Supporting Information

Synthesis of a Sterically Demanding Dispiropiperidine and Its Application in Monoamidodialkyl Zincate Complexes

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Experimental Section

Preparation of 1,2,2,6,6-pentamethylpiperidin-4-one



The desired product is commercially available. However, we prepared from 2,2,6,6-tetaramethylpiperidin-4-one according to the literature method.^[S1] Formic acid (15.1 mL, 400 mmol) was added to a heated toluene solution (90 °C) of 2,2,6,6-tetaramethylpiperidin-4-one (62.1 g, 400 mmol) and paraformaldehyde (18.2 g, 603 mmol). Fitted with a Dean-Stark apparatus, the reaction mixture was then refluxed for 11 h to remove the water azeotropically at 130 °C. The reaction mixture was kept at 100 °C for another hour before allowed to cool to room temperature, to which NaOH (8.11g, 203 mmol) was added. After 1 hours of stirring, the NaOH was filtered and the filtrate was freed of solvent under reduced pressure. The crude product was purified by distillation under reduced pressure (70–72 °C/2.0 mmHg) to provide analytically pure desired product (58.6 g, 346 mmol, 87%) as a yellow oil. ¹H NMR (CDCl₃, 400 MHz): $\delta = 2.37$ (4H, s), 2.32 (3H, s), 1.13 ppm (12H, s).

Preparation of 7-azadispiro[5.1.5.3]hexadecan-15-one (1)



Compound **1** was prepared from 1,2,2,6,6-pentamethylpiperidin-4-one according to the previously reported procedure.^[S2] To a flask charged with NH₄Cl (19.3 g, 361 mmol), a DMSO (90 mL) solution of 1,2,2,6,6-Pentamethylpiperidin-4-one (10.1 g, 59.4 mmol) and cyclohexanone (18.7 mL, 180 mmol) were added in sequence at room temperature. The reaction mixture solution was warmed to 60 °C and stirred for 5 h in a sealed reaction vessel before being cooled to the room temperature, to which water (400 mL) was added. After stirring for 1 h, the reaction solution was treated with aqueous HCl (7%, 120 mL) and stirred for 13 h.* The reaction mixture solution was washed with ether (×3) to remove byproducts. The aqueous phase was adjusted to pH 9 using aqueous K₂CO₃ (10%) and extracted with AcOEt (×4). The combined organic layer (AcOEt) was washed with saturated aqueous NaCl solution, dried over Na₂SO₄ and freed of volatiles under reduced pressure. The residual solid was purified by column chromatography (silica gel) with hexane/AcOEt (1:1) as the eluent to give 7-azadispiro[5.1.5.3]hexadecane-15-one (**1**) (9.23 g, 39.2 mmol, 66%) as a pale yellow solid (R_f = 0.54). ¹H NMR (CDCl₃, 400 MHz): δ = 2.31 (4H, s), 1.7–1.3 ppm (20H, m); ¹³C NMR (100 MHz, CDCl₃): δ = 211.55 (C), 56.85 (CH₂), 52.28 (C), 40.75 (CH₂), 25.67 (CH₂), 22.34 ppm (CH₂).

*: In large scale reactions, precipitates are often generated. In these cases, the reaction mixture was filtered. The filtrate was treated as described above. The filtered solid was mainly the ammonium salt of 1. The water slurry

of this ammonium salt was treated with aqueous K_2CO_3 (10%) to pH 9 and extracted with AcOEt (×4). The combined organic layer (AcOEt) was washed with saturated aqueous NaCl solution, dried over Na₂SO₄ and freed of volatiles under reduced pressure to give an additional batch of product.

Preparation of di-tert-butylzinc, tBu₂Zn

700	<i>t</i> BuLi	1Bu 7a
211012	Et ₂ O, 0 °C, 1 h	<i>и</i> Би ₂ ∠П

*t*Bu₂Zn was prepared from ZnCl₂ according to the literature method.^[S3] *tert*-Butyl lithium (1.61 M in pentane, 31.5 mL, 50.7 mmol) was added dropwise to ZnCl₂ (3.42 g, 25.1 mmol) in Et₂O (38 mL) at 0 °C. The mixture was stirred for 1 h and warmed to room temperature slowly. The white suspension was filtered through a glass filter padded with glass wool, and the solid was washed with Et₂O (3×4 mL). The filtrate was subjected to reduced pressure at -40 °C and allowed to be warmed to -10 °C during solvent evaporation. The residual solid was sublimed at room temperature in vacuo to afford pure *t*Bu₂Zn (3.65 g, 20.3 mmol, 81%) as a white solid. ¹H NMR (400 MHz, C₆D₆): $\delta = 1.12$ ppm (18H, s); ¹³C NMR (100 MHz, C₆D₆): $\delta = 30.93$ (CH₃), 28.42 ppm (C).

Preparation of tert-butyl 3-bromobenzoate (7)



7 was prepared according to the literature method for similar compounds.^[S4] A mixture of *t*BuOH (82 mL) and KOtBu (7.64 g, 68.1 mmol) in THF (82 mL) was stirred at room temperature for 30 min before 3-bromobenzoyl chloride (6.00 mL, 45.4 mmol) was added dropwise. The resulting reaction mixture was then refluxed for 12 h with stirring. After cooling to the room temperature, the solvent was removed under reduced pressure. The residual reaction mixture was dissolved in AcOEt, washed with water (×2) and saturated aqueous Na₂CO₃ solution and dried over MgSO₄. The organic layer was concentrated under reduced pressure. The residual liquid was purified by column chromatography (silica gel) with hexane/AcOEt (19:1) as the eluent to give *tert*-butyl 3-bromobenzoate (**7**) (9.93 g, 38.6 mmol, 85%) as a colorless liquid ($R_f = 0.53$). ¹H NMR (400 MHz, CDCl₃): $\delta = 8.10$ (1H, t, ⁴*J* = 1.7 Hz), 7.92 (1H, dt, ³*J* = 8.0 Hz, ⁴*J* = 1.5 Hz), 7.65 (1H, m), 7.29 (1H, t, ³*J* = 8.0 Hz), 1.59 ppm (9H, s).

Competitive methylation reaction



n-Butyl lithium (1.60 M in hexane, 3.50 mL, 5.60 mmol) was added to a THF solution of TMP(H) (393 mg, 2.78 mmol) and **2** (616 mg, 2.78 mmol) dropwise at -78 °C. After addition, the reaction mixture was slowly warmed to 0 °C and stirred at 0 °C for 1 h. MeOTf (0.300 mL, 2.65 mmol) was added to the resulting suspension and the reaction mixture was stirred at 0 °C or -30 °C for 12 h. The residual lithium amides were quenched by addition of *i*PrOH at 0 °C. Afterwards, the solution was adjusted to pH 10 with aqueous HCl solution (10%) before extracted with CH₂Cl₂ (4×40 mL). The combined organic layer was washed with saturated aqueous NaCl solution, dried over Na₂SO₄ and concentrated under reduced pressure. The product ratio was determined by ¹H NMR of this crude product mixture and is summarized in Table S1.

Entry	THF	Reaction temp.	Ratio
		(°C)	PMP: 3
1	12.4 mL	0	1.26 : 1.00
2	28.0 mL	0	1.26 : 1.00
3	28.0 mL	0	1.26 : 1.00
4	28.0 mL	-30	1.16:1.00
5	28.0 mL	-30	1.16:1.00

The reproducibility was observed. The product ratio of PMP to **3** was lower at -30 °C (entries 4 and 5) than that observed at 0 °C (entries 1–3), most likely due to the more suppressed ring flipping of cyclohexyl rings at lower temperature.

NMR Spectra of New Compounds

Dispiro[cyclohexane-2,2'-piperidine-6',2''-cyclohexane] (CPC(H) (2))





mqq \ 6 Ó

1'-Methyldispiro-[cyclohexane-2,2'-piperidine-6',2''-cyclohexane] (CPC(Me) (3))



Figure S3. ¹H NMR spectrum (400 MHz) of 3 in CDCl₃.



Figure S4. ¹³C{¹H} NMR spectrum (100 MHz) of 3 in CDCl₃.

Lithium dispiro[cyclohexane-2,2'-piperidine-6',2''-cyclohexane]-1'-ide (LiCPC (4))



Figure S5. ¹H NMR spectrum (400 MHz) of **4** in C_6D_6 .

Figure S6. ${}^{13}C{}^{1}H$ NMR spectrum (100 MHz) of 4 in C₄D₈O.

Figure S7. ⁷Li NMR spectrum (155 MHz, LiCl in D₂O) of 4 in C₆D₆.

$[(THF)_2Li(\mu-CPC)(\mu-Et)Zn(Et)](5\cdot(THF)_2)$

Figure S8. ¹H NMR spectrum (400 MHz) of $5 \cdot (THF)_2$ in C₆D₆.

Figure S9. ¹³C{¹H} NMR spectrum (100 MHz) of $5 \cdot (THF)_2$ in C₆D₆.

Figure S10. ⁷Li NMR spectrum (155 MHz, LiCl in D_2O) of $5 \cdot (THF)_2$ in C_6D_6 .

Figure S11. ¹H NMR spectrum (400 MHz) of $6 \cdot (THF)_2$ in C₆D₆.

Figure S12. ¹³C{¹H} NMR spectrum (100 MHz) of $6 \cdot (THF)_2$ in C₆D₆.

Figure S13. ⁷Li NMR spectrum (155 MHz, LiCl in D₂O) of 6·(THF)₂ in C₆D₆.

 $[(TMEDA)Li(\mu-CPC)(\mu-Et)Zn(Et)] (5 \cdot TMEDA)$

Figure S14. ¹H NMR spectrum (400 MHz) of 5•TMEDA in C₆D₆.

Figure S15. ${}^{13}C{}^{1}H$ NMR spectrum (100 MHz) of 5. TMEDA in C₆D₆.

Figure S16. ⁷Li NMR spectrum (155 MHz, LiCl in D₂O) of 5. TMEDA in C₆D₆.

Figure S17. ¹H NMR spectrum (400 MHz) of 6•TMEDA in C₆D₆.

Figure S18. ¹³C{¹H} NMR spectrum (100 MHz) of 6•TMEDA in C_6D_6 .

Figure S19. ⁷Li NMR spectrum (155 MHz, LiCl in D_2O) of 6·TMEDA in C_6D_6 .

Variable Temperature ¹H NMR Spectra

Variable-temperature ¹H NMR (500 MHz) spectra were recorded using JEOL JNM-ECA500 NMR spectrometer in toluene- d_8 . The ¹H chemical shifts (δ scale) were determined by residual protons of the solvent (¹H, C₆D₅CD₃, δ = 2.11 ppm). Anhydrous toluene- d_8 was used for these measurements.

$VT^{1}H NMR of CPC(H) (2)$

Figure S20. ¹H NMR spectrum (500 MHz) of 2 in toluene- d_8 (ca. 0.02 mmol/0.55 mL).

The secondary amine **2** showed the coalescence of the signals with lowering the temperature from -30 °C to -60 °C. The broad signals gradually sharpened as the temperature dropped below -60 °C.

 $VT^{1}H NMR of CPC(Me)$ (3)

Figure S21. ¹H NMR spectrum (500 MHz) of 3 in toluene- d_8 (ca. 0.02 mmol/0.55 mL).

In the case of the tertiary amine 3, no coalescence was observed between -80 °C and 20 °C.

Crystal Structure Determination

Crystals suitable for X-ray structural determination were mounted on a *Bruker SMART APEXII* CCD diffractometer. Samples were irradiated with graphite monochromated Mo-K α radiation (λ = 0.71073 Å) at 173 K for data collection. The data were processed using the *APEX* program suite. All structures were solved by the *SHELXT* program (*ver.* 2014/5). Refinement on F^2 was carried out by full-matrix least-squares using the *SHELXL* in the *SHELX* software package (*ver.* 2014/7)^[S5] and expanded using Fourier techniques. All non-hydrogen atoms were refined using anisotropic thermal parameters. The hydrogen atoms except for *N*–H (in **2**) were assigned to idealized geometric positions and included in the refinement with isotropic thermal parameters. The *SHELXL* was interfaced with *ShelXle* GUI (*ver.* 742) for most of the refinement steps.^[S6] The pictures of molecules were prepared using *Pov-Ray* 3.7.0.^[S7] The crystallographic data are summarized in Table S2 and S3 and can be obtained from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

Table S2	Crystal	lographic	data.
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	2	3	4 ₃ ^[a]
Formula	$C_{15}H_{27}N$	$C_{16}H_{29}N$	C ₁₅ H ₂₆ LiN
Mol wt	221.37	235.40	227.31
Crystal system	orthorhombic	monoclinic	Hexagonal
Space group	$P2_{1}2_{1}2_{1}$	$P2_{1}/n$	P6/mcc
Color	colorless	colorless	colorless
Habit	block	needle	plate
Cryst dimens, mm	$0.11 \times 0.10 \times 0.10$	$0.08 \times 0.04 \times 0.02$	$0.12 \times 0.11 \times 0.05$
<i>a</i> , Å	6.0545(7)	8.3640(11)	15.6814(7)
b, Å	11.8787(15)	31.759(4)	15.6814(7)
<i>c</i> , Å	18.202(2)	10.5541(14)	22.5674(10)
α, deg	90	90	90
β , deg	90	92.253(2)	90
γ, deg	90	90	120
<i>V</i> , Å ³	1309.1(3)	2801.4(6)	4806.0(5)
Z	4	8	12
$D_{\rm calc}, {\rm g \ cm}^{-3}$	1.123	1.116	0.942
Abs coeff, mm^{-1}	0.064	0.063	0.053
<i>F</i> (000)	496	1056	1512

Temp, K	173(2)	173(2)	173(2)
Reflections	7952	16980	26065
Independent	3067	7014	1979
Rint	0.0179	0.0362	0.0332
Parameters	149	309	82
$R_1 \left[I > 2\sigma(I) \right]$	0.0358	0.0580	0.0471
wR_2 (all data)	0.0968	0.1518	0.1591
Goodness of fit	1.043	1.019	1.184
solv for	CH ₂ Cl ₂ , −30 °C	CH ₃ CN	hexane
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CCDC-1491871 (2), 1491872 (3) and 1491873 (4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

[a] In this crystal structure, there are disordered solvent molecules, and their contribution to the scattering values have been removed by using the PLATON SQUEEZE program (*ver.* 1.16).^[S8]

	5 •(THF) ₂	6·(THF) ₂	5·TMEDA	6·TMEDA
Formula	C ₂₁ H ₄₄ LiNO ₂ Zn	C ₂₇ H ₅₂ LiNO ₂ Zn	$C_{19}H_{44}LiN_3Zn$	C ₂₅ H ₅₂ LiN ₃ Zn
Mol wt	414.88	495.00	386.88	467.00
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_{1}/n$	$P2_{1}/c$	Cc	$P2_{1}/c$
Color	colorless	colorless	colorless	colorless
Habit	plate	plate	needle	needle
Cryst dimens, mm	$0.15 \times 0.14 \times 0.06$	$0.26 \times 0.16 \times 0.06$	$0.10 \times 0.09 \times 0.01$	$0.13 \times 0.09 \times 0.03$
<i>a</i> , Å	11.2358(13)	9.5012(7)	8.5884(12)	9.7336(10)
b, Å	18.399(2)	18.7387(14)	25.543(3)	17.1347(18)
<i>c</i> , Å	12.1072(14)	16.3221(12)	10.5895(14)	16.1465(17)
α , deg	90	90	90	90
β , deg	104.549(2)	104.3260(10)	103.379(2)	100.1190(10)
γ, deg	90	90	90	90
<i>V</i> , Å ³	2422.7(5)	2815.6(4)	2285.0(5)	2651.1(5)

Table S3 Crystallographic data.

Ζ	4	4	4	4
$D_{\rm calc}$, g cm ⁻³	1.137	1.168	1.125	1.170
Abs coeff, mm ⁻¹	1.026	0.894	1.080	0.942
<i>F</i> (000)	904	1080	848	1024
Temp, K	173(2)	173(2)	173(2)	173(2)
Reflections	14116	15919	6681	15472
Independent	5521	6459	3951	6191
Rint	0.0248	0.0256	0.0189	0.0576
Parameters	374	383	267	325
$R_1 \left[I > 2\sigma(I) \right]$	0.0562	0.0370	0.0297	0.0534
wR_2 (all data)	0.1759	0.0976	0.0687	0.1214
Goodness of fit	1.020	1.028	1.027	1.010
solv for	havana -20 °C	hoveno -20 °C	TMEDA _20.°C	TMEDA _20 °C
crystallization	nexane, -30°C	nexane, -50°C	1 WIEDA, -30 C	1 MEDA, -30 C

CCDC-1491874 (**5**·(**THF**)₂), 1491875 (**6**·(**THF**)₂), 1491876 (**5**·**TMEDA**) and 1491877 (**6**·**TMEDA**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

¹H Diffusion-Ordered Spectroscopy NMR Analysis

General considerations

Instrumental details

All measurements were carried out with 3 mm NMR tubes (Wilmad-LabGlass) filled with argon (sealed). The Diffusion-Ordered Spectroscopy (DOSY) NMR experiments were performed on JEOL JNM-ECA500 NMR spectrometer operating at 500 MHz for proton resonance under Delta (*ver.* 5.0.4) and equipped with a 50H3X/FG3 probe. ¹H-DOSY experiments were performed with the BPPSTE (Bipolar Pulse Pairs STimulated Echo) pulse sequence. The gradient amplitude was changed from 0.3 G cm⁻¹ to 50.3 G cm⁻¹ in 51 steps for **5**·(**THF**)₂, and from 0.3 G cm⁻¹ to 35.3 G cm⁻¹ in 51 steps for **6**·(**THF**)₂. The measurement conditions for ¹H-DOSY were: diffusion time, 0.1 s; field gradient pulse width, 1 ms; relaxation delay, 7.0 s; duration of the 90° pulse, 4.4 μ s.

Sample preparation^[S9]

All samples were prepared in a glovebox filled with argon. The solvated zincate $5 \cdot (THF)_2$ (23.8 mg) or $6 \cdot (THF)_2$ (19.9 mg) was dissolved in THF- d_8 along with 1,2,3,4-tetraphenylnaphthalene (TPhN, 14.6 mg),

1-phenylnaphthalene (PhN, 13.2 μ L) and tetramethylsilane (TMS, 19.1 μ L) as inert reference standards. The solution surface was 3.0 cm from the bottom of the NMR tube. The ¹H-DOSY NMR data was recorded at 27 °C without spinning.

Analysis

Linear calibration graphs were prepared by plotting log D versus log FW and log D versus log V, in which log D was calculated from the diffusion coefficients of the internal standards (FW= formula weight; V= volume). The FW_{DOSY} and V_{DOSY} of the species in THF- d_8 were estimated from the average value of the diffusion coefficients for the signals corresponding to a zincate (**5** or **6**) using the calibration equation. To determine the volumes of the standards used and candidate zincates **5**·(**THF**)_n and **6**·(**THF**)_n (n= 0, 1, 2), DFT calculations were carried out. The volumes used for creating graphs (logD versus logV) were average values of volumes from four independent calculations.

DOSY NMR study of $5 \cdot (THF)_2$

Table S4 shows the D_{AV} for each standard and also their FW and volumes, and Table S5 shows FW and volumes of candidate CPC-zincate **5**·(**THF**)_n (n= 0, 1, 2). The D_{AV} values are average values of the diffusion coefficients obtained for each signal which corresponds to the inert standard. Graph S1 shows the observed D_{AV} for **5** versus log FW of candidate CPC-zincate on the linear calibration graph of log D versus log FW. Graph S2 shows the observed D_{AV} for **5** versus log V of candidate CPC-zincate on the linear calibration graph of log D versus log FW. Graph S2 shows the observed D_{AV} for **5** versus log V of candidate CPC-zincate on the linear calibration graph of log D versus log D ver

Compound	$10^{-10} \ D_{AV}$	logD	FW	logFW	V	logV
	$(m^2 s^{-1})$		$(g \text{ mol}^{-1})$		$(\text{cm}^3 \text{ mol}^{-1})$	
TPhN	5.22	-9.282336985	432.57	2.636056397	365.8	2.563243701
PhN	9.34	-9.029504238	204.27	2.310204589	170.1	2.230704314
TMS	13.6	-8.866751783	88.23	1.945616279	100.3	2.001300933

Table S4. Diffusion coefficients of internal standards and their FW and volumes in THF- d_8 .

Table S5. FW and volumes of candidate CPC-zincates in THF- d_8 .

Compound	FW	logFW	V	logV
	$(g \text{ mol}^{-1})$		$(\text{cm}^3 \text{ mol}^{-1})$	
(THF) ₂ Li(CPC)ZnEt ₂	495.04	2.694640292	414.3	2.617314933
(THF)Li(CPC)ZnEt ₂	422.93	2.626268492	348.1	2.541704023
Li(CPC)ZnEt ₂	350.82	2.545084344	281.1	2.448860846

Graph S1. log D – log FW representation from the ¹H DOSY NMR data obtained for candidate CPC-zincate and the standards TPhN, PhN, TMS at 27 °C in THF- d_8 .

Graph S2. log D – log V representation from the ¹H DOSY NMR data obtained for candidate CPC-zincate and the standards TPhN, PhN, TMS at 27 °C in THF- d_8 .

From the Graph S1 and S2, **5**•**THF** (n= 1, triangle) best fits the calibration (black line). The D_{AV} for **5** which was calculated from D values for the signals corresponding to the components of **5** was $D_{AV} = 5.45 \times 10^{-10}$ (m² s⁻¹). This D_{AV} could convert to log D = -9.263654341. Assigning this log D to y in linear calibration equations for log D versus log FW and log D versus log V, FW and volume for chemical species corresponding to **5**•(**THF**)₂ dissolved in THF-*d*₈ were estimated to be FW_{DOSY} = 434.88 (g mol⁻¹) and V_{DOSY} = 347.29 (cm³ mol⁻¹) respectively. Table S6 shows the FW and V, and Error_{FW}, Error_V between calculated data and DOSY data.

Compound	FW	Error _{FW}	V	Error _V
	$(g \text{ mol}^{-1})$	(%)	$(\text{cm}^3 \text{ mol}^{-1})$	(%)
(THF) ₂ Li(CPC)ZnEt ₂	495.04	12.2	414.3	16.2
(THF)Li(CPC)ZnEt ₂	422.93	2.8	348.1	0.2
Li(CPC)ZnEt ₂	350.82	24.0	281.1	23.5

Table S6. FW, V and errors between calculated data and DOSY data.

From the DOSY study for $5 \cdot (THF)_2$ in THF- d_8 , $5 \cdot THF$ showed a much smaller error in comparison to $5 \cdot (THF)_2$ and 5. This indicate that 5 could form at complex with Et₂Zn in THF- d_8 and one THF molecule coordinated to the Li center on average.

DOSY NMR study of 6 · (THF)₂

Table S7 shows the D_{AV} for each standard and also their FW and volumes, and Table S8 shows FW and volumes of candidate TMP-zincate **6**·(**THF**)_n (n= 0, 1, 2). Graph S3 shows the observed D_{AV} for **6** versus log FW of candidate TMP-zincate on the linear calibration graph of log D versus log FW. Graph S4 shows the observed D_{AV} for **6** versus log V of candidate TMP-zincate on the linear calibration graph of log D versus log D versus log V. In both graphs, square, triangle and circle mean n= 0, 1 and 2 respectively.

Table S7. Diffusion coefficients of internal standards and their FW and volumes in THF- d_8 .

Compound	$10^{-10} \: D_{AV}$	logD	FW	logFW	V	logV
	$(m^2 s^{-1})$		$(g \text{ mol}^{-1})$		$(\text{cm}^3 \text{ mol}^{-1})$	
TPhN	6.30	-9.200543826	432.57	2.636056397	365.8	2.563243701
PhN	11.8	-8.928868228	204.27	2.310204589	170.1	2.230704314
TMS	17.4	-8.760080186	88.23	1.945616279	100.3	2.001300933

Table S8. FW and volumes of candidate TMP-zincates in THF- d_8 .

Compound	FW	logFW	V	logV	
	$(g \text{ mol}^{-1})$		$(\text{cm}^3 \text{ mol}^{-1})$		
(THF) ₂ Li(TMP)ZnEt ₂	414.91	2.694640292	318.8	2.617314933	
(THF)Li(TMP)ZnEt ₂	342.80	2.626268492	291.5	2.541704023	
Li(TMP)ZnEt ₂	267.69	2.545084344	241.5	2.448860846	

Graph S3. log D – log FW representation from the ¹H DOSY NMR data obtained for candidate TMP-zincate and the standards TPhN, PhN, TMS at 27 °C in THF- d_8 .

Graph S4. log D – log V representation from the ¹H DOSY NMR data obtained for candidate TMP-zincate and the standards TPhN, PhN, TMS at 27 °C in THF- d_8 .

From the Graph S3 and S4, **6** (n= 0, square) best fits the calibration (black line). The D_{AV} for **6** which was calculated from D values for the signals corresponding to the components of **6** was $D_{AV} = 9.04 \times 10^{-10}$ (m² s⁻¹). This D_{AV} could convert to log D = -9.043978441. Assigning this log D to y in linear calibration equations for log D versus log FW and log D versus log V, FW and volume for chemical species corresponding to **6** (**THF**)₂ dissolved in THF-*d*₈ were estimated to be FW_{DOSY} = 265.89 (g mol⁻¹) and V_{DOSY} = 233.25 (cm³ mol⁻¹) respectively. Table S9 shows the FW and V, and Error_{FW}, Error_V between calculated data and DOSY data.

Compound	FW	Error _{FW}	V	Errorv
	$(g \text{ mol}^{-1})$	(%)	$(\text{cm}^3 \text{ mol}^{-1})$	(%)
(THF) ₂ Li(TMP)ZnEt ₂	414.91	35.9	318.8	26.8
(THF)Li(TMP)ZnEt ₂	342.80	22.4	291.5	20.0
Li(TMP)ZnEt ₂	267.69	1.8	241.5	3.4

Table S9. FW, V and error between calculated data and DOSY data.

From the DOSY study for $6 \cdot (THF)_2$ in THF- d_8 , 6 showed a smaller error than $6 \cdot (THF)_2$ and $6 \cdot (THF)$. This indicates that 6 could form at complex with Et₂Zn in THF- d_8 and no THF molecules coordinated to the Li center on average.

DFT calculations

General considerations

Density Functional Theory (DFT) Calculations were performed using the Gaussian 09 package of programs^[S10] to estimate the relative energy gaps of possible conformational isomers **2A**–**F** and **3A**–**F**, and the volumes of inert reference standards, TPhN, PhN and TMS, and candidate zincates, **5**·(**THF**)_{**n**} and **6**·(**THF**)_{**n**} (n= 0, 1, 2) for DOSY analysis. For the conformational isomers **2A**–**F** and **3A**–**F**, the B3LYP^[S11] hybrid functional was used with 6-31G(d,p) basis set for geometry optimization after geometry pre-optimization at the HF/6-31G(d) level of theory. For TPhN, PhN, TMS, **5**·(**THF**)_{**n**} and **6**·(**THF**)_{**n**} (n= 0, 1, 2), the B3LYP hybrid functional was used with 6-311G(d,p) basis set for geometry optimization. For PhN and TMS, the HF/6-31G(d) level of theory was used for geometry pre-optimization. For TPhN, Spartan'04^[S12] was used for geometry pre-optimization. All structures were optimized without any symmetry assumptions. After each geometry optimization at the B3LYP/6-31G(d,p) or B3LYP/6-311G(d,p) level of thory, a frequency calculation at the same level was performed to verify that all the stationary points had no imaginary frequency. The relative energy gaps (kcal/mol) were calculated from the sum of the electronic (E) and zero-point energies (ZPE). The volume for each species were determined by DFT calculations of all optimized structures using volume keyword at the same level of B3LYP/6-311G(d,p).

Figure S22. Relative energy gaps of possible conformational isomers 2A-F at the level of B3LYP/6-31G(d,p).

	2A	2B	2C	2D	2 E	2F
Е	-642.6286522	-642.6273861	-642.6285862	-642.6281033	-642.627284	-642.6280868
ZPE	0.4048	0.4047	0.405282	0.404941	0.405045	0.404931
E+ZPE	-642.2238522	-642.2226861	-642.2233042	-642.2231623	-642.222239	-642.2231558

Table S10. The electronic energies of 2A–F at the B3LYP/6-31G(d,p) level of theory in Hartrees.

The energy gaps between each isomer are very small (<1.01 kcal/mol).

The energy gaps of possible conformational isomers of CPC(Me) (3)

Figure S22. Relative energy gaps of possible conformational isomers 3A-F at the level of B3LYP/6-31G(d,p).

	3A	3B	3C	3D	3 E	3F
Е	-681.9116736	-681.9042846	-681.9113832	-681.9109826	-681.9095918	-681.9179246
ZPE	0.434457	0.433487	0.434277	0.433434	0.434041	0.433736
E+ZPE	-681.4772166	-681.4707976	-681.4771062	-681.4775486	-681.4755508	-681.4841886

Table S11. The electronic energies of **3A–F** at the B3LYP/6-31G(d,p) level of theory in Hartrees.

In comparison to 2, the energy gaps between conformational isomers of 3 are larger (4.17–8.40 kcal/mol).

Optimized structures for DOSY analysis

5-(THF)₂

5-THF

5

6.THF

Volume of each species

	TPhN	PhN	TMS	5-(THF) ₂	5·THF ₂	5	6 •(THF) ₂	6·THF	6
1st	333.693	180.216	104.246	405.624	338.422	288.372	292.099	309.515	250.611
2nd	382.675	163.255	100.712	395.224	359.574	294.853	332.929	261.435	216.821
3rd	382.675	161.134	100.712	388.29	363.099	239.77	295.239	294.49	247.795
4th	364.307	175.976	95.411	468.028	331.372	301.333	354.915	300.5	250.611
Average	365.8375	170.1453	100.2703	414.2915	348.1168	281.082	318.7955	291.485	241.4595

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