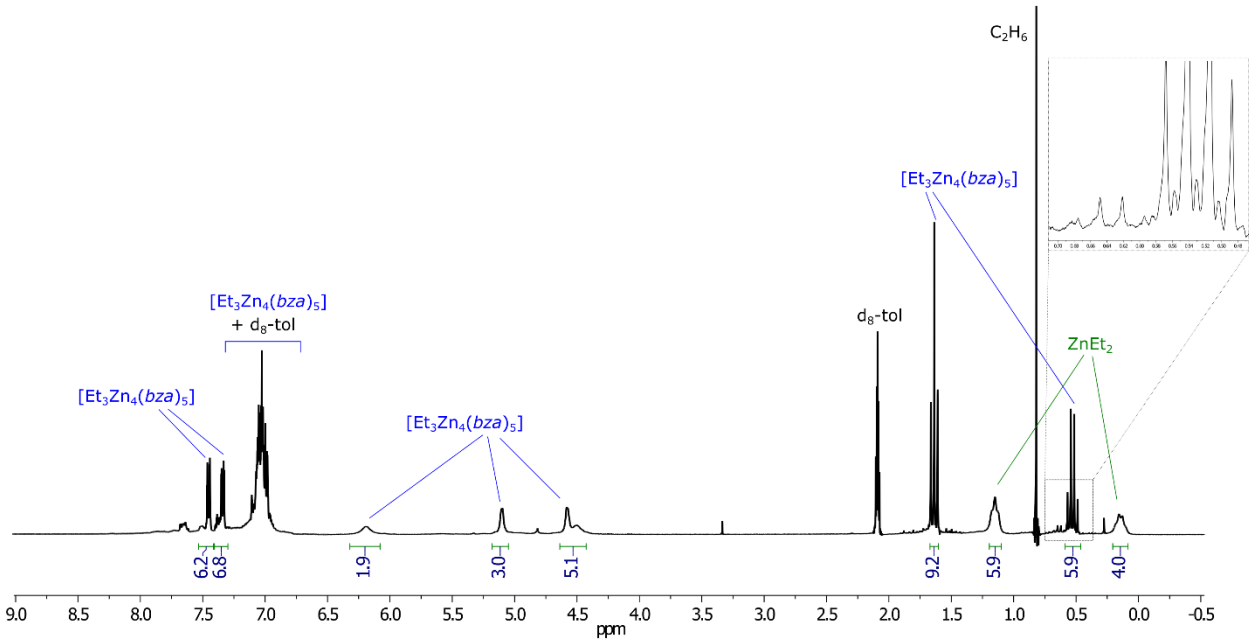


Fig. S22. ^{1}H NMR spectrum from the 1:1 reaction of $ZnEt_2$ with *bza*-H in d_8-toluene.

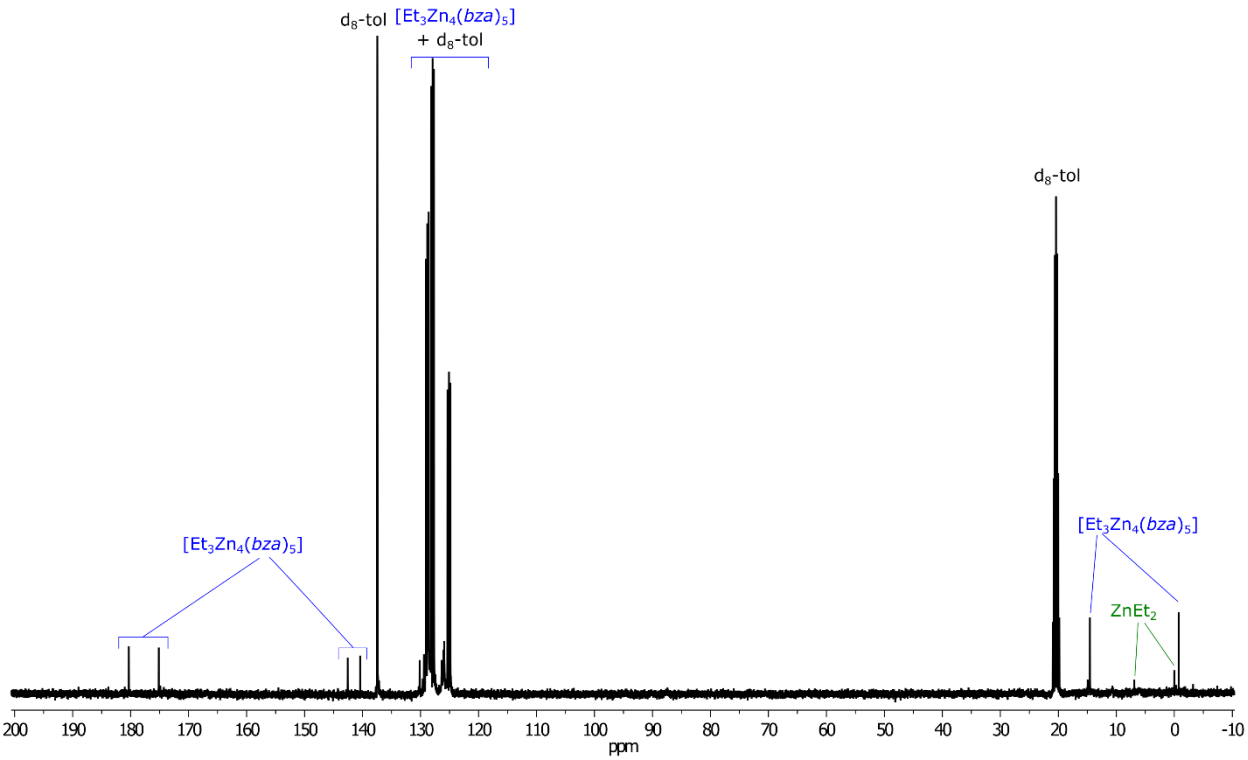


Fig. S23. ^{13}C NMR spectrum from the 1:1 reaction of $ZnEt_2$ with *bza*-H in d_8-toluene.

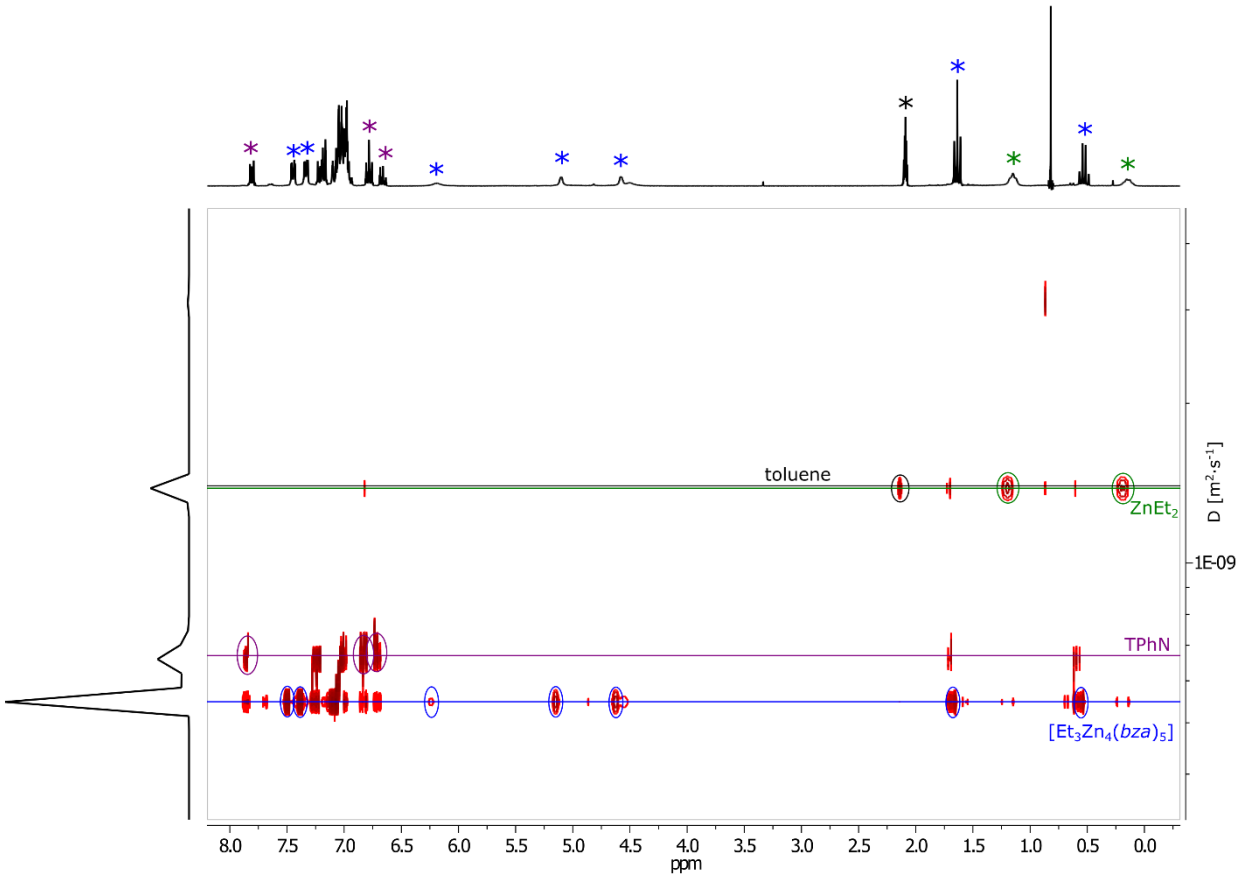


Fig. S24. 2D DOSY-NMR spectrum from the 1:1 reaction of $ZnEt_2$ with *bza*-H in d_8-toluene (signals used to estimate *MW* are marked with asterisks).

Table S7. Calculated molecular weights (*MW*), van-der Waals densities (MD_W), and corrected molecular weights (MW_{cor}) of respective compounds.

Compound	*MW* [g·mol^{-1}]	MD_W [g·mol^{-1}·m^{-3}]	χ_{cor}	MW_{cor} [g·mol^{-1}]
$[Et_3Zn_4(bza)_5]$	944	$6.71 \cdot 10^{29}$	1.44	**655**
$ZnEt_2$	123	$7.44 \cdot 10^{29}$	1.56	**79**

Table S8. Determined diffusion coefficients *D* and estimated molecular weights *MW* based on analysis of DOSY ^{1}H NMR spectrum from the 1:1 reaction of $ZnEt_2$ with *bza*-H in d_8-toluene.

Internal reference (TPhF)		Sample		
[ppm]	*D* [$m^2 \cdot s^{-1}$]	[ppm]	*D* [$m^2 \cdot s^{-1}$]	*MW* [$g \cdot mol^{-1}$]
7.76-7.84	$6.68 \cdot 10^{-10}$	Complex		
6.74-6.83	$6.81 \cdot 10^{-10}$	7.42-7.49	$5.31 \cdot 10^{-10}$	767
6.62-6.70	$7.16 \cdot 10^{-10}$	7.30-7.38	$5.42 \cdot 10^{-10}$	742
Average Reference *D*	$6.88 \cdot 10^{-10}$	6.10-6.28	$5.66 \cdot 10^{-10}$	690
		5.03-5.17	$5.56 \cdot 10^{-10}$	710
		4.54-4.63	$5.47 \cdot 10^{-10}$	731
		Average Estimated *MW*		**706**
		1.57-1.70	$5.81 \cdot 10^{-10}$	662
		0.46-0.60	$5.91 \cdot 10^{-10}$	642
		Average Estimated *MW*		**653**
		Dialkylzinc		
		1.07-1.23	$1.59 \cdot 10^{-9}$	127
		0.05-0.23	$1.59 \cdot 10^{-9}$	120
		Average Estimated *MW*		**124**
		Toluene		
		2.15-2.05	$1.92 \cdot 10^{-9}$	93

2.5. Solution of complex 3

^{1}H and ^{13}C NMR spectra of **3** in d_8-toluene indicate the presence of various forms of bza complexes after dissolution (Fig. S11 and S12). Like in the case of methyl- and ethylzinc derivatives of *bza*, the ^{1}H DOSY spectrum of **3** exhibits a significant discrepancy in estimated *MW* based on signals from the organic ligand and alkylzinc groups (Fig. S26). Analysis of the ^{t}Bu signals indicates three main components with *MW* of about 696, 748, and 158 $g \cdot mol^{-1}$, which fit well to the MW_{cor} of about 706, 744, and 139 $g \cdot mol^{-1}$ calculated for $[^tBuZn(bza)]_4$, $[^tBu_3Zn_4(bza)_5]$, and Zn^tBu_2, respectively (Table S10). Other signals of aliphatic groups are also visible, but their analysis is hampered due to the low intensity.

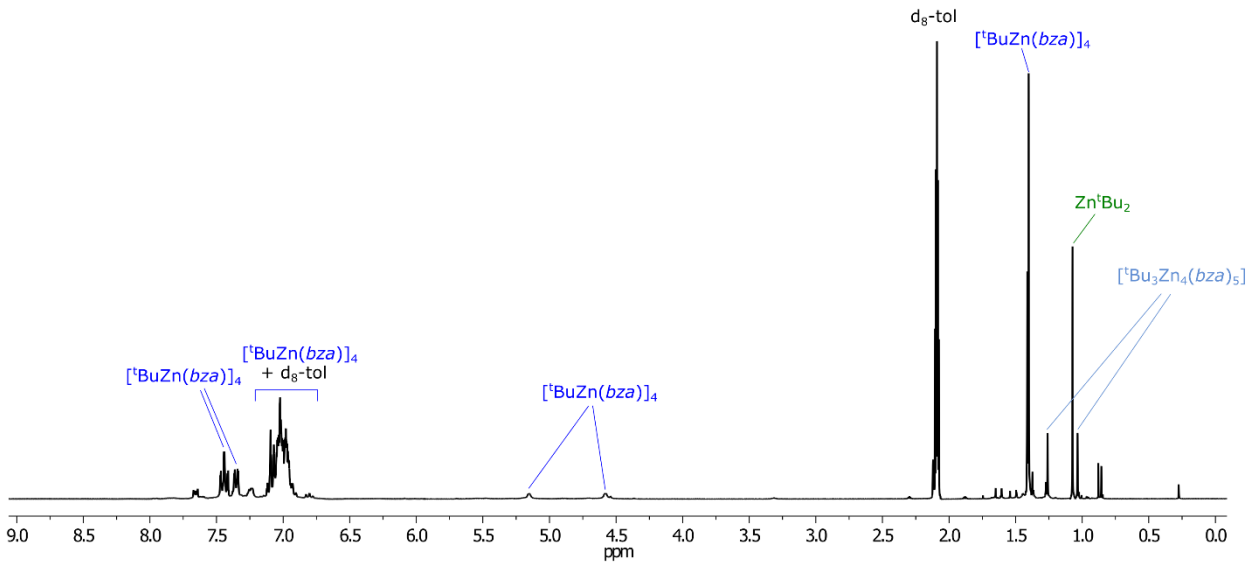


Fig. S25. ^{1}H NMR spectrum of **3** in d_8-toluene.

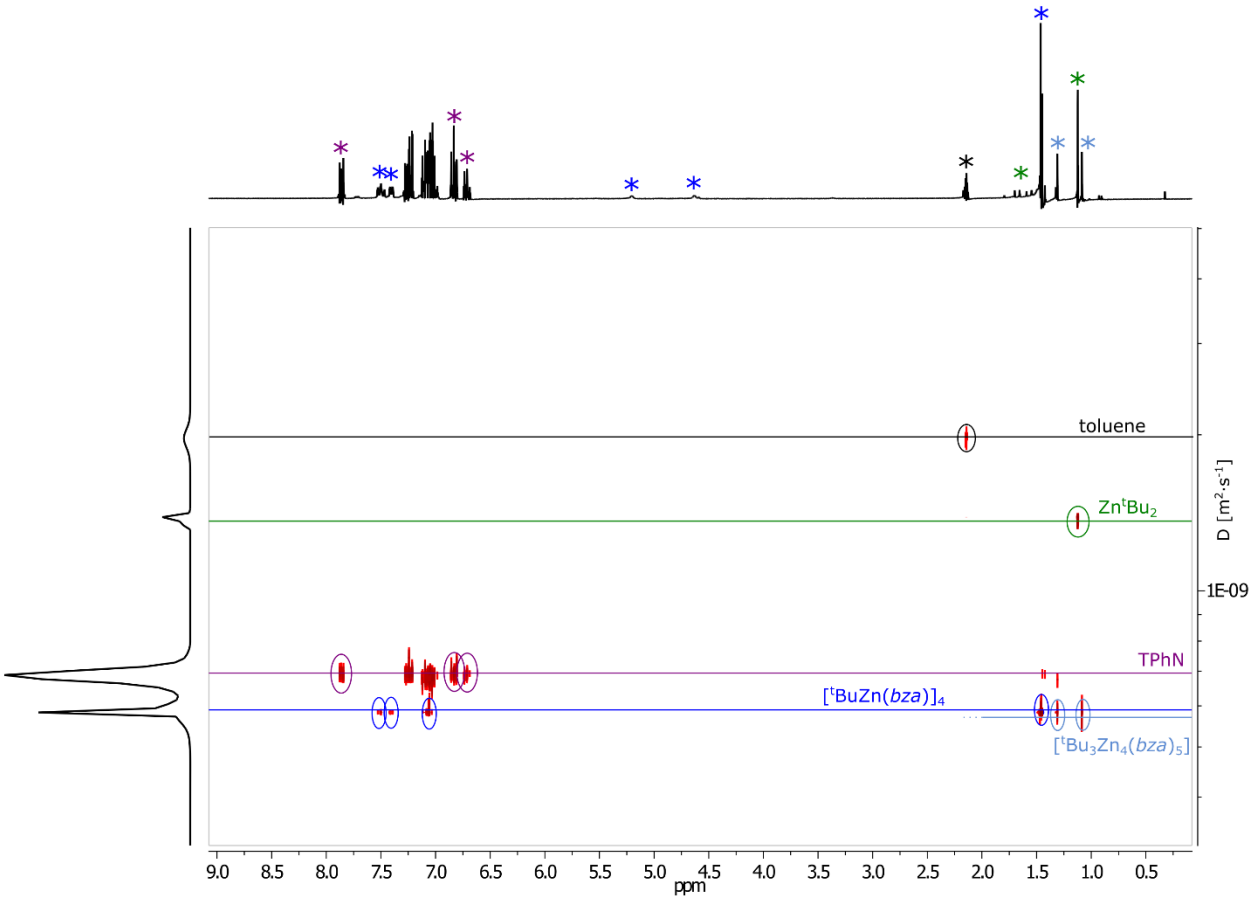


Fig. S26. 2D DOSY-NMR spectrum of **3** in d_8-toluene (signals used to estimate *MW* are marked with asterisks).

Table S9. Calculated molecular weights (*MW*), van-der Waals densities (MD_W), and corrected molecular weights (MW_{cor}) of respective compounds.

Compound	*MW* [g·mol^{-1}]	MD_W [g·mol^{-1}·m^{-3}]	χ_{cor}	MW_{cor} [g·mol^{-1}]
[^{t}BuZn(*bza*)]$_4$	966	$6.28 \cdot 10^{29}$	1.37	**706**
[^{t}Bu$_3$Zn$_4$(*bza*)$_5$]	1028	$6.36 \cdot 10^{29}$	1.38	**744**
Zn^{t}Bu$_2$	179	$5.86 \cdot 10^{29}$	1.29	**139**

Table S10. Determined diffusion coefficients *D* and estimated molecular weights *MW* based on analysis of DOSY ^{1}H NMR spectrum of **3** in d_8-toluene.

Internal reference (TPhF)		Sample		
[ppm]	*D* [m^2·s^{-1}]	[ppm]	*D* [m^2·s^{-1}]	*MW* [g·mol^{-1}]
7.76-7.84	$7.07 \cdot 10^{-10}$	Complex		
6.74-6.83	$7.06 \cdot 10^{-10}$	7.40-7.50	$5.59 \cdot 10^{-10}$	733
6.62-6.70	$7.04 \cdot 10^{-10}$	7.33-7.38	$5.57 \cdot 10^{-10}$	737
Average Reference *D*	$7.06 \cdot 10^{-10}$	5.11-5.23	$5.71 \cdot 10^{-10}$	709
		4.56-4.63	$5.65 \cdot 10^{-10}$	721
		1.38-1.43	$5.78 \cdot 10^{-10}$	**696**
		1.24-1.29	$5.53 \cdot 10^{-10}$	**746**
		1.01-1.05	$5.55 \cdot 10^{-10}$	**743**
		Dialkylzinc		
		1.05-1.10	$1.42 \cdot 10^{-9}$	**158**
		Toluene		
		2.15-2.05	$2.00 \cdot 10^{-9}$	91

3. X-Ray Crystallography Data

Table S11. Crystal data and structure refinement for **1^{Me}**.

Empirical formula	$C_{54}H_{50}N_8Zn_3$	
Formula weight	1007.13	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*P* 2_1/n	
Unit cell dimensions	a = 18.5634(3) Å	a= 90°.
	b = 24.5535(4) Å	b= 107.018(2)°.
	c = 22.3642(4) Å	g = 90°.
Volume	9747.2(3) Å^3	
Z	8	
Density (calculated)	1.373 Mg/m^3	
Absorption coefficient	1.509 mm^{-1}	
F(000)	4160	
Crystal size	0.15 x 0.11 x 0.07 mm^3	
Theta range for data collection	3.015 to 27.000°.	
Index ranges	-20<=h<=23, -31<=k<=28, -28<=l<=16	
Reflections collected	49944	
Independent reflections	21042 [R(int) = 0.0392]	
Completeness to theta = 25.242°	99.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	21042 / 0 / 1175	
Goodness-of-fit on F^2	1.044	
Final R indices [I>2sigma(I)]	R1 = 0.0407, wR2 = 0.0763	
R indices (all data)	R1 = 0.0640, wR2 = 0.0844	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.554 and -0.532 e.Å^{-3}	

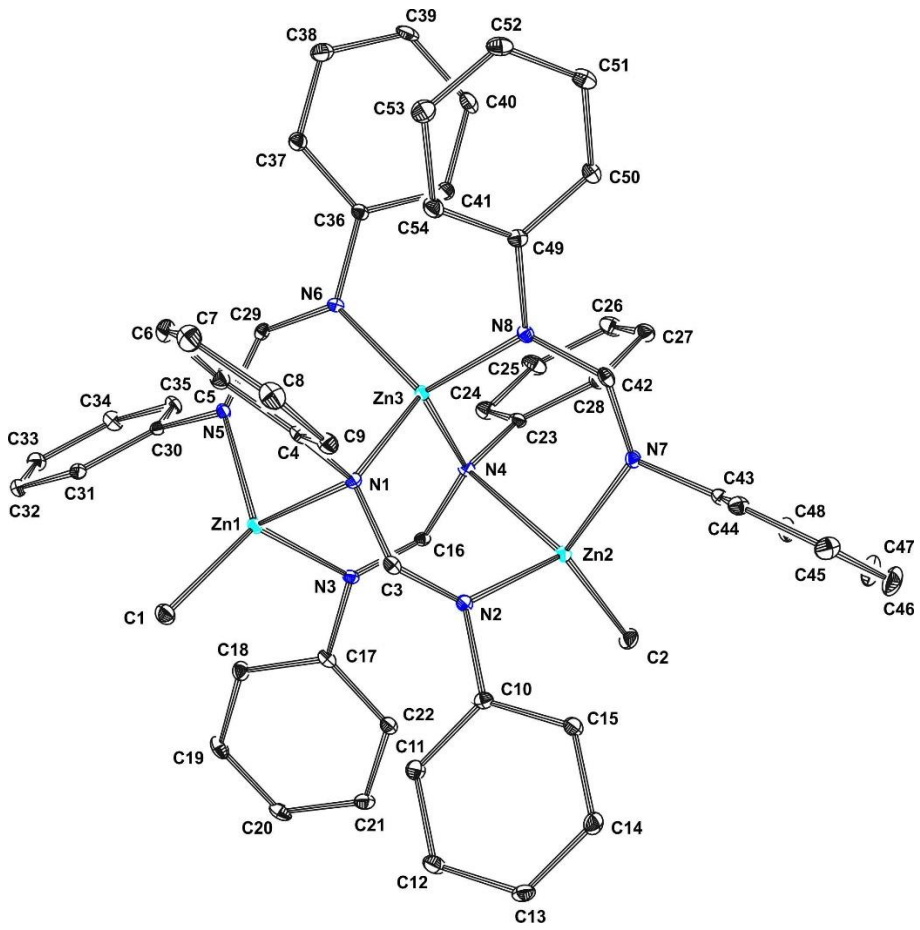


Fig. S27. The molecular structure of $\mathbf{1^{Me}}$ with thermal ellipsoids set at 30% probability. Hydrogen atoms have been omitted for clarity.

Table S12. Selected intermolecular bond lengths [Å] and angles [°] for $\mathbf{1^{Me}}$.

Zn1-C1	1.989(3)	Zn1-N1-C3	100.79(16)
Zn1-N1	2.261(2)	Zn1-N3-C16	128.76(19)
Zn1-N3	2.073(2)	Zn1-N5-C29	131.02(19)
Zn1-N5	2.045(2)	Zn2-N2-C3	134.0(2)
Zn2-C2	1.969(3)	Zn2-N4-C16	96.18(16)
Zn2-N2	2.073(2)	Zn2-N7-C42	131.04(19)
Zn2-N4	2.307(2)	Zn2-N4-Zn3	91.21(8)
Zn2-N7	2.045(2)	Zn3-N1-C3	120.46(19)
Zn3-N1	2.045(2)	Zn3-N4-C16	124.64(18)
Zn3-N4	2.061(2)	Zn3-N6-C29	122.62(19)
Zn3-N6	1.997(2)	Zn3-N8-C42	124.1(2)
Zn3-N8	2.004(2)		

Table S13. Crystal data and structure refinement for $\mathbf{1}^{Et}$.

Empirical formula	$C_{56}H_{54}N_8Zn_3$	
Formula weight	1035.18	
Temperature	100(2) K	
Wavelength	0.71073 Ĺ	
Crystal system	Monoclinic	
Space group	*P* 2_1/c	
Unit cell dimensions	a = 11.7300(2) Å	a= 90°.
	b = 13.4060(3) Å	b= 100.5050(10)°.
	c = 31.6940(7) Å	g = 90°.
Volume	4900.42(18) $Å^3$	
Z	4	
Density (calculated)	1.403 Mg/m^3	
Absorption coefficient	1.503 mm^{-1}	
F(000)	2144	
Crystal size	0.16 x 0.11 x 0.08 mm^3	
Theta range for data collection	1.996 to 27.419°.	
Index ranges	-15<=h<=15, -17<=k<=17, -40<=l<=40	
Reflections collected	21718	
Independent reflections	11110 [R(int) = 0.0598]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.887 and 0.820	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11110 / 0 / 606	
Goodness-of-fit on F^2	1.039	
Final R indices [I>2sigma(I)]	R1 = 0.0474, wR2 = 0.0883	
R indices (all data)	R1 = 0.0789, wR2 = 0.0957	
Largest diff. peak and hole	0.401 and -0.421 e.$Å^{-3}$	

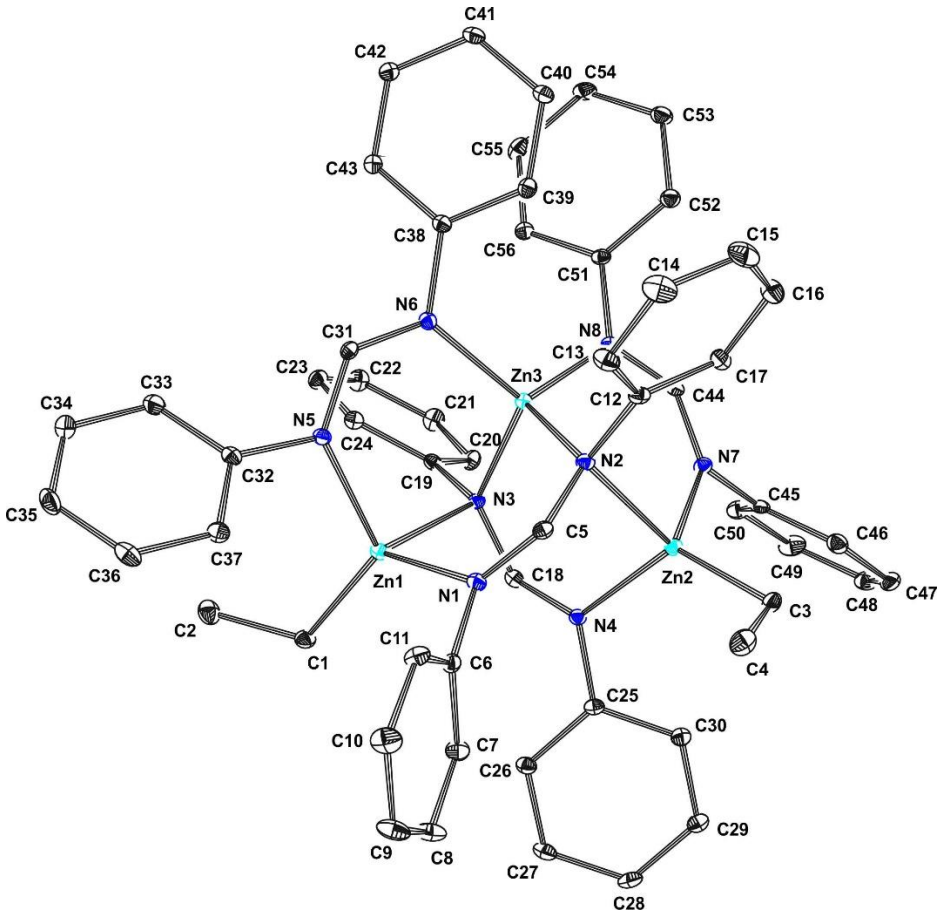


Fig. S28. The molecular structure of $\mathbf{1}^{Et}$ with thermal ellipsoids set at 30% probability. Hydrogen atoms have been omitted for clarity.

Table S14. Selected intermolecular bond lengths [Å] and angles [°] for $\mathbf{1}^{Et}$.

Zn1-C1	1.986(3)	Zn1-N1-C5	129.5(2)
Zn1-N1	2.068(2)	Zn1-N3-C18	98.19(18)
Zn1-N3	2.317(2)	Zn1-N5-C31	132.1(2)
Zn1-N5	2.048(2)	Zn2-N2-C5	101.12(18)
Zn2-C3	1.993(3)	Zn2-N4-C18	122.9(2)
Zn2-N2	2.277(2)	Zn2-N7-C44	132.0(2)
Zn2-N4	2.070(2)	Zn2-N2-Zn3	91.98(10)
Zn2-N7	2.055(3)	Zn3-N2-C5	122.6(2)
Zn3-N2	2.045(2)	Zn3-N3-C18	128.2(2)
Zn3-N3	2.057(2)	Zn3-N6-C31	124.3(2)
Zn3-N6	1.992(2)	Zn3-N8-C44	121.7(2)
Zn3-N8	1.987(2)		

Table S15. Crystal data and structure refinement for **2**.

Empirical formula	$C_{34}H_{40}N_4Zn_2$	
Formula weight	635.44	
Temperature	100(2) K	
Wavelength	0.71073 Ĺ	
Crystal system	Monoclinic	
Space group	*P* 2_1	
Unit cell dimensions	a = 15.2257(2) Å	a= 90°.
	b = 22.1226(2) Å	b= 104.4370(10)°.
	c = 19.5545(2) Å	g = 90°.
Volume	6378.59(12) $Å^3$	
Z	8	
Density (calculated)	1.323 Mg/m^3	
Absorption coefficient	1.532 mm^{-1}	
F(000)	2656	
Crystal size	0.16 x 0.09 x 0.05 mm^3	
Theta range for data collection	1.381 to 25.981°.	
Index ranges	-18<=h<=12, -24<=k<=26, -24<=l<=23	
Reflections collected	25876	
Independent reflections	18795 [R(int) = 0.0355]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.926 and 0.848	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	18795 / 1 / 1466	
Goodness-of-fit on F^2	1.025	
Final R indices [I>2sigma(I)]	R1 = 0.0434, wR2 = 0.1111	
R indices (all data)	R1 = 0.0469, wR2 = 0.1148	
Absolute structure parameter	0.240(10)	
Largest diff. peak and hole	0.522 and -0.813 $e.Å^{-3}$	

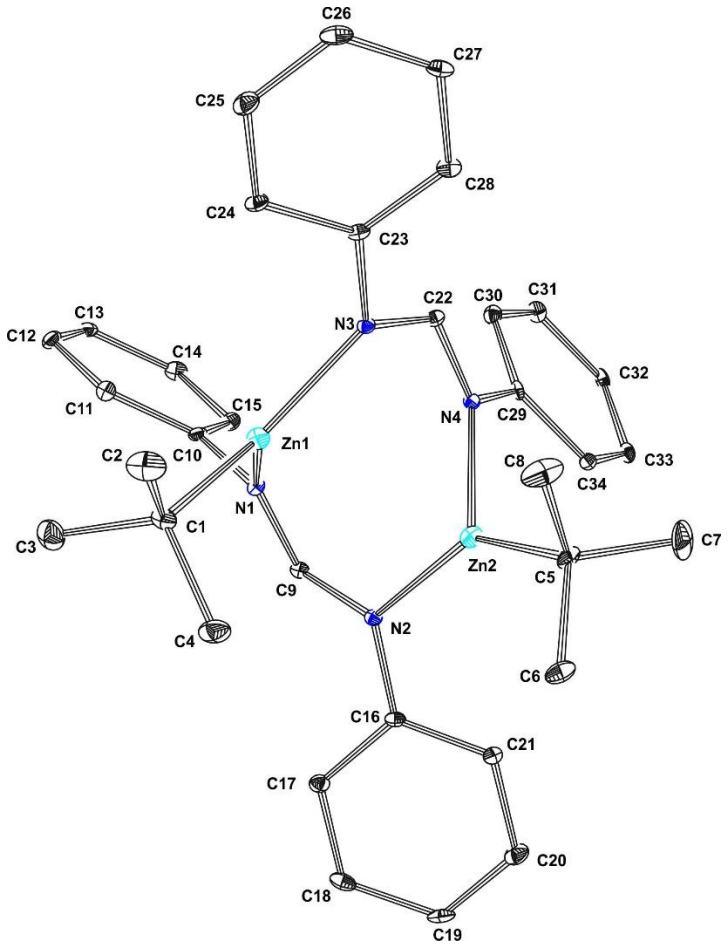


Fig. S29. The molecular structure of **2** with thermal ellipsoids set at 30% probability. Hydrogen atoms have been omitted for clarity.

Table S16. Selected intermolecular bond lengths [Å] and angles [°] for **2**.

Zn1-C1	1.991(6)	Zn1-N1-C9	122.3(4)
Zn1-N1	2.034(5)	Zn1-N1-C10	119.9(4)
Zn1-N3	1.980(5)	Zn1-N3-C22	121.0(4)
Zn2-C5	1.998(6)	Zn1-N3-C23	122.2(4)
Zn2-N2	1.987(5)	Zn2-N2-C9	120.1(4)
Zn2-N4	2.034(5)	Zn2-N2-C16	120.9(4)
		Zn2-N4-C22	116.7(4)
		Zn2-N4-C29	123.7(4)

Table S17. Crystal data and structure refinement for **3**.

Empirical formula	$C_{44}H_{64}N_8Zn_4$	
Formula weight	966.51	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	$I4_1/a$	
Unit cell dimensions	a = 19.5833(3) Å	□= 90°.
	b = 19.5833(3) Å	□= 90°.
	c = 12.0916(3) Å	□ = 90°.
Volume	4637.20(18) Å	
Z	4	
Density (calculated)	1.384 Mg/m^3	
Absorption coefficient	2.083 mm^{-1}	
F(000)	2016	
Crystal size	0.17 x 0.10 x 0.06 mm^3	
Theta range for data collection	3.547 to 29.148°.	
Index ranges	-20<=h<=26, -26<=k<=25, -16<=l<=13	
Reflections collected	8268	
Independent reflections	2758 [R(int) = 0.0336]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.883 and 0.779	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2758 / 0 / 130	
Goodness-of-fit on F^2	1.064	
Final R indices [I>2sigma(I)]	R1 = 0.0286, wR2 = 0.0651	
R indices (all data)	R1 = 0.0360, wR2 = 0.0682	
Largest diff. peak and hole	0.342 and -0.454 e.$Å^3$	

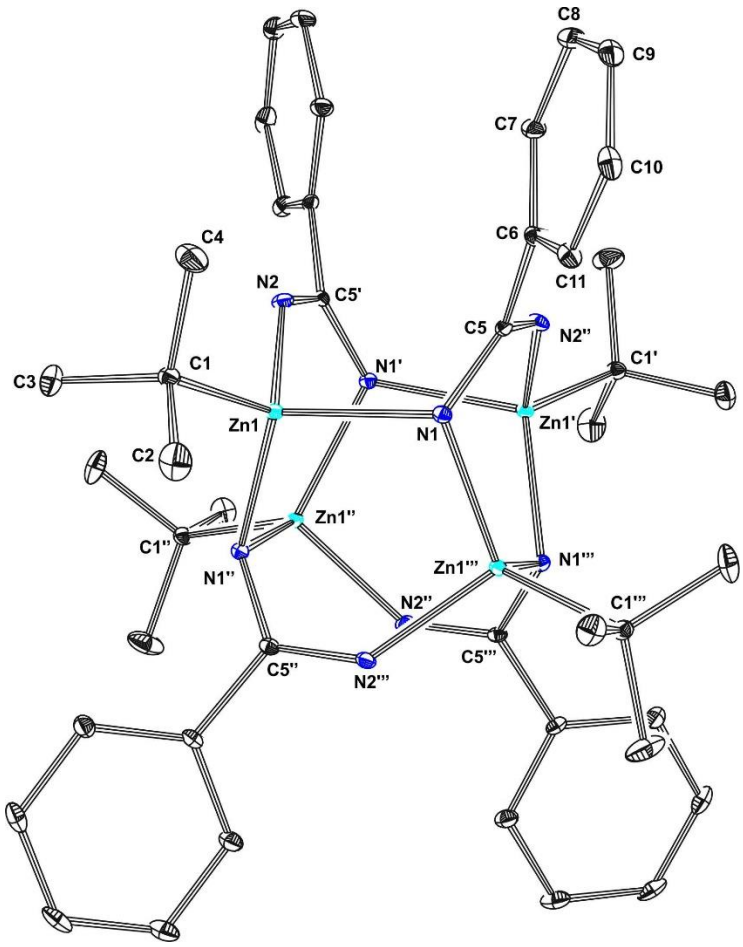
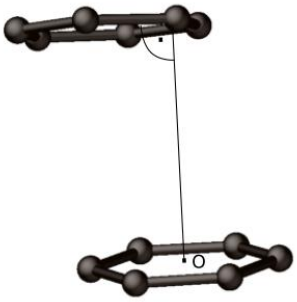


Fig. S30. The molecular structure of **3** with thermal ellipsoids set at 30% probability. Hydrogen atoms have been omitted for clarity. Symmetry transformations used to generate equivalent atoms: (*-x+2,-y+1/2,z*); (*-y+5/4,x-3/4,-z+1/4*); (*y+3/4,-x+5/4,-z+1/4*).

Table S18. Selected intermolecular bond lengths [Å] and angles [°] for **3**.

Zn1-C1	2.0121(19)	Zn1-N1-C5	116.50(12)
Zn1-N1	2.1653(15)	Zn1-N1-Zn1’’’	105.26(6)
Zn1-N2	2.0004(15)	C1-Zn1-N1	110.72(7)
Zn1-N1’’	2.0832(15)	C1-Zn1-N2	115.06(7)
		C1-Zn1-N1’’	114.61(7)
		N1-Zn1-N2	100.56(6)
		N2-Zn1-N1’’	104.95(6)

Table S19. Distances between the ring planes in π-π interactions measured as the distance of the center of one ring (O) from the plane of the other



$\mathbf{1^{Me}}$
3.503 Å
3.664 Å
3.670 Å
3.126 Å
$\mathbf{1^{Et}}$
3.513 Å

Table S20. Distances of H atoms to respective ring planes in CH-π interactions

$\mathbf{1^{Me}}$
2.727 Å
2.682 Å
2.709 Å
2.939 Å
2.694 Å
2.882 Å
2.883 Å
2.772 Å
$\mathbf{1^{Et}}$
2.842 Å
2.913 Å
2.542 Å
2.425 Å
2.674 Å

References:

1 R. Neufeld and D. Stalke, *Chem. Sci.*, 2015, **6**, 3354–3364.

2 A. Kreyenschmidt, S. Bachmann, T. Niklas and D. Stalke, *ChemistrySelect*, 2017, **2**, 6957–6960.