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Synthesis, structure and catalytic activity of tridentate, base-functionalized β -ketiminate zinc complexes in ROP of lactide

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Zinc complexes containing tridentate β -ketiminate ligands with an additional side-arm donor (referred to as [NNO] ligand) [L^1/L^2 ZnR] ($L^1 = \{(OC(Me)C(H)C(Me)NCH_2CH_2CH_2NMe_2)\}$, R = Me **1**, Et **2**, Cl **3**; $L^2 = \{(OC(Me)C(H)C(Me)NCH_2CH_2NMe_2)\}$, R = Me **6**, Et **7**, Cl **9**) as well as cationic derivatives with a weakly coordinating anion [L^1/L^2 Zn][Al(OC(CF₃)₃)₄] ($L^1 = \mathbf{4}$, $L^2 = \mathbf{10}$), a base-stabilized complex [L^2 Zn(dmap)Et] **8** and a base-free complex without a side-arm donor [L^3 ZnEt] **12** ($L^3 = \{(OC(Me)-C(H)C(Me)N-2,6-i-Pr_2C_6H_3)\}$) were synthesized and characterized by single crystal X-ray diffraction (**1**, **2**, **3**, **8**, **9**, **11**, **12**). Ring-opening polymerization (ROP) of *rac*-lactide was studied using the zinc complexes **1** – **4**, **6** – **10** and **12**, mixtures of **7** and Lewis bases (DBU **15**, *t*-BuPy **16**) as well as **12** and DBU (**17**). Lithium-

β -ketiminates L^1 Li **5**, L^2 Li **11** as well as DBU **13** and a mixture of L^2 Li and DBU **14** were also investigated. The compounds except for **3**, **4**, **10** and **12** are active *rac*-lactide polymerization catalysts by a slightly modified activated monomer mechanism. The catalytic activity of the complexes in *rac*-lactide polymerization reactions at ambient temperature increases with addition of Lewis bases to the β -ketiminate zinc compounds. The highest activity was found for the mixture of L^2 ZnEt **7** in the presence of the strong base DBU **15**, which was found to convert 200 equivalents of *rac*-lactide within 1.5 min into polylactide at ambient temperature.

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Introduction

Polylactide (PL) is a promising material due to its bioassimilability and biodegradability in natural environments as well as in the human body since the degradation compounds such as lactic acid are nontoxic and easily eliminated via the Krebs cycle to water and carbon dioxide.^[1-4] Therefore, the synthesis of PL from renewable resources such as corn or sugar beets has received increasing interest over the last decade.^[5] Unfortunately, the toxicity of the well-known (commercially still used) catalyst SnOct₂ causes problems in the biomedical field.^[2,6] As a consequence, the synthesis of non-toxic and low cost catalysts is currently under investigation and some very active zinc, aluminum, magnesium or lanthanide catalysts have been discovered within the last two decades.^[7-10]

Organozinc-based catalysts are of particular interest since they are nontoxic and rather cheap.^[11] However, it was not before the end of the last century when the pioneering work of Coates et al. set the focus on neutral zinc alkoxide complexes of the type [HC{C(Me)NR¹}₂ZnOR] containing a chelating N,N'- β -diketiminato ligand (**1**). In particular weakly-bonded dimeric

complexes of this type showed excellent activities in lactide polymerization reactions.^[12,13] The formation of either monomeric or dimeric complexes was found to be largely influenced by the steric properties of the organic substituent R bound to the imine centers of the specific β -diketiminato ligands. Moreover, the easy modification of the electronic properties of the β -diketiminato ligands by introduction of electron-withdrawing groups allowed the synthesis of tailor-made catalysts. Table 1. summarizes the polymerization activity of N,N'- β -diketiminato-based and N,O-ligand-based catalysts as shown in scheme 1 with different initiator groups and metal centers as well as other highly active lactide polymerization catalysts.

Table 1. Active catalysts for lactide polymerization at ambient temperature [lactide/catalyst: 200]. For review articles see ref [1]

Catalyst	t [min]	conv. [%]	Ref.
DippnacnacZnN(SiMe ₃) ₂	600	97	12a-c
(DippnacnacZnOt-Pr) ₂	20	95	12a-c
DippnacnacZnOt-Bu	10	95	14
DippnacnacZnCHMeCO ₂ Me	20	97	12c
(DippnacnacZnOAc) ₂	4200	92	12c
DippnacnacZnEt	1200	97	12c
2,4- <i>t</i> -Bu ₂ -6-CH ₂ N(Me)C ₂ H ₄ NMe ₂ -C ₆ H ₂ -ZnOEt	5	96	15
(Me ₃ Si) ₂ NZnO(2-Me-4- <i>t</i> -Bu-6-(CH ₂ N-(C ₂ H ₄ NMe ₂)CH ₂ -3-Me-Ph)C ₆ H ₂	40	95	16
DippnacnacMgOt-Bu	2	99	12c
DBU (100 equivalents)	60	85	17
LiOt-Bu (100 equivalents)	1	93	18
Ca-TPB(N(SiMe ₃) ₂)	1	90	19
Sm(O ₂ N ^{OMe}) ₂ {N(SiHMe ₂) ₂ }(THF)	5	95	20
Zn-Carbene (130 equivalents)	4	99	21

Following Coates et al. initial studies on the use of β -diketiminato complexes in lactide polymerization, the synthesis of metal complexes containing other types of chelating substituents, including bidentate N,O ketiminato (**II**) and N,O Schiff base (**III**) substituents as well as donor-functionalized tridentate-type N,N,N (**IV**), O,N,N (**V**), and O,N,O (**VI**) ligands as shown in scheme 1 has been investigated in detail.^[22] Surprisingly, zinc ketimate complexes of type **VII** containing a pendant donor-function,^[23] which show some similarities to widely used salicylaldehydes, as well as other metal complexes of this specific type have been investigated to a lesser extent in ROP of lactide or other cyclic esters.^[24]

Scheme 1. Typical bidentate- and tridentate-type substituents.

Aside from neutral complexes, cationic metal complexes were also investigated since zwitterionic tris(pyrazolyl)borate complexes were found to be very active polymerization catalysts.^[25] As a consequence, cationic organozinc complexes were expected to show a higher catalytic activity than neutral organozinc complexes.^[26] We recently reported on the synthesis of cationic β -diketiminato zinc complexes, but their catalytic activity could not be investigated at ambient temperature due to their insolubility in organic solvents. However, these cationic complexes were found to convert 200 equivalents of lactide within 8 min into polylactide in bulk polymerization at 160 °C.^[27]

Scheme 2. Drawing of the base-functionalized β -ketiminates L^1H and L^2H .

In order to increase the solubility of the cationic zinc complexes we became interested in tridentate β -ketiminato ligands containing an additional hemilabile pendant donor arm. We also decided to vary the linker of the donor arm (C_2H_4 and C_3H_6) in order to modify the structural flexibility. The dimethylaminopropyl-substituted donor-functionalized β -ketiminato ligand (L^1H) was

initially reported by Pugh et al.,^[28] whereas the dimethylaminoethyl-functionalized ligand (L^2H) was initially prepared by Neculai et al. (Scheme 2).^[29] The Dipp-functionalized ligand (L^3H) (type **II** scheme 1) was also used by Harder et al.,^[30] who synthesize bimetallic metal complexes with bridged β -diketiminato ligands.

Herein, we report on the synthesis and solid state structures of the corresponding zinc alkyl, zinc chloride and the cationic zinc complexes. Furthermore, the catalytic activity of different [NNO] zinc and lithium complexes with or without a hemilabile pendant donor arm as well as the influence of additional strong Lewis bases in the ring opening polymerization of lactide will be summarized.

Results and Discussion

Equimolar amounts of the neutral ligand (L^1H , L^2H) and ZnR_2 ($R = Me, Et$) react in alkane elimination reactions in high yields (>80 %) to the expected heteroleptic zinc complexes L^1ZnMe **1**, L^1ZnEt **2**, L^2ZnMe **6** and L^2ZnEt **7** (Scheme 3).

Scheme 3. Synthesis of [NNO] zinc complexes.

1H NMR spectra of the complexes **1**, **2**, **6** and **7** showed the expected resonances of the β -ketiminato [NNO] ligands as well as of the Zn-Me group at -0.95 ppm (**1**, **6**) or the Zn-Et group (**2** 0.04 and 1.24 ppm; **7** 0.03 and 1.19 ppm). Crystals of **1** and **2** suitable for a single crystal X-ray analysis were obtained from solutions in hexane upon storage at -30 °C (Figure 1).

1 and **2** form monomeric structures in the solid state and their central structural parameters are almost identical (Table 2). The zinc atoms in **1** and **2** adopt slightly distorted coordination geometries as is typical for zinc complexes.^[12c,14,27,31] The Zn1-O1 (**1** 1.9675(7), **2** 1.9815(8) Å), Zn1-N1 (**1** 2.0099(8), **2** 2.0045(9) Å) and Zn1-N2 (**1** 2.1707(8), **2** 2.1800(9) Å) bond lengths are comparable. The same is true for the endocyclic O1-Zn1-N1 bond angles (**1** 94.59(3), **2** 93.92(3)°) as well as the O1-Zn1-N2 (**1** 103.33(3), **2** 101.57(4)°) and N1-Zn1-N2 bond angles (**1** 88.97(3), **2** 88.62(4)°). Comparable bonding parameters were previously observed in O,N,N-chelating tridentate Schiff base and related alkoxide complexes.^[15,16,32]

Figure 1. Crystal structures of $[L^1ZnMe]$ (**1**, left hand side) and $[L^1ZnEt]$ (**2**, right hand side). All hydrogen atoms have been omitted for clarity. Ellipsoids are drawn to a 50 % probability level.

While any attempts to grow single crystals of **6** and **7** failed, the addition of the Lewis base dimethylamino-pyridine (dmap) to **7** resulted in the formation of base-stabilized $L^2ZnEt(dmap)$ **8**, whose solid state structure was determined by single crystal X-ray diffraction. **8** crystallizes in the monoclinic space group $P2_1/c$ with two independent molecules of opposite chirality in the elementary cell. The stronger Lewis-basic pyridine-N atom of the dmap Lewis base coordinates to the electrophilic zinc atom, which again adopts a distorted tetrahedral coordination geometry, whereas the amine donor of the pendant side-arm does not bind to the Zn atom (Figure 2). The central structural parameters of **8** such as Zn(1)–N(1) (2.018(3) Å), Zn(1)–O(1) (1.996(2) Å) and Zn(1)–N(3) (2.123(3) Å) bond lengths as well as O(1)–Zn(1)–N(1) (93.57(10)°), O1–Zn1–N_{amine} (99.30(10)°) and N1–Zn1–N_{amine} bond angles (98.21(11)°) are similar to those observed in **1** and **2**.

Figure 2. Crystal structure of $[L^2ZnEt(dmap)]$ (**8**). All hydrogen atoms have been omitted for clarity. Ellipsoids are drawn to a 50 % probability level.

Treatment of $L^{1/2}ZnR^{1/2}$ ($R^1 = Me$; $R^2 = Et$) (**1**, **2**, **6** and **7**) with one equivalent of ethereal HCl in methylene chloride at ambient temperature almost quantitatively yielded the corresponding zinc chloride complexes $[L^1ZnCl]$ **3** and $[L^2ZnCl]$ **9** (Scheme 3). The 1H NMR spectra of **3** and **9** showed resonances of the β -ketimine [NNO] ligand, which are shifted downfield compared to those observed for the zinc alkyl complexes **1**, **2**, **6** and **7**. The lowfield shift most likely results from the introduction of the electron withdrawing chloride substituents.

Crystals of complexes **3** and **9** suitable for single crystal X-ray structure determinations were obtained upon storage of concentrated solutions of **3** and **9** in CH_2Cl_2 at $-30^\circ C$. **3** $[L^1ZnCl]$

adopts a monomeric structure in the solid state, whereas **9** $[L^2ZnCl]$ forms an oxygen-bridged dimer containing a central four-membered Zn_2O_2 ring (Figure 3). The Zn atom of **3** is tetrahedrally coordinated with very similar bonding parameters compared to **1** and **2** (Table 2.), whereas the zinc atom of **9** shows a coordination number of five.

Figure 3. Crystal structure of $[L^1ZnCl]$ (**3**, left hand side) and $[L^2ZnCl]$ (**9**, right hand side). All hydrogen atoms have been omitted for clarity. Ellipsoids are drawn to a 50 % probability level.

Table 2. Selected bond lengths (Å) and bond angles (°) of $[L^1ZnMe]$ (**1**) $[L^1ZnEt]$ (**2**) and $[L^1ZnCl]$ (**3**).

	1	2	3
Zn–N1	2.0099(8)	2.0045(9)	1.9729(9)
Zn–O1	1.9675(7)	1.9815(8)	1.9253(7)
Zn–N2	2.1707(8)	2.1800(9)	2.0812(8)
Zn–Cl	-	-	2.2033(3)
Zn–C	1.9770(10)	1.9870(12)	-
N1–C1	1.3036(13)	1.3020(14)	1.3028(13)
O1–C3	1.2885(12)	1.2855(14)	1.2974(12)
C1–C2	1.4278(14)	1.4322(16)	1.4307(14)
C2–C3	1.3858(14)	1.3791(16)	1.3833(15)
N1–Zn1–O1	94.59(3)	93.92(3)	98.63(3)
N2–Zn1–O1	103.33(3)	101.57(4)	111.14(3)
N1–Zn1–N2	88.97(3)	88.62(4)	94.92(3)
Zn1–N1–C1	124.49(7)	125.21(7)	122.32(7)
Zn1–O1–C3	122.99(6)	122.88(7)	120.40(6)
C1–C2–C3	128.00(9)	127.70(10)	128.93(9)

As a consequence, the N1–Zn1–O1 bond angle of **9** (86.42(5)°) is significantly (almost 12°) decreased compared to that in the monomeric complex **3** (98.63(3)). In addition, the Zn1–N1 (**3** 1.9729(9), **9** 2.0733(15) Å), Zn1–N2 (**3** 2.0812(8), **9** 2.1922(15) Å) and Zn1–O1 bond lengths (**3** 1.9253(7), **9** 2.0519(12) Å) of **9** are elongated compared to those observed for **3**. The dimerization observed for **9** most likely results from the shorter linker of L^2 compared to L^1 (C_2H_4 vs. C_3H_6). Coordination of the amine-donor group to the electrophilic Zn atom results in the formation of either a five-membered ZnN_2C_2 or a six-membered ZnN_2C_3 ring, with the five-membered ring showing an increased ring strain. The N1–Zn–N_{amine} angles of **9** (80.03(6)°, 80.21(6)°) are significantly smaller compared to that in **3** (94.92(3)). As a result, the Zn atom is less shielded and can be addressed by the oxygen-donor (O1), resulting in a dimerization with subsequent formation of a fivefold coordinated Zn atom. Pulsed-gradient spin echo (PGSE) NMR measurements of complexes **3** and **9** in solution (CD_2Cl_2) revealed that L^2ZnCl **9** with the shorter amine linkage is also dimeric (4.78

Å) in solution (CD₂Cl₂, 25°C), whereas L¹ZnCl **3** with the somewhat longer n-propylamine pendant side-arm is rather monomeric (3.65 Å).

The bonding parameters within the β-ketiminate ligand frameworks are very similar as can be seen in table 2. In addition, the Zn-N (2.0099(8) Å **1**; 2.0045(9) Å **2**; 1.9729(9) Å **3**) and Zn-O (1.9675(7) Å **1**; 1.9815(8) Å **2**; 1.9253(7) Å **3**) bond distances of **1** – **3** and **8** are within the typical range reported for fourfold coordinated Zn atoms.^[22–24,33] In contrast, the Zn-N (2.0733(15) Å) and Zn-O (2.0519(12) Å) bond lengths as observed for **9** are elongated due to the increased coordination number. The Zn-N_{amine} bond distances of the pendant donor group are similar to those of comparable complexes.^[34]

Table 3. Selected bond lengths (Å) and bond angles (°) of [L²ZnEt](dmap) (**8**), [L²ZnCl] (**9**), [L²Li] (**11**) and [L³ZnEt]₂ (**12**); data given for **8** and **9** are only of one molecule.

	8	9	11	12
M-N1	2.018(3)	2.0733(15)	2.0379(15)	2.0373(10)
M-O1	1.996(2)	2.0519(12)	1.9749(15)	2.0169(9)
M-N2	-	2.1922(15)	2.2717(15)	-
M-N _{dmap}	2.123(3)	-	-	-
M-Cl	-	2.2674(4)	-	-
M-C	1.998(4)	-	-	1.983(2)
N1-C1	1.307(4)	1.301(2)	1.1980(10)	1.3079(15)
O1-C3	1.276(4)	1.315(2)	1.2867(9)	1.3115(14)
C1-C2	1.421(4)	1.446(3)	1.4393(11)	1.4370(16)
C2-C3	1.376(5)	1.366(2)	1.3809(11)	1.3679(17)
N1-M-O1	93.57(10)	86.42(5)	91.11(6)	91.30(4)
N _{amine} -M-O1	99.30(10)	140.42(5)	164.60(8)	-
N1-M-N _{amine}	98.21(11)	80.03(6)	81.77(5)	-
M-N1-C1	123.2(2)	127.00(12)	126.98(7)	122.97(8)
M-O1-C3	122.1(2)	122.84(11)	126.13(6)	119.88(8)
C1-C2-C3	128.0(3)	126.60(16)	127.18(7)	127.80(11)

Complexes **3** and **9** were reacted with equimolar amounts of Li[Al(OC(CF₃)₃)₄], yielding the expected monocationic zinc complexes of the type [L^{1/2}Zn][Al(OC(CF₃)₃)₄] (**4**, **10**) (Scheme 3) in good yields (> 83%) as light-yellowish solids. The ¹H NMR spectra of **4** and **10** were similar to those of the starting complexes **3** and **9**, showing resonances of the CH backbone around 5.2 ppm, of the methylene group around 2 ppm, the ethylene/propylene bridge between 2 – 4 ppm as well as the NMe₂ resonances around 2.5 ppm. **4** and **10** were re-crystallized upon slow cooling of hot solutions of **4** and **10** in methylene chloride to ambient temperature, but the quality of the resulting crystals was too poor to allow their characterization by single crystal X-ray diffraction.

The β-ketimines L^{1/2}H were also reacted with *t*-BuLi in a butane elimination reaction, giving the lithium complexes L¹Li **5** and L²Li **11** in high yields (95%). Crystals of complex **11**, suitable for single crystal X-ray crystallography, were obtained by slow cooling of melted **11** (mp 24 °C) from 40 °C to ambient temperature. A single crystal X-ray determination showed that **11** adopts a trimeric structure in the solid state, most likely due to the reduced N1-Zn-N_{amine} angle to 81.77(5)° (Figure 4). The Li1-N1 (2.0379(15) Å), Li1-N2 (2.2717(15) Å) and Li1-O1 bond distances (1.9749(15) Å) within the six-membered LiNC₃O rings of **11** are within the typical range as reported for β-ketiminate lithium complexes without a

hemilabile pendant donor arm, but with additional coordinated THF molecules,^[35] as well as to heterocubane-type complexes as reported by Mair et al.^[36]

Figure 4. Crystal structure of trimeric [L²Li] (**11**). All hydrogen atoms have been omitted for clarity. Ellipsoids are drawn to a 50 % probability level.

The alkane elimination reaction between equimolar amounts of L³H, in which the hemilabile pendant donor arm is replaced by a sterically demanding 2,6-diisopropylphenyl-substituent, and ZnEt₂ gave the expected zinc complex L³ZnEt **12** in high yields (>80 %). The ¹H and ¹³C NMR spectra of **12** showed the expected resonances of the 2,6-diisopropyl substituent, the CH backbone of the ketimine group and the Zn-Et moiety.

Scheme 4. Synthesis of L³ZnEt **12**.

Crystals of **12** suitable for single crystal X-ray crystallography were obtained by slow cooling of a solution of **12** in CH₂Cl₂ to -30 °C. **12** adopts a dimeric structure in the solid state (Figure 5), in which the zinc atoms show slightly distorted tetrahedral coordination geometries as is typical for four-coordinated zinc complexes.^[12c,14,27,30] This finding clearly illustrates the influence of the side-arm donor, since both [L¹ZnMe] (**1**) and [L¹ZnEt] (**2**) adopt monomeric structures in the solid state. The Zn1-O1 2.0169(9) Å and Zn1-N1 2.0373(10) Å bond lengths as well as the O1-Zn1-N1 bond angle (91.30(4)°) are comparable to those observed for other zinc ketimine complexes. The bond distances and angles are also comparable to those recently reported for the homoleptic bis-ketiminate zinc complex Zn(L³)₂ (Zn1-O1 1.9617(9) Å, Zn1-N1 1.9818(9) Å, O1-Zn1-N1 96.69(4)°).^[37]

Figure 5. Crystal structure of dimeric $[L^3ZnEt]$ (**12**). All hydrogen atoms have been omitted for clarity. Ellipsoids are drawn to a 50 % probability level.

Polymerization Activity.

The capability of the zinc complexes **1** – **4**, **6** – **10** and **12** $[L^{1/2/3}ZnR](base)$ ($R = Me/Et/Cl$), ($base = t\text{-Bu-Pyr}$, $dmap$, DBU) to serve as catalyst in the polymerization of *rac*-lactide (Scheme 5) in CH_2Cl_2 solution at ambient temperature was investigated. These studies were expanded on mixtures of **7** and strong Lewis bases (DBU **15**, $t\text{-BuPy}$ **16**), **12** and DBU (**17**) as well as the lithium- β -ketiminates L^1Li **5**, L^2Li **11**, the pure Lewis base DBU **13** and a mixture of L^2Li and DBU **14**.

Scheme 5. Ring opening polymerization of lactide by use of **1** – **17**.

NMR analyses of the crude polymerization products [lactide/catalyst: 1:1 or 30:1 or 50:1 or 200:1] showed resonances due to unchanged zinc complexes. The P_r values of the polymers as determined by homonuclear decoupled 1H NMR spectra showed predominantly atactic polymers. These results were confirmed by MALDI-TOF-MS analyses [lactide/catalyst: 10:1 and 20:1], which showed cyclic and linear n -(72 g/mol) polylactide fragments with OH/OH end groups due to hydrolysis of the pending or external Lewis under workup conditions. The GPC curves showed no traces of bimodal molecular weight distribution. No lactide-alkyl (Me, Et) or lactide-ligand (L^1 , L^2) fragments, which point to an coordination/insertion mechanism, were detected in the spectra (see SI).

Kinetic polymerization studies were performed with solutions of **1** – **16** in CH_2Cl_2 at ambient temperature in order to verify the influence of the pendant amine donor (L^1 or L^2) and the organic substituent bound to the Zn atom (Me, Et or Cl) as well the influence of additional strong Lewis bases ($dmap$, DBU , $t\text{-Bu-Py}$) to the catalytic performance of the L^2 -substituted zinc (**8**, **15**, **16**) and lithium complexes (**14**). The results of the kinetic

polymerization experiments are summarized in Figure 6. The compounds except for **3**, **4** and **10** were found to be active in *rac*-lactide polymerization, which is somehow unexpected since it has been well established that alkyl groups are rather poor initiating groups for lactide polymerization whereas alkoxide-substituted zinc complexes generally show much higher catalytic activities.^[1] In particular the mixture of L^2ZnEt with the strong Lewis base DBU (**15**) was found to be highly active in ring opening polymerization (ROP) of *rac*-lactide at ambient temperature in CH_2Cl_2 solution. In addition, L^1ZnCl **3** as well as the cationic complexes L^1Zn^+ **4** and L^2Zn^+ **10** are active in bulk polymerization in the absence of any solvent. In contrast, the β -ketimines $L^{1/2}H$ did not show any sign of polymerization activity even after 10 hours.

Figure 6. Lactide polymerization kinetics in dichloromethane at ambient temperature [lactide/catalyst: 200] $[c_{cat}: 8.3 \cdot 10^{-3} \text{ mol} \cdot L^{-1}]$ **1** – **17**. L^1ZnCl **3**, L^1Zn^+ **4**, L^2Zn^+ **10** and L^3ZnEt **12** are active in bulk polymerization, but don't show any activity in solution at ambient temperature.

The hemilabile pendant donor arm plays a key role for the polymerization activity of the Zn complexes, since its dissociation from the Zn atom results in the formation of a threefold-coordinated Zn center, which allows the coordination of a lactide monomer. This is a pre-requisite for the lactide polymerization. Complexes with the more strained ethyl linkage (L^2) show a higher catalytic activity than those containing the somewhat longer propyl linkage (L^1). These findings most likely result from the increased ring strain within the five-membered rings (L^2) compared to the six-membered rings (L^1), according to which the hemilabile pendant donor arm is easier released from the zinc atom, resulting in the formation of a three-coordinated, highly electrophilic Zn atom with higher polymerization activity.

The studies also confirm the influence of the substituent bound to the Zn atom (Me, Et, Cl) on the polymerization activity. The zinc ethyl complexes showed the highest polymerization activities at ambient temperature, followed by the zinc methyl complexes and finally the zinc chloride complexes ($ZnEt > ZnMe > ZnCl$). Obviously, the polymerization activity increases with increasing +I-effect of the alkyl groups ($Me < Et$), whereas the electronegative chlorine reduces the catalytic activity significantly. The +I-effect of the organic substituent R decreases the electrophilicity of the Zn atom, resulting in a weakening of the dative $N \rightarrow Zn$ bond and an increased polymerization activity.

The catalytic activity of the zinc complexes was found to increase in the presence of an external Lewis base. Moreover, the stronger the Lewis base (Lewis basicity: $DBU > dmap > t\text{-Bu-Py}$),

the more active are the catalysts. This can clearly be seen when comparing the polymerization results obtained with pure $[L^2ZnEt]$ **7** with those obtained with mixtures of **7** with DBU (**15**) as well as **7** with *t*-BuPy (**16**). The highest polymerization activity was observed for a mixture of **7** with the strongest Lewis base DBU (**15**), resulting in a conversion rate of 200 parts of lactide to polylactide within 1.5 minutes with molecular weight up to $(9.2 \cdot 10^4 \text{ g} \cdot \text{mol}^{-1})$ in CH_2Cl_2 at ambient temperature. In order to rule out that the significant increase of catalytic activity is only related to the Lewis base DBU, we also used pure DBU as catalyst in lactide polymerization (**13**), but its activity (as well as that of pure $[L^2ZnEt]$ **7**) was significantly lower compared to that of the DBU/ $[L^2ZnEt]$ mixture (**15**). L^3ZnEt **12**, which does not contain a hemilabile side arm donor but a sterically demanding Dipp substituent, does not show any activity in solution at ambient temperature. In contrast, mixture of L^3ZnEt with the strong Lewis base DBU (**17**) was found to be highly active in ring opening polymerization, but not as active as L^2ZnEt with a hemilabile pendant donor arm and DBU (**15**).

Table 4 summarizes the M_w and PDI values obtained in our polymerization studies. The molecular weight and the polydispersity index of the resulting polylactide was determined by gel permeation chromatography (GPC) in THF at 23 °C (flow 1 mL $\cdot$ min $^{-1}$). The detection of some very high molecular weights (Tab. 4) points to incomplete activation of the catalyst.

Table 4. Molecular weight and the polydispersity index of the resulting polylactide as obtained from polymerization reactions in solution at room temperature and by bulk polymerization (**3**, **4**, **10**, **12**) [c_{cat} : $8.3 \cdot 10^{-3} \text{ mol} \cdot \text{L}^{-1}$].

Catalyst	Time [min]	conv. ^c [%]	M_w^d [$10^4 \text{ g} \cdot \text{mol}^{-1}$]	PDI ^e	P_r^f
1 L^1ZnMe^a	430	93	8.4	1.6	0.53
2 L^1ZnEt^a	210	94	8.1	1.4	0.55
3 L^1ZnCl^b	10	97	13.9	1.6	0.53
4 L^1Zn^{+b}	22	97	4.7	1.3	0.54
5 L^1Li^a	40	93	7.9	1.7	0.61
6 L^2ZnMe^a	170	93	7.9	1.5	0.63
7 L^2ZnEt^a	130	93	7.8	1.5	0.65
8 $L^2ZnEt(dmap)^a$	40	93	10.8	2.1	0.62
9 L^2ZnCl^a	700	93	28.8	2.1	0.66
10 L^2Zn^{+b}	12	97	4.3	1.3	0.55
11 L^2Li^a	40	94	10.0	1.7	0.60
12 L^3ZnEt^b	5	97	19.1	2.7	0.51
13 DBU ^a	80	93	16.2	1.9	0.30
14 $L^2Li + DBU^a$	1.5	85	3.1	1.6	0.50
15 $L^2ZnEt + DBU^a$	1.5	93	9.2	1.9	0.61
16 $L^2ZnEt + t\text{-BuPyr}^a$	80	93	14.5	2.1	0.65
17 $L^3ZnEt + DBU^a$	10	93	5.6	1.8	0.51

[a] CH_2Cl_2 at ambient temperature; [b] absence of solvent at 160 °C; [c] Estimated from ^1H NMR integration of the relative intensities of the OCHMe resonance and the residual *rac*-lactide and polylactide resonances in CD_2Cl_2 ; [d] Determined by GPC analysis in THF at 23 °C. [e] $\text{PDI} = M_w/M_n$; [f] Determined by analysis of the OCHMe resonances of selectively homonuclear decoupled ^1H NMR spectra.

We also investigated the catalytic activity of the Li-complexes L^1Li (**5**) and L^2Li (**11**), since simple lithium alkoxides such as $\text{LiO}t\text{-Bu}$ are known to be highly active in anionic lactide polymerization.^[18] Conversion rates of up to 100 equivalents of lactide into polylactide with low molecular weight ($3.5 \cdot 10^4$

$\text{g} \cdot \text{mol}^{-1}$) within 1 min at ambient temperature in CH_2Cl_2 were observed.^[18] The counter ions were also found to have a strong influence on the catalytic activity, since $\text{KO}t\text{-Bu}$ only reached these results after 60 min.^[38] Moreover, β -ketiminato lithium complexes without a hemilabile pendant donor arm, with coordinated THF were found to polymerize 200 equivalents of lactide within 20 min.^[35] We observed comparable results with L^1Li (**5**) and L^2Li (**11**). However, their activity can be significantly enhanced upon addition of an additional strong Lewis base. The mixture of L^2Li **11** with the strong Lewis base DBU (**13**) polymerized 200 equivalents of lactide within only 1.5 min.

Our polymerization studies clearly revealed that the polymerization activity strongly correlates with addition of Lewis bases to the zinc or lithium compounds. The cationic complexes **4** and **10**, in which the electron density of the β -ketiminato group is expected to be decreased due to the highly electrophilic cationic zinc atom are only active in bulk polymerization reactions at elevated temperatures, yielding polylactide with low polydispersity index (PDI: 1.3) and moderate molecular weight (M_w : $4.5 \cdot 10^4 \text{ g} \cdot \text{mol}^{-1}$). In contrast, higher molecular weights (up to $2.9 \cdot 10^5 \text{ g} \cdot \text{mol}^{-1}$) were obtained with $[L^2ZnCl]$ **9** at ambient temperature within 10 h.

Based on our experimental findings, the polymerization mechanism most likely proceeds through the initial coordination of the lactide monomer to the electrophilic Zn atom, replacing the pendant amine-donor arm. A high ring strain, which increases with shortening of the alkyl chain of the donor arm from propyl (C_3H_6) to ethyl (C_2H_4), enhances the coordination of the lactide monomer. In a second step, either the pendant (neutral) dimethylamine base or the external, even stronger Lewis base (dmap, DBU) attacks the electrophilic carbonyl atom of the coordinated lactide. Therefore, the mechanism of the lactide polymerization using our complexes can be best described as a slightly modified so-called activated monomer mechanism (AMM), in which the lactide is first coordinated to a metal center and then activated an external alcohol. In our case, the external alcohol is replaced by either an internal amine base (side arm donor) or an external amine base. This mechanism explains the higher catalytic activity influence of the zinc complexes (metal activation) compared to that of the pure ligand $L^{1/2}H$ simple base as well as the increasing catalytic activity upon addition of a stronger external base. Moreover, it explains the missing end group (Me, Et) in the resulting polylactide.

Conclusions

β -ketimines $L^{1/2/3}H$ react with ZnMe_2 and ZnEt_2 with alkane elimination and subsequent formation of $L^{1/2}ZnMe$ and $L^{1/2/3}ZnEt$. Addition of 4-dimethylaminopyridine (dmap) to L^2ZnEt yielded the base stabilized complex $L^2ZnEt(dmap)$, whereas treatment of $L^{1/2}ZnMe$ and $L^{1/2}ZnEt$ with one equivalent of ethereal HCl gave in the corresponding zinc chloride complexes L^1ZnCl and L^2ZnCl in high yields. Cationic zinc complexes $[L^{1/2}Zn][Al\{\text{OC}(\text{CF}_3)_3\}_4]$ are accessible by reactions of $[L^{1/2}ZnCl]$ with $\text{Li}[Al\{\text{OC}(\text{CF}_3)_3\}_4]$. The complexes except for **3**, **4**, **10** and **12** are active *rac*-lactide polymerization catalysts by a slightly modified activated monomer mechanism (AMM). The polymerization activity was found to increase with addition of strong Lewis bases to the zinc and lithium complexes. The interplay of strong Lewis bases and the complexes leads to active polymerization catalysts. A mixture of $L^2ZnEt + \text{DBU}$ was found to convert 200 equivalents of *rac*-lactide into polylactide at ambient temperature in CH_2Cl_2 within only 1.5 min.

The polymerization activity, molecular weight and polydispersity index clearly depend on the steric and electronic properties of the metal complexes, possibly allowing a fine-tuning by careful catalyst design in the near future. Further studies on the catalytic activity of the corresponding β -ketiminato zinc alkoxides $L^{1/2}ZnOR$ and amides $L^{1/2}ZnNR_2$, which might allow an insertion/polymerization mechanism, in ROP of lactide are currently under investigation.

Experimental Section

General: All manipulations involving air-sensitive materials were performed using standard vacuum techniques and inert gas atmosphere (argon, < 0.3 ppm O_2) or in a glove box (MBraun Unilab V2.0). Solvents were carefully dried over CaH_2 (CH_2Cl_2) or Na/K alloy (pentane, hexane), respectively, degassed and stored in teflon-sealed glass vessel over molecular sieve. L^1H ,^[28] L^2H ,^[29] L^3H ,^[39] and $Li[Al\{OC(CF_3)_3\}_4]$ ^[40] were synthesized according to literature methods. 1H , ^{13}C and ^{19}F NMR spectra were collected with a Bruker Avance 300 spectrometer and are referenced to internal CD_2Cl_2 (1H : δ = 5.36, ^{13}C : δ = 53.4) and external CCl_3F (^{19}F : δ = 0.31). Homonuclear decoupled 1H NMR spectra are determined by analysis of the $OCHMe$ resonances with a Bruker Avance III HD 600 spectrometer. Elemental analyses were performed at the Labor für Elementaranalyse of the University of Duisburg-Essen. GPC data, the average molar mass (M_n) and molar mass distribution (M_w/M_n) were obtained on a gel permeation chromatography (GPC) in THF at 23 °C (flow rate 1 mL/min). Column (PSS-SDV analytical linear XL 10 μ m) were used with a refractive index detector (Agilent Technologies 1200 Series PSS) and calibrated with polystyrenestandard-Kit (PSS-Kit, Poly(styrene) high; Mp 682-16700000 D; 12 x 1 g; Lot No.: PSS-pskit). Kuhn-Mark-Houwink parameters for polystyrene standards ($KPS = 0.011\text{ mL} \cdot \text{g}^{-1}$, α (alpha) PS = 0.725) were taken from literature.^[41] GPC measurements using a viscosimetric detector had not been carried out. The polymer samples were dissolved in THF (1 mg $\cdot$ mL $^{-1}$) at 23 °C. MALDI-TOF-MS analysis was performed on a Bruker Autoflex III, 200Hz, Smart beam laser 355nm. The polymer samples were dissolved in THF and potassium trifluoroacetate as cationization agent was used. The matrix used was 2,5-dihydroxybenzoic acid. The spectra were recorded in linear and reflectron mode.

[L^1ZnMe] (1): A solution of L^1H (1.84 g, 10 mmol) in hexane (20 mL) was added to a solution of $ZnMe_2$ (8.3 mL, 1.2 M in hexane, 10 mmol) at -30 °C and stirred for 5 h at ambient temperature. The solution was concentrated to 5 mL and stored at -30 °C, resulting in the formation of colorless crystals of **1** within 24 h (2.30 g, 87 %). Mp. 92 °C. Elemental analysis calcd (%) for $C_{11}H_{22}N_2OZn$: C 50.1, H 8.4, N 10.6; found: C 51.6, H 8.7, N 10.1. 1H NMR (300 MHz, CD_2Cl_2 , 25 °C): δ = -0.95 (s, 3H, $ZnCH_3$), 1.71 (m, $^3J_{HH}$ = 4.9 Hz, 2H, NCH_2CH_2), 1.87 (s, 3H, $C_\beta CH_3$), 1.90 (s, 3H, $C_\delta CH_3$), 2.25 (s, 6H, $N(CH_3)_2$), 2.63 (t, $^3J_{HH}$ = 5.6 Hz, 2H, $CH_2N(CH_3)_2$), 3.57 (t, $^3J_{HH}$ = 5.6 Hz, 2H, $C_\beta NCH_2$), 4.67 (s, 1H, $C_\gamma H$); ^{13}C NMR (75 MHz, CD_2Cl_2 , 25 °C): δ = -19.8 ($ZnCH_3$), 19.6 ($C_\beta CH_3$), 27.3 ($C_\delta CH_3$), 27.4 (NCH_2CH_2), 45.7 ($N(CH_3)_2$), 50.1 ($CH_2N(CH_3)_2$), 60.8 ($C_\beta NCH_2$), 96.0 (C_γ), 168.8 ($C_\beta N$), 180.9 ($C_\delta O$).

[L^1ZnEt] (2): A solution of L^1H (1.84 g, 10 mmol) in hexane (20 mL) was added to a solution of $ZnEt_2$ (10.0 mL, 1.0 M in hexane, 10 mmol) at -30 °C and stirred for 5 h at ambient temperature. The solution was concentrated to 5 mL and stored at -30 °C. Colorless crystals of **2** were formed within 24 h (2.28 g, 82 %). Mp 57 °C. Elemental analysis calcd (%) for $C_{12}H_{24}N_2OZn$: C 51.9, H 8.7, N 10.1; found: C 51.6, H 8.7, N 9.8. 1H NMR (300 MHz, CD_2Cl_2 , 25 °C): δ = 0.04 (q, $^3J_{HH}$ = 8.1 Hz, 2H, $ZnCH_2$), 1.24 (t, $^3J_{HH}$ = 8.1 Hz, 3H, $ZnCH_2CH_3$), 1.71 (m, $^3J_{HH}$ = 4.9 Hz, 2H, NCH_2CH_2), 1.86 (s, 3H, $C_\beta CH_3$), 1.90 (s, 3H, $C_\delta CH_3$), 2.26 (s, 6H, $N(CH_3)_2$), 2.65 (t, $^3J_{HH}$ = 5.6 Hz, 2H, $CH_2N(CH_3)_2$), 3.57 (t, $^3J_{HH}$ = 5.6 Hz,

2H, $C_\beta NCH_2$), 4.66 (s, 1H, $C_\gamma H$); ^{13}C NMR (75 MHz, CD_2Cl_2 , 25 °C): δ = -4.4 ($ZnCH_2CH_3$), 13.4 ($ZnCH_2CH_3$), 19.6 ($C_\beta CH_3$), 27.3 ($C_\delta CH_3$), 27.4 (NCH_2CH_2), 45.8 ($N(CH_3)_2$), 50.4 ($CH_2N(CH_3)_2$), 61.1 ($C_\beta NCH_2$), 95.9 (C_γ), 168.8 ($C_\beta N$), 180.9 ($C_\delta O$).

[L^1ZnCl] (3): **2** (1.67 g, 6.0 mmol) was dissolved in CH_2Cl_2 (20 mL), an ethereal solution of HCl (3.0 mL, 2.0 M in ether, 6.0 mmol) was added and the resulting mixture was stirred for 4h at ambient temperature. The solution was concentrated to 5 mL and stored at -30 °C. Colorless crystals of **3** were formed within 24 h (1.55 g, 91 %). Mp. 79 °C. Elemental analysis calcd (%) for $C_{10}H_{19}N_2OZnCl$: C 42.3, H 6.7, N 9.9; found: C 42.3, H 6.8, N 9.6. 1H NMR (300 MHz, CD_2Cl_2 , 25 °C): δ = 1.86 (m, $^3J_{HH}$ = 4.6 Hz, 2H, NCH_2CH_2), 1.93 (s, 3H, $C_\beta CH_3$), 1.95 (s, 3H, $C_\delta CH_3$), 2.49 (s, 6H, $N(CH_3)_2$), 3.02 (t, $^3J_{HH}$ = 5.6 Hz, 2H, $CH_2N(CH_3)_2$), 3.64 (t, $^3J_{HH}$ = 5.6 Hz, 2H, $C_\beta NCH_2$), 4.81 (s, 1H, $C_\gamma H$); ^{13}C NMR (75 MHz, CD_2Cl_2 , 25 °C): δ = 20.3 ($C_\beta CH_3$), 27.1 ($C_\delta CH_3$), 27.3 (NCH_2CH_2), 45.8 ($N(CH_3)_2$), 50.0 ($CH_2N(CH_3)_2$), 61.5 ($C_\beta NCH_2$), 96.8 (C_γ), 171.8 ($C_\beta N$), 182.3 ($C_\delta O$).

[L^1Zn^+][$Al\{OC(CF_3)_3\}_4$] (4): **3** (0.28 g, 1.0 mmol) and $Li[Al(OC(CF_3)_3)_4]$ (0.97 g, 1.0 mmol) were dissolved in 50 mL of CH_2Cl_2 and heated to 60 °C for 1h. The resulting suspension was hot filtered and the solvent of the filtrate evacuated under vacuum, yielding **4** as a light yellowish solid (1.01 g, 83 %). Mp. 126 °C. Elemental analysis calcd (%) for $C_{26}H_{19}N_2O_5AlF_{36}Zn$: C 25.7, H 1.6, N 2.3; found: C 25.4, H 1.7, N 2.2. 1H NMR (300 MHz, CD_2Cl_2 , 25 °C): δ = 2.02 (m, $^3J_{HH}$ = 4.9 Hz, 2H, NCH_2CH_2), 2.07 (s, 3H, $C_\beta CH_3$), 2.13 (s, 3H, $C_\delta CH_3$), 2.58 (s, 6H, $N(CH_3)_2$), 2.91 (t, $^3J_{HH}$ = 5.6 Hz, 2H, $CH_2N(CH_3)_2$), 3.69 (t, $^3J_{HH}$ = 5.6 Hz, 2H, $C_\beta NCH_2$), 5.19 (s, 1H, $C_\gamma H$); ^{13}C NMR (75 MHz, CD_2Cl_2 , 25 °C): δ = 21.9 ($C_\beta CH_3$), 25.7 ($C_\delta CH_3$), 28.1 (NCH_2CH_2), 47.6 ($N(CH_3)_2$), 50.9 ($CH_2N(CH_3)_2$), 62.2 ($C_\beta NCH_2$), 101.4 (C_γ), 121.1 (q, J_{C-F} = 292.3 Hz, CF_3), 177.6 ($C_\beta N$), 184.1 ($C_\delta O$). ^{19}F NMR (282 MHz, CD_2Cl_2 , 25 °C) δ = -75.4.

[L^1Li] (5): A solution of L^1H (1.84 g, 10 mmol) in pentane (20 mL) was added to a solution of $t\text{-BuLi}$ (8.3 mL, 1.2 M in pentane, 10 mmol) at 0 °C and stirred for 5 h at ambient temperature. Removal of pentane gave **5** as light yellow powder (1.82 g, 96 %). Mp. 99 °C. Elemental analysis calcd (%) for $C_{10}H_{19}N_2OLi$: C 63.1, H 10.1, N 14.7; found: C 61.8, H 10.1, N 13.7. 1H NMR (300 MHz, CD_2Cl_2 , 25 °C): δ = 1.70 (m, $^3J_{HH}$ = 6.3 Hz, 2H, NCH_2CH_2), 1.80 (s, 3H, $C_\beta CH_3$), 1.81 (s, 3H, $C_\delta CH_3$), 2.20 (s, 6H, $N(CH_3)_2$), 2.39 (t, $^3J_{HH}$ = 5.6 Hz, 2H, $CH_2N(CH_3)_2$), 3.32 (t, $^3J_{HH}$ = 5.6 Hz, 2H, $C_\beta NCH_2$), 4.63 (s, 1H, $C_\gamma H$); ^{13}C NMR (75 MHz, CD_2Cl_2 , 25 °C): δ = 19.8 ($C_\beta CH_3$), 27.8 ($C_\delta CH_3$), 28.9 (NCH_2CH_2), 45.6 ($N(CH_3)_2$), 50.1 ($CH_2N(CH_3)_2$), 59.6 ($C_\beta NCH_2$), 97.4 (C_γ), 167.3 ($C_\beta N$), 173.9 ($C_\delta O$).

[L^2ZnMe] (6): L^2H (1.70 g, 10.0 mmol) was dissolved in hexane (20 mL) and added to a solution of $ZnMe_2$ (8.3 mL, 1.2 M in hexane, 10.0 mmol) at -30 °C and stirred for 5 h at ambient temperature. The solvent was evacuated under vacuum to give **6** as a light yellow solid (2.17 g, 87 %). Mp. 95 °C. Elemental analysis calcd (%) for $C_{10}H_{20}N_2OZn$: C 48.1, H 8.1, N 11.2; found: C 46.9, H 7.8, N 10.6. 1H NMR (300 MHz, CD_2Cl_2 , 25 °C): δ = -0.95 (s, 3H, $ZnCH_3$), 1.89 (s, 3H, $C_\beta CH_3$), 1.90 (s, 3H, $C_\delta CH_3$), 2.33 (s, 6H, $N(CH_3)_2$), 2.57 (t, $^3J_{HH}$ = 6.3 Hz, 2H, $CH_2N(CH_3)_2$), 3.42 (t, $^3J_{HH}$ = 6.3 Hz, 2H, $C_\beta NCH_2$), 4.83 (s, 1H, $C_\gamma H$); ^{13}C NMR (75 MHz, CD_2Cl_2 , 25 °C): δ = -18.0 ($ZnCH_3$), 20.9 ($C_\beta CH_3$), 27.3 ($C_\delta CH_3$), 44.7 ($N(CH_3)_2$), 45.1 ($CH_2N(CH_3)_2$), 58.1 ($C_\beta NCH_2$), 96.7 (C_γ), 171.1 ($C_\beta N$), 181.4 ($C_\delta O$).

[L^2ZnEt] (7): L^2H (1.70 g, 10.0 mmol) was dissolved in hexane (20 mL) and added to a solution of $ZnEt_2$ (10.0 mL, 1.0 M in hexane, 10.0 mmol) at -30 °C and stirred for 5 h at ambient temperature. The solvent was evacuated under vacuum to give **7** as a light yellow solid (2.48 g, 94 %). Mp. 109 °C. Elemental analysis calcd (%) for $C_{11}H_{22}N_2OZn$: C 50.1, H 8.4, N 10.6; found: C 49.4, H 8.2, N 10.4. 1H NMR (300 MHz, CD_2Cl_2 , 25 °C): δ = 0.03 (q, $^3J_{HH}$ = 8.1 Hz, 2H, $ZnCH_2$), 1.19 (t, $^3J_{HH}$ = 8.1 Hz, 3H, $ZnCH_2CH_3$), 1.89 (s, 3H, $C_\beta CH_3$), 1.90 (s, 3H, $C_\delta CH_3$), 2.35 (s, 6H, $N(CH_3)_2$), 2.57 (t, $^3J_{HH}$ = 6.2 Hz, 2H, $CH_2N(CH_3)_2$), 3.41 (t, $^3J_{HH}$ = 6.2 Hz, 2H, $C_\beta NCH_2$), 4.82 (s, 1H, $C_\gamma H$); ^{13}C NMR (75 MHz, CD_2Cl_2 , 25 °C): δ = -

3.0 (ZnCH₂CH₃), 12.8 (ZnCH₂CH₃), 21.2 (C_βCH₃), 27.3 (C_δCH₃), 44.8 (N(CH₃)₂), 45.1 (CH₂N(CH₃)₂), 58.4 (C_βNCH₂), 96.6 (C_γ), 171.1 (C_βN), 181.8 (C_δO).

[L²ZnEt](dmap) (8): L²H (1.70 g, 10.0 mmol) was dissolved in hexane (20 mL) and added to a solution of ZnEt₂ (10.0 mL, 1.0 M in hexane, 10.0 mmol) at -30 °C. dmap (1.22 g, 10.0 mmol) was added and the solution was stirred for 5 h at ambient temperature. The solvent was evacuated under vacuum, resulting in the formation of **8** as colorless crystals within 24 h (2.70 g, 70 %). Mp. 54 °C. Elemental analysis calcd (%) for C₁₈H₃₂N₄OZn: C 56.0, H 8.4, N 14.5; found: C 55.8, H 8.2, N 14.6. ¹H NMR (300 MHz, CD₂Cl₂, 25 °C): δ = 0.10 (q, ³J_{HH} = 8.1 Hz, 2H, ZnCH₂), 1.25 (t, ³J_{HH} = 8.1 Hz, 3H, ZnCH₂CH₃), 1.88 (s, 3H, C_βCH₃), 1.93 (s, 3H, C_δCH₃), 2.22 (s, 6H, N(CH₃)₂), 2.41 (t, ³J_{HH} = 7.3 Hz, 2H, CH₂N(CH₃)₂), 3.04 (s, 6H, N_{dmap}(CH₃)₂), 3.41 (t, ³J_{HH} = 7.3 Hz, 2H, C_βNCH₂), 4.76 (s, 1H, C_γH), 6.54 (d, ³J_{HH} = 6.8 Hz, 2H, m-CH_{dmap}), 8.07 (d, ³J_{HH} = 6.8 Hz, 2H, o-CH_{dmap}); ¹³C NMR (75 MHz, CD₂Cl₂, 25 °C): δ = -3.2 (ZnCH₂CH₃), 13.2 (ZnCH₂CH₃), 20.9 (C_βCH₃), 27.3 (C_δCH₃), 38.9 (N_{dmap}(CH₃)₂), 45.3 (N(CH₃)₂), 47.9 (CH₂N(CH₃)₂), 59.4 (C_βNCH₂), 96.1 (C_γ), 106.5 (o-C_{dmap}), 148.5 (m-C_{dmap}), 154.8 (C_{dmap}), 170.4 (C_βN), 181.2 (C_δO).

[L²ZnCl] (9): **7** (1.58 g, 6.0 mmol) was dissolved in CH₂Cl₂ (20 mL), an ethereal solution of HCl (3.0 mL, 2.0 M in ether, 6.0 mmol) was added and the resulting mixture was stirred for 4h at ambient temperature. The solution was concentrated to 5 mL and stored at -30 °C, yielding colorless crystals of **9** within 24 h (1.47 g, 91 %). Mp. 134 °C. Elemental analysis calcd (%) for C₉H₁₇N₂OZnCl: C 40.0, H 6.3, N 10.4; found: C 38.9, H 6.3, N 9.2. ¹H NMR (300 MHz, CD₂Cl₂, 25 °C): δ = 1.96 (s, 3H, C_βCH₃), 1.97 (s, 3H, C_δCH₃), 2.44 (s, 6H, N(CH₃)₂), 2.75 (t, ³J_{HH} = 5.6 Hz, 2H, CH₂N(CH₃)₂), 3.41 (t, ³J_{HH} = 5.6 Hz, 2H, C_βNCH₂), 4.95 (s, 1H, C_γH); ¹³C NMR (75 MHz, CD₂Cl₂, 25 °C): δ = 22.0 (C_βCH₃), 27.2 (C_δCH₃), 44.3 (N(CH₃)₂), 45.2 (CH₂N(CH₃)₂), 58.0 (C_βNCH₂), 98.2 (C_γ), 173.3 (C_βN), 180.0 (C_δO).

[L²Zn⁺][Al(OC(CF₃)₃)₄] (10): **9** (0.27 g, 1.0 mmol) and Li(Al(OC(CF₃)₃)₄) (0.97 g, 1.0 mmol) were dissolved in 50 mL of CH₂Cl₂ and heated to 60 °C for 1h. The resulting hot suspension was immediately filtered and the solvent of the filtrate evacuated under vacuum to give **10** as a light yellow solid (1.06 g, 88 %). Mp. 246 °C. Elemental analysis calcd (%) for C₂₅H₁₇N₂O₅AlF₃₆Zn: C 25.0, H 1.4, N 2.3; found: C 25.1, H 1.7, N 2.5. ¹H NMR (300 MHz, CD₂Cl₂, 25 °C): δ = 1.88 (s, 3H, C_βCH₃), 2.15 (s, 3H, C_δCH₃), 2.46 (s, 3H, N(CH₃)₂), 2.51 (s, 3H, N(CH₃)₂), 2.86 (t, ³J_{HH} = 5.6 Hz, 2H, CH₂N(CH₃)₂), 3.61 (t, ³J_{HH} = 5.6 Hz, 2H, C_βNCH₂), 5.23 (s, 1H, C_γH); ¹³C NMR (75 MHz, CD₂Cl₂, 25 °C): δ = 23.0 (C_βCH₃), 26.7 (C_δCH₃), 43.5 (N(CH₃)₂), 44.2 (N(CH₃)₂), 46.4 (CH₂N(CH₃)₂), 58.1 (C_βNCH₂), 101.5 (C_γ), 121.6 (q, J_{C-F} = 292.3 Hz, CF₃), 173.6 (C_βN), 178.6 (C_δO). ¹⁹F NMR (282 MHz, CD₂Cl₂, 25 °C) δ = -75.7.

[L²Li] (11): A solution of L²H (1.70 g, 10 mmol) in pentane (20 mL) was added to a solution of *t*-BuLi (8.3 mL, 1.2 M in pentane, 10 mmol) at 0 °C and stirred for 5 h at ambient temperature. Pentane was removed and light yellow crystals of **11** were formed within 24 h at ambient temperature (1.67 g, 95 %). Mp. 24 °C. Elemental analysis calcd (%) for C₉H₁₇N₂OLi: C 61.4, H 9.7, N 15.9; found: C 61.0, H 9.7, N 15.0. ¹H NMR (300 MHz, CD₂Cl₂, 25 °C): δ = 1.70 (s, 3H, C_βCH₃), 1.80 (s, 3H, C_δCH₃), 2.13 (s, 6H, N(CH₃)₂), 2.41 (t, ³J_{HH} = 5.6 Hz, 2H, CH₂N(CH₃)₂), 3.25 (t, ³J_{HH} = 5.6 Hz, 2H, C_βNCH₂), 4.63 (s, 1H, C_γH); ¹³C NMR (75 MHz, CD₂Cl₂, 25 °C): δ = 20.5 (C_βCH₃), 27.6 (C_δCH₃), 44.7 (N(CH₃)₂), 47.0 (CH₂N(CH₃)₂), 59.9 (C_βNCH₂), 96.7 (C_γ), 168.8 (C_βN), 177.1 (C_δO).

[L³ZnEt] (12): L³H (5.19 g, 20.0 mmol) was dissolved in hexane (20 mL) and added to a solution of ZnEt₂ (20.0 mL, 1.0 M in hexane, 20.0 mmol) at -30 °C and stirred for 5 h at ambient temperature. The solvent was evacuated under vacuum and the resulting solid dissolved in 5 mL of CH₂Cl₂. Storage of the solution at -30 °C gave colorless crystals of **16**

within 24 h (6.72 g, 95 %). Mp. 140 °C. Elemental analysis calcd (%) for C₁₉H₂₉NOZn: C 64.7, H 8.3, N 4.0; found: C 65.1, H 8.3, N 4.0. ¹H NMR (300 MHz, CD₂Cl₂, 25 °C): δ = 0.18 (q, ³J_{HH} = 8.1 Hz, 2H, ZnCH₂), 0.91 (t, ³J_{HH} = 8.1 Hz, 3H, ZnCH₂CH₃), 1.17 (d, ³J_{HH} = 6.9 Hz, 6H, CH(CH₃)₂), 1.21 (d, ³J_{HH} = 6.9 Hz, 6H, CH(CH₃)₂), 1.71 (s, 3H, C_βCH₃), 2.10 (s, 3H, C_δCH₃), 2.93 (m, ³J_{HH} = 6.9 Hz, 2H, CH(CH₃)₂), 5.27 (s, 1H, C_γH), 7.17-7.26 (m, 3H, Ar-H); ¹³C NMR (75 MHz, CD₂Cl₂, 25 °C): δ = -2.4 (ZnCH₂CH₃), 11.4 (ZnCH₂CH₃), 23.1 (C_βCH₃), 23.9 (C_δCH₃), 27.4 ((CH(CH₃)₂), 28.0 ((CH(CH₃)₂), 97.5 (C_γ), 123.6 (*m*-C), 125.9 (*p*-C), 141.1 (*o*-C), 143.0 (*i*-C), 173.0 (C_βN), 184.7 (C_δO).

Polymerization studies.

Polymerization in solution: A mixture of freshly prepared catalyst (0.05 mmol) and lactide (1.4413g, 10 mmol) was dissolved in 6 mL CH₂Cl₂. After polymerization the crude polymer was dried in vacuo. Monomer conversion was determined by ¹H NMR (integration of the methyl protons at 1.53 ppm for the monomer versus the methyl protons at 1.47 ppm for the polymer) (catalyst (0.005 mmol), lactide (0.1441g, 1 mmol) 0.6 mL CD₂Cl₂) (Table 4).

Bulk polymerization: A mixture of freshly prepared catalyst (0.05 mmol) and lactide (1.4413g, 10 mmol) was heated in a glass reactor in the absence of any solvents to 160 °C (> melting point of lactide) for different times (see Table 4). After cooling to ambient temperature, remaining lactide monomer sticking on the reactor wall was dissolved in CH₂Cl₂ and separated. The crude polymer was dried in vacuo. The monomer conversion rate was determined by ¹H NMR spectroscopy (integration of the methyl protons at 1.53 ppm for the monomer versus the methyl protons at 1.47 ppm for the polymer).

Single crystal X-ray analyses. Crystallographic data of **1**, **2**, **3**, **8**, **9**, **11** and **12** which were collected on a Bruker AXS D8 Kappa diffractometer (MoK_α radiation, λ = 0.71073 Å) at T = 180(1) K (except **9** and **11**: 100(1)K), are summarized in Table 2. Figures 1 - 5 show diagrams of the solid-state structure of **1**, **2**, **3**, **8**, **9**, **11** and **12**. The structures were solved by Direct Methods (SHELXS-97)^[42] and refined by full-matrix least-squares on F₂. Semi-empirical absorption corrections from equivalent reflections on basis of multi-scans (Bruker AXS APEX2) were applied. All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model.^[43]

Supporting Information: Syntheses of L¹H and L²H, MALDI-TOFF spectra of selected polymers and X-ray crystallographic data of **1**, **2**, **3**, **8**, **9**, **11** and **12** are given in the electronic supplement. The crystallographic data (without structure factors) were also deposited as „supplementary publication no. CCDC 972514 (**1**), 972512 (**2**), 972513 (**3**), 972517 (**8**), 972515 (**9**), 972516 (**11**), 985010 (**12**) at the Cambridge Crystallographic Data Centre. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre: CCDC, 12 Union Road, Cambridge, CB21EZ (Fax: (+44)1223/336033; E-mail: deposit@ccdc.cam.ac.uk).

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Table 1. Crystallographic data for **1** - **3**, **8**, **9**, **11** and **12**.

	1	2	3	8	9	11	12
Empirical formula	C ₁₁ H ₂₂ N ₂ OZn	C ₁₂ H ₂₄ N ₂ OZn	C ₁₀ H ₁₉ ClN ₂ OZn	C ₁₈ H ₃₂ N ₄ OZn	C ₂₁ H ₃₇ Cl ₁₁ N ₄ O ₂ Zn ₂	C ₂₇ H ₅₁ Li ₃ N ₆ O ₃	C ₃₈ H ₅₈ N ₂ O ₂ Zn ₂
<i>M</i>	263.67	277.70	284.09	385.84	898.23	528.55	705.60
Crystal size [mm]	0.40 × 0.25 × 0.15	0.38 × 0.32 × 0.22	0.45 × 0.30 × 0.20	0.38 × 0.12 × 0.08	0.38 × 0.35 × 0.32	0.34 × 0.32 × 0.25	0.50 × 0.47 × 0.38
<i>T</i> [K]	180(1)	180(1)	180(1)	180(1)	100(1)	100(1)	180(1)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1	<i>P</i> -1
<i>a</i> [Å]	7.6269(4)	9.6644(8)	7.4600(4)	30.608(2)	10.6351(5)	9.1378(2)	8.3250(12)
<i>b</i> [Å]	12.9044(7)	10.9529(9)	12.7923(7)	8.3830(6)	23.2845(11)	10.2062(2)	9.8754(14)
<i>c</i> [Å]	13.5247(7)	13.6327(12)	13.5904(8)	16.1146(12)	15.5326(7)	17.9596(3)	11.6288(17)
<i>α</i> [°]	90	90	90	90	90	84.1030(10)	78.467(4)
<i>β</i> [°]	97.591(2)	102.587(3)	95.655(3)	93.993(3)	109.669(2)	78.1510(10)	82.015(4)
<i>γ</i> [°]	90	90	90	90	90	77.5200(10)	87.283(5)
<i>V</i> [Å ³]	1319.44(12)	1408.4(2)	1290.63(12)	4124.8(5)	3622.0(3)	1597.54(5)	927.5(2)
<i>Z</i>	4	4	4	8	4	2	1
<i>D</i> _{calc} [g · cm ⁻³]	1.327	1.310	1.462	1.243	1.647	1.099	1.263
<i>μ</i> (MoK _α [mm ⁻¹])	1.841	1.728	2.088	1.202	2.163	0.071	1.326
Transmissions	0.75/0.56	0.75/0.49	0.75/0.58	0.75/0.66	0.75/0.60	0.75/0.70	0.75/0.58
<i>F</i> (000)	560	592	592	1648	1816	576	376
Index ranges	-11 ≤ <i>h</i> ≤ 11 -19 ≤ <i>k</i> ≤ 19 -19 ≤ <i>l</i> ≤ 20	-13 ≤ <i>h</i> ≤ 13 -11 ≤ <i>k</i> ≤ 15 -18 ≤ <i>l</i> ≤ 18	-11 ≤ <i>h</i> ≤ 10 -19 ≤ <i>k</i> ≤ 19 -20 ≤ <i>l</i> ≤ 20	-37 ≤ <i>h</i> ≤ 37 -10 ≤ <i>k</i> ≤ 10 -19 ≤ <i>l</i> ≤ 19	-14 ≤ <i>h</i> ≤ 14 -31 ≤ <i>k</i> ≤ 31 -21 ≤ <i>l</i> ≤ 21	-13 ≤ <i>h</i> ≤ 13 -15 ≤ <i>k</i> ≤ 15 -26 ≤ <i>l</i> ≤ 26	-11 ≤ <i>h</i> ≤ 11 -14 ≤ <i>k</i> ≤ 14 -16 ≤ <i>l</i> ≤ 16
<i>θ</i> _{max} [°]	33.119	29.675	33.233	25.969	29.243	32.083	25.242
Reflections collected	30806	23415	20290	40363	51792	60613	44168
Independent reflections	4661	3965	4942	8017	9711	10797	5626
<i>R</i> _{int}	0.0240	0.0277	0.0226	0.0467	0.0204	0.0239	0.0254
Refined parameter	141	145	136	433	361	365	226
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0203	0.0197	0.0204	0.0470	0.0265	0.0398	0.0250
<i>wR</i> ₂ [all data]	0.0578	0.0551	0.0562	0.1101	0.0644	0.1131	0.0718
GooF	1.051	1.052	1.024	1.015	1.110	1.027	1.061
<i>Δρ</i> _{final} (max/min) [e · Å ⁻³]	0.365/-0.297	0.300/-0.230	0.402/-0.342	0.632/-0.372	0.859/-0.661	0.442/-0.233	0.375/-0.245

[a] $R I = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ (for $I > 2\sigma(I)$). - [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. - [c] Goodness of fit = $\{\Sigma[w(|F_o^2| - |F_c^2|)^2]/(N_{\text{observns}} - N_{\text{params}})\}^{1/2}$. $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ with $P = [F_o^2 + 2F_c^2]/3$, *a* and *b* are constants chosen by the programme.

Entry for the Table of Contents

Layout 1:

((Key Topic))

Several NNO zinc complex were synthesized and structurally characterized by single crystal X-ray diffraction. In addition, their catalytic activity in ring opening polymerization (ROP) of lactide is presented. The polymerization was found to occur through a modified activated monomer mechanism .

C. Scheiper, D. Dittrich, C. Wölper, D. Bläser, J. Roll, S. Schulz*. Page No. – Page No.

Synthesis, structure and catalytic activity of tridentate, base-functionalized β -ketiminate zinc complexes in ROP of lactide.

Keywords: NNO ligand / Zinc / Ring-Opening Polymerization

Supporting Information

Syntheses of **L¹H** and **L²H**

Synthesis of **L¹H**

Acetylacetone (6.10 mL, 0.060 mol) and N,N-dimethylaminopropylamine (6.13 g, 0.060 mol) were dissolved in 100 mL of benzene and heated for two days. The solvent and the byproduct water were evacuated under reduced pressure, giving **L¹H** in almost quantitative yield as oily liquid (10.84 g, 98 %). Elemental analysis calcd. (%) for C₁₀H₂₀N₂O (M = 184.28 g/mol): C 65.2, H 10.6, N 15.2, found: C 64.7, H 10.2, N 15.0. ¹H-NMR (300 MHz, CD₂Cl₂, 25 °C): δ = 1.72 (m, ³J_{HH} = 6.8 Hz, 2H, NCH₂CH₂CH₂N(CH₃)₂), 1.94 (s, 3H, C_δCH₃), 1.95 (s, 3H, C_βCH₃), 2.20 (s, 6H NCH₂CH₂CH₂N(CH₃)₂), 2.32 (t, ³J_{HH} = 6.8 Hz, 2H, NCH₂CH₂CH₂N(CH₃)₂), 3.29 (q, ³J_{HH} = 6.8 Hz, 2H, NCH₂CH₂CH₂N(CH₃)₂), 4.96 (s, 1H, C_γ), 10.82 (s, 1H, NH). ¹³C-NMR (125 MHz, CD₂Cl₂, 25 °C): δ = 20.4 (C_δCH₃), 30.0 (NCH₂CH₂CH₂N(CH₃)₂), 30.3 (C_βCH₃), 42.7 (NCH₂CH₂CH₂N(CH₃)₂), 47.0 (NCH₂CH₂CH₂N(CH₃)₂), 58.3 (NCH₂CH₂CH₂N(CH₃)₂), 96.6 (C_γ), 165.0 (C_βN), 195.9 (C_δO).

Synthesis of **L²H**

Acetylacetone (6.10 mL, 0.060 mol) and N,N-dimethylaminoethylamine (5.29 g, 0.060 mol) were dissolved in 100 mL benzene and heated for two days. The solvent and the byproduct water were evacuated under reduced pressure, giving **L²H** in almost quantitative yield as oily liquid (9.91 g, 97 %). Elemental analysis calcd. (%) for C₉H₁₈N₂O (M = 170.25 g/mol): C 63.5, H 10.7, N 16.4, found: C 62.9, H 10.8, N 15.6. ¹H-NMR (300 MHz, CD₂Cl₂, 25 °C): δ = 1.94 (s, 3H, C_δCH₃), 1.95 (s, 3H, C_βCH₃), 2.27 (s, 6H NCH₂CH₂N(CH₃)₂), 2.47 (t, ³J_{HH} = 6.0 Hz, 2H, NCH₂CH₂N(CH₃)₂), 3.29 (q, ³J_{HH} = 6.4 Hz, 2H, NCH₂CH₂N(CH₃)₂), 4.97 (s, 1H, C_γ), 10.77 (s, 1H, NH). ¹³C-NMR (125 MHz, CD₂Cl₂, 25 °C): δ = 20.6 (C_δCH₃), 30.4 (C_βCH₃), 42.8 (NCH₂CH₂N(CH₃)₂), 47.1 (NCH₂CH₂N(CH₃)₂), 60.7 (NCH₂CH₂N(CH₃)₂), 96.7 (C_γ), 164.4 (C_βN), 195.9 (C_δO).

Fig S1: Assignment of carbon atoms.

MALDI-TOF Experiment

Fig S1: Unpurified PLA with KTFAC; MS⁺ of crude reaction product of L²ZnEt (7) / rac-lactide (1:20). Region m/z = 750 to 1550.

Crystallographic Details

L¹ZnMe (1)

Table 1. Crystal data and structure refinement for dd_22_0m.

Identification code	dd_22_0m	
Empirical formula	C ₁₁ H ₂₂ N ₂ O Zn	
Formula weight	263.67 Da	
Density (calculated)	1.327 g cm ⁻³	
<i>F</i> (000)	560	
Temperature	180(1) K	
Crystal size	0.400 x 0.250 x 0.150 mm	
Crystal color	colourless	
Crystal description	tablet	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	<i>P</i> 2 ₁ /c	
Unit cell dimensions	<i>a</i> = 7.6269(4) Å	$\alpha = 90^\circ$
	<i>b</i> = 12.9044(7) Å	$\beta = 97.591(2)^\circ$
	<i>c</i> = 13.5247(7) Å	$\gamma = 90^\circ$
Volume	1319.44(12) Å ³	
<i>Z</i>	4	
Cell measurement reflections used	9809	
Cell measurement theta min/max	2.69° to 32.4°	
Diffraction control software	Bruker AXS APEX 2 Vers.3.0/2009	
Diffraction measurement device	Bruker D8 KAPPA series II with APEX II area detector system	
Diffraction measurement method	Data collection strategy APEX 2/COSMO	
Theta range for data collection	2.191° to 33.119°	
Completeness to theta = 30.000°	99.9 %	
Index ranges	-11 ≤ <i>h</i> ≤ 11, -19 ≤ <i>k</i> ≤ 19, -19 ≤ <i>l</i> ≤ 20	
Computing data reduction	Bruker AXS APEX 2 Vers.3/2009	
Absorption coefficient	1.841 mm ⁻¹	
Absorption correction	Semi-empirical from equivalents	
Empirical absorption correction	Bruker AXS APEX 2 Vers.3/2009	
Max. / min. transmission	0.75 / 0.56	
<i>R</i> (merg) before/after correction	0.0554 / 0.0312	
Computing structure solution	Bruker AXS SHELXTL Vers. 2008/1	
Computing structure refinement	Bruker AXS SHELXL-2013/4	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Reflections collected	30806	
Independent reflections	4661 [<i>R</i> (int) = 0.0240]	
Data / restraints / parameters	4086 / 0 / 141	
Goodness-of-fit on <i>F</i> ²	1.051	
Weighting details	$w = 1/[\sigma^2(F_o^2) + (0.0294 \cdot P)^2 + 0.2681 \cdot P]$ where $P = (F_o^2 + 2F_c^2)/3$	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0203, <i>wR</i> 2 = 0.0557	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0254, <i>wR</i> 2 = 0.0578	
Largest diff. peak and hole	0.365 and -0.297 eÅ ⁻³	
Treatment of hydrogen atoms	Riding model on idealized geometries with the 1.2 fold isotropic displacement parameters of the equivalent U _{ij} of the corresponding carbon atom. The methyl groups are idealized with tetrahedral angles in a combined rotating and rigid group refinement with the 1.5 fold isotropic displacement parameters of the equivalent U _{ij} of the corresponding carbon atom.	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for dd_22_0m. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Zn(1)	2346(1)	2280(1)	794(1)	24(1)
O(1)	1553(1)	3726(1)	866(1)	30(1)
N(1)	4908(1)	2606(1)	1234(1)	26(1)
N(2)	2939(1)	2139(1)	-727(1)	27(1)
C(1)	5513(1)	3525(1)	1495(1)	27(1)
C(2)	4377(1)	4396(1)	1552(1)	28(1)
C(3)	2578(1)	4464(1)	1233(1)	26(1)
C(4)	7476(2)	3732(1)	1750(1)	50(1)
C(5)	1660(2)	5492(1)	1312(1)	38(1)
C(6)	6079(1)	1757(1)	1024(1)	36(1)
C(7)	6138(2)	1657(1)	-95(1)	39(1)
C(8)	4392(2)	1374(1)	-723(1)	36(1)
C(9)	3431(2)	3149(1)	-1118(1)	33(1)
C(10)	1360(2)	1743(1)	-1370(1)	41(1)
C(11)	1075(2)	1049(1)	1201(1)	36(1)

Table 3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for dd_22_0m.

Zn(1)-O(1)	1.9675(7)	N(1)-Zn(1)-N(2)	88.97(3)
Zn(1)-C(11)	1.9770(10)	C(3)-O(1)-Zn(1)	122.99(6)
Zn(1)-N(1)	2.0099(8)	C(1)-N(1)-C(6)	121.93(9)
Zn(1)-N(2)	2.1707(8)	C(1)-N(1)-Zn(1)	124.49(7)
O(1)-C(3)	1.2885(12)	C(6)-N(1)-Zn(1)	112.35(7)
N(1)-C(1)	1.3036(13)	C(9)-N(2)-C(10)	108.71(9)
N(1)-C(6)	1.4651(13)	C(9)-N(2)-C(8)	111.36(9)
N(2)-C(9)	1.4734(13)	C(10)-N(2)-C(8)	108.71(9)
N(2)-C(10)	1.4802(14)	C(9)-N(2)-Zn(1)	111.14(6)
N(2)-C(8)	1.4839(14)	C(10)-N(2)-Zn(1)	109.33(7)
C(1)-C(2)	1.4278(14)	C(8)-N(2)-Zn(1)	107.54(6)
C(1)-C(4)	1.5149(14)	N(1)-C(1)-C(2)	122.32(9)
C(2)-C(3)	1.3858(14)	N(1)-C(1)-C(4)	121.76(10)
C(3)-C(5)	1.5108(14)	C(2)-C(1)-C(4)	115.92(9)
C(6)-C(7)	1.5258(16)	C(3)-C(2)-C(1)	128.00(9)
C(7)-C(8)	1.5264(17)	O(1)-C(3)-C(2)	126.79(9)
		O(1)-C(3)-C(5)	114.36(9)
O(1)-Zn(1)-C(11)	125.64(4)	C(2)-C(3)-C(5)	118.84(9)
O(1)-Zn(1)-N(1)	94.59(3)	N(1)-C(6)-C(7)	110.71(9)
C(11)-Zn(1)-N(1)	125.39(4)	C(6)-C(7)-C(8)	115.74(10)
O(1)-Zn(1)-N(2)	103.33(3)	N(2)-C(8)-C(7)	116.03(9)
C(11)-Zn(1)-N(2)	111.56(4)		

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for dd_22_0m. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Zn(1)	25(1)	24(1)	24(1)	0(1)	4(1)	-3(1)
O(1)	26(1)	28(1)	36(1)	-4(1)	4(1)	1(1)
N(1)	24(1)	28(1)	26(1)	0(1)	1(1)	2(1)
N(2)	34(1)	25(1)	22(1)	-1(1)	3(1)	-2(1)
C(1)	24(1)	34(1)	23(1)	-1(1)	2(1)	-4(1)
C(2)	32(1)	26(1)	27(1)	-3(1)	6(1)	-7(1)
C(3)	32(1)	24(1)	24(1)	0(1)	9(1)	0(1)
C(4)	25(1)	55(1)	66(1)	-10(1)	-2(1)	-7(1)
C(5)	45(1)	28(1)	44(1)	-4(1)	11(1)	6(1)
C(6)	32(1)	36(1)	38(1)	0(1)	0(1)	10(1)
C(7)	36(1)	40(1)	42(1)	-2(1)	12(1)	12(1)
C(8)	49(1)	30(1)	31(1)	-5(1)	9(1)	7(1)
C(9)	42(1)	30(1)	28(1)	7(1)	6(1)	-2(1)
C(10)	47(1)	46(1)	28(1)	-7(1)	-2(1)	-10(1)
C(11)	38(1)	34(1)	38(1)	5(1)	8(1)	-9(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and i displacement parameters ($\text{\AA}^2 \times 10^3$) for dd_22_0m.

	x	y	z	U(eq)
H(2)	4922	5005	1845	34
H(4A)	7989	3232	2252	74
H(4B)	7656	4436	2015	74
H(4C)	8053	3662	1147	74
H(5A)	1024	5680	659	58
H(5B)	2540	6026	1529	58
H(5C)	820	5436	1798	58
H(6A)	5651	1100	1284	43
H(6B)	7287	1889	1368	43
H(7A)	7025	1123	-203	47
H(7B)	6554	2324	-343	47
H(8A)	4618	1267	-1420	43
H(8B)	3982	705	-478	43
H(9A)	4403	3451	-662	50
H(9B)	2409	3615	-1174	50
H(9C)	3809	3052	-1777	50
H(10A)	370	2222	-1347	61
H(10B)	1045	1059	-1131	61
H(10C)	1622	1684	-2058	61
H(11A)	507	1218	1790	54
H(11B)	1915	480	1361	54
H(11C)	172	839	654	54

L¹ZnEt (2)

Table 1. Crystal data and structure refinement for dd_010m.

Identification code	dd_010m	
Empirical formula	C ₁₂ H ₂₄ N ₂ O Zn	
Formula weight	277.70 Da	
Density (calculated)	1.310 g cm ⁻³	
<i>F</i> (000)	592	
Temperature	180(1) K	
Crystal size	0.380 x 0.320 x 0.220 mm	
Crystal color	colourless	
Crystal description	block	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	<i>P</i> 2 ₁ / <i>c</i>	
Unit cell dimensions	<i>a</i> = 9.6644(8) Å	$\alpha = 90^\circ$
	<i>b</i> = 10.9529(9) Å	$\beta = 102.587(3)^\circ$
	<i>c</i> = 13.6327(12) Å	$\gamma = 90^\circ$
Volume	1408.4(2) Å ³	
<i>Z</i>	4	
Cell measurement reflections used	15885	
Cell measurement theta min/max	2.85° to 29.64°	
Diffraction control software	Bruker AXS APEX 2 Vers.3.0/2009	
Diffraction measurement device	Bruker D8 KAPPA series II with APEX II area detector system	
Diffraction measurement method	Data collection strategy APEX 2/COSMO	
Theta range for data collection	2.159° to 29.675°	
Completeness to theta = 25.242°	99.5 %	
Index ranges	-13 ≤ <i>h</i> ≤ 13, -11 ≤ <i>k</i> ≤ 15, -18 ≤ <i>l</i> ≤ 18	
Computing data reduction	Bruker AXS APEX 2 Vers.3/2009	
Absorption coefficient	1.728 mm ⁻¹	
Absorption correction	Semi-empirical from equivalents	
Empirical absorption correction	Bruker AXS APEX 2 Vers.3/2009	
Max. / min. transmission	0.75 / 0.49	
<i>R</i> (merg) before/after correction	0.0808 / 0.0381	
Computing structure solution	Bruker AXS SHELXTL Vers. 2008/1	
Computing structure refinement	Bruker AXS SHELXL-2013/4	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Reflections collected	23415	
Independent reflections	3965 [<i>R</i> (int) = 0.0277]	
Data / restraints / parameters	3579 / 0 / 145	
Goodness-of-fit on <i>F</i> ²	1.051	
Weighting details	$w = 1/[\sigma^2 (Fo^2) + (0.027*P)^2 + 0.3526*P]$ where $P = (Fo^2 + 2Fc^2)/3$	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0197, <i>wR</i> 2 = 0.0524	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0235, <i>wR</i> 2 = 0.0551	
Largest diff. peak and hole	0.300 and -0.230 eÅ ⁻³	
Treatment of hydrogen atoms	Riding model on idealized geometries with the 1.2 fold isotropic displacement parameters of the equivalent U _{ij} of the corresponding carbon atom. The methyl groups are idealized with tetrahedral angles in a combined rotating and rigid group refinement with the 1.5 fold isotropic displacement parameters of the equivalent U _{ij} of the corresponding carbon atom.	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for dd_010m. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Zn(1)	2638(1)	9615(1)	1756(1)	24(1)
N(1)	1114(1)	8549(1)	2083(1)	26(1)
N(2)	4048(1)	8038(1)	1971(1)	31(1)
O(1)	3103(1)	10378(1)	3106(1)	31(1)
C(1)	650(1)	8598(1)	2910(1)	27(1)
C(2)	1194(1)	9458(1)	3690(1)	29(1)
C(3)	2352(1)	10216(1)	3766(1)	27(1)
C(4)	-472(1)	7725(1)	3111(1)	42(1)
C(5)	2851(2)	10936(1)	4724(1)	39(1)
C(6)	762(1)	7523(1)	1385(1)	35(1)
C(7)	1953(1)	6581(1)	1579(1)	39(1)
C(8)	3356(1)	7003(1)	1352(1)	38(1)
C(9)	5353(2)	8367(2)	1631(1)	53(1)
C(10)	4440(2)	7688(1)	3039(1)	46(1)
C(11)	2670(2)	10526(1)	501(1)	36(1)
C(12)	1983(2)	9908(2)	-484(1)	47(1)

Table 3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for dd_010m.

Zn(1)-O(1)	1.9815(8)	N(1)-Zn(1)-N(2)	88.62(4)
Zn(1)-C(11)	1.9870(12)	C(1)-N(1)-C(6)	121.32(9)
Zn(1)-N(1)	2.0045(9)	C(1)-N(1)-Zn(1)	125.21(7)
Zn(1)-N(2)	2.1800(9)	C(6)-N(1)-Zn(1)	112.38(7)
N(1)-C(1)	1.3020(14)	C(10)-N(2)-C(9)	108.63(11)
N(1)-C(6)	1.4641(14)	C(10)-N(2)-C(8)	110.54(10)
N(2)-C(10)	1.4728(16)	C(9)-N(2)-C(8)	108.49(10)
N(2)-C(9)	1.4798(17)	C(10)-N(2)-Zn(1)	110.97(8)
N(2)-C(8)	1.4827(15)	C(9)-N(2)-Zn(1)	108.37(8)
O(1)-C(3)	1.2855(14)	C(8)-N(2)-Zn(1)	109.78(7)
C(1)-C(2)	1.4322(16)	C(3)-O(1)-Zn(1)	122.88(7)
C(1)-C(4)	1.5150(15)	N(1)-C(1)-C(2)	122.05(10)
C(2)-C(3)	1.3791(16)	N(1)-C(1)-C(4)	121.71(11)
C(3)-C(5)	1.5126(15)	C(2)-C(1)-C(4)	116.22(10)
C(6)-C(7)	1.5249(18)	C(3)-C(2)-C(1)	127.70(10)
C(7)-C(8)	1.5272(19)	O(1)-C(3)-C(2)	127.17(10)
C(11)-C(12)	1.5207(19)	O(1)-C(3)-C(5)	114.21(10)
O(1)-Zn(1)-C(11)	123.04(4)	C(2)-C(3)-C(5)	118.61(10)
O(1)-Zn(1)-N(1)	93.92(3)	N(1)-C(6)-C(7)	110.25(9)
C(11)-Zn(1)-N(1)	129.37(5)	C(6)-C(7)-C(8)	115.46(10)
O(1)-Zn(1)-N(2)	101.57(4)	N(2)-C(8)-C(7)	115.21(10)
C(11)-Zn(1)-N(2)	112.78(5)	C(12)-C(11)-Zn(1)	116.83(9)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for dd_010m. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Zn(1)	29(1)	22(1)	21(1)	0(1)	8(1)	-2(1)
N(1)	24(1)	27(1)	25(1)	-2(1)	2(1)	-3(1)
N(2)	30(1)	28(1)	35(1)	-4(1)	6(1)	3(1)
O(1)	38(1)	29(1)	26(1)	-6(1)	11(1)	-9(1)
C(1)	22(1)	28(1)	31(1)	5(1)	5(1)	1(1)
C(2)	33(1)	31(1)	26(1)	2(1)	13(1)	4(1)
C(3)	36(1)	22(1)	22(1)	-1(1)	6(1)	4(1)
C(4)	35(1)	49(1)	46(1)	4(1)	14(1)	-13(1)
C(5)	58(1)	34(1)	26(1)	-8(1)	11(1)	-4(1)
C(6)	35(1)	36(1)	31(1)	-8(1)	2(1)	-10(1)
C(7)	50(1)	25(1)	40(1)	-10(1)	7(1)	-7(1)
C(8)	44(1)	31(1)	38(1)	-10(1)	9(1)	4(1)
C(9)	35(1)	50(1)	78(1)	-10(1)	25(1)	3(1)
C(10)	49(1)	43(1)	38(1)	-1(1)	-9(1)	11(1)
C(11)	53(1)	32(1)	26(1)	4(1)	13(1)	-3(1)
C(12)	54(1)	58(1)	27(1)	5(1)	4(1)	-3(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and i displacement parameters ($\text{\AA}^2 \times 10^3$) for dd_010m.

	x	y	z	U(eq)
H(2)	699	9512	4219	35
H(4A)	-1327	7799	2574	64
H(4B)	-702	7925	3758	64
H(4C)	-113	6887	3131	64
H(5A)	3814	10681	5048	59
H(5B)	2212	10785	5180	59
H(5C)	2848	11809	4566	59
H(6A)	617	7824	685	42
H(6B)	-131	7138	1470	42
H(7A)	1628	5849	1167	47
H(7B)	2125	6333	2294	47
H(8A)	4020	6303	1450	45
H(8B)	3187	7242	635	45
H(9A)	6009	7673	1738	79
H(9B)	5803	9071	2016	79
H(9C)	5110	8574	915	79
H(10A)	5024	6949	3111	69
H(10B)	3579	7530	3288	69
H(10C)	4977	8352	3428	69
H(11A)	2193	11321	531	44
H(11B)	3671	10700	488	44
H(12A)	2483	9144	-551	70
H(12B)	2037	10451	-1046	70
H(12C)	988	9731	-490	70

L¹ZnCl (3)

Table 1. Crystal data and structure refinement for dd_17_0m.

Identification code	dd_17_0m	
Empirical formula	C ₁₀ H ₁₉ Cl N ₂ O Zn	
Formula weight	284.09 Da	
Density (calculated)	1.462 g cm ⁻³	
<i>F</i> (000)	592	
Temperature	180(1) K	
Crystal size	0.450 x 0.300 x 0.200 mm	
Crystal color	colourless	
Crystal description	prism	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	<i>P</i> 2 ₁ /c	
Unit cell dimensions	<i>a</i> = 7.4600(4) Å	$\alpha = 90^\circ$
	<i>b</i> = 12.7923(7) Å	$\beta = 95.655(3)^\circ$
	<i>c</i> = 13.5904(8) Å	$\gamma = 90^\circ$
Volume	1290.63(12) Å ³	
<i>Z</i>	4	
Cell measurement reflections used	9939	
Cell measurement theta min/max	2.74° to 33.19°	
Diffractometer control software	Bruker AXS APEX 2 Vers.3.0/2009	
Diffractometer measurement device	Bruker D8 KAPPA series II with APEX II area detector system	
Diffractometer measurement method	Data collection strategy APEX 2/COSMO	
Theta range for data collection	2.191° to 33.233°	
Completeness to theta = 25.242°	99.8 %	
Index ranges	-11 ≤ <i>h</i> ≤ 10, -19 ≤ <i>k</i> ≤ 19, -20 ≤ <i>l</i> ≤ 20	
Computing data reduction	Bruker AXS APEX 2 Vers.3/2009	
Absorption coefficient	2.088 mm ⁻¹	
Absorption correction	Semi-empirical from equivalents	
Empirical absorption correction	Bruker AXS APEX 2 Vers.3/2009	
Max. / min. transmission	0.75 / 0.58	
<i>R</i> (merg) before/after correction	0.0554 / 0.0318	
Computing structure solution	Bruker AXS SHELXTL Vers. 2008/1	
Computing structure refinement	Bruker AXS SHELXL-2013/4	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Reflections collected	20290	
Independent reflections	4942 [<i>R</i> (int) = 0.0226]	
Data / restraints / parameters	4434 / 0 / 136	
Goodness-of-fit on <i>F</i> ²	1.024	
Weighting details	$w = 1/[\sigma^2 (Fo^2) + (0.0271 * P)^2 + 0.3191 * P]$ where $P = (Fo^2 + 2Fc^2)/3$	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0204, <i>wR</i> 2 = 0.0542	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0248, <i>wR</i> 2 = 0.0562	
Largest diff. peak and hole	0.402 and -0.342 eÅ ⁻³	
Treatment of hydrogen atoms	Riding model on idealized geometries with the 1.2 fold isotropic displacement parameters of the equivalent Uij of the corresponding carbon atom. The methyl groups are idealized with tetrahedral angles in a combined rotating and rigid group refinement with the 1.5 fold isotropic displacement parameters of the equivalent Uij of the corresponding carbon atom.	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for dd_17_0m. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Zn(1)	7444(1)	2400(1)	750(1)	20(1)
Cl(1)	6033(1)	1045(1)	1312(1)	35(1)
O(1)	6538(1)	3799(1)	869(1)	27(1)
N(1)	9982(1)	2656(1)	1245(1)	23(1)
N(2)	7981(1)	2085(1)	-694(1)	23(1)
C(1)	10558(1)	3570(1)	1558(1)	24(1)
C(2)	9377(1)	4445(1)	1609(1)	25(1)
C(3)	7574(1)	4530(1)	1268(1)	24(1)
C(4)	12525(2)	3765(1)	1886(1)	43(1)
C(5)	6634(2)	5565(1)	1357(1)	35(1)
C(6)	11192(1)	1794(1)	1049(1)	29(1)
C(7)	11253(1)	1646(1)	-65(1)	30(1)
C(8)	9484(2)	1316(1)	-648(1)	29(1)
C(9)	8485(2)	3072(1)	-1167(1)	32(1)
C(10)	6394(2)	1628(1)	-1284(1)	38(1)

Table 3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for dd_17_0m.

Zn(1)-O(1)	1.9253(7)	N(2)-Zn(1)-Cl(1)	108.53(3)
Zn(1)-N(1)	1.9729(9)	C(3)-O(1)-Zn(1)	120.40(6)
Zn(1)-N(2)	2.0812(8)	C(1)-N(1)-C(6)	123.02(9)
Zn(1)-Cl(1)	2.2033(3)	C(1)-N(1)-Zn(1)	122.32(7)
O(1)-C(3)	1.2974(12)	C(6)-N(1)-Zn(1)	113.66(7)
N(1)-C(1)	1.3028(13)	C(9)-N(2)-C(10)	108.98(9)
N(1)-C(6)	1.4652(13)	C(9)-N(2)-C(8)	111.06(8)
N(2)-C(9)	1.4813(14)	C(10)-N(2)-C(8)	108.63(9)
N(2)-C(10)	1.4829(14)	C(9)-N(2)-Zn(1)	108.97(7)
N(2)-C(8)	1.4893(14)	C(10)-N(2)-Zn(1)	111.62(7)
C(1)-C(2)	1.4307(14)	C(8)-N(2)-Zn(1)	107.59(6)
C(1)-C(4)	1.5122(15)	N(1)-C(1)-C(2)	122.25(9)
C(2)-C(3)	1.3833(15)	N(1)-C(1)-C(4)	121.60(10)
C(3)-C(5)	1.5083(14)	C(2)-C(1)-C(4)	116.14(9)
C(6)-C(7)	1.5306(15)	C(3)-C(2)-C(1)	128.93(9)
C(7)-C(8)	1.5299(16)	O(1)-C(3)-C(2)	127.05(9)
		O(1)-C(3)-C(5)	113.82(9)
O(1)-Zn(1)-N(1)	98.63(3)	C(2)-C(3)-C(5)	119.13(9)
O(1)-Zn(1)-N(2)	111.14(3)	N(1)-C(6)-C(7)	110.61(8)
N(1)-Zn(1)-N(2)	94.92(3)	C(8)-C(7)-C(6)	115.99(9)
O(1)-Zn(1)-Cl(1)	121.25(2)	N(2)-C(8)-C(7)	116.54(9)
N(1)-Zn(1)-Cl(1)	119.18(3)		

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for dd_17_0m. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Zn(1)	18(1)	21(1)	22(1)	-1(1)	1(1)	-2(1)
Cl(1)	33(1)	33(1)	38(1)	9(1)	5(1)	-10(1)
O(1)	22(1)	25(1)	34(1)	-4(1)	1(1)	2(1)
N(1)	19(1)	24(1)	25(1)	0(1)	0(1)	1(1)
N(2)	26(1)	22(1)	22(1)	0(1)	1(1)	0(1)
C(1)	20(1)	28(1)	22(1)	0(1)	1(1)	-5(1)
C(2)	27(1)	23(1)	26(1)	-2(1)	4(1)	-5(1)
C(3)	28(1)	21(1)	23(1)	0(1)	7(1)	0(1)
C(4)	22(1)	43(1)	62(1)	-10(1)	-5(1)	-7(1)
C(5)	39(1)	24(1)	42(1)	-2(1)	10(1)	5(1)
C(6)	23(1)	29(1)	34(1)	1(1)	-2(1)	7(1)
C(7)	26(1)	30(1)	36(1)	1(1)	9(1)	8(1)
C(8)	36(1)	24(1)	28(1)	-4(1)	5(1)	6(1)
C(9)	38(1)	31(1)	29(1)	10(1)	6(1)	3(1)
C(10)	36(1)	45(1)	30(1)	-11(1)	-5(1)	-4(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and i displacement parameters ($\text{\AA}^2 \times 10^3$) for dd_17_0m.

	x	y	z	U(eq)
H(2)	9904	5051	1921	30
H(4A)	12999	3190	2312	64
H(4B)	12650	4424	2253	64
H(4C)	13202	3806	1304	64
H(5A)	6007	5757	715	52
H(5B)	7524	6104	1567	52
H(5C)	5760	5507	1847	52
H(6A)	10768	1142	1341	35
H(6B)	12418	1946	1363	35
H(7A)	11651	2311	-346	36
H(7B)	12177	1112	-167	36
H(8A)	9736	1152	-1333	35
H(8B)	9069	662	-353	35
H(9A)	9428	3426	-737	49
H(9B)	7426	3527	-1272	49
H(9C)	8934	2916	-1805	49
H(10A)	5385	2121	-1307	56
H(10B)	6055	973	-977	56
H(10C)	6695	1487	-1957	56

Table 6. Torsion angles [°] for dd_17_0m.

C(6)-N(1)-C(1)-C(2)	170.77(9)
Zn(1)-N(1)-C(1)-C(2)	2.96(13)
C(6)-N(1)-C(1)-C(4)	-9.06(15)
Zn(1)-N(1)-C(1)-C(4)	-176.87(9)
N(1)-C(1)-C(2)-C(3)	-7.25(16)
C(4)-C(1)-C(2)-C(3)	172.58(11)
Zn(1)-O(1)-C(3)-C(2)	2.71(13)
Zn(1)-O(1)-C(3)-C(5)	-176.78(7)
C(1)-C(2)-C(3)-O(1)	4.08(16)
C(1)-C(2)-C(3)-C(5)	-176.45(9)
C(1)-N(1)-C(6)-C(7)	-104.89(11)
Zn(1)-N(1)-C(6)-C(7)	63.87(10)
N(1)-C(6)-C(7)-C(8)	-64.06(12)
C(9)-N(2)-C(8)-C(7)	60.28(11)
C(10)-N(2)-C(8)-C(7)	-179.88(9)
Zn(1)-N(2)-C(8)-C(7)	-58.90(10)
C(6)-C(7)-C(8)-N(2)	65.62(13)

L²ZnEt (8)

Table 1. Crystal data and structure refinement for dd_009m.

Identification code	dd_009m	
Empirical formula	C ₁₈ H ₃₂ N ₄ O Zn	
Formula weight	385.84 Da	
Density (calculated)	1.243 g cm ⁻³	
<i>F</i> (000)	1648	
Temperature	180(1) K	
Crystal size	0.380 x 0.120 x 0.080 mm	
Crystal color	yellow	
Crystal description	rod	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	<i>P</i> 2 ₁ /c	
Unit cell dimensions	<i>a</i> = 30.608(2) Å	$\alpha = 90^\circ$
	<i>b</i> = 8.3830(6) Å	$\beta = 93.993(3)^\circ$
	<i>c</i> = 16.1146(12) Å	$\gamma = 90^\circ$
Volume	4124.8(5) Å ³	
<i>Z</i>	8	
Cell measurement reflections used	9893	
Cell measurement theta min/max	2.50° to 25.85°	
Diffractometer control software	Bruker AXS APEX 2 Vers.3.0/2009	
Diffractometer measurement device	Bruker D8 KAPPA series II with APEX II area detector system	
Diffractometer measurement method	Data collection strategy APEX 2/COSMO	
Theta range for data collection	2.001° to 25.969°	
Completeness to theta = 25.242°	99.7 %	
Index ranges	-37 ≤ <i>h</i> ≤ 37, -10 ≤ <i>k</i> ≤ 10, -19 ≤ <i>l</i> ≤ 19	
Computing data reduction	Bruker AXS APEX 2 Vers.3/2009	
Absorption coefficient	1.202 mm ⁻¹	
Absorption correction	Semi-empirical from equivalents	
Empirical absorption correction	Bruker AXS APEX 2 Vers.3/2009	
Max. / min. transmission	0.75 / 0.66	
<i>R</i> (merg) before/after correction	0.0775 / 0.0509	
Computing structure solution	Bruker AXS SHELXTL Vers. 2008/1	
Computing structure refinement	Bruker AXS SHELXL-2013/4	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Reflections collected	40363	
Independent reflections	8017 [<i>R</i> (int) = 0.0467]	
Data / restraints / parameters	4968 / 0 / 433	
Goodness-of-fit on <i>F</i> ²	1.015	
Weighting details	$w = 1/[\sigma^2 (Fo^2) + (0.0411 * P)^2 + 3.4529 * P]$ where $P = (Fo^2 + 2Fc^2)/3$	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0470, <i>wR</i> 2 = 0.0935	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0963, <i>wR</i> 2 = 0.1101	
Largest diff. peak and hole	0.632 and -0.372 eÅ ⁻³	
Treatment of hydrogen atoms	Riding model on idealized geometries with the 1.2 fold isotropic displacement parameters of the equivalent Uij of the corresponding carbon atom. The methyl groups are idealized with tetrahedral angles in a combined rotating and rigid group refinement with the 1.5 fold isotropic displacement parameters of the equivalent Uij of the corresponding carbon atom.	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for dd_009m. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Zn(1)	3638(1)	4151(1)	5243(1)	36(1)
O(1)	3498(1)	4378(3)	4020(1)	40(1)
N(1)	4115(1)	2528(3)	5105(2)	31(1)
N(2)	5120(1)	3005(3)	6574(2)	37(1)
N(3)	3131(1)	2553(4)	5525(2)	36(1)
N(4)	2172(1)	-636(5)	6267(2)	56(1)
C(1)	4160(1)	1761(4)	4410(2)	33(1)
C(2)	3905(1)	2100(4)	3660(2)	37(1)
C(3)	3620(1)	3348(5)	3500(2)	36(1)
C(4)	4494(1)	437(5)	4354(2)	50(1)
C(5)	3434(1)	3607(5)	2610(2)	58(1)
C(6)	4412(1)	2205(4)	5843(2)	37(1)
C(7)	4804(1)	3335(4)	5871(2)	36(1)
C(8)	5529(1)	3859(5)	6467(3)	62(1)
C(9)	4949(1)	3469(5)	7360(2)	55(1)
C(10)	3666(2)	5988(5)	6035(3)	72(1)
C(11)	3944(2)	7350(6)	5864(3)	90(2)
C(12)	2749(1)	3057(5)	5803(2)	40(1)
C(13)	2425(1)	2069(5)	6043(2)	45(1)
C(14)	2478(1)	406(5)	6023(2)	42(1)
C(15)	2875(1)	-111(5)	5730(2)	41(1)
C(16)	3178(1)	966(4)	5495(2)	38(1)
C(17)	1775(1)	-55(6)	6614(3)	77(2)
C(18)	2263(1)	-2332(6)	6314(3)	69(1)
Zn(2)	1310(1)	4108(1)	4787(1)	36(1)
O(21)	1400(1)	4422(3)	6008(1)	44(1)
N(21)	780(1)	5578(3)	4643(2)	36(1)
N(22)	439(1)	4895(4)	2383(2)	51(1)
N(23)	1798(1)	5639(3)	4362(2)	35(1)
N(24)	2763(1)	8711(4)	3564(2)	49(1)
C(21)	642(1)	6392(4)	5263(2)	37(1)
C(22)	833(1)	6326(5)	6088(2)	45(1)
C(23)	1175(1)	5398(5)	6412(2)	40(1)
C(24)	244(1)	7487(5)	5138(3)	55(1)
C(25)	1300(1)	5491(6)	7333(2)	68(1)
C(26)	537(1)	5784(6)	3824(2)	66(1)
C(27)	651(1)	4601(6)	3204(2)	61(1)
C(28)	-22(1)	4583(5)	2321(3)	60(1)
C(29)	641(1)	3860(7)	1805(3)	83(2)
C(30)	1377(1)	1898(4)	4383(2)	43(1)
C(31)	993(1)	778(5)	4474(2)	50(1)
C(32)	2189(1)	5109(4)	4157(2)	35(1)
C(33)	2517(1)	6060(4)	3903(2)	38(1)
C(34)	2454(1)	7712(4)	3828(2)	36(1)
C(35)	2042(1)	8267(5)	4042(2)	44(1)
C(36)	1741(1)	7222(5)	4299(2)	43(1)
C(37)	3195(1)	8140(5)	3388(3)	66(1)
C(38)	2670(1)	10398(5)	3424(3)	67(1)

Table 3. Bond lengths [Å] and angles [°] for dd_009m.

Zn(1)-O(1)	1.996(2)	C(9)-N(2)-C(7)	111.3(3)
Zn(1)-C(10)	1.998(4)	C(8)-N(2)-C(7)	110.0(3)
Zn(1)-N(1)	2.018(3)	C(16)-N(3)-C(12)	114.8(3)
Zn(1)-N(3)	2.123(3)	C(16)-N(3)-Zn(1)	122.5(2)
O(1)-C(3)	1.276(4)	C(12)-N(3)-Zn(1)	122.5(3)
N(1)-C(1)	1.307(4)	C(14)-N(4)-C(18)	120.8(3)
N(1)-C(6)	1.472(4)	C(14)-N(4)-C(17)	120.5(4)
N(2)-C(9)	1.457(4)	C(18)-N(4)-C(17)	118.0(3)
N(2)-C(8)	1.463(4)	N(1)-C(1)-C(2)	123.0(3)
N(2)-C(7)	1.464(4)	N(1)-C(1)-C(4)	121.6(3)
N(3)-C(16)	1.340(4)	C(2)-C(1)-C(4)	115.4(3)
N(3)-C(12)	1.349(4)	C(3)-C(2)-C(1)	128.0(3)
N(4)-C(14)	1.359(5)	O(1)-C(3)-C(2)	126.9(3)
N(4)-C(18)	1.450(5)	O(1)-C(3)-C(5)	114.7(3)
N(4)-C(17)	1.458(5)	C(2)-C(3)-C(5)	118.4(3)
C(1)-C(2)	1.421(4)	N(1)-C(6)-C(7)	110.5(3)
C(1)-C(4)	1.516(4)	N(2)-C(7)-C(6)	112.4(3)
C(2)-C(3)	1.376(5)	C(11)-C(10)-Zn(1)	118.8(3)
C(3)-C(5)	1.521(5)	N(3)-C(12)-C(13)	124.5(4)
C(6)-C(7)	1.525(4)	C(12)-C(13)-C(14)	120.5(3)
C(10)-C(11)	1.461(6)	N(4)-C(14)-C(15)	122.0(4)
C(12)-C(13)	1.369(5)	N(4)-C(14)-C(13)	123.3(3)
C(13)-C(14)	1.404(5)	C(15)-C(14)-C(13)	114.8(3)
C(14)-C(15)	1.403(5)	C(16)-C(15)-C(14)	120.6(4)
C(15)-C(16)	1.366(5)	N(3)-C(16)-C(15)	124.8(3)
Zn(2)-C(30)	1.979(3)	C(30)-Zn(2)-O(21)	116.07(13)
Zn(2)-O(21)	1.985(2)	C(30)-Zn(2)-N(21)	128.86(13)
Zn(2)-N(21)	2.039(3)	O(21)-Zn(2)-N(21)	95.00(10)
Zn(2)-N(23)	2.117(3)	C(30)-Zn(2)-N(23)	111.74(13)
O(21)-C(23)	1.277(4)	O(21)-Zn(2)-N(23)	100.84(10)
N(21)-C(21)	1.304(4)	N(21)-Zn(2)-N(23)	99.82(11)
N(21)-C(26)	1.479(4)	C(23)-O(21)-Zn(2)	123.2(2)
N(22)-C(28)	1.431(5)	C(21)-N(21)-C(26)	117.0(3)
N(22)-C(29)	1.444(5)	C(21)-N(21)-Zn(2)	121.8(2)
N(22)-C(27)	1.454(4)	C(26)-N(21)-Zn(2)	121.3(2)
N(23)-C(32)	1.340(4)	C(28)-N(22)-C(29)	108.1(3)
N(23)-C(36)	1.341(4)	C(28)-N(22)-C(27)	114.1(3)
N(24)-C(34)	1.354(4)	C(29)-N(22)-C(27)	107.5(3)
N(24)-C(37)	1.453(5)	C(32)-N(23)-C(36)	115.0(3)
N(24)-C(38)	1.457(5)	C(32)-N(23)-Zn(2)	122.7(2)
C(21)-C(22)	1.416(5)	C(36)-N(23)-Zn(2)	122.2(2)
C(21)-C(24)	1.528(5)	C(34)-N(24)-C(37)	121.5(3)
C(22)-C(23)	1.377(5)	C(34)-N(24)-C(38)	121.2(3)
C(23)-C(25)	1.509(5)	C(37)-N(24)-C(38)	117.3(3)
C(26)-C(27)	1.467(5)	N(21)-C(21)-C(22)	124.3(3)
C(30)-C(31)	1.520(5)	N(21)-C(21)-C(24)	120.7(3)
C(32)-C(33)	1.368(5)	C(22)-C(21)-C(24)	115.0(3)
C(33)-C(34)	1.402(5)	C(23)-C(22)-C(21)	129.2(3)
C(34)-C(35)	1.409(5)	O(21)-C(23)-C(22)	126.3(3)
C(35)-C(36)	1.358(5)	O(21)-C(23)-C(25)	115.2(3)
O(1)-Zn(1)-C(10)	123.62(17)	C(22)-C(23)-C(25)	118.5(3)
O(1)-Zn(1)-N(1)	93.57(10)	C(27)-C(26)-N(21)	113.6(3)
C(10)-Zn(1)-N(1)	126.23(16)	N(22)-C(27)-C(26)	113.1(4)
O(1)-Zn(1)-N(3)	99.30(10)	C(31)-C(30)-Zn(2)	116.7(2)
C(10)-Zn(1)-N(3)	110.43(15)	N(23)-C(32)-C(33)	124.6(3)
N(1)-Zn(1)-N(3)	98.21(11)	C(32)-C(33)-C(34)	120.1(3)
C(3)-O(1)-Zn(1)	122.1(2)	N(24)-C(34)-C(33)	122.9(3)
C(1)-N(1)-C(6)	120.3(3)	N(24)-C(34)-C(35)	121.9(3)
C(1)-N(1)-Zn(1)	123.2(2)	C(33)-C(34)-C(35)	115.2(3)
C(6)-N(1)-Zn(1)	116.5(2)	C(36)-C(35)-C(34)	120.0(3)
C(9)-N(2)-C(8)	109.5(3)	N(23)-C(36)-C(35)	125.0(3)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for dd_009m. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Zn(1)	30(1)	34(1)	45(1)	-7(1)	1(1)	4(1)
O(1)	30(1)	45(2)	45(1)	8(1)	2(1)	10(1)
N(1)	21(1)	36(2)	37(2)	2(1)	-1(1)	1(1)
N(2)	26(1)	46(2)	38(2)	-3(1)	-2(1)	0(1)
N(3)	29(2)	42(2)	35(2)	0(1)	0(1)	6(1)
N(4)	38(2)	69(3)	62(2)	9(2)	6(2)	-8(2)
C(1)	20(2)	33(2)	46(2)	1(2)	6(2)	0(1)
C(2)	32(2)	37(2)	41(2)	-8(2)	2(2)	-3(2)
C(3)	24(2)	47(2)	35(2)	6(2)	-3(2)	-9(2)
C(4)	43(2)	44(3)	64(3)	-2(2)	10(2)	15(2)
C(5)	51(2)	76(3)	46(2)	14(2)	-9(2)	-8(2)
C(6)	27(2)	44(2)	41(2)	7(2)	-3(2)	-2(2)
C(7)	31(2)	39(2)	39(2)	4(2)	0(2)	-2(2)
C(8)	33(2)	78(3)	73(3)	-11(2)	-4(2)	-15(2)
C(9)	52(2)	67(3)	46(2)	-7(2)	-2(2)	1(2)
C(10)	73(3)	47(3)	97(4)	-23(3)	19(3)	1(2)
C(11)	81(3)	68(4)	123(5)	-33(3)	7(3)	3(3)
C(12)	34(2)	48(3)	38(2)	2(2)	-1(2)	12(2)
C(13)	25(2)	67(3)	42(2)	2(2)	3(2)	9(2)
C(14)	32(2)	58(3)	34(2)	4(2)	-5(2)	-3(2)
C(15)	36(2)	44(3)	43(2)	-2(2)	-1(2)	0(2)
C(16)	29(2)	46(3)	37(2)	-6(2)	2(1)	4(2)
C(17)	37(2)	111(4)	85(3)	23(3)	19(2)	-7(2)
C(18)	60(3)	72(4)	73(3)	17(3)	4(2)	-21(2)
Zn(2)	36(1)	37(1)	34(1)	-3(1)	-1(1)	8(1)
O(21)	46(1)	57(2)	29(1)	1(1)	-4(1)	7(1)
N(21)	34(2)	44(2)	29(2)	-2(1)	-5(1)	10(1)
N(22)	57(2)	62(2)	33(2)	8(2)	-10(2)	-18(2)
N(23)	36(2)	35(2)	34(2)	1(1)	2(1)	9(1)
N(24)	47(2)	40(2)	61(2)	10(2)	-1(2)	-3(1)
C(21)	29(2)	34(2)	48(2)	0(2)	13(2)	-2(1)
C(22)	50(2)	53(3)	35(2)	-9(2)	17(2)	2(2)
C(23)	47(2)	45(2)	30(2)	0(2)	7(2)	-15(2)
C(24)	41(2)	50(3)	75(3)	0(2)	13(2)	12(2)
C(25)	82(3)	93(4)	29(2)	0(2)	1(2)	-14(3)
C(26)	77(3)	69(3)	48(2)	-4(2)	-15(2)	33(2)
C(27)	62(3)	75(3)	43(2)	1(2)	-6(2)	-2(2)
C(28)	48(2)	65(3)	65(3)	-12(2)	-4(2)	7(2)
C(29)	49(3)	141(5)	62(3)	-3(3)	14(2)	-13(3)
C(30)	39(2)	43(2)	46(2)	-10(2)	1(2)	11(2)
C(31)	52(2)	44(3)	53(2)	-2(2)	5(2)	5(2)
C(32)	37(2)	28(2)	41(2)	3(2)	1(2)	8(2)
C(33)	32(2)	38(2)	42(2)	2(2)	-1(2)	10(2)
C(34)	40(2)	37(2)	29(2)	3(2)	-8(2)	1(2)
C(35)	52(2)	31(2)	47(2)	2(2)	-2(2)	14(2)
C(36)	41(2)	41(3)	47(2)	-1(2)	6(2)	16(2)
C(37)	46(2)	60(3)	91(3)	13(3)	8(2)	-10(2)
C(38)	61(3)	49(3)	87(3)	22(2)	-14(2)	-9(2)

Table 5. Hydrogen coordinates ($\times 10^4$) and i displacement parameters ($\text{\AA}^2 \times 10^3$) for dd_009m.

	x	y	z	U(eq)
H(2)	3935	1376	3215	44
H(4A)	4789	875	4459	75
H(4B)	4465	-38	3797	75
H(4C)	4443	-384	4770	75
H(5A)	3116	3743	2602	87
H(5B)	3502	2680	2271	87
H(5C)	3566	4565	2383	87
H(6A)	4517	1088	5826	45
H(6B)	4253	2341	6352	45
H(7A)	4952	3238	5346	44
H(7B)	4698	4446	5913	44
H(8A)	5642	3557	5935	92
H(8B)	5745	3584	6922	92
H(8C)	5474	5011	6472	92
H(9A)	4882	4612	7348	83
H(9B)	5169	3247	7817	83
H(9C)	4682	2862	7443	83
H(10A)	3364	6392	6071	86
H(10B)	3765	5571	6592	86
H(11A)	4247	6987	5826	136
H(11B)	3934	8131	6315	136
H(11C)	3839	7846	5337	136
H(12)	2702	4174	5834	48
H(13)	2162	2511	6224	54
H(15)	2934	-1220	5695	49
H(16)	3441	560	5295	45
H(17A)	1848	387	7170	116
H(17B)	1568	-940	6655	116
H(17C)	1641	776	6252	116
H(18A)	2367	-2697	5784	103
H(18B)	1995	-2909	6426	103
H(18C)	2489	-2537	6762	103
H(22)	709	7022	6473	55
H(24A)	300	8304	4724	82
H(24B)	188	8002	5666	82
H(24C)	-13	6857	4943	82
H(25A)	1213	4503	7602	103
H(25B)	1149	6397	7571	103
H(25C)	1617	5636	7425	103
H(26A)	219	5712	3898	79
H(26B)	597	6863	3611	79
H(27A)	973	4606	3166	73
H(27B)	567	3528	3393	73
H(28A)	-75	3482	2491	89
H(28B)	-138	4737	1744	89
H(28C)	-168	5318	2684	89
H(29A)	579	2746	1937	125
H(29B)	959	4033	1847	125
H(29C)	524	4099	1237	125
H(30A)	1435	1945	3787	51
H(30B)	1639	1426	4685	51
H(31A)	966	545	5065	75
H(31B)	1041	-217	4175	75
H(31C)	723	1284	4241	75
H(32)	2242	3993	4191	42
H(33)	2789	5601	3776	45
H(35)	1976	9373	4006	52
H(36)	1469	7645	4446	51

H(37A)	3299	7379	3819	99
H(37B)	3398	9044	3383	99
H(37C)	3179	7613	2844	99
H(38A)	2424	10513	3007	100
H(38B)	2929	10923	3224	100
H(38C)	2596	10894	3946	100

L²ZnCl (9)

Table 1. Crystal data and structure refinement for dd_047lt.

Identification code	dd_047lt	
Empirical formula	C ₁₈ H ₃₄ Cl ₂ N ₄ O ₂ Zn ₂ , 3(CHCl ₃)	
Formula weight	898.23 Da	
Density (calculated)	1.647 g cm ⁻³	
<i>F</i> (000)	1816	
Temperature	100(1) K	
Crystal size	0.380 x 0.350 x 0.320 mm	
Crystal color	brown	
Crystal description	block	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	<i>P</i> 2 ₁ / <i>c</i>	
Unit cell dimensions	<i>a</i> = 10.6351(5) Å	$\alpha = 90^\circ$
	<i>b</i> = 23.2845(11) Å	$\beta = 109.669(2)^\circ$
	<i>c</i> = 15.5326(7) Å	$\gamma = 90^\circ$
Volume	3622.0(3) Å ³	
<i>Z</i>	4	
Cell measurement reflections used	30883	
Cell measurement theta min/max	2.22° to 29.23°	
Diffractometer control software	Bruker AXS APEX 2 Vers.3.0/2009	
Diffractometer measurement device	Bruker D8 KAPPA series II with APEX II area detector system	
Diffractometer measurement method	Data collection strategy APEX 2/COSMO	
Theta range for data collection	1.644° to 29.243°	
Completeness to theta = 25.242°	99.5 %	
Index ranges	-14 ≤ <i>h</i> ≤ 14, -31 ≤ <i>k</i> ≤ 31, -21 ≤ <i>l</i> ≤ 21	
Computing data reduction	Bruker AXS APEX 2 Vers.3/2009	
Absorption coefficient	2.163 mm ⁻¹	
Absorption correction	Semi-empirical from equivalents	
Empirical absorption correction	Bruker AXS APEX 2 Vers.3/2009	
Max. / min. transmission	0.75 / 0.60	
<i>R</i> (merg) before/after correction	0.0509 / 0.0320	
Computing structure solution	Bruker AXS SHELXTL Vers. 2008/1	
Computing structure refinement	Bruker AXS SHELXL-2013/4	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Reflections collected	51792	
Independent reflections	9711 [<i>R</i> (int) = 0.0204]	
Data / restraints / parameters	8805 / 0 / 361	
Goodness-of-fit on <i>F</i> ²	1.110	
Weighting details	$w = 1/[\sigma^2 (Fo^2) + (0.0224*P)^2 + 4.231*P]$ where $P = (Fo^2 + 2Fc^2)/3$	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0265, <i>wR</i> 2 = 0.0616	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0317, <i>wR</i> 2 = 0.0644	
Largest diff. peak and hole	0.859 and -0.661 eÅ ⁻³	
Treatment of hydrogen atoms	Riding model on idealized geometries with the 1.2 fold isotropic displacement parameters of the equivalent Uij of the corresponding carbon atom. The methyl groups are idealized with tetrahedral angles in a combined rotating and rigid group refinement with the 1.5 fold isotropic displacement parameters of the equivalent Uij of the corresponding carbon atom.	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for dd_047lt. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Zn(1)	9386(1)	3186(1)	7477(1)	13(1)
Zn(21)	7008(1)	2322(1)	7439(1)	12(1)
Cl(1)	11293(1)	3447(1)	8599(1)	17(1)
Cl(21)	7017(1)	1656(1)	8518(1)	18(1)
O(1)	8938(1)	2326(1)	7372(1)	16(1)
O(21)	7832(1)	3084(1)	7992(1)	15(1)
N(1)	9821(1)	3088(1)	6280(1)	16(1)
N(2)	8621(1)	4004(1)	6804(1)	16(1)
N(21)	5180(1)	2740(1)	7062(1)	15(1)
N(22)	6073(1)	1956(1)	6094(1)	15(1)
C(1)	10120(2)	2614(1)	5953(1)	17(1)
C(2)	10141(2)	2067(1)	6399(1)	17(1)
C(3)	9600(2)	1949(1)	7062(1)	16(1)
C(4)	10456(2)	2609(1)	5082(1)	24(1)
C(5)	9752(2)	1366(1)	7503(1)	21(1)
C(6)	9811(2)	3627(1)	5793(1)	20(1)
C(7)	9654(2)	4123(1)	6386(1)	19(1)
C(8)	8567(2)	4492(1)	7397(1)	23(1)
C(9)	7294(2)	3929(1)	6103(1)	21(1)
C(21)	4893(2)	3195(1)	7444(1)	15(1)
C(22)	5898(2)	3495(1)	8167(1)	16(1)
C(23)	7250(2)	3433(1)	8405(1)	15(1)
C(24)	3501(2)	3438(1)	7141(1)	21(1)
C(25)	8179(2)	3759(1)	9201(1)	20(1)
C(26)	4138(2)	2472(1)	6296(1)	17(1)
C(27)	4662(2)	1911(1)	6043(1)	17(1)
C(28)	6537(2)	1379(1)	5949(1)	19(1)
C(29)	6220(2)	2349(1)	5387(1)	18(1)
C(31)	3870(2)	1609(1)	8677(1)	20(1)
C(32)	6705(2)	154(1)	8571(2)	26(1)
C(33)	2449(2)	4560(1)	10085(1)	24(1)
Cl(3)	3919(1)	1186(1)	9636(1)	33(1)
Cl(4)	3226(1)	1197(1)	7670(1)	24(1)
Cl(5)	2917(1)	2232(1)	8628(1)	22(1)
Cl(6)	7058(1)	48(1)	7553(1)	30(1)
Cl(7)	7997(1)	-156(1)	9498(1)	37(1)
Cl(8)	5174(1)	-155(1)	8499(1)	39(1)
Cl(9)	1880(1)	5064(1)	9186(1)	28(1)
Cl(10)	4022(1)	4762(1)	10848(1)	37(1)
Cl(11)	1299(1)	4503(1)	10672(1)	31(1)

Table 3. Bond lengths [Å] and angles [°] for dd_047lt.

Zn(1)-O(1)	2.0519(12)	C(3)-O(1)-Zn(1)	122.84(11)
Zn(1)-N(1)	2.0733(15)	C(3)-O(1)-Zn(21)	132.24(11)
Zn(1)-O(21)	2.0781(12)	Zn(1)-O(1)-Zn(21)	101.85(5)
Zn(1)-N(2)	2.1922(15)	C(23)-O(21)-Zn(21)	122.66(11)
Zn(1)-Cl(1)	2.2674(4)	C(23)-O(21)-Zn(1)	133.11(11)
Zn(21)-O(21)	2.0343(12)	Zn(21)-O(21)-Zn(1)	102.88(5)
Zn(21)-N(21)	2.0734(14)	C(1)-N(1)-C(6)	119.11(15)
Zn(21)-O(1)	2.0904(12)	C(1)-N(1)-Zn(1)	127.00(12)
Zn(21)-N(22)	2.1644(14)	C(6)-N(1)-Zn(1)	113.87(11)
Zn(21)-Cl(21)	2.2812(4)	C(9)-N(2)-C(8)	108.84(14)
O(1)-C(3)	1.315(2)	C(9)-N(2)-C(7)	111.47(14)
O(21)-C(23)	1.313(2)	C(8)-N(2)-C(7)	108.67(14)
N(1)-C(1)	1.301(2)	C(9)-N(2)-Zn(1)	111.02(11)
N(1)-C(6)	1.463(2)	C(8)-N(2)-Zn(1)	117.24(11)
N(2)-C(9)	1.475(2)	C(7)-N(2)-Zn(1)	99.28(10)
N(2)-C(8)	1.475(2)	C(21)-N(21)-C(26)	119.21(14)
N(2)-C(7)	1.478(2)	C(21)-N(21)-Zn(21)	126.54(12)
N(21)-C(21)	1.299(2)	C(26)-N(21)-Zn(21)	114.24(11)
N(21)-C(26)	1.465(2)	C(28)-N(22)-C(29)	109.03(14)
N(22)-C(28)	1.474(2)	C(28)-N(22)-C(27)	108.29(13)
N(22)-C(29)	1.478(2)	C(29)-N(22)-C(27)	111.28(14)
N(22)-C(27)	1.479(2)	C(28)-N(22)-Zn(21)	115.99(11)
C(1)-C(2)	1.446(3)	C(29)-N(22)-Zn(21)	110.11(10)
C(1)-C(4)	1.511(2)	C(27)-N(22)-Zn(21)	101.97(10)
C(2)-C(3)	1.366(2)	N(1)-C(1)-C(2)	121.79(16)
C(3)-C(5)	1.503(2)	N(1)-C(1)-C(4)	121.30(17)
C(6)-C(7)	1.521(3)	C(2)-C(1)-C(4)	116.90(16)
C(21)-C(22)	1.444(2)	C(3)-C(2)-C(1)	126.60(16)
C(21)-C(24)	1.505(2)	O(1)-C(3)-C(2)	123.75(16)
C(22)-C(23)	1.367(2)	O(1)-C(3)-C(5)	115.05(15)
C(23)-C(25)	1.501(2)	C(2)-C(3)-C(5)	121.19(16)
C(26)-C(27)	1.522(2)	N(1)-C(6)-C(7)	108.69(14)
C(31)-Cl(5)	1.7558(19)	N(2)-C(7)-C(6)	111.91(14)
C(31)-Cl(4)	1.7650(19)	N(21)-C(21)-C(22)	121.58(15)
C(31)-Cl(3)	1.7714(19)	N(21)-C(21)-C(24)	121.45(16)
C(32)-Cl(8)	1.749(2)	C(22)-C(21)-C(24)	116.97(15)
C(32)-Cl(6)	1.761(2)	C(23)-C(22)-C(21)	126.55(16)
C(32)-Cl(7)	1.774(2)	O(21)-C(23)-C(22)	123.95(16)
C(33)-Cl(10)	1.757(2)	O(21)-C(23)-C(25)	115.32(15)
C(33)-Cl(11)	1.760(2)	C(22)-C(23)-C(25)	120.71(15)
C(33)-Cl(9)	1.767(2)	N(21)-C(26)-C(27)	109.41(14)
O(1)-Zn(1)-N(1)	86.42(5)	N(22)-C(27)-C(26)	112.24(14)
O(1)-Zn(1)-O(21)	74.05(5)	Cl(5)-C(31)-Cl(4)	111.35(10)
N(1)-Zn(1)-O(21)	141.15(5)	Cl(5)-C(31)-Cl(3)	110.48(10)
O(1)-Zn(1)-N(2)	140.42(5)	Cl(4)-C(31)-Cl(3)	109.62(10)
N(1)-Zn(1)-N(2)	80.03(6)	Cl(8)-C(32)-Cl(6)	111.12(12)
O(21)-Zn(1)-N(2)	93.88(5)	Cl(8)-C(32)-Cl(7)	109.58(11)
O(1)-Zn(1)-Cl(1)	116.50(4)	Cl(6)-C(32)-Cl(7)	109.32(11)
N(1)-Zn(1)-Cl(1)	107.88(4)	Cl(10)-C(33)-Cl(11)	109.93(11)
O(21)-Zn(1)-Cl(1)	110.87(4)	Cl(10)-C(33)-Cl(9)	110.54(11)
N(2)-Zn(1)-Cl(1)	103.06(4)	Cl(11)-C(33)-Cl(9)	110.33(11)
O(21)-Zn(21)-N(21)	86.58(5)		
O(21)-Zn(21)-O(1)	74.15(5)		
N(21)-Zn(21)-O(1)	145.78(5)		
O(21)-Zn(21)-N(22)	138.02(5)		
N(21)-Zn(21)-N(22)	80.21(6)		
O(1)-Zn(21)-N(22)	95.33(5)		
O(21)-Zn(21)-Cl(21)	112.85(4)		
N(21)-Zn(21)-Cl(21)	107.37(4)		
O(1)-Zn(21)-Cl(21)	106.13(4)		
N(22)-Zn(21)-Cl(21)	109.12(4)		

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for dd_047lt. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Zn(1)	13(1)	12(1)	13(1)	-1(1)	4(1)	-1(1)
Zn(21)	12(1)	11(1)	13(1)	0(1)	4(1)	0(1)
Cl(1)	15(1)	17(1)	16(1)	-2(1)	3(1)	-2(1)
Cl(21)	17(1)	17(1)	19(1)	5(1)	6(1)	-1(1)
O(1)	15(1)	14(1)	20(1)	-3(1)	9(1)	-2(1)
O(21)	15(1)	13(1)	18(1)	-3(1)	7(1)	-1(1)
N(1)	15(1)	18(1)	14(1)	0(1)	4(1)	-1(1)
N(2)	15(1)	15(1)	18(1)	1(1)	5(1)	-1(1)
N(21)	13(1)	16(1)	15(1)	1(1)	3(1)	0(1)
N(22)	15(1)	13(1)	16(1)	0(1)	5(1)	-1(1)
C(1)	11(1)	24(1)	15(1)	-4(1)	3(1)	-2(1)
C(2)	14(1)	18(1)	19(1)	-6(1)	5(1)	1(1)
C(3)	12(1)	14(1)	19(1)	-4(1)	4(1)	-1(1)
C(4)	21(1)	34(1)	17(1)	-4(1)	9(1)	1(1)
C(5)	20(1)	15(1)	29(1)	0(1)	8(1)	1(1)
C(6)	19(1)	22(1)	18(1)	4(1)	7(1)	-1(1)
C(7)	18(1)	18(1)	20(1)	3(1)	5(1)	-3(1)
C(8)	28(1)	16(1)	25(1)	-2(1)	9(1)	1(1)
C(9)	15(1)	22(1)	22(1)	3(1)	3(1)	1(1)
C(21)	16(1)	16(1)	16(1)	4(1)	7(1)	2(1)
C(22)	19(1)	15(1)	17(1)	-1(1)	8(1)	2(1)
C(23)	20(1)	12(1)	15(1)	0(1)	8(1)	0(1)
C(24)	16(1)	20(1)	26(1)	2(1)	8(1)	5(1)
C(25)	21(1)	20(1)	17(1)	-4(1)	6(1)	0(1)
C(26)	13(1)	19(1)	18(1)	0(1)	3(1)	-1(1)
C(27)	14(1)	17(1)	20(1)	-2(1)	4(1)	-3(1)
C(28)	20(1)	15(1)	21(1)	-3(1)	6(1)	1(1)
C(29)	20(1)	19(1)	16(1)	2(1)	6(1)	-2(1)
C(31)	20(1)	21(1)	19(1)	1(1)	6(1)	2(1)
C(32)	32(1)	16(1)	35(1)	0(1)	17(1)	0(1)
C(33)	24(1)	18(1)	27(1)	-4(1)	6(1)	-2(1)
Cl(3)	49(1)	27(1)	21(1)	6(1)	9(1)	6(1)
Cl(4)	25(1)	27(1)	21(1)	-4(1)	8(1)	0(1)
Cl(5)	20(1)	20(1)	22(1)	0(1)	3(1)	2(1)
Cl(6)	35(1)	28(1)	30(1)	6(1)	15(1)	2(1)
Cl(7)	36(1)	46(1)	26(1)	-9(1)	5(1)	1(1)
Cl(8)	28(1)	38(1)	57(1)	13(1)	21(1)	4(1)
Cl(9)	38(1)	24(1)	21(1)	-2(1)	10(1)	-6(1)
Cl(10)	22(1)	33(1)	48(1)	-4(1)	0(1)	1(1)
Cl(11)	30(1)	36(1)	28(1)	8(1)	9(1)	-2(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and i displacement parameters ($\text{\AA}^2 \times 10^3$) for dd_047lt.

	x	y	z	U(eq)
H(2)	10575	1759	6212	21
H(4A)	9670	2725	4567	35
H(4B)	10727	2221	4972	35
H(4C)	11189	2877	5139	35
H(5A)	10413	1387	8119	32
H(5B)	10049	1090	7136	32
H(5C)	8891	1243	7541	32
H(6A)	9062	3627	5204	23
H(6B)	10656	3669	5663	23
H(7A)	10518	4194	6876	22
H(7B)	9409	4474	6009	22
H(8A)	9431	4531	7886	35
H(8B)	7868	4423	7665	35
H(8C)	8367	4845	7033	35
H(9A)	7028	4286	5756	31
H(9B)	6641	3833	6400	31
H(9C)	7331	3618	5687	31
H(22)	5588	3763	8511	20
H(24A)	3251	3566	6505	31
H(24B)	3469	3764	7531	31
H(24C)	2875	3141	7191	31
H(25A)	8503	3503	9731	29
H(25B)	7703	4083	9349	29
H(25C)	8939	3902	9041	29
H(26A)	3878	2735	5763	21
H(26B)	3339	2396	6469	21
H(27C)	4580	1605	6462	21
H(27B)	4107	1801	5414	21
H(28A)	6493	1122	6437	28
H(28B)	7461	1403	5957	28
H(28C)	5967	1230	5356	28
H(29A)	5699	2203	4780	27
H(29B)	7163	2373	5441	27
H(29C)	5895	2732	5472	27
H(31)	4802	1727	8745	24
H(32)	6667	575	8681	32
H(33)	2533	4177	9819	28

L²Li (11)

Table 1. Crystal data and structure refinement for cs_306m.

Identification code	cs_306m	
Empirical formula	C ₂₇ H ₅₁ Li ₃ N ₆ O ₃	
Formula weight	528.55 Da	
Density (calculated)	1.099 g cm ⁻³	
<i>F</i> (000)	576	
Temperature	100(1) K	
Crystal size	0.340 x 0.320 x 0.250 mm	
Crystal color	orange	
Crystal description	block	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	<i>P</i> $\bar{1}$	
Unit cell dimensions	<i>a</i> = 9.1378(2) Å	α = 84.1030(10)°
	<i>b</i> = 10.2062(2) Å	β = 78.1510(10)°
	<i>c</i> = 17.9596(3) Å	γ = 77.5200(10)°
Volume	1597.54(5) Å ³	
<i>Z</i>	2	
Cell measurement reflections used	30287	
Cell measurement theta min/max	2.29° to 32.05°	
Diffractometer control software	Bruker AXS APEX 2 Vers.3.0/2009	
Diffractometer measurement device	Bruker D8 KAPPA series II with APEX II area detector system	
Diffractometer measurement method	Data collection strategy APEX 2/COSMO	
Theta range for data collection	2.047° to 32.083°	
Completeness to theta = 25.242°	99.7 %	
Index ranges	-13 ≤ <i>h</i> ≤ 13, -15 ≤ <i>k</i> ≤ 15, -26 ≤ <i>l</i> ≤ 26	
Computing data reduction	Bruker AXS APEX 2 Vers.3/2009	
Absorption coefficient	0.071 mm ⁻¹	
Absorption correction	Semi-empirical from equivalents	
Empirical absorption correction	Bruker AXS APEX 2 Vers.3/2009	
Max. / min. transmission	0.75 / 0.70	
<i>R</i> (merg) before/after correction	0.0534 / 0.0345	
Computing structure solution	Bruker AXS SHELXTL Vers. 2008/1	
Computing structure refinement	Bruker AXS SHELXL-2013/4	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Reflections collected	60613	
Independent reflections	10797 [<i>R</i> (int) = 0.0239]	
Data / restraints / parameters	9092 / 0 / 365	
Goodness-of-fit on <i>F</i> ²	1.026	
Weighting details	$w = 1/[\sigma^2(F_o^2) + (0.0603 \cdot P)^2 + 0.329 \cdot P]$	
	where $P = (F_o^2 + 2F_c^2)/3$	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0398, <i>wR</i> 2 = 0.1051	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0498, <i>wR</i> 2 = 0.1131	
Largest diff. peak and hole	0.442 and -0.233 eÅ ⁻³	
Treatment of hydrogen atoms	Riding model on idealized geometries with the 1.2 fold isotropic displacement parameters of the equivalent U _{ij} of the corresponding carbon atom. The methyl groups are idealized with tetrahedral angles in a combined rotating and rigid group refinement with the 1.5 fold isotropic displacement parameters of the equivalent U _{ij} of the corresponding carbon atom.	
Disorder	Carbon atoms C(27) to C(29) disordered over two sites with SOF 0.9 and 0.1 together with the riding hydrogen atoms. Hydrogen atoms of C(26) disordered over two sites with occupancies factor 0.9 and 0.1	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for cs_306m. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
N(1)	4314(1)	-418(1)	1237(1)	19(1)
N(2)	6014(1)	296(1)	2226(1)	21(1)
N(3)	104(1)	3500(1)	3146(1)	18(1)
N(4)	469(1)	5339(1)	1864(1)	21(1)
N(5)	3309(1)	4121(1)	3767(1)	21(1)
N(6)	2107(1)	1933(1)	4629(1)	26(1)
O(1)	2166(1)	2087(1)	1270(1)	19(1)
O(2)	2369(1)	1096(1)	2854(1)	17(1)
O(3)	3609(1)	3232(1)	2278(1)	17(1)
Li(1)	3763(2)	1239(1)	1859(1)	20(1)
Li(2)	1585(2)	3299(1)	2033(1)	20(1)
Li(3)	2495(2)	2727(1)	3303(1)	19(1)
C(1)	3634(1)	-658(1)	713(1)	18(1)
C(2)	2306(1)	255(1)	524(1)	20(1)
C(3)	1675(1)	1513(1)	793(1)	18(1)
C(4)	4193(1)	-1900(1)	257(1)	25(1)
C(5)	308(1)	2332(1)	488(1)	27(1)
C(6)	5650(1)	-1383(1)	1409(1)	24(1)
C(7)	5892(1)	-1101(1)	2186(1)	23(1)
C(8)	7456(1)	565(1)	1780(1)	32(1)
C(9)	5885(1)	577(1)	3020(1)	31(1)
C(11)	-770(1)	2625(1)	3399(1)	18(1)
C(12)	-269(1)	1214(1)	3306(1)	19(1)
C(13)	1199(1)	553(1)	3012(1)	16(1)
C(14)	-2412(1)	3048(1)	3809(1)	25(1)
C(15)	1453(1)	-919(1)	2866(1)	25(1)
C(16)	-573(1)	4926(1)	3240(1)	24(1)
C(17)	280(1)	5787(1)	2637(1)	22(1)
C(18)	-1004(1)	5419(1)	1639(1)	30(1)
C(19)	1356(1)	6184(1)	1324(1)	33(1)
C(21)	4041(1)	5020(1)	3401(1)	17(1)
C(22)	4612(1)	5018(1)	2592(1)	18(1)
C(23)	4429(1)	4137(1)	2098(1)	16(1)
C(24)	4404(1)	6122(1)	3800(1)	25(1)
C(25)	5253(1)	4211(1)	1277(1)	24(1)
C(26)	2911(1)	4100(1)	4597(1)	31(1)
C(27)	3080(1)	2636(1)	4913(1)	24(1)
C(28)	2531(2)	485(1)	4778(1)	37(1)
C(29)	493(1)	2374(1)	5014(1)	33(1)
C(27A)	1589(10)	3193(9)	4826(5)	27(2)
C(28A)	3900(12)	1501(11)	4859(6)	34(2)
C(29A)	1578(17)	837(14)	4808(8)	48(3)

Table 3. Bond lengths [Å] and angles [°] for cs_306m.

N(1)-C(1)	1.2980(10)	C(7)-N(2)-Li(1)	96.04(6)
N(1)-C(6)	1.4588(10)	C(11)-N(3)-C(16)	117.71(7)
N(1)-Li(1)	2.0379(15)	C(11)-N(3)-Li(2)	119.59(6)
N(2)-C(9)	1.4599(11)	C(16)-N(3)-Li(2)	108.71(6)
N(2)-C(8)	1.4603(12)	C(11)-N(3)-Li(3)	112.23(6)
N(2)-C(7)	1.4641(11)	C(16)-N(3)-Li(3)	119.24(6)
N(2)-Li(1)	2.2717(15)	Li(2)-N(3)-Li(3)	71.10(5)
N(3)-C(11)	1.3111(10)	C(19)-N(4)-C(18)	109.25(7)
N(3)-C(16)	1.4657(10)	C(19)-N(4)-C(17)	108.92(7)
N(3)-Li(2)	2.1719(16)	C(18)-N(4)-C(17)	111.90(7)
N(3)-Li(3)	2.2224(15)	C(19)-N(4)-Li(2)	115.73(7)
N(4)-C(19)	1.4662(12)	C(18)-N(4)-Li(2)	111.03(7)
N(4)-C(18)	1.4662(11)	C(17)-N(4)-Li(2)	99.73(6)
N(4)-C(17)	1.4710(11)	C(21)-N(5)-C(26)	119.14(7)
N(4)-Li(2)	2.1320(15)	C(21)-N(5)-Li(3)	127.03(7)
N(5)-C(21)	1.2964(10)	C(26)-N(5)-Li(3)	113.73(7)
N(5)-C(26)	1.4598(11)	C(29A)-N(6)-C(27A)	133.2(8)
N(5)-Li(3)	2.0562(15)	C(27)-N(6)-C(28)	111.41(9)
N(6)-C(29A)	1.298(14)	C(27)-N(6)-C(29)	109.79(8)
N(6)-C(27A)	1.329(9)	C(28)-N(6)-C(29)	107.76(9)
N(6)-C(27)	1.4502(12)	C(29A)-N(6)-C(28A)	103.2(8)
N(6)-C(28)	1.4561(13)	C(27A)-N(6)-C(28A)	104.6(5)
N(6)-C(29)	1.4882(14)	C(29A)-N(6)-Li(3)	117.7(6)
N(6)-C(28A)	1.725(10)	C(27A)-N(6)-Li(3)	89.7(4)
N(6)-Li(3)	2.4152(16)	C(27)-N(6)-Li(3)	100.50(6)
O(1)-C(3)	1.2867(9)	C(28)-N(6)-Li(3)	115.80(7)
O(1)-Li(2)	1.8589(15)	C(29)-N(6)-Li(3)	111.40(7)
O(1)-Li(1)	1.9747(15)	C(28A)-N(6)-Li(3)	105.8(4)
O(2)-C(13)	1.2768(9)	C(3)-O(1)-Li(2)	144.15(7)
O(2)-Li(3)	1.9577(14)	C(3)-O(1)-Li(1)	126.13(6)
O(2)-Li(1)	1.9816(15)	Li(2)-O(1)-Li(1)	83.72(6)
O(2)-Li(2)	2.6075(16)	C(13)-O(2)-Li(3)	123.59(6)
O(3)-C(23)	1.2876(9)	C(13)-O(2)-Li(1)	128.19(6)
O(3)-Li(2)	1.9728(15)	Li(3)-O(2)-Li(1)	100.58(6)
O(3)-Li(3)	1.9875(15)	C(13)-O(2)-Li(2)	105.68(5)
O(3)-Li(1)	2.2060(15)	Li(3)-O(2)-Li(2)	66.31(5)
Li(1)-Li(2)	2.5597(19)	Li(1)-O(2)-Li(2)	66.18(5)
Li(1)-Li(3)	3.0305(19)	C(23)-O(3)-Li(2)	126.94(6)
Li(2)-Li(3)	2.555(2)	C(23)-O(3)-Li(3)	128.05(6)
Li(2)-C(17)	2.7873(16)	Li(2)-O(3)-Li(3)	80.36(6)
Li(3)-C(27A)	2.750(9)	C(23)-O(3)-Li(1)	133.62(6)
C(1)-C(2)	1.4393(11)	Li(2)-O(3)-Li(1)	75.31(6)
C(1)-C(4)	1.5166(11)	Li(3)-O(3)-Li(1)	92.40(6)
C(2)-C(3)	1.3809(11)	O(1)-Li(1)-O(2)	96.35(6)
C(3)-C(5)	1.5144(11)	O(1)-Li(1)-N(1)	91.11(6)
C(6)-C(7)	1.5213(12)	O(2)-Li(1)-N(1)	115.79(7)
C(11)-C(12)	1.4291(11)	O(1)-Li(1)-O(3)	87.98(6)
C(11)-C(14)	1.5198(11)	O(2)-Li(1)-O(3)	79.68(5)
C(12)-C(13)	1.3875(10)	N(1)-Li(1)-O(3)	164.50(8)
C(13)-C(15)	1.5116(11)	O(1)-Li(1)-N(2)	164.60(8)
C(16)-C(17)	1.5185(13)	O(2)-Li(1)-N(2)	99.04(6)
C(21)-C(22)	1.4389(11)	N(1)-Li(1)-N(2)	81.77(5)
C(21)-C(24)	1.5208(11)	O(3)-Li(1)-N(2)	95.24(6)
C(22)-C(23)	1.3838(10)	O(1)-Li(1)-Li(2)	46.21(4)
C(23)-C(25)	1.5141(11)	O(2)-Li(1)-Li(2)	68.73(5)
C(26)-C(27)	1.5303(14)	N(1)-Li(1)-Li(2)	136.08(7)
C(26)-C(27A)	1.639(9)	O(3)-Li(1)-Li(2)	48.21(4)
		N(2)-Li(1)-Li(2)	142.13(7)
C(1)-N(1)-C(6)	119.33(7)	O(1)-Li(1)-Li(3)	98.59(6)
C(1)-N(1)-Li(1)	126.98(7)	O(2)-Li(1)-Li(3)	39.42(4)
C(6)-N(1)-Li(1)	113.67(6)	N(1)-Li(1)-Li(3)	154.02(7)
C(9)-N(2)-C(8)	109.81(7)	O(3)-Li(1)-Li(3)	40.94(4)
C(9)-N(2)-C(7)	109.50(7)	N(2)-Li(1)-Li(3)	93.63(5)
C(8)-N(2)-C(7)	111.35(7)	Li(2)-Li(1)-Li(3)	53.60(5)
C(9)-N(2)-Li(1)	108.25(6)	O(1)-Li(2)-O(3)	98.71(7)
C(8)-N(2)-Li(1)	120.89(7)	O(1)-Li(2)-N(4)	123.52(8)

O(3)-Li(2)-N(4)	109.85(7)	N(3)-Li(3)-C(27A)	89.3(2)
O(1)-Li(2)-N(3)	138.18(8)	N(6)-Li(3)-C(27A)	28.89(19)
O(3)-Li(2)-N(3)	102.18(6)	Li(2)-Li(3)-C(27A)	141.4(2)
N(4)-Li(2)-N(3)	82.15(5)	O(2)-Li(3)-Li(1)	40.00(4)
O(1)-Li(2)-Li(3)	120.95(7)	O(3)-Li(3)-Li(1)	46.66(4)
O(3)-Li(2)-Li(3)	50.07(5)	N(5)-Li(3)-Li(1)	130.57(7)
N(4)-Li(2)-Li(3)	114.72(7)	N(3)-Li(3)-Li(1)	99.85(6)
N(3)-Li(2)-Li(3)	55.37(5)	N(6)-Li(3)-Li(1)	131.40(6)
O(1)-Li(2)-Li(1)	50.07(5)	Li(2)-Li(3)-Li(1)	53.73(5)
O(3)-Li(2)-Li(1)	56.48(5)	C(27A)-Li(3)-Li(1)	160.3(2)
N(4)-Li(2)-Li(1)	156.73(8)	N(1)-C(1)-C(2)	121.66(7)
N(3)-Li(2)-Li(1)	117.65(7)	N(1)-C(1)-C(4)	122.45(7)
Li(3)-Li(2)-Li(1)	72.67(6)	C(2)-C(1)-C(4)	115.89(7)
O(1)-Li(2)-O(2)	80.72(5)	C(3)-C(2)-C(1)	127.18(7)
O(3)-Li(2)-O(2)	70.32(5)	O(1)-C(3)-C(2)	125.99(7)
N(4)-Li(2)-O(2)	154.32(7)	O(1)-C(3)-C(5)	115.75(7)
N(3)-Li(2)-O(2)	72.99(5)	C(2)-C(3)-C(5)	118.23(7)
Li(3)-Li(2)-O(2)	44.56(4)	N(1)-C(6)-C(7)	107.77(6)
Li(1)-Li(2)-O(2)	45.09(4)	N(2)-C(7)-C(6)	112.55(7)
O(1)-Li(2)-C(17)	154.86(8)	N(3)-C(11)-C(12)	123.06(7)
O(3)-Li(2)-C(17)	94.79(6)	N(3)-C(11)-C(14)	121.94(7)
N(4)-Li(2)-C(17)	31.34(3)	C(12)-C(11)-C(14)	115.00(7)
N(3)-Li(2)-C(17)	57.45(4)	C(13)-C(12)-C(11)	126.67(7)
Li(3)-Li(2)-C(17)	83.87(5)	O(2)-C(13)-C(12)	124.77(7)
Li(1)-Li(2)-C(17)	150.53(7)	O(2)-C(13)-C(15)	116.82(7)
O(2)-Li(2)-C(17)	123.98(6)	C(12)-C(13)-C(15)	118.41(7)
O(2)-Li(3)-O(3)	85.90(6)	N(3)-C(16)-C(17)	109.94(6)
O(2)-Li(3)-N(5)	162.23(8)	N(4)-C(17)-C(16)	112.52(7)
O(3)-Li(3)-N(5)	89.71(6)	N(4)-C(17)-Li(2)	48.93(5)
O(2)-Li(3)-N(3)	86.25(6)	C(16)-C(17)-Li(2)	82.08(5)
O(3)-Li(3)-N(3)	99.96(6)	N(5)-C(21)-C(22)	122.32(7)
N(5)-Li(3)-N(3)	111.48(7)	N(5)-C(21)-C(24)	122.38(7)
O(2)-Li(3)-N(6)	98.77(6)	C(22)-C(21)-C(24)	115.27(7)
O(3)-Li(3)-N(6)	158.54(8)	C(23)-C(22)-C(21)	126.76(7)
N(5)-Li(3)-N(6)	79.46(5)	O(3)-C(23)-C(22)	125.24(7)
N(3)-Li(3)-N(6)	101.24(6)	O(3)-C(23)-C(25)	115.99(6)
O(2)-Li(3)-Li(2)	69.14(5)	C(22)-C(23)-C(25)	118.76(7)
O(3)-Li(3)-Li(2)	49.57(5)	N(5)-C(26)-C(27)	108.62(7)
N(5)-Li(3)-Li(2)	119.95(7)	N(5)-C(26)-C(27A)	104.7(3)
N(3)-Li(3)-Li(2)	53.53(5)	N(6)-C(27)-C(26)	111.85(8)
N(6)-Li(3)-Li(2)	151.34(7)	N(6)-C(27A)-C(26)	112.2(6)
O(2)-Li(3)-C(27A)	124.5(2)	N(6)-C(27A)-Li(3)	61.4(4)
O(3)-Li(3)-C(27A)	148.9(2)	C(26)-C(27A)-Li(3)	80.6(4)
N(5)-Li(3)-C(27A)	59.40(19)		

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for cs_306m. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
N(1)	21(1)	17(1)	17(1)	-3(1)	-3(1)	0(1)
N(2)	19(1)	25(1)	19(1)	-3(1)	-5(1)	-2(1)
N(3)	18(1)	15(1)	22(1)	-4(1)	-2(1)	-1(1)
N(4)	20(1)	19(1)	24(1)	-1(1)	-7(1)	-1(1)
N(5)	27(1)	21(1)	15(1)	-4(1)	-4(1)	-8(1)
N(6)	37(1)	23(1)	18(1)	0(1)	-6(1)	-10(1)
O(1)	22(1)	18(1)	18(1)	-5(1)	-7(1)	-1(1)
O(2)	16(1)	18(1)	19(1)	-4(1)	0(1)	-5(1)
O(3)	18(1)	16(1)	17(1)	-2(1)	-3(1)	-5(1)
Li(1)	20(1)	20(1)	19(1)	-3(1)	-4(1)	-1(1)
Li(2)	19(1)	20(1)	22(1)	-5(1)	-5(1)	-2(1)
Li(3)	21(1)	20(1)	19(1)	-3(1)	-4(1)	-6(1)
C(1)	22(1)	17(1)	15(1)	-3(1)	1(1)	-6(1)
C(2)	23(1)	22(1)	16(1)	-5(1)	-4(1)	-6(1)
C(3)	19(1)	21(1)	14(1)	-1(1)	-4(1)	-5(1)
C(4)	31(1)	20(1)	23(1)	-9(1)	1(1)	-6(1)
C(5)	26(1)	29(1)	28(1)	-2(1)	-14(1)	-2(1)
C(6)	25(1)	19(1)	25(1)	-4(1)	-5(1)	3(1)
C(7)	22(1)	22(1)	22(1)	2(1)	-6(1)	1(1)
C(8)	26(1)	41(1)	29(1)	2(1)	-4(1)	-11(1)
C(9)	26(1)	45(1)	23(1)	-8(1)	-10(1)	-2(1)
C(11)	15(1)	20(1)	19(1)	-4(1)	-3(1)	-2(1)
C(12)	16(1)	18(1)	23(1)	-2(1)	-2(1)	-6(1)
C(13)	19(1)	15(1)	16(1)	-1(1)	-3(1)	-4(1)
C(14)	16(1)	27(1)	30(1)	-7(1)	0(1)	-3(1)
C(15)	25(1)	16(1)	34(1)	-5(1)	0(1)	-6(1)
C(16)	24(1)	17(1)	27(1)	-7(1)	0(1)	1(1)
C(17)	24(1)	14(1)	29(1)	-5(1)	-6(1)	-2(1)
C(18)	25(1)	28(1)	39(1)	-8(1)	-15(1)	4(1)
C(19)	33(1)	29(1)	33(1)	10(1)	-7(1)	-4(1)
C(21)	19(1)	15(1)	20(1)	-3(1)	-9(1)	-2(1)
C(22)	20(1)	16(1)	21(1)	-1(1)	-5(1)	-6(1)
C(23)	16(1)	15(1)	17(1)	0(1)	-3(1)	-2(1)
C(24)	35(1)	18(1)	27(1)	-4(1)	-13(1)	-7(1)
C(25)	28(1)	23(1)	19(1)	-1(1)	1(1)	-8(1)
C(26)	50(1)	30(1)	17(1)	-6(1)	-4(1)	-17(1)
C(27)	29(1)	30(1)	16(1)	1(1)	-8(1)	-9(1)
C(28)	62(1)	24(1)	22(1)	4(1)	-3(1)	-12(1)
C(29)	29(1)	50(1)	22(1)	-3(1)	-1(1)	-13(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and i displacement parameters ($\text{\AA}^2 \times 10^3$) for cs_306m.

	x	y	z	U(eq)
H(2)	1809	-40	176	23
H(4A)	5192	-1860	-62	37
H(4B)	3463	-1938	-67	37
H(4C)	4283	-2704	606	37
H(5A)	-541	2576	914	40
H(5B)	3	1799	144	40
H(5C)	576	3150	210	40
H(6A)	6559	-1288	1015	28
H(6B)	5482	-2312	1418	28
H(7A)	5028	-1305	2581	28
H(7B)	6836	-1704	2297	28
H(8A)	7532	1489	1842	47
H(8B)	7498	448	1241	47
H(8C)	8307	-63	1957	47
H(9A)	4903	421	3314	46
H(9B)	5951	1516	3048	46
H(9C)	6716	-16	3232	46
H(12)	-1017	674	3463	23
H(14A)	-2451	3641	4211	37
H(14B)	-2808	2249	4035	37
H(14C)	-3035	3527	3444	37
H(15A)	1852	-1044	2323	38
H(15B)	483	-1226	3016	38
H(15C)	2189	-1442	3165	38
H(16A)	-521	5163	3753	28
H(16B)	-1660	5099	3193	28
H(17A)	-285	6731	2654	26
H(17B)	1299	5759	2754	26
H(18A)	-1597	6340	1681	45
H(18B)	-1568	4802	1975	45
H(18C)	-832	5169	1111	45
H(19A)	775	7111	1312	49
H(19B)	1563	5844	814	49
H(19C)	2323	6163	1485	49
H(22)	5172	5692	2375	22
H(24A)	3463	6604	4105	38
H(24B)	4856	6751	3419	38
H(24C)	5127	5720	4135	38
H(25A)	6049	3401	1181	35
H(25B)	5719	5006	1182	35
H(25C)	4524	4274	937	35
H(26A)	1848	4588	4758	37
H(26B)	3596	4549	4797	37
H(26C)	2527	4994	4766	37
H(26D)	3784	3699	4821	37
H(27A)	4156	2169	4767	29
H(27B)	2817	2610	5477	29
H(28A)	3593	163	4532	55
H(28B)	1861	42	4574	55
H(28C)	2421	273	5329	55
H(29A)	-152	1860	4841	50
H(29B)	151	3334	4888	50
H(29C)	416	2218	5567	50
H(27C)	1205	3192	5383	32
H(27D)	724	3606	4570	32
H(28D)	3822	1614	5402	50
H(28E)	4552	2084	4555	50
H(28F)	4345	561	4749	50

H(29D)	1430	648	5362	71
H(29E)	2307	89	4555	71
H(29F)	599	945	4642	71

L³ZnEt (12)

Table 1. Crystal data and structure refinement for cs_360m.

Identification code	cs_360m	
Empirical formula	C ₃₈ H ₅₈ N ₂ O ₂ Zn ₂	
Formula weight	705.60 Da	
Density (calculated)	1.263 g cm ⁻³	
F(000)	376	
Temperature	180(1) K	
Crystal size	0.500 x 0.470 x 0.380 mm	
Crystal color	colourless	
Crystal description	block	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	$a = 8.3250(12)$ Å	$\alpha = 78.467(4)^\circ$
	$b = 9.8754(14)$ Å	$\beta = 82.014(5)^\circ$
	$c = 11.6288(17)$ Å	$\gamma = 87.283(5)^\circ$
Volume	927.5(2) Å ³	
Z	1	
Cell measurement reflections used	31613	
Cell measurement theta min/max	2.86° to 30.52°	
Diffraction control software	Bruker AXS APEX 2 Vers.3.0/2009	
Diffraction measurement device	Bruker D8 KAPPA series II with APEX II area detector system	
Diffraction measurement method	Data collection strategy APEX 2/COSMO	
Theta range for data collection	2.860° to 30.594°	
Completeness to theta = 25.242°	99.8 %	
Index ranges	-11 ≤ h ≤ 11, -14 ≤ k ≤ 14, -16 ≤ l ≤ 16	
Computing data reduction	Bruker AXS APEX 2 Vers.3/2009	
Absorption coefficient	1.326 mm ⁻¹	
Absorption correction	Semi-empirical from equivalents	
Empirical absorption correction	Bruker AXS APEX 2 Vers.3/2009	
Max. / min. transmission	0.75 / 0.58	
R(merg) before/after correction	0.0727 / 0.355	
Computing structure solution	Bruker AXS SHELXTL Vers. 2008/4/(c) 2008	
Computing structure refinement	Bruker AXS SHELXTL Vers. 2008/4/(c) 2008	
Refinement method	Full-matrix least-squares on F ²	
Reflections collected	44168	
Independent reflections	5626 [R(int) = 0.0254]	
Data / restraints / parameters	5170 / 0 / 226	
Goodness-of-fit on F ²	1.061	
Weighting details	$w = 1/[\sigma^2 (F_o^2) + (0.0357 \cdot P)^2 + 0.3255 \cdot P]$ where $P = (F_o^2 + 2F_c^2)/3$	
Final R indices [I > 2σ(I)]	R1 = 0.0250, wR2 = 0.0673	
R indices (all data)	R1 = 0.0292, wR2 = 0.0718	
Largest diff. peak and hole	0.375 and -0.245 eÅ ⁻³	
Treatment of hydrogen atoms	Riding model on idealized geometries with the 1.2 fold isotropic displacement parameters of the equivalent Uij of the corresponding carbon atom. The methyl groups are idealized with tetrahedral angles in a combined rotating and rigid group refinement with the 1.5 fold isotropic displacement parameters of the equivalent Uij of the corresponding carbon atom.	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for cs_360m. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Zn(1)	4040(1)	4804(1)	6294(1)	28(1)
O(1)	3805(1)	4269(1)	4741(1)	31(1)
N(1)	4645(1)	2821(1)	7010(1)	24(1)
C(1)	4222(2)	1752(1)	6623(1)	27(1)
C(2)	3535(2)	1866(1)	5540(1)	30(1)
C(3)	3427(2)	3016(1)	4673(1)	30(1)
C(4)	4446(2)	296(1)	7284(2)	49(1)
C(5)	2857(2)	2897(2)	3523(1)	44(1)
C(6)	5488(1)	2643(1)	8037(1)	23(1)
C(7)	7195(1)	2586(1)	7873(1)	29(1)
C(8)	8004(2)	2530(1)	8857(1)	34(1)
C(9)	7166(2)	2529(1)	9966(1)	34(1)
C(10)	5486(2)	2581(1)	10115(1)	31(1)
C(11)	4610(1)	2637(1)	9162(1)	25(1)
C(12)	8168(2)	2546(2)	6675(1)	40(1)
C(13)	9548(2)	3550(2)	6365(2)	54(1)
C(14)	8864(3)	1090(2)	6634(2)	83(1)
C(15)	2764(1)	2638(1)	9380(1)	29(1)
C(16)	2162(2)	1226(2)	10036(2)	68(1)
C(17)	2061(2)	3729(2)	10070(2)	53(1)
C(18)	2658(4)	6024(3)	7203(2)	37(1)
C(19)	2089(3)	7395(2)	6513(2)	47(1)
C(18A)	3161(7)	6472(7)	6912(6)	32(1)
C(19A)	1321(6)	6606(7)	7092(5)	45(2)

Table 3. Bond lengths [Å] and angles [°] for cs_360m.

Zn(1)-C(18)	1.983(2)	N(1)-Zn(1)-O(1)#1	107.12(4)
Zn(1)-C(18A)	1.994(5)	C(3)-O(1)-Zn(1)	122.32(7)
Zn(1)-O(1)	2.0169(9)	C(3)-O(1)-Zn(1)#1	119.88(8)
Zn(1)-N(1)	2.0373(10)	Zn(1)-O(1)-Zn(1)#1	98.82(4)
Zn(1)-O(1)#1	2.1502(10)	C(1)-N(1)-C(6)	120.87(9)
O(1)-C(3)	1.3115(14)	C(1)-N(1)-Zn(1)	122.97(8)
O(1)-Zn(1)#1	2.1502(10)	C(6)-N(1)-Zn(1)	116.04(7)
N(1)-C(1)	1.3079(15)	N(1)-C(1)-C(2)	123.24(10)
N(1)-C(6)	1.4448(14)	N(1)-C(1)-C(4)	121.86(11)
C(1)-C(2)	1.4370(16)	C(2)-C(1)-C(4)	114.90(11)
C(1)-C(4)	1.5058(18)	C(3)-C(2)-C(1)	127.80(11)
C(2)-C(3)	1.3679(17)	O(1)-C(3)-C(2)	125.12(11)
C(3)-C(5)	1.5066(17)	O(1)-C(3)-C(5)	114.71(11)
C(6)-C(11)	1.4058(15)	C(2)-C(3)-C(5)	120.16(11)
C(6)-C(7)	1.4076(16)	C(11)-C(6)-C(7)	121.16(10)
C(7)-C(8)	1.3964(17)	C(11)-C(6)-N(1)	119.97(10)
C(7)-C(12)	1.5178(18)	C(7)-C(6)-N(1)	118.68(10)
C(8)-C(9)	1.3784(19)	C(8)-C(7)-C(6)	118.31(11)
C(9)-C(10)	1.3847(19)	C(8)-C(7)-C(12)	119.57(11)
C(10)-C(11)	1.3991(16)	C(6)-C(7)-C(12)	122.10(11)
C(11)-C(15)	1.5228(16)	C(9)-C(8)-C(7)	121.43(12)
C(12)-C(13)	1.511(2)	C(8)-C(9)-C(10)	119.58(11)
C(12)-C(14)	1.532(3)	C(9)-C(10)-C(11)	121.56(11)
C(15)-C(17)	1.518(2)	C(10)-C(11)-C(6)	117.96(11)
C(15)-C(16)	1.520(2)	C(10)-C(11)-C(15)	119.52(10)
C(18)-C(19)	1.520(3)	C(6)-C(11)-C(15)	122.49(10)
C(18A)-C(19A)	1.520(8)	C(13)-C(12)-C(7)	112.95(13)
C(18)-Zn(1)-O(1)	130.33(8)	C(13)-C(12)-C(14)	108.57(14)
C(18A)-Zn(1)-O(1)	128.93(18)	C(7)-C(12)-C(14)	110.61(13)
C(18)-Zn(1)-N(1)	122.91(9)	C(17)-C(15)-C(16)	109.27(15)
C(18A)-Zn(1)-N(1)	136.1(2)	C(17)-C(15)-C(11)	112.57(11)
O(1)-Zn(1)-N(1)	91.30(4)	C(16)-C(15)-C(11)	110.56(11)
C(18)-Zn(1)-O(1)#1	115.29(11)	C(19)-C(18)-Zn(1)	117.20(18)
C(18A)-Zn(1)-O(1)#1	97.0(2)	C(19A)-C(18A)-Zn(1)	115.0(4)
O(1)-Zn(1)-O(1)#1	81.18(4)		

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for cs_360m. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Zn(1)	40(1)	25(1)	19(1)	-7(1)	-5(1)	6(1)
O(1)	48(1)	26(1)	20(1)	-5(1)	-10(1)	0(1)
N(1)	27(1)	26(1)	18(1)	-3(1)	-3(1)	0(1)
C(1)	32(1)	26(1)	24(1)	-2(1)	-5(1)	-3(1)
C(2)	36(1)	28(1)	27(1)	-7(1)	-8(1)	-4(1)
C(3)	36(1)	31(1)	23(1)	-9(1)	-9(1)	0(1)
C(4)	76(1)	27(1)	45(1)	4(1)	-27(1)	-12(1)
C(5)	66(1)	40(1)	32(1)	-13(1)	-24(1)	2(1)
C(6)	27(1)	22(1)	19(1)	-2(1)	-4(1)	-2(1)
C(7)	28(1)	31(1)	26(1)	-3(1)	-3(1)	-2(1)
C(8)	29(1)	38(1)	34(1)	-5(1)	-9(1)	-2(1)
C(9)	40(1)	37(1)	30(1)	-7(1)	-15(1)	0(1)
C(10)	39(1)	35(1)	21(1)	-7(1)	-6(1)	1(1)
C(11)	30(1)	24(1)	20(1)	-3(1)	-3(1)	-1(1)
C(12)	29(1)	58(1)	29(1)	-7(1)	2(1)	-3(1)
C(13)	50(1)	44(1)	58(1)	-1(1)	19(1)	-5(1)
C(14)	108(2)	52(1)	82(2)	-34(1)	51(1)	-26(1)
C(15)	29(1)	32(1)	23(1)	-3(1)	-2(1)	1(1)
C(16)	38(1)	42(1)	109(2)	14(1)	2(1)	-7(1)
C(17)	43(1)	64(1)	56(1)	-31(1)	0(1)	10(1)
C(18)	48(1)	37(1)	27(1)	-13(1)	-3(1)	7(1)
C(19)	52(1)	36(1)	52(1)	-12(1)	-3(1)	9(1)
C(18A)	34(3)	34(3)	32(3)	-16(2)	-1(2)	-3(2)
C(19A)	36(2)	61(4)	46(3)	-27(3)	-7(2)	7(2)

Table 5. Hydrogen coordinates ($\times 10^4$) and i displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for cs_360m.

	x	y	z	U(eq)
H(2)	3103	1044	5410	35
H(4A)	5036	307	7955	73
H(4B)	5066	-252	6752	73
H(4C)	3382	-117	7576	73
H(5A)	1919	3519	3389	65
H(5B)	2546	1943	3562	65
H(5C)	3735	3153	2871	65
H(8)	9156	2493	8760	40
H(9)	7737	2493	10625	41
H(10)	4915	2578	10881	38
H(12)	7421	2794	6058	47
H(13A)	9126	4482	6418	81
H(13B)	10068	3545	5556	81
H(13C)	10345	3275	6918	81
H(14A)	9510	1090	5862	125
H(14B)	7973	442	6751	125
H(14C)	9553	807	7262	125
H(15)	2353	2839	8594	34
H(16A)	2588	992	10797	102
H(16B)	2537	530	9560	102
H(16C)	974	1247	10174	102
H(17A)	878	3769	10099	79
H(17B)	2507	4631	9679	79
H(17C)	2345	3492	10877	79
H(18A)	1686	5503	7612	44
H(18B)	3266	6222	7822	44
H(19A)	3029	7902	6057	70
H(19B)	1519	7942	7065	70
H(19C)	1353	7223	5972	70
H(18C)	3560	6453	7679	39
H(18D)	3600	7304	6354	39
H(19D)	896	6479	6377	68
H(19E)	1000	7526	7251	68
H(19F)	880	5900	7766	68

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